ISOTOPIC LABELLING APPLIED TO THE INFRARED SPECTRA OF METAL COMPLEXES

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by

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In memory of my father.

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SUMMARY

An investigation of a series of imidazole complexes of first transition metal(II) nitrates, perchlorates and halides is reported. Deuteration of the imidazole ring provides reliable assignments for the internal vibrations of imidazole. This technique also permits unambiguous assignments of the internal vibrations of nitrate or perchlorate by their lack of deutero-sensitivity. The infrared spectra of imidazole and its complexes are examined in order to determine the ratio ν^D/ν^H for bands assigned to the C-H, N-H and ring modes of the heterocyclic ring. With very few exceptions, ν^D/ν^H falls within the ranges 0.74 to 0.84 and 0.93 to 1.00 for C-H and ring vibrations, respectively. The potential usefulness of the results is discussed. Assignments of the M-N and M-halide vibrations are based on the results of the deuteration studies, metal ion substitution and on halogen substitution. The number of M-L vibrations in the far-infrared satisfies the selection rules for the molecular point or site group symmetries and facilitates accurate structural assignments.

Essentially complete assignments have been deduced for $[Cu(NO_3)_2(pz)]_n$ in the 4000-300 cm^{-1} range of the mull infrared spectrum. The number of vibrational modes for the nitrato and pyrazine ligands and their activities in the infrared are deduced on theoretical predictions based on the known site and factor group symmetries of the linear polymer. Band assignments for the internal vibrations of the ligands are based on pyrazine-d_4 substitution. The complete far-infrared spectrum (350-25 cm^{-1}) is reported together with assignments for the metal-ligand stretching vibrations.

The metal(II) complexes of acetylacetone $[M(AA)_2(B)_2]$ (M = Co, Ni,

Zn; B = imidazole, pyridazine) and $[M(AA)_2(B)]_n$ (M = Co, Ni, Zn; B= pyrazine, pyrimidine) were prepared and their infrared spectra determined over the range 700-140 cm^{-1}. Metal-oxygen and metal-nitrogen stretching vibrations, νM-O and νM-N are assigned on the basis of the band shifts induced by deuteration of the adducted base and by metal ion substitution. Three or four νM-O bands are observed within the range 600-200cm^{-1}. The two νM-O bands of higher frequency are considered to be coupled with internal ligand modes. Two νM-N bands are observed within the range 280-170 cm^{-1}. The metal-nitrogen stretching frequencies are in good agreement with the values previously established for these vibrations in the complexes $[M(imidazole)_6]^{2+}$, $[M(pyrazine)_2Cl_2]_n$ and $[Ni(AA)_2(pyridine)_2]$.

The infrared spectra (700-140 cm^{-1}) of the metal (II) complexes of salicylaldehyde $[M(Sal)_2]$ (M = Co, Ni, Zn), $[M(Sal)_2(B)_2]$ (M = Co, Ni, Zn; B = water, imidazole, pyridine) and $[M(Sal)_2(B)]_n$ (M = Co, Ni, Zn; B = pyrazine, pyrimidine) are discussed. On the basis of their infrared spectra all these complexes are assigned octahedral structures. Assignments of the M-O and M-N stretching vibrations are made by comparison with the spectra of the analogous acetylacetonate complexes, the effects of metal ion substitution and deuteration of the adducted base. The νM-O bands near 500 and 300 cm^{-1} are considered to originate in the two species of the M-O bonds which (unlike the analogous acetylacetonates) have differing bond lengths. These differences, and vibrational coupling between νM-O and salicylaldehyde ligand modes, give rise to a greater number of bands which comprise a contribution from νM-O than occur in the spectra of the analogous acetylacetonate adducts.

The infrared spectra (4000-400 cm^{-1}) of the complex *trans*-$[Pt(glycinate)_2]$ and its ^{18}O, ^{15}N, 1-^{13}C-, 2-^{13}C-, 2,2-d_2- and *N*,*N*-d_2-labelled analogues

have been determined. Each spectral band has been assigned on the basis of the shifts induced by the various forms of isotopic labelling. The N-H, C-H, C=O and Pt-O stretching vibrations and the CH_2 scissoring, CH_2 twisting and NH_2 twisting modes are vibrationally pure but all other bands represent vibrationally coupled modes. The spectra reveal that some earlier assignments require revision.

A study of the infrared spectra of *cis*-$[Ni(gly)_2(Him)_2]$ (gly = glycinate ion, Him = imidazole) and its isotopically labelled analogues are made over the range 4000-140 cm^{-1}. ^{18}O-, ^{15}N-, 1-^{13}C-, 2-^{13}C- and 2,2-d_2-Labelling of the coordinated glycinate yields assignments for the internal glycinate modes and nickel-oxygen and nickel-nitrogen stretching and bending vibrations, while deuteration of imidazole (Him-d_3) provides assignments for the internal modes of the coordinated imidazole rings and for nickel-imidazole vibrations. The results, combined with those of previous multiple isotopic labelling studies on glycinate complexes, enable some general conclusions to be reached on the infrared spectra of these complexes.

An investigation of the infrared spectra (4000-140 cm^{-1}) of the complex *trans*-[Pt(L-alaninate)$_2$] and its ^{18}O-, ^{15}N-, 2-d, 3-d_3- and N,N-d_2-labelled analogues has been made. Spectral bands are assigned on the basis of the shifts induced by the various forms of labelling and by substitution of Pd(II) for Pt(II). The labelling study reveals that very few bands represent vibrationally pure modes and that a small increase in the complexity of the coordinated amino acid induces a large increase in the complexity of the spectrum.

The infrared spectra of some metal(II) complexes of glycylglycine are discussed in relation to their known or probable structures. A distinction between various structures is possible on the basis of

differences in the spectral band patterns of these complexes. Firm assignments are presented for the majority of the internal ligand vibrations and metal-ligand modes by observing the band shifts resulting from ^{15}N-labelling, metal ion substitution and halogen substitution.

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ABBREVIATIONS

AA	acetylacetonate anion
ala	alaninate anion
B	generalized base
B.M.	Bohr Magneton
CFT	crystal field theory
CFSE	crystal field stabilization energy
gg	glycylglycinate dianion
gly	glycinate anion
Hgg	glycylglycinate anion
H_2gg	glycyglycine
Him	imidazole
im	imidazolinium ion
ir	infrared
L	generalized ligand
M	generalized metal ion
pd	pyridazine (1,2-diazine)
pm	pyrimidine (1,3-diazine)
py	pyridine
pz	pyrazine (1,4-diazine)
R	generalized substituent
Sal	salicylaldehyde anion
X	generalized halide
ν	infrared stretching mode
δ	infrared bending mode : in-plane
γ	infrared bending mode : out-of-plane
ω	infrared bending mode : wag
τ	infrared bending mode : torsion

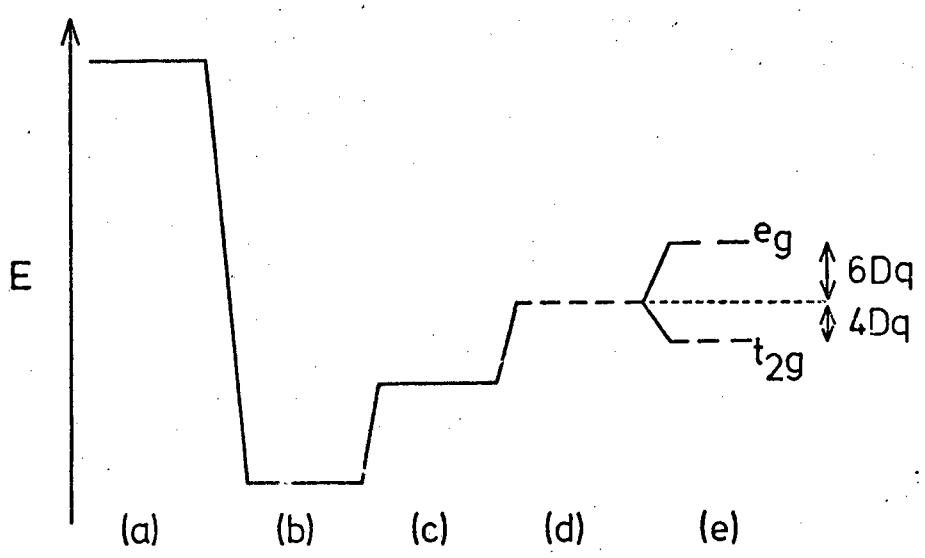
I. INTRODUCTION

1. CRYSTAL FIELD ASPECTS OF INFRARED SPECTRA

The way in which certain properties of compounds of the first and second transition series metal ions vary with *d*-orbital population may be rationalized in terms of the splitting which these orbitals suffer under the influence of the crystal field. The electrostatic crystal field theory (CFT) which considers metal ions and ligands as point charges, has proved adequate for the explanation of many fundamental properties of transition metal complexes. These encompass the manner in which[1] bond distances, lattice energies, heats of ligation and other thermodynamic properties vary through a series of transition metal complexes of constant ligand composition as also their magnetic characteristics, electronic spectra and metal-ligand stretching frequencies.

The electrostatic field created by the presence of the ligands, which is likened, in octahedral symmetry, to a spherical set of negative point charges (comprising, for instance, the negative ends of the ligand dipoles) removes the degeneracy of the metal ion inner orbitals. The *s*-, *p*- and *d*-orbitals are affected differently, according to their spatial orientation with respect to the axes of ligand approach. On ligand approach the *s*-orbitals of the metal ion, being spherically symmetrical with regard to the three dimensional coordinate system, are raised in energy. A similar repulsion is experienced by the *p*-orbitals which are directed along the three cartesian axes. The $d_{x^2-y^2}$- and d_{z^2}-orbitals, collectively termed the e_g-orbitals, suffer a greater repulsion than those which are orientated between the axes (d_{xy}-, d_{xz}- and d_{yz}-orbitals, collectively termed the t_{2g}-orbitals) such that the degeneracy of the five *d*-orbitals

is removed as depicted in Fig. 1. *f*-Orbitals undergo a corresponding removal of degeneracy but the splitting is much smaller.



(a) Free ion.

(b) Attraction of ligand charges.

(c) Destabilization of electrons in orbitals other than *d*.

(d) Destabilization of electrons in *d*-orbitals.

(e) Crystal field splitting.

Figure 1.

Crystal field splitting results in stabilization of the complex relative to the situation which would obtain in the absence of such splitting. Each t_{2g}-orbital is stabilized by $4Dq$ about the baricentre of the split orbitals, and each e_g-orbital is destabilized by $6Dq$, where $10Dq$ represents the total splitting energy. The more closely the ligands approach the metal ion, the more extensive the *d*-orbital

repulsion suffered and the larger the magnitude of $10Dq$. In strong fields $10Dq$ may attain a value of the order of 100 K cal mol^{-1}.

For all configurations other than d^0, high-spin d^5 and d^{10} (or f^0, high-spin f^7 and f^{14}) the splitting lowers the potential energy of the system. This energy decrease which results from the splitting of the d-orbital levels is termed the crystal field stabilization energy (CFSE). It is a function of, *inter alia*, the population of the d-orbitals. Hence, the CFSE of a transition metal ion in an octahedral field may be expressed[2]

$$\text{CFSE} = -(0.4n_{t_{2g}} - 0.6n_{e_g})10Dq + P \qquad (1)$$

where $n_{t_{2g}}$ and n_{e_g} are the occupation numbers of the t_{2g} and e_g orbitals, respectively and P is the pairing energy appropriate to spin-paired complexes. Jørgensen[3] expressed $10Dq$ as the product

$$10Dq = fg \qquad (2)$$

where f provides a measure of the CF splitting power of the ligand (equivalent to its position in the spectrochemical series) and g is the spectroscopically-determined value of $10Dq$ for an octahedrally hydrated metal ion (for which f is unity). From this relationship $10Dq$ may be estimated for ions where experimental values are not available. From examples where $10Dq$ has been empirically determined, f values for a variety of ligands have been obtained. These data are valuable since they provide an index of the relative CF splitting powers of various ligands.

Despite the small magnitude of the CFSE contribution to complex formation its significant influence on complex properties[2,4] may readily be detected on passing through an isostructural transition series of complexes of a common ligand with varying metal ion of constant oxidation

state. This implies that all other influences such as ionic radius and mass are constant or vary smoothly through the series of ions from d^0 to d^{10}. The part played by CFSE is superimposed upon these effects and varies irregularly with d-orbital population. The total bonding energy is primarily dependent on such factors as the attraction between the metal ion and ligands and on interelectronic repulsion of electrons in orbitals other than those of the d-shell.

Since the CFSE influences the M-L bond strength, the M-L force constants of such an isostructural series of complexes as has been defined above are expected[5] to exhibit a variation with d-orbital population similar to that shown[1] by numerous thermodynamic properties. Apart from CFSE, those properties of the metal ion which have most influence on νM-L are the ionic radius and mass of M. Ionic contraction and increasing ionic mass on passing through a transition series will have opposed effects on νM-L. The former will increase νM-L and the latter will decrease νM-L. The fact[5] that there is almost invariably an overall increase in νM-L from d^0 through d^{10} suggests that the effect of ionic contraction on νM-L outweighs the mass effect. It therefore appears probable[5] that, in the absence of any appreciable mass effect, the M-L stretching frequencies in the infrared spectra of these complexes should vary in parallel with their CFSE's.

To obtain the crystal field contribution[5-15] to νM-L, the stretching frequency, ν, is plotted against d-orbital population. Complexes of first transition series ions with $3d^0$, high-spin $3d^5$ and $3d^{10}$ electronic configurations are not stablized by the crystal field. Their spectra may be considered as reference spectra from which CF effects are absent. Thus, an interpolation line drawn through the points for these ions represents the frequencies (ν_0) which, other factors being equal, would

also be realized for the complexes of the remaining ions where CF stabilization is absent. The difference $(\nu-\nu_o)$ between the observed and interpolated frequencies is therefore that part of νM-L contributed by the CFSE. The variation in $(\nu-\nu_o)$ is found to qualitatively follow the variation in CFSE. There is also an increase in νM-L (i.e. ν_o) in the order $d^0 < d^5 < d^{10}$ which is expected from the ionic contraction through the transition series.

Thornton and co-workers[5-18] have made extensive studies in this field. νM-O of many β-ketoenolates of trivalent ions show a correlation with *d*-orbital population which is consistent with the relative CFSE's of the metal(III) ions[5]. Good correlations were obtained for νM-L vibrations in metal(II) and metal(III) tropolonate complexes[6], metal(II) acetylacetonates and their nitrogenous base adducts[7], in metal(II) 2,2'-bipyridyl and 1,10-phenanthroline complexes[8], 2-thenoyltrifluoroacetonates[9], metal(II) anthranilates[10], the di- and trivalent γ-substituted acetylacetonates[11], a range of complexes with nitrogen donor ligands[12], and in metal(II) oxalate and metal(III) cyanide complexes[13]. The same correlation was demonstrated for νM-O in the second transition series metal(III) acetylacetonates[13] and the lithium salts of the lanthanide(III) tetrakis(tropolonates)[14], and lanthanide(III) tris(tropolonates)[15]. Support for the assignments made for νM-L in a variety of metal(II) salicylaldimine complexes[16-18], was obtained from such correlations with CFSE.

2. METHODS OF ASSIGNING METAL-LIGAND VIBRATIONS IN THE INFRARED SPECTRA OF TRANSITION METAL COMPLEXES

Direct information regarding structural features of inorganic and coordination compounds may be obtained from their low frequency infrared spectra (i.e. below 650 cm^{-1}). Bands in the far infrared region arise from vibrations of relatively weak bonds or those involving heavy atoms encompassing such motions as lattice modes, vibrations in which hydrogen bonding participates, modes arising from coordinated water and low frequency torsional oscillations. Of prime interest are the metal-ligand stretches and bends (generally occuring below 650 cm^{-1}) since these yield important information for structural characterization. The interpretation and assignment of M-L vibrations is, however, frequently complicated by vibrational coupling, by lowering of symmetry and by the occurence of ligand modes activated by complex formation.[19]

Use has been made of the following methods, in particular, for the assignment of metal-ligand vibrations:

1. A method distinguished by its simplicity, involves comparison of the spectrum of the free ligand with that of its complex. Bands in the spectrum of the complex which are absent from that of the ligand, may be assigned to M-L modes. Ambiguity often arises since ligand vibrations activated by complexation may appear in the same region as the M-L vibrations.[20]
2. Metal-sensitive vibrations will appear in the same regions in the infrared spectra of complexes constituting an identical metal ion, and a series of similar substituted ligands. νCu-N in the complexes, CuX_2L_2 (X = Cl, Br; L = substituted pyridine) were

assigned[21] by this method. The method has also been used for the assignment of νNi-O in a series of variously substituted pyridine adducts of Ni(II) acetylacetonate[22] and for νM-O assignments in the spectra of metal acetylacetonates with various α-, β-, and γ-substituents[11,23].

3. A series of isostructural complexes in which the coordinated metal ion is replaced successively by metal ions of equivalent oxidation state from the same transition series, while the ligand composition remains constant, will yield values of νM-L in the order of the CFSE's of the respective metal ions. The bands in the spectrum which follow this trend are regarded as having metal-ligand characteristics. This technique is discussed and exemplified in chapters three and four.

4. Metal-ligand and other frequencies are predicted by calculations (normal coordinate analysis) based on a model of the complex[24-27]. It is, however, difficult to determine a unique set of physically reasonable force constants and, as a consequence, the values of metal-ligand stretching force constants differing sometimes by an appreciable factor have been published[24]. More accurate values are obtained by methods involving the calculation of force constants using such data as isotopic shifts and Coriolis coupling constants[25-27].

5. The isotopic labelling technique[28] employs labelling of the metal ion or ligand atoms with preferably stable isotopes. Bands shifted by labelling are assigned to vibrations involving the labelled atoms. It is assumed that the force constants are

unaltered by isotopic substitution. Thus the shift in observed frequency is attributed to the mass effect. The isotope-induced shift will be greater as the m^i/m ratio increases, where m^i is the higher mass of the labelled atom and m is the mass of the atom with natural isotopic abundance. The greatest isotope effect can therefore be expected for deuterated and tritiated molecules which show band shifts of up to 1000 and 1300 cm^{-1}, respectively. In the case of lower m^i/m ratios, for instance ^{18}O-labelled molecules[28], shifts as high as 40 cm^{-1} may be observed. However, the frequency shifts which result from labelling depend directly upon the extent to which the labelled atoms participate in the specific vibration. The greater the extent to which the molecular species comprising the labelled atom contributes to a vibration, the greater is the isotopic shift effected by the mass change resulting from isotopic substitution. The magnitudes of these shifts are subject to constraints such as vibrational coupling, the number and nature of the atoms in the molecule which have been labelled and the extent of hydrogen bonding. The smaller the coupling with a vibration not involving the labelled atom, the purer is the vibration and the greater will be the observed shift.

To a reasonable approximation, isotopic shifts may be calculated[28] by assuming the labelled atom to be part of a simple diatomic oscillator. The vibrational frequency of an harmonic diatomic molecule may be represented

$$\nu = \frac{1}{2\pi c}\left[\frac{f}{\mu}\right]^{\frac{1}{2}} \qquad (3a)$$

and, for the corresponding isotopically-labelled species

$$\nu^{i} = \frac{1}{2\pi c}\left[\frac{f}{\mu^{i}}\right]^{\frac{1}{2}} \qquad (3b)$$

where ν = vibrational frequency (wavenumber),
f = harmonic force constant,
μ = reduced mass of molecule,
c = velocity of light.

and the superscript i pertains to the labelled system.

The frequency shift may be obtained from the ratio

$$\frac{\nu^{i}}{\nu} = \left[\frac{\mu}{\mu^{i}}\right]^{\frac{1}{2}} \qquad (4)$$

Equation (4) approximates the observed ratio well if most of the energy of the vibration is contained within the diatomic oscillator, *i.e.* where vibrational coupling, hydrogen bonding, *etc.* are absent. Good agreement between calculated and observed shifts ($|\nu-\nu^{i}|$) have been obtained for instance, for N-H and C=O stretching vibrations in the infrared spectra[29-31] of glycine, and L- and β-alanine complexes of Cu(II) and Ni(II).

A variety of commercially available ligands with labelled donor or other atoms, of high isotopic purity are obtainable. The most commonly employed stable isotopes are ^{2}H, ^{18}O, ^{13}C and ^{15}N. *^{2}H-*Labelling is useful in ascertaining the extent of vibrational purity of N-H, O-H and C-H vibrational modes and also for the detection of hydrogen bonding, by comparison of the observed and calculated shifts. The favourable mass advantage of ring deutration relative to donor atom labelling in heterocyclic nitrogenous bases (*e.g.* aniline-d_5 or -d_7, pyridine-d_5 and pyridine-*N*-oxide-d_5) facilitates the unambiguous assignment[32-34] of νM-L vibrations, as well as the various ring

deformations. The work reported on ^{18}O-labelling involves various ^{18}O=X stretching vibrations where X is C, N, P, As, S, V and U, but significant shifts are also obtained for ^{18}O-H, C-^{18}O and M-^{18}O vibrations. The νM-O bands of acetylacetonate complexes[35-36] have been assigned by replacement of the donor ^{16}O-atoms by ^{18}O. Labelling of the ligand donor atom has been used to assign νM-L in salicylaldimine complexes[16,18], anthranilate complexes[10] and tropolonate complexes[37]. Assignments of νM-L and other vibrations in the glycine and L- and β-alanine complexes of Cu(II) and Ni(II) have been achieved by multiple labelling[29-31] of the ligand atoms.

Another method which is often costly and limited by the availability of the appropriate (preferably) stable isotope, is metal ion labelling. This method has the inherent advantage of generating shifts in M-L vibrations only but the shifts are generally small (because of the relatively unfavourable mass ratio between labelled and unlabelled metal ion), and may fall within the range of experimental error. The method fails also in distinguishing between M-L vibrations in complexes of mixed donor atoms. For instance, νM-N and νM-Cl in $[M(py)_2Cl_2]$, would be indistinguishable by this technique. In an extensive review, Nakamoto[38] has surveyed the use of isotopes of various transition metal ions for the assignments of M-L vibrations. This technique has been used for assignment purposes in a vast range of molecules such as complexes of phosphines, quinoline, acetylacetone, 2,2'-bipyridyl, amines and pyridine. It has also been utilized in amino acid complexes[39] and tropolonate complexes[40].

3. GROUP THEORY APPLIED TO MOLECULAR VIBRATIONS

Using symmetry considerations[41-43] alone, it is possible to predict the number of vibrational modes and their Raman/infrared activities. If the symmetry elements of a molecule are known, one may deduce the point group to which the molecule belongs. From the character table for that particular point group, the symmetry species of the normal modes of vibration of the molecule are determined. These vibrations may then be separated out into stretches and bends, and their activities in the infrared and Raman deduced.

All movements of the atoms in a molecule may be resolved into components along three axes, x, y and z. There are 3N possible movements in a molecule composed of N atoms. Six of these motions correspond to translation and rotation, while the remaining 3N-6 (3N-5 for a linear molecule) are associated with internal molecular vibrations. To categorize these vibrations, each atom is labelled with three orthogonal position vectors. Under the symmetry operations for the particular point group, the atomic displacements are expressed as transformation matrices whose characters, χ, form a reducible representation, Γ_{total}, for this set of vectors. Consider as an illustration, the H_2O molecule (point group C_{2v}) for which Γ_{total} is

C_{2v}	E	C_2	δ_v	$\delta_v{}^1$
Γ_{total}	9	-1	1	3

To determine the symmetry species of all possible molecular motions, the following reduction formula is used.

$$n_i = \frac{1}{h} \Sigma \chi_R \chi_I N \qquad (5)$$

where n_i = the number of times each irreducible representation appears in the reducible representation,

h = the order of the group,

χ_R = character of the reducible representation,

χ_I = character of the irreducible representation,

N = the number of symmetry operations in the class.

Thus, the nine possible molecular motions in the water molecule are:

$$\Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 3B_2$$

The vectors for any point group individually represent translation with the x, y and z directions and are obtained from the character table containing columns listing the transformation properties of x, y and z, x^2, y^2, z^2, xz, yz and xy. Rotational properties associated with a point group are listed as R_x, R_y and R_z. Removing these irreducible representations relating to translation and rotation leaves the representations responsible for vibration. For the water molecule:

Symmetries for all molecular motions	$3A_1 + A_2 + 2B_1 + 3B_2$
Symmetries for translations	$A_1 + B_1 + B_2$
Symmetries for rotations	$A_2 + B_1 + B_2$
Symmetries for vibrations = Γ_{vib}	$2A_1 + B_1 = 3N - 6$

In order to determine how the stretches and bends contribute to the normal modes, a new basis for the representations of the point group is chosen, using internal displacement vectors. To determine the reducible representations for the stretches, vectors are drawn along the bonds. Any vector shifted to a different position by a symmetry operation contributes nothing to the character of the matrix, while unshifted vectors contribute +1 or -1 depending on whether they are unchanged or

reversed. For water the operations E and δ_ν^1 do not move the vectors, while C_2 and δ_ν interchange them,

$C_{2\nu}$	E	C_2	δ_ν	δ_ν^1
$\Gamma_{stretch}$	2	0	0	2

which reduces using equation (5) to

$$\Gamma_{stretch} = A_1(\text{sym.}) + B_2 \ (\text{asym.})$$

The bends are obtained by subtracting $\Gamma_{stretch}$ from Γ_{vib} yielding,

$$\Gamma_{bend} = A_1 \ (\text{sym.}).$$

Symmetry does not permit the separation of two vibrations of the same irreducible representation. Stretching vibrations usually require more energy than bending modes, resulting in a considerable frequency difference between the two. Hence the symmetric A_1 stretch and A_1 bend in water would have little influence on one another although symmetry permits their interaction. However, vibrations of the A_1 type do not interact with those of the B_2 type since they are orthogonal representations.

A vibration will be infrared active if, during vibration, there is a resultant change in dipole. Since the dipole moment changes in the same way as the x, y and z coorindates, a vibration will be infrared active if it belongs to the same representation as any of the internal displacement vectors. This is read directly from the character table. Similarly, a fundamental transition will be Raman active if the mode involved belongs to the same representation as any of the operations in the last column of the character table. These operations are related to the polarizability of the bonds. For water, all modes are infrared and Raman active.

The vibrations of a molecule in the gaseous phase are governed only by the restrictions[42] of its own point symmetry. These are the conditions described above. When a molecule occupies a site in a crystal it may no longer be regarded as an isolated unit, since it now becomes subject to the symmetry restrictions of its solid environment. This change in symmetry can split degenerate vibrations, activate inactive vibrations and generate lattice modes arising from translatory and rotatory motions of the molecule within the solid.

For a rigorous vibrational analysis, the entire array of molecules should be considered but there are two frequently used approximations: Site group[44] and factor group analyses.[45-46] In the site group analysis by Halford,[44] the interactions between one molecule and its surroundings are ignored. The surroundings are treated as static but its symmetry is imposed on that of the molecule occupying a site within it. The site symmetry is found using the following conditions:

1. The site group must be a subgroup of the space group of the crystal and the point group of the isolated molecule.
2. The number of equivalent sites must be equal to the number of molecules in the unit cell.

The site symmetry, which is generally lower than the molecular symmetry, may be found if the space group, the number of molecules per unit cell and the point group of the isolated molecule are known. Halford[44] derived tables listing the possible site symmetries and the number of equivalent sites for the 230 space groups.

Factor group analysis[45-46] is more complete in that it accounts for lattice modes and solid state splittings of non-degenerate vibrations of the free molecule. The information necessary for the analysis is a full X-ray crystal structure analysis with atomic coordinates in

terms of the Wykoff notation. Adams and Newton[47] have published tables of reduced representations which readily facilitate the vibrational analysis of solids belonging to any of the 230 space groups.

4. INFRARED SPECTRA OF IMIDAZOLE AND ITS COMPLEXES

Imidazole (Him) is a monodentate ligand known to form complexes with metal ions through the tertiary rather than through the imino (pyrrole) nitrogen.[48-58] The proton at the pyrrole nitrogen is labile and the resulting anion behaves as a uninegative bridging ligand. This has been confirmed by numerous x-ray structural analyses.[48-58] Imidazole, however, forms such a large and diverse number of complexes with most transition metal ions that few of their structures are known with any degree of certainty. By far the most common techniques used for their structural elucidation have been infrared spectroscopy,[57-65] electronic spectroscopy[55-60] and magnetic measurements.[58-61]

The coordination chemistry of Him has often been compared with that of other nitrogenous bases such as ammonia but more especially, pyridine (py).[58-60] Both Him and py are heterocycles which complex through a tertiary nitrogen atom. One interesting feature of Him is its ready formation of $[M(Him)_6]X_2$ systems where X ranges from halide through many simple inorganic anions. By contrast, confirmation of the existence of only two hexakis-complexes of py has been obtained and those reported are certainly not very stable, e.g. $[Cr(py)_6]Br_2$.[66] The reason why Him readily forms stable hexakis-complexes is not clearly understood. Some consider[60] that the smaller five-membered ring might be favoured from a steric point of view. The greater availability of the lone-pair on the Him tertiary nitrogen than that on py, as shown by their respective pK_a values (pK_a Him = 6.95; pK_a py = 5.3) may[58] also account for this ability. However, the isomer of Him, pyrazole (also a five-membered ring, pK_a = 2.47) has been found[67] to form stable hexakis-complexes with Co(II) and Ni(II) salts even though it is a weaker base

than py. There are further anomalies. For instance, the stable form[33] of $Co(py)_2Cl_2$ is polymeric octahedral, while $Co(NH_3)_2Cl_2$[68] is monomeric tetrahedral and the intense blue colour, electronic spectrum[59] and infrared spectrum[64] of $Co(Him)_2Cl_2$ is convincing evidence for its tetrahedral structure. Differences such as these have been explained[58] in terms of differences in σ-electron donor and π-electron acceptor properties of these ligands.

Complete band assignments in the infrared spectrum of solid Him have been proposed by Perchard and co-workers.[69-71] While the band assignments proposed in this work for the spectra of Him (and its deuterated analogues Him-d_1, Him-d_3 and Him-d_4) are essentially identical to those reported,[69,70] these spectra are now re-examined with the aim of determining the ratio ν^D/ν^H for bands assigned to C-H, ring and N-H modes of the heterocyclic ring. Without exception, the ratios ν^{D_3}/ν^{H_4} and ν^{D_4}/ν^{H_4} fall within the range 0.74 to 0.83 for bands involving C-H vibrations and 0.83 to 1.00 for essentially ring modes. The potential usefulness of these results is discussed with respect to the assignments of Him vibrations occurring in complexes of this ligand since the ratios for the complexes are similar to those observed for the free ligand.

The infrared spectra (4000 - 140 cm^{-1}) of the following series of complexes derived from the reaction of Him with metal(II) halides, nitrates and perchlorates are studied in the present work.

$M(Him)_6(X)_2$	where M = Mn(II), Fe(II), Co(II), Ni(II); X = ClO_4^-, and $[Zn(Him)_5](ClO_4)_2$ or M = Co(II), Ni(II), Zn(II); X = NO_3^-.
$M(Him)_4(X)_2$	where M = Cu(II), Zn(II); X = ClO_4^-, NO_3^- M = Cu(II); X = Cl^-, Br^-, I^-.
$M(Him)_2(X)_2$	where M = Co(II), Zn(II); X = Cl^-, Br^-.

This work was also undertaken in order to assign the metal-ligand vibrations occurring below 350 cm^{-1} by determining the band shifts induced by deuteration of the Him ring and by determining the extent to which the number of M-L bands yielded by the deuteration studies are consistent with symmetry requirements based on known or likely structures of the complexes. Band patterns in the mid-infrared relating to perchlorate or nitrate modes in the spectra of these particular complexes, show interesting correlations (based on symmetry requirements) on going from essentially ionic perchlorate or nitrate, to structures known to contain essentially monodentate perchlorate or nitrate.

5. INFRARED VIBRATIONAL ANALYSIS OF $[Cu(NO_3)_2(pz)]_n$

$[Cu(NO_3)_2(pz)]_n$ has been investigated by x-ray crystallography[72] in terms of its space group and atomic coordinates, and has also received attention in the fields of PMR,[73] magnetic measurements[74,75] and electronic and ESR studies.[76] The molecular structure of pyrazine has been determined by electron diffraction[77] and x-ray analysis[78] and, on the basis of these studies, detailed vibrational assignments have been made.[79-84]

The normal modes of vibration of an isolated nitrate ion of D_{3h} point group symmetry are well known.[85] A number of studies, such as those by Vratny[86] and Ferraro[87] on nitrates, have sought to relate deviations from the free ion selection rules to the covalent character of the nitrate group. Some studies have been aimed at determining whether certain deviations from the free ion selection rules could be used as a criterion for distinguishing between monodentate,[88-91] bidentate[92] and bridging nitrato groups.

A study of the infrared spectrum of $[Cu(NO_3)_2(pz)]_n$ was undertaken for several reasons. Firstly, this system has not previously been studied by infrared spectroscopy. The availability of the wealth of symmetry data on this compound and its component molecules, makes this a suitable system for the application of symmetry consideration. Present facilities allow the spectrum to be extended from 250-30 cm^{-1}, thus enabling an investigation of all the metal-ligand and related modes expected to arise at lower frequency. Of particular interest is a study of the behaviour of the internal modes of pz and nitrate as their vibrational selection rules are changed on lowering the symmetry of the crystalline environment. This is especially interesting in the case of the nitrate groups which are

bidentate towards the Cu(II) ion. Finally, the availability of deuterated pz has enabled accurate assignments of the stretches involving the N-Cu-N skeleton and unambiguous assignments of the internal nitrate modes in the mid-infrared on the basis of their insensitivity towards deuteration of the pz ring.

6. HETEROCYCLIC BASE ADDUCTS OF METAL(II) ACETYLACETONATES

Since Werner[93] first employed acetylacetone as a chelating ligand, β-diketones have proved to be one of the most versatile classes of organic donors available for the study of coordination complexes. Ironically, the M(II) and M(III) complexes of acetylacetone remain a subject of controversy among coordination chemists, at least so far as their infrared spectra are concerned.

In earlier infrared studies, attention was directed primarily at the mid-infrared region. More recently, research has been extended to the region below 700 cm^{-1} where the metal-ligand vibrations are expected to occur. In 1960, Nakamoto and Martell[94] carried out an approximate normal coordinate analysis on $[Cu(AA)_2]$. At this time no spectral data below 400 cm^{-1} were available and no isotopically-labelled metal acetylacetonates had been studied. A number of investigators[95-97] have recently extended measurements to the far-infrared region, and the spectra of metal complexes containing ^{13}C- and ^{18}O-labelled acetylacetonates,[35,98] as well as their metal ion-labelled[99] analogues, have been reported.

Recent work in this laboratory has included studies of the adducts formed between first row transition M(II) acetylacetonates and monodentate nitrogen donor ligands such as alkylamines, anilines and pyridines.[22,100] The complexes generally have the formula *trans*-$[M(AA)_2B_2]$. Bidentate ligands such as 1,10-phenanthroline, 2,2'-bipyridine and 2,2'-biquinoline[8] which form complexes of the type *cis*-$[M(AA)_2(B\text{-}B)]$ have also received attention. Many heterocyclic bases including imidazole (Him), pyrazine (pz), pyrimidine (pm) and pyridazine (pd) are known to form stable adducts with M(II) β-ketoenolates.[101-105] These heterocycles

(with the exception of imidazole) have the capacity to form neutral polymers in which each of the two nitrogen donors are bonded to discrete planar $M(AA)_2$ units and formulated $[M(AA)_2B]_n$.

Assignments of the metal-ligand stretching frequencies in the bis (pyridine) adducts of Ni(II) acetylacetonate[106] have been established by observing the shifts induced by metal ion substitution and by deuteration of the pyridine adduct. In view of the success achieved and because virtually no infrared data concerning the adducts formed between Him, pz, pm and pd and M(II) acetylacetonates are available, the present work was undertaken to determine the infrared spectra of these complexes (700 - 140 cm^{-1}) and to use these techniques for assignment of the metal-ligand vibrations. Some eighteen adducts of Co(II), Ni(II) and Zn(II) acetylacetonates were synthesized and the Him and pz adducts were labelled with the deuterated base to facilitate assignments of the M-N stretching and bending modes. It has also proved possible to distinguish M-N vibrations by ^{15}N-labelling of the heterocyclic nitrogen atom.[106] However, a much greater mass difference is achieved by employing the deuterated base which, apart from allowing unambiguous assignments of the internal ring deformations, may generate low frequency shifts in νM-N of as much as 10 cm^{-1}.

7. METAL CHELATES OF SALICYLALDEHYDE

Many of the reactions of salicylaldehyde as a bidentate ligand are rather similar to those of acetylacetone. However, the complexes of salicylaldehyde do not have the stability of the corresponding acetylacetonates. This has been attributed[107] to the interference of resonance in the chelate ring which results from the presence of the *o*-phenylene ring of salicylaldehyde. This has been illustrated by comparing the formation constants[107] of the Cu(II) chelates of acetylacetone and salicylaldehyde. Stability constants of M(II) complexes of salicylaldehyde have been determined by several workers[108-109] and the relationship between proton dissociation constants and stability constants of substituted salicylaldehydes has been studied.[110-111] Crystal structure determinations,[112-118] magnetic measurements[117-119] and a discussion of the absorption spectra[120] in terms of σ- and π-bonding of various salicylaldehydate complexes have been reported.

The first infrared study of salicylaldehydate complexes was carried out by Bellamy and Branch,[121] who noted from the values of νC-O and νC=O, that the phenoxide and carbonyl groups appear to retain their independent character on chelation by contrast with acetylacetone, where electron delocalization tends to equalize the C ⟷ O bond orders. Graddon and Mockler[122-125] have reported νC=O values for many bis-(*o*-hydroxyarylcarbonyl) metal(II) compounds to be in the 1660-1600 cm^{-1} region. In a later study[126] the infrared spectra of some M(I), M(II) and M(III) complexes were extended down to 300 cm^{-1}, and assignments of νM-O were made by comparison with the analogous acetylacetonates.

In a recent investigation[127] in this laboratory, the effects of metal ion substitution and ligand substitution on the spectra (1700-250 cm^{-1})

of the Co(II), Ni(II) and Cu(II) complexes of salicylaldehyde were studied. It was found that replacement of one metal(II) ion by another of higher CFSE, or replacement of one ligand substituent by another of greater electron releasing resonance capacity, has the effect of increasing the M-O and phenolic C-O bond orders at the expense of the aldehydic C=O bonding. These effects were considered[127] to cause increased electron delocalization in the chelate ring, thus facilitating metal-ligand π-bonding. Formation of bis(pyridine) adducts was found[127] to cause depletion of electron density in the M-O and C=O bonds relative to the anhydrous complexes or bis(aquo) adducts, in accordance with the π-electron acceptor properties of pyridine.

The aim of the present study was to extend the spectra of the complexes of Co(II) and Ni(II) salicylaldehydates to 140 cm^{-1} and to extend earlier work[127] to incorporate the complexes of Zn(II) salicylaldehydate. In order to facilitate band assignments, the effects of adduct formation on the infrared spectra of these complexes have been studied. For this purpose the nitrogen-donor bases pyridine (py), imidazole (Him), pyrazine (pz) and pyrimidine (pm) were employed. The effects of bis(aquo) adduct formation on the spectra of the anhydrous complexes are also discussed. In addition, the deuterated species, py-d_5 , pz-d_4 and Him-d_4 have assisted in providing reliable assignments of νM-N in the spectra of these adducts.

8. BAND ASSIGNMENTS IN THE INFRARED SPECTRA OF METAL(II) CHELATES OF AMINO ACIDS BY ISOTOPIC LABELLING

Vibrational spectroscopic techniques have been widely applied to systems of biological interest. Such studies when applied to metal-amino acid systems, are of importance since the identification of metal-ligand vibrations provides information on both the nature of the metal binding site and the strength of the metal-ligand interaction. This information, obtained from such simple models as these, may be of value in the study of more complex metallopeptide and metalloprotein systems.

Isotopic labelling of the ligand atoms has led to reliable band assignments in the infrared spectra of glycine[128-130] and its Ni(II) and Cu(II) complexes.[29-30] Assignments in the spectrum of *cis*-$[Cu(gly)_2(H_2O)]$ have been based on deuteration studies,[131] isotopic ^{65}Cu-substitution,[132] and recently[29] an elaborate study was made in which the glycinate ligand was labelled using ^{15}N-, ^{18}O-and 1-^{13}C-isotopic substitution. A similar study[30] has been made on *trans*-$[Ni(gly)_2(H_2O)_2]$. Crystal structure determinations indicate that the dimensions of the glycinate residues in most glycinate complexes[133-134] are almost identical and are very close to those of the free ligand. However, because of differences in symmetry (structure and coordination number) assignments in the spectra of *trans*-$[Pt(gly)_2]$ and *cis*-$[Ni(gly)_2(Him)_2]$ are difficult to accomplish by direct comparison with those reported[30] for *trans*-$[Ni(gly)_2(H_2O)_2]$.

There exists some measure of disagreement on the assignment of the infrared bands in the spectra of glycinate and other amino acid complexes.[131,136-138] One view assumes low covalency in the M-O bonds[136,137] with essentially monodentate M-N coordination of the amino acid while another[131,138] considers the M-O bonds to be highly covalent.

Independent normal coordinate analyses[131,136] have not succeeded in unambiguously resolving the problem, the two sets of assignments showing considerable differences.

In the present work, the infrared spectra (4000-140 cm^{-1}) of *trans*-[Pt(gly)$_2$], *cis*-[Ni(gly)$_2$(Him)$_2$] and *trans*-[Pt(L-ala)$_2$] were studied. Each band in the spectra of the glycinate complexes has been assigned on the basis of the shifts induced by ^{18}O-, ^{15}N-, 1-^{13}C-, 2-^{13}C-, 2,2-d_2- and N,N-d_2-labelling of the glycinate ligand. The results show that the N-H, C-H, C=O and Pt-O stretching vibrations and the CH_2 scissoring, CH_2 twisting and NH_2 twisting modes in the spectrum of *trans*-[Pt(gly)$_2$] are vibrationally pure but all other bands represent vibrationally coupled modes. The spectra reveal also that certain earlier assignments require revision.

While the above forms of isotopic labelling yield assignments for the internal glycinate modes in the spectrum of *cis*-[Ni(gly)$_2$(Him)$_2$] as well as the nickel-oxygen and nickel-nitrogen stretching and bending modes, deuteration of imidazole (Him-d_3) provides assignments for the internal modes of the coordinated imidazole rings and for the nickel-imidazole vibrations. This complex represents the first example to be studied by this technique in which all of the donor atoms in an heterocyclic adduct of a metal glycinate complex have the *cis*-configuration. The results, combined with those of previous multiple isotopic labelling studies on glycinate complexes, enable some general conclusions to be reached on the infrared spectra of these complexes.

Less attention has been given to the infrared spectra of alanine complexes than those of glycine. The infrared spectra of *trans*-[Pt(L-ala)$_2$] and its ^{18}O-, ^{15}N- 2-d, 3-d_3- and N,N-d_2-labelled analogues have been determined. The spectral bands were assigned on the basis of the shifts induced by the various modes of isotopic labelling and by

substitution of Pd(II) for Pt(II). The labelling study reveals (again) that very few bands represent vibrationally pure modes and that a small increase in the complexity of the coordinated amino acid (on going from glycine to L-alanine) induces a large increase in the complexity of the spectrum.

9. METAL COMPLEXES OF GLYCYLGLYCINE

Infrared spectra of dipeptides have previously been investigated,[139-142] and extensive studies have been made on the interactions of metal ions with dipeptides in solution.[140,143-148] Results of these studies, which were largely confined to the effects of pH and pD variation on the infrared spectra in the 1700 - 1500 cm^{-1} region, have been discussed[143-148] in relation to coordinate bonding and formation constants. Reports on the mull spectra of M(II) peptide systems are sparse, although some of the complexes studied here have previously been investigated in the 1700 - 1400 cm^{-1} region. Attempts to use frequency differences[149] in the asymmetric and symmetric vibrations of the carboxylate group as an indication of the mode of carboxylate bonding have met with little success. There still exists some disagreement as to the nature of the functional groups coordinated to the metal as well as differences of opinion on the formulation of metal-peptide chelates.

The *trans*-amide group in dipeptides (which is invariably planar[150]) gives rise to characteristic absorption bands in the infrared spectrum, due to combinations of N-H, C=O and C-N stretching and bending motions. Typical frequencies for these highly coupled vibrations or "Amide Bands" for free peptides and their approximate assignments[150] are given in Table 1. The inherent complexity of the infrared spectra of dipeptides and their metal chelates is well known. It has been shown[151,152] that some relationship exists between the Amide A, B, II and III vibrations. When coordination of the peptide group to a metal ion occurs, the Amide II frequency increases, while the Amide B band[152] undergoes a corresponding high frequency shift, indicating some resonance effect between the two species.[151,152] A correspondingly low frequency shift of the Amide III

Table 1.

Band	ν cm^{-1}	Approximate assignment
Amide A	3300	νN-H
Amide B	3100	Amide II first overtone
Amide I	1660	νC=O
Amide II	1570	δi.p. N-H + νC-N
Amide III	1300	νC-N + δi.p. N-H
Amide IV	630	δi.p. O=C-N
Amide V	730	δo.o.p. N-H
Amide VI	600	δo.o.p. C=O

band indicates that the origins of the Amide II and III bands are also related.

The infrared spectra of sixteen first row transition metal(II) complexes of glycylglycine (gg) are reported here. For those complexes of known structure, structural correlations are possible on the basis of differences between their infrared band patterns. These correlations, together with information obtained from ^{15}N-labelled glycylglycine, are used to assign structures to related complexes, many of which do not appear to have previously been investigated.

II. EXPERIMENTAL

1. PHYSICAL METHODS

1.1 Infrared Spectra

Infrared spectra were determined as nujol mulls between caesium bromide or caesium iodide plates on a Beckman IR-12 spectrophotometer, and as nujol mulls between polyethylene plates on a Digilab FTS 16 B/D interferometer and a Perkin-Elmer 180 spectrophotometer. Infrared spectra of liquid heterocyclic ligands, acetylacetone and salicylaldehyde were determined as liquid films using the same window materials. The Digilab interferometer and Perkin-Elmer spectrophotometer were used mainly over the range 300-150 cm^{-1} whereas the Beckman IR-12 spectrophotometer was used for the 4000-250 cm^{-1} region. The wavenumber precision of the latter instrument is quoted by the manufacturers as 0.2 cm^{-1} at 200 cm^{-1}, 0.3 cm^{-1} at 400 cm^{-1}, 0.4 cm^{-1} at 740 cm^{-1}, 0.6 cm^{-1} at 1330 cm^{-1} and 0.7 cm^{-1} at 2220 cm^{-1}. The wavenumber reproducibility of the spectrophotometer is given by the manufacturers as 0.1 cm^{-1} at 200 cm^{-1}, 0.15 cm^{-1} at 400 cm^{-1}, 0.2 cm^{-1} at 740 cm^{-1}, 0.3 cm^{-1} at 1330 cm^{-1} and 0.35 cm^{-1} at 2220 cm^{-1}. For maximum precision, the frequencies were read directly from the wavenumber drum, not from the chart paper. Bands in the spectra of labelled compounds and their unlabelled analogues were repeated at least five times. Reproducibility of quoted frequencies is better than 0.5 cm^{-1}.

The Beckman IR-12 and Perkin-Elmer 180 spectrophotometers were calibrated against carbon dioxide, water vapour and polystyrene film.

1.2 Electronic Spectra

Electronic spectra were taken as solids supported on filter paper circles in the reflectance mode on a Beckman Dk-2A ratio recording spectrophotometer. The instrument was calibrated with a didymium filter.

1.3 Magnetic Measurements

Magnetic susceptibilities were determined at ambient temperatures on a Newport-Stanton Gouy magnetic balance. The instrument was calibrated with mercury(II) tetrathiocyanatocobaltate. Pascal's constants[153] were used to estimate the diamagnetism of the ligands. Accuracy was checked with copper(II) acetate (found: 1.43 B.M. at 293 K; reported[154]: 1.40 B.M. at 293 K).

1.4 Microanalyses

Microanalyses were performed on a Heraeus Universal Combustion Analyser Model CHN-Micro, by Mr. W.R.T. Hemsted of the Department of Organic Chemistry, University of Cape Town. The calculated values are based on the assumption that the effect of the mass change (due to labelling) on the heat conductivity of nitrogen or water vapour is negligible.

2. PREPARATION OF COMPOUNDS

The isotopically labelled ligands used in this study together with their commercial sources and reported isotopic purities are listed in Table 2.

Table 2.

Isotopically labelled ligand	Isotopic purity (atom %)	Commercial source
Imidazole-d_4	98	Merck, Sharp & Dohme (Canada) Ltd.
Imidazole-d_3[a]		
Imidazole-d_1[b]		
Pyridine-d_5	99	BOC Prochem Ltd.
Pyrazine-d_4[c]	84	Merck, Sharp & Dohme (Canada) Ltd.
^{18}O-glycine	78	BOC Prochem Ltd.
^{15}N-glycine	97	BOC Prochem Ltd.
1-^{13}C-glycine	91	BOC Prochem Ltd.
2-^{13}C-glycine	91	BOC Prochem Ltd.
N,N-d_2-glycine[b]		
2,2-d_2-glycine	97	Merch, Sharp & Dohme (Canada) Ltd.
^{18}O-L-alanine	76	BOC Prochem Ltd.
^{15}N-L-alanine	95	Merck, Sharp & Dohme (Canada) Ltd.
2-d,3-d_3-L-alanine	98	Merck, Sharp & Dohme (Canada) Ltd.
N,N-d_2-L-alanine[b]		
^{15}N-glycylglycine	99	Stohler Isotope Chemicals.

[a] Obtained by successive recrystallization of imidazole-d_4 from water.
[b] Obtained under inert conditions by successive recrystallization from D_2O.
[c] Infrared spectrum gives reason to believe that the compound has less than the reported isotopic purity.

2.1 The Imidazole Complexes of Metal(II) Nitrates, Perchlorates and Halides

2.1.1 The Hexakis(Imidazole) Complexes of Metal(II) Nitrates and Perchlorates $[M(Him)_6](X)_2$ (M = Co, Ni, Zn, X = NO_3; M = Mn, Fe, Co, Ni, X = ClO_4) and $[Zn(Him)_5](ClO_4)_2$

The nitrate complexes (except for that of Zn(II)) were prepared[51,58,60-61,65] by slow addition of imidazole (0.003 mole) in water (2 ml) to a solution of the metal(II) nitrate (0.0005 mole) in water (2 ml). The precipitates were collected by filtration and washed with a small volume of cold water. The zinc(II) complex was crystallized from a concentrated ethonolic solution of the metal(II) nitrate (0.0005 mole) and imidazole (0.003 mole) which was left at room temperature for two days. The colourless crystals were collected by filtration and washed with cold ethanol. All complexes were dried under reduced pressure over silica gel.

Complexes of metal(II) perchlorates and $[Zn(Him)_5](ClO_4)_2$ were similarly prepared from aqueous solutions of imidazole (0.003 mole) and metal(II) perchlorate (0.0005 mole). The labelled complexes were similarly prepared from imidazole-d_4. The deuteroimine (ND) groups of imidazole-d_4 undergo rapid exchange in solution so that synthesis of the labelled complexes with imidazole-d_4 yields imidazole-d_3 complexes. Unless otherwise stated, this applies to all the labelled imidazole complexes studied here.

2.1.2 The Tetrakis(Imidazole) Complexes of Copper(II) and Zinc(II) Nitrates and Perchlorates

Both Copper(II) complexes[53,56,58,61] were readily precipitated as

blue or violet crystals for the perchloroate and nitrate, respectively, on combining imidazole (0.002 mole) in ethanol with the copper(II) salt (0.0005 mole) in ethanol. The zinc(II) complexes, being more soluble, were crystallized[54,61] by slow evaporation of concentrated solutions of imidazole (0.002 mole) and zinc(II) nitrate or perchlorate (0.0005 mole) in ethanol. All products were collected by filtration, washed with ethanol followed by acetone, and dried under reduced pressure over silica gel. The labelled complexes were similarily prepared using imidazole-d_4.

2.1.3 The Tetrakis(Imidazole) Complexes of Copper(II) Chloride, Bromide and Iodide

Crystals of the chloride and bromide complexes[58,61] were readily precipitated on combining imidazole (0.002 mole) in ethanol, with the appropriate copper(II) halide (0.0005 mole) in ethanol. The crystals were recovered by filtration, washed successively with ethanol and acetone and dried under reduced pressure over silica gel.

Solutions of copper(II) ions are normally reduced by iodide ions. It was found that in the presence of imidazole, the copper(II) ion is stable in solutions containing iodide ions. The stability of such solutions has been reported[50] to be both solvent and temperature dependent, reduction to Cu(I) being favoured in relatively non-polar solvents and by high temperatures. The complex $[Cu(Him)_4I_2]$ was prepared by a method similar to that reported.[50] An aqueous solution containing a slight excess of imidazole (0.0025 mole) was introduced, with stirring, to an aqueous solution of copper(II) chloride (0.0005 mole). On treating this clear blue solution with an excess of aqueous KI (0.0008 mole) a copious precipitate of the violet crystalline iodide complex was formed.

This was collected by filtration, washed with water and stored over silica gel. The complex showed no evidence of contamination with $[Cu(Him)_4Cl_2]$. Labelled complexes were similarly prepared using imidazole-d_4.

2.1.4 The Bis(Imidazole) Complexes $[M(Him)_2X_2]$ (M = Co, X = Cl, Br; M = Zn, X = Cl, Br)

Several preparative methods[58-59,61] for the cobalt(II) complexes have been reported. Thermal decomposition of hexakis(imidazole) cobalt(II) chloride (or bromide) yields the bis-complexes but their purity was questionable. The bis-complexes were therefore prepared by the following reported method.[61] To an ethanolic solution of the cobalt(II) halide (0.001 mole) was added with stirring, a solution of imidazole (0.002 mole) in ethanol. The volume of the resulting deep blue solution was reduced to a minimum by warming and a few drops of dichloromethane were added. Upon standing at $0^{o}C$ for two days, the royal blue crystals which were formed were filtered, washed with ice-cold ethanol followed by anhydrous ether and stored under reduced pressure over silica gel.

The chloride and bromide complexes of Zn(II) were prepared by reported methods.[49,62] Concentrated ethanolic solutions containing 0.002 mole imidazole and 0.001 mole zinc(II) halide were mixed and the solution allowed to stand overnight at room temperature. The crystals were collected by filtration, washed with ethanol and dried in vacuo over silica gel.

Labelled complexes were prepared from imidazole-d_4 according to the above methods.

2.2 The Complex Bis(nitrato)mono(pyrazine)copper(II)

The royal blue crystals were synthesised according to the literature method.[72] A concentrated aqueous solution of pyrazine (0.001 mole) and copper(II) nitrate (0.001 mole) was left to evaporate at room temperature. The crystals which separated were collected by filtration, washed with water and dried over silica gel. The labelled complex was similarly prepared using pyrazine-d_4.

2.3 The Imidazole, Pyrazine, Pyrimidine and Pyridazine Adducts of Metal(II) Acetylacetonates $[M(AA)_2(B)_n]$ (M = Co, Ni, n = 2, B = Imidazole, Pyridazine; M = Co, Ni, Zn, n = 1, B = Pyrazine, Pyrimidine; M = Co, Ni, n = 1, B = Pyridazine

Except for the bis(pyridazine) complexes, well-crystallized adducts were synthesised[102,104] from hot ethanolic solutions of the metal(II) acetylacetonate and heterocyclic base in the correct stoichiometric proportions. The products were collected by filtration, washed with ethanol followed by petroleum ether and dried over silica gel.

Preparation of the bis(pyridazine) adducts required recrystallization of the anhydrous metal(II) acetylacetonate from excess pyridazine. The adducts, once formed, are stable and were collected by filtration, washed with ethanol and dried over silica gel. Labelled adducts were similarly prepared from imidazole-d_4 in deuterated ethanol or pyrazine-d_4.

2.4 The Metal(II) Complexes of Salicylaldehyde [$M(Sal)_2$] (M = Co, Ni, Zn) and their Aquo, Imidazole, Pyridine, Pyrazine and Pyrimidine Adducts, [$M(Sal)_2(B)_n$] (M = Co, Ni, Zn, n = 2, B = H_2O, Pyridine; M = Co, Ni, n = 2, B = Imidazole; M = Co, Ni, Zn, n = 1, B = Pyrazine, Pyrimidine)

The bis(aquo) adducts were prepared[127] by the following general procedure. A solution of the ligand (0.02 mole) in methanol was treated with 20 ml of 1M sodium hydroxide. This solution was then added, dropwise, to a solution of metal(II) acetate in hot methanol. After allowing the solution to cool, the crystals were collected by filtration, washed thoroughly (methanol) and dried under reduced pressure over silica gel. When heated over silica gel at 130°C under reduced pressure, the bis(aquo) adducts yielded the anhydrous complexes.

The pyridine, imidazole, pyrazine and pyrimidine adducts were prepared by addition of the appropriate ligand in ethanol (in slight excess of the stoichiometric quantity) to a hot ethanolic solution of the bis(aquo) adduct. It was necessary to induce precipitation of the pyridine adducts by the addition of petroleum ether. The products were washed with a small volume of ethanol and stored over silica gel. The labelled adducts were similarly prepared from pyridine-d_5, imidazole-d_4 or pyrazine-d_4.

2.5 The Complex *Trans*-Bis(glycinato)Platinum(II)

The synthesis is similar to that reported.[155] An aqueous solution of glycine (0.002 mole) and K_2PtCl_4 (0.001 mole) was heated on a water bath and the pH of the solution adjusted to 6.0 by dropwise addition of 1M KOH. On evaporation of the water white crystals of the complex were formed which were collected by filtration,

washed with warm water, and dried over silica gel. The labelled analogues were similarly obtained from ^{15}N-, ^{18}O-, 1-^{13}C-, 2-^{13}C- and 2,2-d_2- labelled glycine. The N,N-d_2-labelled complex was similarly prepared in D_2O from samples of glycine (or 2,2-d_2-glycine) previously recrystallized from D_2O.

2.6 The *Trans*-Bis(L-Alaninato) Complexes of Platinum(II) and Palladium(II)

The complexes were prepared by the same method used for the synthesis of *trans*-[Pt(gly)$_2$]. The labelled analogues of *trans*-[Pt(L-ala)$_2$] were similarly obtained from ^{18}O-, ^{15}N- and 2-d, 3-d_3-L-alanine. The N,N-d_2-labelled complex was prepared in D_2O from a sample of L-alanine previously recrystallized from D_2O.

2.7 The Complex *Cis,cis*-Bis(Glycinato)*cis*-Bis(Imidazole) Nickel(II)

The complex may be synthesised according to the reported method.[156] Since discrete crystals of the complex were not required, the following procedure was followed using a stock supply of *trans*-[Ni(gly)$_2$(H$_2$O)$_2$]. A slight excess of imidazole (0.0025 mole) in ethanol was slowly introduced to a suspension of *trans*-[Ni(gly)$_2$(H$_2$O)$_2$] (0.001 mole) in hot ethanol. On continued heating, the blue solution turned purple and a deposit of *cis*-[Ni(gly)$_2$(Him)$_2$] formed. This was retrieved by filtration, washed with hot ethanol and dried under reduced pressure over silica gel. The preparation yields a complex, the infrared spectrum of which is

identical to that synthesised by the literature method.[156] The labelled complexes were similarly prepared from ^{18}O-, ^{15}N-, 1-^{13}C-, 2-^{13}C- and 2,2-d_2-glycine and imidazole-d_4. The deuteroimine (ND) groups of the imidazole-d_4 ring undergo exchange in solution so that synthesis of the labelled complex with imidazole-d_4 yields the imidazole-d_3 complex. The reaction cannot be carried out in ethanol-OD since this will induce deuteration of the amino group of glycine.

2.8 Metal(II) complexes of Glycylglycine

2.8.1 The complexes $[M(Hgg)X(H_2O)]$ with Hgg = $(NH_2CH_2CONHCH_2CO_2)^-$ (M = Mn, Co, Ni, Zn; X = Cl, Br) and $[Cu(Hgg)X]$ (X = Cl, Br)

Glycylglycine (0.001 mole) in hot ethanol was added (with stirring) to the metal(II) halide (0.0014 mole) in hot ethanol. The resultant precipitate was collected by filtration, washed (ethanol) and dried over silica gel. The labelled complexes were similarly prepared using ^{15}N-glycylglycine.

2.8.2 The complexes $[Cu(Hgg)Cl(H_2O)]$ and $[Cd(Hgg)Cl(H_2O)]$

Crystals of $[Cu(Hgg)Cl(H_2O)]$ were prepared by the following method.[149] An aqueous solution of glycylglycine (0.001 mole) was added to a solution of copper(II) chloride (0.0014 mole). The volume of the blue-green solution was reduced to a minimum by heating, and upon standing blue-green crystals were deposited which were collected by filtration, washed with ethanol and dried over silica gel. The labelled complex was similarly prepared from ^{15}N-glycylglycine.

Crystals of $[Cd(Hgg)Cl(H_2O)]$ were obtained[157] from an aqueous solution containing cadmium(II) chloride (0.001 mole) and glycylglycine (0.002 mole) whose pH was adjusted to 8 by addition of 0.1 M NaOH. Upon evaporation

of the clear solution white crystals were deposited which were collected by filtration, washed with ethanol and dried under reduced pressure over silica gel.

2.8.3 The complexes $Na_2[Ni(gg)_2].nH_2O$ where gg = $(NH_2CH_2CONCH_2CO_2)^{2-}$ (M = Mn, n = 2; M = Ni, n = 9; M = Zn, n = 5

The complex $Na_2[Ni(gg)_2].9H_2O$ was prepared by the addition of glycylglycine in ethanol to a hot aqueous suspension of nickel(II) carbonate. The mixture was heated with stirring for ½ hour before the excess nickel(II) carbonate was removed by filtration. Blue-green crystals precipitated after the filtrate had stood overnight. These were collected by filtration, washed (ethanol) and dried over silica gel.

The Mn(II) and Zn(II) complexes were prepared by the addition of glycylglycine (0.002 mole) in ethanol to an aqueous suspension of freshly prepared metal(II) hydroxide (0.001 mole). The mixture was heated gently (with stirring) until precipitation was complete. The products were collected by filtration, washed (ethanol) and dried over silica gel.

2.8.4 The complex $[Cu(gg)(H_2O)_2]$

The complex was synthesised according to the reported method.[144] A freshly prepared aqueous suspension of copper(II) hydroxide (0.001 mole) was treated with a solution of glycylglycine (0.001 mole). The excess cupric hydroxide was removed by filtration and the volume of the deep-blue filtrate reduced to a minimum. Upon standing crystals of the dihydrate were deposited which were recovered by filtration, washed with a small volume of water and dried over silica gel. The labelled analogue was similarly prepared using ^{15}N-glycylglycine.

III. RESULTS

1. ANALYSES OF COMPOUNDS

Table 3. Analytical data on the complexes $[M(Him)_6](NO_3)_2$, $[M(Him)_6](ClO_4)_2$ and $[Zn(Him)_5](ClO_4)_2$

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Co(Him)_6](NO_3)_2$	36.6	4.1	33.2	36.6	4.0	33.2
$[Co(Him\text{-}d_1)_6](NO_3)_2$	36.2	4.0	32.8	36.3	4.0	33.0
$[Co(Him\text{-}d_3)_6](NO_3)_2$	35.5	4.0	32.2	35.5	4.0	32.0
$[Co(Him\text{-}d_4)_6](NO_3)_2$	35.1	3.9	31.9	35.1	4.0	32.0
$[Ni(Him)_6](NO_3)_2$	36.6	4.1	33.2	36.6	4.0	33.2
$[Ni(Him\text{-}d_3)_6](NO_3)_2$	35.5	4.0	32.2	35.6	4.0	32.0
$[Ni(Him\text{-}d_4)_6](NO_3)_2$	35.1	3.9	31.9	35.3	4.0	32.0
$[Zn(Him)_6](NO_3)_2$	36.2	4.0	32.8	36.1	4.1	32.7
$[Zn(Him\text{-}d_3)_6](NO_3)_2$	35.1	3.9	31.8	35.2	4.0	32.0
$[Mn(Him)_6](ClO_4)_2$	32.6	3.7	25.4	32.6	3.7	25.3
$[Mn(Him\text{-}d_3)_6](ClO_4)_2$	31.8	3.6	27.7	31.7	3.6	27.7
$[Fe(Him)_6](ClO_4)_2$	32.6	3.6	25.3	31.6	3.6	25.4
$[Fe(Him\text{-}d_3)_6](ClO_4)_2$	31.7	3.6	24.7	31.8	3.5	24.7
$[Co(Him)_6](ClO_4)_2$	32.4	3.6	25.2	32.4	3.6	25.0
$[Co(Him\text{-}d_3)_6](ClO_4)_2$	31.6	3.5	24.6	31.8	3.5	24.7
$[Ni(Him)_6](ClO_4)_2$	32.5	3.6	25.2	32.4	3.6	25.1
$[Ni(Him\text{-}d_3)_6](ClO_4)_2$	31.6	3.5	24.6	31.7	3.6	24.6
$[Zn(Him)_5](ClO_4)_2$	29.8	3.3	23.2	30.0	3.3	23.3
$[Zn(Him\text{-}d_3)_5](ClO_4)_2$	29.1	3.3	22.6	29.2	3.2	22.7

Table 4: Analytical data on the tetrakis(imidazole) complexes of metal(II) perchlorates and nitrates

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Cu(Him)_4(ClO_4)_2]$	27.0	3.0	21.0	27.0	3.0	20.7
$[Cu(Him\text{-}d_3)_4(ClO_4)_2]$	26.4	2.9	20.5	26.4	3.0	20.4
$[Zn(Him)_4](ClO_4)_2$	26.9	3.0	20.9	26.9	3.0	20.9
$[Zn(Him\text{-}d_3)_4](ClO_4)_2$	26.3	2.9	20.4	26.2	2.9	20.4
$[Cu(Him)_4(NO_3)_2]$	31.3	3.5	30.5	31.4	3.5	30.3
$[Cu(Him\text{-}d_3)_4(NO_3)_2]$	30.5	3.4	29.7	30.5	3.4	29.8
$[Zn(Him)_4(NO_3)_2]$	31.2	3.5	30.3	31.1	3.5	30.1
$[Zn(Him\text{-}d_3)_4(NO_3)_2]$	30.4	3.4	29.6	30.6	3.4	29.5

Table 5. Analytical data on the tetrakis(imidazole) complexes of copper(II) halides

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Cu(Him)_4Cl_2]$	35.4	4.0	27.5	35.3	4.0	27.3
$[Cu(Him\text{-}d_3)_4Cl_2]$	34.4	3.9	26.8	34.5	3.9	26.8
$[Cu(Him)_4Br_2]$	29.1	3.3	22.6	29.1	3.3	22.5
$[Cu(Him\text{-}d_3)_4Br_2]$	28.4	3.2	22.1	28.3	3.2	22.0
$[Cu(Him)_4I_2]$	24.4	2.7	19.0	24.4	2.7	19.2
$[Cu(Him\text{-}d_3)_4I_2]$	24.0	2.7	18.6	24.2	2.7	18.7

Table 6. Analytical data on the bis(imidazole) complexes of metal(II) halides

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Co(Him)_2Cl_2]$	27.1	3.0	21.1	27.1	3.0	20.0
$[Co(Him\text{-}d_3)_2Cl_2]$	26.5	3.0	20.6	26.6	3.0	20.5
$[Co(Him)_2Br_2]$	20.3	2.3	15.8	20.3	2.3	15.9
$[Co(Him\text{-}d_3)_2Br_2]$	20.0	2.2	15.5	20.1	2.3	15.7
$[Zn(Him)_2Cl_2]$	26.5	3.0	20.6	26.3	3.1	20.3
$[Zn(Him\text{-}d_3)_2Cl_2]$	25.9	2.9	20.1	25.5	3.0	20.0
$[Zn(Him)_2Br_2]$	19.9	2.2	15.5	20.1	2.3	15.7
$[Zn(Him\text{-}d_3)_2Br_2]$	19.6	2.2	15.2	19.7	2.3	15.4

Table 7. Analytical data on the complex $[Cu(NO_3)_2(pz)]_n$ and its pz-d_4 analogue

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Cu(NO_3)_2(pz)]_n$	18.0	1.5	21.0	18.0	1.5	21.0
$[Cu(NO_3)_2(pz\text{-}d_4)]_n$	17.7	1.5	20.6	17.6	1.4	20.5

Table 8. Analytical data on the heterocyclic base adducts of metal(II) acetylacetonates and their deuterated analogues

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Co(AA)_2(Him)_2]$	48.9	5.6	14.3	48.9	5.5	14.2
$[Co(AA)_2(Him\text{-}d_4)_2]$	47.9	4.5	14.0	47.9	4.5	14.2
$[Ni(AA)_2(Him)_2]$	48.9	5.6	14.2	48.9	5.6	14.2
$[Ni(AA)_2(Him\text{-}d_4)_2]$	47.9	4.5	14.0	47.8	4.5	14.0
$[Co(AA)_2(pz)]_n$	49.9	5.4	8.3	49.9	5.5	8.4
$[Co(AA)_2(pz\text{-}d_4)]_n$	49.3	5.3	8.2	49.4	5.5	8.2
$[Ni(AA)_2(pz)]_n$	49.9	5.4	8.3	49.9	5.4	8.4
$[Ni(AA)_2(pz\text{-}d_4)]_n$	49.3	5.3	8.2	49.3	5.4	8.4
$[Zn(AA)_2(pz)]_n$	48.9	5.3	8.2	48.8	5.2	8.1
$[Zn(AA)_2(pz\text{-}d_4)]_n$	48.4	5.2	8.1	48.3	5.1	8.0
$[Co(AA)_2(pm)]_n$	49.9	5.4	8.3	49.8	5.4	8.3
$[Ni(AA)_2(pm)]_n$	49.9	5.4	8.3	49.8	5.4	8.3
$[Zn(AA)_2(pm)]_n$	48.9	5.3	8.2	49.9	5.3	8.2
$[Co(AA)_2(pd)_2]$	51.8	5.3	13.4	51.8	5.3	13.4
$[Ni(AA)_2(pd)_2]$	51.8	5.3	13.4	51.8	5.3	13.4
$[\{Co(AA)_2\}_2(pd)]$	48.5	5.4	4.7	48.5	5.4	4.7
$[\{Ni(AA)_2\}_2(pd)]$	48.5	5.4	4.7	48.6	5.4	4.7

Table 9. Analytical data on the M(II) chelates of salicylaldehyde and their heterocyclic base adducts

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Co(Sal)_2]$	55.8	3.3		55.4	3.3	
$[Ni(Sal)_2]$	55.9	3.3		55.4	3.3	
$[Zn(Sal)_2]$	54.7	3.3		54.8	3.3	
$[Co(Sal)_2(H_2O)_2]$	49.9	4.2		50.0	4.3	
$[Ni(Sal)_2(H_2O)_2]$	49.9	4.2		49.8	4.1	
$[Zn(Sal)_2(H_2O)_2]$	48.9	4.1		48.2	3.9	
$[Co(Sal)_2(py)_2]$	62.7	4.4	6.1	62.7	4.4	5.9
$[Co(Sal)_2(py\text{-}d_5)_2]$	61.4	4.3	6.0	61.0	4.5	5.9
$[Ni(Sal)_2(py)_2]$	62.8	4.4	6.1	62.6	4.3	6.2
$[Ni(Sal)_2(py\text{-}d_5)_2]$	61.4	4.3	6.0	61.5	4.3	6.0
$[Zn(Sal)_2(py)_2]$	61.9	4.3	6.0	61.5	4.4	5.6
$[Zn(Sal)_2(py\text{-}d_5)_2]$	60.8	4.2	5.9	60.0	4.5	5.8
$[Co(Sal)_2(Him)_2]$	55.0	4.1	12.8	54.9	4.1	12.7
$[Co(Sal)_2(Him\text{-}d_4)_2]$	54.0	4.1	12.6	53.7	4.3	12.5
$[Ni(Sal)_2(Him)_2]$	55.0	4.1	12.8	54.9	4.1	12.9
$[Ni(Sal)_2(Him\text{-}d_4)_2]$	54.0	4.1	12.6	54.0	4.4	12.5
$[Co(Sal)_2(pz)]_n$	56.7	3.7	7.3	56.6	3.7	7.2
$[Co(Sal)_2(pz\text{-}d_4)]_n$	56.1	3.7	7.3	56.0	3.5	7.3
$[Ni(Sal)_2(pz)]_n$	56.7	3.7	7.3	56.5	3.7	6.9
$[Ni(Sal)_2(pz\text{-}d_4)]_n$	56.1	3.6	7.3	56.3	3.8	7.0

continued/

Table 9 continued/

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Zn(Sal)_2(pz)]_n$	55.8	3.6	7.2	56.5	3.7	6.9
$[Zn(Sal)_2(pz\text{-}d_4)]_n$	55.2	3.6	7.1	55.5	3.5	7.4
$[Co(Sal)_2(pm)]_n$	56.7	3.7	7.3	56.5	3.7	7.4
$[Ni(Sal)_2(pm)]_n$	56.7	3.7	7.3	56.3	3.7	7.3
$[Zn(Sal)_2(pm)]_n$	55.8	3.6	7.2	55.8	3.6	7.0

Table 10. Analytical data on the complex *trans*-$[Pt(gly)_2]$ and its isotopically labelled analogues

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
trans-$[Pt(gly)_2]$	14.0	2.4	8.2	14.0	2.4	8.2
trans-$[Pt(^{18}O\text{-}gly)_2]$	13.7	2.3	8.0	13.7	2.3	8.0
trans-$[Pt(^{15}N\text{-}gly)_2]$	13.9	2.3	8.1	13.9	2.4	8.2
trans-$[Pt(1\text{-}^{13}C\text{-}gly)_2]$	14.0	2.3	8.1	14.3	2.3	8.1
trans-$[Pt(2\text{-}^{13}C\text{-}gly)_2]$	14.0	2.3	8.1	14.4	2.3	8.1
trans-$[Pt(2,2\text{-}d_2\text{-}gly)_2]$	13.8	2.3	8.0	13.8	3.5	8.0

Table 11. Analytical data on the complex *cis*-$[Ni(gly)_2(Him)_2]$ and its isotopically labelled analogues

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
cis-$[Ni(gly)_2(Him)_2]$	35.0	4.7	24.5	34.8	4.5	24.2
cis-$[Ni(^{18}O\text{-gly})_2(Him)_2]$	34.2	4.6	23.9	34.1	4.5	24.0
cis-$[Ni(^{15}N\text{-gly})_2(Him)_2]$	34.8	4.7	24.4	34.8	4.6	24.5
cis-$[Ni(1\text{-}^{13}C\text{-gly})_2(Him)_2]$	34.8	4.7	24.4	34.8	4.7	24.5
cis-$[Ni(2\text{-}^{13}C\text{-gly})_2(Him)_2]$	34.8	4.7	24.4	34.7	4.7	24.3
cis-$[Ni(2,2\text{-}d_2\text{-gly})_2(Him)_2]$	34.6	4.6	24.2	34.5	4.5	24.2
cis-$[Ni(gly)_2(Him\text{-}d_3)_2]$	34.4	4.6	24.1	34.4	4.5	24.0

Table 12. Analytical data on the complex *trans*-$[Pt(L\text{-ala})_2]$ and its isotopically labelled analogues

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
trans-$[Pt(L\text{-ala})_2]$	19.4	3.3	7.5	19.2	3.1	7.3
trans-$[Pt(^{18}O\text{-L-ala})_2]$	19.0	3.2	7.4	19.1	3.1	7.4
trans-$[Pt(^{15}N\text{-L-ala})_2]$	19.3	3.2	7.5	19.2	3.2	7.5
trans-$[Pt(2\text{-}d,3\text{-}d_3\text{-L-ala})_2]$	19.0	3.2	7.4	19.0	3.2	7.5
trans-$[Pd(L\text{-ala})_2]$	25.5	4.3	9.9	25.5	4.3	10.0

Table 13. Analytical data on the M(II) halide complexes of glycylglycine

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
[Mn(Hgg)Cl(H_2O)]	20.1	3.8	11.7	20.1	3.7	11.5
[Co(Hgg)Cl(H_2O)]	19.7	3.7	11.5	19.9	3.8	11.7
[Co(^{15}N-Hgg)Cl(H_2O)]	19.6	3.7	11.4	19.6	3.7	11.5
[Ni(Hgg)Cl(H_2O)]	19.7	3.7	11.5	19.6	3.6	11.5
[Ni(^{15}N-Hgg)Cl(H_2O)]	19.6	3.7	11.4	19.5	3.6	11.4
[Cu(Hgg)Cl(H_2O)]	19.4	3.7	11.3	19.4	3.7	11.3
[Cu(^{15}N-Hgg)Cl(H_2O)]	19.2	3.6	11.2	19.2	3.5	11.2
[Zn(Hgg)Cl(H_2O)]	19.2	3.6	11.2	19.2	3.5	11.0
[Mn(Hgg)Br(H_2O)]	16.9	3.2	9.9	16.8	3.2	10.0
[Co(Hgg)Br(H_2O)]	16.7	3.1	9.7	16.8	3.1	9.8
[Co(^{15}N-Hgg)Br(H_2O)]	16.6	3.1	9.7	16.5	3.1	9.7
[Ni(Hgg)Br(H_2O)]	16.7	3.2	9.7	16.7	3.2	9.5
[Ni(^{15}N-Hgg)Br(H_2O)]	16.6	3.1	9.7	16.5	3.2	9.8
[Cu(Hgg)Br(H_2O)]	16.4	3.1	9.6	16.4	3.1	9.6
[Cu(^{15}N-Hgg)Br(H_2O)]	16.3	3.1	9.5	16.4	3.1	9.5
[Cu(Hgg)Cl]	20.9	3.1	12.2	20.8	3.1	12.2
[Cu(^{15}N-Hgg)Cl]	20.7	3.0	12.1	20.6	3.0	12.0
[Cu(Hgg)Br]	17.5	2.6	10.2	17.6	2.6	10.1
[Cu(^{15}N-Hgg)Br]	17.4	2.5	10.1	17.4	2.4	10.0

Table 14. Analytical data on the M(II) complexes of glycylglycine

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$Na_2[Mn(gg)_2]\cdot 2H_2O$	24.2	4.1	14.1	24.5	4.8	14.0
$Na_2[Ni(gg)_2]\cdot 9H_2O$	18.2	5.7	10.6	18.1	5.7	10.5
$Na_2[Zn(gg)_2]\cdot 5H_2O$	20.8	4.8	12.1	21.1	5.1	12.2
$[Cu(gg)(H_2O)_2]$	20.9	4.4	12.2	21.2	4.6	12.1
$[Cu(gg)(H_2O)](H_2O)$	19.4	4.9	11.3	19.4	4.9	11.3

2. INFRARED RESULTS

All values are cm^{-1}.

Table 15. Frequencies, ν^D/ν^H ratios and band assignments[a] in the infrared spectrum of Imidazole and its d_1-, d_3- and d_4-analogues

Him	Him-d_1	Him-d_3	Him-d_4	ν^{D_1}/ν^{H_4}	ν^{D_3}/ν^{H_4}	ν^{D_4}/ν^{H_4}	Species	Assignment
3143	3142		2354	1.0	0.76	0.75	A^1	νC-H
3123	3121	2335	2334	1.0	0.75	0.75	A^1	νC-H
3123	3121	2320	2323	1.0	0.75	0.74	A^1	νC-H
3100	3098							
	3020							
	2909							
2800	2150	2850	2140	0.77	1.0	0.76	A^1	νN-H
1573	1538	1507	1510					Comb.
		1468						
1541	1497	1460	1461	0.97	0.95	0.95	A^1	νring
		1454	1457					
	1474	1443	1434					
1490	1442	1423	1414	0.97	0.96	0.95	A^1	νring
	1353^{sh}							
1450	1348	1412	1338	0.93	0.97	0.92	A^1	νring
		1397						
		1340						
		1317	1317					
		1305						
		1292						
		1281						
	1325^{sh}	1274	1273					
1323	1319	1265	1260	1.0	0.96	0.96	A^1	νring
	1303							
	1260	1244	1244					
	1248							
1260	1243^{sh}	959	947	0.99	0.76	0.75	A^1	δC-H
1243	916	1212	914	0.74	0.98	0.74	A^1	δN-H
	1209	1198	1195[b]					
		1178	1178					
		1159						
1174	1140							Comb.
1145								
1140	1126	1116^{sh}	1106	0.99	0.97	0.97	A^1	νring
		1105						
	1110^{sh}	854	849					
1099	1103^{sh}	834	833	1.0	0.77	0.77	A^1	δC-H
	1086	1049	1048					
		807	804					
1052	1060	791	796^{sh}	1.0	0.76	0.76	A^1	δC-H
			1018					
			990					

Table 15 continued.

Him	Him-d_1	Him-d_3	Him-d_4	ν^{D_1}/ν^{H_4}	ν^{D_3}/ν^{H_4}	ν^{D_4}/ν^{H_4}	Species	Assignment
972								Comb.
934[c]	554	920	566	0.60	0.99	0.61	A^{11}	γN-H
934	964	959	953	1.03	1.03	1.02	A^{1}	δring
924	927	769 763[sh]	768 760	1.0	0.83	0.83	A^{11}	γC-H
894	895	879 867	881	1.0	0.98	0.99	A^{1}	δring
835	838	672	666	1.0	0.80	0.80	A^{11}	γC-H
827	831	656						
755	758	597	597	1.0	0.78	0.78	A^{11}	γC-H
736	740	569	586					
		729	728					
	721	721	724					
657	660 648	547	547	1.0	0.83	0.83	A^{11}	γring
619	622 610	522	521	1.0	0.84	0.84	A^{11}	γring
174[w]								Translational lattice mode

a Assignments based on those of Perchard *et al.*[69-71]

b Mean of doublet.

c Frequency of γN-H estimated[70] within this region.

sh Shoulder.

w Weak.

Table 16. Frequencies, ratios ν^D / ν^H and band assignment in the infrared spectra of $[M(Him)_6](NO_3)_2$, (M = Co(II), Ni(II) or Zn(II))

$[Co(Him)_6](NO_3)_2$				$[Ni(Him)_6](NO_3)_2$			$[Zn(Him)_6](NO_3)_2$					
Him	$-d_1$	$-d_3$	$-d_4$	Him	$-d_3$	$-d_4$	Him	$-d_3$	ν^{D_1}/ν^{H_4}	ν^{D_3}/ν^{H_4}	ν^{D_4}/ν^{H_4}	Assignment
3185	2403 2389	3185	2393 2375	3173	3173	2398 2380	3100	3100	0.75	1.0	0.75	νN-H
3135	3135	2374		3135	2378		3134	2384	1.0	0.76	0.74±0.01	νC-H
3135	3135	2352	2331	3135	2353	2337	3134	2350	1.0	0.75	0.74±0.01	νC-H
3135	3135	2332		3135	2336		3134	2340	1.0	0.75±0.01	0.74±0.01	νC-H
1536	1536	1489 1473	1485 1474	1540	1489 1474	1483 1477	1537	1490	1.0	0.96±0.01	0.96	νring
1505 1490	1505 1488	1445	1447	1503 1490^{sh}	1447	1449	1505^{sh} 1490	1448	1.0	0.96±0.01	0.97	νring
1455^{sh}	1455^{sh}	1455^{sh}	1455^{sh}	1460^{sh}	1460^{sh}	1460^{sh}						
1436	1436	1340^{sh}	1348^{sh} 1431	1439	1359^{sh}	1359^{sh} 1431	1439	1350	1.0	0.94±0.01	0.93±0.01	νring
1374	1374	1373	1373	1373	1373	1373	1374	1374				$\nu_3 NO_3$
1323	1323	1285 1268	1283 1265	1326	1290 1273	1290 1271	1324	1290 1270	1.0	0.96±0.01	0.96±0.01	νring
1252	1252 1243	941	941	1255	944	944	1247	941	1.0	0.75	0.75	δC-H
1232	918 905	1187 1178	914	1235	1191 1182	918	1234	1195 1178	0.74	0.96	0.74	δN-H
			1187			1191						
1179 1170	1180 1171	1155	1167 1155	1183 1174	1160	1173 1161	1180 1172	1158				Comb.
1136	1144 1136	1112	1112	1141	1117	1119	1138	1112	1.0	0.98	0.98	νring
1101 1095	1112 1095	890 874	886 873	1104 1099	894 877	891 877	1102 1096	890 874	1.0	0.80	0.80	δC-H
1072 1067^{sh}	1072 1067^{sh}	818	814	1072	821	818	1073 1069^{sh}	817	1.0	0.76±0.01	0.76	δC-H
			996^{W}			1001^{W}						
970^{W}				977^{W}								Comb.
(939)^{a}	570 558	899	561^{sh}	(938)^{a}	901	566^{sh}	(935)^{a}	890^{b}	0.60	0.95±0.01	0.60	γN-H

Table 16 continued.

[Co(Him)$_6$](NO$_3$)$_2$				[Ni(Him)$_6$](NO$_3$)$_2$			[Zn(Him)$_6$](NO$_3$)$_2$		ν^{D_1}/ν^{H_4}	ν^{D_3}/ν^{H_4}	ν^{D_4}/ν^{H_4}	Assignment
Him	-d_1	-d_3	-d_4	Him	-d_3	-d_4	Him	-d_3				
939[c]	962	969[sh] 963	969[sh] 958	938	973 965	975 962	935	971 962	1.02	1.03	1.03	δring
939[c]	939	723	723	938[c]	726	726	935[c]	726	1.0	0.77±0.01	0.77	γC-H
918	876	840	835	921	845	839	920	840	0.95	0.91±0.01	0.91	δring
871							870					
861							861	862				
844	843	657	657	848	662	663	848	667	1.0	0.78±0.01	0.78	γC-H
825	825	818[d]	814[d]	827	821[d]	818[d]	828	817[d]				ν_2NO_3
773[w]	771[w]	771[w]	771[w]	770[w]	770[w]	770[w]	770[w]	770[w]				
760[w]	760[w]	760[w]	760[w]	760[w]	760[w]	760[w]	760[w]	760[w]				
746	745	590 577	590 576	747	594 581	594 580	749	592 579	1.0	0.78±0.01	0.78±0.01	γC-H
710	710	710	710	715	715	715	712	712	1.0			ν_4NO_3
666	666	563	561	670	568	566	667	564	1.0	0.85	0.84	γring
614	614	521	520	616	524	524	616	520	1.0	0.84±0.01	0.85	γring
238		235		261	257		200	194				νasym. M-N
201		193		212	205		159	150				δ_τ+δM-N-C
172		164		185	175							δ_τ+δM-N-C

a Frequency of γN-H estimated within this region.
b γN-H masked by band at 890 cm^{-1}.
c γC-H and δring coincident at this wavenumber.
d Nitrate vibration in spectra of Him-d_3 and Him-d_4 are coincident with δC-D, hence the low frequency shift and intensity change on going from the unlabelled spectrum to that of Him-d_3 and Him-d_4.
sh Shoulder.
w Weak.
δ_τ Metal-imidazole torsion.

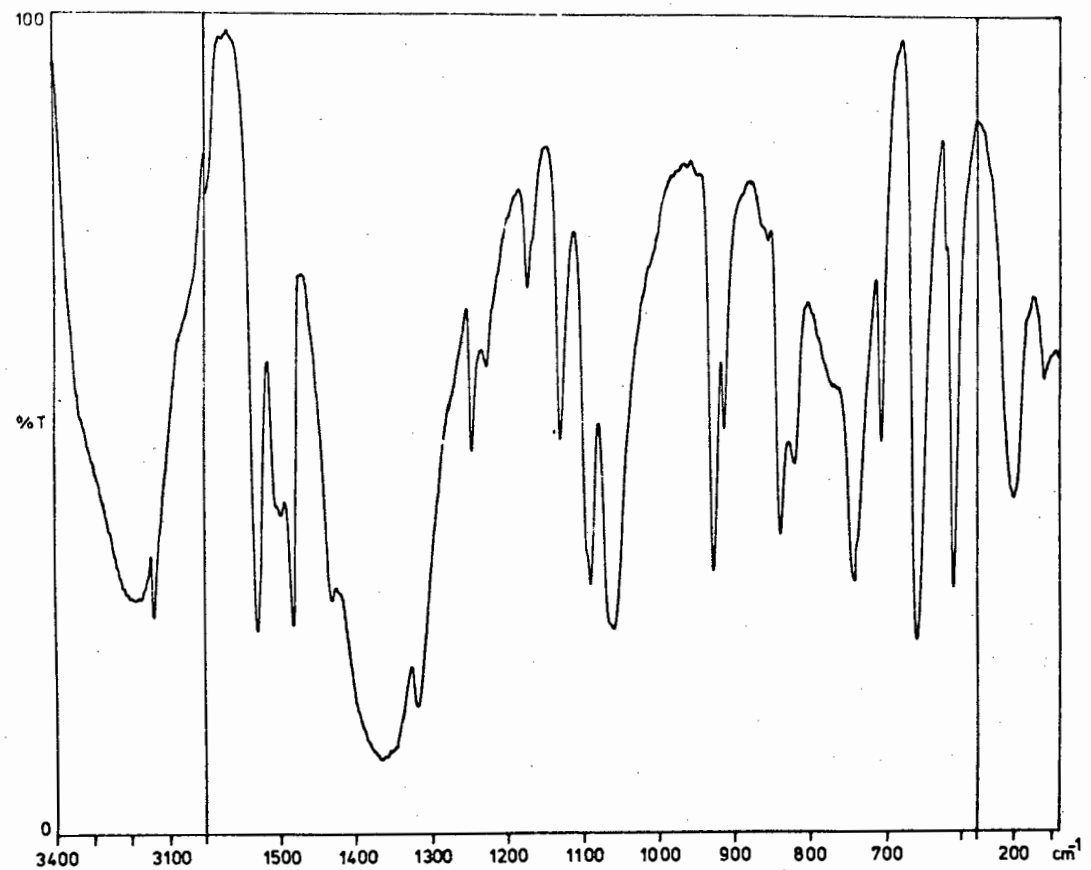


Fig. 2. The infrared spectrum of $[Zn(Him)_6](NO_3)_2$

Table 17. Frequencies, ratios ν^{D}/ν^{H} and band assignments in the infrared spectra of $[M(Him)_6](ClO_4)_2$, (M = Mn(II), Fe(II), Co(II), Ni(II)) and $[Zn(Him)_5](ClO_4)_2$

Mn	Fe	Co	Ni		Zn		ν^{D_3}/ν^{H_4}	Assignment
			Him	Him-d_3	Him	Him-d_3		
3437	3437	3437	3438	3438	3320	3320	1.0	νN-H
3350	3355	3355	3360	3360				
3165	3165	3165	3165	2363	3145	2360	0.75	νC-H
3143	3145	3145	3150	2335	3130	2335	0.74±0.01	νC-H
1535	1535	1535	1536	1497 1484	1545	1475	0.96±0.01	νring
1486	1486	1486	1486	1440	1510 1497	1458	0.97	νring
1421	1421	1421	1424	1461 1411 1403	1432	1425	1.0	νring
1325	1325	1325	1326	1287 1273	1330_{sh} 1323_{sh}	1275 1260	0.96±0.01	νring
1255	1255	1255	1257	948 932	1265	947 933	0.74±0.01	δC-H
1223	1223	1223	1223	1166 1159	1245	1190	0.95±0.01	δN-H
1156_{sh} 1130_{sh}	1156_{sh} 1130_{sh}	1156_{sh} 1130_{sh}	1156_{sh} 1130_{sh}	a 1130_{sh}	1170_{sh} 1130_{sh}	a 1130_{sh}		νring
1111 1084	1111 1084	1111 1084	1111 1085	1111 1085	1110 1087	1110 1087		ν_3ClO_4
b	b	b	b	883 871	b	891 875		δC-D
1049	1049	1049	1054	820	1071	826	0.77±0.01	δC-H
975	975	975	975	972	980			Comb.
936	936	936	936	961	953	973	1.03±0.01	δring
919	919	919	919	725	920	733_{sh}	0.79±0.01	γC-H
876 864	876 864	876 864	876 864					Comb.
845	845	845	845	771	847	778	0.91±0.01	δring
826	826	826	826	648	833 824	653	0.78±0.01	γC-H
770 758	770 758	770 758	771 758	593 579	767 757	577	0.76±0.01	γC-H
727	727	727	725	715	725	725	1.0	γN-H
656	656	656	660	567 557	670 650	547	0.84±0.01	γring
621	621	621	621	621	621	621		ν_4ClO_4
607 595	607 595	607 595	607 595	531 520	609_{sh}	525	0.86±0.01	γring
464_w	464_w	464_w	464_w	464_w	464_{vw}	464_{vw}		ν_2ClO_4
211(3)[c]	231(5)	243(4) 224(4)	260(4)		322(12) 310(7)			νM-N
					257(9)			νM-N
278(7) 268(8)	275(3) 264(10)	185(3) 175(6)	199(6) 185(11)		195(11) 176(0)		coupled	δ_τ M-Him + δM-N-C δN-M-N

cont./

Table 17 continued.

[a] Corresponding band in spectrum of labelled complex is obscured by perchlorate absorption in 1100 cm^{-1} region.

[b] Corresponding band in spectrum of unlabelled complex is obscured by perchlorate absorption in 1100 cm^{-1} region.

[c] Figures in parentheses following metal-ligand frequencies are the shifts towards lower frequency induced by Him-d_3 labelling.

sh Shoulder.

w Weak.

vw Very weak.

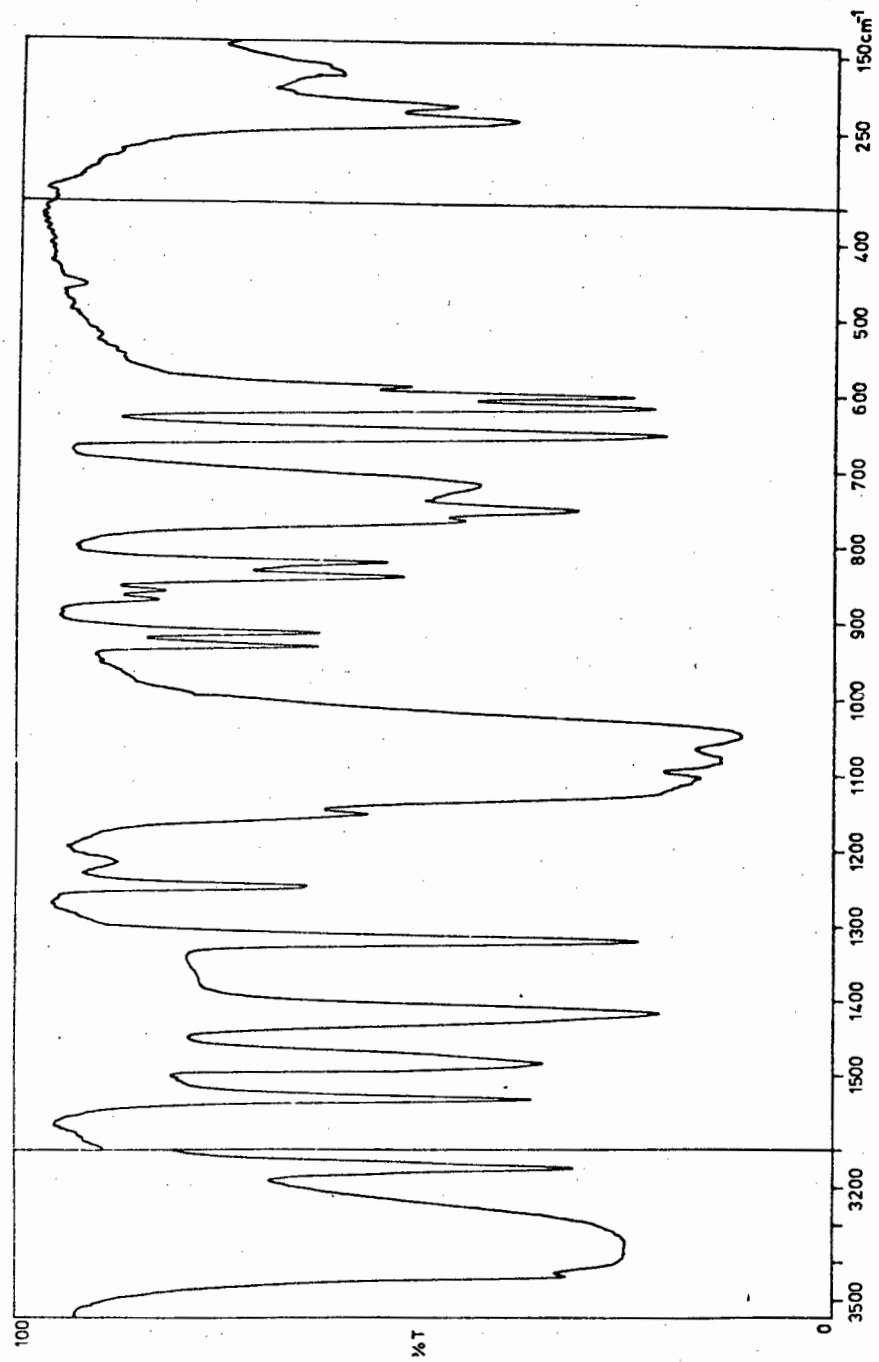


Fig. 3. The infrared spectrum of $[Co(Him)_6](ClO_4)_2$

Table 18. Frequencies, ratios ν^{D_3}/ν^{H_4} and band assignments in the infrared spectra of $[Cu(Him)_4(ClO_4)_2]$ and $[Zn(Him)_4](ClO_4)_2$

Cu(II)		Zn(II)			
Him	Him-d_3	Him	Him-d_3	ν^{D_3}/ν^{H_4}	Assignment
3381 3351	3381 3351	3380	3380	1.0	νN-H
3164	2372	3160	2379	0.75	νC-H
3144	2340	3145	2355	0.75±0.01	νC-H
		3131	2337	0.75	νC-H
1545	1486 1471	1546	1493	0.96±0.01	νring
1513 1493	1465 1454	1512 1508^{sh}	1471 1453	0.97	νring
1434	1421 1409	1431	1404	0.98±0.01	νring
			1347 1339		
1330	1303 1276	1331	1273	0.96±0.01	νring
1266	950	1267	948	0.75	δC-H
1225	1198 1183	1230	1188		Comb.
1175	a	1183	a		νring
b	b	1133	a		δN-H
1135^{sh}	1135^{sh}				
1111	1111	1120–1060^{c}			ν_3ClO_4
1070	1070				
e	890 877^{d}	e	889		δC-D
1056	827	1050	828	0.78±0.01	δC-H
	980				
950	970	953	974	1.02	δring
930^{w}	930^{w}				ν_1ClO_4
			930		
917	745 738^{d}	920	759 741	0.81±0.01	γC-H
870	845	873			
847	781 776	854 847	776	0.92±0.01	δring
f	650 644	833	f		γC-H
764 757	598 586^{d}	760	600	0.78±0.01	γC-H
	760				
721	715	730	720	0.99	γN-H
660 650	565 552	652	556	0.85	γring
625	625	622	622		ν_4ClO_4
610	521	614	524	0.85	γring

continued/

Table 18 continued.

Cu(II)		Zn(II)			
Him	Him-d_3	Him	Him-d_3	ν^{D_3}/ν^{H_4}	Assignment
462^{vw}	462^{vw}	464^{vw}	464^{vw}		ν_2ClO_4
307	303				νasym. Cu-N
286	284				νsym. Cu-N
		271	268		νZn-N
246	238	199	189		δ_τM-Him+δM-N-C
228	219	185	175		δ_τM-Him+δM-N-C
167	162				δN-Cu-N

a Corresponding band in spectrum of labelled complex obscured by perchlorate absorption near 1100 cm^{-1}.

b Band obscured by perchlorate absorption near 1100 cm^{-1}.

c Perchlorate band in spectrum of the Zn(II) complex occurs as a continuous absorption in the range 1120 to 1060 cm^{-1}.

d Mean of doublet.

e Corresponding band in spectrum of unlabelled complex obscured by perchlorate absorption near 1100 cm^{-1}.

f Corresponding band not observed.

sh Shoulder.

w Weak.

vw Very weak.

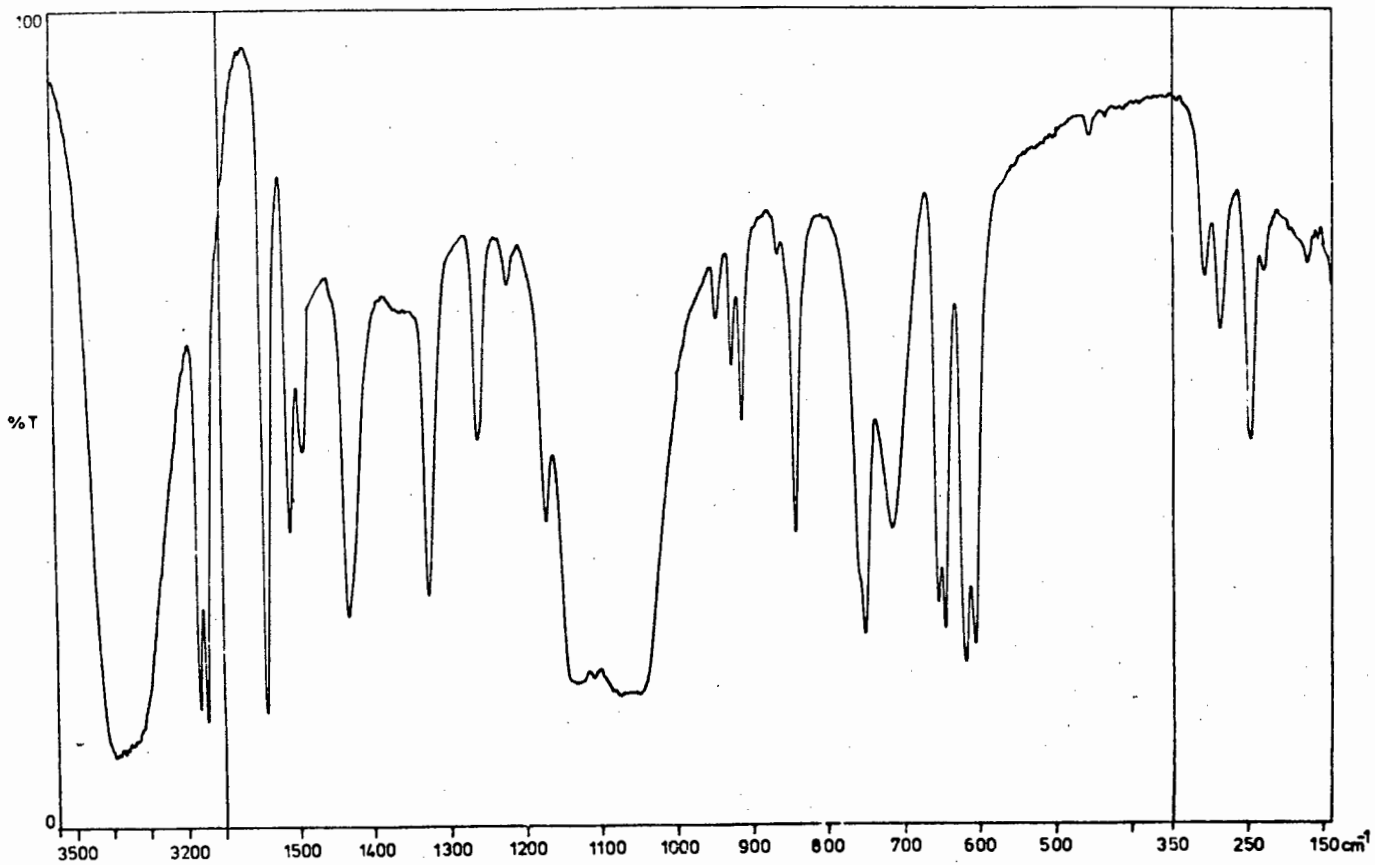


Fig.4. The infrared spectrum of $[Cu(Him)_4(ClO_4)_2]$

Table 19. Frequencies, ratios ν^{D_3}/ν^{H_4} and band assignments in the infrared spectra of $[Cu(Him)_4(NO_3)_2]$ and $[Zn(Him)_4(NO_3)_2]$

Cu(II)		Zn(II)			
Him	Him-d_3	Him	Him-d_3	ν^{D_3}/ν^{H_4}	Assignment
3315	3310	3237	3237	1.0	νN-H
	2356	3160[a]	2363	0.75	νC-H
3155	2343	3148	2355	0.75±0.01	νC-H
3134	2329	3136[a]	2334[a]	0.74	νC-H
1537	1484 1472	1544	1498	0.96±0.01	νring
			1478		
		1512	1466		
1498	1450	1505	1453	0.97	νring
1432	1404[sh]	1461	1431	0.98	νring
1399	1390	1406	1494		ν_4NO_3
1343	1337	1324	1335		ν_1NO_3
1322	1292	1315	1289	0.97	νring
1311[sh]	1272		1270		
1257	946 937	1261	945 940	0.75	δC-H
1242	1190	1248	1210		
	1174	1238	1196		
	1166				
	1147				
1167	1110	1189	1117	0.94±0.01	νring
1132	1080	1136	1079	0.95	δN-H
1097	888[a] 876	1104 1092	891	0.80±0.01	δC-H
1068	819	1069	831 819	0.77	δC-H
1044	1049	1035	1035 1010		ν_2NO_3
949 942	975 968	954	971	1.03±0.01	δring
931 925	757 736	919 912	736	0.80	γC-H
890		865			
856	773	842[sh]	770	0.91±0.01	δring
846		835			
823	823[sh]	813	813[sh]		ν_6NO_3
761	595[a]	768	597	0.78	γC-H
746	580[a]	760	593		
739[sh]	722	745	b	0.98	γN-H
		718	718		ν_3NO_3
709	709	703	703		ν_5NO_3
660	567 560	644	551 549	0.85	γring
619	529	623	530[sh]	0.85	γring
610	519	618	524		

continued/

Table 19 continued.

Cu(II)		Zn(II)		ν^{D_3}/ν^{H_4}	Assignment
Him	Him-d_3	Him	Him-d_3		
290	287	271	267		νM-N
254	246				δ_TM-Him+δM-N-C
223	216	202	194		δ_TM-Him+δM-N-C
165	157	156	154		δN-M-N

a Mean of doublet.

b Corresponding band in spectrum of labelled complex not observed. Could be coincident with 736 cm^{-1} absorption.

sh Shoulder.

Table 20. Frequencies and band assignments in the infrared spectra of $[Cu(Him)_4(X)_2]$, (X = Cl, Br or I)

Cl	Br	I	Assignment
3298	3285[w] 3235[w]	3220[sh]	νN-H
3188	3180	3173	νN-H
3134			νN-H
3154 3141			νC-H
3116	3123	3120	νC-H
3110	3112	3105	νC-H
1537	1533	1533	νring
1494	1501[sh] 1489	1490 1472	νring
1427 1422	1420	1422	νring
1348 1337	1330 1325	1347 1328	νring
1330[sh]	1310		Comb.
1262	1258	1256	δC-H
1245 1222[w]	1240 1218[w]	1234 1222[w]	Comb.
1175 1165	1169	1166	νring
1142			δN-H
1127	1131	1128	δN-H
1112	1101	1095	δN-H
1094	1094	1081	δC-H
1066	1064	1066	δC-H
953 943	949 941	947 941	δring
920	920	919	γC-H
890	888		Comb.
870 860	871	860 852	δring
845	853 833	833	γC-H
804	801		γN-H
775 756	770	775 770	γC-H
747	747	745	
730	728	720 701	γN-H
663	659	657	γring
622 610	619 608	620 604	γring
284(4)[a]	292(4)	289(4)	νCu-N
254(8)	253(8)	250(8)	δ_TCu-Him+δCu-N-C
225(8)	223(8)	218(6)	δ_TCu-Him+δCu-N-C
170(4)[sh]			δN-Cu-N
156(3)			δN-Cu-N

Cont./

Table 20 continued.

[a] Figures in parentheses following metal-ligand frequencies are the shifts towards lower frequency induced by Him-d_3 labelling.

[sh] Shoulder.

[w] Weak.

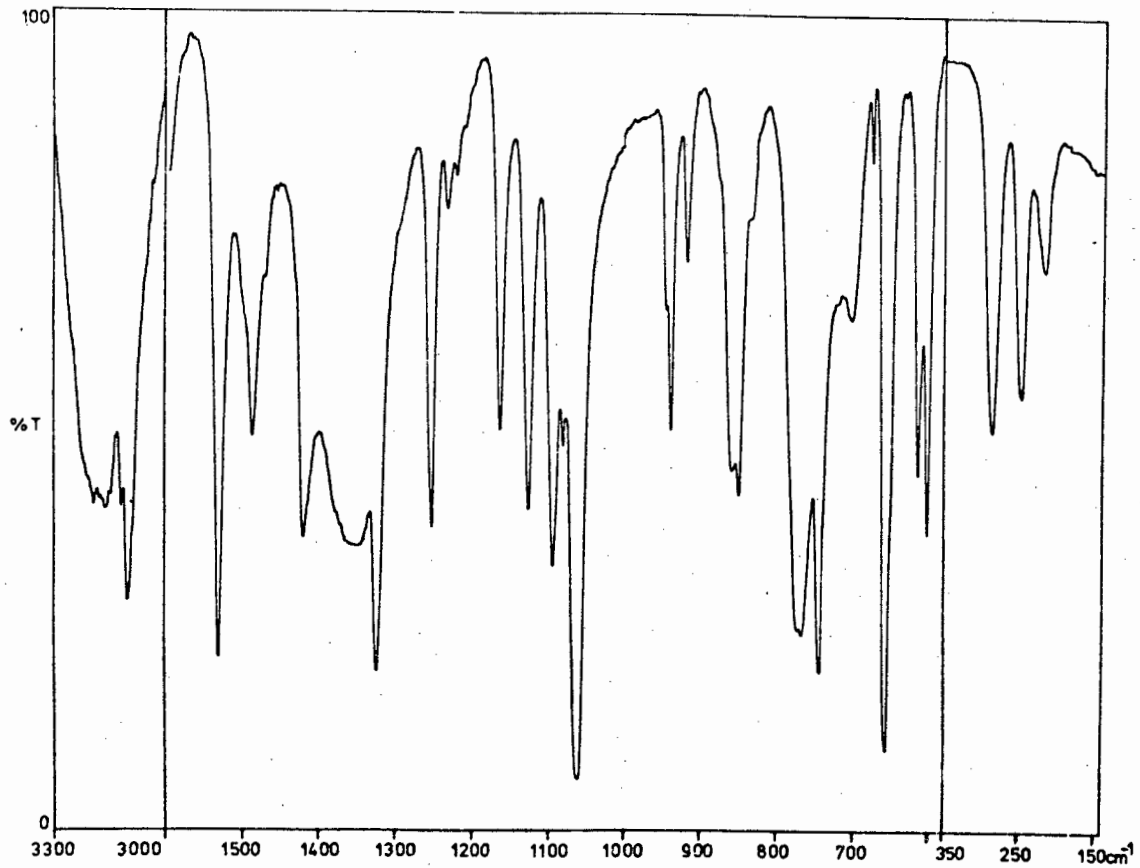


Fig. 5. The infrared spectrum of $[Cu(Him)_4I_2]$

Table 21. Frequencies and band assignments in the infrared spectra of $[M(Him)_2(X)_2]$, (M = Co(II) or Zn(II); X = Cl or Br)

Co		Zn		
Cl	Br	Cl	Br	Assignment
3308	3339	3309	3350[sh]	
3272	3313	3260	3270[sh]	νN-H
3152	3160	3154	3165	
3141	3152	3141	3151	νC-H
3133	3139	3133	3139	νC-H
3120	3120	3120	3126	νC-H
1538	1538	1540	1540	νring
1512	1507	1515	1508	
1497	1489	1501		νring
1492[sh]		1493	1491	
1422	1422	1432	1425	νring
1412		1422		
1350[br]	1350[br]	1355[br]	1348[br]	
1315	1325	1328	1329[a]	νring
1257	1255	1260	1260	δC-H
1254		1256		
1236		1236		comb.
1220	1222	1226	1214	
1177		1177		νring
1168	1169	1170	1171	
1132	1127	1135	1129	δN-H
1122	1122	1124	1125	
1101	1097	1101	1100	δC-H
1098	1091	1098	1091	
1071	1069	1071	1069	δC-H
	1063		1062	
952	951	952	950[a]	δ ring
917	918	918	919	γC-H
863	869	870[sh]		
852	845	865	864	δ ring
842	839	853	846	γC-H
833	833	844	832	
753	753[a]	754	758	γC-H
735	723	740	706	γN-H
702	704	704		
	679		682	γN-H
650	648	649	642	γring
	643[sh]			
616	609	617	608	γring
612		613		
321	255[br]	298	231[br]	νasym. M-X
310		288		νsym. M-X
276(3)[b]	283(2)	250(3)	250(3)	νasym. M-N
240(1)	c	238(4)		νsym. M-N
205	187(2)	195(9)	192(10)[sh]	δ_τM-Him + δM-N-C
193(8)	183(9)[sh]		184(5)	δ_τM-Him + δM-N-C
			170(10)	δ_τM-Him + δM-N-C
159(6)	149(6)	160(10)	148(4)	δ N-M-N
		153(4)[sh]		

Cont./

Table 21 continued.

[a] Mean of doublet.

[b] Figures in parentheses following metal-ligand frequencies are the shifts towards lower frequencies induced by Him-d_3 labelling.

[c] νsym. Co-N masked by strong absorption at 255 cm^{-1}.

sh Shoulder.

br Broad.

Table 22. Vibrational frequencies of pyrazine[a] and $[Cu(NO_3)_2(pz)]_n$

pyrazine	species(D_{2h})	$[Cu(NO_3)_2pz]_n$	species(C_{2h})	Assignment
3080		3132		Comb.
3060(785)	B_{3u}	3112(793)	A_u	νC-H
3060(803)	B_{2u}	3100(806)	B_u	νC-H
3008		3078 3061 3033		Comb.
2965		3011		
2931		2949		
		1494(0)	B_u	ν_1 NO_3
1492 1482	B_{3u}	1486	A_u	νring
1410	B_{2u}	1429	B_u	νring
1351 1335	B_{2u}	1386	B_u	νring
		1290(0)	B_u	ν_4 NO_3
1181				
1143 1139	B_{2u}	1166	B_u	δC-H
1113		1108		Comb.
1064	B_{3u}	1123	A_u	δC-H
1019	B_{3u}	1081	A_u	δring
		1015(0)	B_u	ν_2 NO_3
1004				Comb.
[950][b]	A_u	1051	A_u	γC-H
825		835		
801	B_{1u}	823	B_u	γC-H
786		814		
		805(0)	B_u	ν_3 NO_3
		751(0)	B_u	ν_5 NO_3
		708(0)	A_u	ν_6 NO_3
413(14)	B_{1u}	498(29)	B_u	γring
[400][b]	A_u	493(32)	A_u	γring
		341(2)		νasym. Cu-O
		224(2)		νCu-N
		205(4)		
		140(3)		
		115(1)		
		95(2)		
		73(0)		
		46(4)		
		35[vw]		

[a] Assignments based on those of Simmons[83] and those of Lord *et al*[80].

[b] Figures in square brackets represent estimated frequencies[80,83-84].

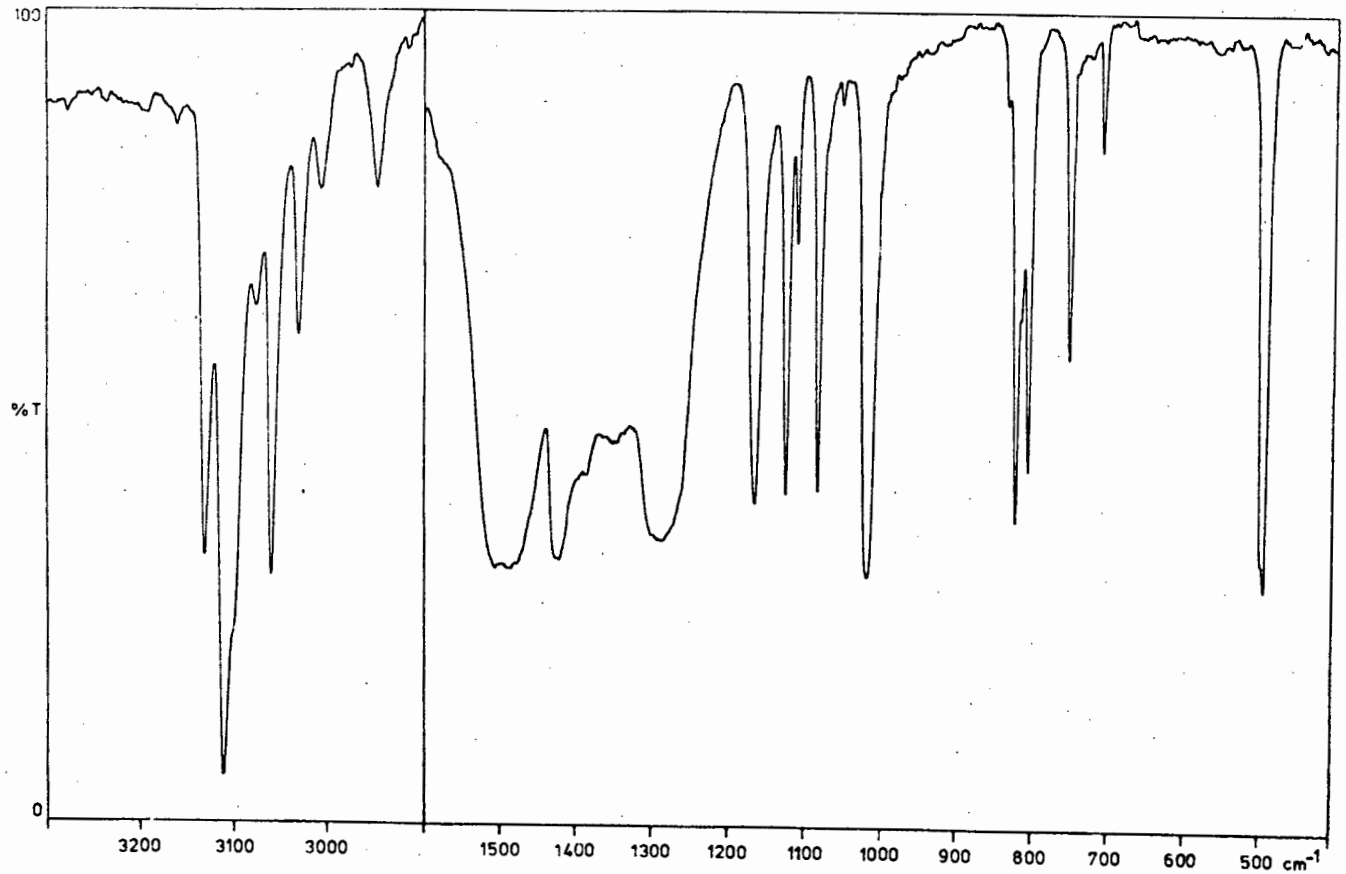


Fig. 6. The infrared spectrum (3300-400 cm^{-1}) of the complex $[Cu(NO_3)_2(pz)]_n$

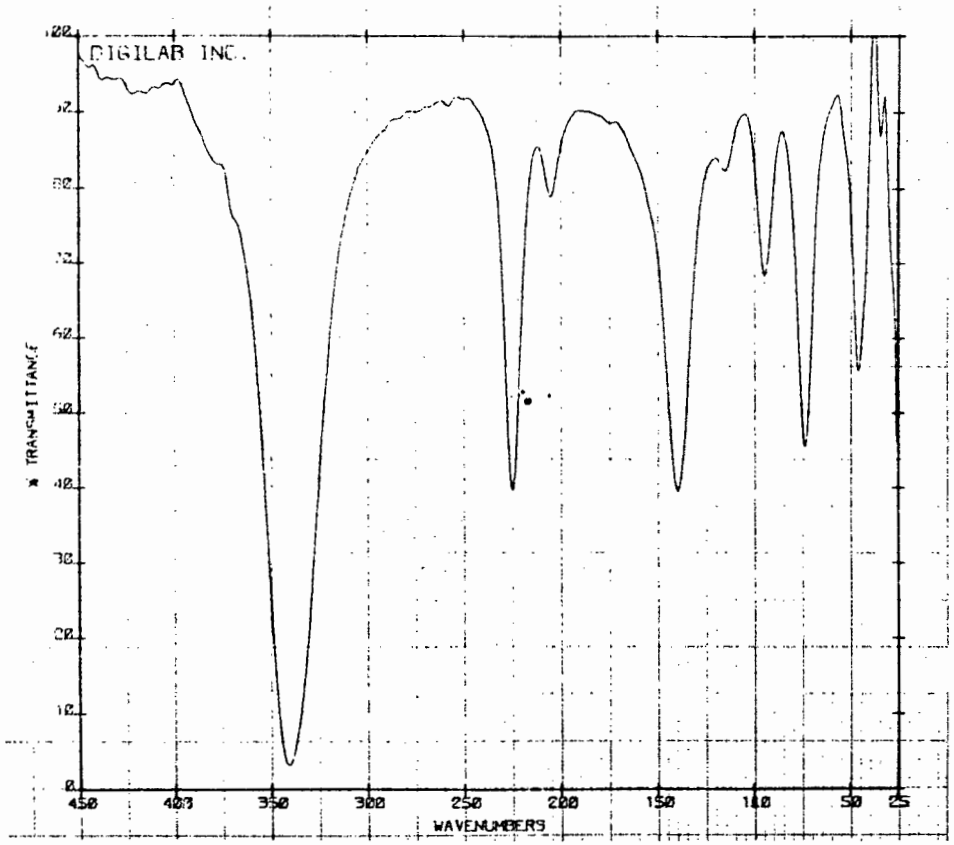


Fig. 7. The infrared spectrum (450-25 cm^{-1}) of the complex $[Cu(NO_3)_2(pz)]_n$

Table 23. Vibrational Frequencies (and d-sensitivities) of the metal(II) acetylacetonates and their base adducts

$[M(AA)_2(Him)_2]$		$[M(AA)_2(pz)]_n$			$[M(AA)_2(pm)]_n$			$[M(AA)_2(pd)_2]$		$[\{M(AA)_2\}_2(pd)]$		Assignment
Co	Ni	Co	Ni	Zn	Co	Ni	Zn	Co	Ni	Co	Ni	
658(0)	658(0)	655(0)	658(0)	652(0)	652	659	648	654	655	655	655	Chelate ring def.
616(97)	616(96)				688	689	683	669	670	678	680	γring(Him,pm) δring(pd)
					666	666	655	639	641	669	669	δring(pm,pd)
					578	580	572			569	562	δring(pm), ring def.(pd)
556(0)	572(0)	557(0)	577(0)	554(1)	555	566	558	558	575	555	575	coupled νM-O
416(0)	422(0)	410(0)	417(0)	412(1)	416	423	416	414	422	417	421	
		469(18)	480(20)	460(16)	374	379	360	399	406	401	407	γring(pz,pm,pd)
								384	385			ring def.(pd)
262(3)	278(4)	216(2)	234(2)	217(0)	212	233	184	173	185	194	211	νM-N
229(2)	253(1)	201(3)	213(2)	202(4)	201	221	175					
202(0)	220(0)	281(0)	298(0)	258(0)	276	281	248	267	272	270	274	νM-O
		257(0)	267(0)	227(0)	254	265	231	218	237	234	246	
		237(1)	252(1)	227(0)								νM-O + νM-N
180(2)	195(4)	148(0)	161(3)	149(2)	155	164	154					δL-M-L
170(0)	174(0)											

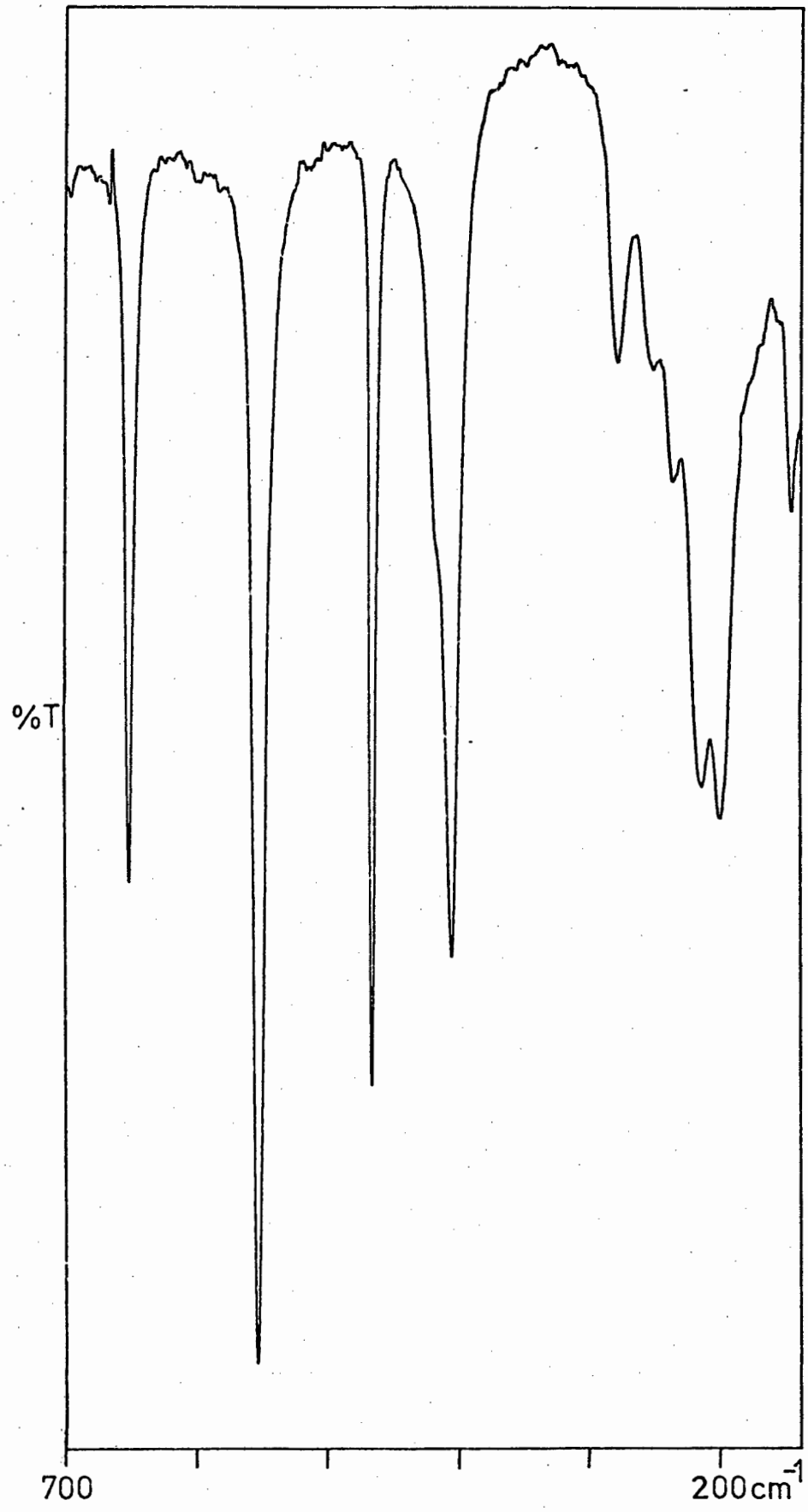


Fig. 8. The infrared spectrum (700-140 cm^{-1}) of the complex $[Co(AA)_2(pz)]_n$

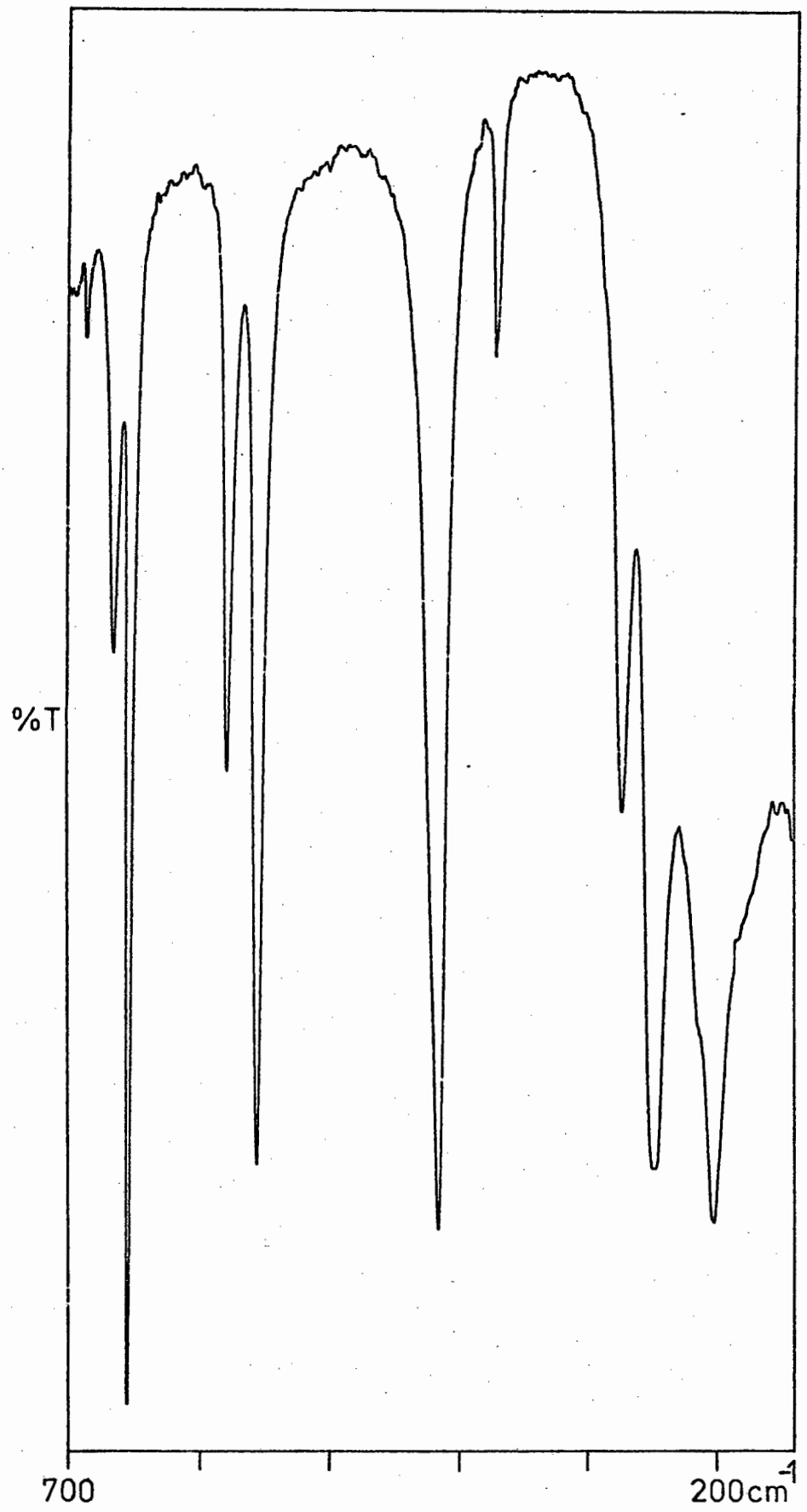


Fig. 9. The infrared spectrum (700-140 cm^{-1}) of the complex $[Co(AA)_2(pm)]_n$

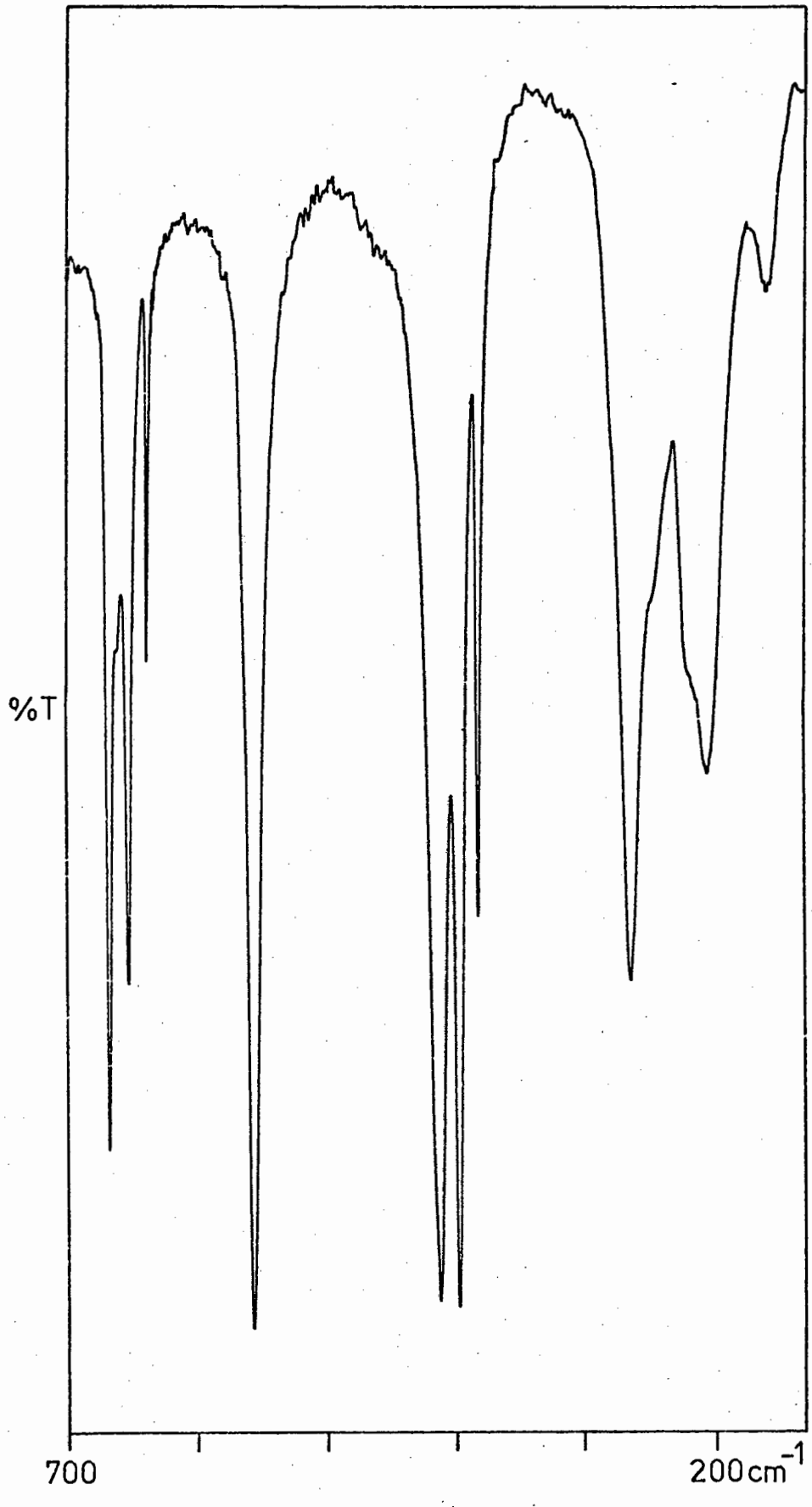


Fig. 10. The infrared spectrum (700-140 cm^{-1}) of the complex $[Co(AA)_2(pd)_2]$

Table 24. Vibrational frequencies (and d-sensitivities) of the M(II) salicylaldehydates and their base adducts.

$[M(Sal)_2]$			$[M(Sal)_2(H_2O)_2]$			$[M(Sal)_2(py)_2]$			$[M(Sal)_2(Him)_2]$		$[M(Sal)_2(pz)]_n$			$[M(Sal)_2(pm)]_n$			Assignment
Co	Ni	Zn	Co	Ni	Zn	Co	Ni	Zn	Co	Ni	Co	Ni	Zn	Co	Ni	Zn	
						696(91)	700(92)	699(92)									γC-H(py)
														687	690	688[a]	γring(pm)
664	666	663	663	666	663	658(0)	659(0)	659(0)	664(1)	664(2)	659(1)	661(0)	658(0)	659	663	658	νSal
			630	637	635												νSal
						631(10)	631(10)	631(10)									δring(py)
									625(90)	623(92)							γring(Him)
587	592	583	598	592	590	589(0)	592(0)	588(0)	583(0)	587(0)	592(0)	593(0)	591(0)	591	592	588	νSal
														564	564	560	νSal
545	552	542	543	565	544	546(0)	539(0)	544(0)	543(0)	546(0)	539(0)	537(0)	538(0)	544	543	540	νSal
521	526	504	526	535	514	505(0)	523(0)	497(0)	509(0)	524(0)	505(0)	523(0)	504(0)	508	524	503	νM-O
440	445	438	440	439	436	447(0)	446(1)	442(0)			443(0)	447(0)	445(0)	445	445	445	νSal
						437(0)	438(0)	434(0)	434(0)	437(0)	437[b]	436(0)	437[c]	436	435	434	νSal
						425(39)	431(38)	420(37)			470(20)	480(21)	458(20)	370	376	367	γring(py,pz,pm)
			370[d]	383[d]	380[d]												M-OH$_2$ or H$_2$O rock
											366(0)	361(0)	364(0)				νSal
														346	361	355	νSal + νM-O
343	357	343				331(0)	339(0)	317(0)	332(0)	355(0)	338(0)	344(0)	322(0)	336	345	326	νSal + νM-O
318	331	315	318	327	311	287(0)	296(0)	244(0)	312(0)	347(0)	281(0)	296(0)	250(0)	290	304	242	νSal + νM-O
276	306	270	257	277	245	254(0)	269(0)	230(0)			257(0)	270(1)	244(2)	[e]257	260	221	νM-O
			245	265	239	230(0)	242(0)	208(0)	232(0)	250(0)	231(0)	244(0)	205(0)				νM-O[e]
225,185	238[a],206	212,172	215	231	190												νSal + νM-O
						207(0)	209(0)	198(0)								201	νSal
						193(10)	192(0)	158(1)	266(1)	284(5)	221(2)	240(1)	198(0)	185	203	168	νM-N[f]
							181(10)	153(1)	239(1)	263(2)				171	185	160	νM-N
173	188	160	165	174	158	160(0;sh)											δO-M-O
			143	154	b.1.	152(0)	157(0)	b.1.									
									195(3)	197(5)	167(0)	181(0)	151(1)				δO-M-N or δN-M-N
									185(2)	186(2)	149(0)	161(0)	b.1.	145	159	b.1.	
									162(2)	166(3)							

[a] Mean of doublet. [b] Does not recur in the deuterated spectrum. [c] Obscured in the deuterated spectrum by pz-d_4 ring mode at 438 cm^{-1}. [d] Broad band of low intensity. [e] Coupled with νM-N in the spectra of the Him and pz adducts. [f] Coupled with νM-O in the spectrum of the pz adducts. b.1. = Beyond limit of measurement. sh = Shoulder.

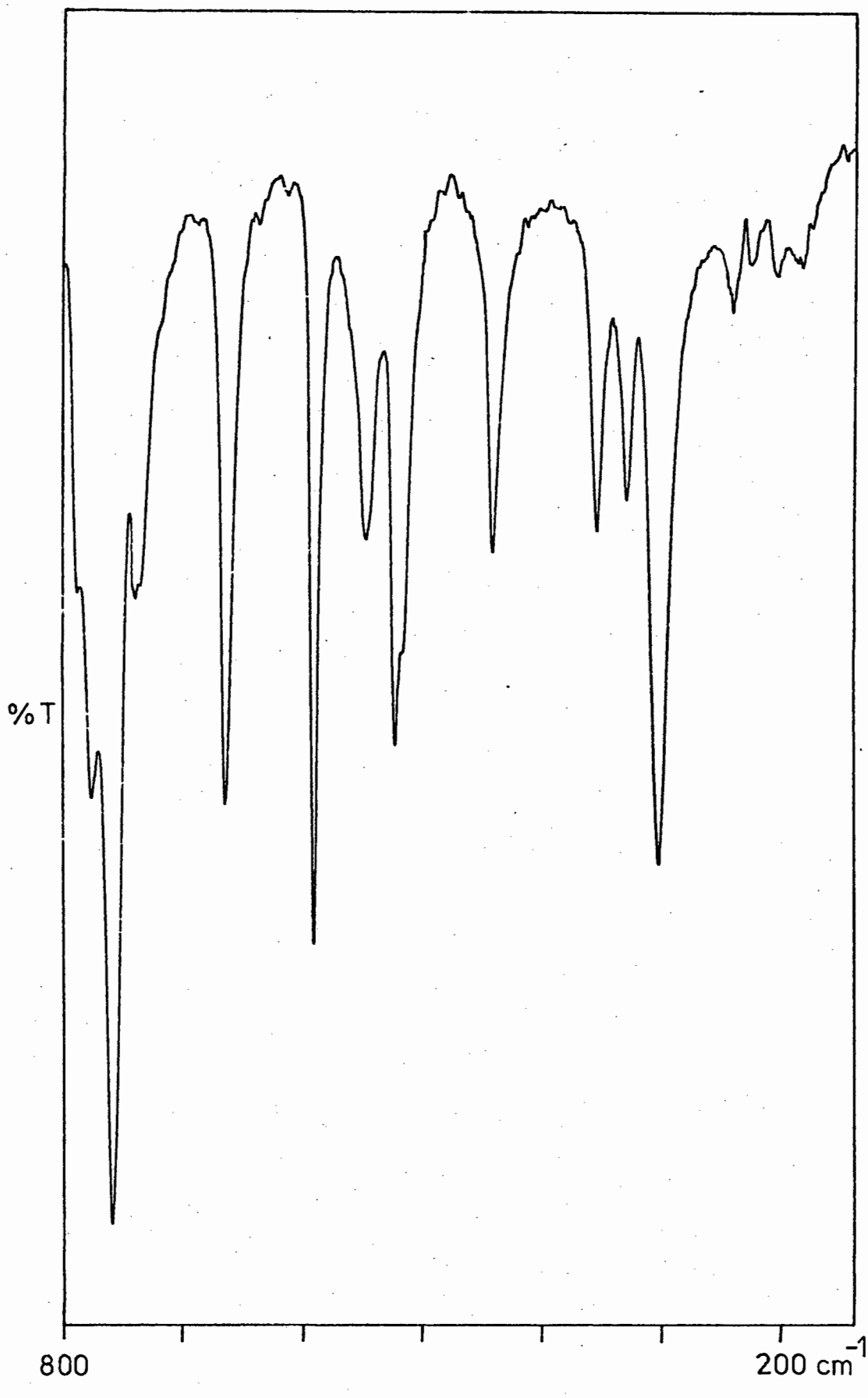


Fig. 11. The infrared spectrum (800-140 cm^{-1}) of the complex $[Ni(Sal)_2]$

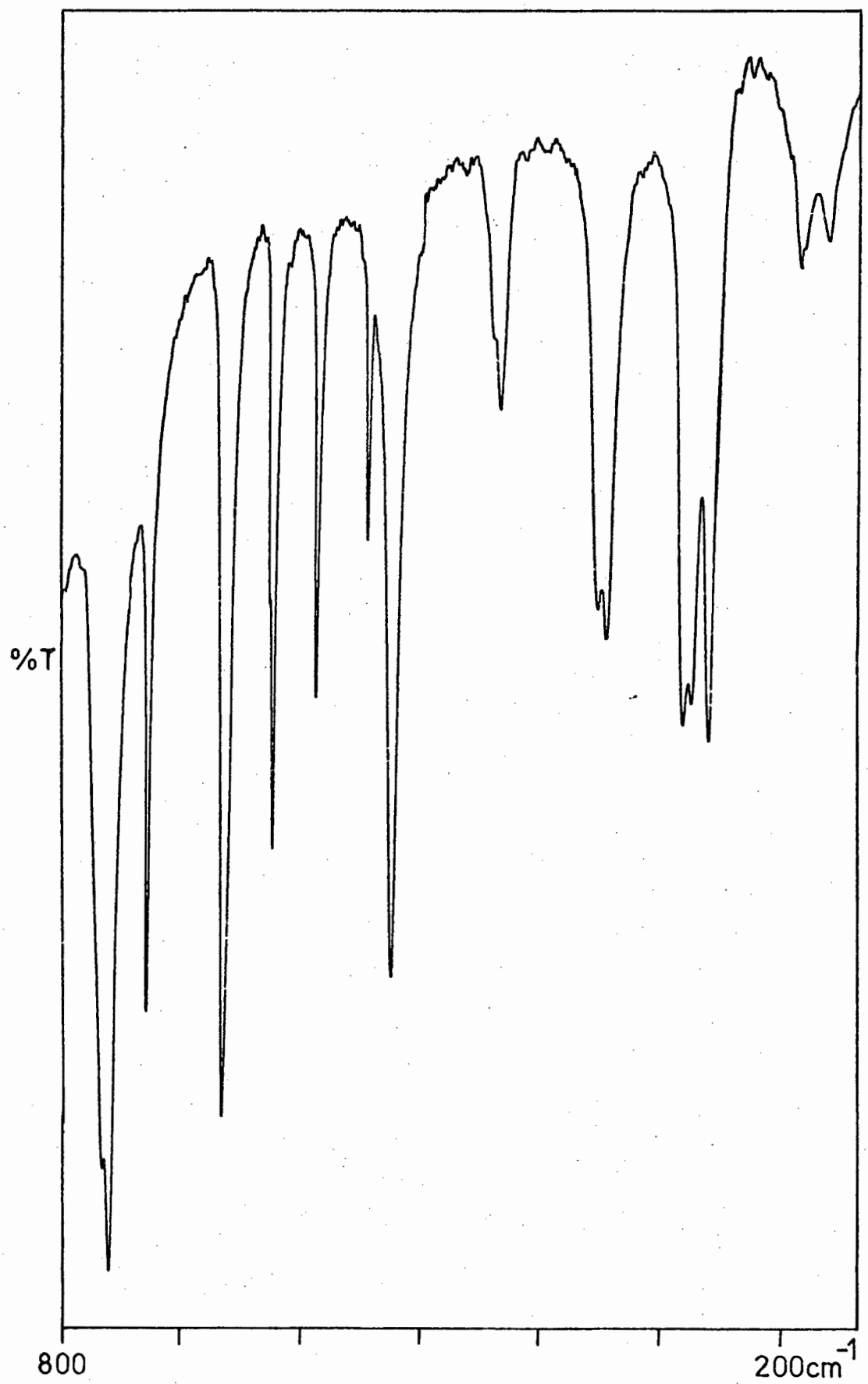


Fig. 12. The infrared spectrum (800-140 cm^{-1}) of the complex $[Ni(Sal)_2(Him)_2]$

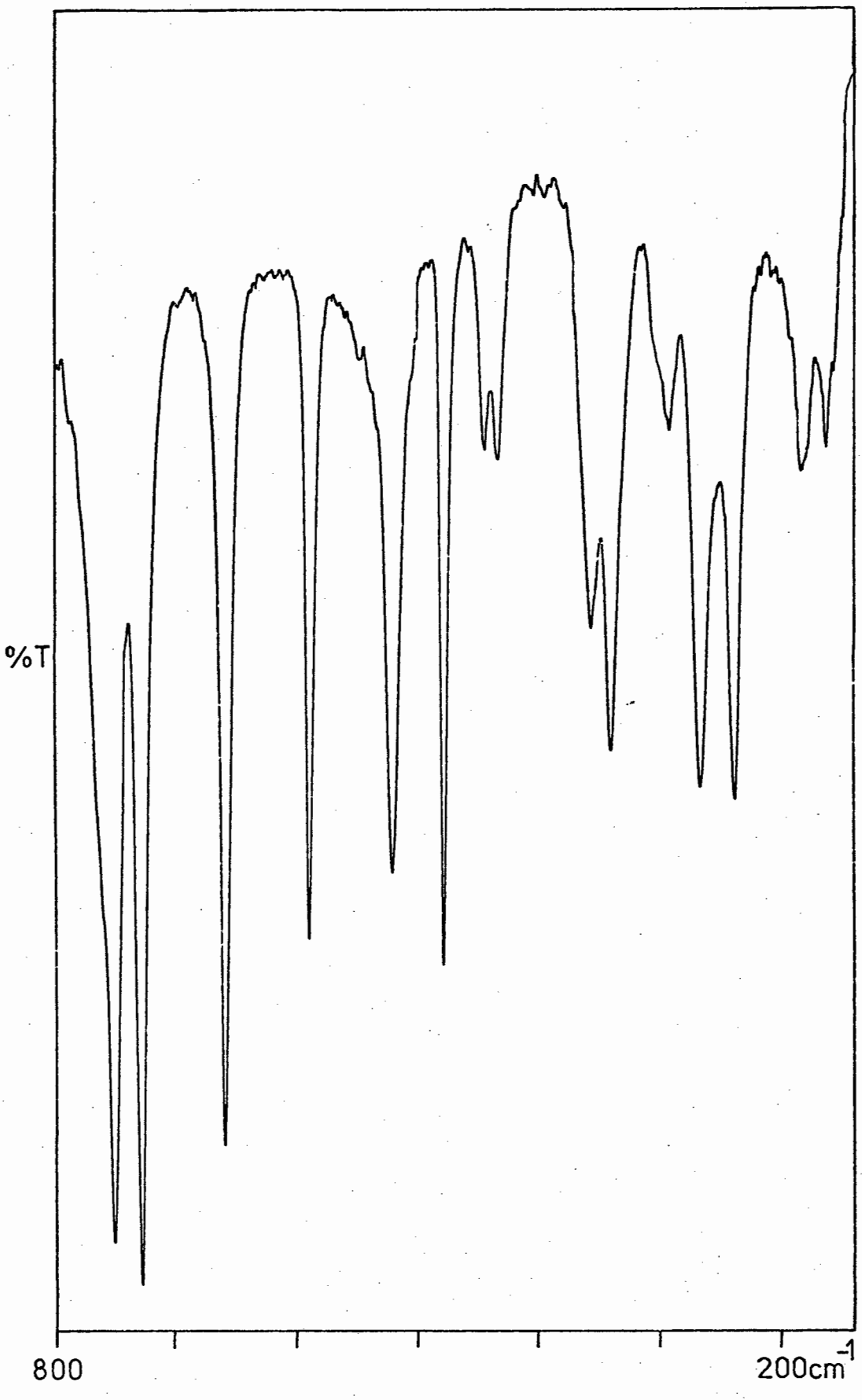


Fig. 13. The infrared spectrum (800-140 cm^{-1}) of the complex $[Ni(Sal)_2(pz)]_n$

Table 25. Frequencies, isotopically-induced shifts and infrared band assignments for *trans*-$[Pt(gly)_2]$[a]

ν		$\Delta\nu$							Assignment
		^{18}O	^{15}N	1-^{13}C	2-^{13}C	2,2-d_2	*N*,*N*-d_2	2,2-d_2 + *N*,*N*-d_2	
ν_1	3230		4				822	819	νN-H asym.
ν_2	3094						795	797	νN-H sym.
ν_3	2984			2	12	829		823	νC-H asym.
ν_4	2934				4	831		823	νC-H sym.
ν_5	1650	18		29			6	4	νC=O
ν_6	1607	6	2	15		6	400	475	νC=O + NH_2 scissor
ν_7	1439				2	374		369	CH_2 scissor
ν_8	1431sh	24	5	-[b]	10	70	56	76	νC-O+νC-C+NH_2 twist
ν_9	1375	5		4	9	18	22	44	νC-O + νC-C
ν_{10}	1333	8		10			25	136	νC-O + NH_2 twist
ν_{11}	1294	5		14	3		247	242	νC-O+νC-C+NH_2 twist
ν_{12}	1247		4				217	239	NH_2 twist
ν_{13}	1187			2		248		256	CH_2 twist
ν_{14}	1026	3	12		18	101	171	234	νC-N + CO_2 scissor
ν_{15}	968			8	9	91		111	νC-C + CH_2 rock
ν_{16}	921	31[c]		3	7	29	31	29	CO_2 scissor + CH_2 rock
ν_{17}	798	3			2	21	34	58	CO_2 rock + CH_2 rock + NH_2 rock
ν_{18}	754	13		2	5	29	120	125	
ν_{19}	619	8	8	2		9	21	43	CO_2 wag + NH_2 rock
ν_{20}	548	3	4	7		53	22	81	ring def. + νPt-N
ν_{21}	497	8	5			27	18	39	νPt-N + νPt-O
ν_{22}	415	11			2	8		10	νPt-O
ν_{23}	338	3					3	6	δO-Pt-O
ν_{24}	263		4			4	31	42	δN-Pt-N
ν_{25}	150	3				10			δPt-O-C
ν_{26}	128[d]								
ν_{27}	90[d]								

[a] All shifts to lower wavenumber. Absence of date implies shift <1 cm^{-1}.

[b] Shoulder.

[c] Proceded by a residual ^{16}O-band.

[d] See ref. 137.

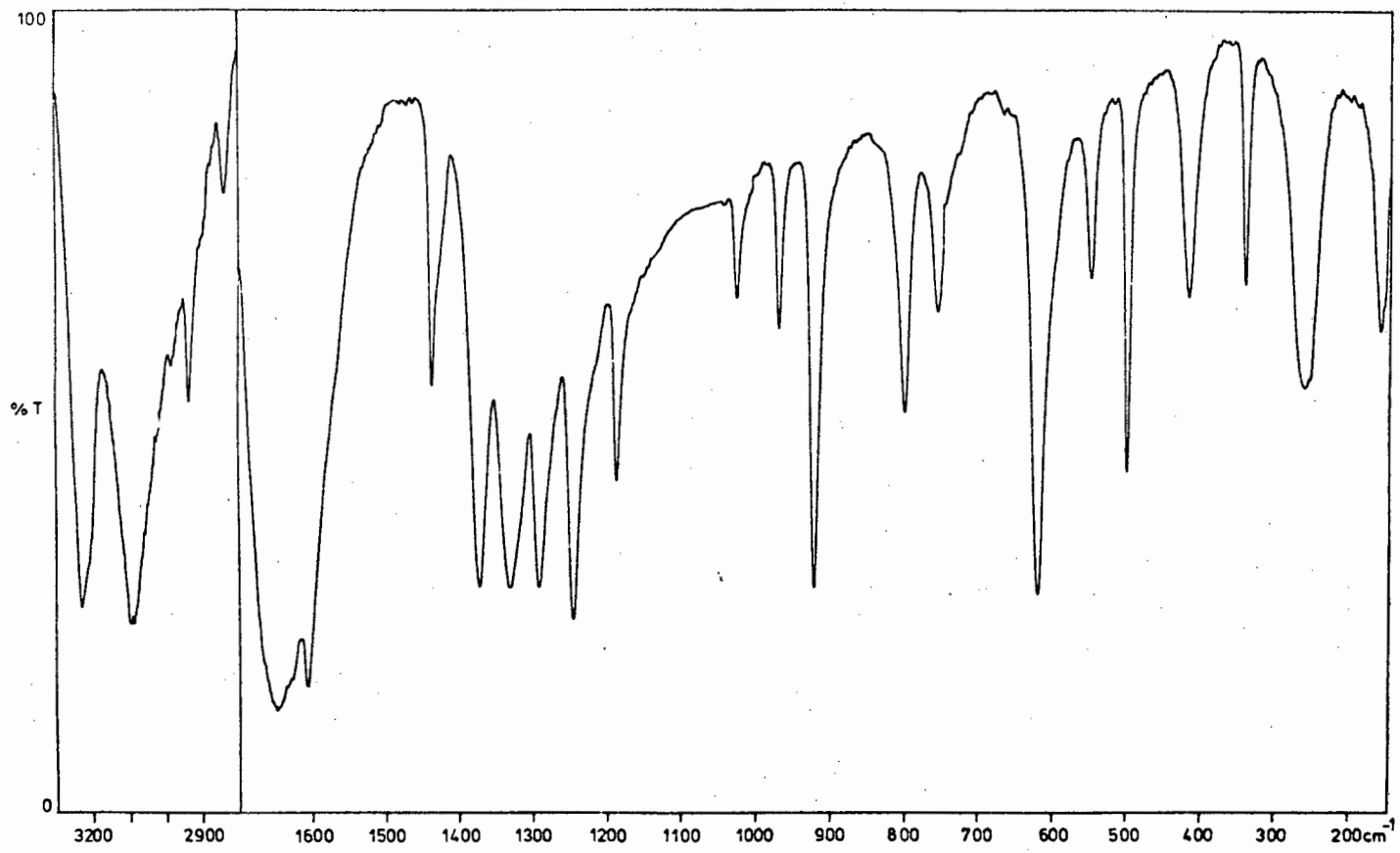


Fig. 14. The infrared spectrum (3300-140 cm^{-1}) of *trans*-$[Pt(gly)_2]$

Table 26. Frequency and isotopic shift data (cm^{-1}) for the complex *cis*-$[Ni(gly)_2(Him)_2]$. Shifts of <1.5 cm^{-1} are ignored.

Band*	Frequency	Shift						Assignment
		^{18}O	^{15}N	1-^{13}C	2-^{13}C	2,2-d_2	Him-d_3	
ν_1	3318		8				20	νN-H(gly)
ν_2	3282		7				14	
ν_3	3195		7				17	
ν_4	3150						790	νC-H(Him)
ν_5	3139						905	
ν_6	3127						820	
ν_7	2940				13	798		νC-H(gly)
ν_8	2920				5	810		
ν_9	1632	9		12		2		νC=O
ν_{10}†	1601	19		35				
ν_{11}	1586	18		31	2			
ν_{12}	1541		3	6				NH_2 scissor + νC=O
ν_{13}	1516		5			9	18	NH_2 scissor+ν(Him ring)
ν_{14}	1492						56	ν(Him ring)
ν_{15}	1448					3	100	
ν_{16}	1434				4	5	17	CH_2 scissor +ν(Him ring)
ν_{17}	1416	15		19	7	9		νC-O + νC-C(gly)
ν_{18}	1401			4	6	220	9	CH_2 scissor + νC-C(gly)
ν_{19}	1355	20	3	19	5	20	4	νC-O + νC-C(gly) + NH_2 wag
ν_{20}	1344		4		8	193	19	CH_2 wag + NH_2 wag
ν_{21}	1327						57	δC-H(Him)
ν_{22}	1310	4		4	6	18	8	CH_2 wag +νC-C(gly) + νC-O
ν_{23}	1294		3		6	97	16	CH_2 wag + NH_2 wag
ν_{24}	1257						284	δC-H(Him)
ν_{25}	1253						280	
ν_{26}	1245						48	δN-H(Him)
ν_{27}	1188			4	2	104	7	CH_2 twist + νC-C(gly)
ν_{28}	1145						45	δN-H(Him)
ν_{29}	1133		3	2	2	28	10	NH_2 twist + νC-C(gly)
ν_{30}	1093	2	2				213	δC-H(Him)
ν_{31}	1067						250	

Table 26 continued.

Band*	Frequency	Shift						Assignment
		^{18}O	^{15}N	1-^{13}C	2-^{13}C	2,2-d_2	Him-d_3	
ν_{32}	1052		14		18	4	4	νC-N(gly)
ν_{33}	957			11	10	11		νC-C(gly)
ν_{34}	944	3		3	4	4		νC-C(gly) + CO_2 scissor
ν_{35}	916	6		2		4	36	CO_2 scissor + γC-H(Him)
ν_{36}	905	25		7	7	31	10	CO_2 scissor + CH_2 rock
ν_{37}	898						28	δ(Him ring)
ν_{38}	850						118	γC-H(Him)
ν_{39}	834						102	
ν_{40}	831						99	
ν_{41}	763						129	
ν_{42}	753						119	
ν_{43}	729	9	2	6	6	23	9	CO_2 rock + CH_2 rock + NH_2 rock
ν_{44}	667						112	γ(Him ring)
ν_{45}	664						109	
ν_{46}	624						100	
ν_{47}	601	4	2	6		18	13	CO_2 wag + chelate ring def.
ν_{48}	583	9	6		2	31	10	
ν_{49}	536	15	7	2	2	5	12	
ν_{50}	510	11	4	2		42		CO_2 wag + νNi-N(gly)
ν_{51}	498	7	2	2		40	15	
ν_{52}	418	6	6			4		νNi-N(gly) + νNi-O
ν_{53}	401	7	5			4	81?	
ν_{54}	306	6	2	2		2	13	νNi-O + νNi-N(Him) + νNi-N(gly)
ν_{55}	256	4	2		3		21	νNi-N(Him) + δO-Ni-N(gly)
ν_{56}	236	6	2				16	
ν_{57}	203	3		2			15	δO-Ni-O + νNi-N(Him)
ν_{58}	164					2	6	δ(Him)N-Ni-N(Him)
ν_{59}	149							

* Hydrogen bonded νN-H(Him) bands occur at 3093, 3046, 3037, 3015, 2921, 2845, 2832, 2785, 2715, 2690, 2618 and 2595 cm^{-1}.

† ν_{10} masks a ν(Him ring) band which becomes resolved from the νC=O band in the 1-^{13}C-labelled spectrum.

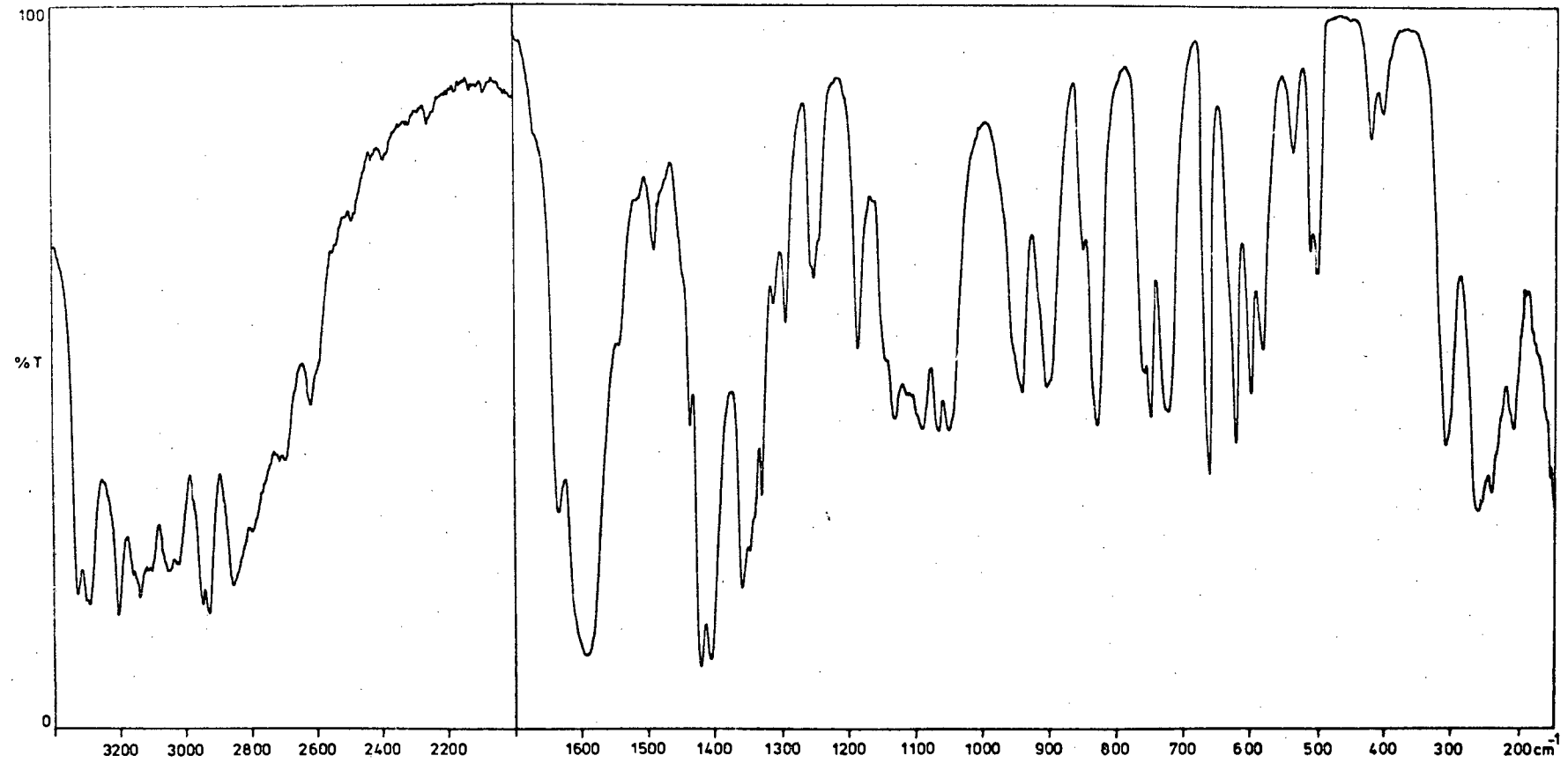


Fig. 15. The infrared spectrum (3300-140 cm^{-1}) of *cis*- $[Ni(gly)_2(Him)_2]$

Table 27. Frequencies (cm^{-1}), shifts ($\Delta\nu$, cm^{-1}) and infrared band assignments for the complex $[Pt(L\text{-ala})_2]$ and its Pd(II)- and isotopically-substituted analogues*

Band	Frequency	Δν (Pt-Pd)†	Δν ^{18}O	Δν ^{15}N	Δν $N,N\text{-}d_2$	Δν $2\text{-}d,3\text{-}d_3$	Assignment
ν_1	3225	-5		5	818		
ν_2	3209	-8		8	808		νN-H
ν_3	3103	-18		5	795		
ν_4	3003	3				751	
ν_5	2985	1				749	νC-H
ν_6	2943	3				744	
ν_7	1655	11	26	2	2	2	νC=O
ν_8	1606	3	9	3	422		νC=O + NH_2 scissor
ν_9	1457	-18				337	CH_3 deg.def.
ν_{10}	1450	-7			2	337	
ν_{11}	1392	2	4	2	9	30	νC-O + νC-C
ν_{12}	1384	0	3		20	71	
ν_{13}	1360	-3			2	365	CH_3 sym.def.
ν_{14}	1348	5	2	2	32	377	CH_3 sym.def. + NH_2 twist
ν_{15}	1307	3	15	2	18	19	νC-O + νC-C + NH_2 twist
ν_{16}	1289	-1	8	2	15	40	
ν_{17}	1268	‡			319	130	NH_2 twist + νC-CH_3
ν_{18}	1246	22		4	284	64	
ν_{19}	1231	32		4	283	94	
ν_{20}	1119	1		2	10	56	
ν_{21}	1108	-3	2	2	37	52	coupled νC-N
ν_{22}	1094	8	4	2	35	45	
ν_{23}	1038	2	3	2	200	117	νC-N + CO_2 scissor + CH_2 rock
ν_{24}	928	4	11	3	4	26	CO_2 scissor + νC-C
ν_{25}	917	‡		4	27	16	νC-N
ν_{26}	862	3	20	4	14	13	CO_2 scissor + νC-N
ν_{27}	819	21	5	5	178	21	
ν_{28}	772	2	7		15	13	CO_2 rock + CH_3 rock
ν_{29}	765	3		3	2	97	+ NH_2 rock
ν_{30}	747	-1	3	3	180	34	
ν_{31}	699	5	9	2	3	10	CO_2 rock
ν_{32}	632	9	5	4	13	19	
ν_{33}	617	18	14	9	31	22	CO_2 wag + ring def.
ν_{34}	605	18	7	9	19	10	
ν_{35}	527	18	6	7	27	22	νPt-N + νPt-O
ν_{36}	418	8	10		4	13	νPt-O
ν_{37}	402	11	10	2	23	18	νPt-O + ring def.
ν_{38}	359	3	5		16	14	
ν_{39}	324	36	4	2	9	10	ring def.
ν_{40}	289	7	5	2		4	
ν_{41}	266	2	3	2		7	
ν_{42}	234	1	6	2	8	9	δO-Pt-N
ν_{43}	223	2		4	15		δN-Pt-N
ν_{44}	158	6	8				δO-Pt-O

* Shifts <2 cm^{-1} ignored. † Frequency for Pt(II) complex minus frequency for Pd(II) complex. ‡ No corresponding band observed in spectrum of Pd(II) complex.

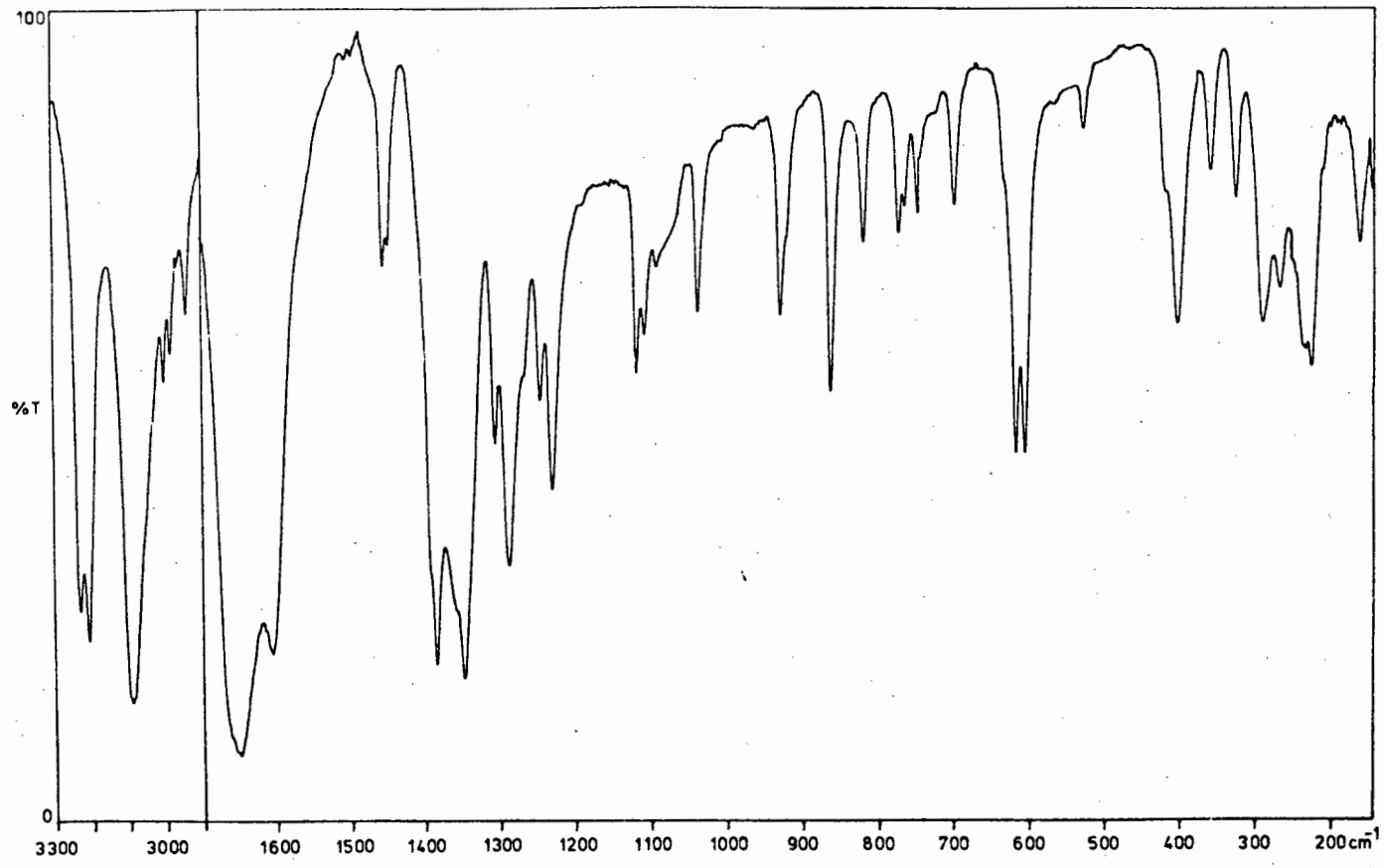


Fig. 16. The infrared spectrum (3300-140 cm^{-1}) of *trans*- $[Pt(L\text{-}ala)_2]$

Table 28. Frequencies, ^{15}N-induced shifts (in parentheses) and band assignments in the infrared spectra of [M(Hgg)X(H_2O)] (M = Mn, Co, Ni, Cu, Zn; X = Cl or Br)

Mn		Co		Ni		Cu	Zn	Assignment
Cl	Br	Cl	Br	Cl	Br	Cl	Cl	
3455	3450	3450	3439	3460	3450	3450	3500	νasym. O-H(water)
3380	3375	3389	3383	3385	3374	3425	(broad)	νsym. O-H(water)
3360(8)	3364(7)	3362(8)	3364(5)	3360(9)	3364(8)	3327(8)	3329	νN-H (amino)
3345(8)	3330(7)	3345(7)	3331(8)	3344(9)	3329(6)	3290(7)	3279	νN-H (amino)
3270(7)	3268(5)	3277(6)	3273(4)	3369(3)	3369(6)	3257(5)	3240	Amide A (νN-H)
						3218(4)		Amide A
3180(8)	3180(8)	3170(7)	3175(1)	3180(9)	3193(18)	3167(15)	3158	Amide B
						2989	3107	νC-H
3000	2995	3003[a]	2995	3006	2999	2976	3006	νC-H
2950	2950	2948[a]	2946	2950	2951	2953	2961	νC-H
2930	2930	2932	2929	2933	2931	2932	2930	νC-H
1644	1645	1643	1637	1642	1638(3)	1642(3)	1650	Amide I (νC=O)
1615	1618	1617(1)	1625(6)	1617	1620	1607	1616	Amide I (νC=O)
1584	1595	1591(5)	1597(7)	1593(3)	1597(2)	1586(6)	1576	NH_2 scissor
1571	1571	1571	1569	1572	1570(2)	1627(3)	1566	νC=O (carboxyl)
1544	1543	1549(17)	1539(16)	1551(14)	1543(17)	1576(16)	1558	Amide II (δN-H)
						1557[a](23)		Amide II (δN-H)
1440	1439	1440	1439	1440	1438(1)	1428(1)	1440	νC-O + CH_2 scissor
1429	1429	1429	1429	1429	1429	1418(1)	1430	
						1404(1)		
1399	1400	1400	1400	1401	1401	1393	1400	νC-O + νC-C and
1372	1372	1372(1)	1373(1)	1371	1371	1375(1)	1371	νC-O + CH_2 wag
1324	1325	1322	1323	1320	1322(1)	1325(3)	1333	
1314	1315	1315	1315	1311	1315	1309	1325	
1273	1272	1271(2)	1271(2)	1271(2)	1271(2)	1282[a](2)	1278	NH_2 twist
1256	1255	1256(2)	1256(3)	1257(2)	1256(3)	1259(2)	1268	NH_2 twist
						1237(1)		NH_2 twist
						1183(1)		NH_2 twist
						1145(2)		NH_2 twist
1104	1105	1101(8)	1102(8)	1100(8)	1101(7)	1102(12)	1108	Coupled νC-N

Cont./

Table 28 continued.

Mn		Co		Ni		Cu	Zn	Assignment
Cl	Br	Cl	Br	Cl	Br	Cl	Cl	
1062	1066	1062(8)	1066(5)	1065(7)	1074(9)	1092(10)	1077	Coupled νC-N
						1048(16)		Coupled νC-N
						1040[b]		Coupled νC-N
1029	1028	b	b	1030(10)	1030(9)	1028(7)	1029	Coupled νC-N
999	1008	1017(22)	1022(11)	1023(13)	1025(11)	1020(10)	1026	Coupled νC-N
932	932	935	935	935	935	937	936	CO_2 scissor
922	923	925	926	928	928(1)	928	930	CO_2 scissor
						918		CO_2 scissor
890	891	893(4)	891(2)	895(3)	894(2)	895(3)	892	NH_2 wag + δN-H
883	883	886(3)	886(4)	889(4)	888(4)	895	888	NH_2 wag + δN-H
749	748	753(2)	751(2)	757(2)	756(3)	749(7)	759	NH_2 rock + δN-H
723	711	718(5)	716(4)	723(2)	721(3)	723(3)	723	NH_2 rock + δN-H
						707(2)		NH_2 rock + δN-H
		663	645	691	672			H_2O rock
						645(5)		CO_2 rock + δring
624	618	624	619(1)	624(1)	621(1)	618	612	CO_2 rock + δring
596	595	603(2)	598(1)	608(2)	604(1)	589(2)	601	CO_2 rock + δring
		577(2)	c	595(3)	593(3)		577	CO_2 rock + δring
567	564							CO_2 rock + δring
548	543	570(3)	565(4)	573(4)	572(4)	550(2)	562	CO_2 rock + δring
491	490	532(1)	526	537(2)	534(3)		539	CO_2 rock + δring
439	438	467(11)	469(9)	481(8)	483(6)	506(8)	478	νM-N (amino)
402	404	418(1)	417(1)	431	422	451(2)	435	νM-O
346	345	360(4)	357(3)	367(2)	368(3)	368(2)	369	ligand (?)
			316(4)		340(1)			ligand
259	271	285	280(1)	299	303(1)	306(2)	275	νM-O
259	261	272	270(4)	293	292(1)	300	270	νM-Cl + νM-O
210	206	227(1)	226(1)	256(8)	240(1)	268(1)	250	νM-Br + δL-M-L
183	181	195	188(1)	205	205	207	189	δL-M-L
		185	179	195	200(1)	196		δL-M-L
		154	157	171	174	130	158	δL-M-L
						160		δL-M-L

[a] Mean of doublet. [b] Band masked by 1017 cm^{-1} absorption but observed in the spectrum of the ^{15}N-labelled complex. [c] Shoulder to band at 565 cm^{-1}. Frequency cannot be accurately determined.

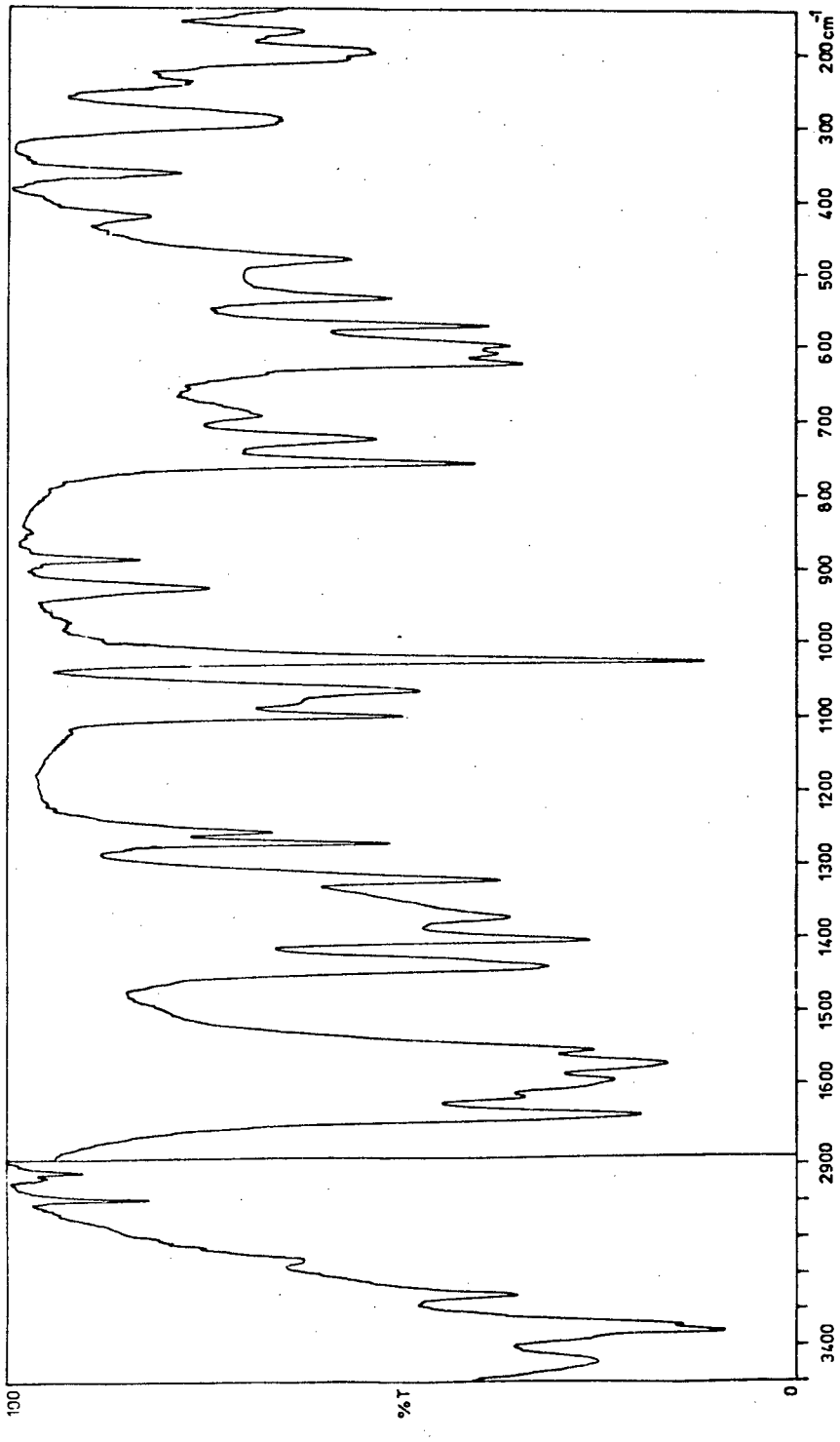


Fig. 17 The infrared spectrum (3500-140 cm^{-1}) of $[Ni(Hgg)Cl(H_2O)]$

Table 29. Frequencies, ^{15}N-induced shifts (in parentheses) and band assignments in the infrared spectra of [Cu(Hgg)X] (X = Cl or Br)

Cl	Br	Assignment
3325(6)	3321(10)	νasym. N-H (amino)
3268(8)	3291(12)	νsym. N-H (amino)
3261[a]	3261[a]	νO-H
3112(20)	3111(19)	νN-H-----O
3012	3008	νC-H
2970	2969	νC-H
2938	2934	νC-H
2924[a]	2924[a]	νC-H
1642(5)	1641(10)	νC=N
1594	1591(3)	νC=O (carboxyl)
1579(7)	1578(8)	NH_2 scissor
1562(8)[a]	1562(11)	NH_2 scissor
1419	1422	νC-O + CH_2 scissor,
1392	1392	νC-O + νC-C and
1371(1)	1367	νC-O + CH_2 wag
1301(1)	1301	
1273(2)	1276(3)	NH_2 twist
1251(2)	1253(2)	NH_2 twist
1100(4)	1102(5)	νC-N
1086(11)	1086(11)	νC-N
1038(9)	1037(9)	νC-N
1023(8)	1023(9)	νC-N
937(2)	935	CO_2 scissor
927	930	CO_2 scissor
896(3)	896(2)	NH_2 wag
746(3)	740(4)	NH_2 rock
720	720(1)	δring
715(3)	699(2)	δring
612(5)	619(4)	δring
588(2)	591(3)	δring
567(3)	570(2)	δring
503(8)	506(8)	νCu-N
383(1)	390(5)	Coupled νCu-N
363(2)	360(3)	Coupled νCu-N
324(3)	317(3)	Coupled νCu-N
271	271(1)	νCu-O
262(1)	235(1)	νCu-X
187	170	δL-Cu-L
160	151	δL-Cu-L

[a] Shoulder.

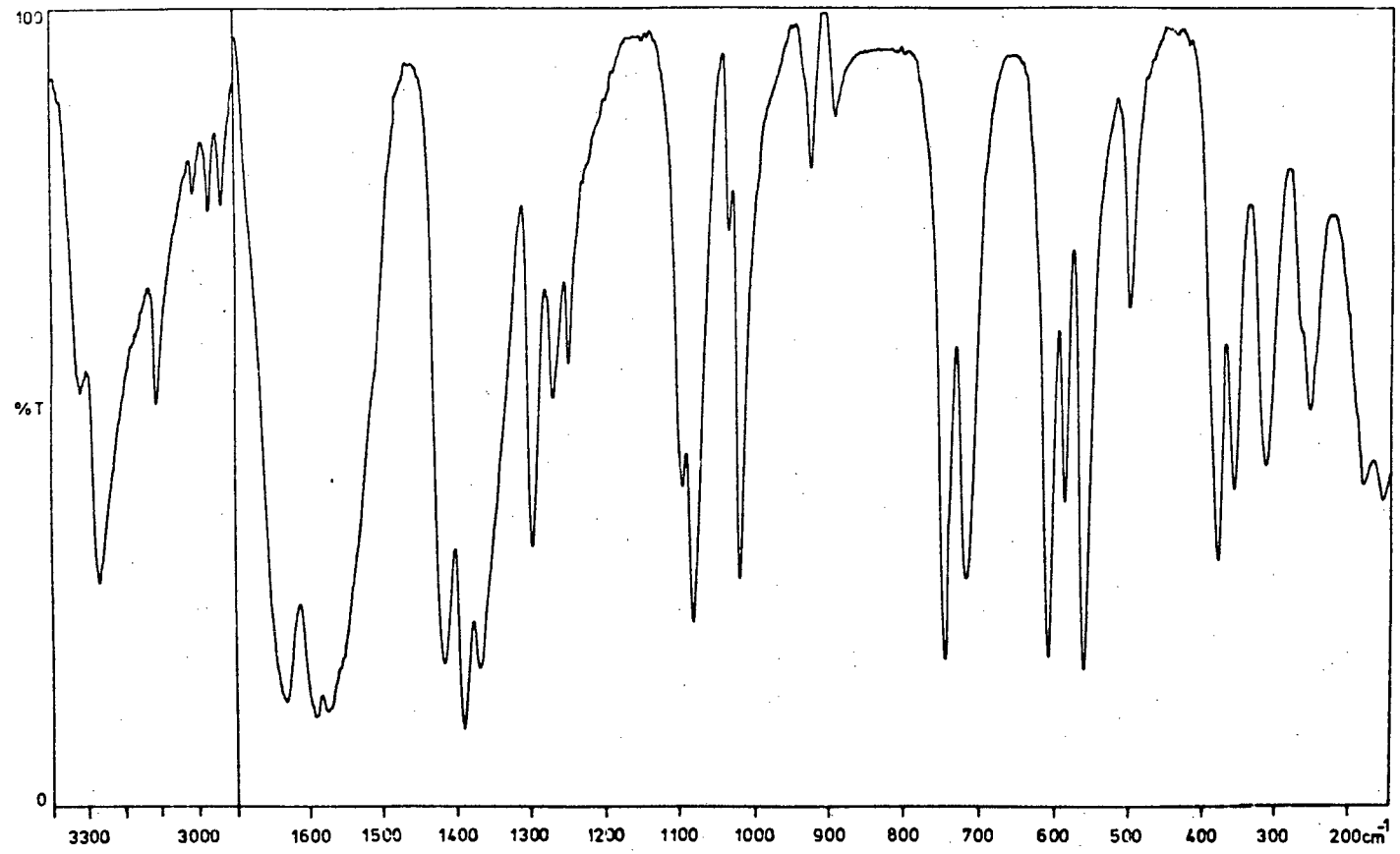


Fig. 18. The infrared spectrum (3400-140 cm^{-1}) of [Cu(Hgg)Cl]

Table 30. Frequencies and band assignments in the infrared spectra of $Na_2[M(gg)_2].nH_2O$ (M = Mn, n = 2; M = Ni, n = 9; M = Zn, n = 5)

Mn	Ni	Zn	Assignment
3545	3527	3542	νO-H (water)
3442br	3451br	3450br	νO-H (water)
3338	3339	3338	νasym. N-H (amine)
3243br	3236br	3240br	νsym. N-H(amine) + νO-H(water)
3147	3157	3140	νN-H---O
3088	3094	3092	νN-H---O
2971	2971	2971	νC-H
2936	2923	2932	νC-H
1659	1652	1660	Amide I (νC=O)
1643	1627	1645	Amide I (νC=O)
1600	1594	1600	NH_2 scissor
1569	1575	1572	νC=O (Carboxylate)
1427	1426	1427	}
1404	1406	1405	}
1381	1384	1383	}
1324	1322	1324	} νC-O + CH_2 scissor, νC-O
1311	1311	1312	} + νC-C and νC-O + CH_2 wag
1280	1282	1280	}
1260	1257	1260	}
1211	1206	1212	}
1159	1157	1160	}
1111	1107	1111	Coupled νC-N
1095	1090	1095	Coupled νC-N
1078	1076	1078	Coupled νC-N
1041	1037	1040	Coupled νC-N
1028	1025	1028	Coupled νC-N
		1003	
950	949	951	CO_2 scissor
925	925	924	CO_2 scissor
893	896	889	NH_2 wag + δN-H
753	754	754	NH_2 rock + δN-H
734	739	738	NH_2 rock + δN-H
611	614	612	CO_2 rock
524	528	527	νM-N (amine)
459	465	465	νM-N + νM-O
425	427	411	νM-N + νM-O
355	370	355	νM-O
329	335	325	νM-O
294		304	δL-M-L
	240	226	δL-M-L
203	210	197	δL-M-L
	185		δL-M-L
152		150	δL-M-L

br Broad.

Table 31. Frequencies and band assignments in the infrared spectrum of $[Cu(gg)(H_2O)_2]$

3386[br]	νO-H (water)
3309	νasym. N-H
3266	νsym. N-H
3092	νN-H---O
2936	νasym. C-H
2910	νsym. C-H
1688	Amide I
1622	NH_2 scissor
1592	νC=O (carboxylate)
1427	νC-O + CH_2 scissor, νC-O + νC=C and νC-C + CH_2 wag.
1383	
1336	
1293	
1202	
1173	
1138	
1088	Coupled νC-N
1038	Coupled νC-N
1000	Coupled νC-N
932	CO_2 scissor
918	CO_2 scissor
819[br]	H_2O rock
755	NH_2 wag + NH_2 rock + δN-H.
725	
620	CO_2 twist
543	νCu-N (amine)
514	νCu-N (amine) or νCu-O (water)
473	νCu-N + νCu-O
416	νCu-N + νCu-O
381	νCu-O
337	νCu-O
305	δL-M-L
263	δL-M-L
206	δL-M-L
188	δL-M-L
160	δL-M-L

br Broad.

3. ELECTRONIC SPECTRA AND MAGNETIC MOMENTS

Table 32. Electronic transition energies and magnetic moments for the base adducts of metal(II) acetylacetonates

Complex	Transition energy (kK)	Assignment	$\mu_{eff.}$ (B.M.)
$[Co(AA)_2(Him)_2]$	9.9	$^4T_{2g} \leftarrow {}^4T_{1g}$	4.26
	19.1	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$	
$[Ni(AA)_2(Him)_2]$	10.5	$^3T_{2g} \leftarrow {}^3A_{2g}$	2.62
	17.2	$^3T_{1g} \leftarrow {}^3A_{2g}$	
$[Co(AA)_2(pz)]_n$	10.1	$^4T_{2g} \leftarrow {}^4T_{1g}$	
	18.7	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$	
$[Ni(AA)_2(pz)]_n$	10.2	$^3T_{2g} \leftarrow {}^3A_{2g}$	
	17.4	$^3T_{1g} \leftarrow {}^3A_{2g}$	
$[Co(AA)_2(pm)]_n$	10.3	$^4T_{2g} \leftarrow {}^4T_{1g}$	
	21.5	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$	
$[Ni(AA)_2(pm)]_n$	10.6	$^3T_{2g} \leftarrow {}^3A_{2g}$	
	17.7	$^3T_{1g} \leftarrow {}^3A_{2g}$	
$[Co(AA)_2(pd)_2]$	10.4	$^4T_{2g} \leftarrow {}^4T_{1g}$	
	19.6	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$	
$[Ni(AA)_2(pd)_2]$	10.6	$^3T_{2g} \leftarrow {}^3A_{2g}$	
	17.7	$^3T_{1g} \leftarrow {}^3A_{2g}$	
$[\{Co(AA)_2\}_2(pd)]$	8.9	$^4T_{2g} \leftarrow {}^4T_{1g}$ [a]	4.09
	17.1	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$	
$[\{Ni(AA)_2\}_2(pd)]$	8.5	$^3T_{2g} \leftarrow {}^3A_{2g}$ [a]	2.71
	16.8	$^3T_{1g} \leftarrow {}^3A_{2g}$	

[a] Assuming octahedral goemetry for the complexes $[\{M(AA)_2\}_2(pd)]$.

Table 33. Electronic transition energies for the metal(II) complexes of salicylaldehyde and their adducts

Complex	Transition energy (kK)	Assignment
$[Co(Sal)_2]$	9.5	$^4T_{2g} \leftarrow {}^4T_{1g}$
	19.6	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$
$[Co(Sal)_2(H_2O)_2]$	9.7	$^4T_{2g} \leftarrow {}^4T_{1g}$
	19.6	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$
$[Co(Sal)_2(py)_2]$	10.4	$^4T_{2g} \leftarrow {}^4T_{1g}$
	18.5	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$
$[Co(Sal)_2(Him)_2]$	9.5	$^4T_{2g} \leftarrow {}^4T_{1g}$
	20.0	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$
$[Co(Sal)_2(pz)]_n$	10.1	$^4T_{2g} \leftarrow {}^4T_{1g}$
	18.0	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$
$[Co(Sal)_2(pm)]_n$	10.3	$^4T_{2g} \leftarrow {}^4T_{1g}$
	18.9	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$
$[Ni(Sal)_2]$	9.7	$^3T_{2g} \leftarrow {}^3A_{2g}$
	16.3	$^3T_{1g} \leftarrow {}^3A_{2g}$
$[Ni(Sal)_2(H_2O)_2]$	9.7	$^3T_{2g} \leftarrow {}^3A_{2g}$
	16.4	$^3T_{1g} \leftarrow {}^3A_{2g}$
$[Ni(Sal)_2(py)_2]$	10.9	$^3T_{2g} \leftarrow {}^3A_{2g}$
	18.0	$^3T_{1g} \leftarrow {}^3A_{2g}$
$[Ni(Sal)_2(Him)_2]$	10.4	$^3T_{2g} \leftarrow {}^3A_{2g}$
	17.7	$^3T_{1g} \leftarrow {}^3A_{2g}$
$[Ni(Sal)_2(pz)]_n$	10.4	$^3T_{2g} \leftarrow {}^3A_{2g}$
	18.0	$^3T_{1g} \leftarrow {}^3A_{2g}$
$[Ni(Sal)_2(pm)]_n$	10.2	$^3T_{2g} \leftarrow {}^3A_{2g}$
	17.5	$^3T_{1g} \leftarrow {}^3A_{2g}$

IV. DISCUSSION

1. INFRARED SPECTRA OF IMIDAZOLE COMPLEXES OF METAL(II) HALIDES, PERCHLORATES AND NITRATES

1.1 Band assignments in the infrared spectrum of imidazole and examination of the ratio ν^D/ν^H for bands assigned to C-H(D), N-H(D) and ring vibrations in imidazole and its complexes

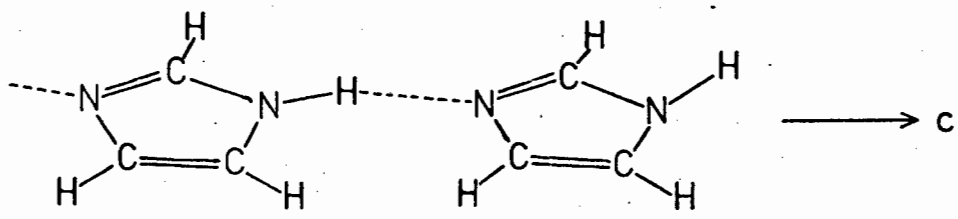
Comparison of the spectrum of imidazole (Him) with that of Him-d_3 and Him-d_4 (Table 15, Fig. 19) shows that the ratio between the frequencies (ν^D/ν^H) of corresponding bands falls into two ranges, 0.74 to 0.83 for bands involving C-H vibrations and 0.83 to 1.00 for ring vibrations. The lower ratio obtained for C-H modes is to be expected since these vibrations involve the hydrogen atoms and are therefore more sensitive to deuterium substitution. Three such ratios may be obtained for Him, namely ν^{D_1}/ν^{H_4}, ν^{D_3}/ν^{H_4} and ν^{D_4}/ν^{H_4}, where the latter two ratios are nearly identical except for the N-H(D) vibrations, in which case the first and third ratios are very close in value, ranging from 0.61 to 0.76.

Such ratios obtained for the C-H and ring vibrations agree very well with those reported[158-159] for other aromatic and heterocyclic bases, 0.74 to 0.83 and 0.83 to 1.00 for C-H and ring modes, respectively. This ratio approach has also been applied to the vibrational spectra of naphthalene and naphthalene-d_8 and values of ν^D/ν^H approximating 0.75 for C-H and 0.90 for ring modes were obtained.[160] Similar ratios have been observed by other workers[161] for pyridine and aniline. The infrared spectra of a diverse variety of metal complexes comprising such ligands as quinoline, pyridine, aniline and their fully deuterated analogues have been examined in this laboratory[158-159] with the aim of

determining the ratio ν^D/ν^H for C-H and ring vibrations as an aid to assignments. With very few exceptions, the ratios parallel those of the free parent ligands.

These ratios may serve as an effective distinction between C-H and ring vibrations in aromatic and heterocyclic compounds.[161] The potential usefulness of such results lies, however, in the absence of overlap between the ratio ranges[159] suggesting that the observed ratios may serve to distinguish between C-H and ring modes in metal complexes as in the parent ligands. The ratios observed for the Him complexes discussed here exactly match those for the free ligand. Distinction between these vibrations and metal-ligand modes, or bands originating in the vibrations of other functional groups or other coordinated ligands has also been achieved,[159] the latter generally yielding ν^D/ν^H ratios very close to unity. Where apparently anomolous ratios are observed, the possibility of incorrect assignments or vibrational coupling must be considered.[161] These ratios will be further discussed with regard to the band assignments in the spectrum of Him and its variously deuterated analogues. When more than one band occurs for each mode of vibration, the mean value of the frequencies is taken for the purpose of determining the ratio.

Imidazole crystallizes in the monoclinic system[162] and belongs to the space group $P2_1/C$ (C_{2h}^5) having four molecules per unit cell. The crystal contains infinite chains of N – H --- N hydrogen-bonded molecules.[162] The only symmetry element of an Him chain (I) is a glide plane parallel to the c-axis,[162] which corresponds with C_s symmetry. Using this, 21 fundamental vibrations are expected for an Him molecule, represented by $15A^1 + 6A^{11}$. Vibrations of the A^1 type involve in-plane motions, while the A^{11} vibrations whose characters are negative with respect to the



(I)

plane of symmetry will be out-of-plane motions, all of which should be both infrared and Raman active. These vibrations are described in Table 34.

Table 34.

Species (C_s symmetry)	Description
$15A^1$	νN-H 3νC-H δN-H 3δC-H 5νring 2δring
$6A^{11}$	γN-H 3γC-H 2γring

The infrared spectrum of Him has been extensively studied in both the solid and solution states.[69-71,163-165] The band assignments in the

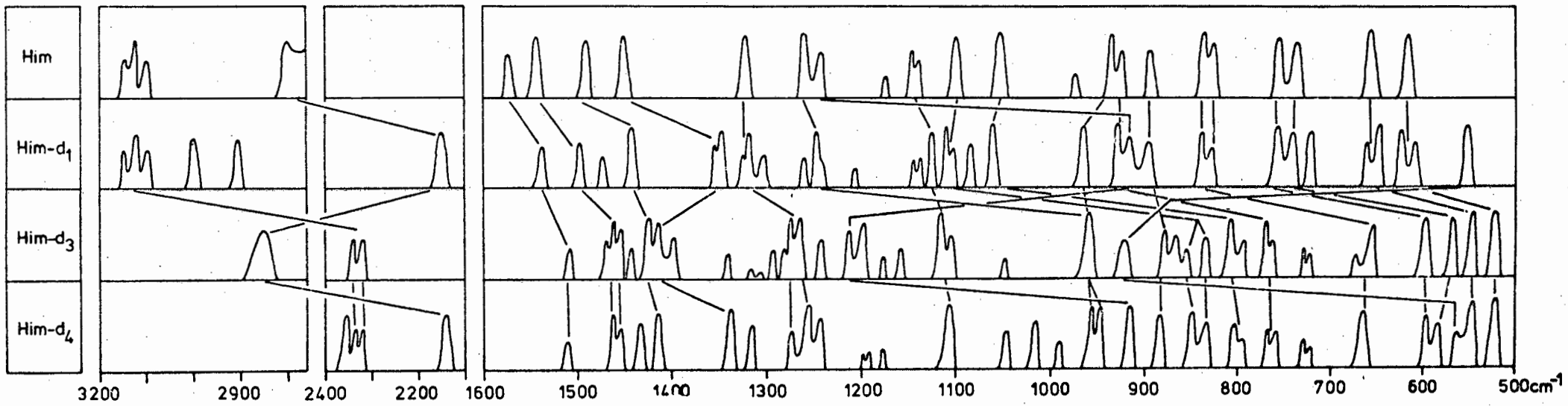


Fig. 19. The infrared spectrum (3400-580 cm^{-1}) of Him and its d_1-, d_3-, and d_4-labelled analogues

spectrum of Him proposed in Table 15 and depicted in Fig. 19 are based on the effects of d_1-, d_3- and d_4-labelling and on the reported assignments by Perchard *et al.*[69-71] whose work appears to be the most conclusive for this system. Assignments for the internal modes of undeuterated Him proposed here are identical with those previously reported.[69-70] However, some assignment changes in the spectra of the variously deuterated molecules are proposed on the basis of the results of the deuteration studies and on the expected values of the ratio ν^D/ν^H.

The 3100-2200 cm^{-1} region of the spectrum consists of a massive envelope of bands attributed[69] to H-bonded N-H stretching modes, with an intensity maximum near 2800 cm^{-1}. It has been suggested[71] that the numerous other bands extending down to 2200 cm^{-1} may involve Fermi resonance of the νN-H fundamental (near 2800 cm^{-1}) with various combinations and overtones. Two sharp bands occur above 3100 cm^{-1} which are attributed to νC-H. The more intense absorption at 3123 cm^{-1} probably[69] comprises overlap of two of the three expected C-H stretching modes. The five ring stretching modes of the A^1 species occur at 1541, 1490, 1450, 1320 and 1145 cm^{-1} (doublet). Of the three δC-H modes, that at 1260 cm^{-1} is shifted to 959 cm^{-1} in the Him-d_3 spectrum, thus overlapping[70] with the δring band at the same frequency. It becomes clearly visible, however, in the spectrum of Him-d_4 at 947 cm^{-1}. The δC-D band corresponding to δC-H at 1099 cm^{-1} in the Him spectrum has been placed[70] at 879 cm^{-1} in the Him-d_3 spectrum, and at 849 cm^{-1} in the spectrum of Him-d_4. It is suggested here that the 849 cm^{-1} and 833 cm^{-1} bands in the Him-d_4 spectrum and the 854 cm^{-1} and 834 cm^{-1} bands in the Him-d_3 spectrum are δC-D since this yields an appropriate ν^D/ν^H value of 0.77. The remaining δC-H mode is assigned to the 1052 cm^{-1} vibration, and the 1243 cm^{-1} band is assigned to δN-H in agreement with previous work.[70]

The δring mode at 894 cm^{-1} in the Him spectrum was left unassigned[70] in the Him-d_3 spectrum, but may originate in the 879 cm^{-1} band previously assigned[70] to δC-D.

Of the six fundamentals of the A^{11} species, the assignments for two of the γC-H modes at 924 and 750 cm^{-1} (doublet) are in agreement with those previously made,[70] while changes in assignment of γC-D (corresponding to γC-H near 830 cm^{-1}) in the Him-d_3 and Him-d_4 spectra are proposed on the basis of their ν^D/ν^H ratios. This vibration was previously[70] ascribed to the band near 725 cm^{-1} in the spectra of Him-d_3 and Him-d_4, yielding ratios of 0.87 which is anomalously high for a C-H vibration.[158-161] For this reason, assignment of the doublet near 660 cm^{-1}, and the band at 666 cm^{-1} in the spectra of Him-d_3 and Him-d_4 respectively, to γC-H, is preferred. These assignments yield ratios of 0.80 which lies within the range expected for such vibrations. No specific band may be assigned to γN-H. Perchard *et al.*[70] estimated it to occur near 930 cm^{-1} and considered that it may be masked by adjacent absorptions. They assigned a 670 cm^{-1} vibration in the spectrum of Him-d_1 to γN-D (this is considered to correspond with the 660 cm^{-1} band in the present work). A unique band in the Him-d_1 spectrum, however, is that at 554 cm^{-1}, which is therefore only reasonably assignable to γN-D. This band recurs in the Him-d_4 spectrum at 566 cm^{-1}. Using the factor group C_{2h} Perchard and co-workers[71] determined the number of lattice vibrations of Him and assigned the weak 174 cm^{-1} band to a translational lattice mode.

Practically all the internal modes in the spectrum of Him recur in the spectra of the complexes and, in both cases, similar values of the ratio ν^D/ν^H are observed. Ratios of the C-H(D) modes and ring modes span ranges of 0.74 to 0.81 and 0.84 to 1.00, respectively, with the exception of the δring band near 950 cm^{-1} which undergoes a slight high frequency

shift[70] on deuteration to yield (as it does in the spectrum of the free base) an anomalous ratio of 1.03. This value approximates the square root of the mass ratio m^i/m, where m^i is the mass of Him-d_3 or Him-d_4. In contrast to the complicated absorptions of the H-bonded N-H stretch in the spectrum of free Him, complexation results in clearly defined N-H stretching bands above 3200 cm^{-1}. The positions of the N-H deformational frequencies in the spectra of Him complexes are known[62] to be highly dependent on the nature and extent to which they partake in H-bonding; δN-H (in the complexes studied here) spanning the frequency ranges 1250 to 1100 cm^{-1} and γN-H 940 to 700 cm^{-1}. The remaining bands are approximately concurrent in the spectra of the free ligand and the complexes. Ratios for the N-H modes in the complexes are almost identical to those pertaining to the free base, ranging from 0.60 to 0.75 for the d_1- and d_4- and from 0.95 to 1.00 for the d_3-labelled complexes.

1.2 The complexes $[M(Him)_6](NO_3)_2$, where M = Co(II), Ni(II) and Zn(II)

Hexakis(imidazole)nickel(II) nitrate appears to be isomorphous with the Co(II) analogue,[51,166] both having the rhombohedral space group $R\bar{3}$. Complete assignments for the low frequency infrared and Raman spectra of the Co(II) complex[65] have been made in single crystal studies (for which this complex is ideally suited since the point group, site group and factor group[65] are all S_6). In the present study the corresponding Zn(II) complex (Fig. 2) is also discussed, and band assignments in the far-infrared are based on the effects of Him-d_3 labelling and metal ion substitution. It is clear from the band-for-band correspondence of the mid- and far-infrared spectra (Table 16, Figs. 20 and 21) of these complexes

that the Zn(II) analogue is octahedral and isostructural (not necessarily isomorphous) with the Co(II) and Ni(II) complexes. Infrared spectra (4000 - 300 cm^{-1}) of d_1-, d_3- and d_4-labelled $[Co(Him)_6](NO_3)_2$ were recorded (Table 16, Fig. 20) for the purpose of facilitating band assignments and to ascertain whether the ratios ν^D/ν^H conform with those for the free base. Examination of the ratios in Tables 15 and 16 show that these values are similar.

Crystal structure analysis[51] of the Ni(II) complex reveals that the nitrate groups are essentially ionic with symmetry C_3, which is not sufficiently distorted[85,91,167] from D_{3h} symmetry (the symmetry of an isolated nitrate ion) to cause splitting of degeneracies or induce activity of infrared inactive modes. Assignments of the nitrate modes are reported in Table 35. Of the four normal modes of vibration of an ionic nitrate group, ν_1 (which occurs in the 1050 cm^{-1} region[85,91,167]) is infrared inactive,[85] but often appears in the spectra of complexes where the nitrate ion is outside the coordination sphere.[91]

Table 35.

Frequency (cm^{-1})			Assignment
Co(II)	Ni(II)	Zn(II)	
1374	1373	1374	ν_3 νasym. NO_3
825	827	828	ν_2 δNO_3
710	715	712	ν_4 δNO_3

This is attributed to relaxation of the free ion selection rules under the constraint of the field within the crystal. All three spectra reveal the absence of ν_1 (νsym. NO_3) while ν_2, ν_3 and ν_4 arise within the regions expected[85,91,167] for ionic nitrate. That the intensity of the ν_2 band increases and shows an apparent shift on Him-d_3 and Him-d_4

labelling is due to its coincidence with δC-D of Him-d_3 and Him-d_4 in these spectra.

All the skeletal vibrations (of which one asymmetric stretch and one N-M-N bending mode are expected on the basis of O_h point group symmetry) are confined to the region below 300 cm^{-1} (Fig. 21). It is generally agreed[57,61,64-65] that the strong band of highest frequency is νasym.M-N. Nakamoto[64] found that the equivalent band in the spectra of $[M(Him)_6]Cl_2$ (M = Ni or Zn) exhibited the largest metal-isotope shifts in this region. The Him-d_3-induced shifts (Table 16) in these bands in the nitrate complexes are lower than the shifts experienced by the remaining bands in the 300-140 cm^{-1} region but are of the magnitude expected for a relatively pure νM-N band. Furthermore, they are strongly metal ion dependent in the order of CFSE's Co(II) < Ni(II) > Zn(II). Four opinions exist as to the origins of the remaining one (or two) bands above 140 cm^{-1}. One view[61] considers that these weaker bands might be components of the T_{1u} stretching mode due to departure from O_h symmetry. Eilbeck and co-workers[57] tentatively assigned the 200 cm^{-1} vibration in $[Co(Him)_6]Cl_2$ to δN-M-N, while Nakamoto[64] suggests them to be ligand modes because the Him spectrum exhibits a weak band near 180 cm^{-1} (assigned[71] to a translational lattice mode). Adams,[65] however, gives good reason to suggest that these bands originate in M-Him torsional modes and modes involving δM-N-C. While these bands were found[64] to yield no appreciable metal-isotope shifts, they are strongly deutero-sensitive.

It is difficult to make reliable assignments for these bands since they are rather close to νM-N to warrant their assignment to δN-M-N. In the past however, similar bands in pyridine complexes have been assigned[33,85,168] to δN-M-N. Adams[65] points out that numerous complicated deformational modes are likely to arise in complexes with donor ligands

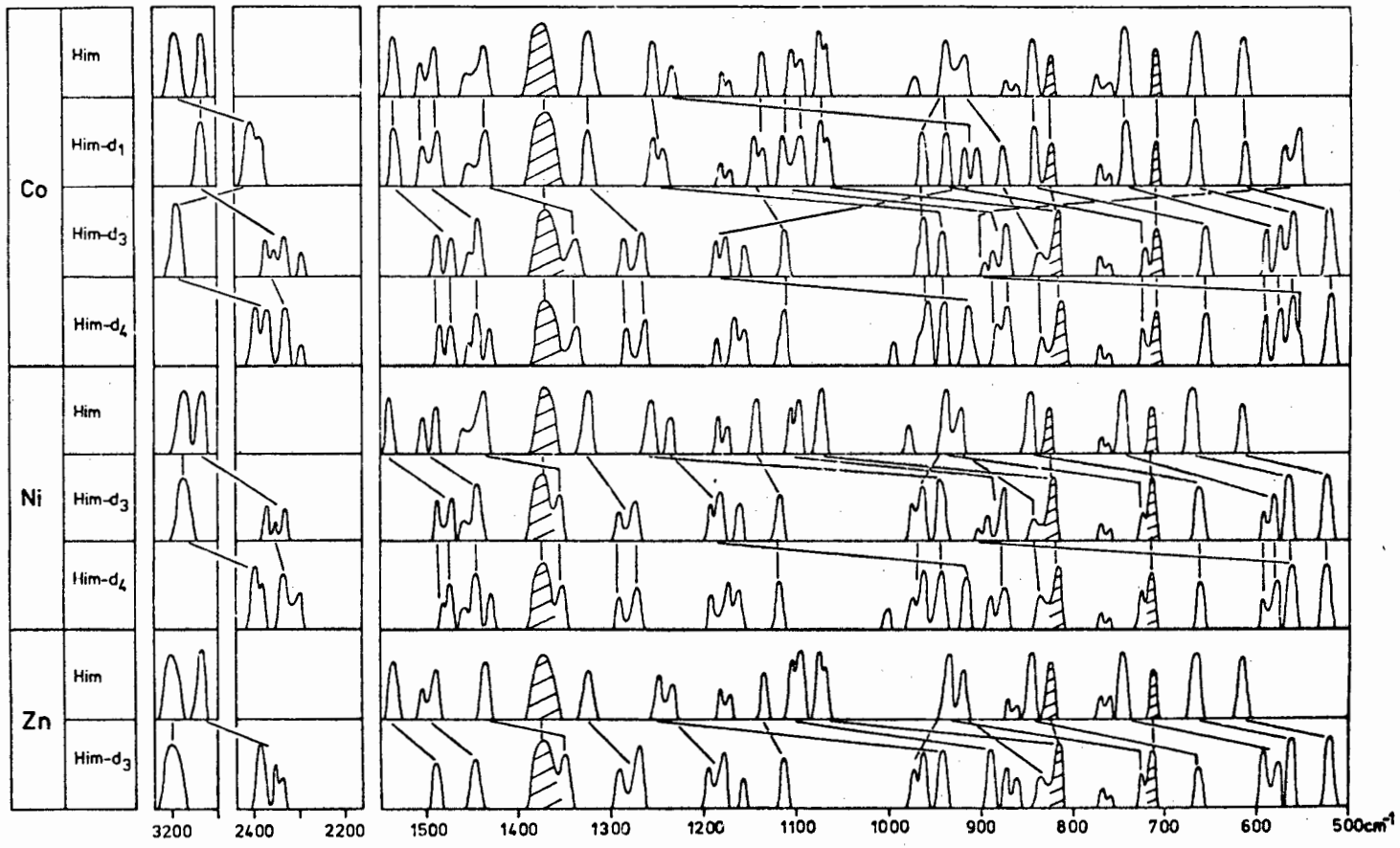


Fig. 20. The infrared spectra (4000-500 cm^{-1}) of the complexes $[M(Him)_6](NO_3)_2$ and their Him-d_1, -d_3 and -d_4 labelled analogues

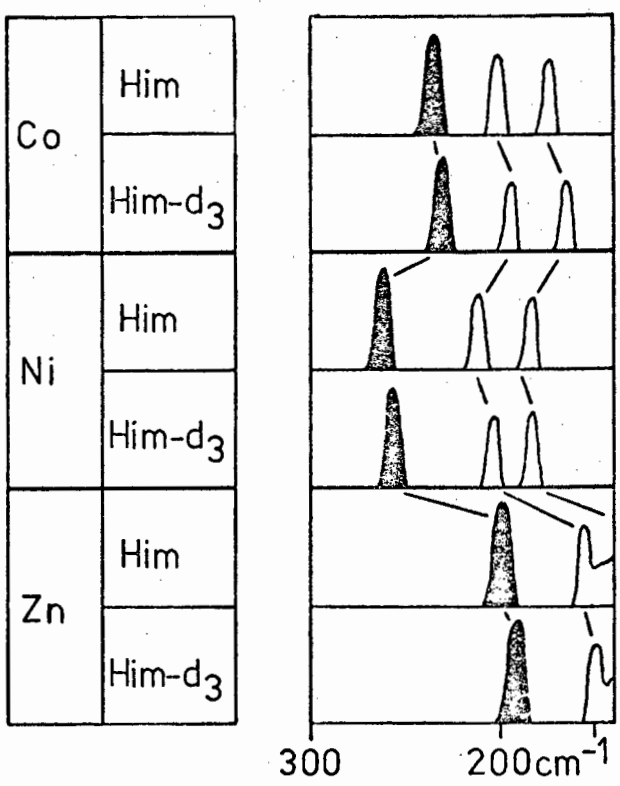


Fig. 21. The infrared spectra (300-140 cm^{-1}) of the complexes $[M(Him)_6](NO_3)_2$ and their Him-d_3 labelled analogues. Solid bands: νM-N

such as these heterocycles, which may manifest themselves in various M-L torsions and deformations in the vibrational spectra. Both bands are nevertheless strongly metal ion dependent indicating some form of M-L character and furthermore, their shifts on d_3-labelling are much greater than the expected shifts ($\Delta\nu \sim 3$ cm^{-1}) based on a simple diatomic oscillator model. It is probable that a deformation of the form δM-N-C will yield a larger shift than that of a M-N stretch or N-M-N bend and on this basis these bands are assigned to δ_τM-Him + δM-N-C.

1.3 The complexes $[M(Him)_6](ClO_4)_2$, where M = Mn(II), Fe(II), Co(II) and Ni(II) and $[Zn(Him)_5](ClO_4)_2$

Imidazole readily forms stable hexakis-complexes with Mn(II), Fe(II), Co(II) and Ni(II) perchlorates, whereas the Zn(II) perchlorate complex prefers five-coordination. With the exception of the far-infrared spectrum of the Co(II) complex (Figs. 3 and 23) the striking similarities in band patterns in the spectra of the complexes of Mn(II) through Ni(II) is sufficient evidence of their isostructural nature. The mid-infrared spectrum (Table 17) is characterised by two N-H stretching bands near 3360 cm^{-1} and a shoulder near 3437 cm^{-1}, whereas the spectrum of the five-coordinate Zn(II) complex exhibits a single broad band at 3320 cm^{-1}. The γ ring mode near 600 cm^{-1} occurs as two bands in the spectra of the complexes of Mn(II) through Ni(II) while that in the Zn(II) spectrum occurs as a shoulder at 609 cm^{-1}. The only complex in this series to have previously received attention[60] is that of the Co(II) salt, for which the value of $\mu_{eff.}$ (5.10 B.M.) is typical of high-spin octahedral Co(II). Reported infrared spectra[60] (4000 - 700 cm^{-1}) summarized the perchlorate

vibrations from which it was concluded that the perchlorate ions are essentially ionic.

The free perchlorate anion has a regular tetrahedral structure[85,167 169-170] and belongs to the T_d point group. Its nine vibrational degrees of freedom are distributed between four fundamental modes of vibration, $A_1(\nu_1) + E(\nu_2) + 2T_2(\nu_3,\nu_4)$. In the spectra of ionic perchlorates, the triply degenerate modes are infrared active; ν_3 occuring[85] near 1100 cm^{-1} as a very broad band which is occasionally split[168] while ν_4 is observed in the 625 cm^{-1} region. The non-degenerate ν_1, theoretically forbidden in the infrared, often occurs[167,169] as a very weak band near 930 cm^{-1} owing to some relaxation of the T_d symmetry criteria in a field of somewhat lower symmetry. While the effect of coordination of the perchlorate group is likely to bring about major differences in the infrared spectrum, minor shifts or splittings may result from lowering of the group's site symmetry or from vibrational coupling between perchlorate groups in the unit cell. The bands assigned to perchlorate modes are listed in Table 36. From the nature and frequencies of these vibrations it may be concluded that the perchlorate groups obey the selection rules for an ionic and tetrahedral anion, although activation of the inactive ν_2 mode is evidenced by a weak band at 464 cm^{-1}. This absorption is extremely weak in the spectrum of the Zn(II) complex. The asymmetric

Table 36.

Frequencies (cm^{-1})						
Mn(II)	Fe(II)	Co(II)	Ni(II)	Zn(II)	Species (T_d)	Assignment
1130	1130	1130	1130	1145		
1111	1111	1111	1111	1110	T_2	ν_3 νasym.
1084	1084	1084	1085	1087		
621	621	621	621	621	T_2	ν_4 δasym.
464	464	464	464	463[a]	E	ν_2 δsym.

a Very weak.

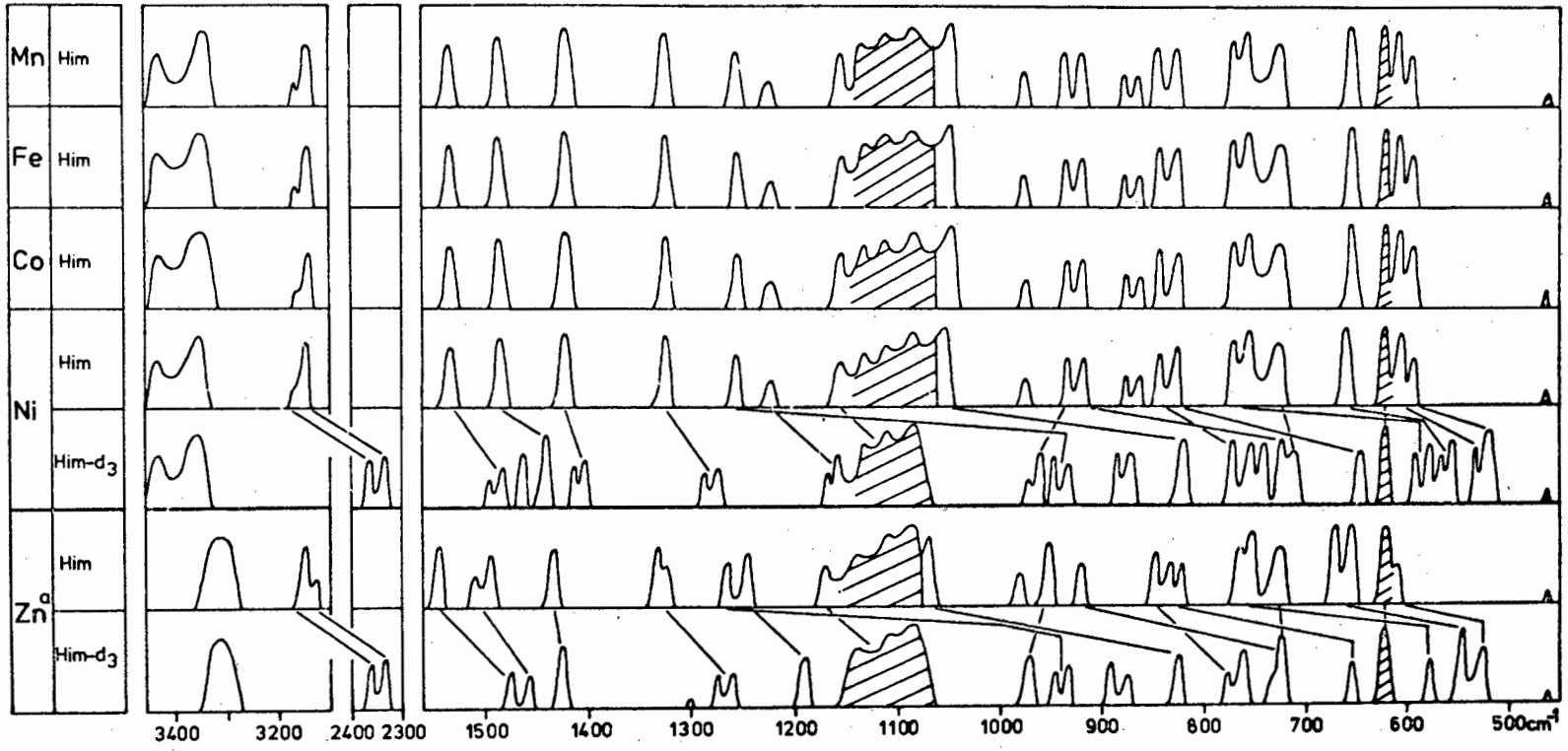


Fig. 22. The infrared spectra (4000-450 cm^{-1}) of the complexes $[M(Him)_6](ClO_4)_2$ and $[Zn(Him)_5](ClO_4)_2$[a]

deformation, ν_4, is readily identified at 621 cm^{-1} by its insensitivity towards deuteration of the Him ring and the broad diffuse ν_3 absorption has three intensity maxima in the 1100 cm^{-1} region.

The metal-ligand vibrations, below 350 cm^{-1} (Fig. 23) in the spectra of the complexes of Mn(II) through Ni(II) exhibit essentially the same band patterns as their corresponding nitrates. The asymmetric Ni-N stretching mode occurs at the same frequency as νasym Ni-N in $[Ni(Him)_6](NO_3)_2$. The spectrum of the Co(II) complex is exceptional in that this band is split, giving two strong absorptions at 243 and 224 cm^{-1}, undergoing equivalent shifts ($\Delta\nu$ = 4 cm^{-1}) on deuteration. In the light of the reported magnetic moment and electronic spectrum,[60] both of which support octahedral sterochemistry, splitting of νCo-N must be considered evidence for some deviation from O_h symmetry. Support for these assignments of νM-N is revealed by their strong metal ion dependence in the order of CFSE's: Mn(II) ≤ Fe(II) < Co(II) < Ni(II). The remaining two bands between 200 and 140 cm^{-1} are probably the same as those bands assigned to torsions and δM-N-C in the spectra of the nitrate complexes. In these spectra they are, however, significantly weaker in intensity. These bands show, with the exception of Fe(II), a correlation with metal ion substitution equivalent to that of νM-N, while their *d*-sensitivities are, once again, equal to or greater than those observed for νM-N. They are therefore similarly assigned to δ_τM-Him + δM-N-C.

The anomalous spectrum obtained for the Zn(II) complex is evidence for its unique structure. Five-coordinate Zn(II), of which there are numerous known examples,[171] appears to form tetragonal pyramidal structures[171] rather than the other idealized geometry of a trigonal bipyramid for five-coordinate complexes. Assuming that the perchlorate ions are not coordinated, as appears to be the case from their band pattern which is

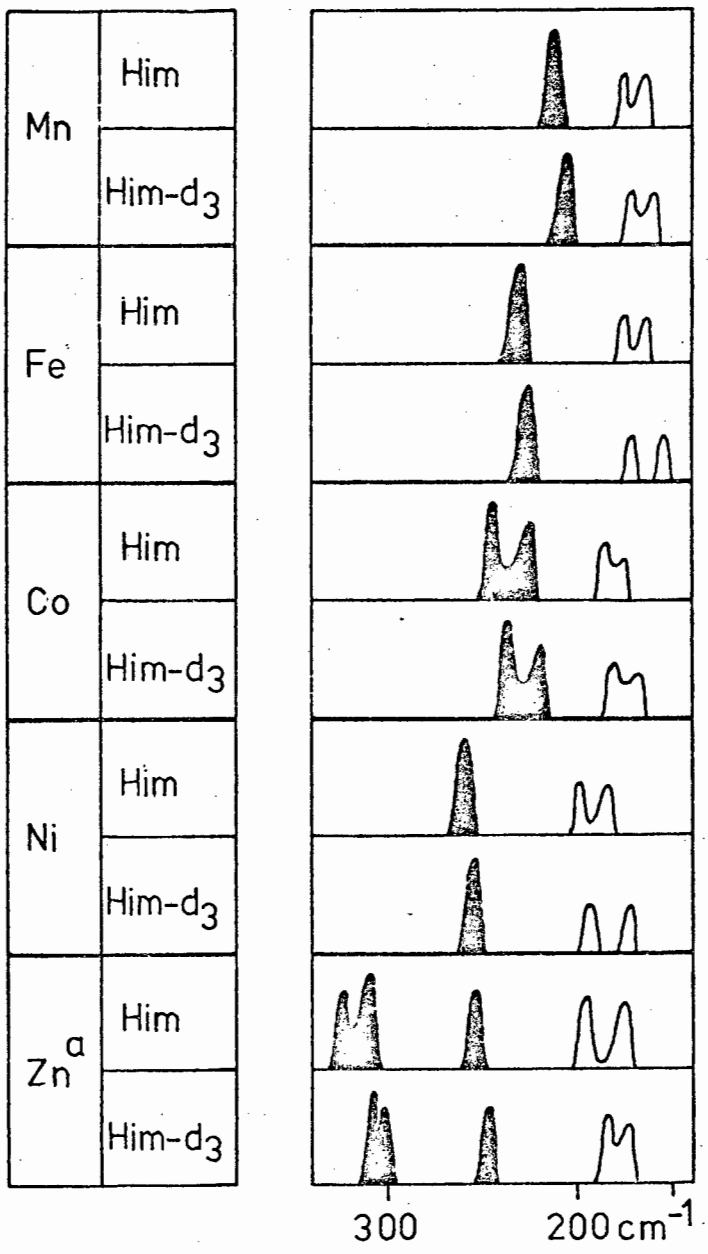


Fig. 23. The infrared spectra (350-140 cm^{-1}) of the complexes $[M(Him)_6](ClO_4)_2$ and $[Zn(Him)_5](ClO_4)_2$.

Solid bands: νM-N

identical to that of the six-coordinate complexes (Table 17), the structure proposed for this complex is that of a square based pyramid. On this basis the three bands above 250 cm^{-1} in the infrared spectrum are assigned to νZn-N. The fact that these bands arise at the same, or higher, frequency than νNi-N in $[Ni(Him)_6](ClO_4)_2$, assists in verifying the structural assignment of the Zn(II) complex. It is well known[172] that when the bonding capacity of the metal ion is distributed over fewer bonds, the values of νM-L will be higher than would be the case for a complex with a greater coordination number. This phenomenon has been demonstrated on numerous occasions, one example[33] being the transformation of polymeric octahedral $[Co(py)_2Cl_2]$, (νCo-N = 182 cm^{-1}) into monomeric tetrahedral $[Co(py)_2Cl_2]$, (νCo-N = 248 and 208 cm^{-1}). In the case of the tetrahedral complex, the bonding capacity of Co(II) is distributed over four bonds rather than six in the octahedral complex. Both values of νCo-N are at higher frequency than that for the octahedral complex. The two bands below 200 cm^{-1} correspond, in position, with those assigned to δ_τM-Him + δM-N-C in the spectra of the octahedral complexes. The 195 cm^{-1} band is similarly assigned, on the basis of its position and its strong *d*-sensitivity, while the 176 cm^{-1} band, which shows no sensitivity towards deuteration, is assigned to a coupled mode involving δN-M-N since this is the region in which such a mode is anticipated i.e. roughly half the frequency of the M-N stretching mode.

1.4 The complexes $[Cu(Him)_4(ClO_4)_2]$, $[Cu(Him)_4(NO_3)_2]$, $[Zn(Him)_4](ClO_4)_2$ and $[Zn(Him)_4(NO_3)_2]$

The crystals of $[Cu(Him)_4(ClO_4)_2]$ are monoclinic,[53] space group $P2_1/n$, with two formula units in the unit cell. The six-coordinate octahedral complex possesses two short Cu-N bonds differing by 0.012 Å and a long Cu-O bond of 2.625 Å completing the *trans*-octahedral stereochemistry.[53] The hydrogen atoms on the pyrrole nitrogens take part in two types of H-bond[53] to oxygen atoms of the perchlorate groups. This is well reflected in the N-H stretching region of the infrared spectrum (Table 18, Fig. 24) by two νN-H peaks. The crystal structure analysis[53] indicates that the symmetry of the monodentate perchlorate groups approximates that of the free ion. Tetragonal distortion along the Cu-O bonds evidently has the effect of lowering the Cu-O covalent character, thus preserving most of the ionic nature of the perchlorate groups. This fact is evident from the infrared spectrum (Table 37, Fig. 24) where the degenerate perchlorate modes, ν_3 and ν_4, which display structure, are essentially the same as those in the spectra of $[M(Him)_6](ClO_4)_2$. The point of significance in the present case is the

Table 37

Frequency (cm^{-1})			
$[Cu(Him)_4(ClO_4)_2]$	$[Zn(Him)_4](ClO_4)_2$	Species (T_d)	Assignment
1135			
1111	1120-1060	T_2	ν_3 νasym.
1070			
930[a]		A_1	ν_1 νsym.
625	622	T_2	ν_4 δasym.
462[b]	464[b]	E	ν_2 δsym.

[a] Weak.
[b] Very weak.

increased frequency separation between the two lower frequency components of ν_3. The asymmetric deformation, ν_4, occurs as a single absorption at 625 cm^{-1}, while ν_1 and ν_2, which are theoretically infrared-inactive in T_d symmetry, but often observed[169-170] in the spectra of ionic perchlorates, occur as weak bands at 930 and 462 cm^{-1}. All these assignments are supported by absence of sensitivity to deuteration.

The Zn(II) ion in $[Zn(Him)_4](ClO_4)_2$ is tetrahedrally coordinated[54] to four Him molecules whose pyrrole N-H groups are H-bonded to oxygen atoms of the approximately tetrahedral ionic perchlorate groups. The perchlorate spectrum (Tables 18 and 37) agrees well with those of the hexakis-complexes, with the exception of ν_3, which occurs as one continuous absorption over the range 1120 to 1060 cm^{-1}. It is distinguished, however, from the spectrum of $[Cu(Him)_4(ClO_4)_2]$ by the absence of ν_1, while ν_2 is again seen as a very weak band at 464 cm^{-1}.

Tetrakis(imidazole)copper(II) nitrate forms orthorhombic crystals[56] (space group $Pna2_1$, Z = 4) whose geometry is similar to that of the perchlorate complex i.e. tetragonally distorted along the Cu-O (nitrate) bonds with four Him molecules defining the equatorial plane. The infrared spectrum (Table 19) exhibits nitrate absorptions differing considerably from those in the spectra of $[M(Him)_6](NO_3)_2$ and this is attributed to their monodentate coordination in $[Cu(Him)_4(NO_3)_2]$. This has the effect of lowering the point symmetry of the nitrate entity so as to approximate[85,91] C_{2v} symmetry, thus lifting degenerate modes and activating all six vibrational degrees of freedom. The $D_{3h} \rightarrow C_{2v}$ correlation is shown in Table 38 together with the corresponding assignments. Both νasym.and νsym.NO_2 occur as strong absorptions at 1399 and 1343 cm^{-1}, respectively. νN-O is observed at 1049 cm^{-1}, and δasym.NO_2 occurs at 709 cm^{-1}, as evidenced by their insensitivity

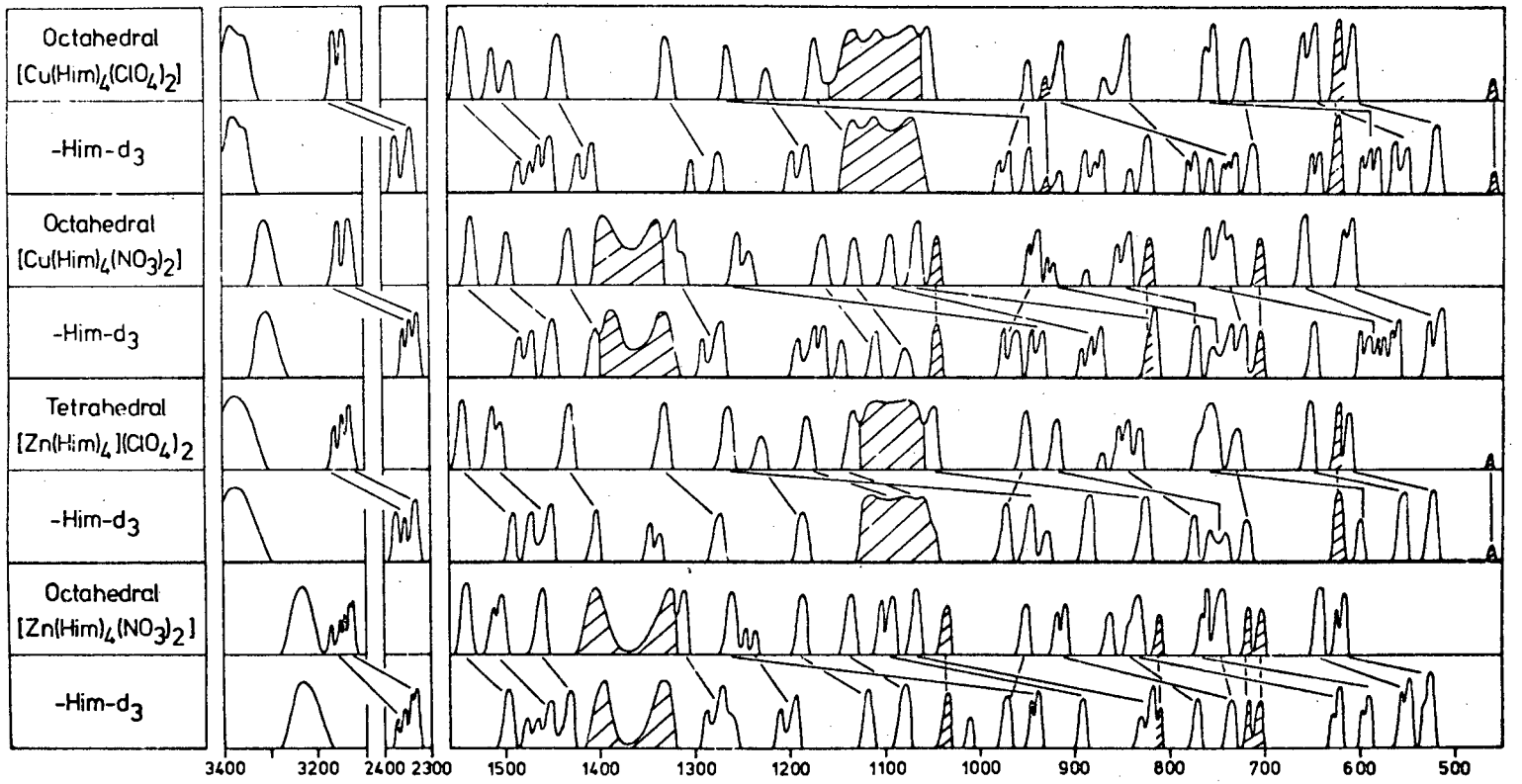


Fig. 24. The infrared spectra (3400-450 cm^{-1}) of $[Cu(Him)_4(ClO_4)_2]$, $[Cu(Him)_4(NO_3)_2]$, $[Zn(Him)_4](ClO_4)_2$ and $[Zn(Him)_4(NO_3)_2]$

towards deuteration. The symmetric bend, ν_3, which generally occurs in the 740 cm^{-1} range[85,91] is probably obscured by the strong Him absorptions in this region.

Table 38.

Ionic nitrate (D_{3h} symmetry)		Monodentate nitrate (C_{2v} symmetry)	Frequency (cm^{-1}) $[Cu(Him)_4(NO_3)_2]$	$[Zn(Him)_4(NO_3)_2]$
ν_1 A_1^1 νsym.NO_2	→	ν_2 A^1 νsym. N-O	1049	1035
ν_2 A_2^{11} δNO_2	→	ν_6 B^1 oop. rock	823	813
ν_3 E^1 νasym.NO_2	→	ν_1 A^1 νsym.NO_2	1343	1324
	↘	ν_4 B_2 νasym.NO_2	1399	1406
ν_4 E^1 Planar rock	→	ν_3 A^1 δsym.NO_2	not observed	718
	↘	ν_5 B^2 δasym.NO_2	709	703

The close similarity between the infrared spectra below 300 cm^{-1} of $[Zn(Him)_4](ClO_4)_2$ and its corresponding nitrato-complex is misleading. Examination of the nitrate spectrum (Tables 19 and 38) of the Zn(II) complex shows that ν_3 is split into two strong absorptions in the 1410-1320 cm^{-1} region, and that ν_4 is also split. In fact, the band pattern is identical to that observed in the nitrate spectrum of $[Cu(Him)_4(NO_3)_2]$ and is consistent[85,91] with covalent bond formation between nitrate and Zn(II). In view of this evidence, the Zn(II) complex is formulated $[Zn(Him)_4(NO_3)_2]$ with monodentate nitrate groups occupying axial sites of the octahedron. This is consistent with the findings of Goodgame and co-workers.[61] It has been established[91] that the position of νN-O in monodentate nitrato-complexes is symptomatic of the strength of

the M-O covalency. Comparison of the frequencies in Table 38 for the Zn(II) and Cu(II) analogues shows that ν_2(νN-O) for monodentate nitrate in the Zn(II) complex is some 14 cm^{-1} lower in frequency than the corresponding nitrate band in the Cu(II) complex, indicating a stronger Zn-O than Cu-O covalent bond. This is consistent with tetragonal distortion[56] in the direction of the Cu-O bond in the Cu(II) complex. That the frequency separation between ν_1 and ν_4 is greater in the Zn(II) complex may also be a measure of the M-O bond strength.

The metal-ligand modes below 350 cm^{-1} in the spectrum of $[Cu(Him)_4(ClO_4)_2]$ are best described in terms of the C_i site symmetry[56] of the Cu atom, rather than the point group symmetry D_{4h}. The distribution of the relevant modes for D_{4h} symmetry together with the corresponding modes for C_i symmetry are shown in the correlation in Table 39. This symmetry has the effect of generating both asymmetric and symmetric Cu-N stretching modes which are recognised as those bands at 307 and 286 cm^{-1} in the infrared spectrum (Fig. 25). It is expected that νCu-O occurs below 140 cm^{-1} since the Cu-O distance[56] is long and all the bands occurring above this frequency exhibit strong *d*-sensitivities.

Table 39.

D_{4h} (Point group)		C_i (Site group)
E_u νM-N	⟶	$2A_u$ (νasym. M-N + νsym. M-N)
A_{2u} νM-O	⟶	Au νM-O
A_{2u}		Au
B_{2u}	⟶	A_u Skeletal deformations
$2E_u$		$2A_u$

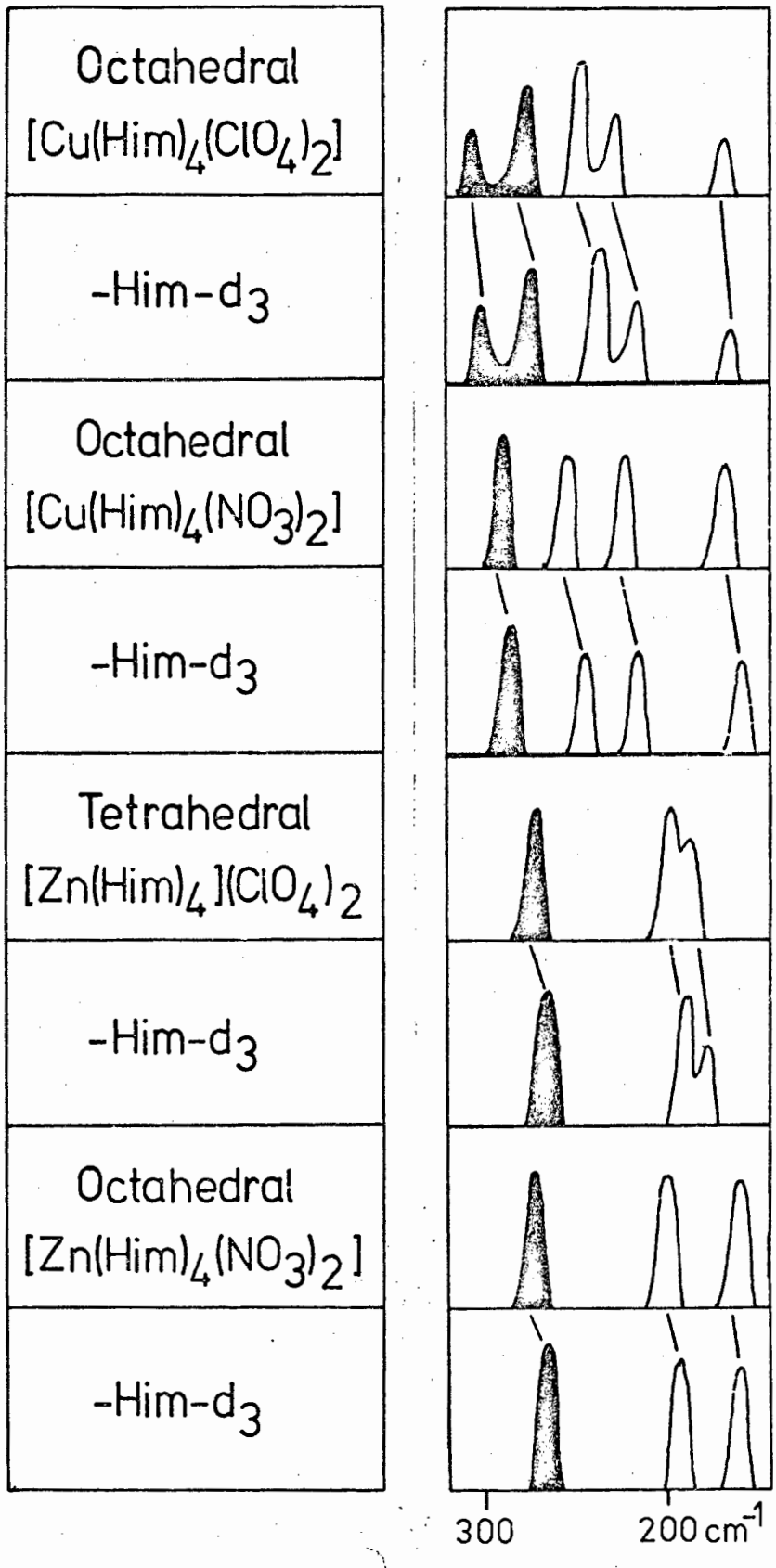


Fig. 25. Infrared spectra (350-140 cm^{-1}) of $[Cu(Him)_4(ClO_4)_2]$, $[Cu(Him)_4(NO_3)_2]$, $[Zn(Him)_4](ClO_4)_2$ and $[Zn(Him)_4(NO_3)_2]$. Solid bands: νM-N (Him)

The bands arising at 246 and 228 cm^{-1} appear to have the same origin as the bands assigned to δ_TM-Him + δM-N-C in the spectra of the hexakis-complexes since they occur at similar positions in relation to νM-N and are equally sensitive to Him-d_3 substitution. The weak 167 cm^{-1} absorption is assigned to δN-Cu-N on the basis of its shift on labelling and its position with respect to the νCu-N bands.

The Cu-N stretches in the spectra of $[Cu(Him)_4(NO_3)_2]$ and $[Zn(Him)_4(NO_3)_2]$ occur as single strong absorptions at 290 and 271 cm^{-1}, respectively. It has been suggested[61] that the 271 cm^{-1} band in the Zn(II) complex is νZn-O (nitrate). This appears unlikely for two reasons. Firstly, it has a *d*-sensitivity matching that of most of the bands assigned to νM-N in the complexes studied here and secondly, it seems unlikely that νZn-O would occur some 69 cm^{-1} higher than any other band that may be assigned to νZn-N. Finally, this assignment agrees well with the corresponding assignments for the Cu(II) complex, being in the expected order of CFSE's of Cu(II) > Zn(II). The remaining one (or two) bands occurring above 180 cm^{-1} are, on the basis of their *d*-sensitivities and positions with respect to similar bands in the hexakis-complexes, assigned to δ_TM-Him + δN-M-C while the band below 170 cm^{-1} is assigned to δN-M-N.

1.5 The complexes $[Cu(Him)_4X_2]$, where X = Cl, Br or I

Perchard and Novak[62] reported a thorough investigation of the ligand modes in the infrared spectra of the chloride and bromide complexes. Together with Him-d_1 labelling these workers were able to distinguish between crystallographically non-equivalent Him molecules

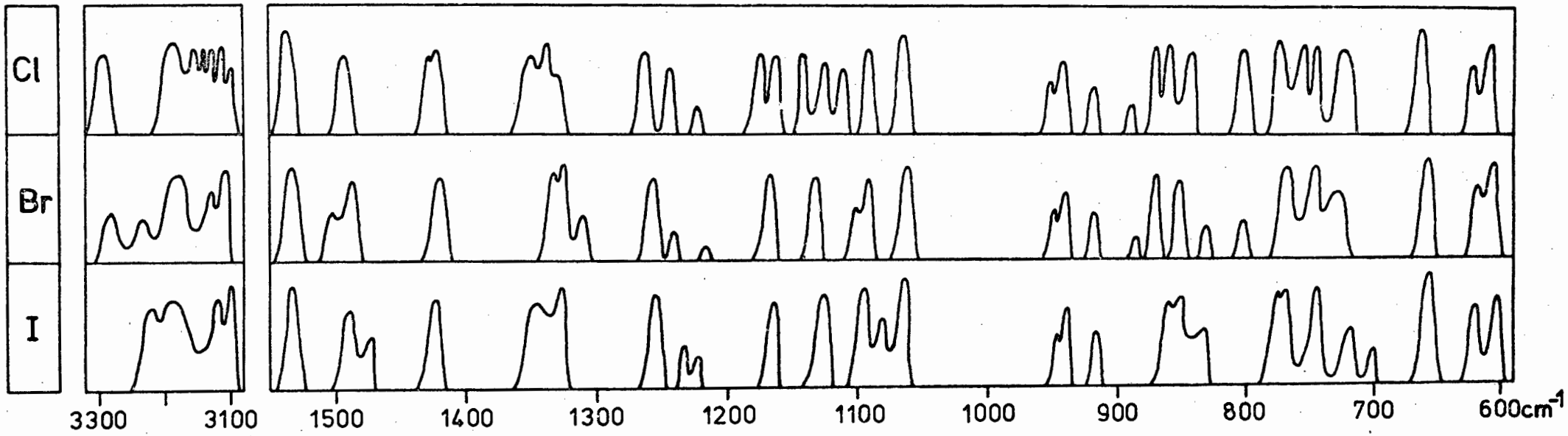


Fig. 26. The infrared spectra (4000-500 cm^{-1}) of the complexes $[Cu(Him)_4(X)_2]$. (X = Cl, Br or I).

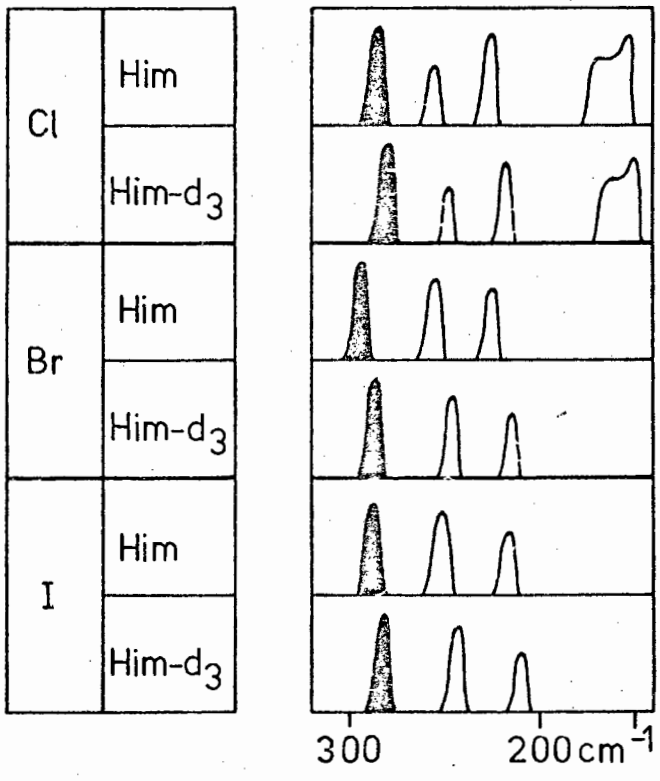


Fig. 27. The infrared spectra (330-140 cm^{-1}) of the complexes $[Cu(Him)_4(X)_2]$. Solid bands: νM-N.

in these complexes, as indicated by the presence of more than one N-H(D) stretching and bending mode. Present assignments in the 4000-600 cm^{-1} range are therefore identical to those reported[66] (Table 20, Fig. 26).

Of the three complexes, only the iodide has been the subject of X-ray crystallographic investigation.[50] The coordination about the copper atom was found to be essentially square planar with two rather distant iodide ions completing a distorted octahedron (Cu-I distances[50] 3.42 and 3.87 Å) suggesting a weak Cu-I interaction. For the chloride and bromide complexes, tetragonally distorted octahedral structures have been suggested,[58] as evidenced by their electronic spectra. Reported infrared spectra[58,61] gave no evidence for a Cu-X vibration above 190 cm^{-1}, in agreement with the suggested[173] long Cu-X bond. However, the energies of the electronic bands in the reflectance spectra were found[61] to change on varying the halogen, suggesting some measure of Cu-X covalency. These workers[61] identified the three halogen-independent bands above 200 cm^{-1} (Table 20, Fig. 27) as possibly νCu-N modes generated by distortion of the CuN_4 plane. This would appear unlikely since the degree of distortion implied would yield spectra for these halide complexes quite different from that of $[Cu(Him)_4(NO_3)_2]$ while each has essentially the same symmetry. On this basis, the band above 280 cm^{-1} is assigned to νCu-N (Fig. 27) while the two bands between 260 and 200 cm^{-1} are assigned to δ_TCu-Him + δCu-N-C. The spectra of the chloride complex has an additional band at 156 cm^{-1} and a shoulder at 170 cm^{-1}, both of which display *d*-sensitivities which distinguish them from possible Cu-Cl vibrations. These bands are assigned to δN-Cu-N.

1.6 The complexes $[M(Him)_2X_2]$, where M = Co(II) or Zn(II); X = Cl or Br

Of these complexes, only $[Zn(Him)_2Cl_2]$ has been studied[49,52] by x-ray crystallography. The Zn(II) complex is tetrahedral[49] and, together with the corresponding bromide and iodide, has been characterized[62-63] by infrared and Raman spectroscopy (4000-40 cm^{-1}). Perchard and Novak[16] classified the low frequency vibrations from a factor group analysis supported by Him-d_4 labelling. The Co(II) complexes are royal blue in colour and generally believed[58-59,61,64] to be tetrahedral with C_{2v} point symmetry.

Complete band assignments (4000-500 cm^{-1}) in the infrared spectra of the Zn(II) complexes have been made[62] using Him-d_1 labelling (Table 21). Similarities between the far-infrared spectra of the Co(II) and Zn(II) complexes (Fig. 28) clearly indicate their isostructural character. The point group approximation of C_{2v} symmetry for the Co(II) and Zn(II) complexes is sufficient to explain band assignments in the 350-200 cm^{-1} region (Fig. 29). On this basis, two M-halogen and two M-N stretching vibrations are expected. In the case of the chloride complexes these are well-resolved. It is generally agreed[59,61,63-64] that the two M-Cl stretches (asymmetric and symmetric) are those bands at highest frequency. These assignments are now substantiated by their total lack of deutero-sensitivity, while they are sensitive towards both metal ion substitution and replacement of chloride by bromide. By contrast, the two bands between 280 and 230 cm^{-1} are assigned to νM-N since they are deutero-sensitive and metal ion sensitive, but show no halogen sensitivity. Band assignments in the bromides are not as easily accomplished because νM-X and νM-N very nearly coincide in the 250 cm^{-1} region of the spectrum. The asymmetric Zn-N stretch occurs

as a shoulder at 250 cm^{-1} and is distinguished from νZn-Br at 231 cm^{-1} by its *d*-sensitivity, while the latter is insensitive to isotopic substitution. By comparison with the position of νsym. Zn-N in the chloro complex, it is likely that the corresponding vibration in the bromo complex is masked by the strong 231 cm^{-1} band.

Some measure of disagreement has arisen over the correct assignments of νasym. and νsym. Zn-Br. It has been noted[174] for complexes of the type $Co(py)_2X_2$, that the frequency separation between the asymmetric and symmetric M-X stretching bands decreases in the order Cl > Br > I, there being very little separation between the M-Br and M-I frequencies. Perchard *et al.*[63] found the reverse order to hold in the spectra of $Zn(NH_3)_2X_2$, and assumed this to be true for the corresponding bis(imidazole) complexes also, assigning νsym. Zn-Br at 186 cm^{-1}. The resulting large νasym.-νsym. frequency difference was explained[63] in terms of coupling of the 186 cm^{-1} band to a rotational mode at 192 cm^{-1}. Although the broad 231 cm^{-1} band apparently[63] shows no splitting in the spectrum at liquid nitrogen temperature, it is now considered preferable to assign νasym. + νsym. Zn-Br as coincident at 231 cm^{-1}. However, all the bands below 200 cm^{-1} are shifted by d_3-labelling which precludes any of them from being assigned to a νZn-Br mode with any degree of vibrational purity. Since all the bands below 200 cm^{-1} in the spectra of these Co(II) and Zn(II) complexes exhibit substantial *d*-sensitivities, no band or bands can be uniquely assigned to δX-M-X. The bands below 160 cm^{-1} in the spectra of the Co(II) complexes are assigned to δN-M-N as are the corresponding bands in the spectra of the Zn(II) complexes. These assignments are based on the observation that, of all the bands below 200 cm^{-1}, these are the only absorptions exhibiting both *d*- and metal ion sensitivity. On the results of their factor group analysis, Perchard and co-workers[63] assigned the shoulder at 153 cm^{-1} in the spectrum

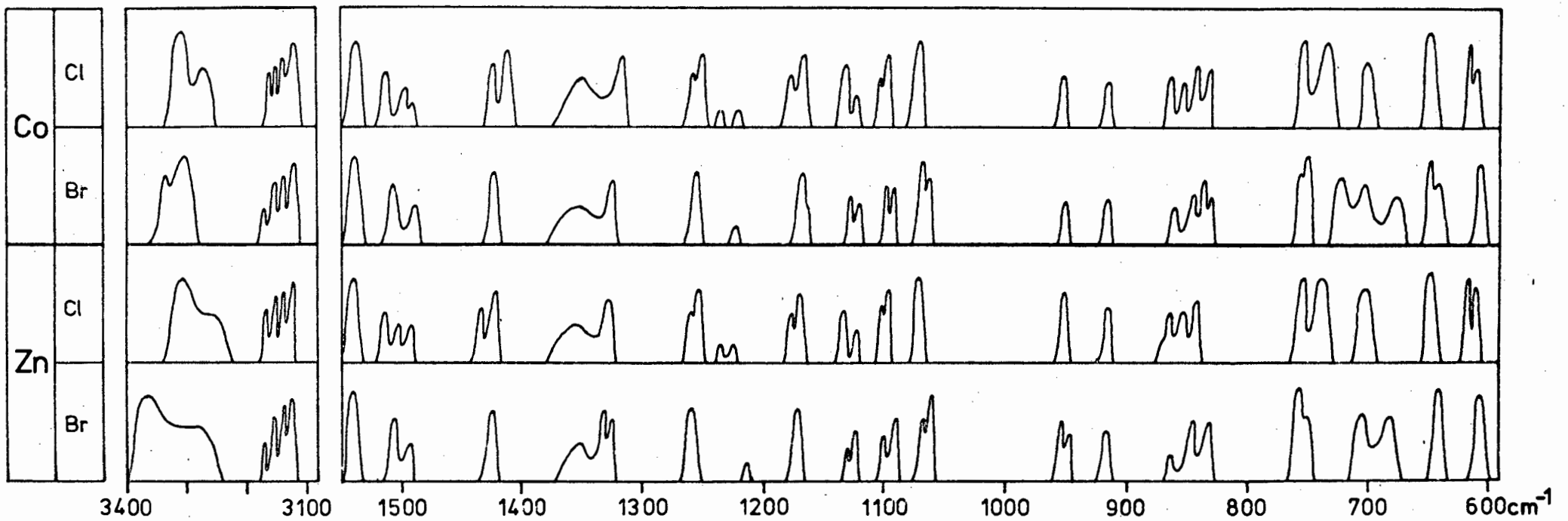


Fig. 28. The infrared spectra (3400-580 cm^{-1}) of the complexes $[M(Him)_2(X)_2]$, (M = Co, Zn; X = Cl, Br)

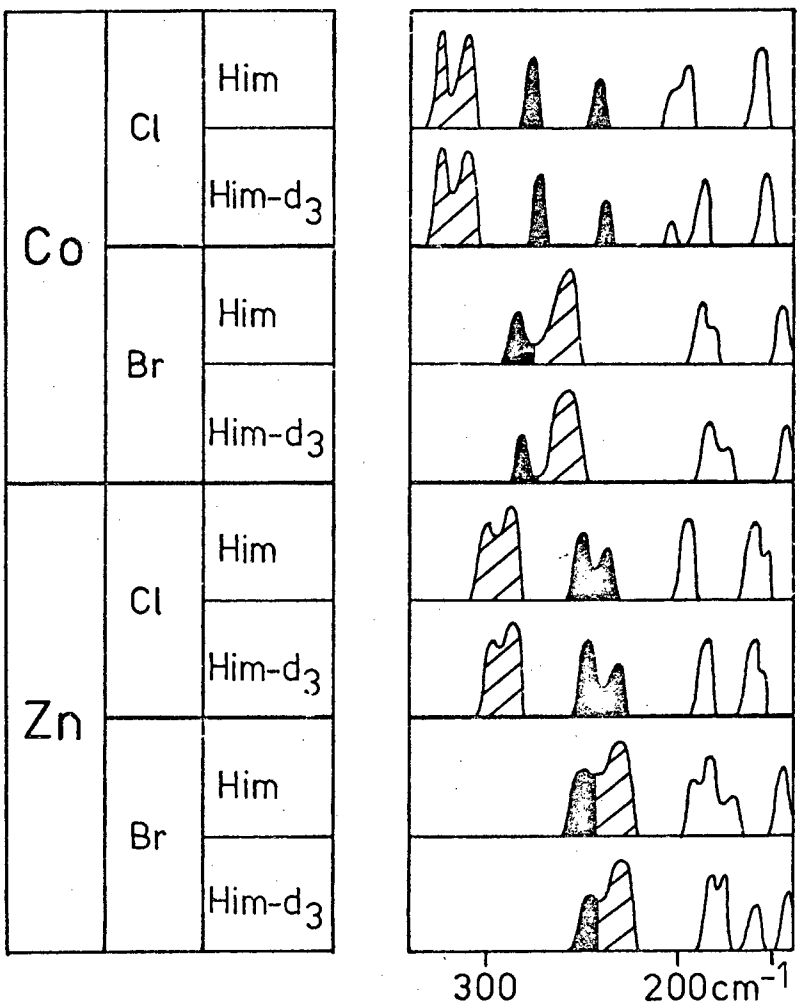


Fig. 29. The infrared spectra (350-140 cm^{-1}) of the complexes $[M(Him)_2(X)_2]$, (M = Co,Zn; X = Cl, Br).
Solid bands: νM-N, shaded bands: νM-X.

of $[Zn(Him)_2Cl_2]$ to δN-M-N, while the 195 cm^{-1} and 160 cm^{-1} bands were[63] assigned to Zn-Him rotations. These motions are similar to those modes described by Adams[65] to account for the bands in the 200-170 cm^{-1} region of $[Co(Him)_6](NO_3)_2$. The results of metal isotope studies[64] have led to the assignment of the 195 and 160 cm^{-1} bands to a ligand mode and δN-Zn-Cl, respectively, while the 153 cm^{-1} shoulder was assigned to a second ligand mode.

2. A VIBRATIONAL ANALYSIS OF BIS(NITRATO)MONO(PYRAZINE)-COPPER(II)

Pyrazine reacts with M(II) ions to form a wide variety of complexes the structural diversity of which has attracted the attention of many workers. The literature is particularly rich in reports on the complexes formed by pz and M(II) halides ranging from those of the first row transition metal ions[175-180] to Cd(II), Hg(II) and also Sn(IV) halides.[180-184]

Structural elucidation has been of primary interest since the various combinations of both terminal and/or bridging pz and halide generate at least four structural possibilities. For the metals Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), the 1:1 complexes $MLCl_2$ are considered[175,177,179-181,183-188] to involve polymeric octahedral structures having both pz and chloride bridging. Similar structures have been proposed for the 1:1 complexes of $NiBr_2$, $CuBr_2$, $CdBr_2$ and CdI_2. The $ZnBr_2$, ZnI_2, $HgCl_2$ and $HgBr_2$ complexes are, however, considered[183] to be polymeric tetrahedral species with terminal halide, polymerisation being achieved by bridging pz units. The 1:1 complexes of Sn(IV) chloride and bromides form octahedral complexes[182] with terminal halide and bridging pz molecules.

When M(II) ion and ligand are combined in the ratio 1:2 the favoured structure is polymeric octahedral.[175,177-180,185-187] The Mn(II), Fe(II), Co(II) and Ni(II) chlorides and Ni(II) bromide form 1:2 complexes considered to be polymeric octahedral species with terminal pz and bridging halide. However, a recent crystal structure determination[178] of $Co(pz)_2Cl_2$ has revealed the presence of bridging pz and terminal chloride. $Sn(pz)_2X_4$ (X = Cl, Br, I) are all considered[182] mononuclear octahedral with terminal pz and halide.

The majority of these structural assignments have been based on infrared and Raman spectra. Changing the halogen is a successful means of assigning M-X modes since bands originating in these vibrations show the usual[85] low frequency shift as one halogen is replaced by another of higher atomic mass. Whether the halide is terminal or bridging may similarly be determined[85] since terminal halides usually absorb at higher frequency. This method becomes unreliable when there is a change in structure within a series, *i.e.* the metal ion in a chloride complex may be octahedral but tetrahedral in the bromide or iodide. In this case the change in coordination number may counteract the mass effect. Assignments of νM-N in pz complexes have been based primarily on emperical methods. The bands usually occur within the region 285-185 cm^{-1}. To date, there has been but one reported study on the effects of deuteration[179] of the pz ring on the spectra of this type of compound.

Bis(nitrato)mono(pyrazine)copper(II) was found[72] to crystallize in the orthorhombic system, with space group *Pmna* (D_{2h}^{7}), and Z = 2. The two nitrate anions are unsymmetrically bonded to the Cu(II) ion through two oxygen atoms, forming two long (2.490 Å) and two short (2.010 Å) bonds, in accordance with the typical tetragonally-distorted Cu(II) stereochemistry. Pyrazine molecules occupy the fifth and sixth coordination sites to form a linear coordination polymer as depicted in Fig. 30. There are two such chains per unit cell[72] with a unimolecular repeat in each cell and the chains are parallel to the crystallographic *a*-axis. The shortest distance between copper atoms belonging to neighbouring chains is as high as 5.142 Å, suggesting the absence of chemical bonding between parallel chains.

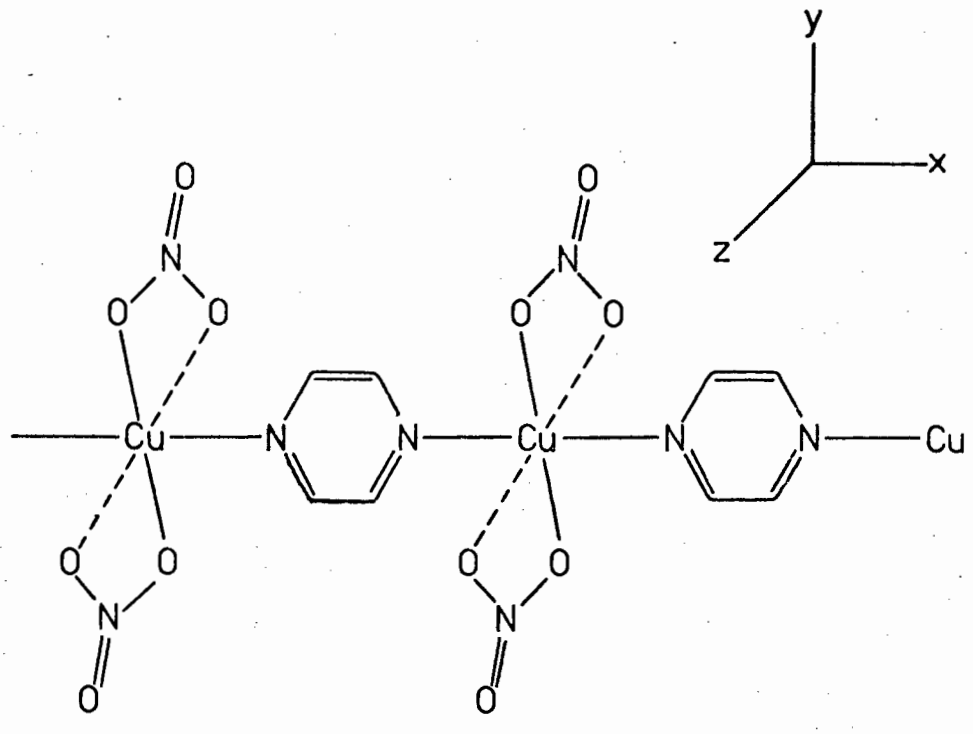


Figure 30.

The structure may therefore be treated as a molecular crystal comprising relatively strong interactions between Cu(II) ions and ligands and relatively weak interactions between neighbouring -Cu-pz-Cu- chains. For the vibrational analysis, the nitrate groups are therefore correctly treated as being covalently bonded to Cu(II) and not as separate ionic entities. Regarding the chains as relatively isolated from one another, the vibrations may be treated,[189] to a first approximation, in terms of their line group symmetry. From the crystal structure data[72] the Wyckoff site occupancy of the various atoms in the unit cell are obtained as follows. The Cu atoms occupy sites *2/m*, and the oxygen and nitrogen atoms of the nitrate groups occupy sites *m*. The nitrogen atoms of pz are on sites *e*, and the remaining carbon and hydrogen atoms

of pz occupy general positions. Since the Cu atom in the crystal is on sites *2/m* (C_{2h}) and the whole chain has the symmetry elements C_2, i and δ, the line group is isomorphous with C_{2h}. Derivation of the selection rules for the line group may be readily achieved by making use of the tables for factor group and point group analysis derived by Adams and Newton.[47] Using group No. 10 in these tables, and choosing the relevant rows corresponding to the site occupancy of the various atoms, the line group vector N_{total} is obtained (Table 40).

Table 40.

			C_{2h}	A_g	B_g	A_u	B_u
	Cu		*a*	0	0	1	2
Ring	C	4	*o*	3	3	3	3
Ring	H	4	*o*	3	3	3	3
Ring	N	2	*i*	1	2	1	2
NO_3^-	N	2	*m*	2	1	1	2
NO_3^-	3xO	3x2	*m*	6	3	3	6
	N_{total}			15	12	12	18

$= 57 = 3N^1$,

where N^1 = half the number of atoms in the unit cell.

This number of vibrations ($3N^1$) is exactly half that expected for the whole unit cell ($3N = 114$). N_{total} (Table 40) may now be separated into the contributions from the internal vibrations of the nitrate and pz groups, the vibrations of the CuO_2N_2 skeleton, and the low frequency acoustic modes (Table 41).

Table 41.

C_{2h}	A_g	B_g	A_u	B_u	
N_{total} [a]	15	12	12	18	
$T_{acoustic}$ [b]	0	0	1	2	
R_z [c]	1	0	0	0	
N_{ring} [d]	6	6	6	6	⟸ in-active modes
$N_{NO_3^-}$ [d]	5	1	1	5	
$N_{skeletal}$ [e]	3	5	4	5	

a From table 40.

b Acoustic modes corresponding with the translational vectors aligned along the three axes, and are read directly from the C_{2h} character table.

c The single rotatory mode of the chain which is read off the z-rotation table of group No. 10, ref. 47.

d N_{ring} and $N_{NO_3^-}$ represent the internal modes of pz and NO_3^- under the symmetry of the line group. N_{ring} is obtained by summing the rows 2 to 4 (Table 40), less translations and rotations of the pz ring. $N_{NO_3^-}$ is a 4 x row $2m$ (Table 40), less translations and rotations for two nitrate groups.

e Row 1 less rows 2 to 5.

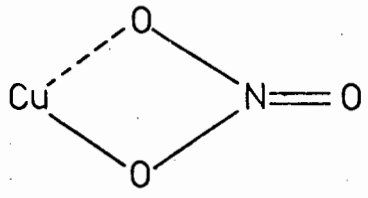
Under the symmetry of the line group the ir spectrum (Table 41) is expected to yield a total of 27 vibrations, 12 of which are pz modes, 6 are nitrate modes and 9 are skeletal modes.

2.1 The nitrate spectrum

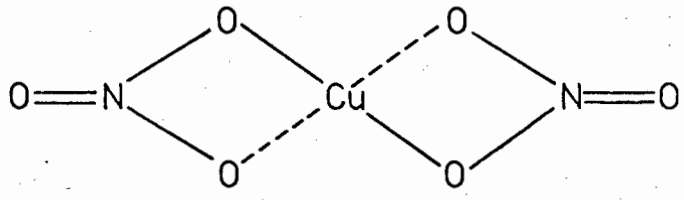
The samples of pz-d_4 used in this study are rated by the manufacturers as being of 84% isotopic purity, insufficient for reliable assignments of the internal modes of pz-d_4 in the spectrum of $[Cu(NO_3)_2(pz)]$. The spectrum of the deuterated complex is included in the discussion since it does nevertheless facilitate assignments of the nitrate modes by their total lack of d-sensitivity .

The row $N_{NO_3^-}$ in table 41 may also be obtained by considering the isolated planar NO_3^- ion of point group D_{3h}. The normal modes of vibration for such an ion[85,167] are $A_1^{\,1}(\nu_1) + A_2^{\,11}(\nu_2) + E^1(\nu_3) + E^1(\nu_4)$, of which three are ir-active and absorb above 650 cm^{-1}. ν_3 And ν_4 are doubly degenerate and, if the symmetry of the ion is lowered, these vibrations may split while the Raman-active mode ν_1 may become ir-active. It may therefore be possible to see six nitrate vibrations above 650 cm^{-1} in the infrared spectrum and, if the symmetry is lowered by coordination to a metal ion, bands attributable to M-O modes will also arise below 600 cm^{-1}.

Each nitrate is bidentate towards the Cu(II) ion in $[Cu(NO_3)_2(pz)]_n$ and occupy sites m, having C_s symmetry (II).



(II)



(III)

A correlation of $D_{3h} \rightarrow C_s$ will give the vibrational species for one NO_3^- coordinated to Cu(II), whereas the correlation $C_s \rightarrow C_{2h}$ will yield the vibrational species for two nitrate groups (III) coordinated to Cu(II) under the symmetry of the line group, C_{2h}. Finally a line group-factor group correlation ($C_{2h} \rightarrow D_{2h}$) should indicate the manner in which the vibrations of all four NO_3^- groups interact under the symmetry conditions of the unit cell (Table 42).

Table 42.

	D_{3h}		$\xrightarrow{\delta_h}$ C_s	$\xrightarrow{x2}$ C_{2h}	$\xrightarrow[C_2(x)]{x2}$ D_{2h}
ν_1	A_1^1	(νsym.NO_3^-)	$\underline{A^1}$	$A_g + \underline{B_u}$ [a]	$A_g + B_{3g} + \underline{B_{1u}} + \underline{B_{2u}}$
ν_2	$\underline{A_2^{11}}$	(δNO_3^-)	A^{11}	$B_g + \underline{A_u}$	$B_{1g} + B_{2g} + A_u + \underline{B_{3u}}$
ν_3	$\underline{E^1}$	(νasym.NO_3^-)	$\underline{2A^1}$	$2(A_g + \underline{B_u})$	$2(A_g + B_{3g} + \underline{B_{1u}} + \underline{B_{2u}})$
ν_4	$\underline{E^1}$	(NO_3rock)	$\underline{2A^1}$	$2(A_g + \underline{B_u})$	$2(A_g + B_{3g} + \underline{B_{1u}} + \underline{B_{2u}})$
	Isolated NO_3^- ion.		One NO_3^- coordinated to Cu(II).	Two NO_3^- coordinated to Cu(II).	Two chains in unit cell containing two NO_3^- groups each.

[a] Species underlined indicate ir-activity.

The increased splitting which the bands in the nitrate spectrum undergo as the symmetry of the environment is lowered,[189] is diagramatically represented in Fig. 31. The six ir-active fundamentals of the nitrate groups under the line group symmetry, are each split into two modes under the factor group symmetry. Thus, the B_u species in C_{2h} is split into two bands $B_{1u} + B_{2u}$ in D_{2h}, both being ir-active. The A_u species is also split in D_{2h} into two bands, $A_u + B_{3u}$, but the

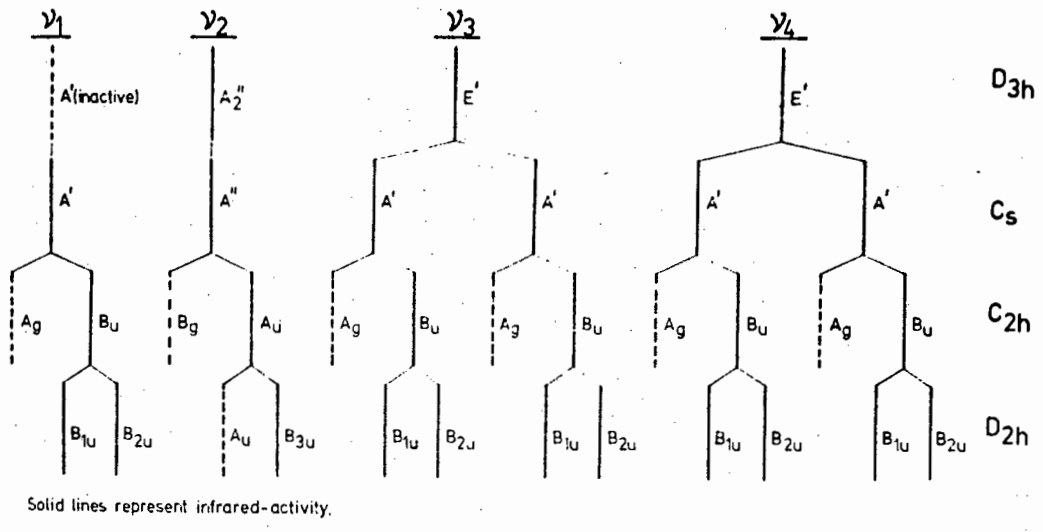


Fig. 31

A_u component is inactive and only the B_{3u} component is observed. The frequency separation of these factor group splittings will be small and were unresolvable under the facilities available. It is therefore necessary only to consider the line group approximation. The six internal modes of the nitrate groups (C_{2h}) and their assignments are given in Table 43.

Table 43.

	Mode [a]	Species	Frequency (cm^{-1})
ν_1	νN=O	B_u	1494
ν_2	νsym.NO_2	B_u	1015
ν_3	δsym.NO_2	B_u	805
ν_4	νasym.NO_2	B_u	1290
ν_5	δasym.NO_2	B_u	751
ν_6	δoop. NO_3	A_u	708

[a] Modes for bidentate nitrate[85].

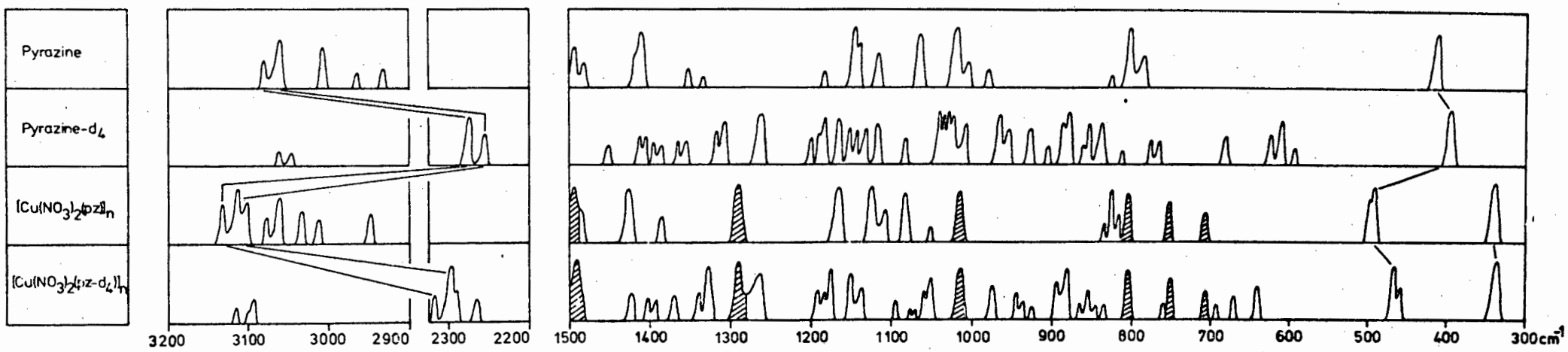


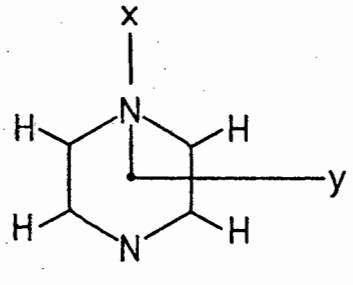
Fig. 32. The infrared spectrum (3400-150 cm^{-1}) of $[Cu(NO_3)_2(pz)]_n$. Shaded bands: nitrate vibrations.

The total lack of *d*-sensitivity exhibited by these bands when pz was replaced by pz-d_4 (Table 22, Figs. 6 and 32) confirms their assignments to vibrations involving the nitrate groups.

2.2 The pyrazine spectrum

The molecular structure of pz has been determined by electron diffraction[77] and x-ray analysis.[78] The molecule is planar and belongs to the D_{2h} point group. The vibrational assignments of pz were first discussed by Ito *et al.*[79] and by Lord *et al.*[80] on the basis of more extensive experimental data. Scully[81] made a zero order calculation of the pz fundamentals using a valence field based on that of benzene. The ir spectra of pz and pz-d_4 have been studied in the liquid and vapour states by Simmons and colleagues,[83] and in the liquid, vapour and crystalline states by Califano and co-workers.[84]

Choosing a set of axes such that the *xy*-plane incorporates the plane of the molecule with the *x*-axis passing through the nitrogen atoms, and the *z*-axis perpendicular to the molecular plane (IV), a point group analysis may be completed using group No. 47 in the Tables by Adams and Newton [47] (Table 44).



(IV)

Table 44.

Atoms	Sites	D_{2h}	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
2xN	C_{2v}	$2i$	1	1	1	0	0	1	1	1
4xC	C_s	$4y$	2	2	1	1	1	1	2	2
4xH	C_s	$4y$	2	2	1	1	1	1	2	2
			5	5	3	2	2	3	5	5
Translatory/Rotatory modes				1	1	1		1	1	1
Internal modes of pz			5	4	2	1	2	2[a]	4	4 = 24 = 3n-6

[a] Modes underlined indicate ir-activity.

Assignments of the internal modes of free pz and its corresponding modes in the complex are listed in Table 22. According to Table 44, free pz is expected to show ten ir-active fundamentals. (The two A_u modes being inactive in D_{2h} symmetry). The two out-of-plane B_{1u} modes of free pz, the γC-H and γring modes (Fig. 32) are located at 801 and 413 cm^{-1}, respectively. Band assignments proposed here are based on the work of Simmons[83] and co-workers and of Lord *et al.*[80] Hence the bands at 3060, 1410 and between 1135 and 1140 cm^{-1} are assigned to fundamentals of the B_{2u} species. The four bands at 3060, 1492, 1143, 1064 and 1019 cm^{-1} to the B_{3u} species.
The two C-H stretching modes, B_{3u} and B_{2u}, are coincident at 3060 cm^{-1} but are split into separate bands in the spectrum of pz-d_4 at 2275 and 2257 cm^{-1}. The remaining bands in the ir spectrum of pz are assigned to various combination bands in accordance with the assignments made by Califano and co-workers.[84] Estimations[80,83] of the frequencies of

the two inactive A_u species have been made at 950 and 340 cm^{-1}. A subsequent study[84] placed the A_u mode of lower frequency near 400 cm^{-1}.

A $D_{2h} \rightarrow C_{2h}$ correlation of the vibrations of the pz molecule indicate the behaviour of the modes under the line group symmetry (Table 45) in agreement with the entry N_{ring} in Table 41. Finally the $C_{2h} \rightarrow D_{2h}$ correlation shows how the bands split on coupling two chains together

Table 45.

D_{2h} (Point Group)	$\xrightarrow{C_{2(x)}}$	C_{2h} (Line Group)	$\xrightarrow{C_{2(x)}}$	D_{2h} (Factor Group)
$5A_g$	———	$6A_g$	———	$6(A_g + B_{3g})$
B_{3g}				
$4B_{1g}$	———	$6B_g$	———	$6(B_{1g} + B_{2g})$
$2B_{2g}$				
$2A_u$	———	$6A_u$	———	$6(A_u + B_{3u})$[a]
$4B_{3u}$				
$2B_{1u}$	———	$6B_u$	———	$6(B_{1u} + B_{2u})$
$4B_{2u}$				

[a] Species underlined indicate ir-activity.

in the crystal. The A_u modes in C_{2h} are now ir-active and therefore twelve fundamentals, $6A_u + 6B_u$, are expected. However, under the D_{2h} factor group symmetry, each A_u mode (Table 45) is split into an A_u and B_{3u} band, of which only the B_{3u} component is ir-active. Similarly each B_u mode will split into a B_{1u} and B_{2u} mode, both

components being ir-active. Such splitting would however require low temperature studies for their observation. The 1051 cm^{-1} band and the shoulder at 493 cm^{-1} (Table 22 , Fig. 32) are assigned to the components of the A_u mode which were inactive in the spectrum of the free ligand. Most low frequency ligand modes tend to shift to higher frequency on complexation.[190] Appearance of the low frequency component of the A_u species at 493 cm^{-1} seems to support earlier assignments[84] of the inactive A_u mode of free pz near 400 cm^{-1} rather than[80,83] near 340 cm^{-1} since the latter would represent a high frequency shift (some 153 cm^{-1}), rather in excess of that expected for such a ligand mode. Complexation has resulted in the separation of the two νC-H bands near 3100 ($B_{1u} + B_{3u}$), which were coincident in the spectrum of free pz. These bands occur as a well-resolved doublet (Table 22) near 2270 cm^{-1} in the spectrum of $[Cu(NO_3)_2(pz\text{-}d_4)]_n$.

Hence, all the nitrate modes and pz modes, apart from the band at 490 cm^{-1} are above 700 cm^{-1}, leaving the skeletal modes (Table 41) expected below 600 cm^{-1} uncluttered by ligand vibrations.

2.3 The skeletal modes

In the line group approximation the skeletal modes (Table 41) of a single chain span the representations:

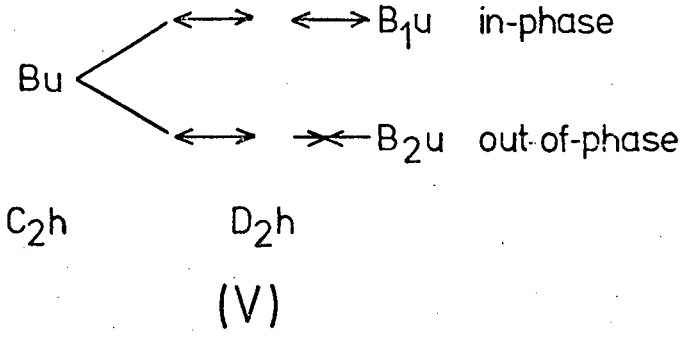
$N_{skeletal} = 3A_g + 5B_g + 4A_u + 5B_u$ of which nine vibrations ($4A_u + 5B_u$) are ir-active. In the full unit cell (correlation $C_{2h} \rightarrow D_{2h}$), Table 46, each mode will couple with the same mode in the second chain generating two modes. Thus each A_u mode should, in theory, generate a doublet of which only the B_{3u} component is ir-active.

Table 46.

C_{2h}	$\xrightarrow{C_{2(x)}}$	D_{2h}
$3A_g$	———	$3(A_g + B_{3g})$
$5B_g$	———	$5(B_{1g} + B_{2g})$
$\underline{4A_u}$	———	$4(A_u + \underline{B_{3u}}^{a})$
$\underline{5B_u}$	———	$5(\underline{B_{1u}} + \underline{B_{2u}})$

a Species underlined indicate ir-activity.

The same applies to the B_u modes, but both components are ir-active. The B_{1u} mode represents the in-phase coupling and the B_{2u} mode represents the out-of-phase coupling (V).



(V)

The frequency separation of these modes may not, however, be large enough to be detectable at room temperature, and for the purpose of this study, it is necessary only to consider the line group approximation.

It is useful to consider the skeletal modes as originating[189] in the three translations and three rotations associated with each nitrate and each pz group, in the hypothetical situation where there is no bonding between them and the Cu(II) ion. The three translations of Cu will correspond with the three translations of the whole chain and are therefore omitted. However, the single rotatory mode R_z of the chain must be included in the skeletal modes. Thus, in C_{2h}, the nitrate groups are on sites *m* and the pz ring on site *a* and, using the tables for factor group analysis,[47] the translations and rotations associated with these groups may be summed to yield the required skeletal modes, as depicted in Table 47.

Table 47.

C_{2h}		A_g	B_g	A_u	B_u	
2 x NO_3 [a]	*m*	2	1	1	2	
2 x NO_3 [b]	*m*	1	2	2	1	
1 x pz [c]	*a*	0	0	1	2	
1 x pz [d]	*a*	1	2	0	0	
		4	5	4	5	= Sum of rows R_z + $N_{skeletal}$ in Table 41.

a Row *m* of group 10 represents[47] translations of 2 x NO_3^-.

b Rotatory table of group 10 represents rotations of 2 x NO_3^-.

c Row *a* of group 10 represents translations of pz.

d Rotatory table of group 10 represents rotations of pz.

The four A_u modes may be divided into one νCu-N(pz) (the longitudinal optic mode of the chain), δN(pz)-Cu-O, δ_τCu-NO_3 and δ_ωCu-O-N(NO_3). The two Cu-O bonds which have covalent bond lengths (2.01 Å) will have νCu-O modes associated with them. These modes span the representations A_g(νsym.Cu-O) + B_u(νasym.Cu-O), the B_u component being infrared-active. The remaining four B_u modes[189] are δCu-O-N(NO_3), δCu-O, plus two modes in which the pz rings move in orthogonal directions normal to the chain axis, i.e. 2δCu-N.

The region 350-25 cm^{-1} (Figs. 7 and 33) in the infrared spectrum agrees well with theoretical predictions of C_{2h}, showing eight of the nine expected bands. The ninth band may be the weak absorption at 35 cm^{-1} or may arise below 25 cm^{-1}. Deuteration alone is, however, insufficient as a means of band assignments in this region since all modes with the same symmetry designation (i.e. A_u or B_u) may, through vibrational mixing, exhibit *d*-sensitivities. This is apparently the case since apart from the 73 cm^{-1} band, all other bands show varying degrees of *d*-sensitivity (Table 22). Therefore, assigments of νCu-N νCu-O only are proposed and no attempt is made to assign the remaining skeletal vibrations.

The 224 cm^{-1} band is assigned to νCu-N. This band lies within the region characteristic of νCu-N in a large variety of complexes of metal(II) ions and pz.[175-181,183-188] Moreover, rough estimates of νCu-N using the relationship[191] obtained by the Wilson FG matrix method

$$\nu = \frac{1}{2\pi c}\left[\frac{2f}{\mu}\right]^{\frac{1}{2}} \qquad (6)$$

(where f is an average Cu-N force constant[192-193] and μ is the reduced mass of the Cu-pz entity) places νCu-N well within this region. Little

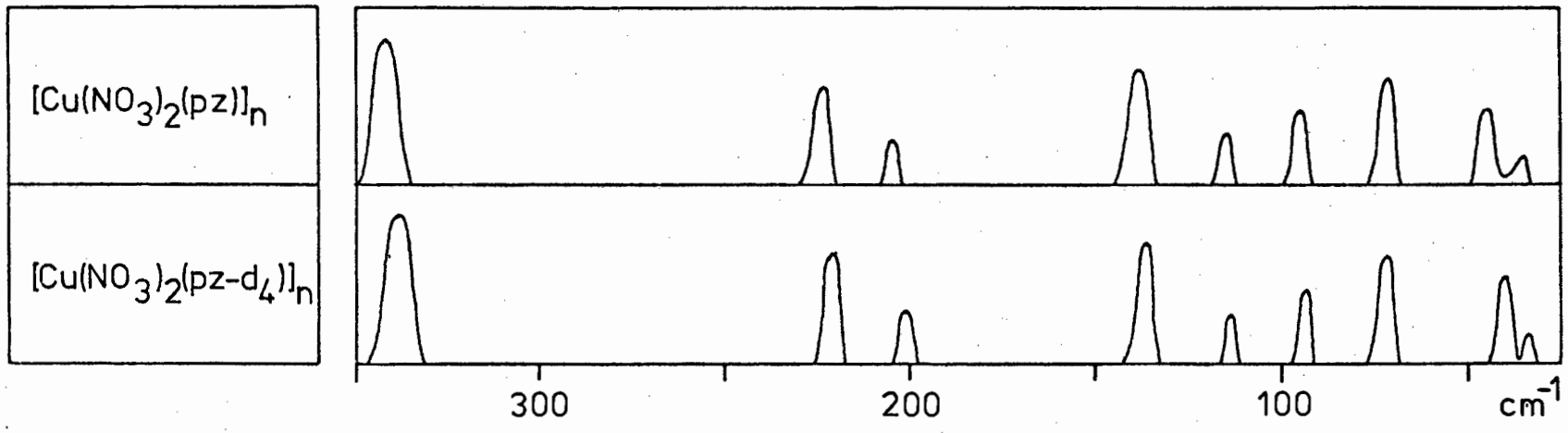


Fig. 33. The infrared spectrum (350-25 cm^{-1}) of $[Cu(NO_3)_2(pz)]_n$

is known of the far-infrared spectra of coordinated nitrato-complexes. It is unlikely that the Cu-L skeletal deformations will occur above νCu-N at 224 cm^{-1}. The strong 341 cm^{-1} band is therefore assigned to νasym.Cu-O, its *d*-sensitivity resulting from mixing with other B_u modes involving N(pz). Support for this assignment comes from studies[194] of the spectra of bidentate nitrato-complexes $L_2Cu(NO_3)_2$ (L = 2-picoline, quinoline, pyridine) where strong bands assignable to νCu-O (NO_3) were found in the 330-250 cm^{-1} region.

3. INFRARED SPECTRA (700-140 cm^{-1}) OF THE IMIDAZOLE, PYRAZINE, PYRIMIDINE AND PYRIDAZINE ADDUCTS OF COBALT(II), NICKEL(II) AND ZINC(II) ACETYLACETONATES

Anhydrous bis(acetylacetonato)Co(II) has been shown[195] by x-ray analysis to be a tetrameric molecule, $[Co(AA)_2]_4$, in which some oxygen atoms of the acetylacetonate group are shared between two Co(II) ions to attain octahedral configuration about each Co(II) ion. The trimeric nature of the analogous Ni(II) and Zn(II) complexes[196-197] is achieved by similar sharing of oxygen atoms of the acetylacetonate ligands. The anhydrous Cu(II) chelate[198] is, however, uniquely monomeric and square planar in the solid state. The anhydrous polymers are readily cleaved by donors such as water and nitrogenous bases which, apart from Zn(II) acetylacetonate, generally assume *trans*-axial positions to yield six-coordinate monomers. Such adducts of Zn(II) acetylacetonate have been shown[199-200] to exist as both five- and six-coordinate species.

When the methyl groups of acetylacetone are replaced by such bulky substituents as tertiary butyl groups, the M(II) complexes obtained do not form polymeric octahedral structures but attain[201] monomeric square planar geometry as a result of steric repulsion. Hence bis(dipavaloylmethanido)Ni(II) and bis(3-methylacetylacetonato)Ni(II) are planar and diamagnetic.[202-203] The bis(aquo) adducts of Co(II) and Ni(II) acetylacetonates are *trans*-octahedral monomers[204-205] while the Zn(II) complex[206] adducts only one molecule of water to yield a five-coordinate trigonal bipyramidal structure. These aquo-adducts of M(II) acetylacetonates are the classical starting materials for the synthesis of a large variety of adducts comprising bases such as amines, pyridines, pyridine-N-oxides and bases with labile oxygen atoms.

Unlike pyridine (which forms *trans*-octahedral monomeric adducts with Co(II) and Ni(II) acetylacetonates,[207-208] and five-coordinate monomers with Zn(II) acetylacetonate) pz, pm and pd have the capacity to behave as bridging ligands, coordinating to two different metal ions forming -M-L-M- links. Formation of bridged species is characteristic of these nitrogen heterocycles in contrast to the common bidentate ligands such as 2,2'-bipyridine and ethylenediamine, which prefer to form *cis*-chelates with a single metal ion.[209] Such polymers have been reported[105] for $[Mn(AA)_2(pz)]_n$. However, molecular weight determinations were of no diagnostic value owing to the facile decomposition of the polymer in chloroform solution. In another study[103] of the first row transition metal(II) acetylacetonates of pz, it was similarly concluded that the pz adducts may form -M-L-M- chains. Although the published powder patterns showed minor differences, they were considered sufficiently alike to suggest that the Mn(II), Fe(II), Co(II) and Zn(II) complexes are structurally analogous, while the Ni(II) complex showed more marked deviations which were considered to indicate a somewhat different structure. Several further examples of such chains have been reported.[72,104,210-211] Belford *et al.*[210] reported a crystal structure determination of $[Cu(hfac)_2(pz)]_n$ (hfac = $CF_3COCH\,COCF_3)^-$ in which the complex is shown to be a linear coordination polymer bridged by pz molecules. Morosin *et al.*[211] found that the pz adduct of Cu(II) acetate has a structure characterised by alternating linear chains in which dimeric units of Cu(II) acetate monohydrate are linked by pz molecules.

While it is expected that pz and pm will form -M-L-M- links to produce polymeric structures with M(II) acetylacetonates, it is doubtful whether pd will have the necessary bite to span the distance across two M(II) acetylacetonato molecules in order to achieve a -M-L-M- chain.

Hence, it is likely that pd will form 1:2 monomers. A variety of metal complexes of Him have been synthesised and their infrared spectra determined but there is little information in the literature on adduct formation by this base.[102] On losing a proton, an Him anion (im) may act as a uninegative bridging ligand, and is thus capable of forming -M-im-M- chains,[212] or two-dimensional networks. This is, however, unlikely to occur in the Him adducts of M(II) acetylacetonates discussed here. In practice Him behaves as a neutral monodentate ligand towards M(II) acetylacetonates[102] forming the species $[M(AA)_2(Him)_2]$. The reflectance spectra and magnetic moments of the Co(II) and Ni(II) complexes are typical[213] of octahedral complexes of these metal ions (Table 32), and they are therefore probably structurally analogous with the *trans*-bis(pyridine) adducts of Co(II) and Ni(II) acetylacetonates (Fig. 34a).

Reaction of pz and pm with Co(II), Ni(II) and Zn(II) acetylacetonates forms complexes which analyse for one molecule of base, indicating polymeric structures of stoichiometry $[M(AA)_2B]_n$, (Figs. 34b and 35). The Co(II) and Ni(II) species also yield reflectance spectra[213] which are in accord with those expected for octahedral complexes of these ions. In the present work, two types of adducts were isolated from the reaction of pd with Co(II) and Ni(II) acetylacetonate. The bis(adducts) having the stoichiometry $[M(AA)_2(pd)_2]$ clearly involve bonding through only one of the nitrogen atoms of the heterocyclic base. These adducts have reflectance spectra[213] indicative of octahedral symmetry (Table 32) and are therefore regarded as monomeric octahedral species similar to the corresponding bis(pyridine) adducts.[106] On reaction between the M(II) acetylacetonate and pd in the ratio 1:1, the resulting adducts analyse for half a molecule of base with a stoichiometry $[\{M(AA)_2\}_2(pd)]$.

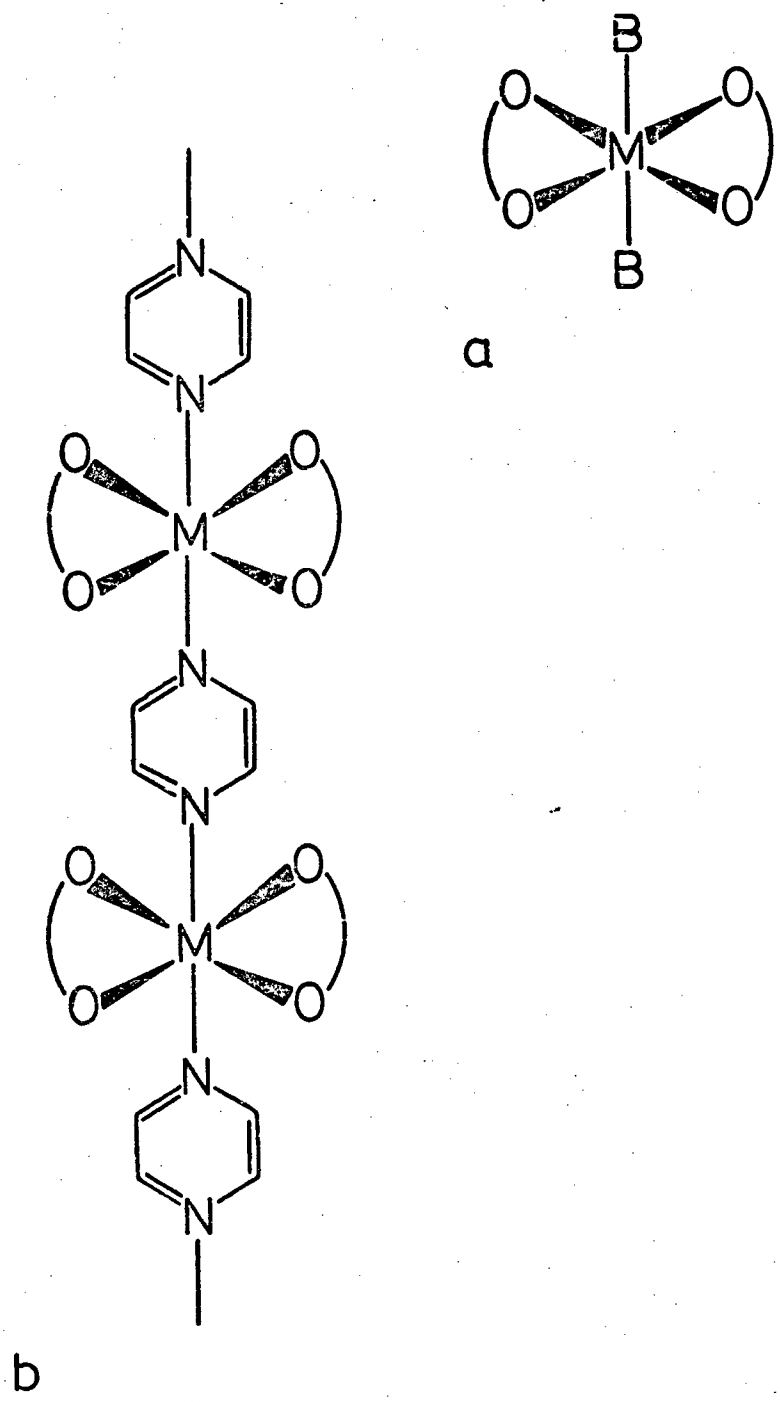


Fig. 34. Proposed structures for the complexes $[M(AA)_2(pz)]_n$ and $[M(AA)_2(B)_2]$, (B= monodentate ligand e.g. Him, py).

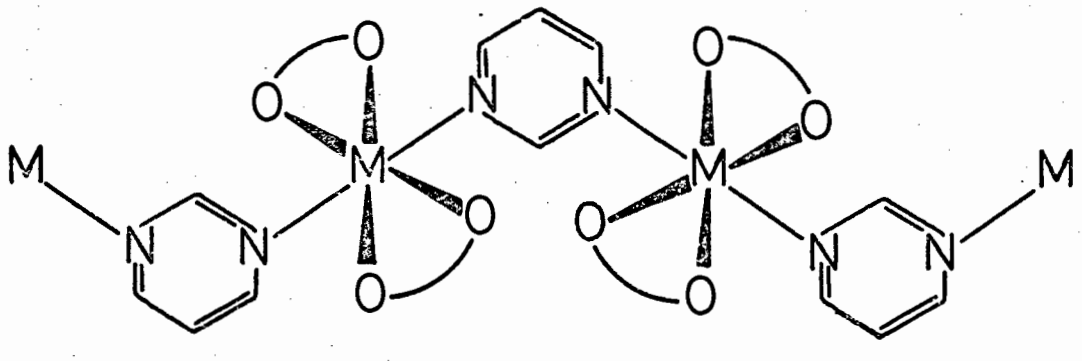


Fig. 35. Proposed sturcture for the complexes $[M(AA)_2(pm)]_n$

The reflectance spectra of the pz, pm and bis(pd) complexes indicate that they all have octahedral stereochemistry. The small differences which arise in the reflectance spectra of the latter pd complexes are not sufficient to suggest five-coordination but rather indicate distorted octahedral structure with bridging pd molecules, as postulated[214] for $[MX_2pd]$, (M = first row transition metal(II) ion; X = halogen).

Rigorous normal coordinate treatments (considering all the atoms in the molecule) of some M(II) and M(III) acetylacetonates[215] have been reported. Band assignments throughout the region 3100-290 cm^{-1} and M-O stretching force constants have been given. It is the M-L stretching vibrations of these complexes which are of primary concern since they provide direct information regarding the strength and electronic characteristics of the M-L bonds. These vibrations were initially assigned on a purely theoretical basis[94,215] without any independent experimental verification. The metal-isotope labelling technique[99] was subsequently used to provide a novel method for detecting M-L vibrations. Nakamoto and co-workers[99] applied this technique to the acetylacetonato complexes of Fe(III), Cr(III), Pd(II), Cu(II) and Ni(II), while Pinchas *et al.*[35] used the ^{18}O-labelled acetylacetonates of Mn(III) and Cr(III) for their assignments. Controversy immediately ensued as to the correct assignment of νCr-O in $[Cr(AA)_3]$. Nakamoto[99] assigned the two bands at 463 and 358 cm^{-1} to Cr-O stretching modes, since these bands exhibit the largest low frequency shifts (3 and 4 cm^{-1}, respectively) on metal ion labelling. The ^{18}O-induced shift (19 cm^{-1}) observed by Pinchas[35] for the band at 592 cm^{-1} was sufficiently close to the calculated value (assuming a diatomic oscillator) of 25 cm^{-1} for a Cr-O stretch, to warrant its assignment to this mode. On the other hand, this band shifted only 0.7 cm^{-1} on ^{50}Cr-^{53}Cr-substitution,[99] and, on this basis, was assigned

to an out-of-plane chelate ring deformation.

The behavior of the band at 355 cm^{-1} in the tris-complex of Cr(III) towards the alternative types of labelling, has also led to confusion. Its insensitivity towards ^{18}O-labelling led to its assignment[35] as an in-plane C-C-C bending mode. This band produced the largest isotopic shift (3.9 cm^{-1}) in the ^{50}Cr-^{53}Cr study,[99] where it was accordingly assigned to νCr-O.

The infrared spectra of the bis(aquo) adducts of M(II) acetylacetonates are known[22,99,106] to exhibit three regions of metal ion sensitivity below 600 cm^{-1}. These metal-sensitive bands occur within the ranges 600-500, 450-400 and 300-180 cm^{-1}, and are also observed to exhibit sensitivity towards the adducted base[22,106] (as a result of the variation in ligand field strength of the bases). Based on the results of normal coordinate analyses, and in view of the large shift recorded for metal ion labelling,[99] the band near 572 cm^{-1} in the spectrum of $[Ni(AA)_2(py)_2]$ has been assigned to a ring deformation coupled with νM-O. Absence of deutero-sensitivity coupled with significant sensitivity towards metal ion substitution[106] were considered evidence in support of this assignment. Substituent effects within the chelate ring of the β-ketoenolate[23,106] have also been cited in support of this assignment.

Although ^{18}O-labelling has not been applied to the base adducts of M(II) acetylacetonates, the assignment[35,216] of νCr-O in $[Cr(AA)_3]$ to the bands near 590 and 456 cm^{-1} has been made on the basis of this technique. The latter band, which is analogous to the 420 cm^{-1} vibration in $[Ni(AA)_2(py)_2]$ was previously assigned[99] to an unspecified chelate ring vibration. It was also claimed that because of their large metal-isotope shifts, the bands at 276 and 249 cm^{-1} represent νNi-O and νNi-N modes, respectively. Subsequently, deuteration of the pyridine ring[106]

led to the unambiguous assignment of the doublet at 197 and 186 cm^{-1} to νNi-N.

Since pz, pm and pd are isomeric, the metal-ligand bands in the infrared spectra of their adducts with M(II) acetylacetonates will be free from mass effects. The position of νM-N will therefore be dependent only on the metal-ligand force constants, which will be determined by the availability of the donor electrons of the heterocyclic base. In addition, the band patterns and the frequencies of the M-O and M-N stretching modes should yield information on the structural characteristics of these complexes.

In the following discussion, bands shifted by metal ion substitution will be referred to as M-sensitive bands, while the term *d*-sensitive will be used to describe those bands which shift to lower frequency on deuteration of the adducted base. For the isotopic labelling technique, only Him and pz were available as their deuterated analogues, Him-d_4 and pz-d_4.

3.1 The imidazole adducts, $[M(AA)_2(Him)_2]$ (M = Co, Ni)

The infrared spectra are depicted in Fig. 36 and the vibrational frequencies are given in Table 23. Band ν_1 has previously been assigned[99] to $\delta C\text{-}CH_3 + \delta$ring + νNi-O in the spectrum of $[Ni(AA)_2(py)_2]$. The fact that it generally shows no M-sensitivity indicates, however, that there is little or no contribution from νM-O. It is also insensitive towards deuteration of the Him ring, and is therefore assigned to a chelate ring deformation. The corresponding band in the spectrum of $[Cr(AA)_3]$ occurs

near 661 cm^{-1} and has been assigned[35] to an out-of-plane chelate ring deformation.

Of all the bands below 700 cm^{-1}, ν_2 has the highest *d*-sensitivity and is unambiguously assigned to the internal mode[70] of Him, γring. The spectra of the deuterated complexes show 3 or 4 unique bands between 600 and 500 cm^{-1}, which are assigned to γC-D and γring deformations of deuterated imidazole. Except for a weak lattice vibration at 174 cm^{-1}, Him has no internal ligand vibrations with a frequency <600 cm^{-1}, nor are there any internal vibrations of coordinated AA in this region. Hence, the seven bands within the range 600-140 cm^{-1} in these spectra all have their origin in M-ligand modes. The bands ν_3 and ν_4 are firmly assigned to νM-O for three reasons. Firstly, they are completely insensitive to deuteration of the Him ring. Secondly, they are strongly M-sensitive in the CFSE sequence Co<Ni.[106] Thirdly, their frequencies lie close to those of the νM-O bands in $[M(AA)_2B_2]$ (M = Co, Ni;B = H_2O, py). In $[Ni(AA)_2(py)_2]$, the νM-O bands are considered[106] to be coupled with the $\delta C\text{-}CH_3$ mode of the AA ring or with a py ligand mode. That ν_3 and ν_4 are coupled νM-O bands is also proposed for the Him adducts since the M-sensitivity of ν_3 and (especially) ν_4 is lower than that of ν_7 (see below).

The bands ν_5 and ν_6 undoubtedly originate in νM-N modes, since they are significantly *d*- and M-sensitive. Their frequencies are very close to those reported[64-65] for νM-N in the complexes $[M(Him)_6]^{2+}$, in which the assignments were based on the metal-isotope labelling technique,[64] and on a single crystal study.[65] Since ν_7 has a higher M-sensitivity than either ν_3 or ν_4 but is completely unaffected by deuteration of Him, it is assigned to a vibrationally pure (uncoupled) νM-O mode. The alternative assignment to δO-M-O proposed[216] for a band in this region

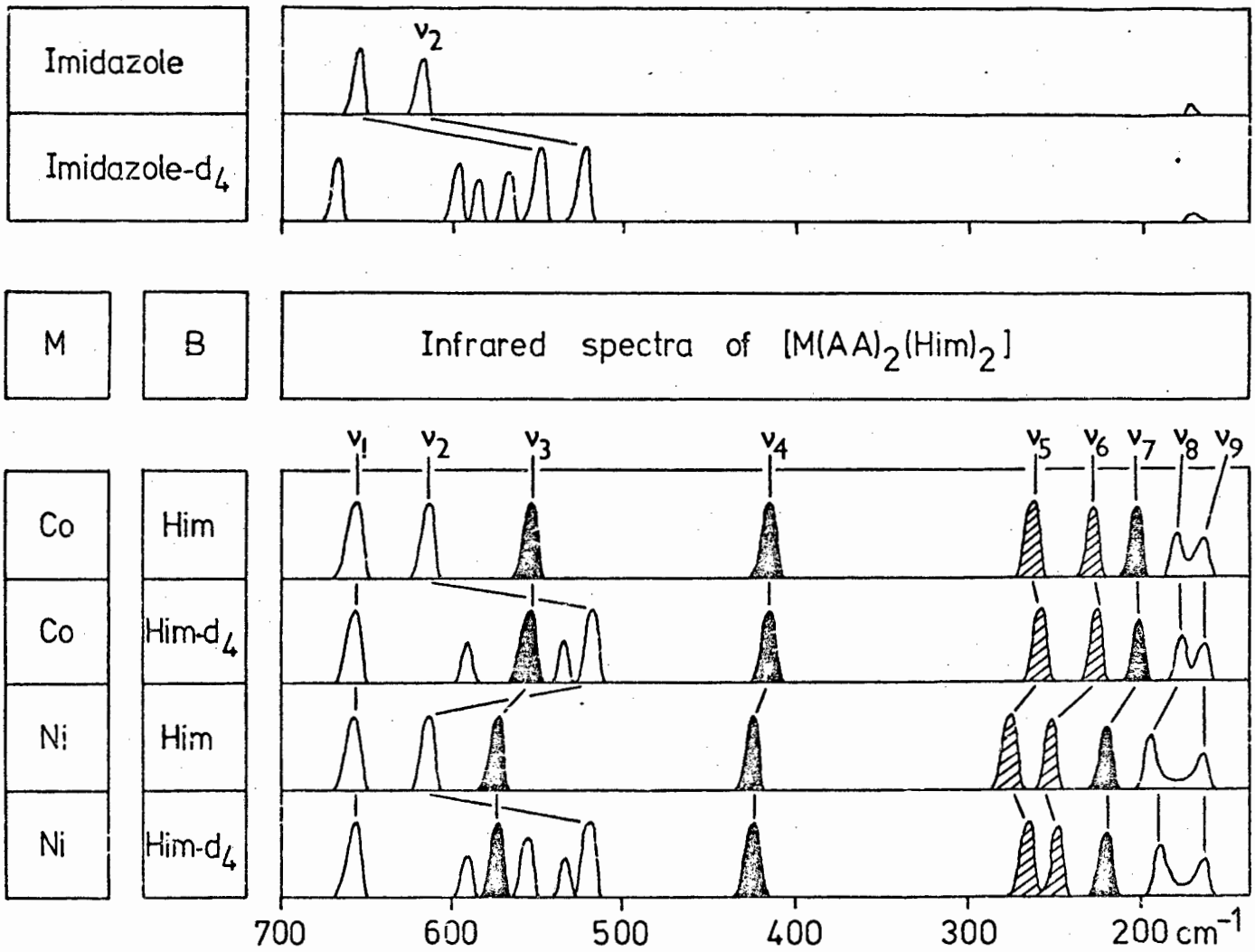


Fig. 36. The infrared spectra (700-140 cm^{-1}) of the complexes $[M(AA)_2(Him)_2]$ and their Him-d_4 analogues. Solid bands: νM-O, shaded bands: νM-N

of the spectrum of $[Cr(AA)_3]$ is considered unlikely since this would place the O-M-O bend at a higher frequency than νM-N.

ν_8, Being both *d*- and M-sensitive, is either a third νM-N band, or, more probably, a bending mode involving nitrogen i.e. δO-M-N, δN-M-N or δM-N-C. The origin of ν_9 is uncertain since it has no M-sensitivity and is too broad for its *d*-sensitivity to be determined in the spectrum of the Ni(II) adduct.

Support for the assignments proposed for νM-O and νM-N is adduced from a comparison between the frequencies of these vibrations in $[Ni(AA)_2(py)_2]$[106] and $[Ni(AA)_2(Him)_2]$. It is now well known[106] that any increase in the strength of the M-base bond on replacing one adducted base by another causes a shift in νM-O towards lower frequency. Since νNi-N in the Him adduct exceeds νNi-N in the py adduct, the reverse trend is expected for νNi-O. This is observed.

3.2 The pyrazine adducts, $[M(AA)_2(pz)]_n$ (M = Co, Ni, Zn)

The infrared spectra are depicted in Figs. 8 and 37. Below 700 cm^{-1}, pz exhibits one internal ligand mode, an out-of-plane deformation[80] of the heterocyclic ring, at 413 cm^{-1}, with a *d*-sensitivity of 14 cm^{-1}. This band recurs in the spectra of the pz adducts in the 470 cm^{-1} region (ν_3). As observed for the py adducts, coordination of pz leads to an increase in the frequency of such internal ligand[190] vibrations. The *d*-sensitivity (which this band retains in the spectra of the pz-d_4 adducts) enables it to be readily distinguished from *d*-insensitive bands near 560 cm^{-1} (ν_2), and 420 cm^{-1} (ν_4). The latter two bands are assigned to coupled νM-O modes on the grounds of their absence of

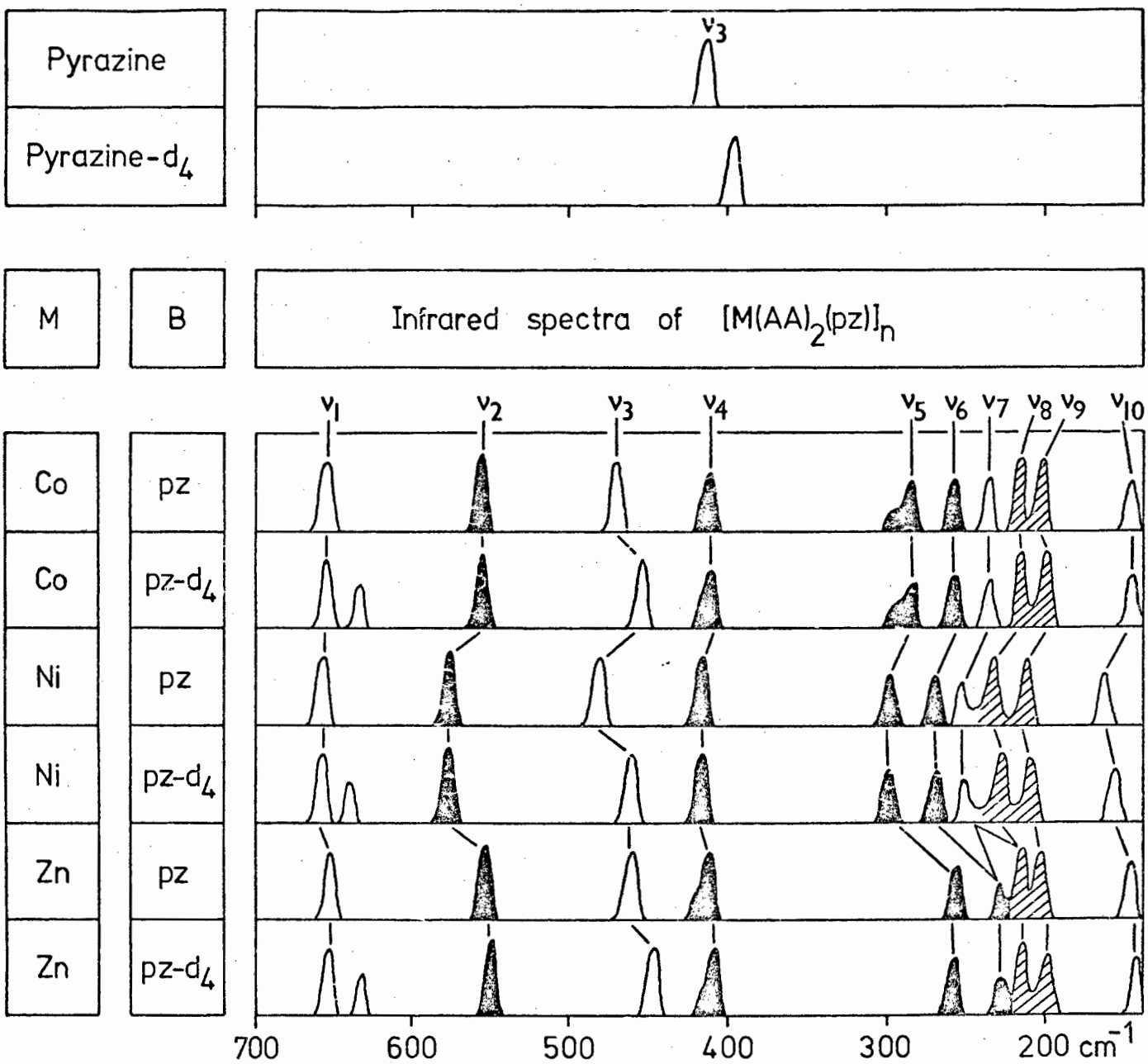


Fig. 37. The infrared spectra (700-140 cm^{-1}) of the complexes $[M(AA)_2(pz)]_n$ and their pz-d_4 analogues. Solid bands: νM-O, shaded bands: νM-N

d-sensitivity and their high M-sensitivity in the CFSE sequence Co < Ni > Zn. By analogy with the Him adducts, ν_1 is assigned to a chelate ring deformation. This band exhibits no *d*-sensitivity, but does, however, yield a small measure of M-sensitivity, indicative of some coupling with νM-O. The spectra of the deuterated adducts reveal one extra band in this region, near 640 cm^{-1}, which is assigned[80] to a pz-d_4 γC-D mode originating above 700 cm^{-1} in the undeuterated complex.

Of the four (or five) bands within the range 300-200 cm^{-1}, only the two of lowest frequency (ν_8 and ν_9) exhibit significant *d*-sensitivity, establishing them firmly as νM-N bands. Their position (near 200 cm^{-1}) agrees with the position of νM-N in the complexes[179] $[Co(pz)_2X_2]$ (X = halogen). The assignment is also supported by the strong M-sensivity of these bands in the sequence Co < Ni > Zn. Of the remaining two (or three) bands (ν_5,ν_6 and ν_7) within the range 300-200 cm^{-1}, ν_5 and ν_6 are assigned to vibrationally pure νM-O modes on the grounds of their absence of *d*-sensitivity, their significant M-sensitivity in the sequence Co < Ni > Zn, and the occurrence of bands in this region in the spectra of the complexes $[M(AA)_2(H_2O)_2]$ (M = Co, Ni), and $[Zn(AA)_2(H_2O)]$, which undoubtedly have the same origin, and the established existence[106] of two νM-O bands in this region of the spectra of $[M(AA)_2(py)_2]$ and $[Zn(AA)_2(py)]$. ν_{10} Is considered to originate in a M-ligand bending mode in view of its M- and *d*-sensitivity.

3.3 The pyrimidine adducts, $[M(AA)_2(pm)]_n$ (M = Co, Ni, Zn)

Figures 9 and 38 depict the spectra of the complexes $[M(AA)_2(pm)]_n$. Deuterated pm-d_4 was not available, but the similarity of these spectra

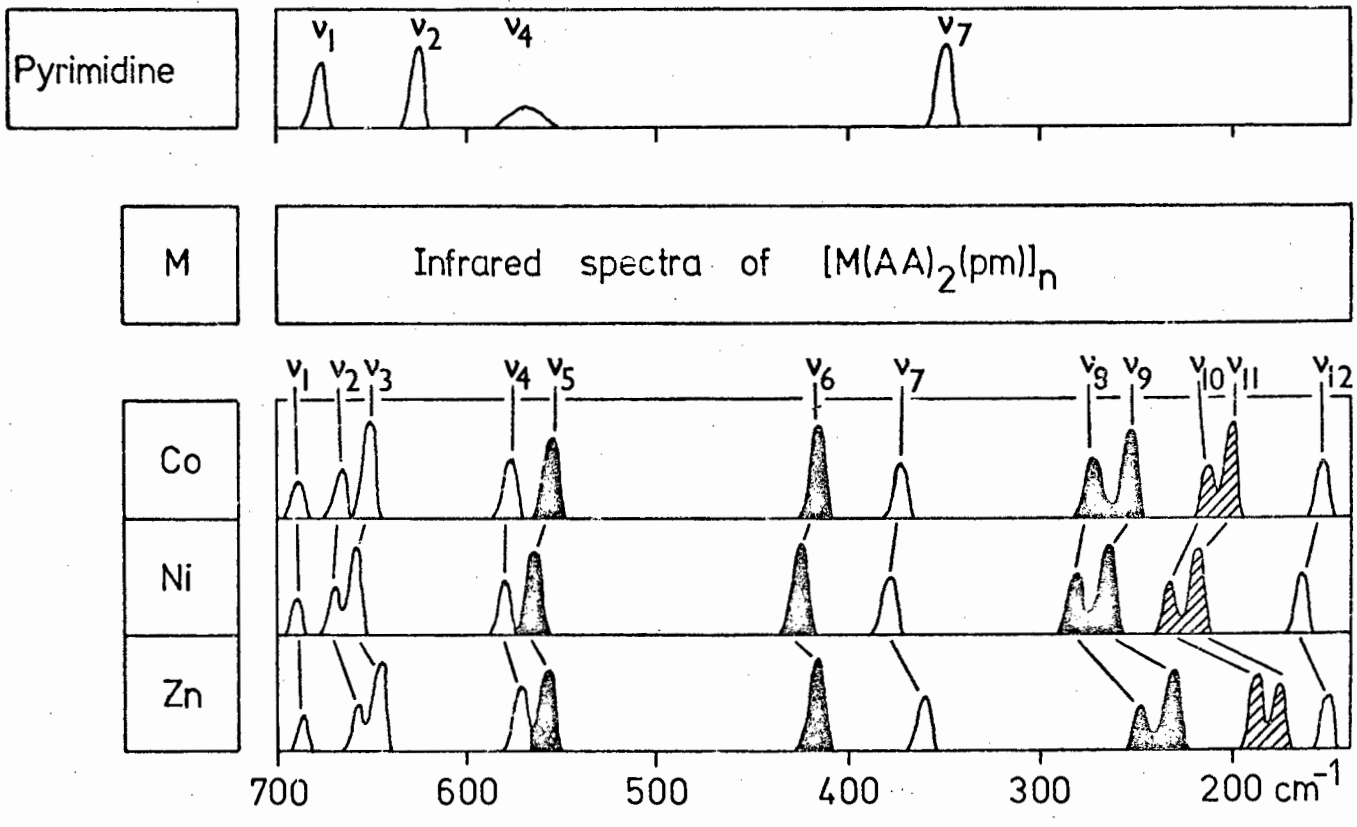


Fig. 38. The infrared spectra (700-140 cm^{-1}) of the complexes $[M(AA)_2(pm)]_n$. Solid bands: νM-O, shaded bands: νM-N.

to those of the corresponding Him and pz adducts provides a basis for reliable empirical assignments. Pyrimidine has four ligand modes below[80] 700 cm^{-1}, at 678 (γring), 624 (δring), 348 (γring) and a very weak band at 567 cm^{-1} (δring). The spectra of the adducts yield seven bands within the range 700-300 cm^{-1}. The band of lowest frequency (ν_7) is considered to correspond with the pm ligand band, raised 31 cm^{-1} by coordination, a shift characteristic[190] of the shift in the out-of-plane ring vibration, on complexation of nitrogen heterocycles. ν_1 And ν_2 are similarly regarded as the internal modes of the pm ring, undoubtedly the out-of-plane ring deformation, and in-plane ring deformations, respectively. ν_3 Is assigned to a chelate ring deformation. Its M-sensitivity suggests that it comprises some contribution from νM-O. Of the remaining three bands in this region (700 - 300 cm^{-1}), that near 420 cm^{-1} (ν_6) and the more M-sensitive band near 560 cm^{-1} (ν_5) are assigned to coupled νM-O modes. The 578 cm^{-1} vibration (ν_4) originates in the B_1 mode (C_{2v}) of pm at 567 cm^{-1} (δring).

Assignment of the two uncoupled M-O bands (ν_8 and ν_9), and the two νM-N bands (ν_{10} and ν_{11}), between 300-170 cm^{-1} is made by comparison with the assignments made for the corresponding Him and pz adducts. ν_{12} Is assigned to a bending mode involving oxygen or nitrogen by analogy with corresponding bands in the spectra of the other adducts.

3.4 The pyridazine adducts, $[M(AA)_2(pd)_2]$ (M = Co, Ni)

Pyridazine exhibits four internal infrared-active vibrational modes below 700 cm^{-1}, at 665 cm (δring[80]), weak bands at 696 (γC-H) and 623 cm^{-1} (δring) and a band at 375 cm^{-1} (γring), (Figs. 10 and 39). In the spectra of the adducts the band of lowest frequency, the out-of-plane heterocyclic ring deformation,[80] is split into two peaks near 400 (ν_6)

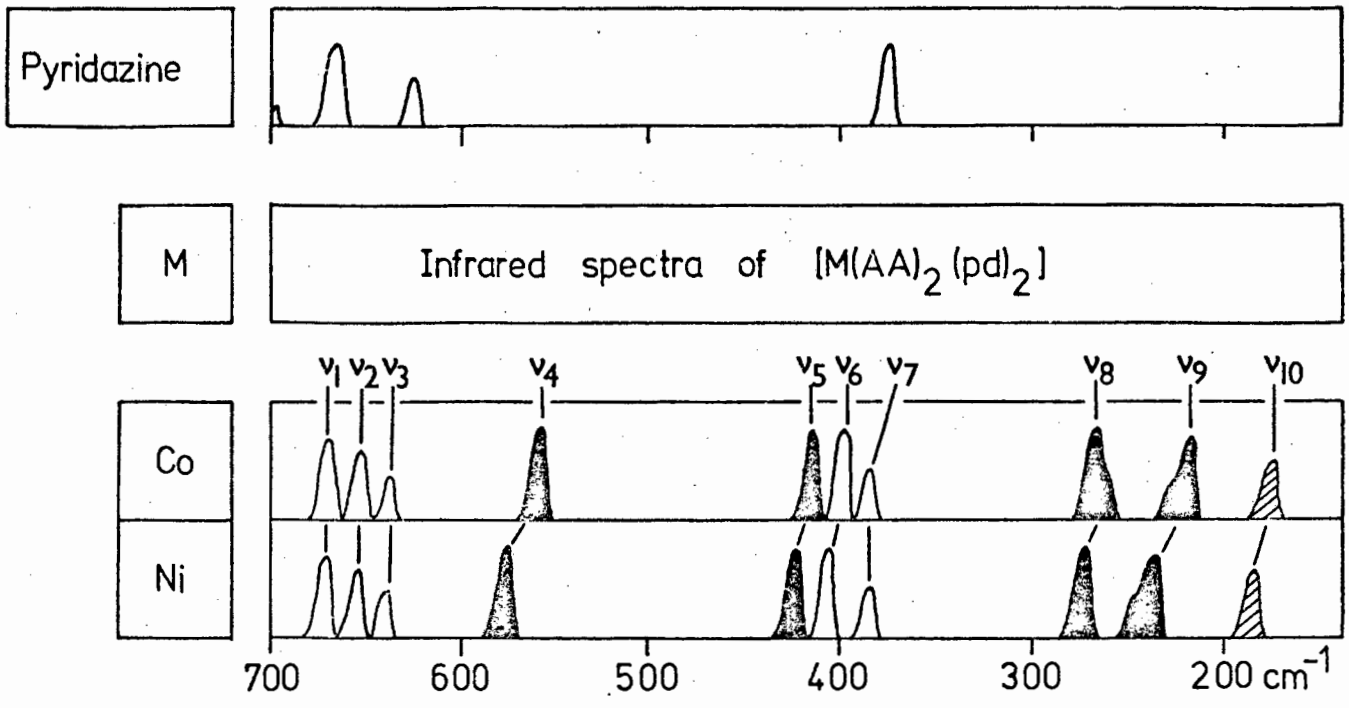


Fig. 39 The infrared spectra (700-140 cm^{-1}) of the complexes $[M(AA)_2(pd)_2]$. Solid bands: νM-O, shaded bands: νM-N.

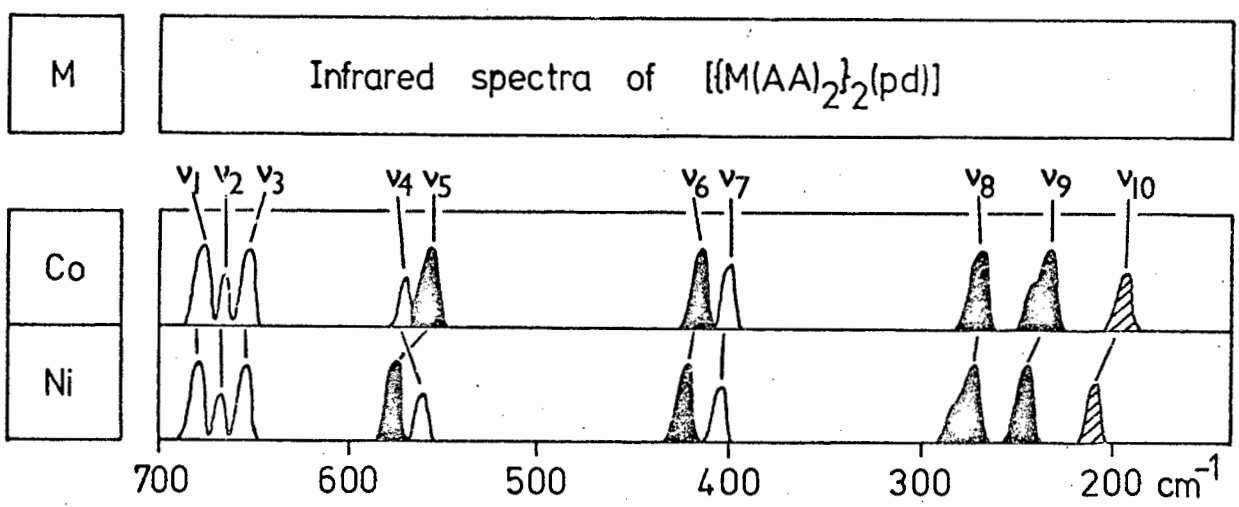


Fig. 40. The infrared spectra (700-140 cm^{-1}) of the complexes $[\{M(AA)_2\}_2(pd)]$. Solid bands: νM-O, shaded bands: νM-N.

and 385 cm^{-1} (ν_7). The appearance of an extra ligand mode could be attributed to different orientations of the pd rings in different $[M(AA)_2(pd)_2]$ molecules, or the activation of an infrared-inactive internal pd mode. Bands ν_1 and ν_3 are assigned to the remaining two pd ring deformations. Band ν_2 is assigned to a chelate ring deformation by comparison with the spectra of the other adducts. The bands ν_4 and ν_5, are almost certainly coupled νM-O vibrations, and ν_8 and ν_9 are assigned to the vibrationally purest νM-O modes. There is only one band below 200 cm^{-1} (ν_{10}). In view of its strong M-sensitivity, it is assigned to νM-N. This band occurs within close proximity to νM-N in the analogous[106] complexes $[M(AA)_2(py)_2]$.

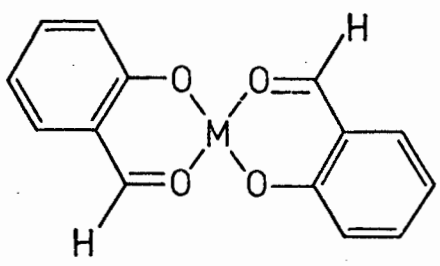
3.5 The pyridazine adducts, $[\{M(AA)_2\}_2(pd)]$ (M = Co, Ni)

The internal pd ligand modes (Fig. 40) are assigned to ν_1, ν_2 and ν_7. The fact that ν_2 occurs at higher frequency than the similarly assigned band in the bis(pd) adducts is attributed to the fact that both nitrogen atoms in these complexes, are involved in bonding, thus imposing a greater stereochemical rigidity upon the adducted base. ν_3 Is assigned to a chelate ring deformation. This assignment is based on its correspondence with the similarly assigned band in the bis(pd) adducts. ν_5 And ν_6 are assigned to the coupled νM-O vibrations. As observed in the spectra of the pm adducts there is an additional band, ν_4, within the region 600-500 cm^{-1}. This band is probably a heterocyclic ligand mode activated by a change in symmetry on complexation. The principal (least-coupled) νM-O vibrations (ν_8 and ν_9) are assigned by comparison with the spectra of the other adducts. ν_{10} Is assigned to νM-N.

4. INFRARED SPECTRA (700-140 cm^{-1}) OF THE ANHYDROUS, AQUO, PYRIDINE, IMIDAZOLE, PYRAZINE AND PYRIMIDINE ADDUCTS OF COBALT(II), NICKEL(II) AND ZINC(II) SALICYL-ALDEHYDATES

By analogy with the corresponding M(II) acetylacetonates, the bis(aquo) adducts of M(II) salicylaldehydates, when heated under reduced pressure over silica gel at temperatures between 120 and 170°C, yield anhydrous complexes. The water molecules are also readily replaced by a variety of nitrogenous bases, of which pyridine is a representative example. Extensive solid state studies have been made on the anhydrous complexes of Co(II), Ni(II) and Cu(II) salicylaldehydates which were originally considered[116-117,217] to be tetrahedral or planar. Anhydrous $[Zn(Sal)_2]$ was considered[217] tetrahedral simply on the grounds that very many tetracoordinate Zn(II) complexes of known structure are tetrahedral.

Magnetic and spectroscopic studies[122-125] of the Co(II), Ni(II) and Cu(II) complexes of salicylaldehyde and its substituted derivatives as well as various other *o*-hydroxyarylcarbonyl complexes of general formula (VI) have shown that the Co(II) and Ni(II) complexes have high-spin configurations and electronic spectra typical of octahedral structure.



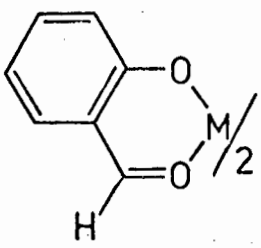
(VI)

It was suggested that the anhydrous complexes are polymeric in the solid state, although they were found to be essentially monomeric in dilute solutions in non-donor solvents. These authors[122-125] concluded that the solution structures were best described as four-coordinate high-spin, *trans*-square planar species, their stability being achieved by back donation of *d*-electrons of the metal ion into the antibonding orbital of the localized C=O double bond.

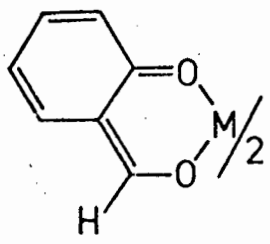
Subsequent evidence from x-ray diffraction studies[112,218], electronic spectra and magnetic moments,[113,218] established polynuclear octahedral structures for the Co(II) and Ni(II) derivatives and approximately square planar coordination[114-115,123,219] for the Cu(II) chelate, which was found[219] to crystallize in the monoclinic system, $P2_1/c$, with Z = 2. The anhydrous Ni(II) complex is trimeric[112] and not isomorphous[118] with the Co(II) complex. The latter is probably a tetramer, resembling the corresponding Co(II) acetylacetonate.[106]

The structures of these complexes are therefore analogous with the acetylacetonates and tropolonates of the same metal ions. However, salicylaldehydate complexes differ from acetylaceonates and resemble tropolonates in possessing two different C-O bond lengths within the chelate ring. This is evident from the infrared spectra[121,127] of salicylaldehydate complexes by the appearance of distinctive aldehydic carbonyl (C=O) and phenolic carbonyl (C-O) vibrations near 1650 and 1330 cm^{-1}, respectively in the bis(aquo) complexes. The νC=O band in the free acetylacetone spectrum occurs[122] near 1660 cm^{-1}. This band disappears on complexation and two new bands[122] appear near 1590 and 1520 cm^{-1}. The high frequency band representing mainly νC=C coupled with νC ⟷ O, and the lower band being mainly νC ⟷ O coupled with νC=C. However, the C=O band in salicylaldehydate complexes is not far removed

from[122] the 1660 cm^{-1} band of the free ligand. Thus the two C-O bonds in these complexes cannot be considered fully equivalent. The C-O frequencies in the Ni(II) and Cu(II) complexes of salicylaldehyde agree remarkably well with the frequencies of this vibration in the corresponding tropolonate complexes[220] which occur near 1340 cm^{-1}. The unsymmetrical nature of the chelate ring was revealed by x-ray analysis of the complexes of Ni(II)[221] and Cu(II).[114] However, the presence of the *o*-phenylene ring in salicylaldehyde has been suggested[116] to interfere with the resonance of the chelate ring, such that the contribution of the benzenoid and non-benzenoid forms (VIIa and VIIb) leads to



(VIIa)



(VIIb)

much localization of electrons[122] in the chelate ring (less than in acetylacetonate complexes).

In an extensive study of the infrared spectra of the Co(II), Ni(II) and Cu(II) complexes of variously-substituted salicylaldehydates[127] the band-for-band correspondence of the spectra of the Co(II) and Ni(II) complexes furnished evidence of their analogous structure. The Cu(II) chelates, on the other hand, yielded[127] unique band patterns in accordance with the uniquely square planar structure. The region 610-550 cm^{-1} in the spectra of the anhydrous complexes, exhibited bands which were

strongly substituent dependent and metal ion dependent, the latter being in the sequence of the CFSE's: Co < Ni < Cu. While assigning νM-O within this region, it was noted[127] that several bands within the CsI region show similar metal ion sensitivity which would justify their assignment, also to (coupled) νM-O vibrations. It has since been found that in the spectra of the analogous acetylacetonate[106] and tropolonate[40,220] complexes, one or two bands below 400 cm^{-1} may be assigned to νM-O on the basis of the shifts induced by isotopic labelling of the coordinated metal ion.

By contrast with Zn(II) acetylacetonate, which is known[106] to adduct only one molecule of water or pyridine, yielding five-coordinate species, the adducts of Zn(II) salicylaldehydate all analyse as six-coordinate complexes and have infrared band patterns which are practically identical with those of their Co(II) and Ni(II) analogues. For this reason, the bis(aquo) and bis(pyridine) adducts of Zn(II) salicylaldehydate are regarded as being *trans*-octahedral and isostructural with the Co(II) and Ni(II) complexes.

The proton magnetic resonance[222] and ligand field spectra[223] of the pz and pm adducts of Co(II) salicylaldehydate have been studied. These bases are weaker than pyridine (pKa = 5.3), their pKa values[224] being 0.65 and 1.30, respectively. In complexes of these ligands, the bases may function either as terminal groups involving only one nitrogen donor, or as bridging groups involving both nitrogen donors. Both types of adduct have been prepared from Co(II) salicylaldehydate[223]. All complexes synthesised in this work analysed for one molecule of base. The reflectance spectra (Table 33) of the Co(II) and Ni(II) complexes of both adducts are those expected[213] for an octahedral environment. The adducts are therefore regarded as polymeric *trans*-octahedral complexes, similar to those of the corresponding acetylacetonates.

The adducts of imidazole (pKa^{58} = 6.95), on the other hand, analysed for two molecules of the base. Their reflectance spectra also conform with those[213] expected for octahedral complexes of these M(II) ions. The remarkable similarity between the infrared spectra of these complexes and those of the bis(pyridine) adducts, supports the view that the Him adducts are monomers. The bis(aquo), bis(py) and bis(Him) adducts are therefore formulated $[M(Sal)_2(B)_2]$ while the pz and pm adducts are formulated $[M(Sal)_2(B)]_n$.

4.1 The anhydrous complexes $[M(Sal)_2]$ (M = Co, Ni, Zn)

It is known that ligand vibrations appearing in the spectra of a complex often occur at higher frequency than in the spectrum of the free ligand. The bands (Table 24) near 665, 587 and 545 cm^{-1} in the spectra of the anhydrous complexes (Figs. 11 and 41) are assigned to ligand modes (νsal) originating in the bands at 660, 564 and 539 cm^{-1}, respectively, in salicylaldehyde. The band at 521 cm^{-1} occurs within a region free from ligand absorption, and is assigned to νM-O in agreement with previous assignments[127]. It is M-sensitive in the CFSE sequence Co < Ni > Zn, and its frequency is close to that of the (coupled νM-O in the spectra of M(II) acetylacetonates. This order of νM-O and the similarity of the spectrum of the Zn(II) complex to those of the Co(II) and Ni(II) complexes indicates that the anhydrous Zn(II) complex is also octahedral since a lower coordination number for the Zn(II) complex would induce a dramatic high-frequency shift in νZn-O.

Salicylaldehyde has three bands between 500-400 cm^{-1}. The band near 440 cm^{-1} in the spectra of the complexes is regarded as originating

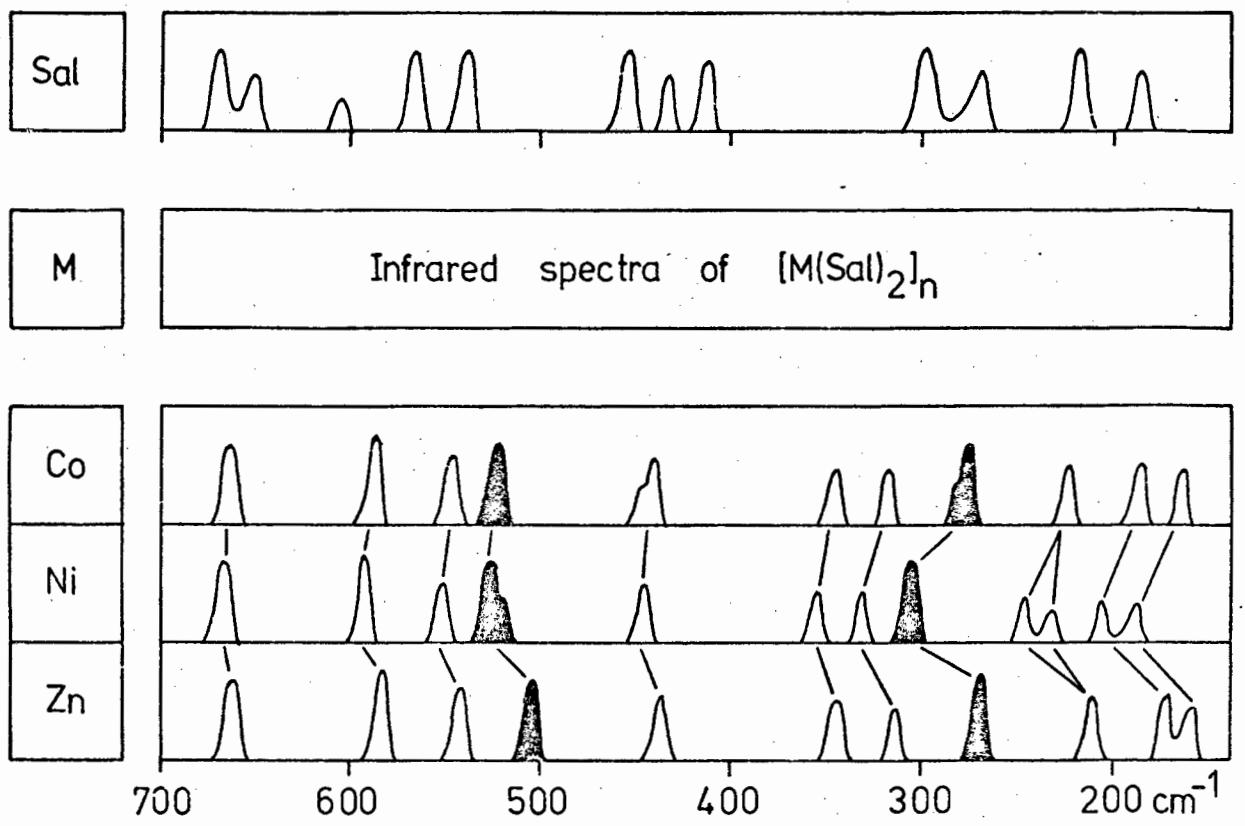


Fig. 41. The infrared spectra (700-140 cm^{-1}) of the complexes $[M(Sal)_2]$. Solid bands: νM-O

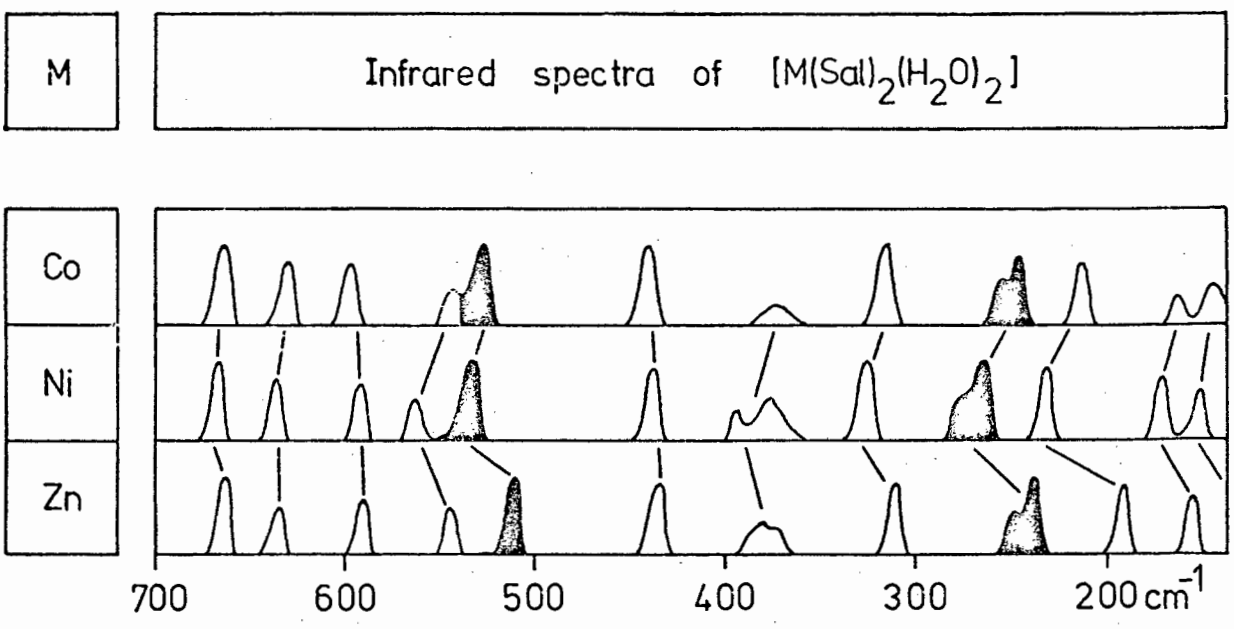


Fig. 42. The infrared spectra (700-140 cm^{-1}) of the complexes $[M(Sal)_2(H_2O)_2]$. Solid bands: νM-O

in one or more of these ligand modes. Although it exhibits slight M-sensitivity indicating the possibility of some coupling with νM-O it is not regarded as a second vibrationally pure νM-O as previously suggested[126] from comparisons with the spectra of the analogous M(II) acetylacetonates. All the bands below 400 cm^{-1} are strongly M-sensitive, but do not arise entirely from M-ligand vibrations, since salicylaldehyde itself has four bands in this region. The bands near 343 cm^{-1} and 318 cm^{-1} probably correspond with the ligand modes near 299 cm^{-1} and 268 cm^{-1}, their M-sensitivity indicating coupling with νM-O. They are therefore assigned to νsal + νM-O. The band of highest frequency and exhibiting the strongest M-sensitivity in this region, i.e. that near 276 cm^{-1}, is assigned to νM-O. A similar assignment was made for a band near this frequency in the complexes of M(II) tropolonates[40] (on the basis of metal isotope substitution) and M(II) acetylacetonates[106] (on the basis of its behaviour towards metal ion substitution and py adduct formation).

The two bands of highest frequency below 250 cm^{-1}, occur within regions of ligand absorption and one thus assigned to ligand modes. Their M-sensitivities indicate the possibility of a contribution from νM-O. The band of lowest frequency probably involves a O-M-O deformation.

4.2 The bis(aquo) adducts $[M(Sal)_2(H_2O)_2]$ (M = Co, Ni, Zn)

There are five vibrations between 700 and 500 cm^{-1}, of which the four bands of highest frequency (Fig. 42) are assigned to νsal since they may be correlated with the free ligand bands in this region. The band at 526 cm^{-1} exhibits the strongest M-sensitivity, and is assigned to νM-O by comparison with the spectra of the anhydrous complexes. The band

near 440 cm^{-1} is assigned to νsal since it shows no M-sensitivity, and occurs within a region of absorption of the free ligand. The broad, weak band near 375 cm^{-1} is not present in the spectra of the anhydrous complexes. A band at 340 cm^{-1} in the spectrum of the bis(aquo) adduct of Ni(II) tropolonate was assigned[40] to νNi-OH_2 on the results of ^{58}Ni-^{62}Ni substitution. The corresponding band shows no M-sensitivity in $[M(Sal)_2(H_2O)_2]$ as would be expected for νM-OH_2. An alternative assignment is to an H-O-H rocking mode.

The band between 327 and 311 cm^{-1} is assigned to νsal + νM-O in view of its proximity to the ligand absorptions which occur below this frequency in the spectrum of the ligand, and because of the strong M-sensitivity which it exhibits. The doublet in the region 257-245 cm^{-1} is assigned to νM-O by analogy with the assignment made for the band in this region in $[M(Sal)_2]_n$. The band at 215cm^{-1} is assigned to νsal including a contribution from νM-O since it is strongly M-sensitive. The bands below 175 cm^{-1} probably involve bending motions of the O-M-O skeleton.

It was noted in earlier work[127] that a low frequency shift in νM-O (assigned to the band between 535 and 514 cm^{-1}) did not accompany the transformation of the anhydrous complexes into their dihydrates. This was regarded as implying that a change in coordination number does not accompany this transformation. When ligand composition remains constant, increased coordination number causes a considerable low frequency shift in νM-L. This may be illustrated[33] by the transformation of mononuclear tetrahedral $[Co(py)_2Cl_2]$, C_{2v} symmetry (νM-N = 248, 208 cm^{-1}), into polynuclear octahedral $[Co(py)_2Cl_2]_n$, C_i symmetry (νM-N = 182 cm^{-1}). The change from $[M(Sal)_2]_n \rightarrow [M(Sal)_2(H_2O)_2]$ does involve a change in ligand composition but the ligand field strength of the

ligand introduced (H_2O) is comparable with that of the ligand replaced (Sal), so that no significant shift in νM-O is expected to accompany the transformation if the anhydrous complex is six-coordinate. The same argument will apply to the Zn(II) complexes where νM-O near 500 cm^{-1} remains constant or has shifted to slightly higher frequency on bis(aquo) adduct formation. This supports the proposal that $[Zn(Sal)_2]_n$ also has the polymeric octahedral structure which pertains to the corresponding acetylacetonate and that $[Zn(Sal)_2(H_2O)_2]$ is monomeric and *trans*-octahedral. Since there is a substantial decrease in the frequency of νM-O near 300 cm^{-1} on bis(aquo) adduct formation, this band is regarded as a coupled, less vibrationally pure νM-O than that near 500 cm^{-1}.

4.3 The pyridine adducts $[M(Sal)_2(py)_2]$ (M = Co, Ni, Zn)

Since the ligand field strength of py is approximately 25% greater than that of water,[2] a significant decrease in νM-O is expected to accompany the transformation $[M(Sal)_2(H_2O)_2] \rightarrow [M(Sal)_2(py)_2]$. It is known[100,225] that an inverse relationship exists between the ligand field strength of the adducted base, and νM-O in the py adducts of M(II) acetylacetonates and tropolonates, i.e. any strengthening of the metal-adduct bond occurs at the expense of the metal-chelate bond. The bands between 523 and 497 cm^{-1} (Fig. 43) are assigned to νM-O for the following reasons. They undergo shifts of as much as 17 cm^{-1} towards lower frequency when the adducted water molecules are replaced by pyridine. They are strongly M-sensitive in the CFSE sequence Co < Ni > Zn.

They also exhibit a total lack of *d*-sensitivity when the adducted pyridine is replaced by pyridine-d_5.

The two bands at 254 and 230 cm^{-1} are also assigned to νM-O. They correspond, in position, with the bands assigned to νM-O in the spectra of $[M(AA)_2(py)_2]$, they are strongly M-sensitive and are insensitive to deuteration of the py ring. The other two bands of higher frequency, below 350 cm^{-1}, are assigned to the coupled vibration, νsal + νM-O, since they correspond with the ligand modes at 299 and 268 cm^{-1}, and are strongly M-sensitive. The band at 207 cm^{-1} probably originates in the ligand mode near 219 cm^{-1} and is assigned to νsal. Thus its M-sensitivity is small and is completely *d*-insensitive. On the basis of its significant *d*-sensitivity, the band at 193 cm^{-1} in the Co(II) complex, and the doublets in the Ni(II) and Zn(II) complexes within the regions 192-181 cm^{-1} and 158-153 cm^{-1}, respectively, are assigned to νM-N. These νM-N frequencies agree well with those of νM-N in $[M(AA)_2(py)_2]$ which were also established[106] by isotopic labelling. The remaining band below 160 cm^{-1} in the Co(II) and Ni(II) complexes (probably below 140 cm^{-1} in the Zn(II) complex) exhibit slight M-sensitivity but no *d*-sensitivity and are therefore assigned to δO-M-O.

Of the remaining bands between 700 and 400 cm^{-1}, those near 660, 590, 546 cm^{-1} and the doublet near 440 cm^{-1} are assigned to νsal, since they occur in regions of absorption by the free ligand, they lack M-sensitivity and are also insensitive towards py deuteration. Deuteration of the py ring has enabled unambiguous assignments of the internal py ring deformations. The bands near 700, 631 and 425 cm^{-1} exhibit *d*-induced shifts of approximately 92, 100 and 39 cm^{-1}, respectively. By comparison with the assignments of pyridine itself,[226] they are assigned to the γC-H, δring and γring modes of the py ring. These bands occur in almost identical positions in the spectra of $[M(AA)_2(py)_2]$.[106]

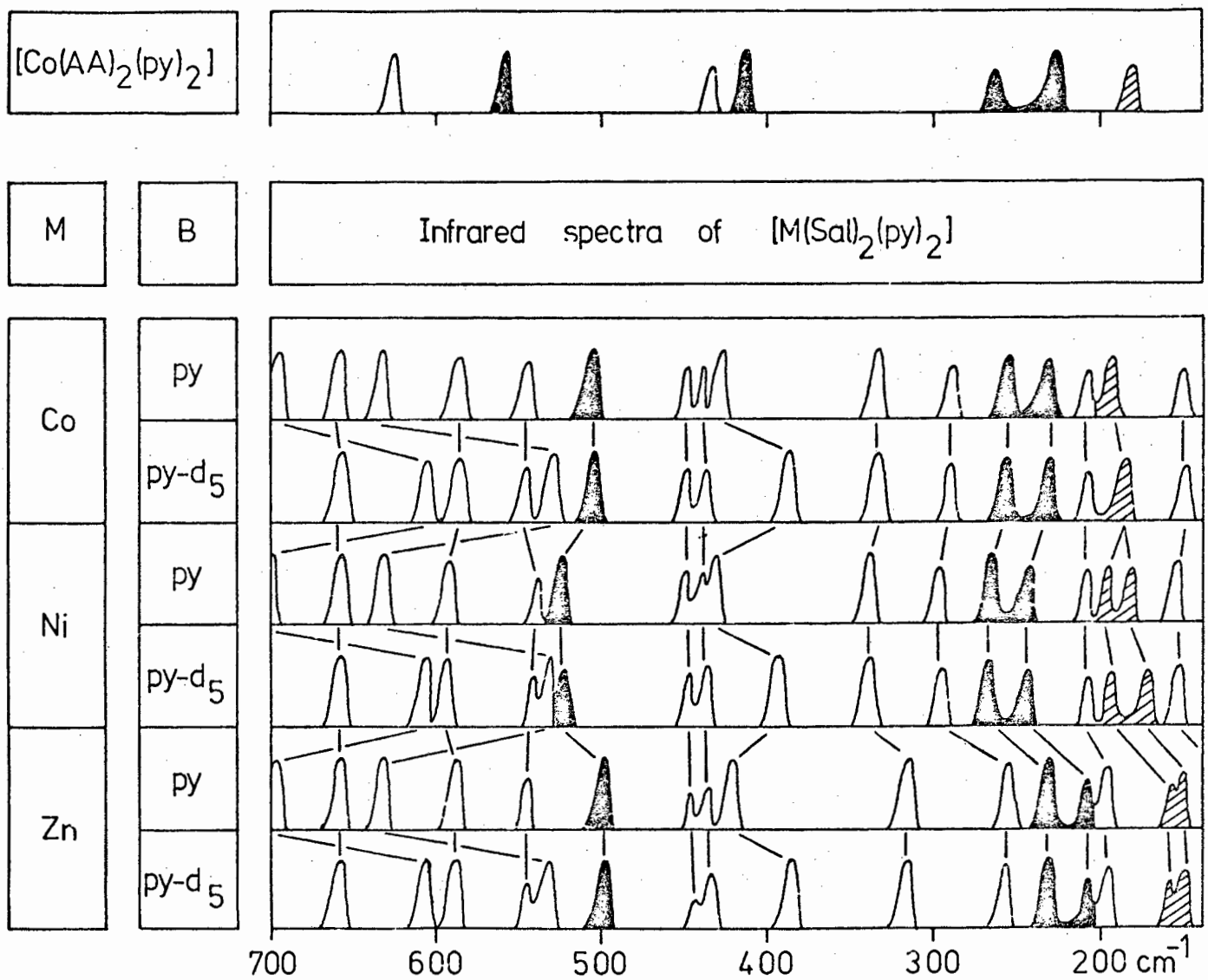


Fig. 43. The infrared spectra (700-140 cm^{-1}) of the complexes $[M(Sal)_2(py)_2]$. Solid bands: νM-O, shaded bands: νM-N

4.4 The imidazole adducts $[M(Sal)_2(Him)_2]$ (M = Co, Ni)

The band (Figs. 12 and 44) at 509 cm^{-1} is assigned to νM-O because it is M-sensitive in the CFSE sequence Co < Ni and is totally insensitive towards deuteration of the Him ring. The band near 435 cm^{-1} is assigned to νsal by analogy with the assignments made for the corresponding band in the complex of salicylaldehyde discussed above. The two bands between 332 and 312 cm^{-1} are similarly assigned to the coupled vibration, νsal + νM-O, on the grounds of their M-sensitivity, the fact that they correspond with the two salicylaldehyde ligand vibrations at slightly lower frequency and because of their *d*-insensitivity.

Apart from the 174 cm^{-1} lattice mode, Him[71] has no internal vibrations below 600 cm^{-1}. Therefore any *d*-sensitive bands below this frequency must arise from the stretching and bending motions of the M-N bonds. That the two bands at 266 and 239 cm^{-1} in the Co(II) complex are νM-N is proposed for the following reasons. Their frequencies are in good agreement with those of νM-N in the complexes $[M(Him)_6]^{2+}$ which were assigned[64] by metal-isotope labelling and a single crystal study.[65] These frequencies also correspond with those of νM-N in $[M(AA)_2(Him)_2]$. Moreover, they exhibit strong M-sensitivity and are shifted to lower frequency on Him-d_4 substitution. The shoulder at 232 cm^{-1} is assigned to νM-O since it is M-sensitive and *d*-insensitive. However, the close proximity of νM-N and νM-O indicate that they are likely to couple. The three bands below 200 cm^{-1} are significantly *d*-sensitive and also exhibit slight M-sensitivity. They are therefore assigned to bending motions involving nitrogen, i.e. δO-M-N or δN-M-N.

Of the remaining bands between 700 and 530 cm^{-1}, those near 664, 585 and 543 cm^{-1} are assigned to νsal. Uncoordinated Him has two bands[70] at 657 and 619 cm^{-1}. Of these, the latter recurs in the spectra

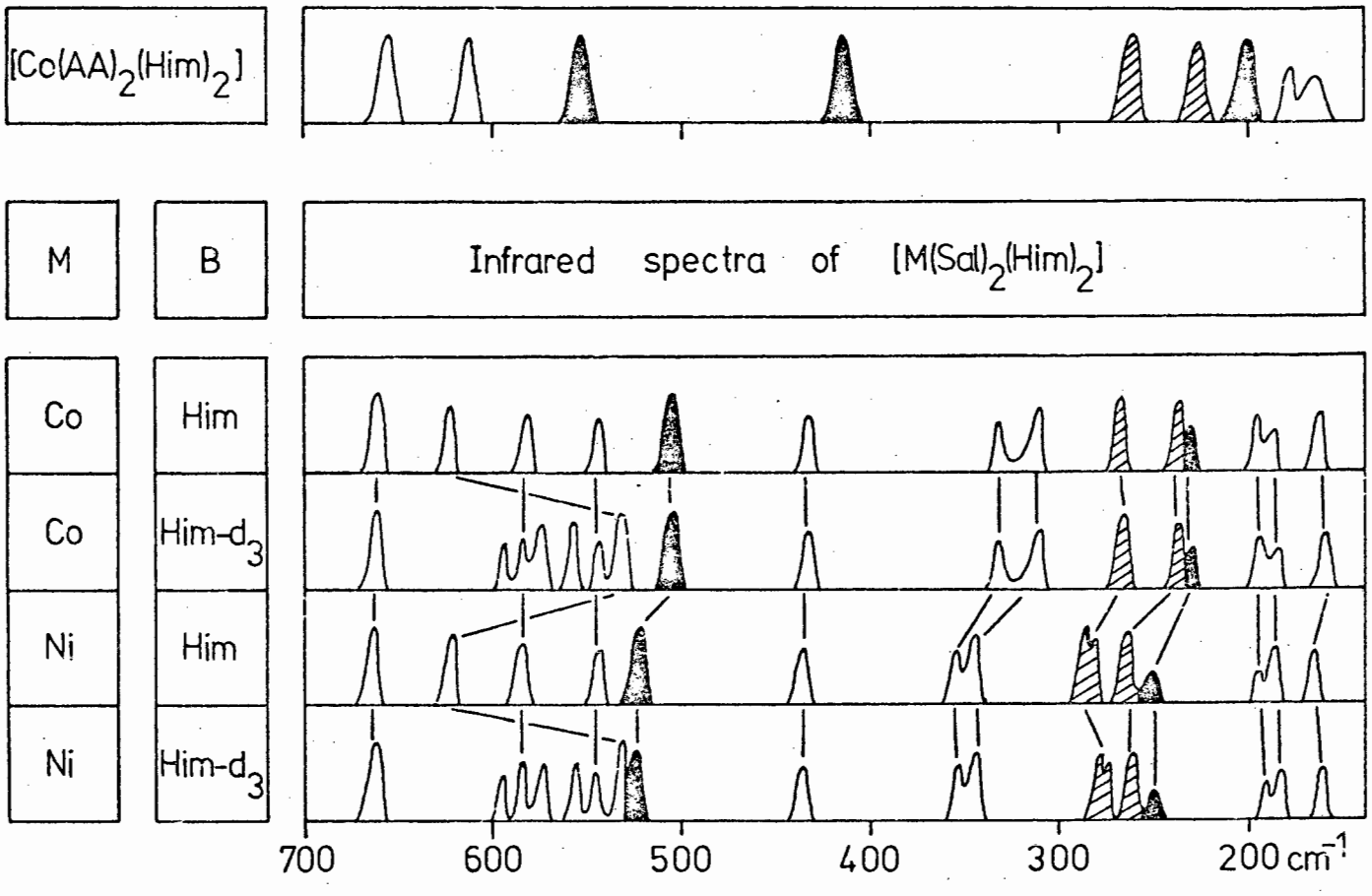


Fig. 44. The infrared spectra (700-140 cm^{-1}) of the complexes $[M(Sal)_2(Him)_2]$. Solid bands: νM-O, shaded bands: νM-N

of the adducts near 625 cm^{-1}, and is identified as the γring(Him) vibration[70] by its *d*-sensitivity. As observed in the spectra of the analogous acetylacetonate, the spectra of the deuterated Him adducts show four new bands between 600 and 500 cm^{-1}. These are undoubtedly deformational modes of deuterated Him-d_3.

4.5 The pyrazine adducts $[M(Sal)_2(pz)]_n$ (M = Co, Ni, Zn)

Pyrazine exhibits one internal mode[80] below 700 cm^{-1}, an out-of-plane ring deformation (γring) near 413 cm^{-1}. This band recurs in the spectra of the adducts (Figs. 13 and 45) near 470 cm^{-1}, and exhibits a *d*-sensitivity of approximately 20 cm^{-1}. It is readily distinguished from the *d*-insensitive ligand bands between 450 and 430 cm^{-1}, which, because of their *d*-insensitivity, are assigned to νsal. The band near 505 cm^{-1} is assigned to νM-O since it is the most strongly M-sensitive band in this region of the spectrum and is totally *d*-insensitive. The three bands near 660, 593 and 538 cm^{-1} are assigned to νsal.

The band near 336 cm^{-1} is both M- and *d*-insensitive and is assigned to νsal, while the band at 338 cm^{-1}, which exhibits strong M-sensitivity, is assigned to the coupled vibration, νsal + νM-O. The band between 300 and 280 cm^{-1} in the Co(II) and Ni(II) complexes, and the high frequency shoulder at 250 cm^{-1} in the Zn(II) complex are assigned to νsal (originating in the free ligand vibration at 268 cm^{-1}). Their M-sensitivity suggests some coupling with νM-O. The band at 257 cm^{-1} is assigned to νM-O because it is strongly M-sensitive and matches, in position, the band at 287 cm^{-1} in $|M(AA)_2(pz)|_n$, also assigned to νM-O. That it is coupled to νM-N in the Zn(II) complex,

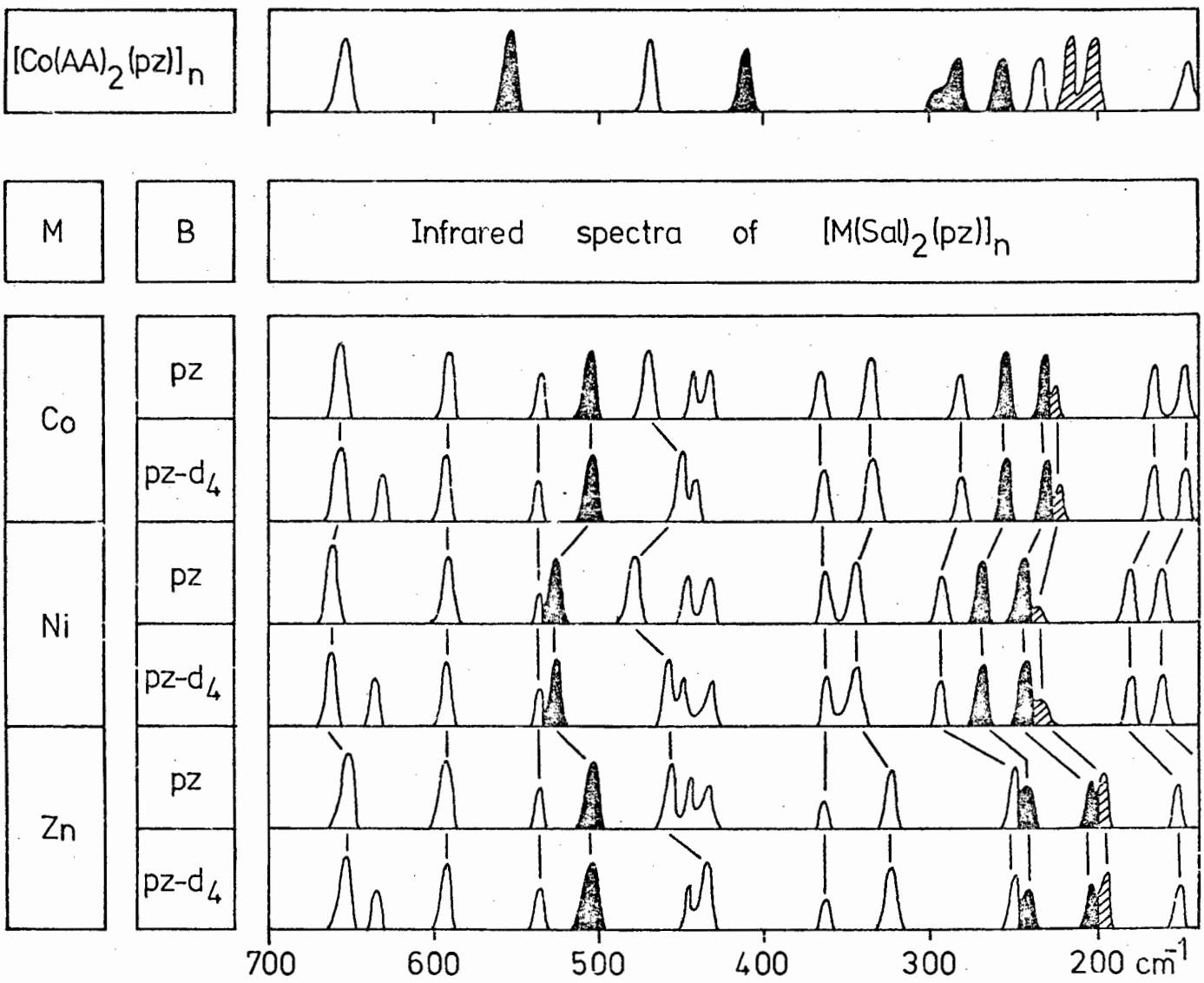


Fig. 45. The infrared spectra (700-140 cm^{-1}) of the complexes $[M(Sal)_2(pz)]_n$. Solid bands: νM-O, shaded bands: νM-N.

is indicated by its *d*-sensitivity of 2 cm^{-1}. The 231 cm^{-1} band is also assigned to νM-O in view of its M-sensitivity and also because it corresponds, in position, with the similarly assigned 237 cm^{-1} band in $[M(AA)_2(pz)]_n$.

The low frequency shoulder at 221 cm^{-1} is assigned to νM-N + νM-O in accordance with the assignment made for the corresponding band in the spectrum of $[M(AA)_2(pz)]_n$, and also by comparison with the assignments made for νM-N in the complexes $[M(pz)_2X_2]$[179] (X = halogen). This band is M-sensitive in the sequence of CFSE's Co < Ni > Zn, but acquires *d*-sensitivity only in the Co(II) complex. This observation, in addition to the fact that it is virtually coincident with the νM-O band at 231 cm^{-1}, indicates that these two bands are probably coupled and both contribute towards νM-O and νM-N. The two bands below 170 cm^{-1} are strongly M-sensitive and are assigned to δL-M-L. The high frequency band is *d*-sensitive only in the Zn(II) complex.

4.6 The pyrimidine adducts $[M(sal)_2(pm)]_n$ (M = Co, Ni, Zn)

The two bands (Fig. 46) at 687 cm^{-1} (in the free base) and 370 cm^{-1} (348 cm^{-1} in the free base) are assigned to pm ring deformations, γring. The bands at 659, 591, 564, 544 cm^{-1} and the doublet near 440 cm^{-1} are assigned to νsal. The strongly M-sensitive band at 508 cm^{-1}, is assigned to νM-O in accordance with the assignments made for the same band in the complexes of salicylaldehyde discussed above. The doublet near 336 cm^{-1} is assigned to νsal + νM-O since it occurs in a region of multiple absorption in the spectrum of uncoordinated

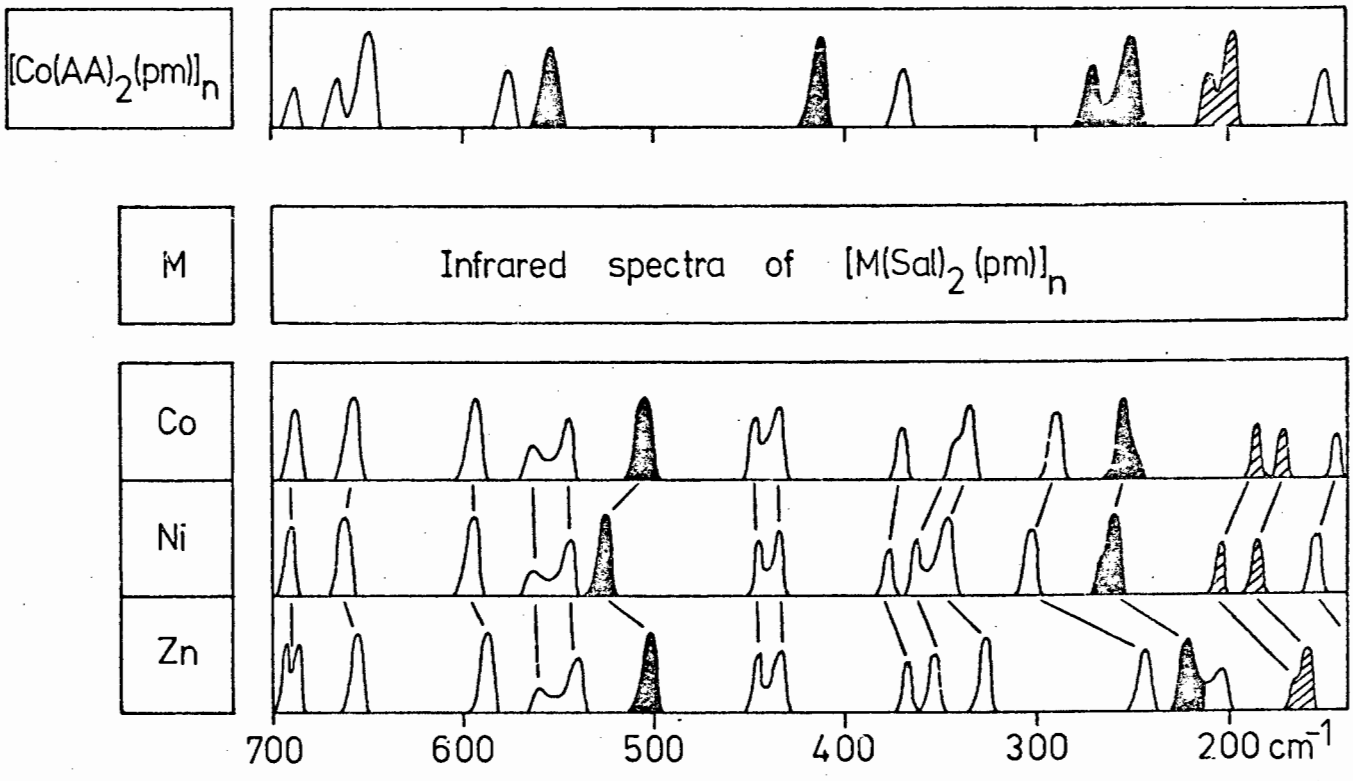


Fig. 46. The infrared spectra (700-140 cm^{-1}) of the complexes $[M(Sal)_2(pm)]_n$. Solid bands: νM-O, shaded bands: νM-N.

salicylaldehyde and because the two components of the doublet exhibit strong M-sensitivity. For similar reasons, the band near 290 cm^{-1} is also assigned to νsal + νM-O. The band at 257 cm^{-1} is strongly M-sensitive and is assigned to νM-O. It corresponds, in position, with νM-O in $[M(AA)_2(pm)]_n$. However, it is probably coupled to the ligand mode occurring at 219 cm^{-1} in the spectrum of salicylaldehyde. The two bands at 185 and 171 cm^{-1} are assigned to νM-N since they correspond with the similarly assigned doublet in this region of the $[M(AA)_2(pm)]_n$ spectrum. The 145 cm^{-1} band is probably a skeletal deformational mode involving nitrogen and oxygen.

5. BAND ASSIGNMENTS IN THE INFRARED SPECTRUM OF *TRANS*-BIS(GLYCINATO)PLATINUM(II) BY MULTIPLE ISOTOPIC LABELLING

Glycine forms several types of complex with Pt(II) ions. Reaction of the anionic ligand with K_2PtCl_4,[227-228] yields the complex $[Pt(gly)_2]$ in which the glycinate groups act as bidentate ligands. A mechanism for this reaction has been postulated[227-229]. Ley and Ficken[230] were the first to investigate this system. They proposed a four-coordinate planar Pt(II) complex with *cis*- and *trans*-isomerides which were isolated as two differing crystal forms. Grinberg and Ptizn[231] found these isomerides to be sparingly soluble in water, giving non-conducting solutions. The less soluble of the isomerides was regarded as being the *trans*-complex.[232-233]

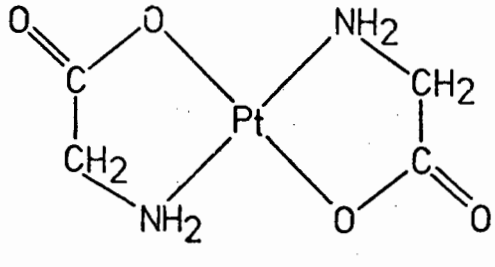
Grinberg *et al.*[234] synthesised bis(glycinato)bis(glycine)-platinum(II), $[Pt(gly)_2(glyH)_2]$, the significance of which with regard to the *cis*- and *trans*-isomerism of $[Pt(gly)_2]$ is of interest. When this compound is heated with water[234] there is an almost quantitative conversion to *cis*-$[Pt(gly)_2]$. The reasons for the formation of the *cis*-isomer only, have been investigated. It was also discovered[235] that when *cis*-$[Pt(gly)_2]$ is heated with excess glycine, in aquous solution, a considerable fraction is converted to the *trans*-isomer. This conversion was found[235] not to occur in the absence of free glycine. In fact, the percentage conversion to the *trans*-isomer increases sharply as the quantity of glycine is increased.[235] To account for this, these authors[235] suggested that $[Pt(gly)_2(glyH)_2]$ is formed as an intermediate in the *cis*- *trans*-conversion. The *trans*-isomer, unlike the *cis*-isomer, does not react in this manner with excess glycine due, probably, to its smaller solubility product.

Infrared spectra for several of these mono- and bidentate complexes of glycine with platinum have been reported.[131,136-138,236-238] Earlier conclusions, regarding the bonding in M(II) complexes of glycine have been based on the observed frequencies of the N-H and carboxylate stretching vibrations of the coordinated N(amino) and carboxyl groups. These conclusions have been criticized on the basis that solid state effects, especially hydrogen-bonding, may be a significant factor in determining these frequencies. It is generally agreed that there exists some measure of covalent nature in the M-N bond. In the absence of other effects the lower the N-H stretching frequency compared with that of the ionic ligand (for example K(gly)), the more covalent the M-N bond.[239] Thus, for a series of *trans*-glycinate complexes of various M(II) ions, the value of νN-H has been found[131,136,236,238] to decrease in the order Ni(II) > Cu(II) > Pd(II) > Pt(II), and νM-N to follow the reverse trend. Such a sequence is in agreement with the stability order of M(II)-glycinato complexes[240] and with their calculated force constants,[131] and is regarded as suggesting that the covalent character of the M-N bond follows the same trend.

For the carboxylate frequencies, one view[136-137] assumes low covalency in the M-O bonds with essentially monodentate coordination. If this were so, the carboxylate frequency should lie unchanged at approximately 1590 cm^{-1} (its value in the alkali metal salts). This is the case[238] with νC=O in the Ni(II) and Zn(II) chelates of glycine. Another view[131,138] considers the M-O bonds as having a significant degree of covalency. The Cu(II) and (especially) the Pt(II) and Pd(II) chelates show a definite high frequency νC=O shift, suggesting that this may be correlated with covalent bond formation. These observations are again subject to solid state effects, *viz.* hydration or hydrogen-bonding.

Independent normal coordinate analyses[131,136] have not succeeded in unambiguously resolving the problem of M-L assignments, the two sets of data showing considerable discrepancies. In their study of the infrared spectrum (670-270 cm^{-1}) of *trans*-$[Pt(gly)_2]$, Lane and co-workers[136] used an approximate normal coordinate treatment as a basis for the assignment of νPt-N. The analysis was made[136] on a five-body problem (PtN_2O_2; point group D_{2h}) in which only the nitrogen and oxygen atoms of the glycinate ligands were considered. By this procedure these workers[136] assigned νPt-N to the band near 418 cm^{-1}, while an extension[137] of this analysis (400-40 cm^{-1}) resulted in the assignment of the band at 155 cm^{-1} to νPt-O. In the spectrum of *cis*-$[Cu(gly)_2(H_2O)]$ these workers[137] assigned the band at 156 cm^{-1} to νCu-O. This band has subsequently[29] been found to be insensitive to the ^{18}O- and 1-^{13}C-forms of isotopic labelling. A more sophisticated treatment[131,138] based on a 1:1 (metal:ligand) model of C_s symmetry, led to the assignment of the Pt-N stretching vibration to the band near 550 cm^{-1}, and of the Pt-O stretch mixed with the Pt-N stretch to the band at 418 cm^{-1}.

The complex *trans*-bis(glycinato)platinum(II) crystallizes[135] in the triclinic system, with space group $P\bar{1}$ (C_i^1). Each molecule (VIII) takes



(VIII)

part in eight hydrogen bonds to each of four neighbouring complexes via the hydrogen atoms on the amino groups, and the carboxylate oxygen atoms. There is one formula unit for unit cell, and the Pt atom lies at a centre of symmetry.[135] The molecule therefore has factor group symmetry C_i and the internal modes of vibration will be described by a calculation using C_i symmetry. Using the procedure outlined by Adams,[47] a factor group analysis has been attempted on this system.

From the crystal structure analysis,[135] the Pt atom at the centre of symmetry, occupies Wyckoff site "*a*". All other ligand atoms lie on general positions "*i*".

Number of atoms in molecule (n) = 19 = number of atoms in unit cell (N).

Table 48.

	C_i	A_g	A_u			
Site of Pt atom	*1a*	0	3			
Sites of all other atoms	*2i*	27	27			
$N_{tot.}$		27	30	=	57	= 3N
T_A		0	3			
$N_{opt.}$		27	27	=	54	= (3N-3)
T		0	0			
R		3	0			
$N_{int.}$		24	27	=	51	= (3n-6)
$N_{ligands}$		21	21			
$N_{skeletal}$		3	6			

where: $N_{tot.}$ = total number of vibrations for the unit cell, of which there are $3N$. Of these, three are,
T_A = acoustic modes corresponding to translational vectors along three axes. This leaves,
$N_{opt.}$ = optical branch modes.

T = optical branch translatory modes.
R = rotatory modes.
$N_{int.}$ = internal modes of vibration for the molecule.
$N_{ligands}$ = internal modes of vibration for the ligands.
$N_{skeletal}$ = vibrations of the PtN_2O_2 skeleton under C_i symmetry.

Thus the internal vibrations (Table 48) for one molecule span the representations $N_{int.} = 24A_g + 27A_u$, and the infrared spectrum should show 27 bands (A_u). If each nine atom ligand is considered as, $NH_2CH_2COO^-$, it has 21 normal modes. With two such ligands arranged centrosymmetrically about the Pt(II) ion, there will be in-phase and out-of-phase combinations of each of these 21 modes; as for example the N-H stretching vibrations of the amino groups (Fig. 47), for which

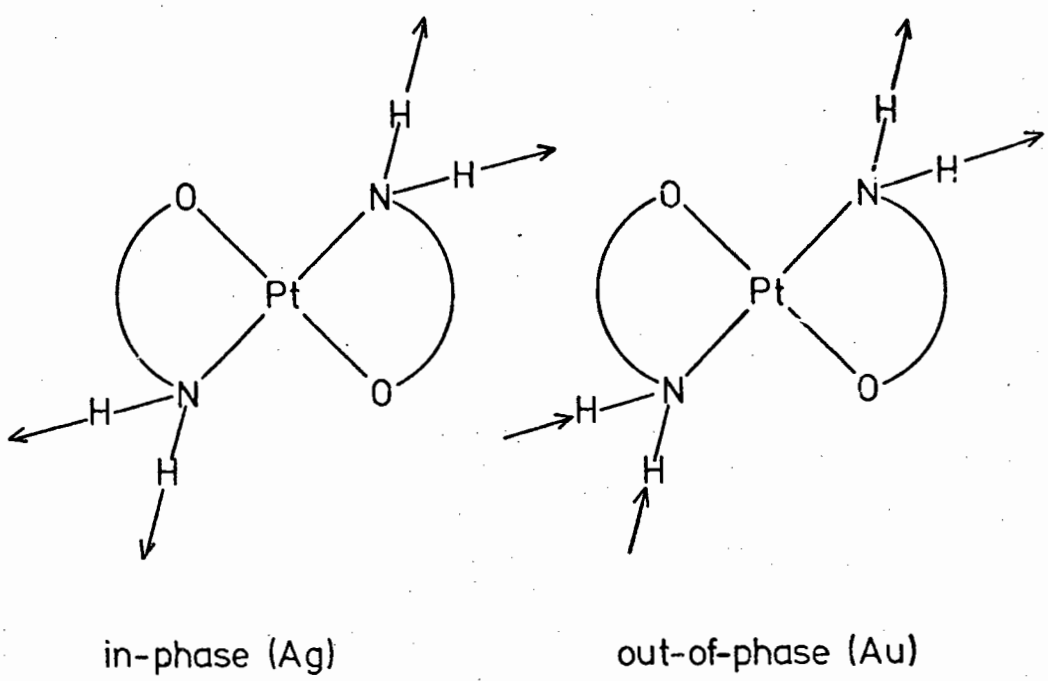
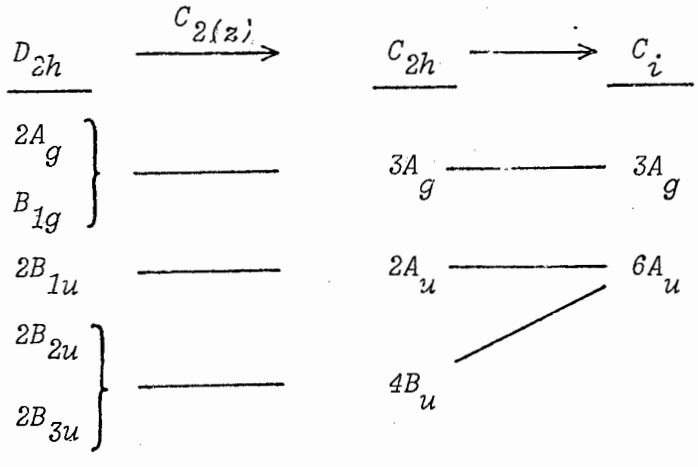


Fig. 47.

the out-of-phase components only, are infrared active. The contribution from the ligand modes towards $N_{int.}$ is thus $21(A_g + A_u)$. Removing these from $N_{int.}$ leaves $3A_g + 6A_u$ modes, which will involve motions of the *trans*-$[Pt(N_2O_2]$ skeleton. The last line in Table 48, $N_{skeletal}$ may similarly be arrived at by considering the vibrational representation of an isolated *trans*-$[PtN_2O_2]$ skeleton of point group D_{2h}, for which the reduced representations are $2A_g + B_{1g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$. A correlation between this result and the factor group of C_i symmetry will yield the representations (Table 49) of the skeletal modes $N_{skeletal}$.

Table 49.



Under C_i symmetry, two of the infrared-active modes will be the asymmetric stretches of the Pt-L bonds, i.e. νasym. Pt-N and νasym. Pt-O. The remaining four A_u modes are likely to be deformations of the *trans*-$[Pt(N_2O_2]$ unit. Since there is only one molecule per unit cell, there are no translatory modes (Table 48) other than those of the acoustic type in which all motions are in-phase (involving no dipole moment change) and therefore infrared-inactive. The three rotatory modes, $3A_g$, will (Table 48) involve motions of the

hydrogen bonds[189] as well as any other intermolecular attractive forces. These are all infrared-inactive. Hence, the infrared spectrum will not show bands corresponding to hydrogen-bond stretches. Such N — H --- O bonding will be detectable only in a decrease in νN-H due to the interaction.

Although this system is relatively simple, the overall symmetry is low, and consequently very little further information regarding the ligand modes and their descriptions can be deduced from $N_{int.}$ Since all the infrared-active modes originate in the same symmetry representations, extensive coupling is expected in the infrared spectrum. This will complicate the analysis of the observed isotopic shifts. The isotopic shifts (Δν) recorded in Table 25 reveal the extent to which vibrational coupling is present in the infrared spectrum of *trans*-$[Pt(gly)_2]$; many bands being sensitive to several forms of labelling. Finally, Table 25 reveals that 27 bands are observed in the range 4000-50 cm^{-1} of the spectrum. (The bands at 120 and 90 cm^{-1} are reported by Walter and co-workers.[137])

The region 4000-1500 cm^{-1}

Four bands occur (Fig. 48) within the range 3300-2900 cm^{-1}. Although the hydrogen atoms of the amino groups take part in intermolecular hydrogen bonding,[135] much of the N-H stretching vibrational energy appears to be localized within the N-H diatomic oscillator. Assuming the N-H oscillator as isolated from the rest of the molecule, it is possible to estimate roughly the expected isotopic shifts of the 3230 and 3094 cm^{-1} frequencies upon deuteration of the amino group, using equation (4).

The equation yields values of ν^i of approximately 2360 and 2258 cm^{-1} for νasym.N-D and νsym.N-D, respectively, indicating that approximately 95% of the energy is localized within the N-H oscillator. The asymmetric C-H stretch (ν_3) appears as a weak shoulder near 2983 cm^{-1} but is clearly visible in the spectrum of the *N,N-*d_2-substituted complex. Shifts of approximately 800 cm^{-1} are induced by deuteration of the methylene groups, and these modes (ν_3 and ν_4) are also vibrationally pure.

The strong absorption at 1650 cm^{-1} (ν_5) is clearly the C=O asymmetric stretch, being sufficiently sensitive towards ^{18}O- and 1-^{13}C-labelling only. The ^{18}O-induced shift of the 18 cm^{-1} is lower than anticipated (40 cm^{-1}), and is probably the result of hydrogen bonding. Its sensitivity to 1-^{13}C-substitution however, is close to the expected value. The NH_2 scissoring mode at 1607 cm^{-1} (ν_6) is recognised by its ^{15}N- and *N,N-*d_2-sensitivity, but is slightly coupled with νC=O since it also exhibits ^{18}O- and 1-^{13}C-sensitivity. The only difference between the present assignments and those previously proposed for the bands in the range 4000-1500 cm^{-1} lies in the coupled nature of ν_6 which is now established by isotopic substitution.

The region 1500 - 600 cm^{-1}

The isotopic shift data reveal that, apart from ν_{12} and ν_{13}, all bands within this region originate in extensively coupled vibrations. Although deuteration is of great value in the assignment problem, which band in the deuterated spectrum corresponds with a particular band in the undeuterated spectrum cannot always be decided with complete certainty. It is nevertheless believed that the shifts indicated in Table 25 and depicted in Fig. 48 are probably correct. The 1439 cm^{-1} band (ν_7),

which is uniquely sensitive to 2-^{13}C-labelling, and is shifted 374 cm^{-1} on 2,2-d_2-labelling is clearly the CH_2 scissoring mode as assigned by Nakamoto.[131]

The C-O stretch appears to be distributed over four bands (ν_8 to ν_{11}). Previous assignments within this region based on normal coordinate analyses,[131,136] are not in entire agreement with each other. Assignment[138] of the absorption at 1375 cm^{-1} (ν_9) to νC-O + νC-C is in agreement with the observed isotopic shifts recorded here. However, the assignment of ν_{10} as predominantly the CH_2 wag[131] appears to be incorrect. It is preferred that this band be assigned to the C-O stretch since it shows significant shifts on both ^{18}O- and 1-^{13}C-substitution. The 1294 cm^{-1} band (ν_{11}) also contains a contribution from the C-O and C-C stretches, but is assigned to predominantly the NH_2 twist, because of its large N,N-d_2-sensitivity. The small ^{15}N-sensitivity of the 1333 cm^{-1} band (ν_{10}) suggests that the NH_2 twist is distributed over two bands. Assignment of ν_{11} to νC-N is therefore incorrect, since such an assignment would be expected to yield considerably larger 2-^{13}C- and ^{15}N-shifts than those observed.

The 1247 cm^{-1} band (ν_{12}) does not show a shift on 2,2-d_2-substitution, hence it cannot be considered as having a contribution from the CH_2 twist,[138] however, its ^{15}N- and N,N-d_2-sensitivities support[131] its assignment to the NH_2 twist. Despite its insensitivity towards 2-^{13}C-labelling, ν^{13} (1187 cm^{-1}) is assigned to the CH_2 twist. This assignment is based on its significant 2,2-d_2-sensitivity and is in agreement with the results of normal coordinate analysis.[131]

Three bands occurring between 1100 and 900 cm^{-1}, have previously[131] been assigned as predominantly NH_2 way + C-N stretch, C-C stretch, and CH_2 rock, respectively. The results of isotopic labelling indicate that two

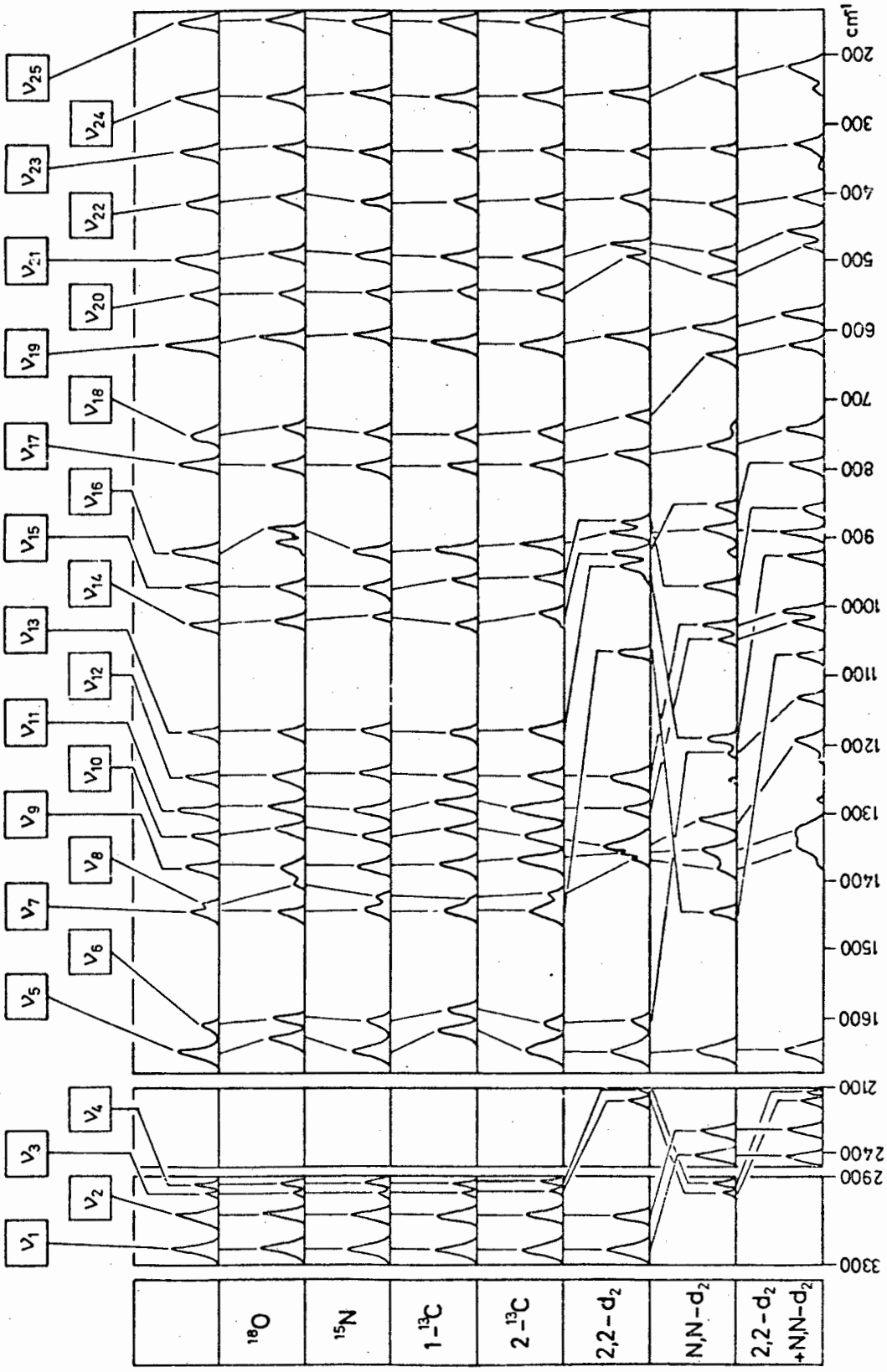


Fig. 48. Infrared spectra of *trans*-$[Pt(gly)_2]$ and its isotopically-labelled analogues.

of these assignments require revision. Strong sensitivity towards ^{15}N- and 2-^{13}C-labelling strongly supports the assignment of ν_{14} to νC-N. Its slight sensitivity to ^{18}O-labelling however, implies that it contains some contribution from the CO_2 scissoring mode. Sensitivities of ν_{15} to the 1-^{13}C- and 2-^{13}C- forms of labelling are in agreement with an earlier assignment[131] to νC-C, although it is more likely that ν_{15} is a νC-C + CH_2 rock since it has a substantial 2,2-d_2-sensitivity. The 921 cm^{-1} band (ν_{16}) is clearly the CO_2 scissor. Coupling of this band to the CH_2 rock is however, indicated by the 2-^{13}C-shift. This band in the spectrum of the ^{18}O-labelled complex, is preceded by a weak high frequency shoulder, probably a residual ^{16}O-band. The NH_2 and CO_2 rocking modes were previously[131] assigned to the bands at 798 cm^{-1} (ν_{17}) and 754 cm^{-1} (ν_{18}), respectively. These modes appear however, to be distributed over both these bands, the chief contribution to both modes being (as evidenced by the isotopic shifts) the 754 cm^{-1} band. These bands exhibit significant 2-^{13}C-sensitivity, suggesting a contribution from the CH_2 rocking mode. Since ν_{19} is sensitive to ^{18}O- and 1-^{13}C-labelling, it is assigned to the CO_2 wag. The fact that it also contains a contribution from the NH_2 rock is shown by its sensitivity towards ^{15}N- and N,N-d_2-labelling.

The frequencies of the various NH_2 and CH_2 deformations provided by the assignments proposed above, generally agree well with those previously[131,138] proposed for these vibrations except that the NH_2 twisting mode is approximately 100 cm^{-1} lower than previously predicted, and no bands can be identified as originating specifically in the wagging modes of the NH_2 and CH_2 groups.

The region 600 - 140 cm^{-1}

It is within this region that the metal-ligand vibrations are expected to occur. The suggestion[136,238] that the Pt-O bonds are ionic is discounted by the structural determination[135] of *trans*-$[Pt(gly)_2]$ which reveals Pt-O and Pt-N distances consistent with high covalency in both bonds. Similar arguments have been advanced[29,131] for the relatively high value of the νCu-O frequency in the spectrum of *cis*-$[Cu(gly)_2(H_2O)]$. Previous[29-30] isotopic labelling studies on *trans*-$[Ni(gly)_2(H_2O)_2]$ and *cis*-$[Cu(gly)_2(H_2O)]$ confirm the suggestion[131] that the νM-N and νM-O frequencies in these glycine chelates follow the sequence Cu > Ni, while the same vibrations in $[Pt(gly)_2]$ are expected to exceed the frequencies of the corresponding asymmetric vibrations in the Cu(II) glycinate complex (476 and 379 cm^{-1}, respectively). The band at 548 cm^{-1} (ν_{20}) has been previously[131,138] assigned to νPt-N. While the present results do not invalidate this assignment (since the band is both ^{15}N- and N,N-d_2-sensitive) concomitant sensitivity to ^{18}O- and 1-^{13}C-labelling shows that there is coupling with a CO_2 vibration, presumably the wagging mode at 619 cm^{-1}. The isotopic sensitivity of the band at 497 cm^{-1} (ν_{21}) is also consistent with its assignment to νPt-N. This band is more sensitive than ν_{20} to ^{18}O-labelling but completely insensitive to 1-^{13}C-labelling, suggesting that it comprises coupling from νPt-O. Hence, the assignment νPt-N + νPt-O is proposed for ν_{21}.

The band at 415 cm^{-1}(ν_{22}) is firmly assigned to the vibrationally pure νPt-O mode, since it has substantial ^{18}O-sensitivity, no 1-^{13}C-sensitivity (i.e. it does not comprise a contribution from a CO_2 deformation). The present assignments of ν_{21} to coupled νPt-N and ν_{22} to νPt-O place these frequencies some 30 cm^{-1} higher than the asymmetric νCu-N and νCu-O modes of *cis*-$[Cu(gly)_2(H_2O)]$ which is qualitatively consistent

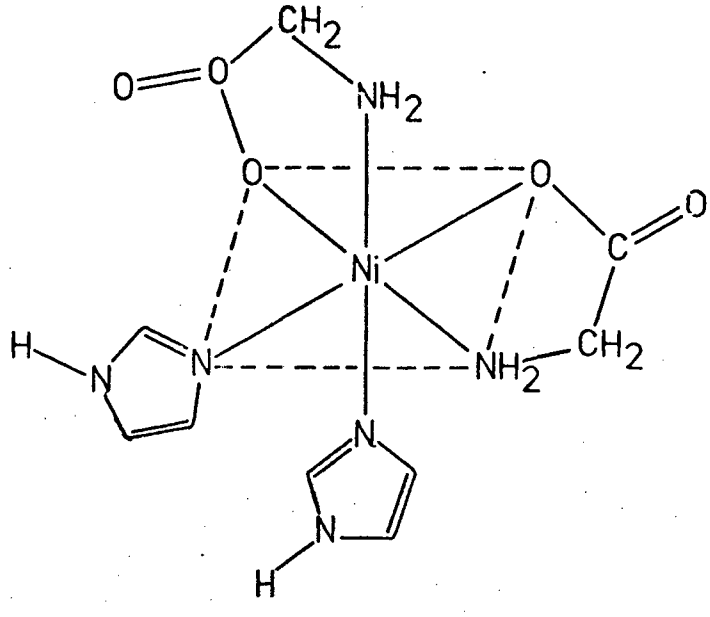
with their relative stability constants[240] and coordination numbers.[172] Earlier assignment[136-137] of ν_{22} to Pt-N is definitely discounted by the absence of sensitivity to ^{15}N- and N,N-d_2-labelling.

The 338 cm^{-1} vibration (ν_{23}) is significantly sensitive towards ^{18}O-labelling only, although the recorded shift is smaller than that of ν_{22}. This band (ν_{23}) is therefore assigned to the O-Pt-O bending mode. This frequency is again higher, as expected, than the copper-ligand bending frequency in the spectrum[29] of *cis*-$[Cu(gly)_2(H_2O)]$. Absence of ^{15}N-, 1-^{13}C- and 2-^{13}C-sensitivity invalidates previous assignments[136-138] of ν_{23} to a C-C-N bending mode.

An earlier assignment[136-137] of the absorption at 263 cm^{-1} (ν_{24}) to a carboxylate twisting mode was supported by the occurrence of a band in this region of the spectrum of uncoordinated glycine. The absence of any significant ^{18}O- and 1-^{13}C-sensitivity requires that this band does not originate in such a mode. Sensitivity of (ν_{24}) to ^{15}N- and N,N-d_2-labelling requires that it be assigned to δN-Pt-N. Results of the normal coordinate analysis,[137] and the assumption of an ionic M-O interaction, yielded an assignment for ν_{25} at 150 cm^{-1} to the asymmetric νPt-O. In view of the present evidence, it would appear unlikely that νM-O in *trans*-$[Pt(gly)_2]$ will occur at such low wavenumber. In view of its ^{18}O- and 2,2-d_2-sensitivities, this band (ν_{25}) probably originates in a δPt-O-C vibration. Two other bands (at 128 and 90 cm^{-1}) have been reported for this system (ν_{26} and ν_{27}), and were assigned[137] to certain intermolecular modes.

6. BAND ASSIGNMENTS (4000-140 cm^{-1}) IN THE INFRARED SPECTRUM OF *CIS*, *CIS*-BIS(GLYCINATO) *CIS*-BIS(IMIDAZOLE)-NICKEL(II) BY MULTIPLE ISOTOPIC LABELLING

It has been shown by x-ray crystal analysis[241] that the title complex crystallizes with a monoclinic unit cell containing four formula units. The space group[241] is $P2_1/C$ (C_{2h}^5). Each pair of chemically equivalent donor atoms occupy adjacent corners of the coordination octahedron, which is unusual for an octahedral bis(glycinate) complex (IX). Furthermore, the two chemically equivalent pairs of ligands are not related by crystallographic symmetry.[241]



(IX)

There are two features which may have important consequences in the infrared spectrum of this complex. Firstly, the two Ni-O (carboxyl), and the two Ni-N(Him) bond lengths[241] were found to differ by a significant

factor of approximately 0.03 Å. Secondly, all acidic hydrogen atoms are involved in H-bonding, except for one hydrogen atom on one of the amino groups.

In the only previously reported study of *cis*-$[Ni(gly)_2(Him)_2]$ and other binary Ni(II) complexes of amino acids, Rao and Li[156] showed that *cis*-$[Ni(gly)_2(Him)_2]$ exists as an octahedral complex in aqueous solution and has a value of 9820 cm^{-1} for the crystal field splitting parameter, $10Dq$. (The $10Dq$ value[156] of *trans*-$[Ni(gly)_2(H_2O)_2]$ is 8910 cm^{-1}).

The infrared spectrum is depicted in Fig. 49 and the isotopically-induced shifts ($\Delta\nu$) are recorded in Table 26. The imino-hydrogen atom in Him, as well as the amino-hydrogen atoms of glycine are acidic and undergo exchange in aqueous solution. Consequently, it is not possible to synthesise the Him-d_4 and *N*,*N*-d_2-gly analogues of *cis*-$[Ni(gly)_2(Him)_2]$ as chemically unique species. For this reason, the spectra of the fully deuterated Him complex and the *N*,*N*-d_2-glycinate complex are not reported.

The region 4000-1700 cm^{-1}

The spectrum of free Him in the region 3100-2200 cm^{-1} consists of a massive envelope of bands attributed[69,163] to H-bonded N-H stretching modes. In the spectrum of *cis*-$[Ni(gly)_2(Him)_2]$, this envelope is better resolved but there remains an extensive band pattern down to 2200 cm^{-1}, which vastly complicates assignments, especially those of the C-H glycinate stretches. The N-H(gly) stretching modes, identified by their sensitivity towards ^{15}N-labelling, are assigned to the bands at 3282 cm^{-1} (ν_2; νasym.N-H) and 3195 cm^{-1} (ν_3; νsym.N-H). One further vibration (ν_1 at 3318 cm^{-1}) exhibits significant ^{15}N-sensitivity, warranting

its assignment to νN-H(gly). The presence of this extra νN-H mode may well be the result of the existence of one N-H bond which does not participate in H-bonding.[241] The mass change which occurs on substitution of Him by Him-d_3 results in a shift of all three N-H stretching modes to lower frequency.

In most M(II) complexes of glycine,[29-30,131] the νC-H modes of the methylene groups occur between 3000 and 2900 cm^{-1} and are of low intensity. In *cis*-[Ni(gly)$_2$(Him)$_2$], these bands are not easily identified because of the complexity of the spectrum in this region. The three bands within the range 3150-3100 cm^{-1} (ν_4-ν_6) are clearly C-H stretching modes of Him, being shifted some 800 cm^{-1} to lower frequency by deuteration. They are unaffected by other modes of labelling. The two νC-H(gly) bands (ν_7; ν_8) occur within the 3000-2800 cm^{-1} range where they are identified by their 2,2-d_2-shifts (~800 cm^{-1}) and 2-^{13}C-sensitivities. All other bands within the range 4000-2200 cm^{-1} (Table 26; Fig. 49) are assigned to H-bonded νN-H modes of the imidazole imino group.

The region 1700-580 cm^{-1}

The majority of the infrared bands of free Him recur in the spectrum of the complex with minor shifts and splittings. The internal Him modes are identified by Him-d_3 sensitivity and absence of sensitivity towards labelling of the glycinate groups, while the species of each internal Him vibration is assigned according to the extensive deuteration studies by Perchard and co-workers[70] on the Him spectrum. Three bands in the 1635-1550 cm^{-1} region (ν_9-ν_{11}) may be assigned to carboxylate stretching modes by virtue of their sensitivities towards ^{18}O- and 1-^{13}C-labelling. Sensitivity of the 1632 cm^{-1} band toward the various

forms of labelling precludes its assignment to the NH_2 scissoring mode which is known[30] to occur in this region of the spectrum of *trans*-$[Ni(gly)_2(H_2O)_2]$. In fact the NH_2 scissoring mode appears to be distributed over two bands (ν_{12},ν_{13}) in the 1550-1510 cm^{-1} region of the spectrum. Sensitivity of the 1541 cm^{-1} vibration to 1-^{13}C-labelling is probably the result of an interaction with the νC=O absorption at 1586 cm^{-1} which undergoes a large low frequency shift on this form of labelling; hence its assignment to the NH_2 scissor + νC=O. The 1516 cm^{-1} band exhibits a similar sensitivity towards Him-d_4 labelling as do the νN-H(gly) modes in the 3300 cm^{-1} region. The 1516 cm^{-1} band (ν_{13}) is assigned to the NH_2 scissor + νring(Him).

The 1492 and 1448 cm^{-1} vibrations (ν_{14},ν_{15}) are assigned to Him ring stretching modes,[70] originating in the 1490 and 1450 cm^{-1} vibrations of free Him. Both bands are sensitive only to Him-d_3 labelling. In the light of its 2-^{13}C-sensitivity, the 1434 cm^{-1} band (ν_{16}) must be regarded as having some CH_2 scissoring character yet its shift on 2,2-d_2-labelling is small. On the basis of its moderate sensitivity to Him-d_3 labelling, this band is assigned to a coupled CH_2 scissor + νring-(Him). The band at 1416 cm^{-1} (ν_{17}) is assigned to νC-O + νC-C(gly) since it is significantly sensitive to both ^{18}O- and 1-^{13}C-labelling and is substantially sensitive also to 2-^{13}C- and 2,2-d_2-labelling. That ν_{18} originates in a C-H deformation of the glycinate methylene group is apparent from its shift on 2,2-d_2-labelling. Its 1-^{13}C- and 2-^{13}C-sensitivity indicates it also has νC-C character. Hence, it is assigned to the CH_2 scissor + νC-C(gly). The νC-C(gly) mode appears to be spread over all three vibrations in this region, since the sensitivities of the 1355 cm^{-1} band (ν_{19}) also require its assignment to νC-C(gly). The isotopic shifts indicate, however, that this band is principally the

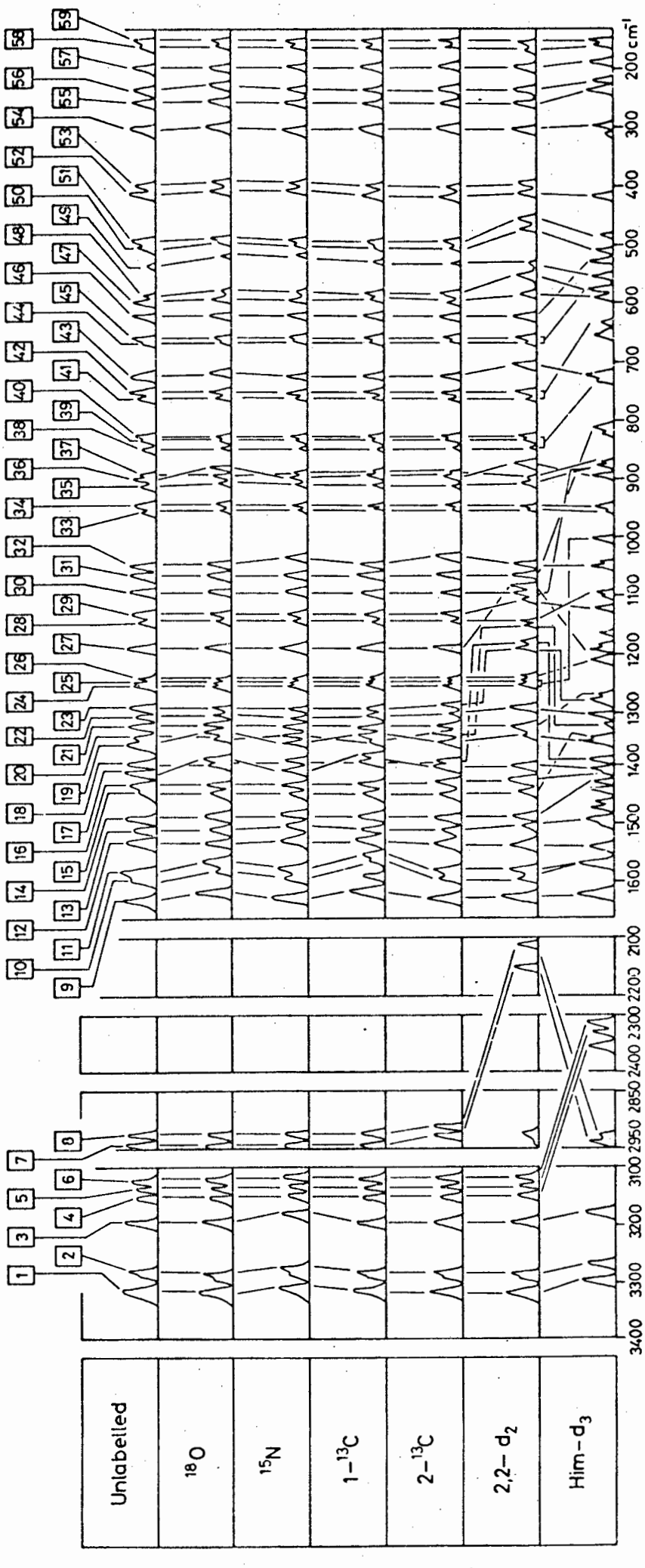


Fig. 49. Infrared spectrum of *cis*-$[Ni(gly)_2(Him)_2]$ and its isotopically-labelled analogues.

C-O stretching mode since it is primarily sensitive to ^{18}O- and 1-^{13}C-labelling. Slight sensitivity to ^{15}N-labelling indicates that ν_{19} is also coupled with the NH_2 wag.

The 1344 cm^{-1} band (ν_{20}) is identified as the CH_2 wagging mode. This assignment is based on the large 2-^{13}C- and 2,2-d_2-shifts. The ^{15}N-sensitivity also shows that it is mixed with NH_2 wagging mode. Absence of sensitivity towards labelling of the glycinate ligands implies that ν_{21} is an internal mode of the Him ring.[70] This band corresponds with the strong 1323 cm^{-1} band in free Him which has been assigned[70] to νring(Him). The 1310 cm^{-1} band (ν_{22}) is sensitive towards most forms of isotopic labelling and is assigned to CH_2wag + νC-C(gly) + νC-O in accordance with the observed shifts. ν_{23} Exhibits shifts similar to those observed for ν_{20} and is therefore similarly assigned although ν_{20} is significantly more sensitive to 2,2-d_2-labelling and thus represents a purer CH_2 wagging vibration. The doublet (ν_{24}, ν_{25}) at 1257 and 1253 cm^{-1} is sensitive only to Him-d_3 labelling and is assigned to the Him ring C-H deformation in accordance with previous assignments[70] for free Him. ν_{26} Corresponds with the 1243 cm^{-1} band in Him, assigned[70] to δN-H(Him). Its sensitivity only to Him-d_3 labelling (in which it shifts 48 cm^{-1}) substantiates this assignment.

Although the 1188 cm^{-1} band (ν_{27}) is only slightly sensitive to 2-^{13}C-labelling, its assignment to the CH_2 twist is based on its large 2,2-d_2-sensitivity. Sensitivity towards 1-^{13}C-labelling, however, suggests that it also receives a contribution from νC-C(gly). Identical assignments have been proposed[29-30] for bands in the same region of the spectra of *trans*-[Ni(gly)$_2$(H$_2$O)$_2$] and *cis*-[Cu(gly)$_2$(H$_2$O)], on the basis of isotopic substitution. The 1145 cm^{-1} absorption (ν_{28}) is assigned to δN-H(Him), and the band at 1133 cm^{-1} (ν_{29}) is assigned to the NH_2 twist + νC-C(gly) since it is sensitive to ^{15}N-, 1-^{13}C- and 2-^{13}C-labelling.

Free Him gives rise to two absorptions at 1099 and 1052 cm^{-1}. The corresponding bands in *cis*-$[Ni(gly)_2(Him)_2]$ occur at 1093 and 1067 cm^{-1}, the latter being totally insensitive to labelling of the glycinate ligands. These bands (ν_{30},ν_{31}) are accordingly assigned[70] to δC-H(Him). The 1052 cm^{-1} band (ν_{32}) is unambiguously assigned to νC-N. It exhibits large shifts towards ^{15}N- and 2-^{13}C-labelling only, and has invariably been found to occur near 1050 cm^{-1} in the spectra of those M(II) complexes of glycine studied[29-30] by the isotopic labelling technique, where it is also characterised by its vibrational purity.

The isotopic shift data indicate that ν_{33} originates purely in the νC-C(gly) mode, as it is sensitive only towards the 1-^{13}C-, and 2-^{13}C-labelling, whereas the neighbouring vibrations at 944 cm^{-1} (ν_{34}) is additionally sensitive to the ^{18}O-label. On the basis of its small 2,2-d_2-shift, the 944 cm^{-1} band is assigned to νC-C + CO_2 scissor. The 916 cm^{-1} band (ν_{35}) is assigned to CO_2 scissor + γC-H(Him) since it is sensitive only to ^{18}O-, 1-^{13}C- and Him-d_3 labelling. ν_{36} Is, however, more sensitive to ^{18}O-labelling and is therefore assigned to a purer CO_2 scissoring mode. Its simultaneous sensitivity towards 2-^{13}C- and (especially) 2,2-d_2-labelling indicates a contribution from the CH_2 rocking vibration.
All the bands in the region 900 - 750 cm^{-1} exhibit a complete absence of sensitivity towards labelling of the glycinate ligands. Furthermore, these bands all occur in regions of strong absorption in the spectrum of Him where they have been assigned to Him ring modes in the spectrum of the free ligand [70]. High sensitivity to ^{18}O- and 1-^{13}C-labelling suggests that ν_{43} is chiefly the CO_2 rock, while simultaneous sensitivity towards 2-^{13}C- and 2,2-d_2-labelling implies mixing with the CH_2 rock. Some NH_2 rocking character is also evident from the small

shift induced by ^{15}N-labelling. The bands in the 700-620 cm^{-1} region are firmly established as Him ring deformations due to their sensitivities only towards deuteration of the Him ring. The band at 657 cm^{-1} in the spectrum of Him splits on complexation, giving rise to a doublet near 665 cm^{-1} in the spectrum of the complex, which is assigned[70] to γring(Him). The band at 624 cm^{-1} is similarly assigned[70] to γring(Him) due to its sensitivity (only) towards Him-d_3 labelling and its correspondence with the 619 cm^{-1} band (γring) in the spectrum of Him. By virtue of the ^{18}O- and 1-^{13}C-shifts of ν_{47}, it is assigned to the CO_2 wag. Sensitivity to all other forms of labelling suggest that the CO_2 wag is mixed with a ring deformation. The same assignments are proposed for ν_{48} and ν_{49} which also show varied magnitudes of sensitivity to all forms of labelling.

The νC=O, NH_2 scissoring, CH_2 scissoring, CO_2 scissoring and νC-N modes are normally most readily identifiable in M(II) complexes of glycine[29-30,131] Of these, only the νC=O and νC-N modes represent pure vibrations in the spectrum of *cis*-$[Ni(gly)_2(Him)_2]$, while the coupled NH_2 scissoring modes are some 70 cm^{-1} lower than generally observed. The isotopic shift values (Table 26) reveal, however, that the extent of vibrational mixing in the 1000-600 cm^{-1} region is comparable[30] with that in the spectrum of *trans*-$[Ni(gly)_2(H_2O)_2]$, where some bands achieve identical assigments in corresponding spectral positions.

The region 580-140 cm^{-1}

Since each chemically equivalent pair of donor atoms in the *cis*-$[NiA_2B_2C_2]$-type skeleton occupy ajacent corners of the octahedron, symmetry considerations require the infrared activity of both asymmetric

and symmetric Ni-L vibrations. The table of isotopic shifts also reveals the extent to which vibrational mixing of the Ni-L absorptions is operative in this region. Assignment of the two bands (ν_{50},ν_{51}) at 510 and 498 cm^{-1} to the CO_2 wag is based on their ^{18}O- and 1-^{13}C-sensitivities. That they also comprise a contribution from νNi-N(gly) is indicated by their ^{15}N-sensitivities. A band at 518 cm^{-1} in the spectrum of *trans*-$[Ni(gly)_2(H_2O)_2]$ has been similarly assigned[30] on the results of isotopic labelling. The presence of two such bands in *cis*-$[Ni(gly)_2(Him)_2]$ is consistent with the *cis*-symmetry of the latter complex. These modes are displaced to lower frequency in the bis(Him) complex compared with $[Ni(gly)_2(H_2O)_2]$. This is consistent with the increase in ligand field strength of Him relative to that of water.

The bands at 418 and 401 cm^{-1} (ν_{52},ν_{53}) exhibit comparable shifts on ^{18}O- and ^{15}N-labelling and are assigned to mixed νasym.Ni-N(gly) + νasym.Ni-O (418 cm^{-1}) and νsym.Ni-N(gly) + νsym.Ni-O (401 cm^{-1}). The latter band reveals an apparently anomolous shift of 81 cm^{-1} on Him-d_3 labelling. This shift is too large for a νNi-N(Him) vibration. An identical assignment has been proposed[30] for the 437 cm^{-1} band in the spectrum of the *trans*-bis(aquo) adduct of Ni(II) glycinate. These bands, furthermore, are regarded as representing purer νNi-L modes than the two bands near 500 cm^{-1}, since they undergo[30] a significantly larger low frequency shift when water is replaced by Him. The band at 306 cm^{-1} is sensitive to ^{18}O-, ^{15}N-, and Him-d_3 labelling, suggesting that it comprises contributions from νNi-O, νNi-N(gly) and νNi-N(Him). Assignments of the ν_{55} and ν_{56} absorptions to νNi-N(Him) is suggested for three reasons. Firstly, these bands are most significantly sensitive to deuteration of the Him ring. Secondly, bands assigned to νM-N in the spectra of the complexes $[M(Him)_6]^{2+}$ occur[64-65] in the similar region of the spectrum.

Thirdly, in the spectra of the Him adducts of M(II) acetylacetonates, the M-N(Him) bands are found in the same spectral region. These bands are nevertheless significantly ^{18}O- and ^{15}N-sensitive, indicating coupling of the Ni-N(Him) stretch with δO-Ni-N(gly). The 203 cm^{-1} band (ν_{57}) is assigned to δO-Ni-O + νNi-N(Him) since it shows ^{18}O-sensitivity, and is also sensitive to Him-d_3 substitution, while the band at 164 cm^{-1} (ν_{58}) is sensitive only to Him-d_3 labelling, confirming its assignment to δ(Him)N-Ni-N(Him).

Although the metal-ligand stretching frequency region of *cis*-$[Ni(gly)_2(Him)_2]$ is espected to be more complex than that of *trans*-$[Ni(gly)_2(H_2O)_2]$ purely on symmetry grounds (both the asymmetric and symmetric νNi-L bands of the former are infrared-active) it is clear from the above discussion that the observed complexity of the spectrum of the *cis*-complex cannot be attributed solely to symmetry conditions but must, at least partially, be ascribed to the extent of vibrational coupling in this complex.

Sufficient multiple isotopic labelling studies[29-30,245-246] have now been performed on glycinate complexes to enable some general conclusions regarding their infrared spectra to be reached.

(1) Very few bands represent vibrationally pure modes. The least coupled bands are generally, νN-H, νC-H, νC=O and νC-N. (2) Metal-ligand stretching frequencies span a wide range of values with νM-N generally >νM-O. Characteristic values for νM-N are ∿ 550 cm^{-1} (Cd(II)[246] and Pt(II) chelates) and ∿ 450 cm^{-1} (Ni(II) chelates[30]). νM-O Is characteristically within the 450-300 cm^{-1} range. In many glycinate complexes, νM-O and νM-N occur as mixed vibrations. (3) Octahedral glycinate complexes comprising adducted heterocyclic bases with nitrogen donors[245] commonly yield νM-N(Base) bands within the range 350-150 cm^{-1}.

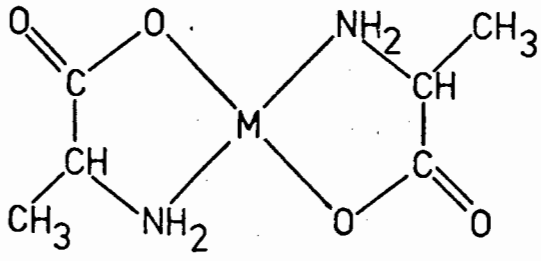
7. BAND ASSIGNMENTS IN THE INFRARED SPECTRA OF *TRANS*-BIS(L-ALANINATO)PLATINUM(II) AND PALLADIUM(II) BY ISOTOPIC LABELLING

Band assignments in the infrared spectrum of alanine were first reported by Mizushima and co-workers[244] by comparing the spectra of N-deuterated alanine and alanine hydrochloride with that of normal alanine. In an attempt to make more conclusive assignments, further measurements of the infrared spectra were later made on *C*-deuterated alanine.[245] The assignments[245] were based on a normal vibration calculation as a seven-body problem, regarding the NH_3^+ and CH_3 groups as dynamical units. Later, the spectra[246] of 2-*d*, 3-d_3- and 2-*d*,3d_3-*N*-d_3-L-alanine were reported and the assignments made supported those previously discussed.[244-245] A subsequent ^{15}N-labelling study (1700-500 cm^{-1}) brought about no assignment changes[247] at all except for the 540 cm^{-1} band previously[244-246] assigned to the CO_2^- bending mode, which was reassigned[247] to a δCCN vibration. These relatively straightforward assignments[244-247] were later shown[31] by ^{15}N- and ^{18}O-labelling to show extensive vibrational coupling, and some modification of the existing assignments were found necessary. Aqueous solutions of L- and β-alanine have also been studied[248] by Raman spectroscopy.

The M(II) complexes formed by L-alanine (L-ala) have been studied by numerous workers[31,152,249-253] in the field of vibrational spectroscopy. Nakamoto *et al.*[249] studied the nature of the metal-carboxylate coordinate linkage of many amino acid complexes in the solid state and in D_2O solution. A normal coordinate treatment[152] of the M(II) complexes of DL-α-ala (4000-80 cm^{-1}) was accomplished using a full 25-body problem, and an approximate discription of the vibrational modes of all observed bands was reported.[152] The most recent report, is that of an ^{18}O- and ^{15}N-labelling study[31] of anhydrous and hydrated Ni(L-ala)$_2$ and anhydrous

Cu(L-ala)2, in which complete band assignments (1700-140 cm^{-1}) were proposed according to the isotopic shifts.

There is, to date, no crystallographic data available for Pt(II) and pd(II) complexes of L-ala. As is characteristic of Pt(II) chemistry, the structure is regarded as a planar monomer (X) and identical to that studied[152] by Durkin and co-workers. With only two exceptions, there



(X)

is a band-for-band correspondence in the infrared spectra of the Pt(II) and Pd(II) complexes (Fig. 50). The isotopic shifts ($\Delta\nu$) recorded in Table 27 for *trans*-[Pt(L-ala)$_2$] reveal the extent to which vibrational coupling is present; exceedingly more so than in the spectrum of *trans*-[Pt(gly)$_2$] studied earlier. Most bands are sensitive to all forms of labelling, especially deuteration. The assignments proposed in Table 27 are based on the effects of isotopic substitutions and on comparisons with previous assignments for L-ala,[31] *trans*-[Cu(L-ala)$_2$][31] and *trans*-[Pt(gly)$_2$]. While the Pt(II) and Pd(II) complexes appear to be isostructural, they are not necessarily isomorphous. However, establishment of the assignments for the Pt(II) complex by multiple isotopic labelling is considered to provide analogous assignments for the corresponding bands of the Pd(II) complex. Frequencies cited in the ensuing discussion refer to the Pt(II) complex.

The region 4000-1500 cm^{-1}

Splitting of the νasym. N-H band (ν_1 and ν_2) in both the Pt(II) and Pd(II) complexes, near 3200 cm^{-1} is ascribed to variations in strength of intermolecular N – H --- O hydrogen bonding within the solid state. Shifts undergone by these bands and the νsym. N-H mode (ν_3) near 3100 cm^{-1}, on ^{15}N- and *N,N*-d_2-labelling, are of the expected magnitude for pure N-H stretching modes. Substitution of Pd(II) for Pt(II) causes a high frequency shift in the νN-H bands, i.e. the opposite trend exhibited by the νM-N bands. While the trend in νN-H might indicate differing H-bond strengths, the corresponding opposite trend in νM-N gives more cause to believe that a higher metal-ligand bond stability in the Pt(II) complex occurs at the expense of the N-H bonding. Two stretching vibrations are expected for the C-H bonds of the methyl group in L-alanine. These bands are regarded as originating in the doublet (ν_4 and ν_5) near 3000 cm^{-1}, while the band near 2940 cm^{-1} (ν_6) is assigned to the C-H stretch. All three bands are sensitive only to 2-*d*, 3-d_3-labelling.

The position of νC=O in *trans*-[Pt(L-ala)$_2$] agrees well with the position of the corresponding band in the glycinate complex, although in the present case a greater ^{18}O-shift is recorded. The NH_2 scissoring mode (ν_8) shows ^{18}O-sensitivity which is induced by overlap with the strong carbonyl stretching absorption i.e. a low frequency shift in νC=O on ^{18}O-labelling influences the frequency of the NH_2 scissor at slightly lower wavenumber. The νC=O value for the Pt(II) complex is 11 cm^{-1} higher than the value for the Pd(II) complex, indicating that the higher electron density of the Pt-O bond is transmitted to the exocyclic C=O bond.

The region 1500 - 600 cm^{-1}

In the spectrum of free L-alanine[31,245-246] the CH_3 degenerate deformation and the CH_3 symmetric deformation occur at 1455 cm^{-1} and 1362 cm^{-1}, respectively. In the spectra of the complexes the degenerate deformation recurs as a doublet (ν_9 and ν_{10}) near 1450 cm^{-1} and are readily identified by their shifts when hydrogen is replaced by deuterium. These shifts agree well with those reported[245-246] for similarly deuterated L-ala. Bands ν_{11} and ν_{12} are shifted slightly by ^{18}O-labelling. Their sensitivities towards *N,N*-d_2- and 2-*d*, 3-d_3-labelling are too small for NH_2 or CH_3 modes but are consistent with a contribution from νC-C. They are thus assigned to νC-O + νC-C. Bands ν_{13} and ν_{14}, near 1350 cm^{-1} clearly originate in the symmetric deformation mode of the methyl group. They occur very close to the position of the corresponding band in free L-ala[31] and are significantly sensitive towards 2-*d*, 3-d_3-labelling. The small ^{15}N- and *N,N*-d_2-sensitivity of ν_{14} indicates some coupling with the NH_2 twisting mode. A band near this frequency in the spectrum of *trans*-[Cu(L-ala)$_2$] was assigned[31] to the NH_2 wag on the basis of its ^{15}N-sensitivity ($\Delta\nu$ = 5 cm^{-1}). The substantial ^{18}O-shifts exhibited by ν_{15} and ν_{16} suggest that they are primarily νC-O modes although coupling with νC-C and some contribution towards the NH_2 twist is indicated by concomitant shifts on 2-*d*, 3-d_3- and *N,N*-d_2-labelling. This assignment is identical to that given for the analogous glycinate complex. The νC-CH_3 mode is expected to occur near 1237 cm^{-1}, which is its position in the spectrum of free L-ala. The three bands ν_{17}-ν_{19} exhibit isotopic sensitivities which are consistent with this assignment. Similar ^{15}N-sensitivity in two of these bands, however, suggests coupling with the NH_2 twisting mode. The 1108 cm^{-1} band (ν_{21}) does not show sufficient *N,N*-d_2- or 2-*d*, 3-d_3-sensitivity to warrant its assignment to

an NH_2 or C-H deformation, as has been proposed.[152] In fact the bands ν_{20} to ν_{22} exhibit *N,N-d*$_2$- shifts which are certainly consistent with those expected for νC-N, although considerable vibrational coupling is indicated by sensitivity to the other isotopic labels. That ν_{23} and ν_{24} are mixed vibrations, is shown by their sensitivities towards all forms of labelling, while ν_{25} appears to represent a pure νC-N mode.

The normal coordinate analysis[152] led to assignments of the CO_2 scissoring modes in the 800-700 cm^{-1} region. The isotopic shift data reveal that these specific modes arise at higher frequency, (ν_{24} and ν_{26}) and that all the bands in the 1000 to 600 cm^{-1} region contribute in some manner towards various deformations of the carboxyl group. That ν_{26} is the more vibrationally pure CO_2 scissoring mode is shown by its greater ^{18}O-sensitivity. As was observed in the spectrum of *trans*-[Pt(gly)$_2$], this absorption exhibits residual high frequency shoulders attributed to ^{16}O-L-ala. This assignment, furthermore, agrees well with that made for the CO_2 scissoring mode[31] in the spectrum of *trans*-[Cu(L-ala)$_2$]. In contrast to the infrared spectra of M(II) complexes of glycine where the νC-N mode generally occurs as a single relatively uncoupled vibration[29-30,242] between 1100 - 1000 cm^{-1}, it is generally observed[245-247] that νC-N in L-ala and its M(II) complexes[31,152] is a coupled vibration and spread over a number of bands in the 1100-850 cm^{-1} region. The bands ν_{27} to ν_{30} are all coupled and the assignments proposed are reasonable in terms of the observed shifts and analogous assignments in the spectrum of *trans*-[Pt(gly)$_2$]. The isotopic shifts reveal that ν_{31} with its substantial ^{18}O-shift, originates predominantly in the CO_2 rocking mode. Ring deformational modes are expected to occur below 700 cm^{-1} and the sensitivity of the bands ν_{32}-ν_{34} to all modes of isotopic substitution suggests that they originate predominantly in skeletal vibrations

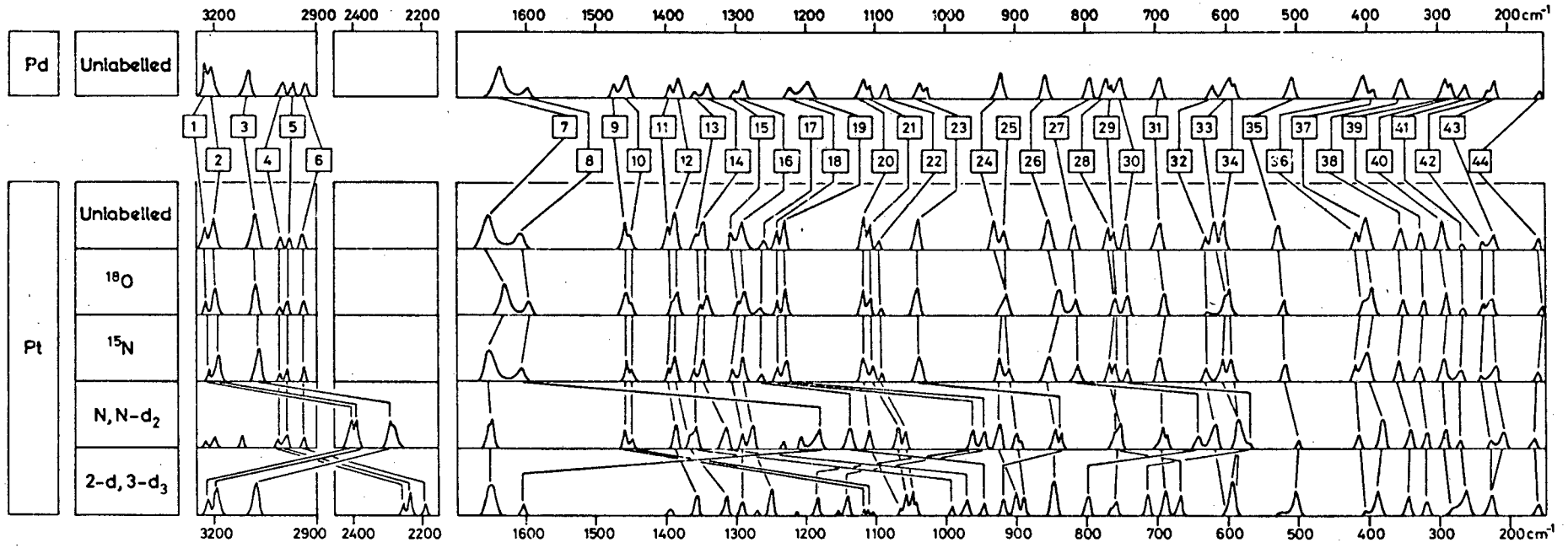


Fig. 50. Infrared spectra of L-alaninate complexes and their isotophically-labelled analogues.

of the chelate ring with some contribution from the CO_2 wagging mode apparent from their ^{18}O-sensitivities.

The region 600-140 cm^{-1}

In the spectrum of *trans*-[Pt(gly)$_2$], a band at 497 cm^{-1} was assigned to the coupled vibration νPt-N + νPt-O, and no vibrationally pure νPt-N was observed. The shifts of ν_{35} in the spectrum of *trans*-[Pt(L-ala)$_2$] are practically identical with those of the corresponding band in the spectrum of the glycinate complex. Hence, a similar assignment is proposed. The large shift (18 cm^{-1}) which this band undergoes on substitution of Pd(II) for Pt(II) is consistent with the generally observed trend[131,136,249] of Pt(II) > Pd(II), based on the degree of covalency of the M-L bond, and is consistent with the assignment proposed.

A relatively pure νPt-O band is observed at 418 cm^{-1}. The frequency is very close to that observed (415 cm^{-1}) for νPt-O in the analogous glycinate complex. The band at 402 cm^{-1} (ν_{37}) is also νPt-O but its slight ^{15}N-sensitivity and its greater sensitivity than ν_{36} towards N,N-d_2-labelling, suggests that it is coupled with a ring deformational mode involving the nitrogen atom.

Below 400 cm^{-1}, bands occur which exhibit sensitivity to several forms of isotopic labelling. These are probably ring deformations and bending modes involving the methyl group of coordinated L-ala. The absence of a methyl group in glycine explains why this region of the spectrum of the L-ala complex is relatively rich in infrared absorptions.

The bands ν_{42}-ν_{44} may be assigned to L-Pt-L bending modes. Of these, ν_{43} is sensitive towards ^{15}N- and N,N-d_2-labelling only, suggesting that it originates in δN-Pt-N. Since ν_{44} is shifted only by ^{18}O-labelling it is assigned to δO-Pt-O. Band ν_{42} , however, is sensitive to ^{18}O-, ^{15}N- and N,N-d_2-labelling and is therefore likely to be δO-Pt-N.

7.1 Influence of Pd(II) substitution on the spectrum of *trans*-[Pt(L-ala)$_2$]

It is now well established[12,245] that substitution of one coordinated metal ion in a complex by another from a higher transition series leads to an increase in the force constant (and hence vibrational frequency) of the metal-ligand bonds provided that no change in coordination number, symmetry or oxidation state of the metal ion accompanies the substitution. Thus, substitution of Pt(II) in *trans*-[Pt(L-ala)$_2$] by Pd(II) should lead to a decrease in νM-N and νM-O. Although the mass effect will favour higher frequencies for the Pd(II) complex, mass effects have been shown[172] to be heavily diluted in metal chelates. The data in Table 27 show that all bands assigned to metal-ligand stretching and bending vibrations exhibit a frequency decrease on Pd(II) substitution and this observation may be cited in support of these assignments.

The effects of metal ion substitution on the metal-ligand frequencies are often further transmitted to affect the frequencies of other vibrations in the molecule. These may vary in parallel with the metal-ligand frequencies or they may exhibit an inverse trend.[12] The NH_2 rocking modes of coordinated amines are generally very sensitive to metal ion substitution, moving in the same direction as νM-N. The data in Table 27 show that many bands assigned to pure or coupled NH_2 rocking and twisting modes exhibit substantially lower frequencies in the spectrum of the Pd(II) L-ala complex.

Metal ion substitution in amine complexes often[255] cause the νN-H band to move in the opposite direction to νM-N. This effect is also observed for the L-ala complexes described here, supporting the assigments for the νN-H bands.

7.2 Comparison between present and previous assignments and conclusions

The only previous assignment study[152] of the alanine complex of Pt(II) was based on a normal coordinate analysis, a method which has previously been shown to yield incorrect assignments in spectra of complexes involving chelating ligands, especially for the metal-ligand stretching modes in amino acid complexes[30-31] Thus, the strong 527 cm^{-1} band was not reported, while νPt-N was assigned to the 418 cm^{-1} band which is now found not to shift at all on ^{15}N-labelling. νPt-O was assigned to a band at 198 cm^{-1} since it was believed that the M-O bonds in amino acid complexes have largely ionic character, a view that has been invalidated by subsequent infrared studies and x-ray structural work on $[Cd(gly)_2].H_2O$ and isomerism studies[155,243,256] on *trans*-$[Pt(gly)_2]$ which reveal normal M-O bond lengths.

In conclusion, the frequency shifts which result from multiple isotopic labelling and Pd(II) substitution enable reliable assignments to be provided for most bands in the spectrum of *trans*-$[Pt(L\text{-}ala)_2]$ over the range 4000-140 cm^{-1}. There are few vibrationally pure bands in the spectrum. This is evident, not only from the observed isotopic shifts, but also from the occurrence of 44 bands in the spectrum of *trans*-$[Pt(L\text{-}ala)_2]$ compared with 25 for *trans*-$[Pt(gly)_2]$ over the same spectral range. Since both complexes have the *trans*-configuration, it is apparent that a small increase in complexity of the coordinated amino acid induces a large increase in complexity of the infrared spectrum.

8. STRUCTURAL INFORMATION ON SOME METAL(II) COMPLEXES OF GLYCYLGLYCINE FROM THEIR INFRARED SPECTRA

The maximum deviation from planarity of the peptide group[257] in complexes of peptides which have thus far been investigated crystallographically,[258] has been found to approximate 6^{o}, which appears[258] to be the limit to which the peptide group may be deformed in order to accommodate chelate ring strain. Furthermore, there is no structural evidence[258] that protonated N(peptide) atoms are ever used in metal-ligand bonding. This observation is explained[258] on the grounds that the tetrahedral configuration thus implied, is energetically and geometrically unfavourable. The average dimensions[150,258] of the complexed peptide do not appear to differ significantly from those of the free peptide, except for the C=O and C-N bonds of the peptide group when the N(peptide) atom takes part in M-L bonding. As regards the M-L bond lengths, those of the M-N(amine) and M-N(amide) bonds are found tc differ considerably,[258] the former generally being longer than the latter.

Initially, the association of Cu(II) ions with peptides was regarded as unique[259-260] in that Cu(II) was the only ion known to induce ionization of the amide proton. Extensive titration,[144,261] spectrophotometric and x-ray diffraction studies[144,150,258,261] reveal that Co(II), Ni(II) and Pd(II) may also promote ionization of amide protons, the Co(II) and Ni(II) complexes usually containing[262] two molecules of glycylglycine (gg) per M(II) ion. The more strongly tetragonal Cu(II) and Pd(II) ions chelate only one molecule[262] of gg per M(II) ion. Types of structure and the functional groups used in bonding to the metal ion are highly pH dependent.[143-148,252,263-264] At low pH, the most basic sites within the peptide are the amino group

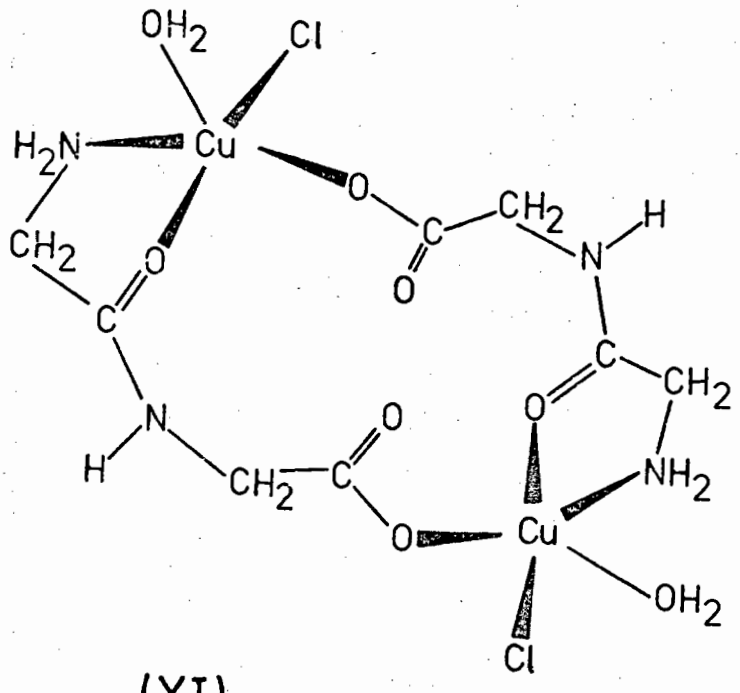
and the O(peptide) atom. It is therefore at these sites that metal ion coordination occurs.[143-148] As pH is raised the N(peptide) atom becomes deprotonated resulting in it becoming the most basic site. Consequently coordination takes place here. The carboxylate oxygen atoms now become the most basic sites and may participate in coordination. Martell and co-workers[144] found that bonding to Zn(II) ions was not pH dependent and put this down to the fact that Zn(II) ions, which are not affected by ligand field stabilization, have nothing to gain energetically by being bound to N(peptide) instead of O(peptide) donor atoms. Accordingly,[260] the dissociation of peptide protons in alkaline solution is not promoted by Zn(II) ions as it is by Cu(II), Co(II) and Ni(II) ions, for which CFSE is important.

8.1 [M(Hgg)X(H_2O)], (M = Mn, Co, Ni, Cu, Zn; X = Cl, Br)

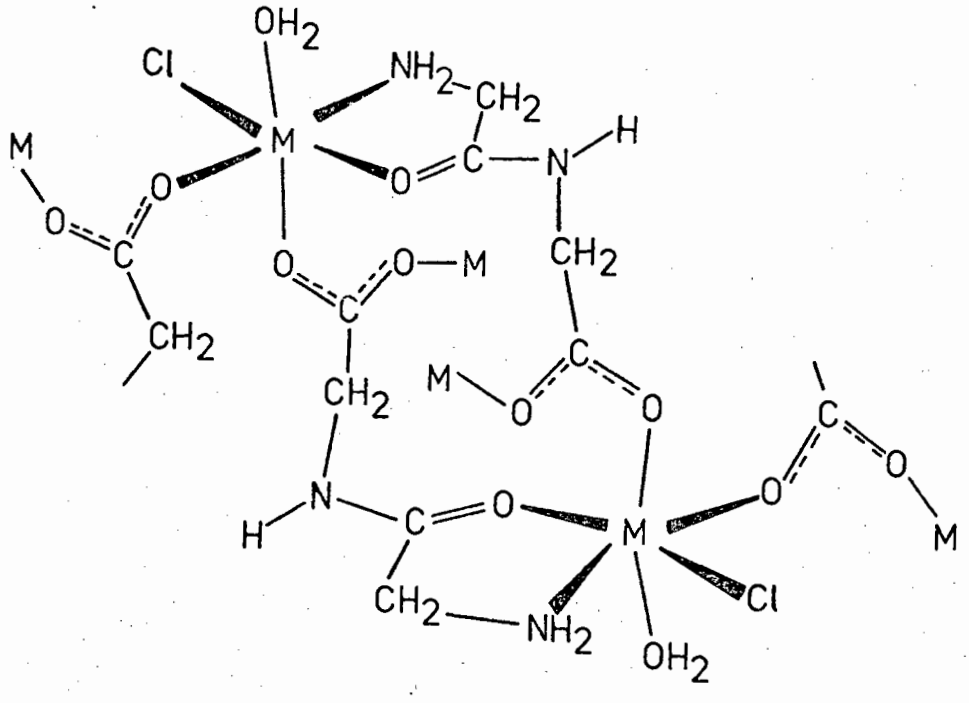
Chloroglycylglycinatocopper(II) monohydrate has been shown by x-ray analysis[265] to be a dimeric structure (XI). The glycylglycinate ligands are coordinated to one Cu(II) ion through the amino nitrogen[265] and peptide oxygen atoms, and to the other Cu(II) ion through the carboxylate oxygen atom, in a dimeric structure having C_2-like symmetry.[265] The coordination polyhedra are distorted square pyramidal, with the water molecule at the apex. This complex is crystallized from acid solution[149] and has retained the proton at the N(peptide) atom.

Although the finer details of the metal-ligand bond lengths and molecular packing were not reported[265] the infrared spectrum (Table 28, Figs. 17 and 51) is consistent with this mode of coordination.

The infrared spectra (Table 28, Figs. 17 and 51) of the Mn(II), Co(II),



(XI)



(XII)

Ni(II) and Zn(II) complexes show, by virtue of their band-for-band correspondence, that these chloro and bromo complexes are isostructural, and resemble, in broader detail, the spectra of the analogous Cu(II) complexes. It is suggested that these complexes have (distorted) octahedral structures (XII) similar to that reported[157] for $[Cd(Hgg)Cl(H_2O)]$, where the dimers, which have a structure identical to that[265] of $[Cu(Hgg)Cl(H_2O)]_2$, complete their octahedral coordination by bridging of the carboxylate oxygen atoms ($M-O^{---}C^{---}O-M$) to neighbouring dimers. Thus, all the carboxylate or amido oxygen atoms are bonded to M(II) ions. Octahedral geometries have previously[149] been suggested for the Ni(II) complex on the basis of magnetic moments, but the form of carboxylate bonding was not deduced.[149]

Because of the nature and extent of H-bonding in most complexes of dipeptides,[258] it is assumed that all acidic protons in the complexes studied here are involved in H-bonding. The broad doublet of low intensity above 3400 cm^{-1} (Fig. 51) in the Cu(II) complex is assigned to νO-H of the coordinated water molecule. This band is totally insensitive to ^{15}N-labelling. Five bands occur between 3400 and 3100 cm^{-1}, all of which are sensitive to ^{15}N-labelling. These bands have previously[149] been assigned to the asymmetric and symmetric N-H stretches of the amino groups. The 3167 cm^{-1} band was assigned to the Amide A band (νN-H). The Amide A band arises near 3280 cm^{-1} in free H_2gg and since chelation does not occur through the N(peptide) atom it seems unlikely that a decrease in frequency of some 110 cm^{-1} would occur in this band on complexation. It is therefore preferred to assign the two bands at 3257 and 3218 cm^{-1} to the Amide A band. The remaining two bands at 3327 and 3290 cm^{-1} are then attributed to the νasym.and νsym.N-H (amine) bands, respectively. These bands occur in close proximity to the

similarly assigned[29] νN-H modes in *cis*-[Cu(gly)$_2$(H$_2$O)].

In the spectra of the Mn(II), Co(II), Ni(II) and Zn(II) complexes, the broad band near 3450 cm^{-1} and the shoulder near 3390 cm^{-1} are assigned to νO-H(water). By contrast with the Cu(II) complexes, only four ^{15}N-sensitive bands are observed in the 3370-3100 cm^{-1} range. The absorption near 3270 cm^{-1} is assigned to the Amide A band, and agrees well with the position of absorption of this mode (for a non-coordinated peptide nitrogen) in the spectrum of H$_2$gg. The other two absorptions near 3360 and 3345 cm^{-1} are attributed to νasym. and νsym. N-H (amine), respectively. The sharp decrease in frequency of the νN-H (amine) vibration on passing from Ni(II) to Cu(II) may arise from differences in strength of N – H --- O = C H-bonding. It may also, however, reflect a stronger M-N (amine) bond order, which is to be expected in the case of Cu(II) due to its increased contribution from CFSE and lower coordination number. The same observations were made[131,136] for the amino acid complexes of Ni(II) and Cu(II) where νN-H in the Ni(II) chelates are invariably higher than those of the Cu(II) chelates. It is suggested that this order[27-28] reflects the relative strengths of the covalent M-N bonds (assuming that solid state effects remain constant throughout).

The bands between 3010 and 2900 cm^{-1}, being insensitive to labelling, are assigned to C-H stretching modes of the methylene groups. The carbonyl region (1700-1500 cm^{-1}) in the spectra of the Cu(II) complex exhibits six bands, of which the two of lowest frequency show significant ^{15}N-sensitivity, confirming their previous assignments[149] to amide II vibrations (δN-H). This assignment agrees well with the frequency of the amide II band in free H$_2$gg (near 1575 cm^{-1}), indicating a free, protonated N(peptide) atom. The two at 1642 and 1627 cm^{-1} are the most intense absorptions in this region. Although they exhibit slight

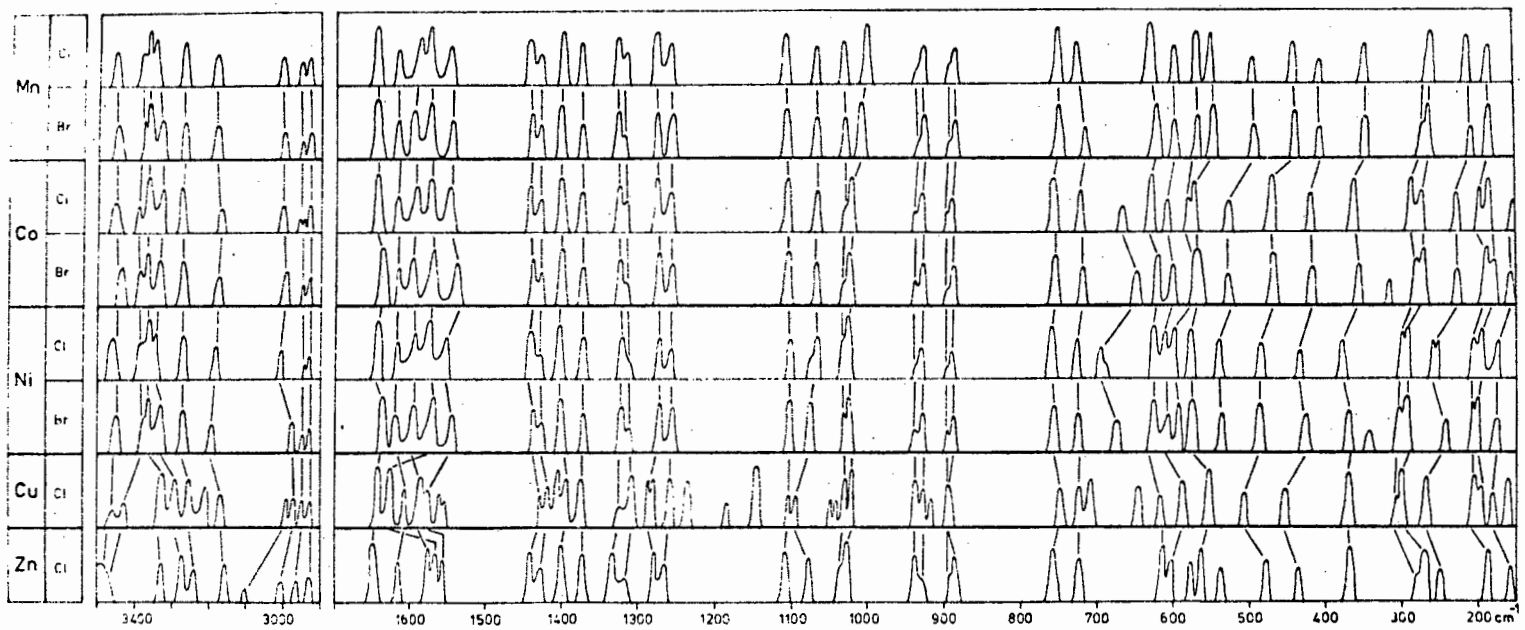


Fig. 51. The infrared spectra (3500-140 cm^{-1}) of the complexes $[M(Hgg)X(H_2O)]$, (X = Cl, Br).

^{15}N-sensitivity (indicative of coupling) they are assigned to the amide I band (νC=O) and νC=O (carboxylate), respectively. Such an assignment of νC=O (carboxylate) is consistent with a monodentate carboxyl group containing an uncoordinated (probably H-bonded) carboxylate oxygen atom. Because the 1607 cm^{-1} vibration is insensitive to the ^{15}N-isotope, it could be assigned to the OH_2 scissoring mode, known[30] to occur near this frequency in the bis(aquo) adduct of Ni(II) glycinate. It is nevertheless, preferred to assign it to a further amide I band. The occurrence of two amide I and II bands could be the result of coupling of the vibrations of the two peptide groups constituting the dimer. Two bands in the spectrum of H_2gg have been assigned[141,149] to amide I bands. In the spectrum of α-chitin, Nakamoto[266] assigned two bands to amide I modes, the one at higher frequency (1656 cm^{-1}) was thought to arise from hydrate formation since it is very weak in the spectrum[266] of anhydrous β-chitin. Similar splitting of the amide I band has been reported[143] for other complexes of gg, and attributed to crystal effects. The remaining band at 1586 cm^{-1} is assigned, by virtue of its ^{15}N-sensitivity, and by comparison with similar assignments in the complexes of glycine,[29-30] to the NH_2 scissoring mode.

It is within the 1700-1500 cm^{-1} region that the most important conclusions may be drawn as to the dissimilarities in structure and bonding between the Cu(II) complex and the Mn(II), Co(II), Ni(II) and Zn(II) complexes. The two bands near 1640 and 1620 cm^{-1}, in the latter series of complexes are assigned to the amide I bands in view of their insensitivity to ^{15}N-labelling. The asymmetric carboxylate stretch occurs near 1571 cm^{-1}. It is the most intense absorption in this region and is totally insensitive to ^{15}N-labelling. This assignment is entirely consistent with the mode of carboxylate bonding proposed for this

series of complexes, by contrast with the free carboxylate oxygen atom in the Cu(II) complexes. The band near 1590 cm^{-1} is assigned to the NH_2 scissoring mode by comparison with the spectra of glycine complexes[29-30] and because it is substantially ^{15}N-sensitive. Only one amide II band (δN-H) is observed in these spectra. It arises near 1550 cm^{-1} and shows strong ^{15}N-sensitivity.

A remarkable feature about the absorptions in the 1500-1200 cm^{-1} range is their almost complete insensitivity to ^{15}N-labelling. This prevents reliable assignments of these bands to vibrations such as NH_2 deformations, known to occur in this region of the spectra of amino acids.[30-31,131,136,144] The bands between 1300-1230 cm^{-1} do, however, exhibit slight ^{15}N-sensitivity, indicating that they may be coupled amide III or NH_2 deformational bands. The bands between 1500 and 1300 cm^{-1} are probably various mixed vibrations involving CH_2 deformations, C-C and C-O stretching modes, since these vibrations dominate this region of the spectra of amino acid complexes.[30-31,131,136,144] In contrast, the 1120-950 cm^{-1} region exhibits bands which undergo dramatic shifts on ^{15}N-substitution (Δν up to 22 cm^{-1}). The two bands of highest frequency are split in the spectra of the Cu(II) complex, while the band near 1000 cm^{-1} appears to show some metal ion sensitivity. Shifts of similar magnitude have been observed for C-N stretching modes in the M(II) complexes of amino acids.[29-31] Three such bands have been assigned to νC-N in the Ni(II) and Cu(II) complexes of L-alanine.[31] On this basis, these bands are assigned to pure C-N stretching modes. Using the same comparisons, the bands between 950 and 900 cm^{-1} are assigned to (coupled) CO_2 scissoring modes, since they are insensitive to ^{15}N-labelling, and arise at a similar frequency in amino acid complexes.[29-31] For similar reasons, the bands near 885 cm^{-1} are

assigned to NH_2 deformations, based on their ^{15}N-sensitivity. Bands exhibiting ^{15}N-sensitivity occur near this frequency in the spectra of all the complexes studied here (as well as those complexes in which the amide group is deprotonated) which precludes ascribing their origin to solely N-H deformations of the amide group. Most of the bands in the 800-550 cm^{-1} range exhibit some measure of ^{15}N-sensitivity. The band patterns in this region of the spectra of the various complexes differ considerably and are probably coupled modes involving contributions from the N-H (amide) and NH_2 deformations. The band near 624 cm^{-1} is insensitive to labelling (except in the Cu(II) chelate, 645 cm^{-1}) and by comparison with the glycine[29-30] and L-alanine[31] complexes previously reported, is regarded as having a significant contribution from the CO_2 rocking mode. This assignment puts the CO_2 rock in the Cu(II) complex at higher frequency than the other M(II) complexes, which is in agreement with the observed shifts in the carboxylate stretch in the 1600 cm^{-1} region and supports the conclusion that both carboxylate oxygen atoms are involved in M-O bonding in the Mn(II), Co(II), Ni(II) and Zn(II) chelates.

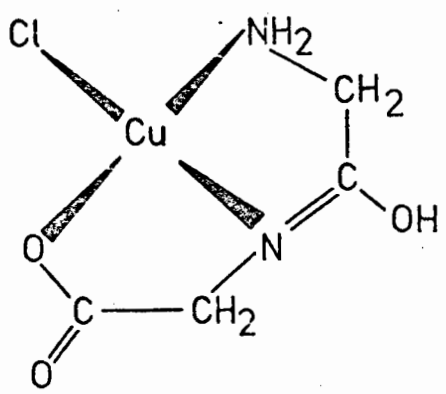
The extent of vibrational coupling is clearly evident in the region below 600 cm^{-1}, the majority of bands being sensitive to ^{15}N-substitution. There are also a number of bands, which, on the basis of their sensitivities towards replacement of the metal ion (in the order of CFSE's Mn < Co < Ni < Cu > Zn) may be assigned to M-L stretching modes. Three bands in the 500-350 cm^{-1} region exhibit both ^{15}N- and M-sensitivity. On the basis of their higher ^{15}N-sensitivity, the bands near 470 cm^{-1} are assigned to the principal νM-N(amine). The neighbouring band in the range 450-400 cm^{-1} is similarly M-sensitive but is completely unaffected by ^{15}N-labelling and is therefore

assigned to the stretching vibration of one of the three species of metal-oxygen bonds present in these complexes. Another νM-O band with similar features occurs within the range 310-250 cm^{-1}. The neighbouring band to lower frequency is assigned to νM-O + νM-Cl since it is ^{15}N-insensitive, M-sensitive and in the bromo complexes of Co(II) and Ni(II), gives rise to additional ^{15}N-insensitive bands at 227 and 220 cm^{-1}, respectively. The lower frequency bands are assigned to the metal-ligand bending modes.

8.2 [Cu(Hgg)X], (X = Cl, Br)

The proposed structure for these complexes (XIII) is that of a four-coordinate planar molecule with a tridentate glycylglycinate residue in which the N(peptide) atom is deprotonated in a similar manner to that observed crystallographically[262] for the bis(glycylglycinato)cobalt(III) ion.

The broad band above 3400 cm^{-1}, assigned to νO-H (coordinated water) in the spectra of the hydrated complexes discussed above, is absent from these spectra. Instead a broad band envelope (Table 29, Fig. 52) occurs in the 3330-3250 cm^{-1} region, due to the O-H stretch of the iminol hydroxyl group. The peak of highest frequency is assigned to νasym. N-H, and that at 3268 cm^{-1} to νsym. N-H, since they are both ^{15}N-sensitive. The magnitudes of their shifts indicate that they are vibrationally pure. The low frequency shoulder near 3261 cm^{-1} is assigned to νO-H (iminol). The remaining ^{15}N-sensitive band near 3112 cm^{-1} is assigned to the H-bonded νN – H --- O which has acquired ^{15}N-sensitivity as a result of



(XIII)

H-bonding to a nitrogen atom of an adjacent complex. The bands between 3100 and 2900 cm^{-1} are clearly the νC-H modes. They are insensitive to ^{15}N-labelling and compare well with the frequencies of νC-H in amino acid complexes.[29-31]

The carbonyl region (1700-1500 cm^{-1}), exhibit only three absorptions. The presence of the 1642 cm^{-1} vibration showing strong ^{15}N-sensitivity excludes it from originating in the amide(I) (νC=O) mode, as is the case in the hydrated complexes. This vibration clearly involves the N(iminol) atom and is therefore assigned to νC=N. Such a C=N stretching vibration is known to occur in the region of the spectra of *N*-alkylsalicylaldimine complexes[17] of Cu(II). Hence, the presence of a νC=N mode and the absence of the amide I mode from the 1650 1600 cm^{-1} region are consistent only with a protonated *O*(peptide) atom to form the iminol tautomer (XIII). The band at 1579 cm^{-1} and its low frequency shoulder are assigned to the NH_2 scissor since they shift in unison on ^{15}N-labelling. The strong 1590 cm^{-1} absorption is assigned to νC=O (carboxylate).

As is observed in the spectra of the hydrated complexes, for which the band pattern is very similar, the 1500-1300 cm^{-1} region exhibits bands which are insensitive to labelling. By analogy with the assignments in the spectra of glycine complexes, these are assigned to νC-C, νC-O and CH_2 deformation modes. The two bands between 1280 and 1200 cm^{-1} are sensitive to ^{15}N-labelling and are assigned to the NH_2 twisting mode. The bands in the 1105-1000 cm^{-1} range are assigned to C-N stretching vibrations by virtue of their strong ^{15}N-sensitivity, and because these modes are known to occur in this region of the spectra of M(II) glycinate and L-alanine complexes.[29-31] By analogy with assignments made for the hydrated complexes, and in view of their ^{15}N-insensitivity, the doublet near 930 cm^{-1} is assigned to the CO_2 scissoring mode. Similarly, the

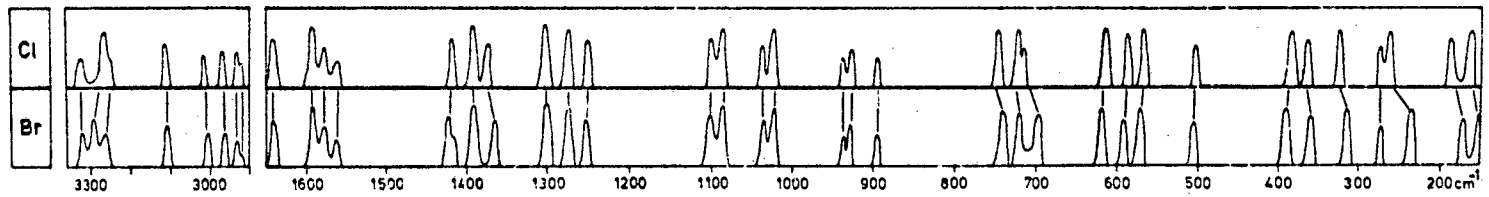


Fig. 52. The infrared spectra (3350-140 cm^{-1}) of the complexes [Cu(Hgg)X], (X = Cl, Br).

896 cm^{-1} vibration, being ^{15}N-sensitive, is assigned to the NH_2 wag. The bands between 750 and 550 cm^{-1}, which all exhibit some measure of ^{15}N-sensitivity, are probably coupled deformations involving the methylene, amino, carboxylate and iminol groups.

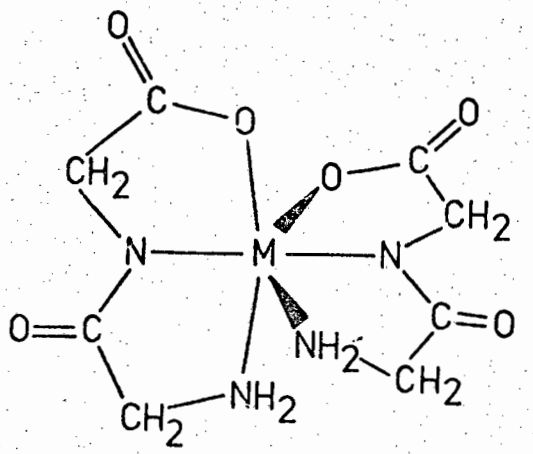
The most substantially ^{15}N-sensitive band occurs near 500 cm^{-1} and is assigned to νCu-N. Since both nitrogen atoms of the complex are labelled, a firm distinction between the two species of νCu-N bands is not possible. That these νCu-N bands occur at exactly the same frequency in the hydrated and anhydrous complexes supports the prediction of a planar anhydrous Cu(II) complex, since the planar geometry is merely an extreme example of a tetragonally distorted square pyramidal complex, and the gain in CFSE is expected to be small. Hence the correspondence of these νCu-N frequencies. Three further vibrations between 400 and 300 cm^{-1} may be assigned to coupled νCu-N on the basis of their ^{15}N-sensitivities. A band in the 400 cm^{-1} region of the spectra of *N*-alkylsalicylaldimine complexes[17] was assigned to νCu-N on the basis of its sensitivity towards change in substituent. The 271 cm^{-1} vibration is completely insensitive to ^{15}N-labelling and is firmly assigned to a νCu-O. The band at 262 cm^{-1} in the chloro complex and 235 cm^{-1} in the bromo complex, are unambiguously assigned to νCu-X, their positions and the shift induced when bromide is substituted for chloride are in agreement with those expected for terminal halide complexes[267] of Cu(II) ions. Their insensitivity to ^{15}N-labelling, furthermore, implies that they represent pure νCu-X vibrations. The lower frequency bands are assigned to M-L bending modes.

8.3 $Na_2[M(gg)_2].nH_2O$, (M(n) = Mn(2), Ni(9) and Zn(5))

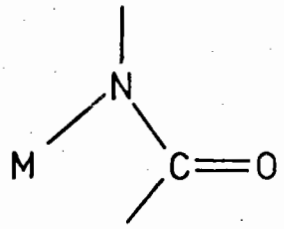
In solutions of Ni(II) ions and gg at pH near 10, dissociation[145] of the peptide protons occurs. Two types of complex, an octahydrate and a nonohydrate, crystallize from such solutions, and differ both in composition and crystal symmetry.[145] Both are disodium salts of the same $[Ni(gg)_2]^{2-}$ ion. The molecular structure[268] (XIV) of $Na_2[Ni(gg)_2].9H_2O$ reveals that each dipeptide ligand is coordinated to the Ni(II) ion through the amino group, deprotonated amide nitrogen and an oxygen of the carboxylate group. This complex is probably identical[268] with the decahydrate studied by Manyak *et al.*[144] The related complexes $Na_2[Mn(gg)_2].2H_2O$ and $Na_2[Zn(gg)_2].5H_2O$ do not appear to have previously been studied. Their infrared spectra generally exhibit a band-for-band correspondence with that of the Ni(II) complex and, on these grounds, these sodium salts appear to be structurally equivalent.

The infrared spectra (Table 30) are depicted in Fig. 53. The band near 3540 cm^{-1} and the broad band at 3442 cm^{-1} are assigned to νO-H(water), while the 3338 cm^{-1} vibration is assigned to νasym. N-H(amine). The broad band at 3240 cm^{-1} is assigned to νsym. N-H + νO-H(water). Since the peptide nitrogen[268] is deprotonated (XIV) there can be no band in this region attributable to the amide A band (νN-H). Hence, the assignments of the vibrations at 3147 and 3088 cm^{-1} to νN – H---O.

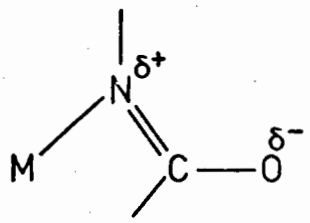
Crystal structure analyses[258] have shown that when the N(peptide) atom is coordinated, there is a significant lengthening of the C-O(peptide) and shortening of the C-N(peptide) bond distances, with respect to those of the free peptide. This implies an increased contribution from the resonance form (XVI). Since the electron shift[258] to the metal is smaller than that to the peptide proton which the M(II) ion replaces,



(XIV)



(XV)



(XVI)

the O(peptide) becomes more negative and the C=O bond order is reduced. This is consistent with the decrease in the amide I frequency (Fig. 53) from near 1675 cm^{-1} in free H_2gg to near 1550 cm^{-1} when the M(II) ion is bonded to the N(peptide) atom. The Ni(II) complex is stabilized by CFSE and as a result, the Ni-N(peptide) bond order is expected to increase over that of the (spin-free) Mn-N and Zn-N bond orders, i.e. the resonance form (XVI) is predominant in the Ni(II) complex, while the Mn(II) and Zn(II) complexes comprise a greater contribution from resonance form (XV). Therefore the C-O(peptide) band should be reduced in the Ni(II) complex, hence the assignment of the 1659 and 1634 cm^{-1} bands as amide I bands. These bands shift in an order which is the opposite of the calculated CFSE's. A similar argument may be put forward for the observed shifts in the NH_2 scissoring modes (1600 cm^{-1}) and C=O (carboxyl) stretching modes near 1569 cm^{-1}. Increased bond order of the Ni-N(amine) bond reduces the effective restoring force of the NH_2 scissoring mode, decreasing its frequency. Conversely, the greater Ni-O (carboxylate) covalent character (due to the extra contribution from CFSE) in the Ni(II) complex, causes an increase in the C=O bond order and a concomitant high frequency shift in νC=O(carboxylate).

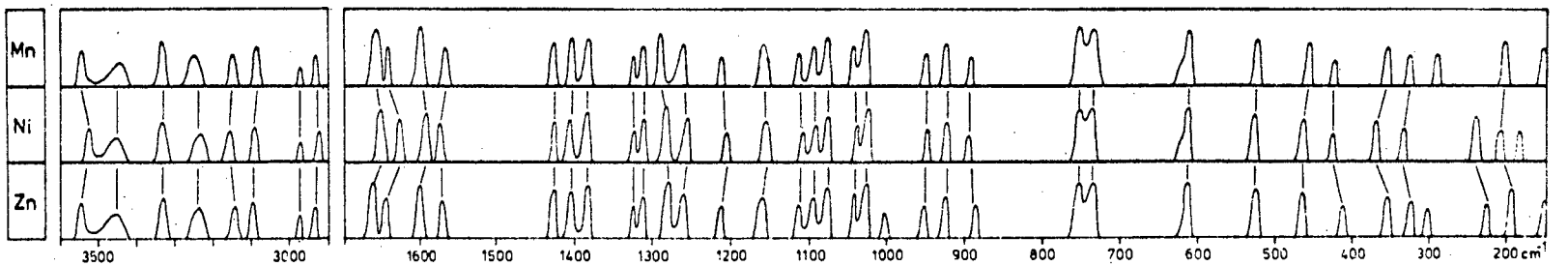
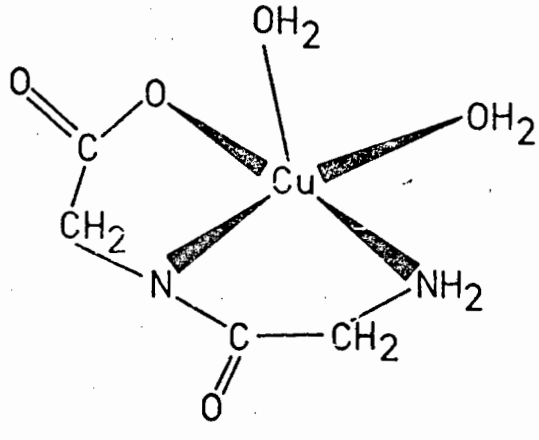


Fig. 53. The infrared spectra (3600-140 cm^{-1}) of the complexes $Na_2[M(gg)_2].nH_2O$

These spectra broadly resemble the spectra of the [Cu(Hgg)X] complexes in the 1500-600 cm^{-1} range and consequently similar assignments may be proposed. (Table 30). Because of the symmetric arrangement of the ligands about the M(II) ion, these spectra are relatively simple, in spite of the number of lattice water molecules present. This is particularly so below 600 cm^{-1}. Although these complexes were not labelled with ^{15}N-gg, tentative assignments of the bands below 600 cm^{-1} may be made by comparison with the spectra of the complexes previously discussed. On this basis, and in view of their M-sensitivities, the bands near 530 cm^{-1} are assigned to νM-N(amine) and those between 470 and 400 cm^{-1} are assigned to νM-N + νM-O. The two highly M-sensitive bands between 380 and 320 cm^{-1} are probably predominantly of νM-O character, since this is the region in which these bands arise in M(II) amino acid complexes.[29-31,131]

8.4 [Cu(gg)$(H_2O)_2$]

The crystal structure has been shown[269] to contain discrete units of [Cu(gg)$(H_2O)_2$] in which the Cu(II) ion has square-based pyramidal coordination (XVII). Tridentate coordination of the gg ligand is achieved by deprotonation[269] of the amide nitrogen atom, being identical to the mode of coordination[268] of gg in $Na_2[Ni(gg)_2].9H_2O$. The five-coordinate structure is completed by coordination of two water molecules. The infrared spectrum (Table 31, Fig. 54) in the N-H stretching region displays a broad band at 3386 cm^{-1} which is attributed to νO-H of water. The asymmetric and symmetric amino group N-H stretches occur in the region 3310-3260 cm^{-1}. Since the amide nitrogen is deprotonated,[269]



(XVII)

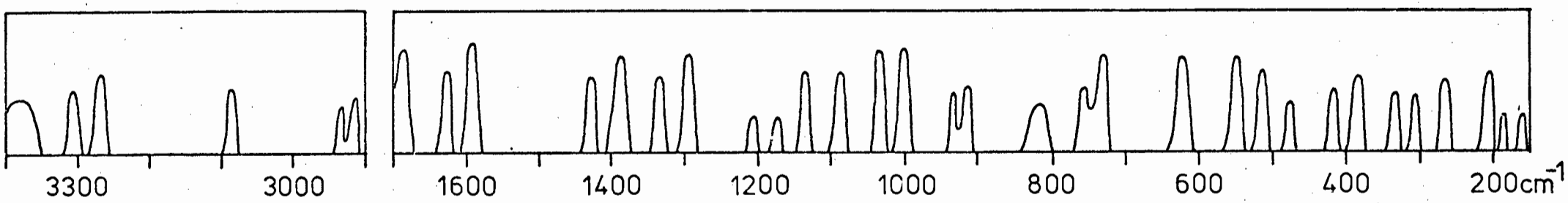


Fig. 54. The infrared spectrum (3400-140 cm^{-1}) of the complex $[Cu(gg)(H_2O)_2]$

the band at 3092 cm^{-1} cannot be attributed to the amide A mode. It appears therefore, that this band is also νN-H(amine) as is the case in the spectra of $Na_2[M(gg)_2].nH_2O$. The remaining two vibrations near 2900 cm^{-1} are assigned to νC-H modes.

The occurrence of three bands in the 1700-1500 cm^{-1} region of the spectrum (Fig. 54) is consistent with the mode of gg bonding. The uncoordinated peptide carbonyl frequency (amide I) occurs at 1688 cm^{-1}. If a direct comparison is drawn between the spectra of $[Cu(gg)(H_2O)_2]$ and $Na_2[M(gg)_2].nH_2O$, it would appear that the exceptionally higher frequency of the amide I band in the former complex, represents an increased contribution of resonance form (XV) over that of (XVII). However, the extent of H-bonding in the disodium complexes (due to the presence of a large number of lattice water molecules) may significantly lower the C=O bond order.

The NH_2 scissoring and νC=O(carboxylate) modes occur at 1622 and 1592 cm^{-1}, respectively. As expected, the amide II band is not observed. Assignments in the spectrum below 1500 cm^{-1} (Fig. 54) are accomplished by comparison with the spectra of $Na_2[M(gg)_2].nH_2O$ (Fig. 53), for which the overall band patterns are similar (except for the two bands at 819 and 514 cm^{-1} in the Cu(II) complex). The crystal structure analysis[269] reveals that the coordinated water molecule completing the basal plane is exceptionally strongly bonded (Cu-O distance[269] 1.946 Å) whereas the apical water molecule is loosely bound with a Cu-O distance[269] of 2.383 Å. On these grounds, the extra band at 514 cm^{-1} is assigned to νCu-N(amine) + νCu-O(water), while the 543 cm^{-1} band is assigned to νCu-N(amine) by comparison with the spectra of the disodium salts. The broad band at 819 cm^{-1} is assigned to an H_2O rocking mode.

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STRUCTURAL INFORMATION ON SOME METAL(II) COMPLEXES OF GLYCYLGLYCINE FROM THEIR INFRARED SPECTRA

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ABSTRACT

The infrared spectra of thirteen metal(II) complexes of glycylglycine have been determined and are discussed in relation to their known or probable structures. A distinction between various structures is possible on the basis of differences in the spectral band patterns of these complexes.

INTRODUCTION

Although metal complexes of peptides have been extensively studied by X-ray crystallographic methods [1], very little structural information has been obtained from IR spectral studies. The IR spectra of peptides have been thoroughly investigated [2—5] but few publications have dealt with the spectra of their complexes.

The results of earlier work, which was largely confined to the effects of pH and pD variation on their spectra in the 1700—1500 cm^{-1} region, have been discussed in terms of coordinate bonding [6—8]. The mull spectra (1700—1400 cm^{-1}) of some of the complexes studied here have previously been obtained [9]. However, attempts to use frequency differences in the symmetric and antisymmetric vibrations of the carboxylate group as an indication of the mode of carboxylate bonding met with little success. In this paper we report correlations between known structures of peptide complexes and their IR spectra. These spectral band patterns are used to assign structures to related complexes.

EXPERIMENTAL

Crystals of $Na_2[Ni(GG)_2].9H_2O$ [where GG = $(NH_2CH_2CONCH_2CO_2)^{2-}$] were prepared by the addition of glycylglycine in ethanol to a hot aqueous suspension of nickel carbonate. The mixture was heated with stirring for $\frac{1}{2}$ hour before the excess nickel carbonate was removed by filtration. The crystals precipitated after the green filtrate had stood overnight. These were collected, washed with ethanol and dried over silica gel.

The complexes $Na_2[M(GG)_2].nH_2O$ (M = Mn, Zn) were prepared by the addition of glycylglycine (2 molar proportions) in ethanol to an aqueous

solution of freshly prepared metal hydroxide (1 molar proportion). The mixture was heated gently (with stirring) until precipitation. The precipitate was collected, washed (ethanol) and dried over silica gel.

The complexes [M(HGG)X(H_2O)] with HGG = $(NH_2CH_2CONHCH_2CO_2)^-$; M = Mn, Co, Ni, Zn; X = Cl or Br, and the complexes [Cu(HGG)X] with X = Cl, Br were prepared by addition of glycylglycine (1 molar proportion) in ethanol to the metal halide (1.4 molar proportions) in ethanol. The resultant precipitate was collected, washed (ethanol) and dried over silica gel.

[Cu(HGG)Cl(H_2O)] and [Cu(GG)(H_2O)$_2$] were prepared by published methods (refs. 9 and 10 respectively).

Analytical data are given in Table 1.

Magnetic susceptibilities of [M(HGG)Cl(H_2O)] were measured at room temperature on a Newport—Stanton Guoy Magnetic Balance. The following results were obtained: M = Mn, μ = 5.75 BM; M = Co, μ = 4.95 BM; M = Ni, μ = 3.22 BM; M = Cu, μ = 1.86 BM.

IR spectra were determined on Nujol mulls between caesium iodide plates (or below 250 cm^{-1} between polyethylene plates) on a Perkin—Elmer 180 Spectrophotometer.

RESULTS AND DISCUSSION

The molecular structure of the bisglycylglycinatonickelate(II) ion of $Na_2[Ni(GG)_2].9H_2O$ reveals that each dipeptide ligand is coordinated to the nickel ion through the amino group, deprotonated amide nitrogen and an oxygen of the carboxylate group [11]. Four bands are present in the 1700—1500 cm^{-1} region (Fig. 1). The two bands at lower wavenumber (1594 and

TABLE 1

Analytical data on complexes of glycylglycine

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$Na_2[Mn(GG)_2].2H_2O$	24.2	4.1	14.1	24.5	4.8	14.0
$Na_2[Ni(GG)_2].9H_2O$	18.2	5.7	10.6	18.1	5.7	10.5
$Na_2[Zn(GG)_2].5H_2O$	20.8	4.8	12.1	21.1	5.1	12.2
[Mn(HGG)Cl(H_2O)]	20.1	3.8	11.7	20.1	3.7	11.5
[Mn(HGG)Br(H_2O)].H_2O	15.9	3.7	9.3	15.9	3.2	9.0
[Co(HGG)Cl(H_2O)]	19.7	3.7	11.5	19.9	3.8	11.7
[Ni(HGG)Cl(H_2O)].$\frac{1}{2}H_2O$	19.0	4.0	11.1	19.0	3.8	10.8
[Ni(HGG)Br(H_2O)]	16.7	3.2	9.7	16.7	3.2	9.5
[Cu(HGG)Cl(H_2O)]	19.4	3.7	11.3	19.4	3.7	11.3
[Zn(HGG)Cl(H_2O)]	19.2	3.6	11.2	19.2	3.5	11.0
[Cu(GG)(H_2O)$_2$]	20.9	4.4	12.2	21.2	4.6	12.1
[Cu(HGG)Cl]	20.9	3.1	12.2	20.8	3.1	12.2
[Cu(HGG)Br]	17.5	2.6	10.2	17.6	2.6	10.1

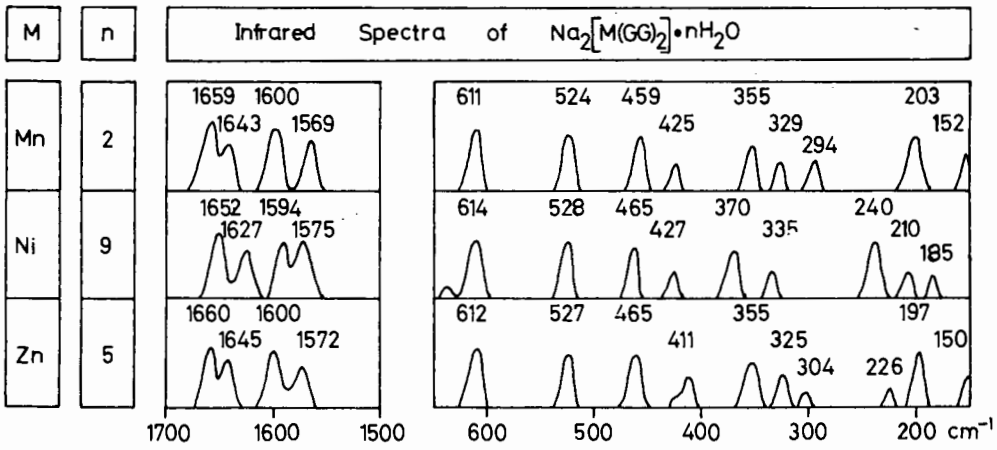

Fig. 1. The IR spectra 1700—1500 and 650—150 cm^{-1} of the complexes $Na_2[M(GG)_2].nH_2O$.

1575 cm^{-1}) are assigned, by comparison with the assignments proposed for the spectrum of *trans*-$[Ni(glycine)_2(H_2O)_2]$ [12], as the NH_2 scissoring and carboxylate stretching modes respectively. The absorption at 1652 cm^{-1} is assigned to the amide I vibration ($\nu C{=}O$). The remaining band at 1627 cm^{-1} may be assigned as the OH_2 scissoring mode. However, we prefer (for reasons discussed below) to suggest that it is a further amide I vibration. The occurrence of two amide I bands could well be the result of coupling of the two peptide carbonyl groups of the complex ion. A similar splitting of the amide I band, which was attributed to crystal effects, has been reported [6] for other complexes of glycylglycine.

The related complexes $Na_2[Mn(GG)].2H_2O$ and $Na_2[Zn(GG)].5H_2O$ do not appear to have been studied previously. Their IR spectra (1700—150 cm^{-1}) generally exhibit a band-for-band correspondence with that of the analogous Ni(II) complex, and on this basis these three sodium salts appear to have identical structures. Figure 1 reveals the spectral similarities for these complexes in the regions 1700—1500 and 650—150 cm^{-1}. That the first two bands below 1700 cm^{-1} show metal-sensitivity strongly supports their assignment to amide I vibrations rather than to the scissoring mode of the uncoordinated water molecules.

The structure of $[Cu(HGG)Cl(H_2O)]_2$ shows both Cu ions of the dimer to be in square based pyramidal coordinations with the glycylglycinate ligands bridging the Cu ions [13]. Each ligand coordinates to one Cu ion via the peptide oxygen and the amino group and to the other Cu ion via one of the carboxylate oxygens. Although the finer details of bond lengths and molecular packing were not reported [13], the IR spectrum (1700—1500 cm^{-1}) is consistent with this mode of coordination (Fig. 2). The additional band near 1550 cm^{-1}, which was absent in the spectra of $Na_2[M(GG)_2].nH_2O$, is assigned as the amide II (N—H bend) mode. Predictably, because of the different modes of coordination of the ligand, the amide I bands occur at lower frequency than in the spectra of the $Na_2[M(GG)_2].nH_2O$ complexes.

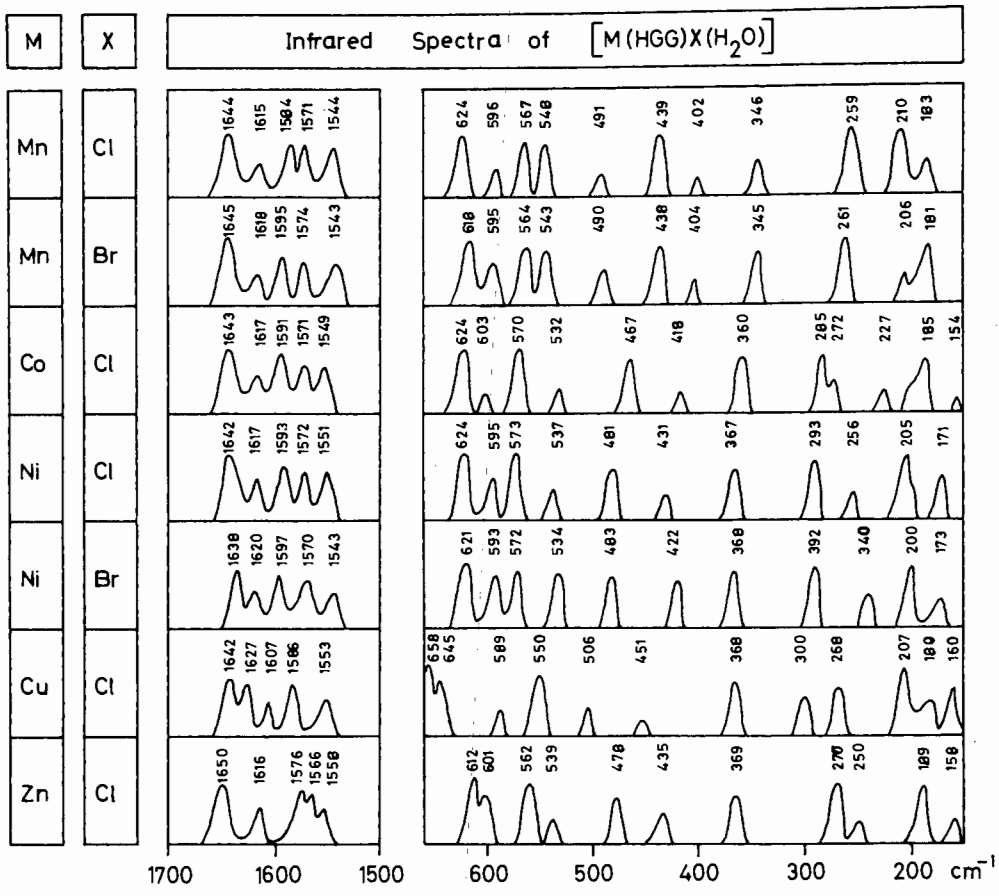

Fig. 2. The IR spectra 1700—1500 and 660—150 cm^{-1} of the complexes $[M(HGG)X(H_2O)]$.

The IR spectra (Fig. 2) of the series $[M(HGG)X(H_2O)]$ with M = Mn(II), Co(II), Ni(II), Zn(II); X = Cl or Br, show, by virtue of their band-for-band correspondence, that these complexes are iso-structural. We suggest that all these complexes have (distorted) octahedral structures similar to that reported [14] for $[Cd(HGG)Cl(H_2O)]_2$ where the dimers, which have a structure identical to $[Cu(HGG)Cl(H_2O)]_2$, complete their octahedral coordination by bridging of carboxylate oxygen atoms to neighbouring dimers. Comparison of the spectra of this series with the spectrum of the analogous Cu(II) complex (Fig. 2) supports the unique five-coordinate structure of $[Cu(HGG)Cl(H_2O)]_2$. In accordance with the presence of the free carboxylate oxygen atom in $[Cu(HGG)Cl(H_2O)]$, νC=O(carboxylate) occurs at higher frequency. The bands at 658 and 645 cm^{-1}, which by comparison with the firmly established assignments in the spectrum of *trans*-$[Ni(glycine)_2(H_2O)_2]$ may reasonably be assigned as CO_2 rocking modes, occur some 30 to 40 cm^{-1} higher in frequency than for the corresponding octahedral analogues of Mn(II), Co(II),

Ni(II) and Zn(II). Apart from these differences arising from the CO_2 modes, the fact that the spectra of all the complexes show such extreme similarities supports our proposed structures. It is of interest to note that octahedral geometries have previously been suggested [9] for [M(HGG)Cl(H_2O)] (M = Ni, Zn), but with no conclusions about the form of the coordinate bonding.

Below 600 cm^{-1}, several absorptions in the spectra of [M(HGG)X(H_2O)] exhibit a metal ion dependence which is the sequence of calculated crystal field stabilisation energies for the high-spin ions. This feature suggests that these bands probably originate from metal—ligand stretching vibrations. However, in view of the fact that isotopic labelling has shown that the majority of bands in the spectra of metal glycinate complexes [12, 15] are the result of mixed vibrations, detailed assignments in the even more complex spectra of these metal glycylglycinates would only be possible after an isotopic labelling study.

[Cu(GG)(H_2O)$_2$] has been shown to have a square based pyramidal structure [16], with the tridentate coordination of the glycylglycinate ligand being identical to that found [11] for Na_2[Ni(GG)$_2$].9H_2O. The five-coordinate structure is completed by the two water molecules. The IR spectrum in the region 1700—1500 cm^{-1} is entirely consistent with this structure. The uncoordinated peptide carbonyl frequency (amide I) is at 1688 cm^{-1} and the NH_2 scissor and νC=O(carboxylate) occur at 1622 and 1592 cm^{-1} respectively. As expected, the amide II band is not observed.

Two further Cu(II) complexes for which elemental analyses suggest the formulation [Cu(HGG)X] (X = Cl, Br) were isolated in this study. Their IR spectra (Fig. 3) have identical band patterns apart from the region below

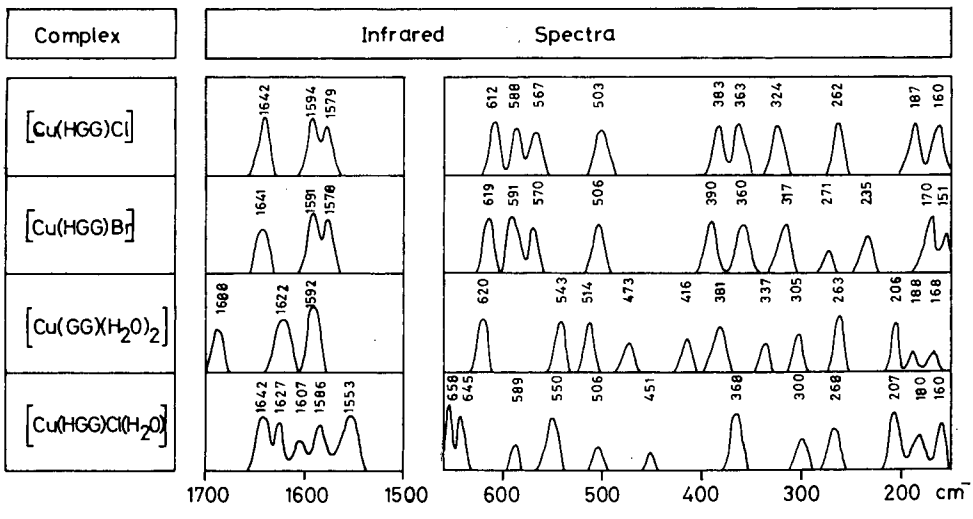

Fig. 3. The IR spectra 1700—1500 and 660—150 cm^{-1} of various Cu(II) complexes of glycylglycine.

200 cm^{-1} where νCu—X are expected to occur. We propose a 4-coordinate structure for these molecules in which the peptide carbonyl has become protonated in a similar manner to that observed crystallographically for the bis(glycylglycinato)cobalt(III) ion [17]. Assuming this to be the structure, the band at 1642 cm^{-1} may reasonably be assigned as a C=N stretching vibration since it occurs in the region found for this mode in *N*-alkylsalicylaldimine complexes of Cu(II) [18].

For comparative purposes, Fig. 3 includes the spectra of the other Cu(II) complexes studied here. The band patterns are clearly dependent both on the mode of coordination of the glycylglycinate anion and on the complex structure.

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EXAMINATION OF THE RATIO ν^D/ν^H FOR INFRARED BANDS ASSIGNED TO THE C-H(D) AND RING VIBRATIONS IN METAL COMPLEXES OF QUINOLINE, PYRIDINE, ANILINE AND THEIR FULLY-DEUTERATED ANALOGUES

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ABSTRACT

The infrared spectra of sixteen metal complexes comprising the ligands quinoline, pyridine, aniline and their fully-deuterated analogues have been examined in order to determine the ratio ν^D/ν^H for bands assigned to the C-H and ring modes of the heterocyclic or aromatic ring. With very few exceptions, ν^D/ν^H falls within the ranges 0.68 to 0.85 for C-H vibrations and 0.85 to 1.00 for ring modes. The ranges are narrower for complexes of a specific amine. The potential usefulness of the results is discussed.

INTRODUCTION

The ratio (ν^D/ν^H) between the frequencies of corresponding bands in the infrared spectra of deuterated and normal molecules serves as an effective distinction between the C-H stretching (or bending) modes and the ring stretching (or bending) vibrations in aromatic and heterocyclic compounds[1]. Naphthalene and naphthalene-d_8, for instance, yield values of ν^D/ν^H which are approximately 0.75 for C-H modes and 0.90 for ring modes[2]. Corresponding ratios are observed for other aromatic and heterocyclic compounds such as aniline and pyridine[1]. The extent to which similar values of ν^D/ν^H are observed for the metal complexes of these amines appears to have been neither examined nor fully exploited as a potential aid to assignments in their infrared spectra although it has long been recognised[3] that the majority of infrared bands which originate in the internal vibrations of pyridine recur on an approximately band-for-band basis in the spectra of pyridine complexes. Some relatively complete (4000 - 150 cm^{-1}) assignment studies[4,5] recently made in this laboratory enable evaluation of the extent to which the ν^D/ν^H ratios for metal complexes mimic those of the parent ligands.

EXPERIMENTAL

The complexes were prepared by reported methods[6-11]. Deuterated complexes were synthesized from pyridine-d_5, quinoline-d_7 and aniline-d_5 of 99.98 and 97% isotopic purity, respectively, supplied by Merck, Sharp and Dohme (Canada) Ltd. Purity of all compounds was determined by microanalyses (C,H,N). Infrared spectra were determined on nujol and hexachlorobutadiene mulls between caesium iodide plates (4000 - 250 cm^{-1}) or poly-

ethylene plates (250 - 150 cm^{-1}) on Beckman IR-12 and Perkin-Elmer 180 spectrophotometers and on a Digilab FTS-16B/D interferometer.

RESULTS AND DISCUSSION

Only the internal modes of the amines are relevant to the discussion; the metal-ligand vibrations and the internal modes of the isothiocyanate, dimethylglyoximate and glycinate ligands will be reported elsewhere[4,5]. The frequencies for the latter vibrations are therefore excluded from Tables 1 and 2.

The complexes $[MQ_2X_2]$ (M = Co, Ni, Cu or Zn; Q = quinoline; X = Cl, Br, I or NCS) and their deuterated analogues represent the most complete series of complexes studied. The frequencies for the internal modes of quinoline, quinoline-d_7 and their complexes are reported in Table 1. Because of the small variation which exists between the frequencies of corresponding bands in their spectra, only the mean frequency is cited for the ten complexes studied. The assignments given for quinoline are those preposed by Chiorboli and Bertoluzzi[12] which are partially based on the study of naphthalene and naphthalene-d_8 by McClellan and Pimentel[2]. Practically every band in the quinoline spectrum recurs in the spectra of the complexes. The ratio ν^D/ν^H spans the ranges 0.74 to 0.83 for the C-H modes and 0.87 to 0.98 for the ring vibrations. The values for the complexes are similar: 0.74 to 0.84 and 0.88 to 0.98, respectively, with the single exception of the δ(ring) mode near 860 cm^{-1} which yields values of 0.80 for the ligand and 0.79 for the complexes, which are anomalously low if the assignment given is correct.

So far as the pyridine complexes are concerned, sufficiently complete data for a meaningful evaluation of the ν^D/ν^H ratio have been

TABLE 1

Frequencies of quinoline vibrations, ν^D/ν^H ratios and assignments for quinoline (Q) and the complexes $[MQ_2X_2]$ (M = Co, X = Cl, Br; M = Ni, X = Br; M = Cu, X = Cl, Br, NCS; M = Zn, X = Cl, Br, I, NCS). The frequencies in parentheses are those for the deuterated species).

Quinoline frequencies (cm^{-1})	ν^D/ν^H for ligand	Mean frequencies for complexes (cm^{-1})	ν^D/ν^H for complexes	Assignments[2,12] (band number)
3054(2275)	0.74	3066±14(2274±14)	0.75±0.01	ν(C-H) (1,41)
3034(2256)	0.74	3053±25(2259±7)	0.74±0.01	ν(C-H) (14,29)
1619(1584)	0.98	1620±1 (1588±9)	0.98	ν(ring) (16)
1594(1551)	0.97	1592±3 (1558±3)	0.98±0.01	ν(ring) (17,31)
1569(1542)	0.98	1583±3 (1544±2)	0.98±0.01	ν(ring) (3)
1549(1290)	0.83	1551±3 (1275±12)	0.82	
1533(1451)	0.95	1546±6 (1462±16)	0.95±0.01	
1500(1438)	0.96	1508±3 (1448±4)	0.96	ν(ring) (44)
1468(1383)	0.94	1463±3 (1381±7)	0.94±0.01	
1453(1366)	0.94	1439±20(1364±3)	0.94±0.01	
1430(1163)	0.81	1437±3 (1155±12)	0.81±0.01	δ(C-H) (18)
1412(1303)	0.92	1410±8 (1321±15)	0.94±0.01	
1391(1281)	0.92	1398±7 (1295±3)	0.93±0.01	ν(ring) (32)
1370(1239)	0.90	1376±3 (1238±4)	0.90	ν(ring) (4)
1336(1257)	0.94	1336±15(1263±5)	0.95	
1332(1232)	0.92	1325±8 (1251±5)	0.94±0.01	
1312(1092)	0.83	1310±3 (1099±2)	0.84	δ(C-H) (33)
1278(1036)	0.81	1283±15(1044±3)	0.81±0.01	γ(C-H) (10)
1253(1015)	0.81	1270±8 (1019±9)	0.80±0.01	δ(C-H) (5)
1230(1024)	0.83	1234±6 (-)		
1215(963)	0.79	1219±13(973±11)	0.80±0.02	
1191(915)	0.78	1200±10(929±4)	0.77±0.01	
1139(891)	0.78	1141±5 (905±4)	0.79±0.01	γ(C-H) (26)
1117(876)	0.78	1130±4 (885±8)	0.78±0.01	δ(C-H) (19,45)
1094(860)	0.79	1090±10(855±24)	0.78±0.03	γ(C-H) (37)
1031(932)	0.90	1054±6 (948±1)	0.90±0.01	δ(ring) (6)
1012(838)	0.83	1021±3 (839±9)	0.82±0.01	δ(C-H) (46)
978(825)	0.84	993±6 (826±9)	0.83±0.02	
952(749)	0.79	970±5 (761±21)	0.78	γ(C-H) (22)
938(780)	0.83	957±4 (781±10)	0.81±0.02	δ(C-H) (7)
924(712)	0.77	889 (718±6)	0.81	
866(696)	0.80[a]	863 (684±29)	0.79±0.04[a]	δ(ring) (20)
842(806)	0.96	- (796±19)		γ(ring) (12)
803(641)	0.80	808±5 (642±5)	0.79±0.01	γ(C-H) (23)
784(613)	0.78	781±4 (611±3)	0.78±0.01	γ(C-H) (38)
758(674)	0.90	722±1 (-)		δ(ring) (8)
742(665)	0.90	741±1 (652±13)	0.88	δ(ring) (47)
736(584)	0.79	739±10(576±7)	0.78±0.01	γ(C-H) (27)
627(589)	0.94	- (-)		δ(ring) (35)
610(568)	0.93	635±3 (590±8)	0.93±0.02	δ(ring) (21)
521(504)	0.97	528±2 (510±7)	0.97±0.02	δ(ring) (9)
477(417)	0.87	488±11(433±11)	0.89±0.01	γ(ring) (24)
469(409)	0.87	464±2 (407±3)	0.88±0.01	δ(ring) (48)
390(351)	0.90	399±5 (363±4)	0.91±0.02	γ(ring) (13)
375(345)	0.92	394±4 (356±4)	0.91±0.01	δ(ring) (36)
178(166)	0.93	187±4 (175±7)	0.93±0.04	γ(ring) (25)

[a] Anomalously low value for the assignment cited.

TABLE 2

Frequencies of pyridine vibrations, ν^D/ν^H ratios and assignments for pyridine (py) and the complexes $[Zn(py)_2Cl_2]$, $[Co(DH)_2(py)X]$ (DH = dimethylglyoximate anion; X = Cl, Br, I, NCS) and $[Ni(gly)_2(py)_2]$. (The frequencies in parentheses are those for the deuterated species).

Pyridine frequencies (cm^{-1})	ν^D/ν^H	$[Zn(py)_2Cl_2]$ frequencies (cm^{-1})	ν^D/ν^H	$[Co(DH)_2(py)X]$ mean frequencies (cm^{-1})[ab]	ν^D/ν^H	$[Ni(gly)_2(py)_2]$ frequencies (cm^{-1})[b]	ν^D/ν^H	Assignments[13-17] (band number)
3083(2293)	0.74	3109(2293)	0.74					(20b)
3054(2293)	0.75	3066(2273)	0.74			3071(2294)	0.75	ν(C-H) (2)
	0.75	3044(-)				3048(2274)	0.75	ν(C-H) (13)
3036(2254)	0.74	2925(-)				2998(2258)	0.75	ν(C-H) (20a,7b)
1633(1585)	0.97	1661(1653)	0.99					(1+6b)
1599(1550)	0.97	1656(1598)	0.96					(1+6a)
1580(1530)	0.97	1607(1566)	0.97	1606±6 (1564±3)	0.97	1610(1557)	0.97	ν(ring) (8a)
1572(1532)	0.98	1573(1539)	0.98			1570(1536)	0.98	ν(ring) (8b)
1482(1340)	0.90	1486(1320)	0.89	1495±5 (1322±4)	0.88	1481(1313)	0.89	ν(ring) (19a)
1439(1301)	0.90	1449(1311)	0.90	1451±4[c] (1322±4)	0.91	1447(1237)	0.83	ν(ring) (19b)
1375(1322)	0.96	1399(1374)	0.98	1370±2[d] (1326±5)	0.97			ν(ring) (14)
		1379(1337)	0.97					
1218(908)	0.74	1245(992)	0.79	1233±7[e] (979±6)	0.79	1238(886)	0.72	(3)
(887)	0.73	1216(890)	0.73	(906±6)	0.73	1213(852)	0.70	δ(C-H) (9a)
1148(887)	0.77	1158[g](843)[g]	0.73	1164±15(856±8)	0.76	1158(844)	0.73	δ(C-H) (15)
1068(833)	0.78	1069(832)	0.78	1070±4 (837±9)	0.78	1065(726)	0.68	δ(C-H) (18b)
1029(1006)	0.98	1045(1025)	0.98	1040±2 (1013±2)	0.97	1035(1009)	0.97	ν(ring) (12)
992(962)	0.97	1015(1013)	0.99	1006±6 (1005±1)	1.00[gh]	1009(975)	0.97	ν(ring) (1)
886(690)	0.78	888(694)	0.78	881±9 (783±6)	0.90[gh]			(10b)
749(567)	0.76	756[g](561)[g]	0.74	765±2 (574±4)	0.75	758(731)	0.96[h]	γ(C-H) (11)
703(530)	0.75	696[g](533)[g]	0.76	696±6 (536±6)	0.77	705(600)	0.85	γ(C-H) (4)
605(582)	0.96	641(615)	0.96	648±1[f] (630±4[g])	0.97	625(542)	0.87	δ(ring) (6a)
405(371)	0.92	423(384)	0.91	422±2[f] (401±5)	0.95	435[gi](398)	0.91	γ(ring) (16b)

[a] Spectra not determined in 3000-3100 cm^{-1} region. [b] Bands not observed are masked by bands from other coordinated ligands. [c] Coupled with ν(C=N). [d] Coupled with $\delta(CH_3)$. [e] Coupled with ν(N-O). [f] Coupled with ν(Co-N). [g] Mean of doublet. [h] Anomalously high value for assignment cited. [i] Coupled with $\nu(Ni-NH_2)$.

obtained[4,5] for six complexes of widely differing chemical type. The assignments for pyridine (py) and pyridine-d_5 (py-d_5) are better established[13-17] than those of quinoline. Table 2 lists the relevant frequency data for pyridine, the complexes $[Zn(py)_2Cl_2]$, $[Co(DH)_2(py)X]$ (DH = dimethylglyoximate anion; X = Cl, Br, I, CH_3), $[Ni(gly)_2(py)_2]$ (gly = glycinate anion) and their py-d_5 analogues. Based on the assignments of Kline and Turkevich[14], the ratio ν^D/ν^H falls within the ranges 0.73 to 0.79 (C-H modes) and 0.90 to 0.98 (ring modes) for py and py-d_5 and 0.68 to 0.85 and 0.85 to 1.00, respectively, for the complexes with the exception of the apparently anomalously high ratios of 0.90 for the γ(C-H) mode 10b in $[Co(DH)_2(py)X]$ and 0.96 for the γ(C-H) mode 11 in $[Ni(gly)_2(py)_2]$. In view of the widely differing types of complexes represented, the ratios for the complexes are remarkably consistent with those observed for the parent ligand.

Sufficiently complete data have been obtained[4] for only one aniline (an) complex, $[Zn(an)_2Cl_2]$ and its an-d_5 analogue. Their spectra reveal ν^D/ν^H ratios within the ranges 0.68 to 0.76 (C-H modes) and 0.93 to 0.99 (ring modes) on the basis of the assignments given by Evans[18] for the parent amine. Similar ratios have been found[5] for a wide range of imidazole complexes.

Over the series of sixteen complexes discussed, the ratio ν^D/ν^H spans the ranges 0.68 to 0.85 for the C-H modes and 0.85 to 1.00 for the ring modes. Absence of overlap between these ranges suggests that the observed ratios serve to distinguish between C-H and ring modes in metal complexes as they do in the parent ligands. Distinction, also, between these vibrations and metal-ligand modes or bands originating in the vibrations of other functional groups or other coordinated ligands may

also be achieved since the latter generally yield ν^D/ν^H ratios very close to unity. Where apparently anomalous ratios are observed, the possibility of incorrect assignments or vibrational coupling must be considered[1].

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THE INFRARED SPECTRA OF *TRANS*-BIS(L-ALANINATO) COMPLEXES OF PLATINUM(II) AND PALLADIUM(II) : BAND ASSIGNMENTS BY MULTIPLE ISOTOPIC LABELLING

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(With 1 figure)

(Read 1978)

SUMMARY

The infrared spectra (4000 - 140 cm^{-1}) of the L-alaninate complex *trans*-[Pt(L-ala)$_2$] and its ^{18}O-, ^{15}N-, 2-d,3-d_3- and N,N-d_2-labelled analogues have been determined. Each spectral band has been assigned on the basis of the shifts induced by the various modes of isotopic labelling and by substitution of Pd(II) for Pt(II). The labelling study reveals that very few bands represent vibrationally-pure modes and that certain earlier assignments require revision.

INTRODUCTION

Less attention has been given to the infrared spectra of alanine complexes than to those of glycine (Ablov *et al.* 1967; Herlinger *et al.* 1970; Jackowitz *et al.* 1967; McAuliffe & Perry 1969; Nakamoto *et al.*

1961; Percy & Stenton 1976*b*; Watt & Knifton 1967). Recent work shows that very few infrared bands in the spectra of glycinate complexes represent vibrationally-pure species although it has been possible to assign the metal-ligand stretching modes by observing the band shifts which are induced by isotopic labelling of the ligand atoms (Hodgson *et al.* 1978; Niven & Thornton 1979; Percy 1976; Percy & Stenton 1976*a*). This paper reports the assignments for *trans*-[Pt(L-ala)$_2$] by observing the infrared band shifts induced by ^{18}O-, ^{15}N-, 2-*d*,3-d_3- and *N*,*N*-d_2-labelling of L-alanine and the effect on the spectrum of substituting Pd(II) for Pt(II).

EXPERIMENTAL

The *trans*-complexes [Pt(L-ala)$_2$] and [Pd(L-ala)$_2$] were prepared by reported methods (Jackowitz *et al.* 1967). The labelled analogues of [Pt(L-ala)$_2$] were similarly obtained from ^{18}O-L-alanine of 76% isotopic purity supplied by BOC Prochem Ltd. and ^{15}N- and 2-*d*,3-d_3-L-alanine of (respectively) 95 and 98% isotopic purity supplied by Merck, Sharp and Dohme (Canada) Ltd. Composition and purity were determined by microanalysis (C, H, N). The *N*,*N*-d_2-labelled complex was similarly prepared in D_2O from a sample of L-alanine previously recrystallized from D_2O.

Infrared spectra were determined on nujol mulls (or, in the region of nujol absorption, on hexachlorobutadiene mulls) between caesium iodide plates on a Beckman IR-12 spectrophotometer (4000 - 250 cm^{-1}) and between polyethylene plates on a Perkin-Elmer 180 spectrophotometer (250 - 140 cm^{-1}). Reproducibility of reported bands is better than 0.5 cm^{-1}.

RESULTS AND DISCUSSION

The band frequencies and shifts ($\Delta\nu$) are reported in Table 1 and the spectra are depicted in Figure 1.

With only two exceptions, there is a band-for-band correspondence between the spectra of the Pt(II) and Pd(II) L-alaninate complexes (Figure 1). Hence, establishment of the assignments for the Pt(II) complex by multiple isotopic labelling is considered to provide analogous assignments for the corresponding bands of the Pd(II) complex. Frequencies cited in the ensuing discussion refer to the Pt(II) complex.

Six bands occur within the range 3300 - 2900 cm^{-1}. The N-H stretching modes (ν_1-ν_3) are distinguished by their sensitivities to ^{15}N- and N,N-d_2-labelling from the neighbouring C-H stretching vibrations (ν_4-ν_6) which are shifted by 2-d,3-d_3-labelling only. The shifts are approximately 800 cm^{-1} for N-H stretches and 750 cm^{-1} for C-H stretches. These values are close to those calculated for isolated N-H or C-H diatomic oscillators (Pinchas & Laulicht 1971). This feature and absence of sensitivity to any other mode of labelling, indicates that these vibrations are essentially free from vibrational coupling. Substitution of Pd(II) for Pt(II) causes a high frequency shift in the ν(N-H) bands, *i.e.* the opposite trend exhibited by the ν(M-N) bands. Hence the higher metal-ligand bond stability of the Pt(II) complex occurs at the expense of the N-H bonding.

The band at 1655 cm^{-1} (ν_7) is clearly a pure ν(C=O) vibration since it is only shifted by ^{18}O-labelling. The neighbouring band (ν_8) is sensitive to ^{13}O-, ^{15}N- and N,N-d_2-labelling; it is therefore assigned to ν(C=O) coupled with the NH_2 scissoring mode which is generally observed near 1600 cm^{-1}. The ν(C=O) value for the Pt(II) complex is

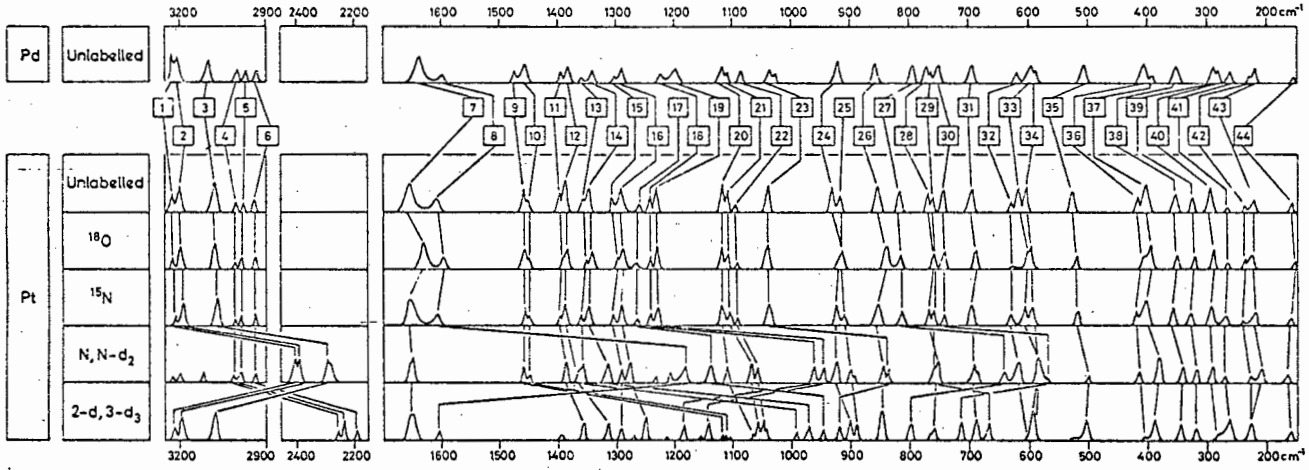

Fig. 1. Infrared spectra of L-alaninate complexes and their isotopically-labelled analogues.

Table 1

Frequencies (cm^{-1}), shifts ($\Delta\nu$, cm^{-1}) and infrared band assignments for the complex $[Pt(L\text{-}ala)_2]$ and its Pd(II)- and isotopically-substituted analogues*

Band	Frequency	Δν (Pt-Pd)†	Δν ^{18}O	Δν ^{15}N	Δν $N,N\text{-}d_2$	Δν $2\text{-}d,3\text{-}d_3$	Assignment
ν_1	3225	-5		5	818		ν(N-H)
ν_2	3209	-8		8	808		
ν_3	3103	-18		5	795		
ν_4	3003	3				751	ν(C-H)
ν_5	2985	1				749	
ν_6	2943	3				744	
ν_7	1655	11	26	2	2	2	ν(C=O)
ν_8	1606	3	9	3	422		ν(C=O)+NH_2 scissor
ν_9	1457	-18				337	CH_3 deg. def.
ν_{10}	1450	-7			2	337	
ν_{11}	1392	2	4	2	9	30	ν(C-O)+ν(C-C)
ν_{12}	1384	0	3		20	71	
ν_{13}	1360	-3			2	365	CH_3 sym.def.
ν_{14}	1348	5	2	2	32	377	CH_3 sym.def.+NH_2 twist
ν_{15}	1307	3	15	2	18	19	ν(C-O)+ν(C-C)+NH_2 twist
ν_{16}	1289	-1	8	2	15	40	
ν_{17}	1268	‡			319	130	NH_2 twist+ν(C-CH_3)
ν_{18}	1246	22		4	284	64	
ν_{19}	1231	32		4	283	94	
ν_{20}	1119	1		2	10	56	coupled ν(C-N)
ν_{21}	1108	-3	2	2	37	52	
ν_{22}	1094	8	4	2	35	45	
ν_{23}	1038	2	3	2	200	117	ν(C-N)+CO_2scissor+CH_3roc
ν_{24}	928	4	11	3	4	26	CO_2 scissor+ν(C-C)
ν_{25}	917	‡		4	27	16	ν(C-N)
ν_{26}	862	3	20	4	14	13	CO_2 scissor+ν(C-N)
ν_{27}	819	21	5	5	178	21	CO_2 rock+CH_3 rock + NH_2 rock
ν_{28}	772	2	7		15	13	
ν_{29}	765	3		3	2	97	
ν_{30}	747	-1	3	3	180	34	
ν_{31}	699	5	9	2	3	10	CO_2 rock
ν_{32}	632	9	5	4	13	19	CO_2 wag+ring def.
ν_{33}	617	18	14	9	31	22	
ν_{34}	605	18	7	9	19	10	
ν_{35}	527	18	6	7	27	22	ν(Pt-N)+ν(Pt-O)
ν_{36}	418	8	10		4	13	ν(Pt-O)
ν_{37}	402	11	10	2	23	18	ν(Pt-O)+ring def.
ν_{38}	359	3	5		16	14	ring def.
ν_{39}	324	36	4	2	9	10	
ν_{40}	289	7	5	2		4	
ν_{41}	266	2	3	2		7	
ν_{42}	234	1	6	2	8	9	δ(O-Pt-N)
ν_{43}	223	2		4	15		δ(N-Pt-N)
ν_{44}	158	6	8				δ(O-Pt-O)

* Shifts <2 cm^{-1} ignored. † Frequency for Pt(II) complex minus frequency for Pd(II) complex. ‡ No corresponding band observed in spectrum of Pd(II) comple

11 cm^{-1} higher than the value for the Pd(II) complex, indicating that the higher electron density of the Pt-O bond is transmitted to the exocyclic C=O bond.

The bands (ν_9,ν_{10}) are sensitive towards 2-*d*,3-d_3-labelling only. They clearly originate in the degenerate deformation mode of the methyl group. The frequencies in the complexes are very similar to those observed in the spectrum of free L-alanine (Percy & Stenton 1976*b*). Bands ν_{11} and ν_{12} are shifted slightly by ^{18}O-labelling. Their sensitivities towards *N*,*N*-d_2- and 2-*d*,3-d_3-labelling are too small for NH_2 or CH_3 modes but are consistent with a contribution from ν(C-C). Hence, the assignment ν(C-O) + ν(C-C) is proposed. Bands ν_{13} and ν_{14}, near 1350 cm^{-1}, clearly originate in the symmetric deformation mode of the methyl group. They occur very close to the position of the corresponding band in free L-alanine (Percy & Stenton 1976*b*) and are significantly sensitive towards 2-*d*,3-d_3-labelling. The small ^{15}N- and *N*,*N*-d_2-sensitivity of ν_{14} indicates some coupling with the NH_2 twisting mode.

The substantial ^{18}O-shifts exhibited by ν_{15} and ν_{16} suggest that they are primarily ν(C-O) bands although coupling with ν(C-C) and an NH_2 mode is indicated by concomitant shifts on 2-*d*,3-d_3- and *N*,*N*-d_2-labelling. The assignment proposed is identical with that given for the analogous glycinate complex (Hodgson *et al.* 1978). The ν(C-CH_3) modes is expected to occur near 1237 cm^{-1}, its value for free L-alanine (Percy & Stenton 1976*b*). The three bands ν_{17}-ν_{19} exhibit isotopic sensitivities which are consistent with this assignment but concomitant ^{15}N-sensitivity in two of them suggests some coupling with the NH_2 twisting mode. The bands ν_{20} to ν_{22} exhibit *N*,*N*-d_2-shifts

which are too small for NH_2 modes but are consistent with those expected for ν(C-N), although considerable vibrational coupling is indicated by sensitivity to the other isotopic labels.

The bands ν_{23} to ν_{30} are highly coupled except for ν_{25} which is a relatively pure ν(C-N) band. The assignments proposed are reasonable in terms of the observed shifts and analogous assignments in the spectrum of $[Pt(gly)_2]$ (Hodgson *et al.* 1978). The band ν_{31}, with its substantial ^{18}O-shift, originates predominantly in the CO_2 rocking mode. Ring deformations are expected below 700 cm^{-1} and the sensitivity of the bands ν_{32}-ν_{34} to all modes of isotopic substitution suggests that they originate predominantly in skeletal vibrations of the chelate ring with some coupling from the CO_2 wagging mode apparent from their ^{18}O-sensitivities.

In the spectrum of $[Pt(gly)_2]$, a band at 497 cm^{-1} has been assigned to the coupled vibration: ν(Pt-N) + ν(Pt-O), no vibrationally-pure ν(Pt-N) band having been observed (Hodgson *et al.* 1978). The shifts exhibited by ν_{35} in the spectrum of $[Pt(L\text{-}ala)_2]$ are practically identical with those of the corresponding band in the spectrum of the glycinate complex. Hence, a similar assignment is proposed. The large shift (18 cm^{-1}) which this band exhibits on substitution of Pd(II) for Pt(II) is also similar to that observed for the glycinate complexes and is consistent with the assignment proposed.

A relatively pure ν(Pt-O) band is observed at 418 cm^{-1}. The frequency is very similar to that (415 cm^{-1}) observed for ν(Pt-O) in the analogous glycinate complex and similar sensitivities to Pd(II) subsititution are also observed for the complexes of the two amino acids. The band at 402 cm^{-1} (ν_{37}) is also ν(Pt-O) but its slight ^{15}N-sensitivity and its greater sensitivity than ν_{36} towards $N,N\text{-}d_2$-

labelling, suggest that it is coupled with a ring deformation mode involving the nitrogen atom.

Below 400 cm^{-1}, bands occur which exhibit sensitivity to several modes of isotopic labelling. These are probably ring deformation bands and bending modes involving the methyl group of coordinated alanine. The absence of a methyl group in glycine explains why this region of the spectrum of the L-alaninate complex is relatively rich in infrared bands.

The L-Pt-L bending modes may be assigned to the bands ν_{42}-ν_{44}. Of these, ν_{43} is sensitive towards ^{15}N- and N,N-d_2-labelling only, suggesting that it originates in δ(N-Pt-N). ν_{44} is only shifted by ^{18}O-labelling and is therefore assigned to δ(O-Pt-O). Band ν_{42} is sensitive to ^{18}O-, ^{15}N- and N,N-d_2-labelling and is therefore probably δ(O-Pt-N).

Influence of Pd(II) substitution on the spectrum of [*Pt(L-ala)*$_2$]

It is now well established that substitution of one coordinated metal ion in a complex by another from a higher transition series leads to an increase in the force constant (and hence vibrational frequency) of the metal-ligand bonds provided that no change in coordination number, symmetry or oxidation state of the metal ion accompanies the substitution (Hulett & Thornton 1973; Thornton 1974). Thus, substitution of Pt(II) in [Pt(L-ala)$_2$] by Pd(II) should lead to a decrease in ν(M-O) and ν(M-N). Although the mass effect will favour higher frequencies for the Pd(II) complex, mass effects have been shown to be heavily diluted in metal chelates (Hulett & Thornton 1973). The data in Table 1 show that all bands assigned to metal-ligand stretching and bending vibrations exhibit a frequency decrease on Pd(II)

substitution and this observation may be cited in support of these assignments.

The effects of metal ion substitution on the metal-ligand frequencies are often further transmitted to affect the frequencies of other vibrations in the molecule. These may vary in parallel with the metal-ligand frequencies or they may exhibit an inverse trend (Haigh *et al.* 1969). The NH_2 rocking modes of coordinated amines are generally very sensitive to metal ion substitution, moving in the same direction as ν(M-N). The data in Table 1 show that many bands assigned to pure or coupled NH_2 rocking and twisting modes exhibit substantially lower frequencies in the Pd(II) L-alanine complex.

Metal ion substitution in amine complexes often causes the ν(N-H) band to move in the opposite direction to ν(M-N) (Engelter *et al.* 1978). This effect is also observed for the L-alanine complexes described here, supporting the assignments for the ν(N-H) bands.

Comparison between present and previous assignments and conclusions

Only one previous assignment study of the alanine complex of Pt(II) has been made (Jackowitz *et al.* 1967). This was based on a normal coordinate treatment, a method which has previously been shown to yield incorrect assignments, especially for the metal-ligand stretching modes, in amino acid complexes (Percy & Stenton 1976*a*, 1976*b*). Thus, the strong 527 cm^{-1} band was not reported, while ν(Pt-N) was assigned to the 418 cm^{-1} band which is now found not to shift at all on ^{15}N-labelling. ν(Pt-O) was assigned to a band at 198 cm^{-1} since it was believed that the M-O bonds in amino acid complexes have largely ionic character, a view that has been invalidated by subsequent infrared studies and X-ray structural work on $[Cd(gly)_2].H_2O$ and isomerism

studies on *trans*-$[Pt(gly)_2]$ which reveal normal M-O bond lengths (Low *et al.* 1959; Niven & Thornton 1978; Pinkard *et al.* 1934).

In conclusion, the frequency shifts which result from multiple isotopic labelling and Pd(II) substitution enable reliable assignments to be provided for most bands in the spectrum of $[Pt(L\text{-}ala)_2]$ over the range 4000 - 140 cm^{-1}. There are few vibrationally-pure bands in the spectrum. This is evident, not only from the observed isotopic shifts, but also from the occurrence of 44 bands in the spectrum of $[Pt(L\text{-}ala)_2]$ compared with 25 for $[Pt(gly)_2]$ over the same spectral range. Since both complexes have *trans*-configuration, it is apparent that a small increase in the complexity of the coordinated amino acid induces a large increase in the complexity of the spectrum.

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Band assignments in the infrared spectrum of *cis*,*cis*-bis(glycinato)*cis*-bis(imidazole)nickel(II) by multiple isotopic labelling

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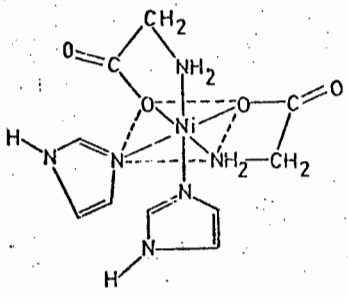
Abstract - The i.r. spectra of *cis*-$[Ni(gly)_2(Him)_2]$ (gly = glycinate ion, Him = imidazole) and its isotopically-labelled analogues have been determined over the range 4000-150 cm^{-1}. ^{18}O-, ^{15}N-, 1-^{13}C-, 2-^{13}C- and 2,2-d_2-Labelling of the coordinated glycinate yields assignments for the internal glycinate modes and the nickel-oxygen and nickel-nitrogen stretching and bending vibrations while deuteration of imidazole (Him-d_3) provides assignments for the internal modes of the coordinated imidazole rings and for the nickel-imidazole vibrations. The results, combined with those of previous multiple isotopic labelling studies on glycinate complexes, enable some general conclusions to be reached on the i.r. spectra of these compounds.

INTRODUCTION

Multiple isotopic labelling of the chelate ring has recently been successfully employed in the assignment of i.r. bands in the spectra of several amino acid complexes [1-5]. The general conclusion emerges from these studies that few bands represent pure, vibrationally-uncoupled modes. Nevertheless, it has proved possible, by labelling all, or almost all, ligand atoms, to provide reasonably firm assignments for each band in the spectrum. The title compound (I) represents the first example to be studied by this technique in which all of the donor atoms in an heterocyclic adduct of a metal glycinate complex have the *cis*-configuration.



(I)

EXPERIMENTAL

Cis-$[Ni(gly)_2(Him)_2]$ was synthesized as described by Rao and Li [6]. The labelled complexes were similarly synthesized from ^{18}O-, ^{15}N-, 1-^{13}C- and 2-^{13}C-labelled glycine of 78, 97, 91 and 91% isotopic purity, respectively, supplied by BOC Prochem Ltd. and 2,2-d_2-glycine and imidazole-d_4 of 97 and 98% isotopic purity, respectively, supplied by

Merck, Sharp and Dohme (Canada) Ltd. Purity of all compounds was established by microanalysis (C,H,N). Infrared spectra were determined on Nujol or hexachlorobutadiene mulls between caesium iodide plates (or, over the range 300-150 cm^{-1}, between polyethylene plates) on a Digilab FTS 16 B/D interferometer and a Perkin-Elmer 180 spectrophotometer.

RESULTS AND DISCUSSION

X-Ray structural determination [7] reveals that the complex (I) is octahedral and the configuration around the metal ion is *cis*-O(carboxyl), *cis*-N(amino), *cis*-N(imidazole). The nickel-ligand bond lengths are characteristic of those determined for *trans*-$[Ni(gly)_2(H_2O)_2]$ and $[Ni(Him)_6](ClO_4)_2$. The molecule has C_i site symmetry.

Figure 1 shows the spectra of the variously-labelled complexes while Table 1 lists the frequencies, isotopic shifts and band assignments. The internal imidazole vibrations and the Ni-N(Him) modes are identified from the band shifts which occur in the Him-d_3-labelled complex while the glycinate and Ni-N(gly) and Ni-O vibrations are distinguished by the shifts which occur on labelling each skeletal atom (and the methylene hydrogen atoms) of the coordinated glycinate groups. The deuteroimine (ND) groups of the imidazole-d_4 ring undergo rapid H-D exchange in air so that synthesis of the labelled complex with imidazole-d_4 yields the imidazole-d_3 complex.

The 4000-2000 cm^{-1} region

The spectrum of free Him in the region 3100-2200 cm^{-1}, consists of a massive envelope of bands atrributed [8,9] to H-bonded N-H stretching modes. This feature and the fact that each molecule of the complex forms ten hydrogen bonds to seven symmetry-related molecules in the crystal [7], vastly complicates the i.r. spectrum in this region. In the absence of ligand labelling, reliable assignments would not be possible. With

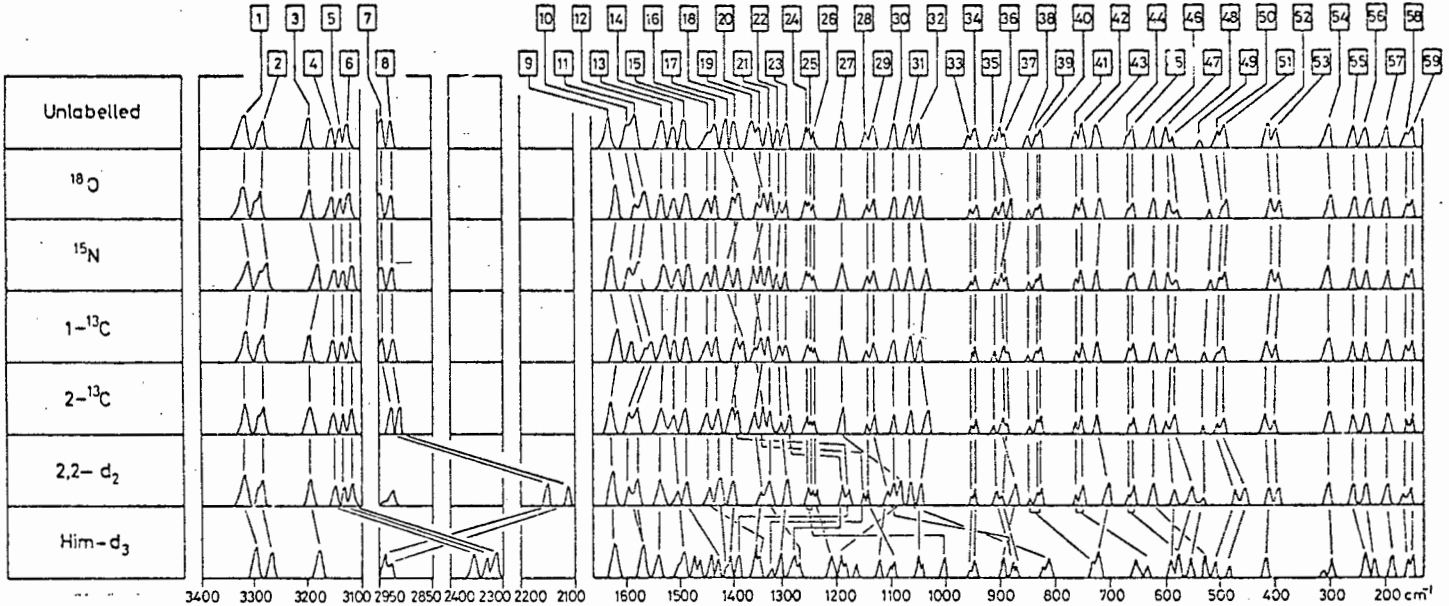


Fig. 1. Infrared spectrum of *cis*-$[Ni(gly)_2(Him)_2]$ and its isotopically-labelled analogues.

Table 1. Frequency and isotopic shift data (cm^{-1}) for the complex *cis*-$[Ni(gly)_2(Him)_2]$. Shifts of $\lesssim 1.5$ cm^{-1} are ignored.

Band*	Frequency	Shift						Assignment
		^{18}O	^{15}N	1-^{13}C	2-^{13}C	2,2-d_2	Him-d_3	
ν_1	3318		8				20	νN-H(gly)
ν_2	3282		7				14	νN-H(gly)
ν_3	3195		7				17	νN-H(gly)
ν_4	3150						790	νC-H(Him)
ν_5	3139						905	νC-H(Him)
ν_6	3127						820	νC-H(Him)
ν_7	2940				13	798		νC-H(gly)
ν_8	2920				5	810		νC-H(gly)
ν_9	1632	9		12		2		νC=O
ν_{10}†	1601	19		35				νC=O
ν_{11}	1586	18		31	2			νC=O
ν_{12}	1541		3	6				NH_2 scissor + νC=O
ν_{13}	1516		5			9	18	NH_2 scissor + ν(Him ring)
ν_{14}	1492						56	ν(Him ring)
ν_{15}	1448					3	100	ν(Him ring)
ν_{16}	1434				4	5	17	CH_2 scissor + ν(Him ring)
ν_{17}	1416	15		19	7	9		νC-O + νC-C(gly)
ν_{18}	1401			4	6	220	9	CH_2 scissor + νC-C(gly)
ν_{19}	1355	20	3	19	5	20	4	νC-O + νC-C(gly) + NH_2 wag
ν_{20}	1344		4		8	193	19	CH_2 wag + NH_2 wag
ν_{21}	1327						57	δC-H(Him)
ν_{22}	1310	4		4	6	18	8	CH_2 wag + νC-C(gly) + νC-O
ν_{23}	1294		3		6	97	16	CH_2 wag + NH_2 wag

Table 1 (continued)

Band*	Frequency	Shift						Assignment
		^{18}O	^{15}N	1-^{13}C	2-^{13}C	2,2-d_2	Him-d_3	
ν_{24}	1257						284	δC-H(Him)
ν_{25}	1253						280	δC-H(Him)
ν_{26}	1245						48	δN-H(Him)
ν_{27}	1188			4	2	104	7	CH_2 twist + νC-C
ν_{28}	1145						45	δN-H(Him)
ν_{29}	1133		3	2	2	28	10	NH_2 twist + νC-C
ν_{30}	1093	2	2				213	δC-H(Him)
ν_{31}	1067						250	δC-H(Him)
ν_{32}	1052		14		18	4	4	νC-N(gly)
ν_{33}	957			11	10	11		νC-C(gly)
ν_{34}	944	3		3	4	4		νC-C(gly) + CO_2 scissor
ν_{35}	916	6		2		4	36	CO_2 scissor + γC-H(Him)
ν_{36}	905	25		7	7	31	10	CO_2 scissor + CH_2 rock
ν_{37}	898						28	δ(Him ring)
ν_{38}	850						118	γC-H(Him)
ν_{39}	834						102	γC-H(Him)
ν_{40}	831						99	γC-H(Him)
ν_{41}	763						129	γC-H(Him)
ν_{42}	753						119	γC-H(Him)
ν_{43}	729	9	2	6	6	23	9	CO_2 rock + CH_2 rock + NH_2 r
ν_{44}	667						112	γ(Him ring)
ν_{45}	664						109	γ(Him ring)
ν_{46}	624						100	γ(Him ring)
ν_{47}	601	4	2	6		18	13	CO_2 wag + chelate ring def.
ν_{48}	583	9	6		2	31	10	CO_2 wag + chelate ring def.
ν_{49}	536	15	7	2	2	5	12	CO_2 wag + chelate ring def.

Table 1 (continued)

Band*	Frequency	Shift						Assignment
		^{18}O	^{15}N	1-^{13}C	2-^{13}C	2,2-d_2	Him-d_3	
ν_{50}	510	11	4	2		42	15	CO_2 wag + νNi-N(gly)
ν_{51}	498	7	2	2		40		
ν_{52}	418	6	6			4	81?	νNi-N(gly) + νNi-O
ν_{53}	401	7	5			4		
ν_{54}	306	6	2	2		2	13	νNi-O + νNi-N(Him) + νNi-N(gly)
ν_{55}	256	4	2		3		21	νNi-N(Him) + δO-Ni-N(gly)
ν_{56}	236	6	2				16	
ν_{57}	203	3		2			15	δO-Ni-O + νNi-N(Him)
ν_{58}	164					2	6	δ(Him)N-Ni-N(Him)
ν_{59}	149							

* Hydrogen bonded νN-H(Him) bands occur at 3093, 3046, 3037, 3015, 2921, 2845, 2832, 2785, 2715, 2690, 2618 and 2595 cm^{-1}

† ν_{10} masks a ν(Him ring) band which becomes resolved from the νC=O band in the 1-^{13}C-labelled spectrum.

labelling, however, the N-H(gly) stretching modes are readily identified by their sensitivities towards ^{15}N-labelling as the group of three bands (ν_1-ν_3) within the range 3350-3150 cm^{-1}. The slight Him-d_3 sensitivity of these bands probably arises from hydrogen bonding between the glycinate and imidazole groups of neighbouring molecules.

The three bands within the range 3150-3100 cm^{-1} (ν_4-ν_6) are clearly C-H stretching modes of Him, being shifted some 800 cm^{-1} to lower frequency by deuteration. They are unaffected by other modes of labelling. The two νC-H(gly) bands (ν_7,ν_8) occur within the range 3000-2800 cm^{-1} where they are identified by their 2,2-d_2-shifts (~800 cm^{-1}) and 2-^{13}C-sensitivities. All other bands within the range 4000-1700 cm^{-1} are assigned to hydrogen-bonded νN-H modes of the imidazole imino group.

The 1650-600 cm^{-1} region

The majority of i.r. bands of free imidazole recur in the spectrum of the complex with the minor shifts and splittings which also characterize the spectra of pyridine complexes [10]. The internal imidazole modes are identified by Him-d_3 sensitivity and absence of sensitivity towards labelling of the glycinate groups while the species of each internal imidazole vibration is allocated according to the extensive deuteration studies of Perchard, Cordes and co-workers [8,9,10] on the imidazole spectrum.

The bands ν_9-ν_{11} are assigned to the carboxylate stretch, νC=O, since they are significantly shifted by ^{18}O- and 1-^{13}C-labelling, only. The NH_2 scissoring mode gives rise to two bands (ν_{12},ν_{13}) at 1541 and 1516 cm^{-1}. These frequencies are considerably lower than that [2] of the corresponding vibration (1610 cm^{-1}) in *trans*-]Ni(gly)$_2$(H_2O)$_2$] as a result of hydrogen bonding and vibrational coupling with νC=O (ν_{12}) or an imidazole ring stretching mode (ν_{13}). Two further imidazole ring stretches (ν_{14},ν_{15}) are identified by their Him-d_3 sensitivities, while the CH_2

scissoring mode (ν_{16}), identified by its sensitivity to 2-^{13}C- and 2,2-d_2-labelling, also comprises a contribution from an imidazole ring stretch. The νC-O band (ν_{17}) is identified by its marked sensitivity to ^{18}O- and 1-^{13}C-labelling but is clearly coupled with νC-C(gly) since it is also 2-^{13}C- and 2,2-d_2-sensitive. In this respect, it resembles the 1412 cm^{-1} band in *trans*-$[Ni(gly)_2(H_2O)_2]$. The NH_2 wagging bands (ν_{19},ν_{20},ν_{23}) are all coupled with other glycinate vibrations.

The in-plane C-H and N-H deformations of the imidazole ring give rise to a set of seven bands within the range 1350-1050 cm^{-1} where they are distinguished from the interspersed glycinate vibrations by their unique sensitivity to imidazole deuteration. The band at 1052 cm^{-1} (ν_{32}) is assigned to νC-N(gly) by its high sensitivity to ^{15}N- and 2-^{13}C-labelling. The position of this band is relatively constant in glycinate complexes [1-5] where it is also characterized by its vibrational purity. The CO_2 scissoring mode spans three bands, none of which is vibrationally pure, within the range 950-900 cm^{-1}.

The out-of-plane C-H deformations of the imidazole ring are identified as a set of five consecutive bands (ν_{38}-ν_{42}) by their Him-d_3 sensitivities. Like their in-plane analogues and the δ- and γ(ring) bands (ν_{44}-ν_{46}), they are all vibrationally pure.

The 600-170 cm^{-1} region

Imidazole yields no bands with frequencies <600 cm^{-1}. Hence, only the CO_2 wagging mode and the various chelate ring deformations of the glycinate group will complicate the assignment of metal-ligand vibrations. The five bands (ν_{47}-ν_{51}) are all sensitive to several modes of labelling and clearly comprise contributions from the CO_2, NH_2 and CH_2 groups of the glycinate ring. Reference to earlier multiple isotopic labelling studies of glycinate complexes [1-5] reveals that a group of such bands characterizes their spectra generally. The extent to which these bands

interfere with the metal-ligand stretching frequency assignments depends on their relative positions. In the present complex, νNi-O and νNi-N(gly) may contribute to ν_{47}-ν_{51} in view of their ^{18}O- and ^{15}N-sensitivities but the band at 418 cm^{-1} (ν_{52}) is significantly sensitive towards ^{18}O- and ^{15}N-labelling only, implying that it originates solely in the coupled vibration νNi-O + νNi-N(gly). The neighbouring band (ν_{53}) at 401 cm^{-1}, exhibits similar isotopic sensitivities except for Him-d_3 labelling where the spectrum reveals an apparently anomalous shift of 81 cm^{-1}. This shift is far too large for a νNi-N(Him) vibration.

The band at 306 cm^{-1} (ν_{54}) is sensitive to ^{18}O-, ^{15}N- and Him-d_3-labelling, suggesting that it comprises contributions from νNi-O, νNi-N(gly) and νNi-N(Him). νNi-O, in *trans*-$[Ni(gly)_2(H_2O)_2]$, occurs as a pure vibration at 334 cm^{-1} [2]. The isotopic sensitivities of ν_{55} and ν_{56} resemble those of ν_{54} but the contributions to νNi-N(Him) from the glycinate portion of the molecule are here more likely to originate in metal-ligand bending modes. The 203 cm^{-1} band (ν_{57}) is sensitive only towards ^{18}O-, 1-^{13}C- and Him-d_3-labelling. It is therefore assigned to νNi-N(Him) + δO-Ni-O, while the band at 164 cm^{-1} (ν_{58}) is sensitive only to Him-d_3 labelling, suggesting its assignment to δ(Him)N-Ni-N(Him).

Although the metal-ligand stretching frequency region of *cis*-$[Ni(gly)_2(Him)_2]$ is expected to be more complex than that of *trans*-$[Ni(gly)_2(H_2O)_2]$ purely on symmetry grounds (both the antisymmetric and symmetric νNi-L bands of the former are i.r.-active) it is clear from the above discussion that the observed complexity of the spectrum of the *cis*-complex cannot be attributed solely to symmetry considerations but must, at least partially, be ascribed to the extent of vibrational coupling in this complex.

CONCLUSIONS

Sufficient multiple isotopic labelling studies have now been performed on glycinate complexes to enable some general conclusions

regarding their infrared spectra to be reached.

1. Very few bands represent vibrationally pure modes. The least-coupled bands are generally, νN-H, νC-H, νC=O and νC-N.
2. Metal-ligand stretching frequencies span a wide range of values with νM-N generally >νM-O. Characteristic values for νM-N are ∿550 cm^{-1} (Cd(II) and Pt(II) chelates) and ∿450 cm^{-1} (Ni(II) chelates) νM-O is characteristically within the range 300-450 cm^{-1}. In many glycinate complexes, νM-O and νM-N are coupled.
3. Octahedral glycinate complexes comprising adducted heterocyclic bases with nitrogen donors commonly yield νM-N(base) bands within the range 150-350 cm^{-1}.

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THC Revised version

Band Assignments in the Infrared Spectrum of *Trans*-bis(glycinato)-platinum(II) by Multiple Isotopic Labelling

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Summary

The infrared spectra (4000-140 cm^{-1}) of the complex *trans*-[Pt(glycinate)$_2$] and its ^{18}O-, ^{15}N-, 1-^{13}C-, 2-^{13}C-, 2,2-d_2- and N,N-d_2-labelled analogues have been determined. Each spectral band has been assigned on the basis of the shifts induced by the various modes of isotopic labelling. The N-H, C-H, C=O and Pt-O stretching vibrations and certain of the CH_2 and NH_2 bending modes are vibrationally pure but all other bands represent vibrationally coupled modes. The spectra reveal that some earlier assignments require revision.

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Introduction

There is some measure of disagreement on the assignment of infrared bands in the spectrum of *trans*-$[Pt(gly)_2]$ and other glycinate complexes[1]. One view[2] assumes low covalency in the M-O bonds with essentially monodentate coordination of the amino acid while another[3] considers the M-O bonds to be highly covalent. Independent normal coordinate analyses[3,4] have not succeeded in unambiguously resolving the problem, the two sets of assignments showing considerable differences. In this paper, isotopic labelling of every ligand atom in *trans*-$[Pt(gly)_2]$ is used to assist in resolving the assignment problem.

Experimental

Trans-$[Pt(gly)_2]$ was prepared by a reported method[5]. The labelled analogues were similarly obtained from ^{15}N-, ^{18}O-, 1-^{13}C- and 2-^{13}C-labelled glycine of (respectively) 95, 74, 92 and 93% isotopic purity supplied by BOC Prochem Ltd. and 2,2-d_2-labelled glycine of 98% isotopic purity supplied by Merck, Sharp and Dohme (Canada) Ltd. $[Pt(gly)_2]$ calc. : C, 14.0; H, 2.4; N, 8.2. Found : C, 14.0; H, 2.4; N, 8.2%. Found for $[Pt(gly\text{-}^{18}O)_2]$: C, 13.7; H, 2.3; N, 8.0%. Found for $[Pt(gly\text{-}^{15}N)_2]$: C, 13.9; H, 2.4; N, 8.6%. Found for $[Pt(gly\text{-}1\text{-}^{13}C)_2]$: C, 14.3; H, 2.3; N, 8.1%. Found for $[Pt(gly\text{-}2\text{-}^{13}C)_2]$: C, 14.4; H, 2.3; N, 8.0%. Found for $[Pt(gly\text{-}2,2\text{-}d_2)_2]$: C, 13.8; H, 3.5; N, 8.0%. The *N,N*-d_2-labelled complexes were similarly prepared in D_2O from samples of glycine (or glycine-2,2-d_2) previously recrystallized from D_2O.

Infrared spectra were determined on nujol mulls (or, in the region of nujol absorption, on hexachlorobutadiene mulls) between caesium iodide plates on a Beckman IR-12 spectrophotometer (4000-250 cm^{-1}) and between

polyethylene plates on a Perkin-Elmer 180 spectrophotometer (250-140 cm^{-1}). Reproducibility of reported bands is better than 0.5 cm^{-1}.

Results and Discussion

The isotopically-induced shifts ($\Delta\nu$) are recorded in Table 1 and the spectra are depicted in Figure 1.

The region 4000-1400 cm^{-1}

Four bands occur within the range 3300-2900 cm^{-1}. The N-H stretching modes (ν_1, ν_2) are readily identified by their sensitivities to ^{15}N- and N,N-d_2-labelling while the neighbouring C-H stretching modes (ν_3, ν_4) are recognised by their sensitivity to 2-^{13}C- and 2,2-d_2-labelling. Shifts of roughly 800 cm^{-1} are induced by deuteration of the NH_2 and CH_2 groups and both modes are vibrationally pure. The band at 1650 cm^{-1} (ν_5) is firmly assigned to ν(C=O), being significantly sensitive towards ^{18}O- and 1-^{13}C- labelling only. The NH_2 scissoring band at 1607 cm^{-1} (ν_6) is recognised by its ^{15}N- and N,N-d_2-sensitivity but is coupled with ν(C=O) since it also exhibits ^{18}O- and 1-^{13}C-sensitivity. The band at 1439 cm^{-1} (ν_7) is uniquely sensitive to 2-^{13}C- and 2,2-d_2-labelling and is therefore assigned to a vibrationally pure CH_2 bending mode. The only difference between the present assignments and those previously proposed[3,6] for bands within the range 4000-1400 cm^{-1} lies in the coupled nature of ν_6 which is now established by isotopic labelling.

The region 1400-600 cm^{-1}

The isotopic shift data reveal that, except for ν_{12} and ν_{13}, all bands within this region originate in extensively coupled vibrations. The bands ν_9, ν_{10} and ν_{11} are all variously-coupled ν(C-O) modes in view of their ^{18}O- sensitivities whereas only ν_9 and ν_{11} have previously been recognized[3,6] as originating in ν(C-O). Earlier assignment[3] of

Table 1 Frequencies, isotopically-induced shifts and infrared band assignments for *trans*-[Pt(gly)$_2$] (cm^{-1})[a)]

	ν	Δν							Assignment
		^{18}O	^{15}N	1-^{13}C	2-^{13}C	2,2-d_2	N,N-d_2	2,2-d_2 + N,N-d_2	
ν_1	3230		4				822	819	ν(N-H) asym.
ν_2	3094						795	797	ν(N-H) sym.
ν_3	2984			2	12	829		823	ν(C-H) asym.
ν_4	2934				4	831		823	ν(C-H) sym.
ν_5	1650	18		29			6	4	ν(C=O)
ν_6	1607	6	2	15		6	400	475	ν(C=O) + NH_2 def.
ν_7	1439				2	374		369	CH_2 def.
ν_8	1431sh	24	5	-[b)]	10	70	56	76	ν(C-O) + ν(C-C) + NH_2 def.
ν_9	1375	5		4	9	18	22	44	ν(C-O) + ν(C-C)
ν_{10}	1333	8		10			25	136	ν(C-O) + NH_2 def.
ν_{11}	1294	5		14	3		247	242	ν(C-O) + ν(C-N) + NH_2 def.
ν_{12}	1247		4				217	239	NH_2 def.
ν_{13}	1187			2		248		256	CH_2 def.
ν_{14}	1026	3	12		18	101	171	234	ν(C-N) + CO_2 def.
ν_{15}	968			8	9	91		111	ν(C-C) + CH_2 def.
ν_{16}	921	31[c)]		3	7	29	31	29	CO_2 + CH_2 defs.
ν_{17}	798	3			2	21	34	58	CO_2 + CH_2 + NH_2 defs.
ν_{18}	754	13		2	5	29	120	125	
ν_{19}	619	8	8	2		9	21	43	CO_2 + NH_2 defs.
ν_{20}	548	3	4	7		53	22	81	coupled ν(Pt-N)
ν_{21}	497	8	5			27	18	39	
ν_{22}	415	11			2	8		10	ν(Pt-O)
ν_{23}	338	3					3	6	δ(O-Pt-O)
ν_{24}	263		4			4	31	42	δ(N-Pt-N)
ν_{25}	150	3				10			δ(Pt-O-C)

a) All shifts are to lower wavenumber. Absence of data implies shift ≤1 cm^{-1}

b) Shoulder

c) Preceded by a residual ^{16}O-band.

ν_{11} to ν(C-N) coupled with the NH_2 wagging mode receives support from the isotopic shift data. Sensitivity of ν_{12} to ^{15}N- and N,N-d_2-labelling only, supports an earlier assignment[3] to the NH_2 twist while agreement with a previous assignment[3] of ν_{13} to the CH_2 twisting mode is now provided by its unique sensitivity to 2-^{13}C- and 2,2-d_2-labelling. Strong sensitivity to ^{15}N- and 2-^{13}C-labelling suggests that ν_{14} is principally ν(C-N) but some coupling with a CO_2 deformation is implied by slight ^{18}O- sensitivity. The bands ν_{15}, ν_{16} and ν_{17} are all variously-coupled CH_2 bending modes of which at least one component of the coupled vibration agrees with earlier assignments[3] The band at 619 cm^{-1}, previously identified[3] as a CO_2 wag, is now seen, from ^{15}N- and N,N-d_2- sensitivities, to be coupled with an NH_2 bending mode. The frequencies of the NH_2 and CH_2 deformations provided by the assignments given above, generally agree well with those previously proposed[3] for these modes.

The region 600-140 cm^{-1}

In this region the metal-ligand vibrations are expected to occur. For the C_i symmetry of the complex, two metal-ligand stretches, ν(Pt-O) and ν(Pt-N), and four bending modes are expected. The suggestion[2,4] that the Pt-O bonds are ionic is discounted by the structural determination[7] of *trans*-[Pt(gly)$_2$] which reveals Pt-O and Pt-N distances consistent with high covalency in both bonds. Similar arguments[3,8] have been advanced for the relatively high value of the ν(Cu-O) frequency in the spectrum of *cis*-[Cu(gly)$_2$(H_2O)]. Both stability constant data[9] and force constant calculations[3] suggest that the metal-ligand stretching frequencies in glycine complexes will increase in the sequence Ni<Cu<Pt. Previous isotopic labelling studies[8,10] on *trans*-[Ni(gly)$_2$(H_2O)$_2$] and *cis*-[Cu(gly)$_2$(H_2O)] confirm the sequence Ni<Cu for ν(M-N) and ν(M-O). Hence, ν(Pt-N) and ν(Pt-O) are expected to exceed the frequencies of the corresponding antisymmetric

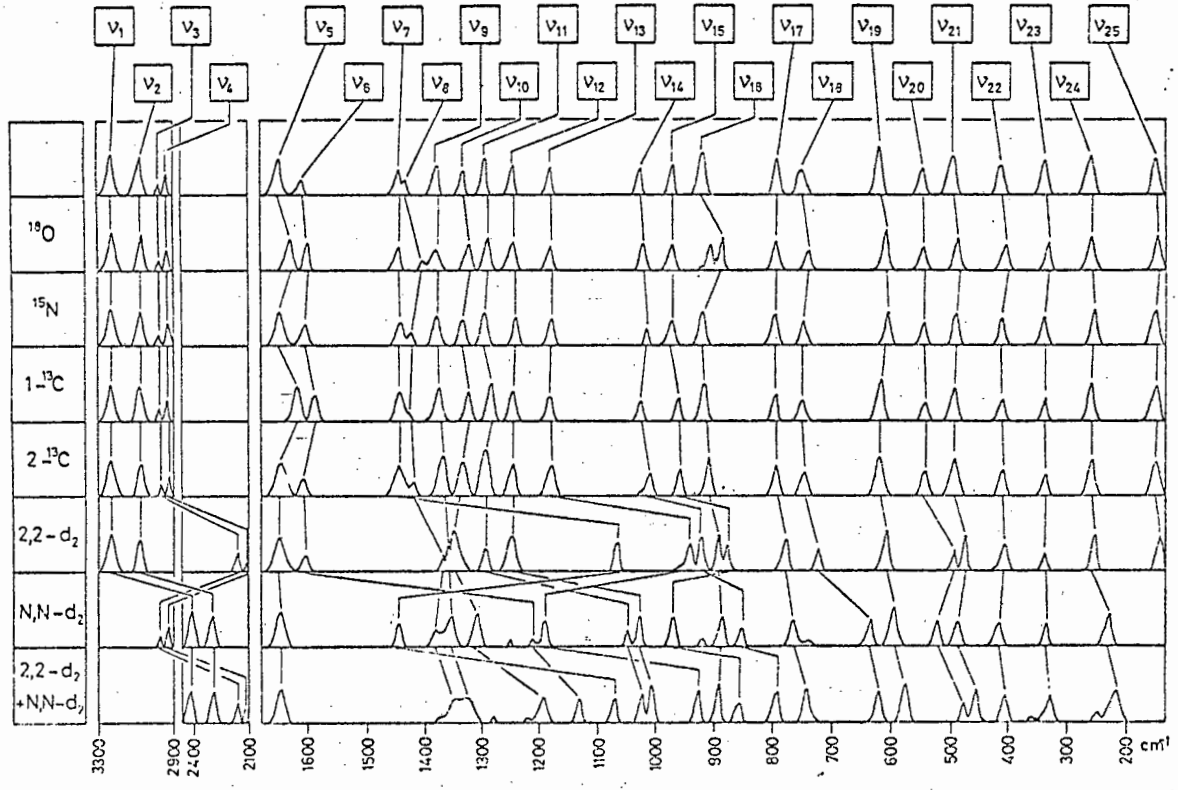

Figure 1. Infrared spectra of *trans*-[Pt(gly)$_2$] and its isotopically-labelled analogues.

vibrations in the Cu(II) glycinate complex (476 and 379 cm^{-1}, respectively). The band at 548 cm^{-1} (ν_{20}) has been assigned[3,6] to ν(Pt-N). While the present results do not invalidate the assignment (since the band is both ^{15}N- and N,N-d_2-sensitive) concomitant sensitivity to ^{18}O- and 1-^{13}C-labelling shows that there is coupling with a vibration involving the CO_2 group. The isotopic sensitivity of the band at 497 cm^{-1} (ν_{21}) is also consistent with its assignment to ν(Pt-N). This band is more sensitive than ν_{20} to ^{18}O-labelling but 2,2-d_2-sensitivity suggests that ν_{21} is also vibrationally coupled.

The band at 415 cm^{-1} (ν_{22}) is firmly assigned to the vibrationally pure ν(Pt-O) mode since it has substantial ^{18}O-sensitivity, no 1-^{13}C-sensitivity (*i.e.* it does not comprise a contribution from a CO_2 deformation) and no ^{15}N- or N,N-d_2-sensitivity. The present assignments of ν_{21} to coupled ν(Pt-N) and ν_{22} to ν(Pt-O) place these frequencies some 30 cm^{-1} higher than the antisymmetric ν(Cu-N) and ν(Cu-O) frequencies of *cis*-$[Cu(gly)_2(H_2O)]$ which is qualitatively consistent with their relative stability constants[9] and coordination numbers[11]. Earlier assignment[4,12] of ν_{22} to ν(Pt-N) is definitely discounted by absence of sensitivity to ^{15}N- and N,N-d_2-labelling.

The band at 338 cm^{-1} (ν_{23}) is significantly sensitive towards ^{18}O-labelling only, although the ^{18}O-shift is smaller than that of ν_{22}; ν_{23} is therefore assigned to the O-Pt-O bending mode. This frequency is again higher, as expected, than the copper-ligand bending frequency in the spectrum of *cis*-$[Cu(gly)_2(H_2O)]$[8]. Absence of ^{15}N-, 1-^{13}C- and 2-^{13}C-sensitivity invalidates previous assignments[4,6,12] of ν_{23} to a CCN bending mode.

The band at 263 cm^{-1} (ν_{24}), sensitive to ^{15}N- and 2,2-d_2-labelling, is assigned to the δ(N-Pt-N) bending mode. Absence of ^{18}O- and 1-^{13}C-

sensitivity invalidates earlier assignments[4,12] to the CO_2 wagging mode coupled with a ring deformation. Finally, ν_{25} at 150 cm^{-1} probably originates in the δ(Pt-O-C) bending vibration in view of its ^{18}O- and 2,2-d_2-sensitivities.

Acknowledgements

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The Infrared Spectra (600-140 cm^{-1}) of the Imidazole, Pyrazine and Pyrimidine Adducts of Cobalt(II), Nickel(II) and Zinc(II) Acetylacetonates

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Summary

The complexes $M(acac)_2(imidazole)_2$ (M = Co or Ni) and $[M(acac)_2B]_n$ (M = Co, Ni or Zn; B = pyrazine or pyrimidine) have been prepared and their i.r. spectra determined over the 600–140 cm^{-1} range. The metal-oxygen and metal-nitrogen stretching frequencies, ν(M–O) and ν(M–N), are assigned on the basis of the band shifts induced by deuteriation of the adducted base and by substitution of the metal ion. Three or four ν(M–C) bands are observed within the 600–200 cm^{-1} range. The two ν(M–O) bands of higher frequency are considered to be coupled with internal ligand modes. Two ν(M–N) bands are observed within the 280–170 cm^{-1} range. The metal-ligand stretching frequencies are in good agreement with the values previously established for these vibrations in the $[M(imidazole)_6]^{2+}$ and $Ni(acac)_2(pyridine)_2$ complexes.

Introduction

Many heterocyclic bases including imidazole (im) and pyrazine (pz) are known to form stable adducts with metal(II) β-ketoenolates[1–5]. Those formed by reaction between monodentate bases, B, such as im and pyridine (py) and the metal(II) acetylacetonate are generally[6, 7] the *trans*-$M(acac)_2B_2$ species whereas bidentate heterocycles such as pz form linear polymers with each of the two nitrogen donors axially bonded to discrete planar $M(acac)_2$ units and formulated as *trans*-$[M(acac)_2B]_n$[8].

Assignments of the metal-ligand stretching frequencies in the bis(pyridine) adducts of Ni^{II} acetylacetonate have been established recently by observing the shifts induced by metal ion substitution and pyridine deuteriation[9]. This paper reports the application of this technique to the im, pz and pyrimidine (pm) adducts of Co^{II}, Ni^{II} and Zn^{II} acetylacetonates.

Experimental

The adducts were prepared by reported methods[2, 4]. Composition and purity were determined by microanalysis (Table 1). Deuteriated complexes were prepared from im-D_4 of 98% isotopic purity and pz-D_4 of 84% isotopic purity supplied by Merck, Sharp and Dohme (Canada) Ltd. The i.r. spectra were determined on nujol mulls between CsI plates

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on a Beckman IR-12 spectrophotometer (600–250 cm^{-1}) and between polyethylene plates on a Perkin-Elmer 180 spectrophotometer (250–140 cm^{-1}). Reflectance spectra were determined on a Beckman DK-2A spectrophotometer.

Table 1. Analytical data and electronic transition energies for base adducts of metal(II) acetylacetonates

Complex	Found (Calcd.)% C	H	N	Transition energy[a]
$Co(acac)_2(im)_2$	48.9 (48.9)	5.5 (5.6)	14.2 (14.3)	9,900 19,100
$Co(acac)_2(im\text{-}D_4)_2$	47.9 (47.9)	7.5 (7.5)	13.9 (13.9)	
$Ni(acac)_2(im)_2$	48.9 (48.9)	5.6 (5.6)	14.2 (14.2)	10,500 17,200
$Ni(acac)_2(im\text{-}D_4)_2$	47.8 (47.9)	7.5 (7.5)	13.9 (14.0)	
$[Co(acac)_2(pz)]_n$	49.9 (49.9)	5.5 (5.4)	8.4 (8.3)	10,100 18,700
$[Co(acac)_2(pz\text{-}D_4)]_n$	49.4 (49.3)	6.5 (6.5)	8.2 (8.2)	
$[Ni(acac)_2(pz)]_n$	49.9 (49.9)	5.4 (5.4)	8.4 (8.3)	10,200 17,400
$[Ni(acac)_2(pz\text{-}D_4)]_n$	49.3 (49.3)	6.4 (6.5)	8.3 (8.2)	
$[Zn(acac)_2(pz)]_n$	48.8 (48.9)	5.2 (5.3)	8.1 (8.2)	
$[Zn(acac)_2(pz\text{-}D_4)]_n$	48.3 (48.4)	6.5 (6.4)	8.0 (8.1)	
$[Co(acac)_2(pm)]_n$	49.8 (49.9)	5.4 (5.4)	8.3 (8.3)	10,300 21,500
$[Ni(acac)_2(pm)]_n$	49.8 (49.9)	5.4 (5.4)	8.3 (8.3)	10,600 17,700
$[Zn(acac)_2(pm)]_n$	48.9 (48.9)	5.3 (5.3)	8.2 (8.2)	

[a] Assigned, in order of increasing energy, to the transitions: $^4T_{2g} \leftarrow {}^4T_{1g}$, $^4T_{1g} \leftarrow {}^4T_{1g}(P)$ (Co complexes) and $^3T_{2g} \leftarrow {}^3A_{2g}$, $^3T_{1g} \leftarrow {}^3A_{2g}$ (Ni complexes).

Results and Discussion

Imidazole behaves as a monodentate ligand towards metal acetylacetonates, forming the $M(acac)_2(im)_2$ species while pz (1,4-diazabenzene) and pm (1,3-diazabenzene) act as bidentate ligands to yield the polymeric adducts $[M(acac)_2B]_n$. The reflectance spectra of the Co^{II} and Ni^{II} complexes of both species are typical[10] of octahedral complexes of these ions (Table 1).

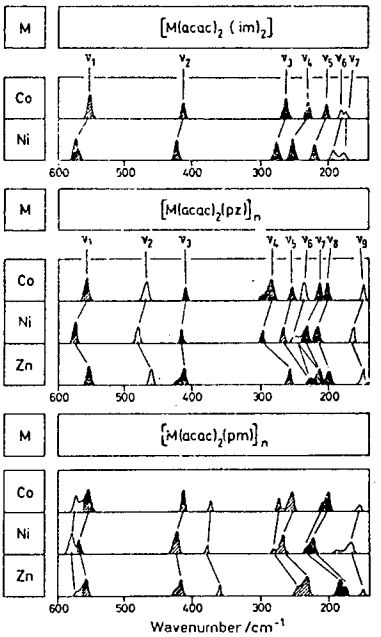

Figure 1. i.r. spectra (600–140 cm^{-1}) of base adducts of metal(II) acetylacetonates. Shaded bands: ν(M–O); solid bands: ν(M–N).

The i.r. spectra are depicted in the Figure and the vibrational frequencies are given in Table 2. In the following discussion, bands shifted by metal ion substitution will be referred to as M-sensitive bands while the term D-sensitive will be used to describe bands which shift to lower frequency on deuteriation of the adducted base. For the isotopic labelling technique, only im and pz were available as their deuteriated analogues, im-D_4 and pz-D_4.

The imidazole adducts, $M(acac)_2(im)_2$ (M = Co or Ni)

Imidazole has no internal ligand vibrations with a frequency < 600 cm^{-1}, nor are there any internal vibrations of

Table 2. Vibrational frequencies and (in parentheses) D-sensitivities of i.r. bands in base adducts of metal(II) acetylacetonates[a]

$M(acac)_2(im)_2$ Co	Ni	$[M(acac)_2(pz)]_n$ Co	Ni	Zn	$[M(acac)_2(pm)]_n$ Co	Ni	Zn	Assignment
556(0)	572(0)	557(0)	577(0)	554(1)	555	566	558	coupled ν(M–O)
416(0)	422(0)	410(0)	417(0)	412(1)	416	423	416	
		469(18)	480(20)	460(16)	374	379	360	pz or pm o.o.p def.
262(3)	278(4)	216(2)	234(2)	217(0)	212	233	184	ν(M–N)
229(2)	253(1)	201(3)	213(2)	202(3)	201	221	175	
202(0)	220(0)	281(0)	298(0)	258(0)	276	28.	248	ν(M–O)
		257(0)	267(0)	227(0)	254	265	231	
		237(1)	252(1)	(227)				ν(M–N) + ν(M–O)?
180(2)	195(4)	148(0)	161(3)	149(2)	155	164	154	δ(L–M–L)
170(0)	174							

[a] cm^{-1}.

coordinated acac in this region. Hence, the seven bands within the 600–140 cm^{-1} range in the spectra of the bis(imidazole) adducts are all assigned to metal-ligand modes. The ν_1 and ν_2 bands are firmly assigned to ν(M–O) for three reasons. Firstly, they are completely insensitive to deuteriation of the imidazole ring. Secondly, they are strongly M-sensitive in the CFSE sequence Co < Ni[9]. Thirdly, their frequencies lie close to those of the ν(M–O) bands in $M(acac)_2B_2$ (M = Co or Ni; B = H_2O or py). In $Ni(acac)_2(py)_2$, the ν(Ni–O) bands are considered[9] to be coupled with the δ(C–Me) mode of the acac ring or with a pyridine ligand mode. That ν_1 and ν_2 are coupled ν(M–O) bands is also proposed here for the im adducts since the M-sensitivity of ν_1 and (especially) ν_2 is lower than that of ν_5 (*vide infra*).

The ν_3 and ν_4 bands are undoubtedly ν(M–N) modes since they are significantly D- and M-sensitive. Their frequencies are very close to those reported[11] for ν(M–N) in the $[M(im)_6]^{2+}$ complexes in which the assignments were based on the metal-isotope labelling technique. Since ν_5 has a higher M-sensitivity than ν_1 or ν_2 but is completely unaffected by deuteriation of im, it is assigned to a vibrationally-pure (uncoupled) ν(M–O) mode. The alternative assignment to δ(O–M–O), proposed[12] for a band in this region of the spectrum of $Cr(acac)_3$, is considered unlikely since this would place the O–M–O bend at a higher frequency than the M–N stretch. ν_6, being both D- and M-sensitive, is either a third ν(M–N) band, δ(O–M–N) or δ(N–M–N). The origin of ν_7 is uncertain since it has no M-sensitivity and is too broad for its D-sensitivity to be determined in the spectrum of the Ni^{11} adduct.

Support for the assignments proposed for ν(M–O) and ν(M–N) is evinced from a comparison between the frequencies for these vibrations in $Ni(acac)_2(py)_2$[9] and $Ni(acac)_2(im)_2$. As is well known[9], any increase in the strength of the M-base bond on replacing one adducted base by another causes a shift in ν(M–O) towards lower frequency. Since ν(Ni–N) in the im adduct exceeds ν(Ni–N) in the py adduct, the reverse trend is expected for ν(Ni–O). This is observed.

The pyrazine adducts, $[M(acac)_2(pz)]_n$ (M = Co, Ni or Zn)

Below 600 cm^{-1}, pz exhibits one internal ligand mode, an out-of-plane deformation of the heterocyclic ring at 412 cm^{-1} with a D-sensitivity of 14 cm^{-1}. This band recurs in the spectra of the pz adducts in the 470 cm^{-1} region (ν_2, Figure). As has been observed for the py adducts[13], coordination of pz leads to an increase in the frequency of such internal ligand vibrations. The D-sensitivity which this band retains in the spectra of the pz-D_4 adducts enables it to be readily distinguished from the D-insensitive bands near 560 cm^{-1} (ν_1) and 420 cm^{-1} (ν_3). The latter two bands are assigned to coupled ν(M–O) on the grounds of their absence of D-sensitivity and their high M-sensitivity in the CFSE sequence Co < Ni > Zn.

Of the four (or five) bands within the 300–200 cm^{-1} range, only the two of lowest frequency (ν_7, ν_8) exhibit significant D-sensitivity, establishing them firmly as ν(M–N) bands. Their position near 200 cm^{-1} agrees well with that of the two ν(M–N) bands in the spectrum of $Ni(acac)_2(py)_2$[9]. The assignment is also supported by the strong M-sensitivity of these bands in the sequence Co < Ni > Zn. Of the remaining two (or three) bands (ν_4, ν_5, ν_6) within the 300–200 cm^{-1} range, ν_4 and ν_5 are assigned to vibrationally-pure ν(M–O) modes on the grounds of their absence of D-sensitivity, their significant M-sensitivity in the sequence Co < Ni > Zn, the occurrence of bands in this region in the spectra of the $M(acac)_2(H_2O)_2$ complexes (M = Co or Ni) and $Zn(acac)_2(H_2O)$ which undoubtedly have the same origin and the established[9] existence of two ν(M–O) bands in this region of the spectra of $M(acac)_2(py)_2$ and $Zn(acac)_2(py)$. The bands below 200 cm^{-1} are considered to originate in metal-ligand bending vibrations.

The pyrimidine adducts, $[M(acac)_2(pm)]_n$ (M = Co, Ni or Zn)

Pyrimidine has only one ligand band below 600 cm^{-1}, namely at 348 cm^{-1}. The spectra of the adducts yield four bands within the 600–300 cm^{-1} range. The band of lowest frequency is considered to correspond with the pm ligand band since it is raised 31 cm^{-1} by coordination, a shift characteristic[13] of the shift in the out-of-plane ring vibration on complexation of nitrogen heterocyclics. Of the remaining three bands, that near 420 cm^{-1} and the more M-sensitive of the two bands near 570 cm^{-1}, are assigned to coupled ν(M–O) modes. Assignment of the two uncoupled ν(M–O) and the two ν(M–N) bands between 300 and 170 cm^{-1} is made by analogy with the assignments of the corresponding py and pz adducts.

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THE INFRARED SPECTRA OF SOME METAL(II) GLYCYLGLYCINATE COMPLEXES : ASSIGNMENTS AND STRUCTURAL ASPECTS

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ABSTRACT

The infrared spectra (4000 - 140 cm^{-1}) of the complexes [Cu(Hgg)X] (Hgg = monoanionic glycylglycinate anion, X = Cl, Br), [M(Hgg)X(H_2O)] (M = Mn, Cu, Zn, X = Cl; M = Co, Ni, X = Cl, Br) and their ^{15}N-labelled analogues, are discussed in relation to their known or proposed structures. Firm assignments are presented for the majority of the internal ligand modes and for metal-ligand vibrations on the basis of the band shifts resulting from ^{15}N-labelling, metal ion substitution and halogen substitution.

INTRODUCTION

The solid state infrared spectra of metal peptide complexes have received very little attention [1,2]. This is undoubtedly due to the diversity of their composition and structure[3], their far greater complexity

than those of simple amino acid complexes and the difficulty of applying reliable assignment techniques.

In an earlier paper[4], it was shown that infrared spectra could be used to distinguish between several stoichiometrically and structurally distinct species of metal glycylglycinate complexes but no firm assignments could be provided for internal ligand vibrations and none at all for metal-ligand modes. This communication presents the first reported assignments for glycylglycinate complexes based on isotopic labelling. It will be shown that ^{15}N-labelling enables firm assignments to be made for certain ligand and metal-ligand modes in the complexes [Cu(Hgg)X] (X = Cl, Br) and, combined with the effects of metal ion substitution, in the complexes [M(Hgg)X(H_2O)] (M = Mn, Co, Ni, Cu, Zn). Hgg is used as an abbreviation for monodentate glycylglycinate.

EXPERIMENTAL

The unlabelled complexes were prepared by reported methods[2,4]. The labelled analogues were similarly obtained from glycylglycine-$^{15}N_2$ of 99% isotopic purity supplied by Stohler Isotope Chemicals, Inc. Composition and purity of all compounds were established by micro-analysis (C, H, N). Infrared spectra were determined on nujol mulls between caesium iodide plates (or, below 250 cm^{-1}, between polyethylene plates) on a Perkin-Elmer 180 spectrophotometer.

RESULTS AND DISCUSSION

The frequencies of the complexes discussed here are reported in Tables 1 and 2.

The Spectra of [Cu(Hgg)X] (X = Cl, Br)

These complexes are considered to have a structure (Fig. 1a) similar to that established[5] crystallographically for the bis(glycylglycinato)-cobalt(III) ion. As will be shown, certain features of the infrared spectra

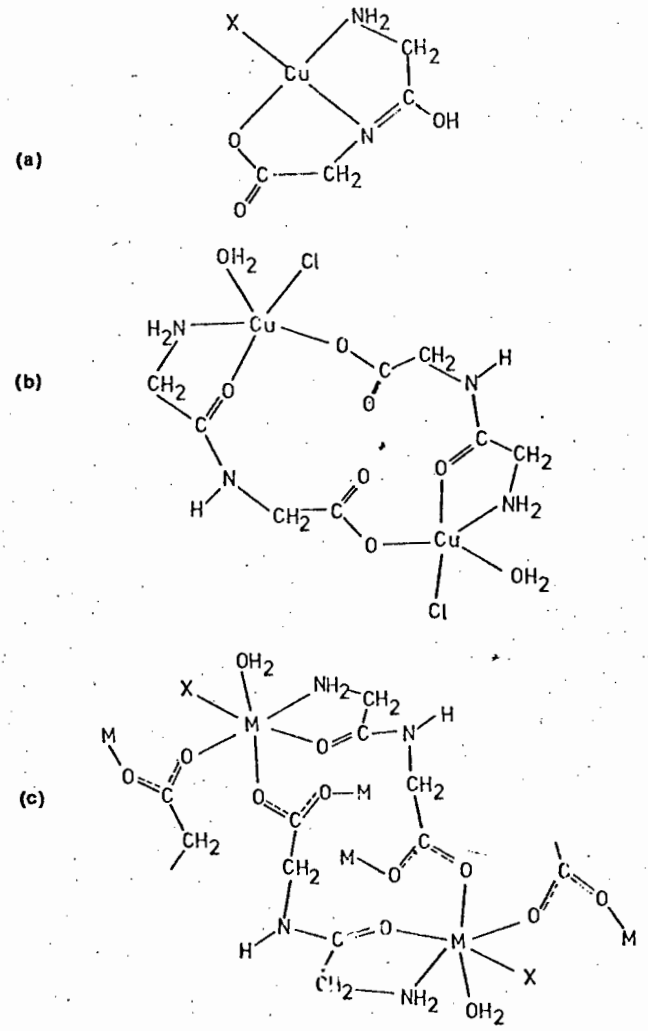

Figure 1. Structures of glycylglycinate complexes: (a) [Cu(Hgg)X], (b) [Cu(Hgg)Cl(H_2O)], (c) [M(Hgg)X(H_2O)] (M = Mn, Co, Ni, Zn).

support the proposed structure. The three significantly ^{15}N-sensitive bands above 3000 cm^{-1} are assigned to the N-H stretching modes of the coordinated amino group, the band at 3112 cm^{-1} resulting from strong N-H---O hydrogen bonding. The ^{15}N-insensitive shoulder at 3261 cm^{-1} is assigned to the O-H stretch of the iminol moiety. The four bands within the range 3100 - 2900 cm^{-1} are completely unaffected by labelling and are therefore assigned to ν(C-H).

Absence of any ^{15}N-insensitive amide I ν(C=O) band within the 1650 - 1600 cm^{-1} region confirms the absence of an amide group as suggested by the proposed structure. Instead, this region comprises a ^{15}N-sensitive band which is assigned to the ν(C=N) mode, being very close to its position[6] in *N*-alkylsalicylaldimine complexes of Cu(II). The carboxylate ν(C=O) band appears below 1600 cm^{-1}. Slight ^{15}N-sensitivity in the bromo complex suggests some coupling with the NH_2 scissoring mode which gives rise to two ^{15}N-sensitive bands in the 1580 - 1560 cm^{-1} region.

From published papers on the spectra of variously-labelled glycinate complexes [7-9], the ν(C-C), ν(C-O) and CH_2 deformations are expected to occur within the 1500 - 1300 cm^{-1} region. Four ^{15}N-insensitive bands within this region are accordingly assigned to these modes. The NH_2 twisting mode gives rise to two ^{15}N-sensitive bands, while four such bands appear in the ν(C-N) region (1100 - 1000 cm^{-1}). Bands insensitive to ^{15}N-labelling near 930 cm^{-1} are assigned to the CO_2 scissoring vibration by analogy with earlier work[7-9] on glycine complexes while, for similar reasons, ^{15}N-sensitive bands near 900 and 750 cm^{-1} are assigned to NH_2 deformations.

Ring deformation modes generally occur within the 750 - 550 cm^{-1} region of glycine complexes[7-9] and are observed here as a group of moderately ^{15}N-

TABLE 1

Vibrational frequencies (cm^{-1}), ^{15}N-induced shifts (cm^{-1}, in parentheses) and infrared band assignments for [Cu(Hgg)X] (X = Cl, Br). Shifts <1 cm^{-1} ignored.

Frequency (shift) X=Cl	Frequency (shift) X=Br	Assignment
3325(6)	3321(10)	ν(N-H)
3268(8)	3291(12)	ν(N-H)
3261sh	3261sh	ν(O-H)
3112(20)	3112(19)	ν(N-H---O)
3012	3008	ν(C-H)
2970	2969	ν(C-H)
2938	2934	ν(C-H)
2924sh	2924sh	ν(C-H)
1642(5)	1641(10)	ν(C=N)
1594	1591(3)	ν(C=O)
1579(7)	1578(8)	NH_2 scissor
1562sh(8)	1562(11)	NH_2 scissor
1419	1422	ν(C-C), ν(C-O) and CH_2 def.
1392	1392	ν(C-C), ν(C-O) and CH_2 def.
1371	1367	ν(C-C), ν(C-O) and CH_2 def.
1301	1301	ν(C-C), ν(C-O) and CH_2 def.
1273(2)	1276(3)	NH_2 twist
1251(2)	1253(2)	NH_2 twist
1100(4)	1102(5)	ν(C-N)
1086(11)	1086(11)	ν(C-N)
1038(9)	1037(9)	ν(C-N)
1023(8)	1023(9)	ν(C-N)
937(2)	935	CO_2 scissor
927	930	CO_2 scissor
896(3)	896(2)	NH_2 wag
746(3)	740(4)	NH_2 rock
720	720	ring def.
715(3)	699(2)	ring def.
612(5)	619(4)	ring def.
588(2)	591(3)	ring def.
567(3)	570(2)	ring def.
503(8)	506(8)	ν(Cu-N)
393(1)	390(5)	coupled ν(Cu-N)
363(2)	360(3)	coupled ν(Cu-N)
324(3)	317(3)	coupled ν(Cu-N)
271	271	ν(Cu-O)
262	235	ν(Cu-X)
187	170	δ(L-Cu-L)
160	151	δ(L-Cu-L)

sensitive bands. The most substantially ^{15}N-sensitive band occurs near 500 cm^{-1} and is assigned to ν(Cu-N). Since both nitrogen atoms of the complex are labelled, a firm distinction between the two species of ν(Cu-N) bands is not possible. Moderately ^{15}N-sensitive bands within the 400 - 300 cm^{-1} region may originate in variously-coupled ν(Cu-N) modes. The 271 cm^{-1} band is the first completely ^{15}N-insensitive band below 700 cm^{-1} and is thus firmly assigned to ν(Cu-O). The neighbouring 262 cm^{-1} band (X = Cl) is also ^{15}N-insensitive and is firmly assigned to ν(Cu-Cl) since it shifts to 235 cm^{-1} on substitution of Br for Cl. Lower frequency bands are assigned to metal-ligand bending modes.

TABLE 2

Vibrational frequencies (cm^{-1}), ^{15}N-induced shifts (cm^{-1}, in parentheses) and infrared band assignments for $[M(Hgg)Cl(H_2O)]_n$ (M = Mn, Co, Ni, Cu, Zn)[a]

Mn[b]	Co	Ni	Cu	Zn[b]	Assignment
3455	3450	3460	3450	3500	ν(O-H) (water)
3380	3389	3385	3425	(broad)	
3360	3362(8)	3360(9)	3327(8)	3329	ν(N-H) (amino)
3345	3345(7)	3344(9)	3290(7)	3278	
3270	3277(6)	3369(3)	3257(5) 3218(4)	3240	ν(N-H) (amide A)
3180	3170(7)	3180(9)	3167(15)	3158	amide B
3000	3003	3006	2989 2976	3107 3006	ν(C-H)
2950	2948[c]	2950	2953	2961	
2930	2932	2933	2932	2930	
1644	1643	1642	1642(3)	1650	ν(C=O) (amide I)
1615	1617	1617	1607	1616	
1571	1571	1572	1627(3)	1566	ν(C=O) (carboxyl)
1544	1549(17)	1551(14)	1576(16) 1553(23)	1558	δ(N-H) (amide II)
1584	1591(5)	1593(3)	1586(6)	1576	NH_2 scissor
-d	-d	-d	-d	-d	coupled ν(C-O)
1273	1271(2)	1271	1282[c](2)	1278	coupled δ(NH_2)
1256	1256(2)	1257(2)	1259(2)	1268	
1104	1101(8)	1100(8)	1102(12)	1108	coupled ν(C-N)
1062	1062(8)	1065(7)	1092(7) 1048(16)	1077	
1029	-e	1030(10)	1028(7)	1029	
999	1017(22)	1023(13)	1020(10)	1026	
932	935	935	937	936	CO_2 scissor
922	925	925	928 918	930	
890	893(4)	895(3)	895(3)	888	δ(NH_2) + δ(N-H)
883	886(3)	889(4)	749(7)	759	
749	753(2)	757(2)	723(3)	724	
723	718(5)	723(2)	707(2)		
	663		645(5)		CO_2 rock + ring def.
624	624	624	618	612	
596	603(2)	608(2)		601	
567	577(2)	595(3)	589(2)		
548	570(3)	573(4)		562	
491	532	537(2)	550(2)	539	
439	467(11)	481(8)	506(8)	478	ν(M-NH_2)
402	418	431	450(2)	435	ν(M-O)
346	360(4)	367(2)	368(2)	369	ligand (?)
259	285	299	306(2)	275	ν(M-O)
	272[f]	293[f]	300	270	ν(M-Cl) + ν(M-O)
210	227	256(8)	268	250	δ(L-M-L)
	195	205	207	189	
183	185	195	196		
	154	171	180	158	

[a] Shifts <1 cm^{-1} ignored. [b] These complexes were not labelled. [c] Mean of doublet. [d] 6 or 7 ^{15}N-insensitive bands occur within the range 1440-1309 cm^{-1}. [e] Masked in unlabelled complex but observed in labelled complex. [f] In the bromo complexes, ν(M-Br) occurs at 226 cm^{-1} (M = Co) and 220 cm^{-1} (M = Ni).

The Spectra of $[M(Hgg)Cl(H_2O)]$ (M = Mn, Cu, Zn, X = Cl; M = Co, Ni; X = Cl, Br)

Frequencies for the chloro complexes are reported in Table 2. The two bromo complexes (M = Co, Ni) yield frequencies and isotopic shifts which, except for ν(M-X), are very similar to those of the chloro analogues.

The structure of the Cu(II) complex has been determined[10]. The dinuclear complex (Fig. 1b) comprises Hgg^- ligands coordinated to one Cu(II) ion through the amino nitrogen and peptide oxygen atoms and to the second Cu(II) ion through carboxylate oxygen atoms. The infrared spectrum is consistent with the structure. The spectrum also broadly resembles those of the corresponding Mn(II), Co(II), Ni(II) and Zn(II) complexes but certain differences to be discussed below indicate that the latter complexes differ in that each metal ion achieves essentially octahedral coordination by bridging via the carboxylate oxygen atoms of neighbouring dimers in the manner crystallographically established[11] for the analogous Cd(II) complex (Fig. 1c). The magnetic moment of the Ni(II) complex[2] (X = Cl) is consistent with such octahedral coordination. In the ensuing discussion, cited frequencies refer to the complexes with X = Cl. Only the Co(II), Ni(II) and Cu(II) complexes were ^{15}N-labelled. Since the assignments for many of the internal ligand modes follow those presented in the previous section, only those which differ and the metal-ligand modes will be discussed below.

Significant differences in the ^{15}N-sensitive bands exist between the spectra of [Cu(Hgg)X] and $[M(Hgg)X(H_2O)]$. The latter complexes comprise peptide links while the former do not. Thus the $[M(Hgg)X(H_2O)]$ complexes yield ^{15}N-sensitive amide A and B bands within the range 3300 - 3100 cm^{-1}.

A further distinction occurs in the 1650 - 1600 cm^{-1} region where the amide I $\nu(C=O)$ mode is observed as a ^{15}N-insensitive pair of bands, the carboxylate $\nu(C=O)$ mode appearing at lower frequency. The amide II $\delta(N-H)$ bands occur as ^{15}N-sensitive bands near 1550 cm^{-1}. The observation that the carboxylate $\nu(C=O)$ frequency in the Cu(II) complex at 1627 cm^{-1} is some 60 cm^{-1} higher than the frequencies for the corresponding vibration in the complexes of the remaining metal ions, supports the suggestion that only the Cu(II) complex is dimeric, the remaining complexes involving cross-linking of the dimers through the carboxylate oxygen atoms to neighbouring dimers. This feature contrasts strongly with the amide I $\nu(C=O)$ band where the spectrum of the Cu(II) complex does not differ from the complexes of the other metal ions.

The band within the range 506 - 439 cm^{-1} is assigned to $\nu(M-NH_2)$ since it is the most significantly ^{15}N-sensitive band in this region and also in view of its strong M-sensitivity which is in the Irving-Williams stability sequence Mn < Co < Ni < Cu > Zn. The neighbouring band within the range 450 - 400 cm^{-1} is similarly M-sensitive but is completely unaffected by ^{15}N-labelling and is therefore assigned to the stretching vibration of one of the three species of metal-oxygen bonds present in these complexes. Another $\nu(M-O)$ band with similar features occurs within the range 310 - 250 cm^{-1}. The neighbouring band to lower frequency is assigned to $\nu(M-O) + \nu(M-Cl)$ since it is ^{15}N-insensitive, M-sensitive and, in the bromo complexes of Co(II) and Ni(II), gives rise to additional ^{15}N-insensitive bands at 227 and 220 cm^{-1}, respectively. Lower frequency bands are assigned to the metal-ligand bending modes.

The fact that all of the metal-ligand stretching frequencies are in the Irving-Williams sequence Mn < Co < Ni < Cu > Zn rather than in the sequence of crystal field stabilization energies: Mn < Co < Ni > Cu > Zn, is consistent with the view that the Cu(II) complex has a lower coordination number than that of the remaining complexes.

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