ISOTOPIC LABELLING: APPLICATION TO BAND ASSIGNMENTS IN THE INFRARED SPECTRA OF METAL COMPLEXES

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CONTENTS

I INTRODUCTION

II EXPERIMENTAL

III RESULTS

IV DISCUSSION

ABBREVIATIONS

DH_2	dimethylglyoxime
acac	acetylacetonate anion
phth	phthalimido anion
py	pyridine
pyO	pyridine *N*-oxide
Him	imidazole
quin	quinoline
am	amine
ν	infrared stretching mode
δ	infrared in-plane bending mode
γ	infrared out-of-plane bending mode
τ	infrared torsional mode
X	generalized halide
B	generalized base
M	generalized metal ion

PUBLICATION

Part of this work has been published as follows:

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SUMMARY

The technique of isotopic labelling is discussed in relation to its application to band assignments in the infrared spectra of metal complexes. ^{15}N- and ^{2}H-labelling are applied to three classes of transition metal coordination compounds.

The infrared spectra (1700 - 140 cm^{-1}) of the cobaloximes [CoX(DH)$_2$py] (DH = dimethylglyoximate monoanion; py = pyridine; X = Cl, Br, I, CH$_3$) are discussed. ^{15}N-Labelling and deuteration of the coordinated pyridine provide firm assignments for the pyridine ligand vibrations and νCo-N(py) while ^{15}N-labelling of the chelated dimethylglyoximate ion provides assignments for its skeletal vibrations and νCo-N(DH). The νCo-X bands are assigned on the basis of their sensitivity to the nature of X and their absence of sensitivity to any of the modes of isotopic labelling employed. νCo-N(DH) occurs near 510 cm^{-1} and νCo-N(py) near 450 cm^{-1}. νCo-X occurs within the range 300 - 400 cm^{-1}. The assignments are discussed in relation to those proposed on the basis of earlier empirical methods.

The internal vibrations of uncoordinated dimethylglyoxime are assigned on the basis of shifts observed in the spectra of dimethylglyoxime-^{15}N and dimethylglyoxime-d_2.

The preparation and infrared spectral characterization of the linkage isomers [Co(CNS)(DH)$_2$py] are discussed. Vibrations involving the thiocyanate group are established by ^{15}NCS labelling. The M-SCN complexes exhibit sharp νSC-N bands at 2112 and 2028 cm^{-1} and νCo-SCN at 356

cm^{-1}. In the Co-NCS complexes νSC-N occurs as a broad band at 2122 cm^{-1} while νCo-NCS is at 376 cm^{-1}. Distinction between the two forms of the complex is proposed on the basis of their infrared spectra.

The infrared spectra of four base adducts of vanadyl acetylacetonate were investigated by means of isotopic labelling. Deuteration of the bases enables the assignment of vibrations originating in the base, while bands insensitive to labelling are ascribed to the acetylacetonate ligand vibrations and the V-O modes. The νV=O and νV-O vibrations are shifted to lower frequency by adduct formation. In the imidazole adduct, these shifts were unusually large and νV-O bands were split, suggesting that this complex has a *cis*-configuration while the pyridine, pyridine *N*-oxide and quinoline adducts have *trans*-configurations. A band occurring between 186 and 197 cm^{-1}, which is sensitive to deuteration of the base is assigned to νV-B. In the $VO(acac)_2quin$ complex the V-N bond is particularly weak and νV-N probably occurs below 140 cm^{-1}.

A series of twelve alkylamine complexes of copper(II) and nickel(II) phthalimide have been prepared and their infrared spectra determined over the range 800 - 140 cm^{-1}. The νM-N(phth) bands near 300 cm^{-1} are identified by their sensitivity to ^{15}N-labelling of the phthalimide nitrogen atom while vibrations involving the amines are identified by their sensitivity to deuteration of the amino group. The dissimilarity between the spectra of the copper and nickel complexes suggests structural differences between the compounds of the two metal ions. The phthalimide ligand bonds to the copper ion via the nitrogen atom. νCo-N(phth) occurs near 300 cm^{-1}. However no firm assignment of νNi-N(phth) can be made, suggesting that in the nickel complexes, the phthalimido ion adopts the *keto* form, bonding to the nickel via the oxygen atom.

I INTRODUCTION

1 BAND ASSIGNMENTS IN THE INFRARED SPECTRA OF TRANSITION METAL COMPLEXES

Arising from the infrared spectra of coordination compounds, the metal-ligand vibrations provide the most useful information regarding structural and bonding problems. Hence, unambiguous assignment of these vibrations is of importance to the coordination chemist. During the past two decades, considerable progress has been made in this field. It has been established that metal-ligand vibrations generally appear in the low frequency (<600 cm^{-1}) region of the infrared spectrum. This results from the comparatively small force constants of the metal-ligand bonds and the relatively high mass of the metal ion. Interpretation of the spectra in this region can be difficult, expecially as the complexity of the system under investigation increases. This is due in part to the multiplicity of bands originating in metal-ligand and activated ligand vibrations, intermolecular interactions such as hydrogen bonding and lattice modes and vibrational coupling of bands with similar force constants.

Various procedures have, in the past, been used for the interpretation of low frequency infrared spectra. Empirical methods employ, for instance, comparisons between the spectra of the metal complex and the free ligand. A band occurring in the spectrum of the complex but not in that of the ligand may be assigned to a metal-ligand vibration. This can, however, only serve as a first approximation since the assignments may become ambiguous if ligand vibrations activated by complex formation occur in the same region as the metal-ligand vibrations. Useful comparisons can also be made between the spectra of a series of complexes in which a common metal ion is coordinated to a series of similar ligands (eg. Cl, I, Br). In these cases the metal-ligand vibrations are expected to vary within a frequency range determined by the electronic and mass differences between the ligands. The crystal field approach to the interpretation of infrared spectra of metal complexes [1 - 3] has been successfully applied to a number of systems [4 - 10]. In this approach, if the transition metal ion is varied through a series of isostructural complexes of a common ligand, the metal ligand vibrations follow the variation in crystal field stabilisation energies of the respective metal ions. The metal-sensitive bands are then attributed to metal-ligand vibrations. Theoretical calculations based on normal coordinate analyses have been used to predict the frequencies of metal-ligand vibrations. However, this method requires a prior knowledge of structural parameters such as bond lengths and angles. These parameters are not always available. Furthermore such calculations are usually based on a simplified model of the coordination complex and often yield results which have been found to be in conflict with other methods of assignment, expecially for molecules with a degree of complexity. Polarised infrared spectra of single crystals complemented with Raman spectroscopy is another method which has been used successfully.

The technique of isotopic labelling provides a simple yet extremely effective means of interpreting infrared spectra. It proves particularly useful in making firm assignments for metal-ligand vibrations of metal complexes in the low frequency region of the spectrum, and is invaluable for systems where molecular (and hence vibrational) complexity excludes the use of experimentally simpler methods.

The frequency of a vibrating molecule is related to the force constant between the vibrating atoms and the masses of the atoms. Isotopic labelling employs the concept of varying the mass of one or more of the atoms in the complex by substitution with an isotope of significantly different mass. Stable non-radioactive isotopes are conveniently used. This has the effect of changing the frequency of any vibration which involves the labelled atom (relative to that of the unlabelled compound).

The isotopic substitution of an atom in a compound does not affect its chemical properties. Thus any resulting shift in frequency of an infrared band may be attributed solely to the mass effect of the labelled atom. It follows that the shifted band may be unambiguously assigned to a vibration involving the labelled atom. The magnitude of shifts observed in the spectra depend on the ratio of the masses of the labelled and unlabelled atoms, *i.e.* the larger the mass differences the greater the isotopic shifts. A good approximation to the expected shift may be calculated if one considers the vibrating molecule to be a simple harmonic oscillator [11]. The vibrational frequency of a diatomic molecule may then be represented:

$$\nu = \frac{1}{2\pi c}(k/\mu)^{\frac{1}{2}} \qquad (1)$$

where k = force constant of oscillator

μ = reduced mass of the molecule

c = velocity of light

When compared with the similar expression for the isotopically labelled molecule:

$$\nu^{i} = \frac{1}{2\pi c}(k/\mu^{i})^{\frac{1}{2}} \qquad (2)$$

the ratio $$\nu^{i}/\nu = (\mu/\mu^{i})^{\frac{1}{2}} \qquad (3)$$

whence the frequency (ν^{i}) of the band in the labelled molecule may be calculated.

Equation 3 can be effectively used to calculate isotopic shifts for stretching and bending modes in polyatomic metal complexes, the diatomic species in the molecule being considered to behave as a free diatomic molecule. Experience shows that the approximation is valid,and good agreement with observed values is generally obtained when most of the vibrational energy is centred in the bond in question. Coupling of vibrational modes brings about deviations from the expected values. Such deviations generally lead to a shift which is progressively smaller than the calculated shift, the greater the extent of coupling.

Two types of labelling are possible in coordination complexes: metal labelling and ligand labelling. Labelling of the metal ion has the distinct advantage of differentiating between metal-ligand vibrations and internal ligand vibrations which may occur in the same frequency range. This method of labelling has been used successfully in assigning metal-ligand vibrations for a number of systems [12]. These include the use of metal isotopes such as ^{50}Cr, ^{53}Cr, ^{62}Ni, ^{65}Cu, ^{64}Zn, ^{68}Zn, ^{104}Pd and ^{124}Sn. However, the unfavourable mass ratio μ/μ^{i} between the labelled and unlabelled ions often results in very small calculated (and therefore observed) shifts. A further drawback of this method is its failure to distinguish between different metal-ligand vibrations (eg. νM-X and νM-N) within the same complex. It is also limited to the few metal ions for which affordable isotopes with a suitable mass difference exist. In the alternative form of labelling, one or more atoms on the ligand are substituted with a heavier isotope. This method is more versatile than metal labelling and usually produces larger isotopic shifts because of the more favourable mass ratio. It has the added advantage of enabling distinction between the different metal-ligand vibrations in the same complex but cannot differentiate between metal-ligand and neighbouring internal ligand vibrations involving the labelled atom. Furthermore its usefulness in inducing isotopic shifts is not confined to the low frequency region but can be used throughout the entire spectrum to confirm assignments of vibrations originating in the ligand itself. The most commonly used labelled atoms are ^{2}H, ^{15}N, ^{18}O and ^{13}C, which have been used in a wide variety of coordination complexes of organic ligands. ^{2}H-induced shifts are generally the largest. N-^{2}H Shifts of ~1000 cm^{-1} have been observed, while C-^{2}H shifts may be as large as 700 cm^{-1}. The magnitude of these shifts do however introduce problems in the more complex organic compounds. Because some bands shift more than others or undergo changes of intensity on labelling, it may become difficult to ascertain which band in the spectrum of the labelled complex corresponds with a particular band in the spectrum of the unlabelled complex. This makes a firm decision on the magnitude of the shift (and hence on the assignment) difficult. However, a rule of thumb distinction between ring stretching and C-H bending vibrations is provided by an earlier isotopic labelling study [13]. In the complexes $[Zn(py)_2Cl_2]$ and $[Zn(an)_2Cl_2]$ the ratio ν^{i}/ν for the deuterated and undeuterated species is ~0.95 for ring stretching modes and ~0.75 for C-H bending modes. Significant (but smaller) shifts are also observed for C-^{15}N, ^{15}N-H, ^{15}N=O, ^{13}C-N, ^{13}C-H, ^{13}C=O, ^{18}O-H, N=^{18}O and C=^{18}O vibrations. These are generally of a size that obviates the problem of band matching, which is characteristic of deuterated complexes. The most convenient forms of labelling for inducing metal-ligand band shifts are ^{2}H and ^{18}O. They normally cause isotopic shifts of between 5 and 25 cm^{-1}. ^{15}N-Labelling, on the other hand, may only induce a shift of between 1 and 5 cm^{-1}. However, it is often the only convenient form of labelling available. The principle of multiple isotopic labelling (in which the various atoms in the ligand are individually labelled) has been successfully used in interpreting the infrared spectra of glycine complexes [14,15]. In these studies, the glycine ligand was independently labelled with ^{18}O,^{15}N and ^{13}C isotopes. The isotopic shifts observed not only enabled complete assignment of the spectrum but also revealed the extent to which vibrational mixing occurs.

In this work, use was made of ligand labelling only. The labelled compounds used in the preparation of the metal complexes are listed in Table 1. Assignments of the infrared bands were based principally upon observed isotopic shifts. This was complemented by empirical methods in which comparisons between spectra of the complexes were made by varying the ligand. Three unrelated classes of transition metal coordination complexes were studied. These will be discussed separately.

2 APPLICATIONS OF ISOTOPIC LABELLING TO THE INFRARED SPECTRA OF METAL COMPLEXES

2.1 COBALOXIMES

The complexity of biological macromolecules introduces considerable difficulty in their study. This has often made worthwhile the study of simpler model compounds that contain the essential features of the biological molecule. The chemistry of Vitamin B_{12} and its derivatives is one such system which has been extensively studied with the aid of model compounds. Since 1964, it has been observed that *bis*(dimethylglyoximato)-cobalt(III) complexes (known as cobaloximes) undergo many of the reactions of the cobalt atom in corrins [16-19]; for example methyl group transfer, reduction and rearrangement reactions.

In the present work, cobaloximes of the type $[CoX(DH)_2py]$ (DH_2 = dimethylglyoxime; X = Cl, Br, I, CNS, CH_3) have been investigated. The structure of these complexes is shown in Fig. 1. The essentially square planar ligand field provided by the dimethylglyoximate ligand, which chelates the copper ion, has the effect of stabilizing Co-C bonds in these complexes. It is primarily this similarity with the stereochemistry of cobalt in Vitamin B_{12} which makes cobaloximes suitable for use as model compounds. Further ligands may easily be bonded in the axial positions. In an attempt to gain an understanding of the nature of the cobalt centre in this type of complex a number of studies have been carried out. These have concentrated principally on the aspect of ground state *cis*- and *trans*-effects in cobaloximes, and have relied mostly upon proton NMR [20-23] and crystallographic [24-30] data. Considerable attention has also been given to the infrared spectra of cobaloximes [31-38]. However, apart from a normal

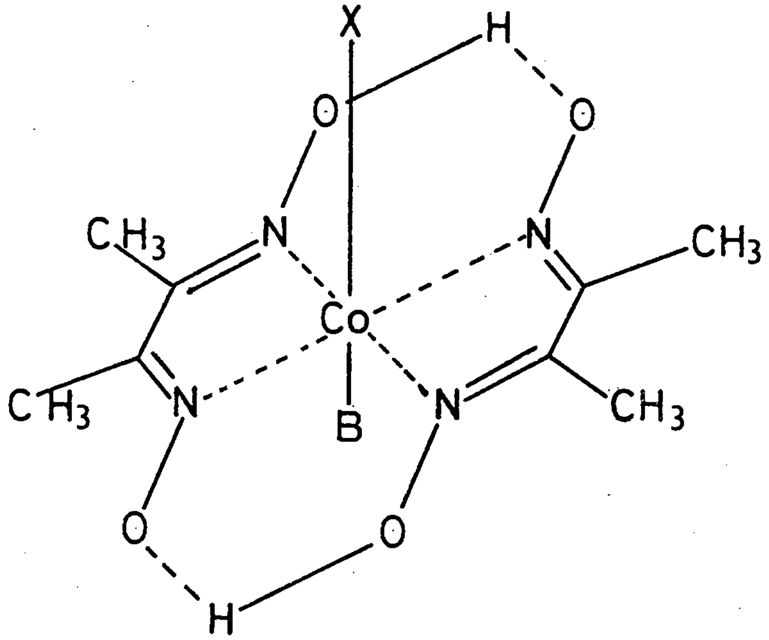


Figure 1. Structure of $[CoX(DH)_2B]$.

X = acid anion, alkyl or aryl group. B ´= Base.

coordinate treatment [32] of the planar cobalt dimethylglyoximate system and a single labelling study [31] involving deuteration of the methyl group of $[CH_3Co(DH)_2py]$, all previous band assignments have been made on a purely empirical basis. In the present work, assignments are based on ^{15}N-labelling of the dimethylglyoximate and pyridine nitrogen atoms, deuteration of the pyridine ring and substitution of the ligand X. This multiple labelling technique has three principal advantages over empirical methods. Firstly, it enables a firm distinction between the internal ligand modes of pyridine and coordinated dimethylglyoxime to be made. Secondly, it serves to distinguish between the metal-ligand stretching vibrations involving the two species of coordinated nitrogen atoms. Thirdly, it provides evidence for the extent of vibrational coupling between pyridine, dimethylglyoximate and metal-ligand modes. The spectra of the unlabelled complexes are reproduced in Figs. 6-9.

An infrared and Raman study [39] using deuterated dimethylglyoxime and polarised infrared of a single crystal specimen has been carried out on uncoordinated dimethylglyoxime. In view of the availability of ^{15}N-labelled dimethylglyoxime it was considered worthwhile extending this work to include the spectrum of dimethylglyoxime-$^{15}N_2$. Generally good agreement of results was obtained, but in the light of the new evidence it was necessary to reassess some of the original assignments. These are presented in Table 9.

Evidence for alternative bonding modes exhibited by the coordinated thiocyanate ion in the complexes $[\mathrm{Co(CNS)(DH)_2py}]$ was first observed by Norbury and co-workers [40]. Consideration of the integrated intensities of the C-N stretching frequencies at ~2120 $\mathrm{cm^{-1}}$ in their infrared spectra confirmed that two species of the complex exist: $[\mathrm{Co(NCS)(DH)_2py}]$ and $[\mathrm{Co(SCN)(DH)_2py}]$. Subsequent work [41-43] has shown that the bonding mode of the thiocyanate ion is solvent-controlled. The solution equilibrium $[\mathrm{Co(SCN)(DH)_2py}] \rightleftarrows [\mathrm{Co(NCS)(DH)_2py}]$ lies to the right for solvents with high dielectric constants. In the solid state no interconversion between the two linkage isomers occurs. As yet, no attempt has been made to characterize the isomers by their infrared spectra other than in the terms of their C-N stretching frequencies. In the present work, the infrared spectra of $[\mathrm{Co(NCS)(DH)_2py}]$ and $[\mathrm{Co(SCN)(DH)_2py}]$ as well as their isotopically labelled analogues were determined in the regions 2200 - 2000 and 1700 - 140 cm^{-1}. Assignments were made on the basis of ^{15}N-labelling of the pyridine and thiocyanato nitrogen atoms and deuteration of the pyridine ring. This enabled distinction between bands originating in the CNS and pyridine ligands. Bands orignating in the dimethylglyoximate moiety were assigned on the basis of those achieved in the study of the complexes [CoX(DH)$_2$py].

2.2 BASE ADDUCTS OF VANADYL ACETYLACETONATE

X-Ray crystallographic studies [44] have shown that vanadyl acetylacetonate has a distorted square pyramidal structure (Fig. 2), the vanadium atom being displaced from the basal plane of the four acetylacetonate oxygen atoms towards the oxygen atom.

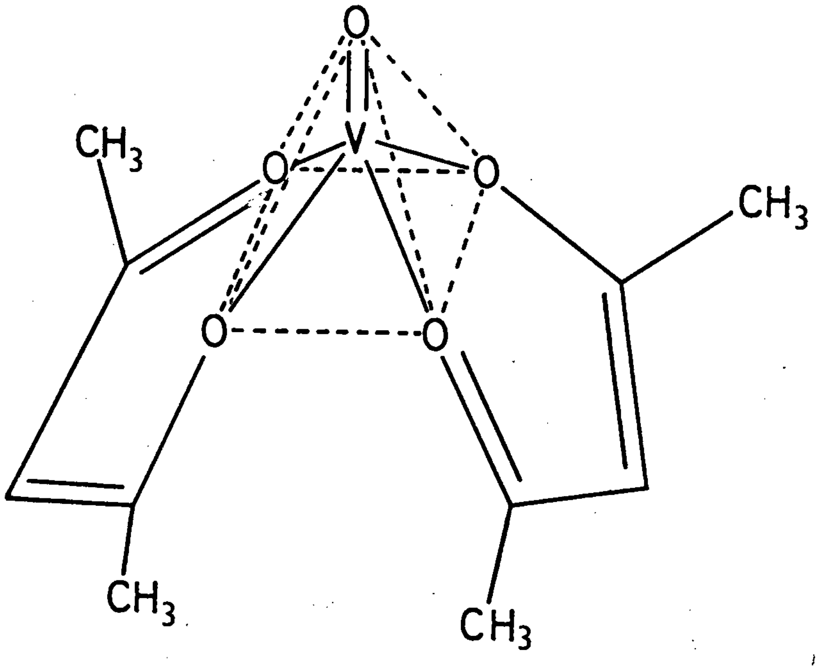


Figure 2. Structure of $VO(acac)_2$.

The V=O bond in vanadyl complexes is a multiple covalent bond consisting of $p\pi \rightarrow d\pi$ donation of electrons by the oxygen atom to the vanadium(IV) ion, superimposed on the V-O σ-bond. The electron accepting capacity of vanadium(IV), which has one half filled and four vacant *d*-orbitals, should be markedly affected by coordination of a sixth ligand. A coordinated base which donates its electron pair will increase the electron density in the metal *d* orbitals and consequently the $p\pi \rightarrow d\pi$ donation from oxygen to vanadium is expected to be reduced to an extent which depends upon the donor ability of the base. As a result there will be a lowering of the V=O bond order and hence νV=O. The above argument has been elegantly demonstrated by a comparison between the infrared spectra of $VO(acac)_2$ and $VO(acac)_2py$ [45], where a decrease in νV=O from 996 to 964 cm^{-1} was observed. It has been calculated [46] that a shift this large cannot be produced simply by mass effects, which may only account for less than 20% of the observed shift. It was soon realized that this lowering of νV=O on adduct formation provides a useful probe with which to establish a quantitative measure of donor strengths of various ligands. Garvey and Ragsdale [47] determined the solution infrared spectra of a series of 4-substituted pyridine *N*-oxide adducts of $VO(acac)_2$. The linear relationship between νV=O and the substituent parameters derived for the pyridine *N*-oxides indicated a decrease in V=O bond strength with increasing donor capacity of the substituent. A similar study on a series of substituted pyridine adducts of $VO(acac)_2$ was carried out by Caira *et al.* [48]. The infrared spectra of fourteen variously substituted pyridine adducts were examined as nujol mulls. These were found to fall into two classes. Those for which νV=O was lowered by 42 ±4 cm^{-1} on adduct formation and showed no dependence upon the electronic nature of the substituent; and those for which νV=O was lowered by 29 ±4 cm^{-1} and showed an inverse relationship with the electron releasing capacity of the substituent. Furthermore, it was noted that in the former class the three bands assigned to νV-O were split. In an attempt to explain these observations it was suggested [48] that the complexes exist as *cis*- and *trans*-isomers of structures a and b (Fig. 3). The series of adducts which display the greatest weakening of V=O being *cis*-isomers, while those displaying the least weakening of V=O being *trans*-isomers. A subsequent X-ray crystallographic structure determination [49], carried out on the 4-phenylpyridine adduct of vanadyl acetylacetonate confirmed the infrared prediction that this compound has a *cis* configuration.

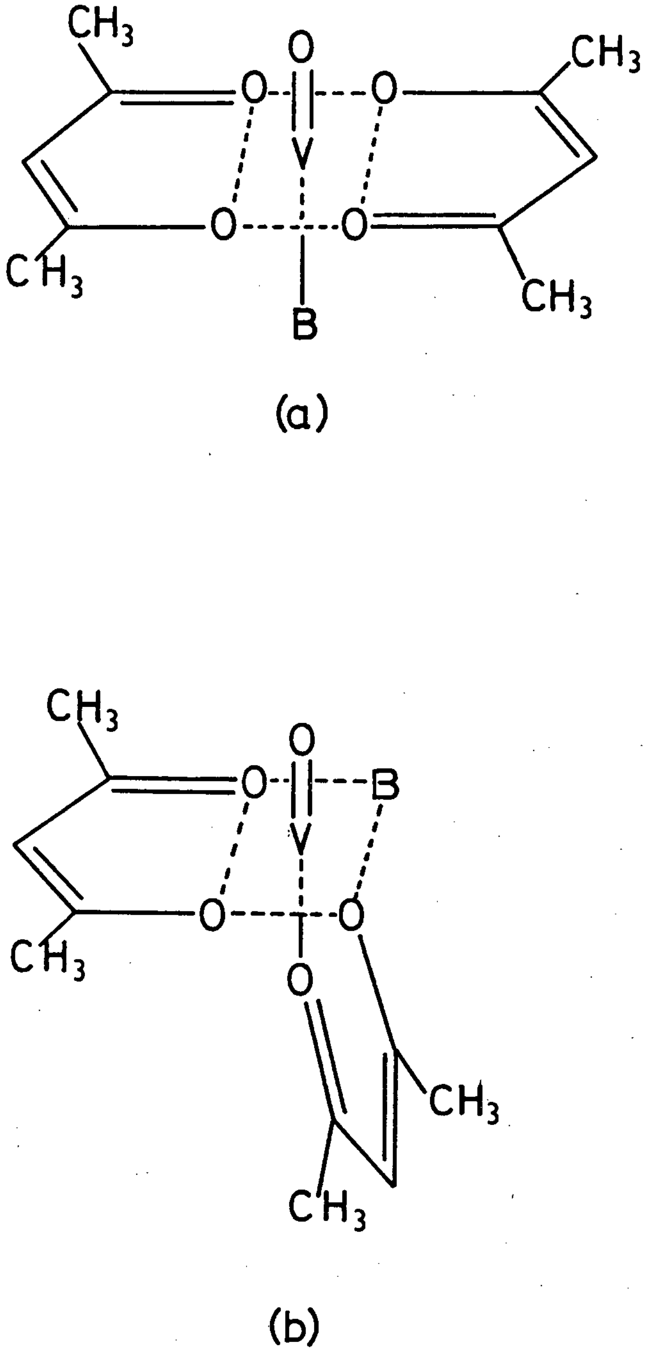


Figure 3. Possible structures of $VO(acac)_2B$

(a) *trans* (b) *cis*

A significant feature which emerged from the crystal structure determination of *cis*-$VO(acac)_2py$-ϕ was that the V-O bond directly opposite the V=O was anomalously long (2.14 Å compared with the 1.97 Å of the other V-O bonds). This accounts for the splitting of νV-O bonds. Furthermore, since the low frequency absorption of each doublet in the *cis*-complexes is weaker than the high frequency absorption, it is suggested [48] that the low frequency absorption is due to the single long V-O bond.

Haigh [50], from his study of substituted pyridine adducts of $VO(acac)_2$, was able to make reasonable empirical assignments of the principal acetylacetonate bands in the spectra of the adducts. These assignments were based on a comparison of the adduct spectra with that of the parent $VO(acac)_2$ complex. The most significant feature of these spectra is the νV=O band which, occurring near 1000 cm^{-1} in the spectrum of $VO(acac)_2$, is lowered considerably by adduct formation as mentioned above. Bands occurring near 608, 484 and 364 cm^{-1} in the spectrum of $VO(acac)_2$, which are also lowered on adduct formation and are split in the case of *cis*-isomers, were assigned to νV-O. No attempt was made to assign νV-N(py) bands since they were either considered beyond the range of measurement at the time (<250 cm^{-1}) or could not be differentiated from other bands in the spectra.

To date, various base adducts of vanadyl acetylacetonate have been isolated and studied [51-53]. However, attention has always been focused upon the V=O bond. In the present work it was proposed to investigate the infrared spectra of some base adducts of vanadyl acetlyacetonate using the technique of isotopic labelling. Labelling of the base should enable the detection of the vanadium-base vibrations as well as the ligand vibrations.

Unfortunately, ^{18}O-labelled acetylacetone was not available at the time this work was completed, so confirmation of the νV-O assignments was not possible. The infrared spectral criteria employed by Caira *et al.* [48] in assigning the geometrical structures of substituted pyridine adducts were then applied to the VO(acac)$_2$B complexes in an attempt to determine their geometric configuration. The bases used in this work were pyridine, pyridine-d_5, pyridine *N*-oxide, pyridine *N*-oxide-d_5, imidazole, imidazole-d_3, quinoline and quinoline-d_7.

2.3 ALKYLAMINE COMPLEXES OF COPPER(II) AND NICKEL(II) PHTHALIMIDE

Considerable interest has in the past accrued to the alkylamine complexes of metal(II) imides [54-61]. Most attention has centred on the structures of these complexes and the mode of bonding of the imide ligand. Previous work has included studies on composition, molecular weight, conductivity, magnetic susceptibility, electron spin resonance and infrared spectroscopy. Monomeric square planar formulation of the solid complexes $[M(imide)_2(am)_2]$ (M = Ni, Cu) has been proposed on the basis of these studies.

From a structural viewpoint, coordination of the imide ion may conceivably occur via either the heterocyclic nitrogen atom or the carbonyl oxygen atom. If the nitrogen atom of the imide is the metal ion donor, then coordination involves the *keto* form of the ligand (Fig. 4a). Alternatively, if the *enol* form (Fig. 4b) is the coordinating species, then the relative donor capacities of the nitrogen and carbonyl oxygen atoms are reversed and coordination occurs via the oxygen atom. All previous speculation of the mode of metal-ligand bonding in these complexes has been based on infrared studies confined to the carbonyl region of the spectrum. The infrared spectra of free imides characteristically exhibit two bands due to carbonyl absorption. These have been attributed either to absorptions of individual carbonyl groups [61] or to symmetric and antisymmetric vibrational coupling between the two carbonyl groups [62]. In the complexes, these carbonyl vibrations are lowered by some 50 to 100 cm^{-1} relative to the ligand values. In a previous infrared study [59] of Cu(II) and Ni(II) imide complexes, it was concluded that coordination occurs through the nitrogen atom of succinimide because both carbonyl vibrations undergo an equal decrease in frequency on complex formation. However it was later found [63] that this was not the case for similar complexes of phthalimide.

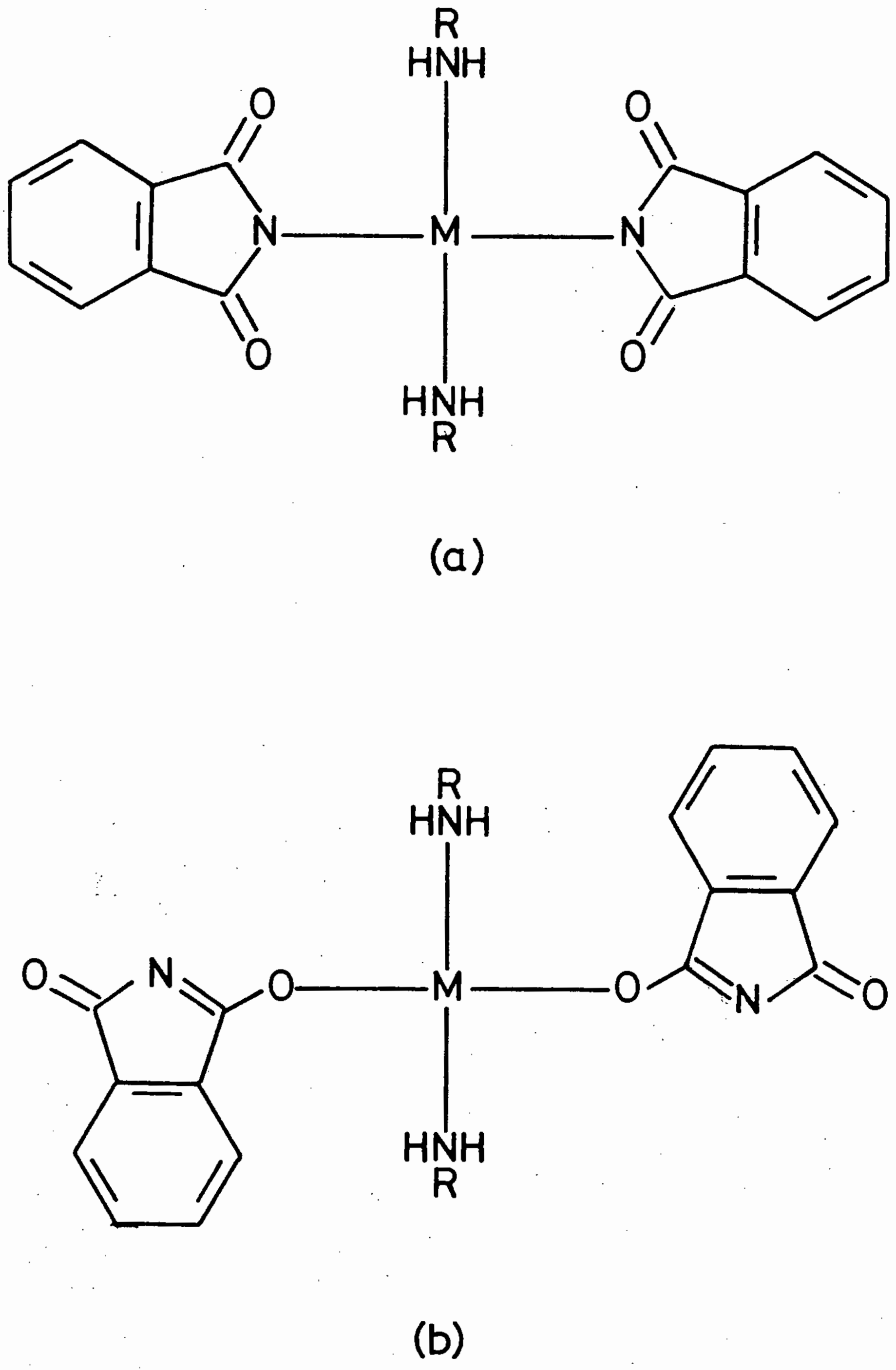


Figure 4. Alternative modes of phthalimide coordination.

In the present work, a labelling study of a series of alkylamine complexes of copper(II) and nickel(II) phthalimide was initiated with a view to assigning the metal-ligand stretching frequencies and thus also establishing the mode of bonding of the phthalimide ligand. Independent labelling of the phthalimide nitrogen with the ^{15}N-isotope and the amino hydrogens with deuterium enables a distinction to be made between the two species of metal-ligand stretching frequency, νM-N(phth) and νM-N(am).

II EXPERIMENTAL

1. PHYSICAL METHODS

1.1 INFRARED SPECTRA

Infrared spectra of the solid complexes were determined as nujol or hexachlorobutadiene mulls. Those of the liquid amine ligands were obtained on liquid films. In the spectral region below 250 cm^{-1}, the samples were supported between polyethylene disks while above 250 cm^{-1}, the window material used was caesium iodide.

Two grating infrared spectrophotometers were used to record the spectra. These were a Perkin-Elmer 180 and a Beckman IR-12. The latter instrument was used only for the spectra of the cobaloximes with axially-coordinated halide and methyl ligands in the region above 250 cm^{-1}. The wavenumber precision and repeatability of the instruments, as quoted by the manufacturers, are given in Table 1. Both spectrophotometers were calibrated against polystyrene and carbon dioxide.

The band frequencies in the spectra obtained from the Perkin-Elmer 180 were recorded by the wavenumber-marker pen. On the Beckman IR-12, however, it was found that maximum precision could be obtained by reading the frequencies directly from the wavenumber drum, not from the chart paper. Reproducibility of the quoted figures is better than 1 cm^{-1}.

1.2 MICROANALYSES

Microanalyses were performed by Mr. W.R.T. Hemsted of the Department of Organic Chemistry, University of Cape Town, on a Heraeus Universal Combustion Analyser.

TABLE 1. Precision and repeatability of infrared spectrophotometers

Frequency (cm^{-1})	Beckman IR-12		Perkin-Elmer 180	
	precision (cm^{-1})	repeatability (cm^{-1})	precision (cm^{-1})	repeatability (cm^{-1})
200	0.20	0.10	0.25	0.10
400	0.30	0.15	0.25	0.10
740	0.40	0.20	0.25	0.10
1330	0.60	0.30	0.25	0.10
2200	0.70	0.35	0.36	0.18

2 PREPARATIVE METHODS

TABLE 2. Source of the labelled chemicals used and atom-% purity with respect to the enriched isotope.

Compound	Atom-% purity of enriched isotope	Source
C_2H_5OD	95	B.O.C. Prochem Ltd.
D_2O	99.7	Merck, Sharp & Dohme(Canada) Ltd.
$H_2{}^{15}NOH.HCl$	97.3	Goss Scientific Instruments Ltd.
$C_5H_5{}^{15}N$	95	Merck, Sharp & Dohme(Canada) Ltd.
C_5D_5N	99	B.O.C. Prochem Ltd.
aniline-^{15}N	96.9	B.O.C. Prochem Ltd.
aniline-d_5	> 97	Merck, Sharp & Dohme(Canada) Ltd.
aniline-N,N-d_2	> 97	Merck, Sharp & Dohme(Canada) Ltd.
imidazole-d_4	98	Merck, Sharp & Dohme(Canada) Ltd.
quinoline-d_7	98	Merck, Sharp & Dohme(Canada) Ltd.
phthalimide-^{15}N	95.5	B.O.C. Prochem Ltd.
pyridine N-oxide-d_5	99	Merck, Sharp & Dohme(Canada) Ltd.
$NaSC^{15}N$	97.1	Merck, Sharp & Dohme(Canada) Ltd.

2.1 COBALOXIMES

2.1.1 Dimethylglyoxime-$^{15}N_2$

$$CH_3(CO)_2CH_3 + 2H_2{}^{15}NOH.HCl \rightarrow CH_3(C^{15}NOH)_2CH_3 + 2HCl + 2H_2O$$

A solution of 0.5 g (7.3 mmole) $H_2{}^{15}NOH.HCl$ in 5 ml distilled water was added dropwise with stirring to a solution of 0.39 ml (4.4 mmole) diacetyl in 5 ml water. The mixture was stirred for 6 hr at room temperature. The resulting white crystals of dimethylglyoxime-$^{15}N_2$ were cooled in ice, washed with water, collected by filtration and dried *in vacuo* over silica gel at 0.1 mm Hg pressure. Yield: 0.33 g (79%).

2.1.2 Dimethylglyoxime-d_2

The hydroxyl hydrogens of dimethyglyoxime were exchanged for deuterium by recrystallization of dimethylglyoxime from a boiling solution of EtOD containing 10% D_2O. To ensure complete exchange, this process was carried out three times. Both the infrared and ^1H n.m.r. spectra indicated that the exchange was essentially complete. The entire preparation was carried out in a glove bag under an atmosphere of dry nitrogen.

2.1.3 The complexes [CoX(DH)$_2$B] (X = Cl, Br, I; B = py, py-^{15}N, py-d_5)

$$CoX_2.nH_2O + 2DH_2 + 2B + \tfrac{1}{4}O_2 \rightarrow [CoX(DH)_2B] + B.HX + (n+\tfrac{1}{2})H_2O.$$

The cobalt(III) complexes were prepared by direct oxidation of Co(II) with air according to the method of Schrauzer [64]. One mmole of the appropriate cobalt(II) halide was dissolved in 2 ml ethanol and added to a hot solution containing 2 mmole dimethylglyoxime dissolved in 10 ml ethanol. After allowing the solution to cool to room temperature, 2 mmole of the required base was added with stirring and a stream of dry air was bubbled through the solution for 10 min. The solution was allowed to stand at room temperature for 20 min, during which period the product crystallized. The brown crystals were collected by filtration on a Büchner funnel and washed with successive 10 ml portions of water, ethanol and diethyl ether. The product was dried *in vacuo* at 0.1 mm Hg pressure.

An identical procedure employing dimethylglyoxime-$^{15}N_2$ was carried out in the preparation of complexes in which the dimethylglyoxime was labelled.

In these reactions, one equivalent of base is consumed to neutralize the HCl produced. Thus a variation of this method [33] employs the addition of one equivalent of NaOH plus one-half of the required amount of base as follows:

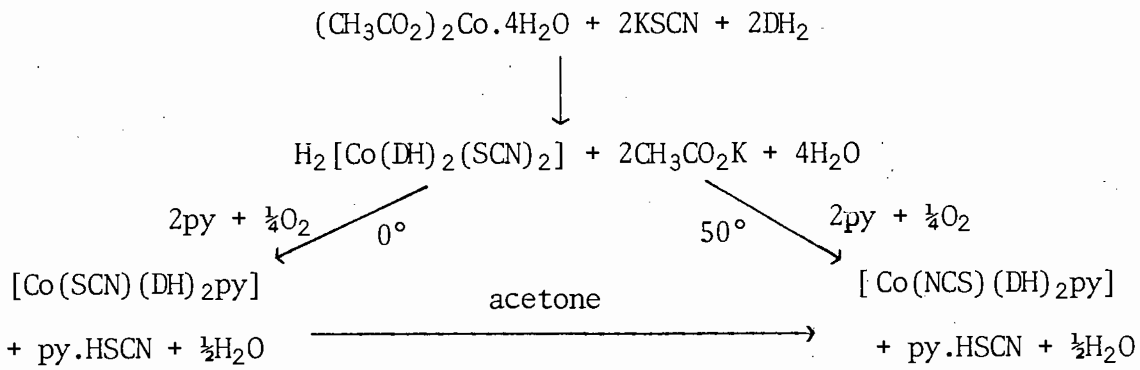
$$CoX_2.nH_2O + 2DH_2 + B + NaOH + \tfrac{1}{4}O_2 \rightarrow [CoX(DH)_2B] + NaX + (n+1\tfrac{1}{2})H_2O$$

This method proved especially useful when using the expensive labelled bases.

The cobaloximes are all yellow-brown crystalline compounds which are stable in air and sparingly soluble in most solvents.

2.1.4 The complexes [Co(CNS)(DH)$_2$py]

The linkage isomers thiocyanato-*bis*(dimethylglyoximato)pyridine cobalt(III) and isothiocyanato-*bis*(dimethylglyoximato)pyridine cobalt(III) were obtained by reaction of the intermediate *bis*(thiocyanate) complex as follows:



An ethanolic solution of 0.25 g (1 mmole) cobalt(II) acetate tetrahydrate and 0.19 g (2 mmole) potassium thiocyanate was added to 0.23 g (2 mmole) dimethylglyoxime dissolved in 10 ml warm ethanol to produce the intermediate *bis*(thiocyanate) complex. This was stirred for 15 min while cooling to 0°C. Air was bubbled through the solution for 10 min to induce precipitation of the complex thiocyanato-*bis*(dimethylglyoximato)pyridine cobalt(III) which was fairly soluble in ethanol. It was filtered, washed with a small amount of cold ethanol and diethyl ether and dried in a vacuum desiccator over silica gel at 0.1 mm Hg pressure. The relatively insoluble isothiocyanato-*bis*(dimethylglyoximato)pyridine cobalt(III) complex was similarly obtained from the *bis*(thiocyanate) intermediate by immediate addition of the pyridine. An alternative means of obtaining the Co-NCS complex has been described by

Norbury *et al.* [40]. The thiocyanato complex was refluxed in acetone until a precipitate formed. Repeated separation and extraction of this precipitate led to the isolation of the isothiocyanato-*bis*(dimethylglyoximato)pyridine complex. A qualitative indication of the isomeric purity of the two linkage isomers was obtained from their infrared spectra.

2.1.5 The complexes $[CH_3Co(DH)_2B]$ (B = py, py-^{15}N, py-d_5)

The synthesis of the base adducts of methylcobaloxime is best achieved by displacement of the coordinated water molecule in methylaquocobaloxime by the appropriate base [33]. Methylaquocobaloxime is prepared *via* the methyl(dimethyl sulphide)cobaloxime complex [64].

$$CoCl_2.6H_2O + 2DH_2 + NaOH \rightarrow \underset{\text{not isolated}}{[Co(DH)_2]} + 2NaCl + 8H_2O$$

$$\xrightarrow[BH_4^+,\ NaOH]{CH_3I,\ DMS} [CH_3Co(DH)_2\{S(CH_3)_2\}]$$

$$\xrightarrow{\Delta\ ,\ H_2O} [CH_3Co(DH)_2(H_2O)]$$

$$\xrightarrow{B} [CH_3Co(DH)_2B]$$

Preparation of methylaquocobaloxime

A suspension of 23.8 g (0.1 mole) cobalt(II) chloride hexahydrate and 23.2 g (0.2 mole) dimethylglyoxime in 100 ml methanol was stirred for 5 min in a 500 ml 3-necked, round-bottomed flask under a nitrogen atmosphere. Subsequently, 8.0 g (0.2 mole) sodium hydroxide in 150 ml water was added. After stirring the solution for 15 min, it was cooled to -20°C and 7.0 g (0.11 mole) dimethyl sulphide was added with continuous stirring. This was followed, after 5 min, by 20.0 g (0.14 mole) methyl iodide. Next, a solution of 4.0 g sodium hydroxide in 20 ml water was added over a period of 5 min, immediately followed by the addition of a solution containing 1.0 g sodium hydroxide and 0.6 g sodium hydroborate in 10 ml water. The solution was stirred for a further 15 min while it returned to room temperature. After filtering, a stream of air was passed through the filtrate to remove the excess of dimethyl sulphide and methyl iodide. The filtrate was diluted with an equal volume of water and set aside for crystallization at -10°C for 24 hr. The orange crystals of methyl(dimethyl sulphide)cobaloxime were collected by filtration on a Büchner funnel, washed with water and dried *in vacuo* over silica gel at 0.1 mm Hg pressure. Yield: 16.7 g (45.6%) based on cobalt(II) chloride hexahydrate.

Methylaquocobaloxime was obtained by boiling a suspension of 15 g (0.04 mole) of the dimethyl sulphide complex in 75 ml water for 30 min. The resulting solution of methylaquocobaloxime was cooled to 0°C and left to stand for 24 hr to crystallize. The product was collected by filtration and air dried. Yield: 9.65 g (75%). The methylaquocobaloxime crystals were dark orange in colour, moderately soluble in water and stable in air but fairly light sensitive. In solution photodecomposition occurs quite readily.

Base substitution of methylaquocobaloxime

The addition of 1.2 mmole of the required base to a suspension of 0.32 g (1 mmole) methylaquocobaloxime in water brought about an immediate colour change from dark orange to yellow indicating formation of the base adduct of methylaquocobaloxime. After stirring the suspension for 30 min, the product was collected by filtration, washed with cold water and dried *in vacuo* at 0.1 mm Hg pressure.

2.2 VANADYL ACETYLACETONATE COMPLEXES

2.2.1 Anhydrous vanadyl acetylacetonate [65]

A mixture of 5 g vanadium(V) oxide (0.03 mole) and 100 ml acetylacetone (0.98 mole) was refluxed for 24 hr in a 200 ml round-bottomed flask fitted with a condenser. The resulting suspension was filtered while hot and the filtrate was cooled. The remaining acetylacetone was removed by evaporation in a stream of air. The solid product was washed (acetone, diethyl ether) and recrystallized from chloroform.

2.2.2 The complexes [VO(acac)$_2$B] (B = py, py-d_5, pyO, pyO-d_5, Him, Him-d_3, quin, quin-d_7)

The varying degrees of solubility of the adducts, the fact that they proved to be more soluble (in most solvents) than the anhydrous complex from which they were prepared and the need to limit the quantity of labelled base used to a microlitre scale, made it difficult to devise a single method of preparation which would be suitable for all of the adducts. Thus the method of preparation used in each case was the one which gave the highest yield and greatest degree of purity.

The pyridine *N*-oxide adduct and its labelled analogue was prepared as reported by Swiel [66]. To 1 mmole of vanadyl acetylacetonate dissolved in 10 ml ethanol, 1.5 mmole of pyridine *N*-oxide was added with a microsyringe. The solution was heated gently and stirred for 5 min. After cooling to room temperature, green crystals of vanadyl *bis*(acetylacetonato)*mono*(pyridine) monhydrate began to form. These were collected by filtration, washed with diethyl ether and dried *in vacuo* at 70°C for 3 hr to remove the single molecule of water of crystallization.

The pyridine adducts could not be consistently prepared by this method and the procedure reported by Haigh [50] (requiring a large excess of base) is unsuitable when using expensive labelled bases. However, it was found that the addition of 20 ml diethyl ether to the hot mixture of 0.27 g (1 mmole) vanadyl acetylacetonate and 0.12 g (1.5 mmole) pyridine in 5 ml ethanol brought about immediate precipitation of the desired product before the vanadyl acetylacetonate itself precipitated from solution. The green vanadyl *bis*(acetylacetonato)*mono*(pyridine) was filtered off, the crystals were washed with diethyl ether and air-dried. Heating the adducts or exposing them to reduced pressure for long periods caused loss of the adducted pyridine molecule.

The vanadyl *bis*(acetylacetonato)*mono*(imidazole) complex was similarly prepared by adding a 50% molar excess of imidazole to vanadyl acetylacetonate. However, the adduct was very soluble in ethanol and, although it could not be precipitated by ether, a pure form of the complex was obtained by allowing the solution to stand for 3 days until all of the solvent had evaporated. The dark green crystals of *bis*(acetylacetonato)*mono*(imidazole) were washed with 20 ml diethyl ether, filtered and air-dried. The labelled analogue was prepared in an identical manner.

The vanadyl *bis*(acetylacetonato)*mono*(quinoline) complex was prepared by adding 0.20 ml (1.7 mmole) quinoline to 0.13 g (0.5 mmole) finely-powdered vanadyl acetylacetonate and mixing thoroughly. Approximately 20 ml diethyl ether was added and the resulting suspension stirred for 1 hr to dissolve all the excess of quinoline. The light green product was collected by filtration and air-dried. Although this method necessitated washing away some of the expensive labelled quinoline (in making the d_7-adduct) it was found to be the only effective means of obtaining this complex.

2.3 ALKYLAMINE COMPLEXES OF COPPER(II) AND NICKEL(II) PHTHALIMIDE

$$MCl_2.nH_2O \quad + \quad 2\ \text{imideH} \quad + \quad 4\text{am} \quad \rightarrow \quad [M(\text{imide})_2(\text{am})_2] \quad + \quad 2\text{am.HCl} \quad + \quad nH_2O$$

The imide complexes were prepared oaccording to the method of Tschugaeff [67]. Because of their instability to water, care was taken to use dry solvents and to avoid prolonged suction during filtration.

2.3.1 The complexes $[Cu(\text{imide})_2(\text{am})_2]$ (imide = phth, phth-^{15}N; am = *ter*-$C_4H_9NH_2$, *ter*-$C_4H_9ND_2$, *cy*-$C_6H_{11}NH_2$, *cy*-$C_6H_{11}ND_2$, *sec*-$C_4H_9NH_2$, *sec*-$C_4H_9ND_2$, *n*-$C_4H_9NH_2$, *n*-$C_4H_9ND_2$, *iso*-$C_4H_9NH_2$, *iso*-$C_4H_9ND_2$, *n*-$C_3H_7NH_2$, *n*-$C_3H_7ND_2$, $\phi CH_2CH_2NH_2$, $\phi CH_2CH_2ND_2$, ϕCH_2NH_2, ϕCH_2ND_2)

Two mmole of the appropriate primary aliphatic amine were syringed into a warm solution of 0.15g (1 mmole) phthalimide and 0.09 g (0.5 mmole) copper(II) chloride dihydrate in 10 ml dry ethanol. The green solution immediately turned blue and the pink complex soon began to precipitate. The solution was made up to 40 ml by the addition of ethanol and stirred vigorously until precipitation was complete. The complex was collected by filtration on a Büchner funnel, washed with ethanol and ether and quickly transferred to a vacuum desiccator where it was dried at 0.1 mm Hg pressure.

2.3.2 The complexes $[Ni(\text{imide})_2(\text{am})_2]$ (imide = phth, phth-^{15}N; am = *cy*-$C_6H_{11}NH_2$, *n*-$C_4H_9NH_2$, *n*-$C_4H_9ND_2$, *n*-$C_3H_7NH_2$, *n*-$C_3H_7ND_2$, $\phi CH_2CH_2NH_2$, $\phi CH_2CH_2ND_2$

These complexes were prepared in a similar manner to the copper complexes but their precipitation was more difficult to effect. The *cyclo*-hexylamine complex was particularly difficult to obtain. This problem was overcome by using a relatively small volume of solvent (7 ml). The pale yellow complexes were collected by filtration and (being fairly soluble in ethanol) were washed with a minimum of the cold solvent and ether before being dried *in vacuo* at 0.1 mm Hg pressure.

The preparation of the amine-d_2 complexes involved the prior deuteration of the amine. This was effected by dissolving the required amount of amine in 1 ml EtOD and adding approximately 4 drops D_2O. The resulting solution, after being shaken well, was allowed to stand for 1 hr. The remainder of the preparation was unchanged except for the fact that EtOD was used in place of the solvent ethanol and the entire procedure was carried out in a glove bag under an atmosphere of dry nitrogen. This ensured that re-exchange of the deuterium atoms was kept to a minimum. Infrared analysis indicated an approximate 50% deuteration of the final product.

III RESULTS

1. ANALYSES OF COMPOUNDS

TABLE 3. Analytical data on dimethylglyoxime and labelled analogues

Compound	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$C_4H_6N_2O_2H_2$	41.4	6.9	24.1	41.4	6.8	24.2
$C_4H_6{}^{15}N_2O_2H_2$	40.7	6.8	23.7	40.8	6.7	23.5
$C_4H_6N_2O_2D_2$	40.7	6.8	23.7	40.7	7.0	23.8

TABLE 4. Analytical data on cobaloximes with axially coordinated pyridine and halide ligands and labelled analogues

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[\mathrm{CoCl(DH)_2py}]$	38.7	4.7	17.4	38.6	4.7	17.3
$[\mathrm{CoI(DH)_2py}]$	31.5	3.9	14.1	31.5	3.9	14.0
$[\mathrm{CoBr(DH)_2py}]$	34.8	4.3	15.6	35.1	4.4	15.5
$[\mathrm{Co(CH_3)(DH)_2py}]$	43.9	5.8	18.3	43.7	5.8	18.3
$[\mathrm{CoCl(DH)_2py}\text{-}^{15}N]$	38.6	4.7	17.3	38.5	4.8	17.4
$[\mathrm{CoI(DH)_2py}\text{-}^{15}N]$	31.5	3.9	14.1	31.1	3.9	13.8
$[\mathrm{CoBr(DH)_2py}\text{-}^{15}N]$	34.8	4.3	15.6	34.6	3.9	15.6
$[\mathrm{Co(CH_3)(DH)_2py}\text{-}^{15}N]$	43.8	5.8	18.2	43.6	6.0	18.3
$[\mathrm{CoCl(DH)_2py}\text{-}d_5]$	38.2	4.7	17.1	38.1	4.8	17.1
$[\mathrm{CoI(DH)_2py}\text{-}d_5]$	31.3	3.8	14.0	31.3	4.1	13.9
$[\mathrm{CoBr(DH)_2py}\text{-}d_5]$	34.5	4.2	15.5	34.4	4.2	15.3
$[\mathrm{Co(CH_3)(DH)_2py}\text{-}d_5]$	43.3	5.7	18.0	43.1	5.8	18.1
$[\mathrm{CoCl(DH}\text{-}^{15}N)_2\mathrm{py}]$	38.3	4.7	17.2	38.2	4.8	17.2
$[\mathrm{CoI(DH}\text{-}^{15}N)_2\mathrm{py}]$	31.3	3.8	14.0	31.3	3.8	13.9
$[\mathrm{CoBr(DH}\text{-}^{15}N)_2\mathrm{py}]$	34.5	4.3	15.5	35.5	4.6	15.2

TABLE 5. Analytical data on thiocyanato-and-isothiocyanato-*bis*-(dimethylglyoximato)pyridine cobalt(III) and labelled analogues

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Co(SCN)(DH)_2py]$	39.4	4.5	19.7	39.3	4.5	19.8
$[Co(SCN)(DH)_2py\text{-}d_5]$	39.0	4.4	19.5	38.6	4.5	19.5
$[Co(SCN)(DH)_2py\text{-}^{15}N]$	39.4	4.5	19.7	39.1	4.5	19.8
$[Co(SC^{15}N)(DH)_2py]$	39.4	4.5	19.7	39.2	4.5	19.7
$[Co(NCS)(DH)_2py]$	39.4	4.5	19.7	39.3	4.5	19.7
$[Co(NCS)(DH)_2py\text{-}d_5]$	39.0	4.4	19.5	38.9	4.4	19.5
$[Co(NCS)(DH)_2py\text{-}^{15}N]$	39.4	4.5	19.7	39.2	4.5	19.8
$[Co(^{15}NCS)(DH)_2py]$	39.4	4.5	19.7	39.3	4.5	19.8

TABLE 6. Analytical data on *bis*(acetylacetonato)oxovanadium(IV) and its base adducts and labelled analogues

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[VO(acac)_2]$	45.3	5.3	-	45.3	5.4	-
$[VO(acac)_2py]$	52.3	5.6	4.1	51.7	5.6	4.1
$[VO(acac)_2py\text{-}d_5]$	51.6	5.5	4.0	51.7	5.5	3.9
$[VO(acac)_2pyO]$	50.0	5.3	3.9	49.8	5.3	3.9
$[VO(acac)_2pyO\text{-}d_5]$	49.3	5.2	3.8	49.2	5.2	3.7
$[VO(acac)_2Him$	46.9	5.4	8.4	46.3	5.4	8.4
$[VO(acac)_2Him\text{-}d_3]$	46.4	5.4	8.3	45.9	5.3	8.4
$[VO(acac)_2quin]$	57.9	5.4	3.6	57.7	5.3	3.6
$[VO(acac)_2quin\text{-}d_7]$	56.9	5.3	3.5	56.9	5.3	3.6

TABLE 7. Analytical data on the alkylamine complexes of copper(II) phthalimide and their labelled analogues

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[\mathrm{Cu(phth)}_2(\mathit{ter}\text{-}\mathrm{C_4H_9NH_2})_2]$	57.4	6.0	11.2	57.5	6.0	11.2
$[\mathrm{Cu(phth)}_2(\mathit{cy}\text{-}\mathrm{C_6H_{11}NH_2})_2]$	60.7	6.2	10.1	60.4	6.0	10.0
$[\mathrm{Cu(phth}\text{-}^{15}\mathit{N})_2(\mathit{cy}\text{-}\mathrm{C_6H_{11}NH_2})_2]$	60.5	6.2	10.1	60.2	6.1	10.1
$[\mathrm{Cu(phth)}_2(\mathit{sec}\text{-}\mathrm{C_4H_9NH_2})_2]$	57.4	6.0	11.2	57.0	6.0	11.0
$[\mathrm{Cu(phth)}_2(\mathit{n}\text{-}\mathrm{C_4H_9NH_2})_2]$	57.4	6.0	11.2	57.3	6.0	11.2
$[\mathrm{Cu(phth}\text{-}^{15}\mathit{N})_2(\mathit{n}\text{-}\mathrm{C_4H_9NH_2})_2]$	57.2	6.0	11.2	56.9	6.0	11.2
$[\mathrm{Cu(phth)}_2(\mathit{iso}\text{-}\mathrm{C_4H_9NH_2})_2]$	57.4	6.0	11.2	57.3	5.8	11.1
$[\mathrm{Cu(phth)}_2(\mathit{n}\text{-}\mathrm{C_3H_7NH_2})_2]$	55.7	5.5	11.8	55.4	5.4	11.6
$[\mathrm{Cu(phth}\text{-}^{15}\mathit{N})_2(\mathit{n}\text{-}\mathrm{C_3H_7NH_2})_2]$	55.5	5.5	11.8	55.4	5.6	11.9
$[\mathrm{Cu(phth)}_2(\phi\mathrm{CH_2CH_2NH_2})_2]$	64.3	5.1	9.4	63.8	4.9	9.3
$[\mathrm{Cu(phth)}_2(\phi\mathrm{CH_2NH_2})_2]$	63.2	4.6	9.8	62.7	4.6	9.7
$[\mathrm{Cu(phth}\text{-}^{15}\mathit{N})_2(\phi\mathrm{CH_2NH_2})_2]$	63.0	4.6	9.8	62.6	4.4	9.8

TABLE 8. Analytical data on the alkylamine complexes of nickel(II) phthalimide and their labelled analogues

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Ni(phth)_2(cy\text{-}C_6H_{11}NH_2)_2]$	61.2	6.2	10.2	60.8	6.2	10.2
$[Ni(phth\text{-}^{15}N)_2(cy\text{-}C_6H_{11}NH_2)_2]$	61.0	6.2	10.2	60.4	6.2	10.1
$[Ni(phth)_2(n\text{-}C_4H_9NH_2)_2]$	58.0	6.1	11.3	57.5	6.1	11.2
$[Ni(phth\text{-}^{15}N)_2(n\text{-}C_4H_9NH_2)_2]$	57.7	6.1	11.2	57.4	6.0	11.3
$[Ni(phth)_2(n\text{-}C_3H_7NH_2)_2]$	56.3	5.6	11.9	55.6	5.6	11.8
$[Ni(phth\text{-}^{15}N)_2(n\text{-}C_3H_7NH_2)_2]$	56.1	5.6	11.9	55.9	5.6	11.8
$[Ni(phth)_2(\phi CH_2CH_2NH_2)_2]$	64.8	5.1	9.4	64.9	5.1	9.6
$[Ni(phth\text{-}^{15}N)_2(\phi CH_2CH_2NH_2)_2]$	64.6	5.1	9.4	64.2	5.0	9.4

2. INFRARED RESULTS

TABLE 9. Vibrational frequencies (cm^{-1}), isotopic shifts and band assignments for crystalline dimethylglyoxime and its labelled analogues.*

DH_2 ν	D-d_2 ν	DH_2-^{15}N ν	Assignment
-	1612	1690	νC=N
1440	1440	1440	CH_3 antisymm.def.
1364	1364	1363	CH_3 symm.def.
1167	1167	1167	νC-C + δO-H
	1152(15)		
1142	1100(42)	1138(4)	δO-H + νC-C
1026	1026	1024(2)	CH_3 rock
		1011(15)	
977	974(3)	972(5)	νN-O
902	888(14)	894(8)	νN-O
~745	736(tb)	722(tb)	skel.def.
706	697	701(5)	skel.def. (δC-N-O)
	580	607	
	558		
468	458(10)	462(6)	γN-O-H
372	368(4)	372	γN-O-H
232	227(7)	237	τCH_3

* All shifts cited (in parentheses) are to lower wavenumber.

Abbreviations: tb = band too broad for shift to be determined.

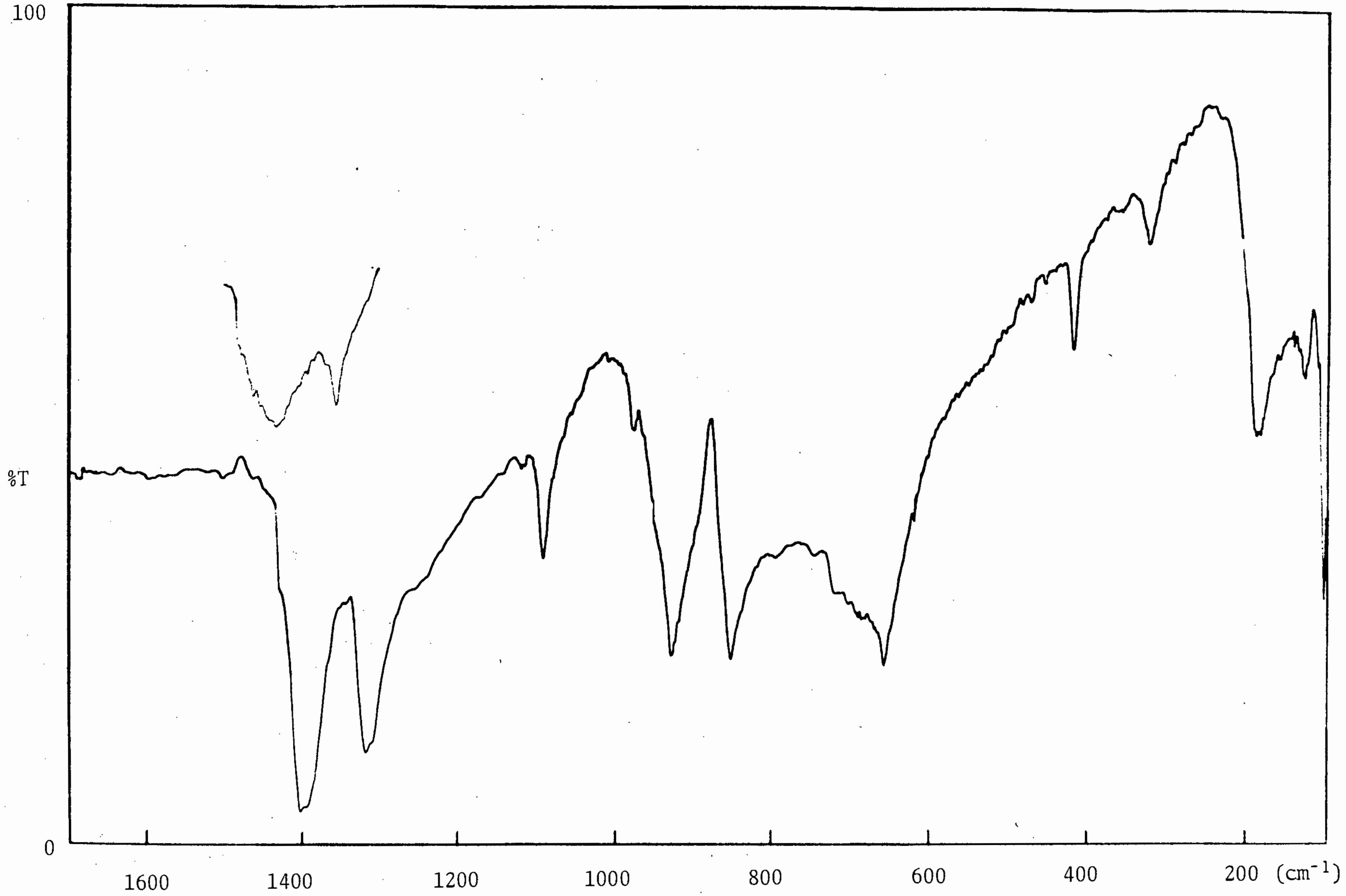


Figure 5. Infrared spectrum of dimethylglyoxime.

TABLE 10. Vibrational frequencies, isotopic shifts (in the sequence DH-^{15}N, py-^{15}N, py-d_5) and band assignments for the complexes $[CoX(DH)_2py]$ (cm^{-1})*.

X = Cl		X = Br		X = I		X = CH_3		Assignment †	
Frequency	Shifts	Frequency	Shifts	Frequency	Shifts	Frequency	Shifts		
1609	0,3,41	1608	0,3,43	1607	0,2,45	1600	-,3,39	ν ring(py)	(8a)
1564	10,0,0	1564	10,0,0	1559	9,0,0	1562	-,2,0	νC=N(DH)	
1498	0,3,170	1496	0,3,171	1493	0,2,169	1491	-,2,178	ν ring(py)	(19a)
1454	0,6,127	1450	3,5,125	1449	0,5,125	1444	-,5,131	ν ring(py) + νC=N(DH)	(19b)
1371	1,1,1/44#	1370	0,0,0/47 #	1368	0,0,0/46#	1370	-,1,1/39#	ν ring(py) + δCH_3(DH)	(14)
1249	1,4,4	1244	1,2,1	1243	1,3,3	1237	-,0,0	νC-C(DH)	
1240	15,8,255/333#	1230	11,12,sh/322#	1228	8,1,248/323#	1237	-,sh,260/330#	δC-H(py) + νN-O(DH)	(3/9a)
1167	0,0,286	1155	0,0,273	1153	1,0,275	1179	-,0,277	δC-H(py)	(15)
1095	5,0,0	1093	2,0,0	1092	3,1,0	1093	-,1,0	νN-O(DH)	
1072	0,2,238	1071	1,1,234	1069	0,3,235	1066	-,2,224	δC-H(py)	(18b)
1042	0,8,27	1041	tb,9,26	1039	0,7,25	1039	-,5,29	ν ring(py)	(12)
1005	tb,2,0	1003	0,0,0	1003	0,0,1	1012	-,0,2	ν ring(py)	(1)
982	13,1,0	980	9,2,0	980	11,0,0	999	-,sh,0	νN-O(DH)	
950	0,0,tb	959	1,0,tb	956	0,0,tb	975	-,2,0	skel.def.(DH)	
874	10,0,98	879	0,0,93	879	0,0,95	890	-,0,104	γC-H(py)	(10b)
765	0,4,190	765	0,3,192	763	0,3,195	767	-,3,187	γC-H(py)	(11)
734	tb,tb,~0	735	tb,tb,~0	735	tb,tb,~0	734	-,tb,0	skel.def.(DH)	

TABLE 10 (Continued)

X = Cl		X = Br		X = I		X = CH_3		Assignment †	
Frequency	Shifts	Frequency	Shifts	Frequency	Shifts	Frequency	Shifts		
721	tb,tb,~0	721	tb,tb,~0	721	tb,tb,~0	722	-,tb,0	skel.def.(DH)	
692	0,3,156	696	0,3,157	694	1,3,159	701	-,3,166	γC-H(py)	(4)
649	0,3,9/22#	647	0,2,8/23#	648	1,6,15/28#	648	-,1,10/25#	δring(py)	(6a)
-		-		-		634	-,6,25		
576	tb,0,1	573	tb,0,0	569	13,0,0	580	-,tb,tb	skel.def.(DH)	
510	3,0,0	512	3,0,0	513	2,0,1	515	-,0,0	νCo-N(DH)	
454	1,3,17	456	0,4,19	453	1,3,17	449	-,2,10	νCo-N(py)	
419	2,2,18	423	2,1,18	423	2,2,21	424	-,2,26	γ ring(py) + νCo-N(DH)	(16b)
378	0,0,0	-		-		-		νCo-Cl	
-		355	0,0,0	-		-		νCo-Br	
-		-		345	0,1,1	-		νCo-I	
-		-		-		316	-,0,0	νCo-CH_3	
280	1,0,0	271	0,0,2	271	0,0,1	253	-,0,0	τCH_3(DH)	
235	1,3,9	238	tb,0,0	228	0,0,4	234	-,0,tb	δL-Co-L	
-		-		-		196	-,0,2	δL-Co-L	
172	0,1,3	174	6,0,5	174	0,1,1	166	-,0,4	δL-Co-L	

TABLE 10 (Continued)

* All shifts cited are to lower wavenumber.

† Figures in parentheses following assignments of pyridine vibrations are the band numbers on the notation of Kline and Turkevich [68].

Extra band observed in the spectrum of py-d_5 complex.

Abbreviations: sh = shoulder (shift masked by adjacent band);
tb = band too broad and weak for shift to be determined.

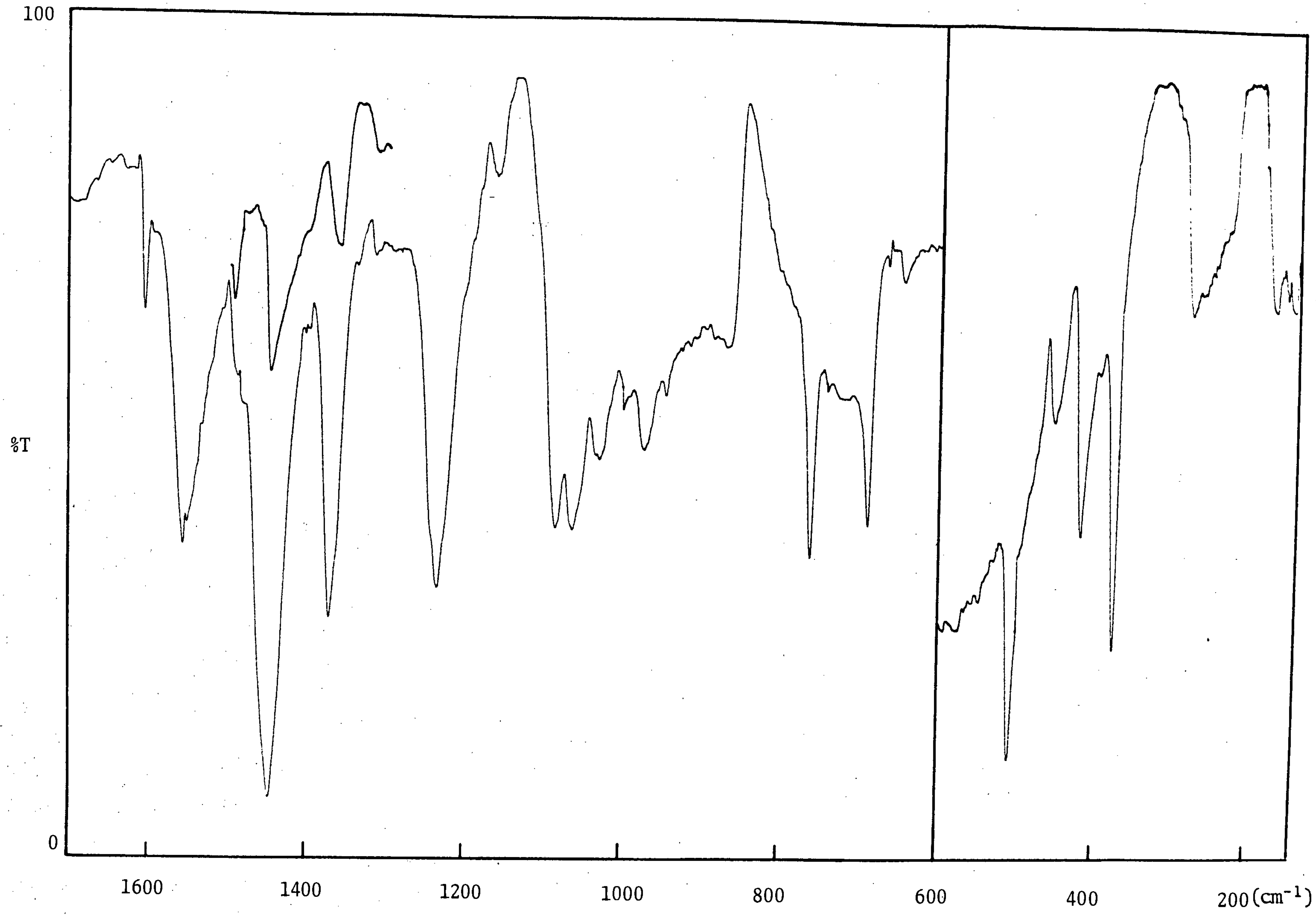


Figure 6. Infrared spectrum of [CoCl(DH)$_2$py].

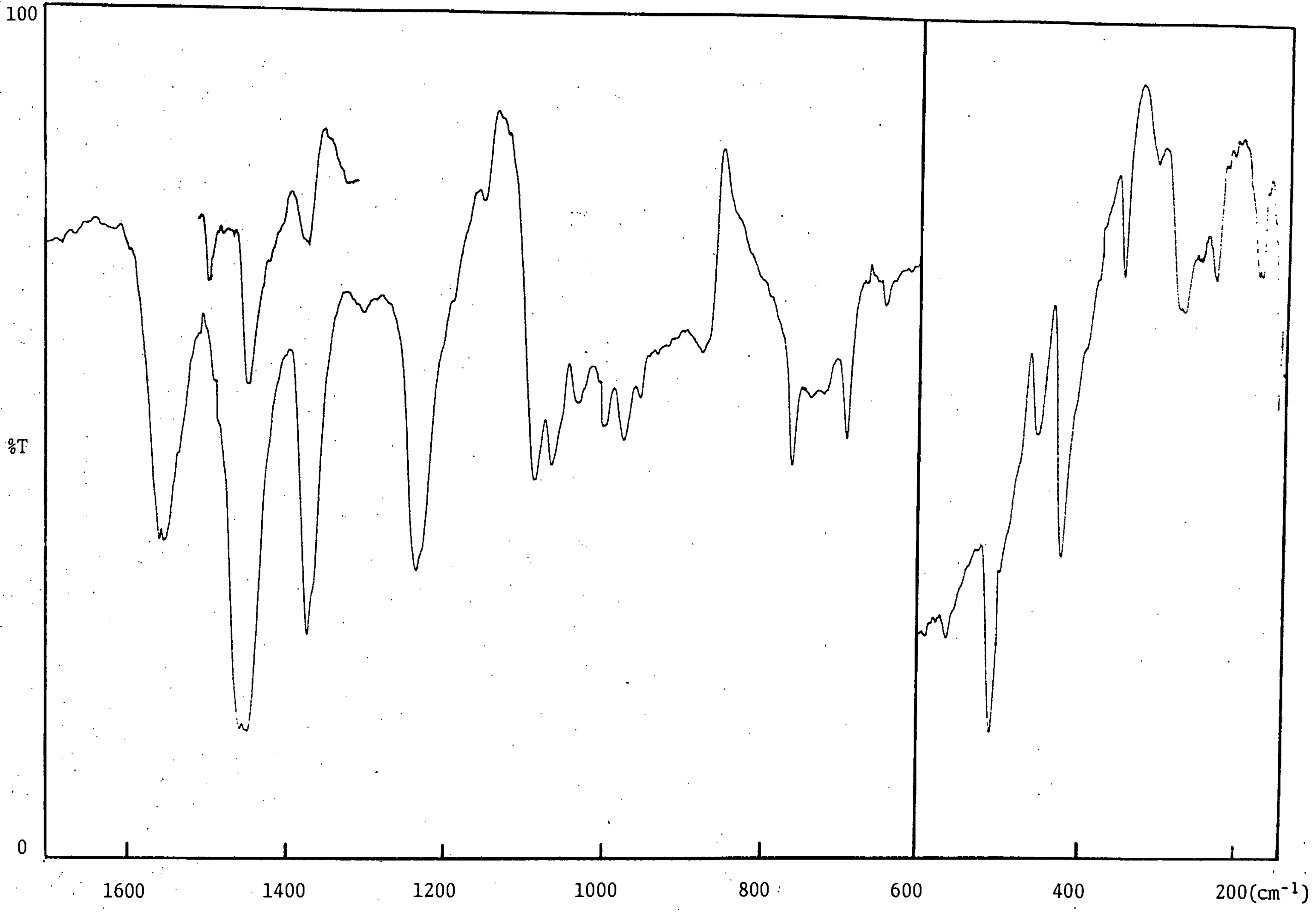


Figure 7. Infrared spectrum of [CoI(DH)$_2$py].

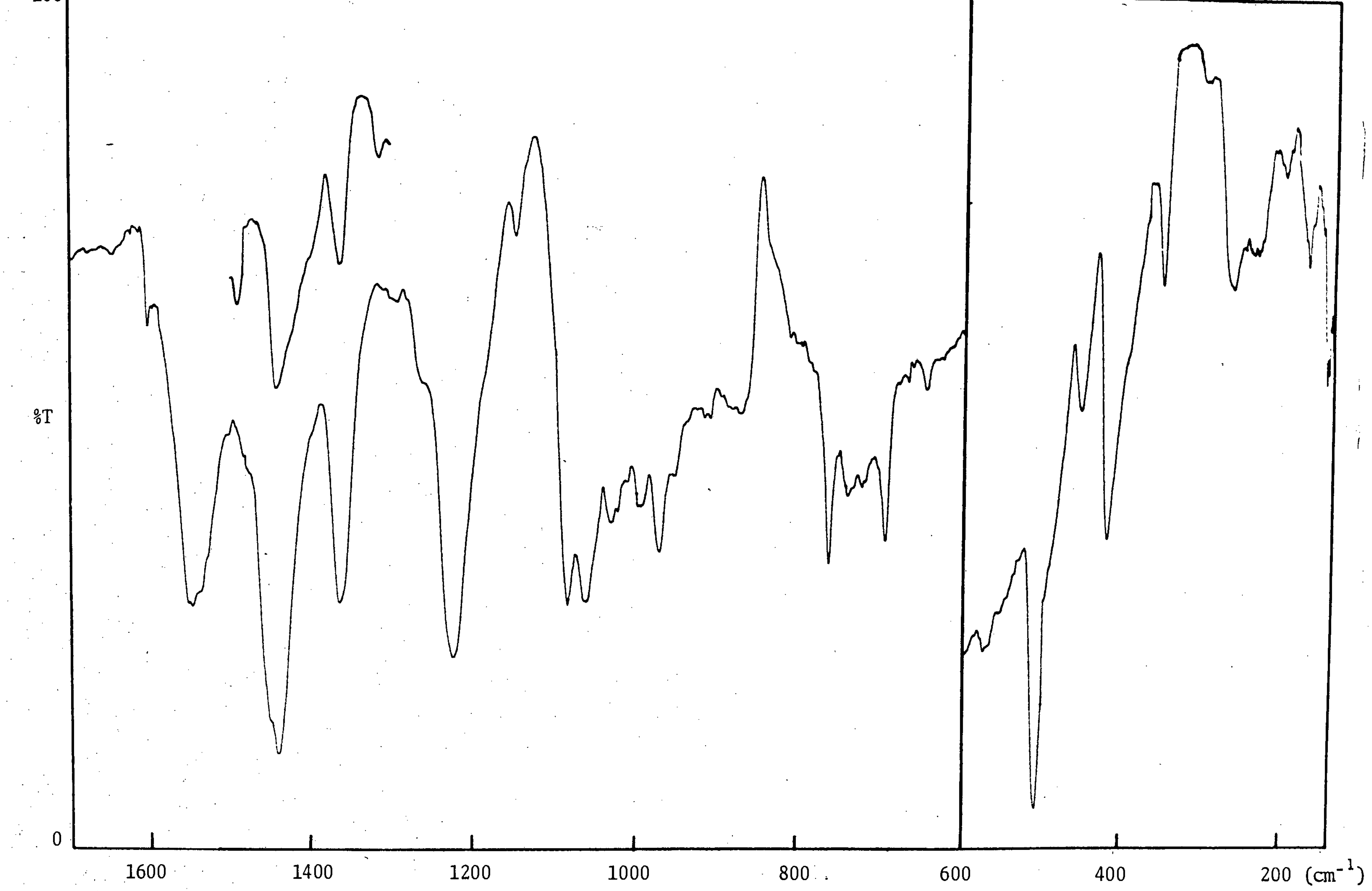


Figure 8. Infrared spectrum of [CoBr(DH)$_2$py]

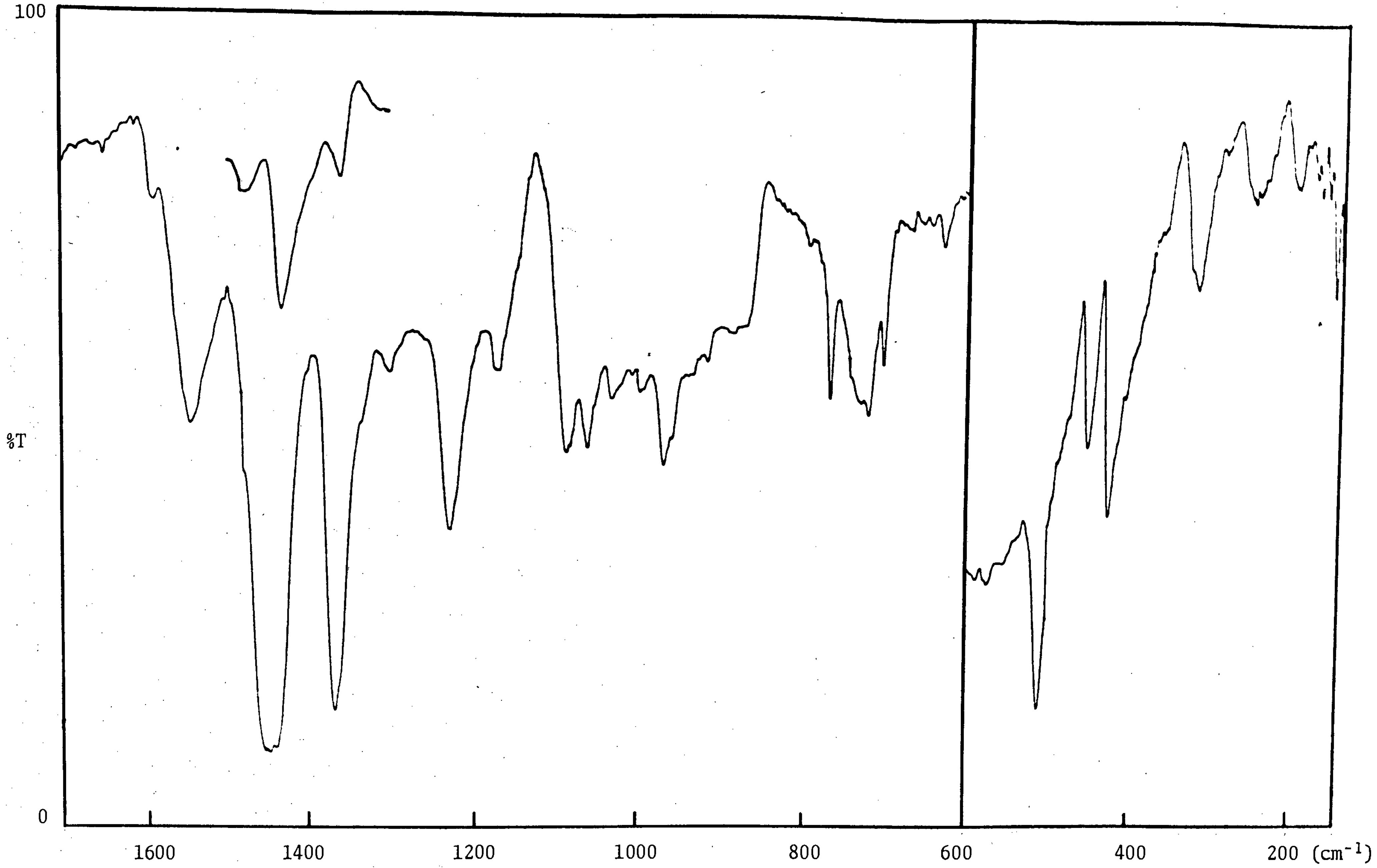


Figure 9. Infrared spectrum of [$CH_3Co(DH)_2py$].

TABLE 11. Vibrational frequencies (cm^{-1}), isotopic shifts (in the sequence ^{15}NCS, py-^{15}N, py-d_5) and band assignments for the linkage isomers of the complex [Co(CNS)(DH)$_2$py]§

[Co(NCS)(DH)$_2$py]		[Co(SCN)(DH)$_2$py]		py		Assignment†	
ν	Δν*	ν	Δν*	ν	Δν*		
2122	30,0,0	2112	29,0,0			νN≡CS	
-		2028	26,0,0			νN≡CS	
				1606	58	ν ring(py)	(6a)
1606	0,2,39	1606	0,0,48	1590	54	ν ring(py)	(8a)
				1581		ν ring(py)	(8a)
1564	0,0,0	1556	0,0,0			νC=N(DH)	
1495	0,3,173	1492	0,2,169	1481	162	ν ring(py)	(19a)
1449	0,5,127	1449	0,6,126	1436	138	ν ring(py) + νC=N(DH)	(19b)
1370	0,0,0/44#	1370	0,0,1/47#	1374	147	ν ring(py) + δCH_3(DH)	(14)
				1291	251	δC-H(py)	
1273	0,0,0	-				νC-CH_3(DH)	
1242	0,0,0	1238	0,0,1			νC-C(DH) + νN-O(DH)	
1231	0,0,134	1224	1,2,127	1215	208	δC-H(py)	(3/9a)
-		1156	3,0,329	1145	183	δC-H(py)	(15)
1094	0,0,0	1093	0,1,0			νN-O(DH)	
1070	0,4,160	1067	0,4,167	1067	182	δC-H(py)	(18b)
1052	0,2,5	1049	1,5,3	1029	197	ν ring(py)	(12)
1019	0,11,15	1025	1,10,19	990	168	ν ring(py)	(1)
982	0,0,1	979	0,0,1			νN-O(DH)	
-		957	0,0,173	940	34		
				882	193	γC-H(py)	(10b)
833	11,0,0	-				νNC-S	
				818			
761	0,4,143	766	0,4,139	748	168	γC-H(py)	(11)
~735	tb,tb,tb	~735	tb,tb,tb			skel.def.(DH)	
694	0,2,155	694	0,2,157	702	168	γC-H(py)	(4)
651	0,8,13	649	0,5,11	675		δ ring(py)	(6a)
645	0,2,22			653	29	δ ring(py)	(6a)
				602	72	δ ring(py)	(6a)

TABLE 11. (Continued)

[Co(NCS)(DH)$_2$py]		[Co(SCN)(DH)$_2$py]		py		Assignment†	
ν	$\Delta\nu$*	ν	$\Delta\nu$*	ν	$\Delta\nu$*		
513	0,0,0	512	0,0,0			νCo-N(DH)	
481	0,1,4	464	0,0,0			δNCS	
464	3,0,26	464	0,0,19			νCo-N(py)	
456	sh,0,1	424	0,0,0			δNCS	
450	0,3,12	-				νCo-N(py)	
423	0,0,22	424	0,0,21	404	37	γ ring(py)	(16b)
397	0,0,-	-					
377	0,0,0	-				νCo-NCS	
-		356	0,0,1			νCo-SCN	
292	1,1,0	309	o,sh,0			τCH$_3$(DH)	
~260	2,0,2	~250	tb,tb,tb			τCH$_3$(DH)	
217	0,0,5	232	0,0,12			δL-Co-L	
195	1,0,0	-				δL-Co-L	
169	0,0,3	168	0,0,2			δL-Co-L	

* All shifts cited are to lower wavenumber.

† Figures in parentheses following assignments of pyridine vibrations are the band numbers on the notation of Kline and Turkevich [68].

Extra band observed in the spectrum of py-d_5 complex.

§ (NCS) and (SCN) represent N- and S-bonded thiocyanato groups, respectively, while (CNS) indicates that the mode of thiocyanate coordination is unspecified.

Abbreviations: sh = shoulder (shift masked by adjacent band)
tb = band too broad and weak for shift to be determined
\- = Band absent in one of the isomers.

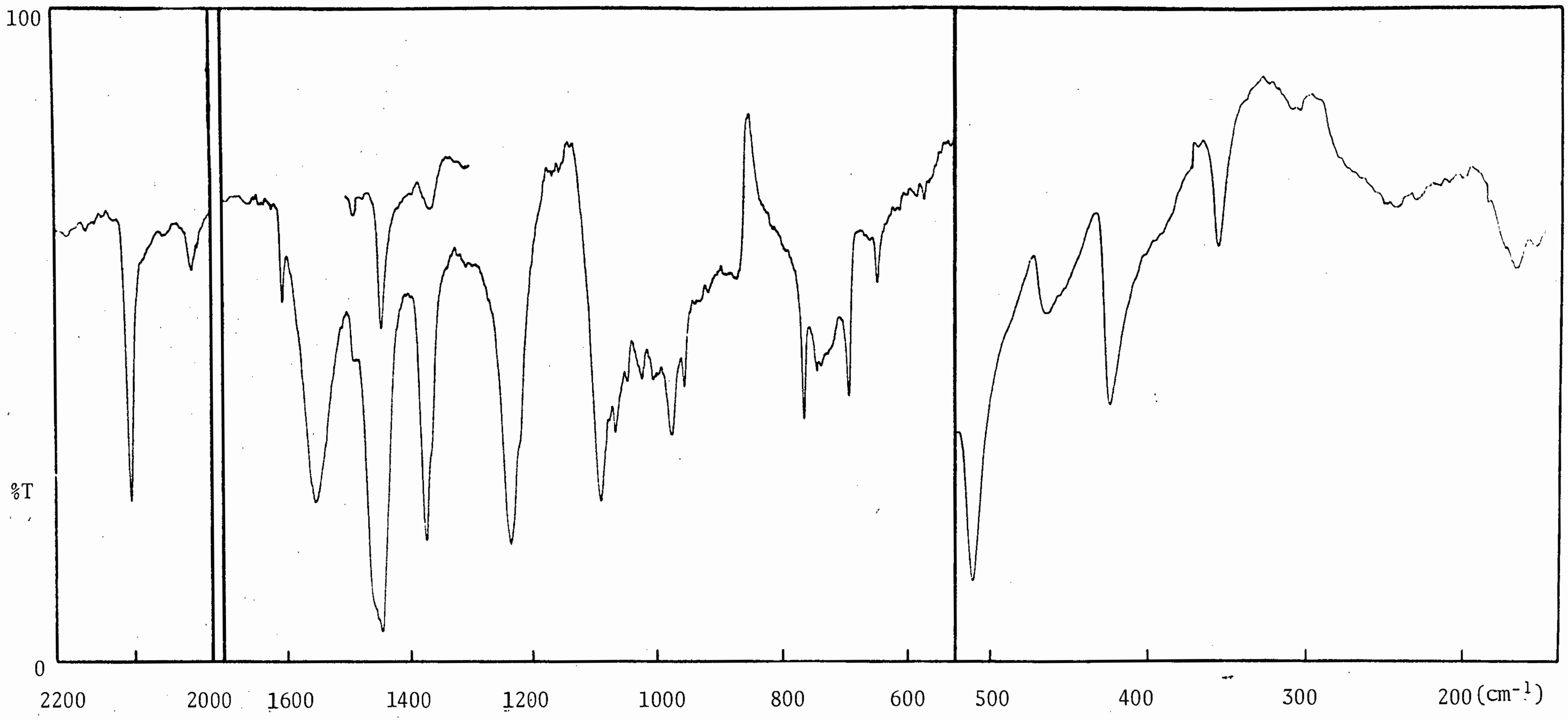


Figure 10. Infrared spectrum of [Co(SCN)(DH)$_2$py].

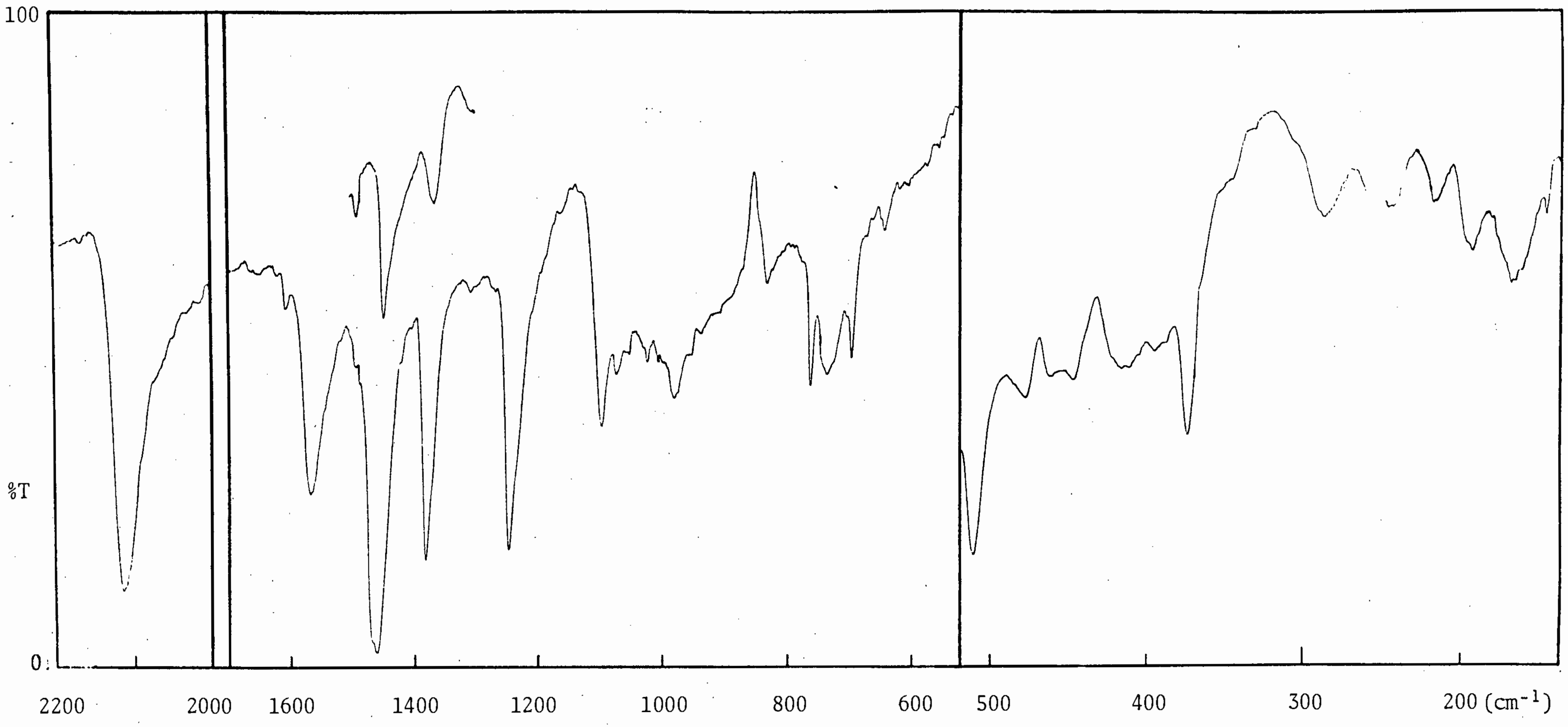


Figure 11. Infrared spectrum of $[Co(NCS)(DH)_2py]$.

TABLE 12. Vibrational frequencies (cm^{-1}), isotopic shifts and band assignments for the complex [VO(acac)$_2$py].

[VO(acac)$_2$py]		[VO(acac)$_2$]	py		Assignment
ν	Δν*	ν	ν	Δν*	
			1606	58	ν ring(py)
			1590	54	ν ring(py)
~1575	0	1587			νC=O(acac)
1559	3	1556			νC=C(acac)
1524	0	1530			
		1521			
1476	166		1481	162	ν ring(py)
1444	134		1436	138	ν ring(py)
1417	0	1418			
1376	1/139#	1372	1374	147	ν ring(py)
1352		1356			
		1343			
1286	246		1291	251	δC-H(py)
1274	1	1286			νC=C + νC-$\mathrm{CH_3}$(acac)
1218	222		1215	208	δC-H(py)
1195	1	1187			δC-H(acac)
1149	173		1145	183	δC-H(py)
1074	185		1067	182	δC-H(py)
1058	sh				
1034	191		1029	197	ν ring(py)
1020	0	1018			$\mathrm{CH_3}$ rock(acac)
1008	0				
998	164		990	168	ν ring(py)
964	4	996			νV=O(acac)
			940	34	
936	2	936			νC=O + νC-$\mathrm{CH_3}$ (acac)
890	169		882	193	γC-H(py)
798	1	798			γC-H(acac)
788	sh				
781	sh	789			
777	0				

TABLE 12. (Continued)

$[VO(acac)_2py]$		$[VO(acac)_2]$	py		Assignment
ν	Δν*	ν	ν	Δν*	
764	197		748	168	γC-H(py)
		720			
709	165		702	168	γC-H(py)
676	1	685	675	51	ring def.(acac) + δ ring(py)
			653	29	
656	0	658			ring def.(acac)
622	78		602	72	δ ring(py)
598	0	608			νV-O(acac)
		579			
561	sh	560			
486	0	461			
463	sh	484			νV-O
448	0				
428	37		404	37	γ ring(py)
418	0	423			
360	2	364			νV-O(acac)
283	2	286			δO-V-O(acac)
256	0	260			δO-V-O(acac)
		238			
		220			
		193			
187	0				
177	5				νV-N(py)
		171			
149	0				δL-V-L

* Δν = py-d_5-induced shifts. All shifts cited are to lower wavenumber.

\# Extra band observed in the spectrum of the py-d_5 complex.

Abbreviations: sh = shoulder (shift masked by adjacent band).

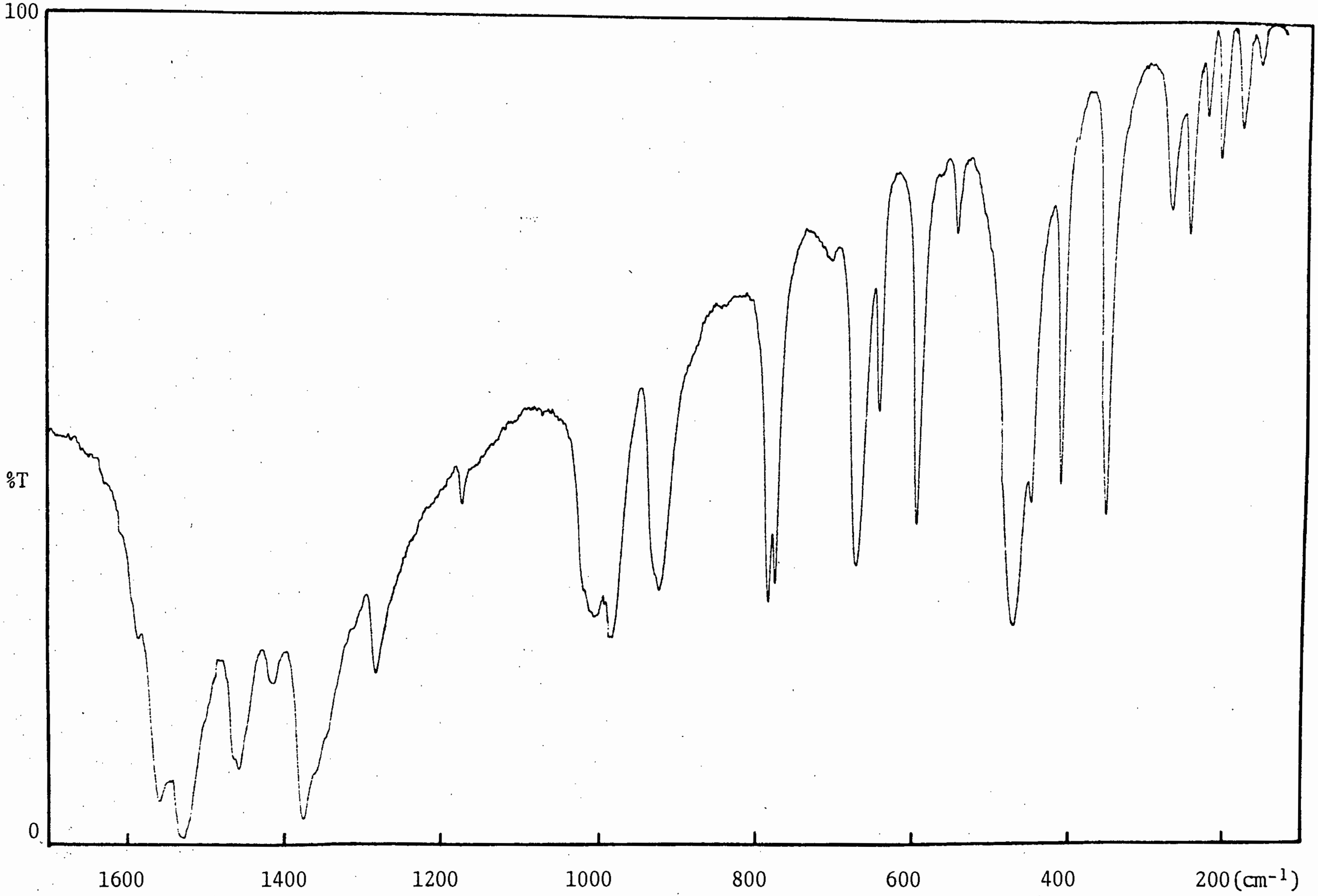


Figure 12. Infrared spectrum of $VO(acac)_2$.

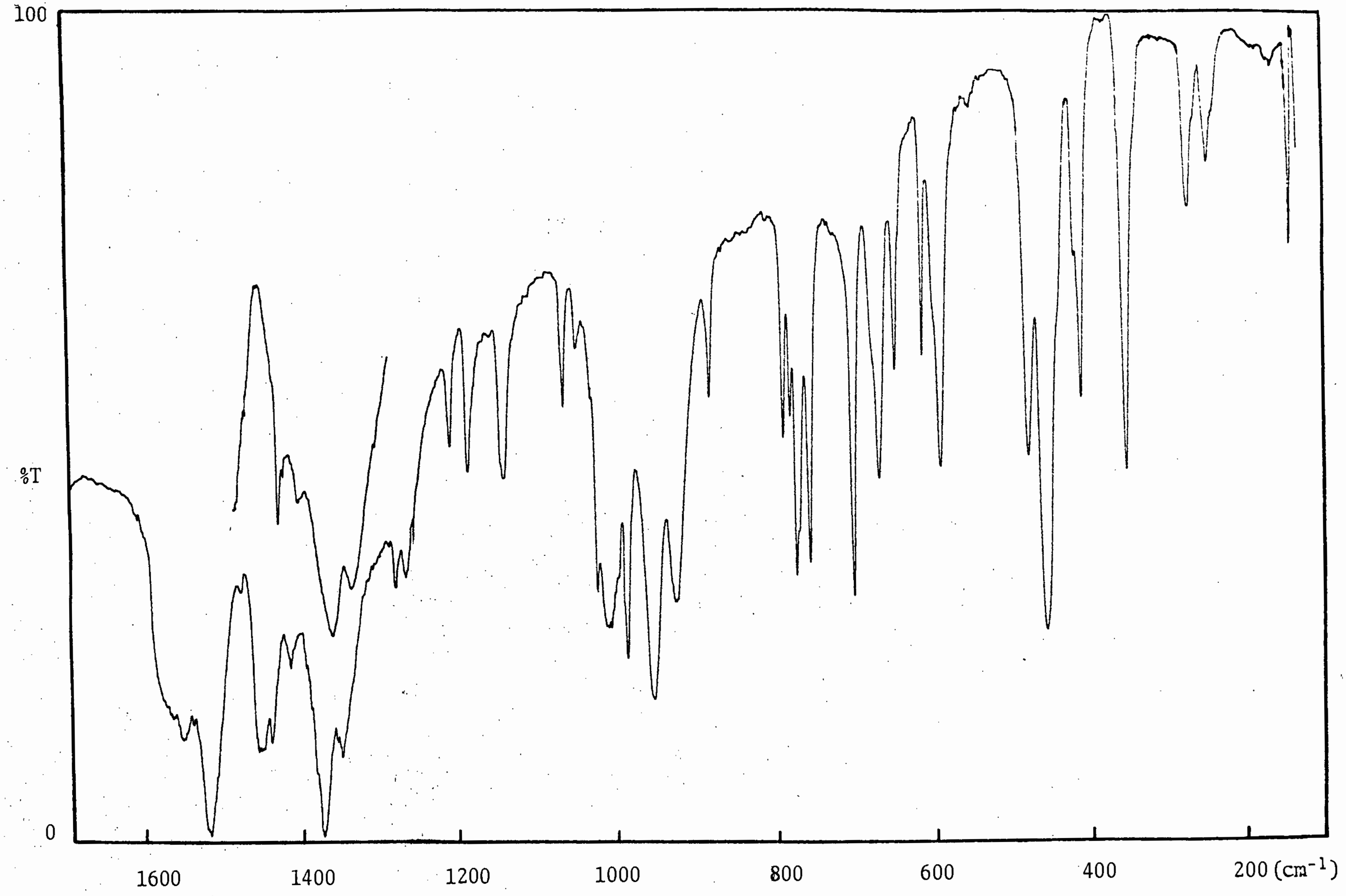


Figure 13. Infrared spectrum of $VO(acac)_2py$.

TABLE 13. Vibrational frequencies (cm^{-1}), isotopic shifts and band assignments for the complexes $[VO(acac)_2pyO]$.

$[VO(acac)_2pyO]$		$[VO(acac)_2]$	pyO		Assignment
ν	$\Delta\nu^*$	ν	ν	$\Delta\nu^*$	
			1650	0	$\nu N-O(pyO)$
			1605	199	ν ring(pyO)
1569	0	1587			$\nu C=O(acac)$
			1560	164	ν ring(pyO)
1556	0	1556			$\nu C=C(acac)$
		1530			
1519	0	1521			
1472	128		1464	122	ν ring(pyO)
1448	2				
1421	0	1418			
			1383	sh	
1380	0	1372			
1366	0	1556			
		1343			
1334	59		1328	58	
1274	0	1286			$\nu C=C + \nu C-CH_3(acac)$
1223	40		1236	44	ν ring(pyO)
1210	27				
1194	2	1187			$\delta C-H(acac)$
1178	sh				
			1172	sh	
1154	sh				
			1149	0	
1074	51		1095	53	$\gamma C-H(pyO)$
			1068	231	$\delta C-H(pyO)$
			1044	228	$\delta C-H(pyO)$
1030	0/42#	1018	1015	40	CH_3 rock(acac) + ν ring(pyO)
1018	2	1018			CH_3 rock(acac)
962	1	996			$\nu V=O(acac)$
932	1/59#	936	913	55	$\nu C=O + \nu C-CH_3(acac) + \gamma C-H(pyO)$

TABLE 13. (Continued)

[VO(acac)$_2$pyO]		[VO(acac)$_2$]	pyO		Assignment
ν	$\Delta\nu$*	ν	ν	$\Delta\nu$*	
842	2				
828	62		835	73	δ ring(pyO) + νN-O(pyO)
788	0	798			γC-H(acac)
784	0	789			
			768	4	
722	0	720			
686	134		675	137	γC-H(pyO)
675	0	685			ring def.(acac)
659	0	658			ring def.(acac)
654	0				
636					
600	0	608			νV-O(acac)
		579			
		560			
550	14		547	14	δ ring(pyO) + νN-O(pyO)
524	sh		511	sh	
471	(0)	461			
460	(0)	484			νV-O
460	(11)		465	20	δN-O(pyO)
418	0	423			
359	0	364			νV-O(acac)
284	0	286			δO-V-O(acac)
245	2	260			δO-V-O(acac)
~237	~5		237	12	γN-O(pyO)
		238			
		220			
		193			
189	4				νV-O(pyO)
		171			
146	sh				δL-V-L

* pyO-d_5-induced shifts. All shifts cited are to lower wavenumber.

\# Extra band observed in the spectrum of the pyO-d_5 complex.

Abbreviations: sh = shoulder (shift masked by adjacent band).

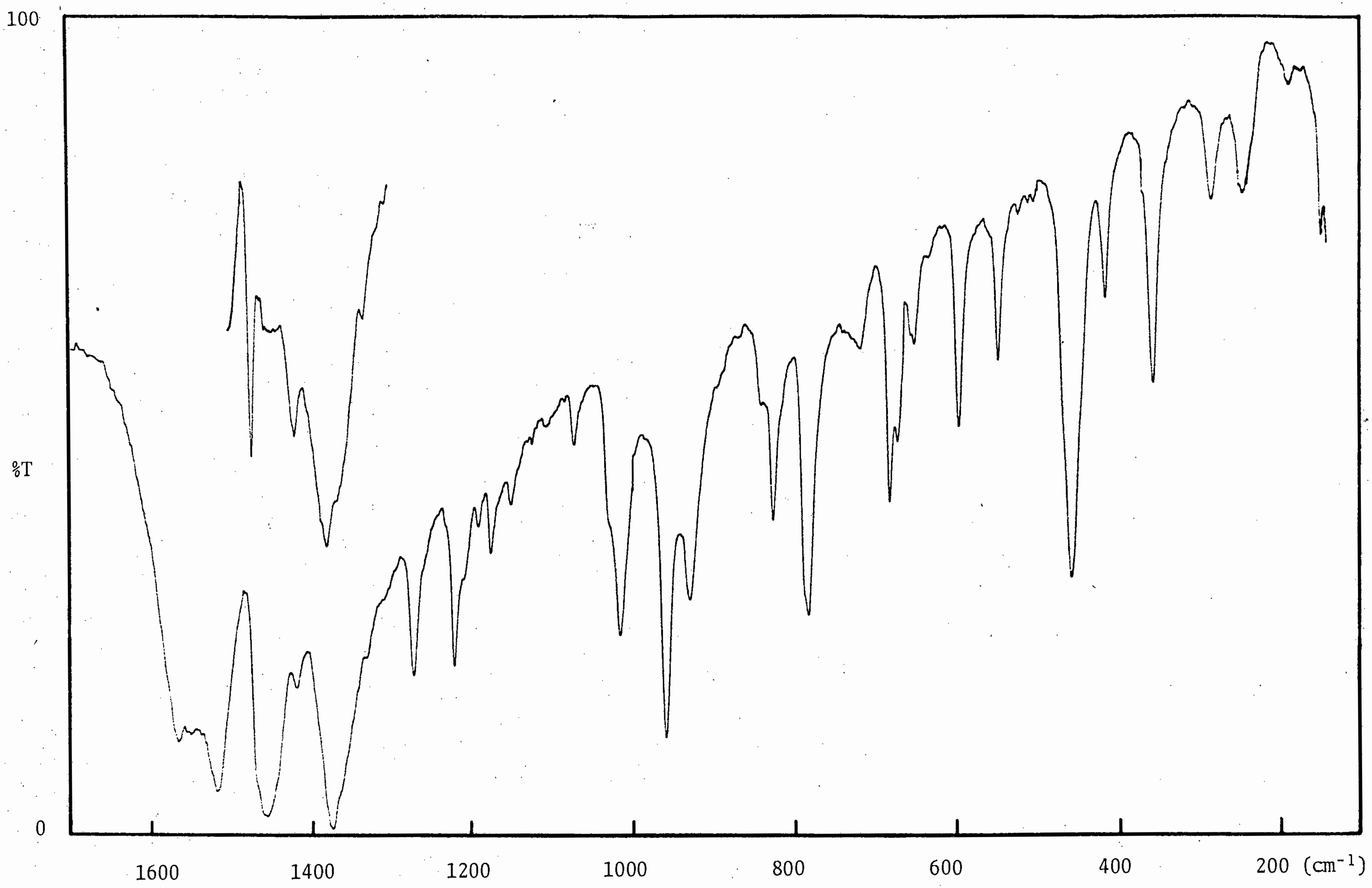


Figure 14. Infrared spectrum of VO(acac)$_2$pyO.

TABLE 14. (Continued)

* Him-d_3-induced shifts. All shifts cited are to lower wavenumber.

† Shifts in the spectrum of free imidazole are assigned only to those bands which are observed in the spectrum of the complex.

Extra band in the spectrum of the Him-d_3 complex.

Abbreviations: sh = shoulder (shift masked by adjacent band).

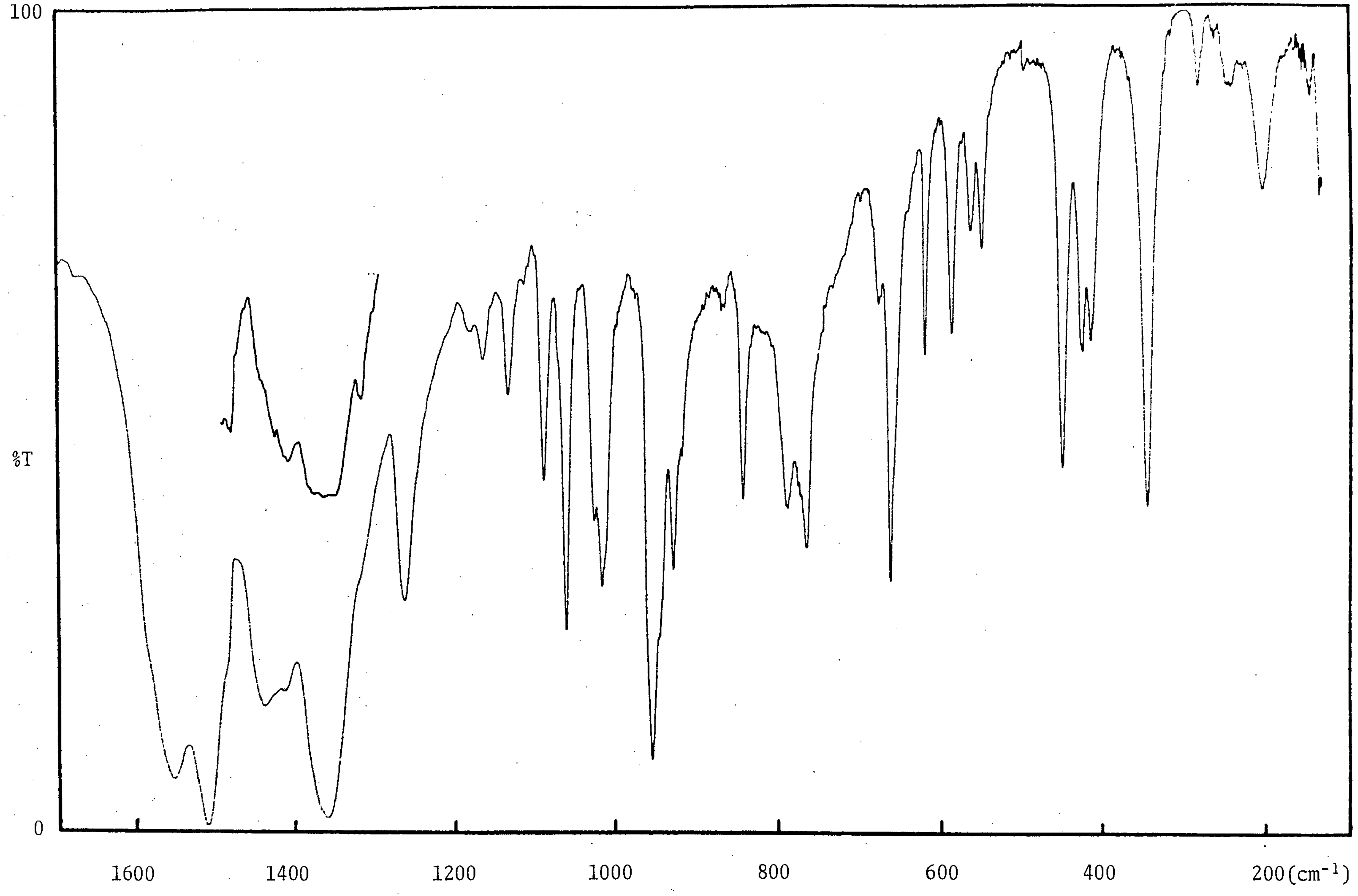


Figure 15. Infrared spectrum of VO(acac)$_2$Him.

TABLE 15. Vibrational frequencies (cm^{-1}), isotopic shifts and band assignments for the complex [VO(acac)$_2$quin].

[VO(acac)$_2$quin]		[VO(acac)$_2$]	quin		Assignment
ν	$\Delta\nu^*$	ν	ν	$\Delta\nu^*$	
			1619	26	ν ring(quin)
1596	sh		1594	43	ν ring(quin)
1589	0				
1574	0	1587			νC=O
1561	0	1556	1569	27	ν ring(quin) + νC=C(acac)
			1549	257	δC-H(quin)
			1533	82	ν ring(quin)
1524	0	1530			
			1514	288	δC-H
1504	sh		1499	61	ν ring(quin)
			1469	86	ν ring(quin)
			1453	87	ν ring(quin)
1430	sh		1430	267	δC-H(quin)
1417		1418			
			1392	111	ν ring(quin)
1375	0	1372			
		1356			
		1343			
			1370	131	ν ring(quin)
			1336	105	ν ring(quin)
			1332	76	ν ring(quin)
1312	218		1312	222	δC-H(quin)
1279	0	1286			δC=C + νC-CH$_3$(acac)
1263	224		1372-8	235	δC-H(quin)
			1353-8	238	δC-H(quin)
1237	0				
			1230	206	δC-H(quin)
1202	204		1215	252	δC-H(quin)
			1191	276	δC-H(quin)
1194	0	1187			δC-H(acac)

TABLE 15. (Continued)

$[VO(acac)_2quin]$		$[VO(acac)_2]$	quin		Assignment
ν	Δν*	ν	ν	Δν*	
1160	sh				
1137	242		1140	249	γC-H(quin)
1121	240		117	241	γC-H(quin)
1101	254		1094	234	γC-H(quin)
1046	91		1031	93	δ ring(quin)
1021	0	1018			CH_3 rock(acac)
			1012	180	δC-H(quin)
979	0	996			νV=O(acac)
			978	153	δCH(quin)
			952	203	γC-H(quin)
941	142		938	158	δC-H(quin)
932	0	936			νC-O + νC-CH_3(acac)
			866	175	δ ring(quin)
821	167		803	162	γC-H(quin)
809	sh				
795	0	798			γC-H(quin)
790	2	789			
			784	171	γC-H(quin)
760	100		758	93	δ ring(quin)
743	155		736	156	γC-H(quin)
		720			
679	0	685			ring def.(acac)
657	4	658			ring def.(acac)
630	34		627	38	δ ring(quin)
619	43		610	42	δ ring(quin)
604	0	608			νV-O
		579			
		560			
523	0				
521	15		520	16	δ ring(quin)
487	55/75#		477	60/68#	γ ring(quin)

TABLE 15. (Continued)

[VO(acac)$_2$quin]		[VO(acac)$_2$]	quin		Assignment
ν	Δν*	ν	ν	Δν*	
467	0	484			νV-O
453	2	461			
417	2	423			
399	29		390	39	γ ring(quin)
390	51		375	30	δ ring(quin)
361	0	364			νV-O
270	0	286			δO-V-O
248	0	260			δO-V-O
		238			
		220			
		193			
193	14		178	12	γ ring(quin)
		171			
149	0				δL-V-L

* = quin-d_7-induced shifts. All shifts cited are to lower wavenumber.

\# Extra band observed in the spectrum of the quin-d_7 complex.

Abbreviations: sh = shoulder (shift masked by adjacent band).

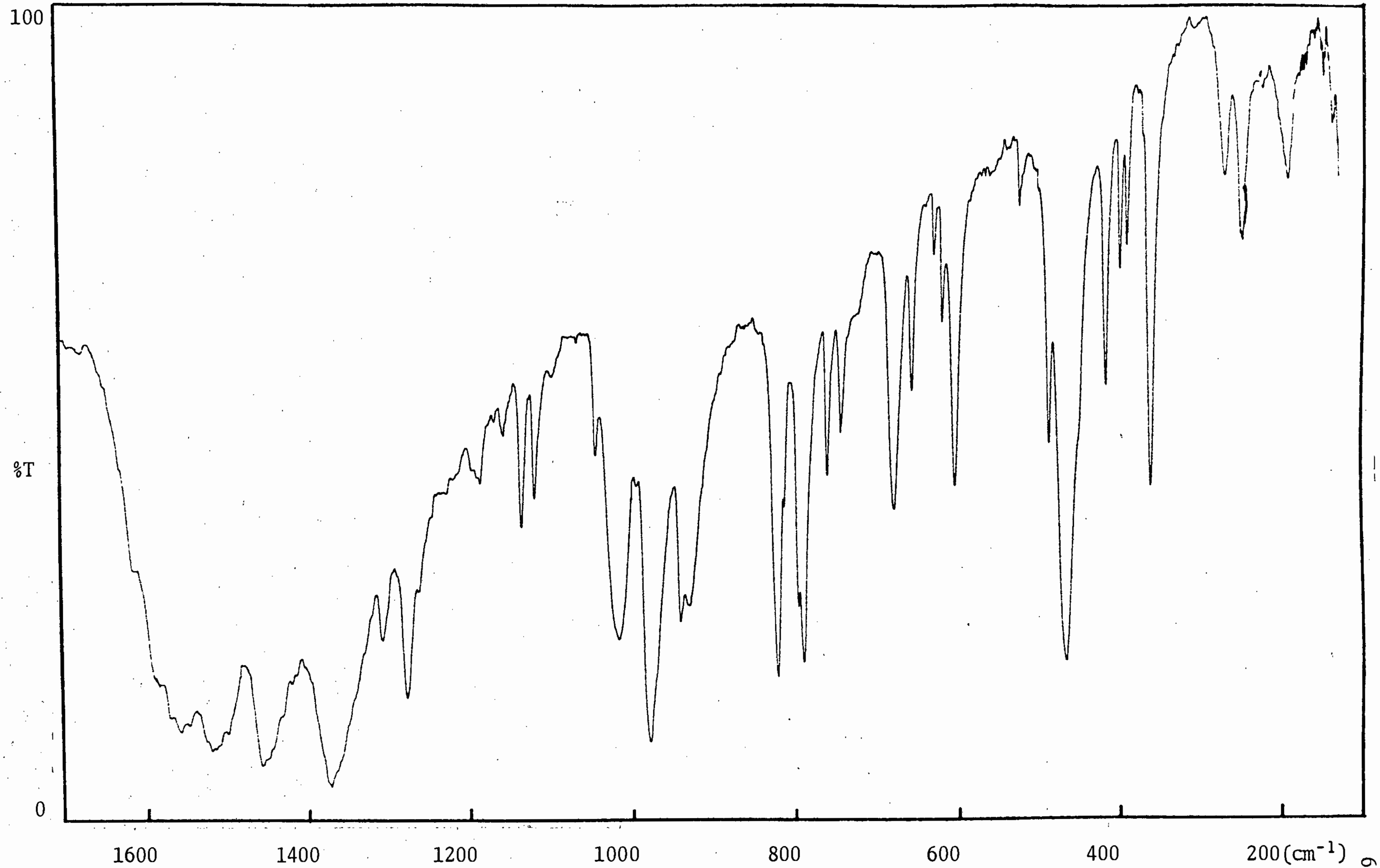


Figure 16. Infrared spectrum of VO(acac)$_2$quin.

TABLE 16. Vibrational frequencies (cm^{-1}) and band assignments for the complexes $[\mathrm{Cu(phth)_2(RNH_2)_2}]$ and their labelled analogues.

Complex	Assignment									
	amine		phth ligand				νCu-N(phth)	phth ligand		
$[\mathrm{Cu(phth)_2}(\mathit{ter}\text{-}\mathrm{C_4H_9NH_2})_2]$	465	450	410		351		294	273	238	189
$[\mathrm{Cu(phth)_2}(\mathit{ter}\text{-}\mathrm{C_4H_9ND_2})_2]$	465	448/424#	410		351		294	272	239	189
$[\mathrm{Cu(phth)_2}(\mathit{cy}\text{-}\mathrm{C_6H_{11}NH_2})_2]$	454	424	409		350		292	262	208	186
$[\mathrm{Cu(phth\text{-}^{15}\mathit{N})_2}(\mathit{cy}\text{-}\mathrm{C_6H_{11}NH_2})_2]$	454	424	409		350		287	261	207	186
$[\mathrm{Cu(phth)_2}(\mathit{cy}\text{-}\mathrm{C_6H_{11}ND_2})_2]$	453/439#	421	408		349		292	261	207	186
$[\mathrm{Cu(phth)_2}(\mathit{sec}\text{-}\mathrm{C_4H_9NH_2})_2]$	452	425	409		351		294	265	204	185
$[\mathrm{Cu(phth)_2}(\mathit{n}\text{-}\mathrm{C_4H_9NH_2})_2]$	-	-	408		357	337	295	252	213	184
$[\mathrm{Cu(phth\text{-}^{15}\mathit{N})_2}(\mathit{n}\text{-}\mathrm{C_4H_9NH_2})_2]$	-	-	408		357	337	290	251	213	184
$[\mathrm{Cu(phth)_2}(\mathit{n}\text{-}\mathrm{C_4H_9ND_2})_2]$	-	-	408		356	333	295	253	213	184
$[\mathrm{Cu(phth)_2}(\mathit{iso}\text{-}\mathrm{C_4H_9NH_2})_2]$	489	433	409	397	351		296	260	232	184
$[\mathrm{Cu(phth)_2}(\mathit{iso}\text{-}\mathrm{C_4H_9ND_2})_2]$	489/468	431	409	395	351		296	260	231	185

TABLE 16. (Continued)

Complex	Assignment									
	amine			phth ligand		νCu-N(phth)				phth ligand
[Cu(phth)$_2$(n-$C_3H_7NH_2$)$_2$]		462	-	410	355	299		259	247	186
[Cu(phth-^{15}N)$_2$(n-$C_3H_7NH_2$)$_2$]		463	-	410	355	294		259	248	186
[Cu(phth)$_2$(n-$C_3H_7ND_2$)$_2$]		464/438#	-	410	355	299		259	249	186
[Cu(phth)$_2$($\phi CH_2CH_2NH_2$)$_2$]		471	452	410	356	297		259	200	186
[Cu(phth)$_2$($\phi CH_2CH_2ND_2$)$_2$]		470	-	410	356	297		264	200	187
[Cu(phth)$_2$(ϕCH_2NH_2)$_2$]	497	488	448	407	355	296	266	253	203	185
[Cu(phth-^{15}N)$_2$(ϕCH_2NH_2)$_2$]	497	488	448	407	355	391	266	253	203	185
[Cu(phth)$_2$(ϕCH_2ND_2)$_2$]	494	486	444	407	354	296	260	sh	203	185

Extra band observed in spectrum of labelled complex.

Abbreviations: sh = shoulder (shift masked by adjacent band).

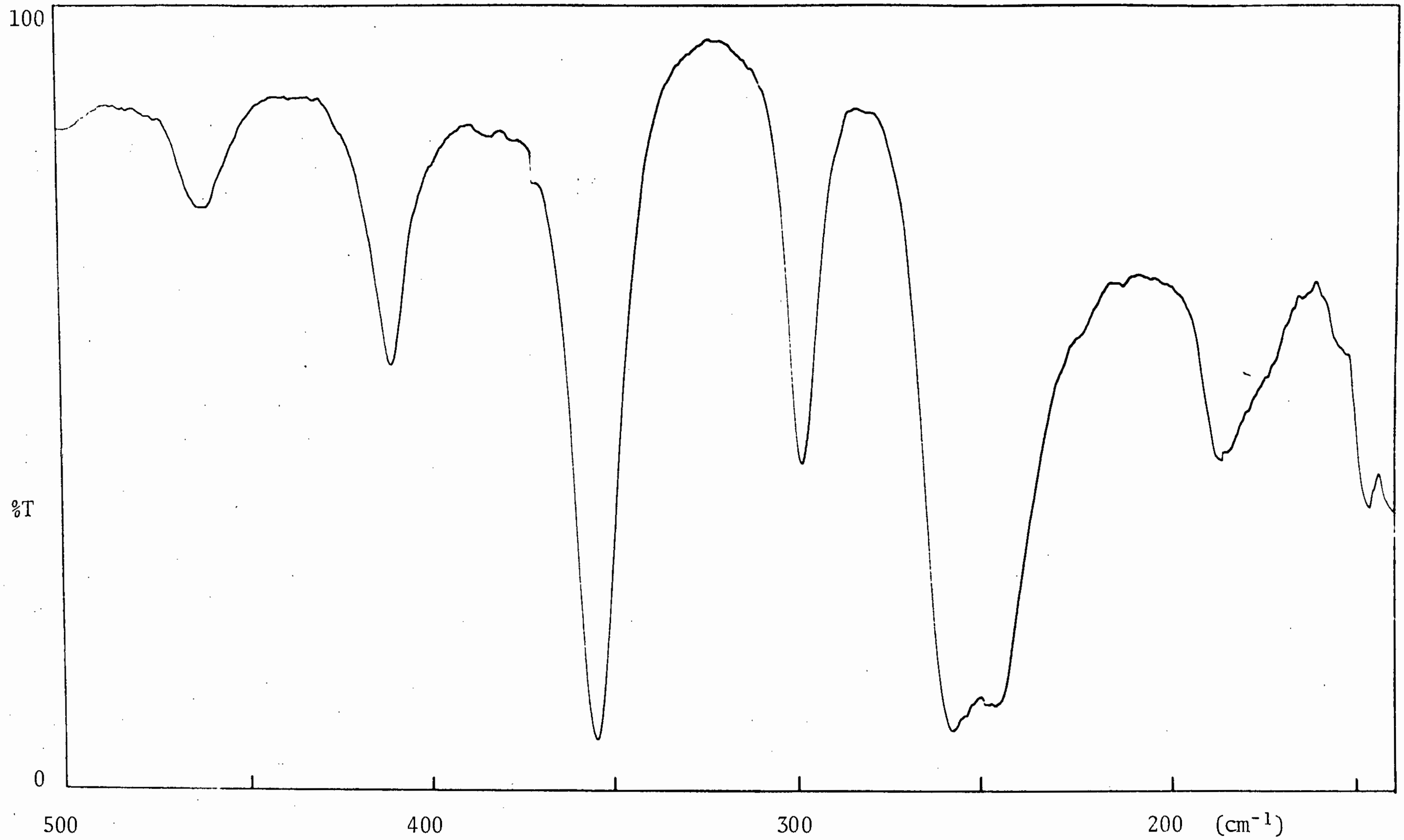


Figure 17. Infrared spectrum of $[Cu(phth)_2(n\text{-}C_3H_7NH_2)_2]$.

TABLE 17. Vibrational frequencies (cm^{-1}) and band assignments for the complexes [Ni(phth)$_2$(RNH$_2$)$_2$] and their labelled analogues.

Complex							Assignments								
		amine ligand			phth			νNi-N(phth)						phth ligand	
[Ni(phth)$_2$(*cy*-C$_6$H$_{11}$NH$_2$)$_2$]		457	435	423	410		372	355	350	327	285	245	220	181	~143
[Ni(phth-^{15}N)$_2$(*cy*-C$_6$H$_{11}$NH$_2$)$_2$]		457	435	423	409		372	sh	351	327	285	245	220	181	~143
[Ni(phth)$_2$(*n*-C$_4$H$_9$NH$_2$)$_2$]		466	430		412		371			338	272	260		185	~137
[Ni(phth-^{15}N)$_2$(*n*-C$_4$H$_9$NH$_2$)$_2$]		466	430		410		371			337	272	259		185	~137
[Ni(phth)$_2$(*n*-C$_4$H$_9$ND$_2$)$_2$]		466	430		412		361			335/319#sh		259		186	
[Ni(phth)$_2$(*n*-C$_3$H$_7$NH$_2$)$_2$]		466			415	406	371	362		338	272	-		185	152
[Ni(phth-^{15}N)$_2$(*n*-C$_3$H$_7$NH$_2$)$_2$]		466			413	406	371	358		338	272	-		185	152
[Ni(phth)$_2$(*n*-C$_3$H$_7$ND$_2$)$_2$]		466			415	402	sh	363		319	261	-		185	151
[Ni(phth)$_2$(ϕCH$_2$CH$_2$NH$_2$)$_2$]	496	468			413		371			337	271	234		186	169
[Ni(phth-^{15}N)$_2$(ϕCH$_2$CH$_2$NH$_2$)$_2$]	496	468			411		371			336	271	234		185	168
[Ni(phth)$_2$(ϕCH$_2$CH$_2$ND$_2$)$_2$]	496	468			413		363			319	252	234		186	165

Extra band observed in spectrum of labelled complex.

Abbreviations: sh = shoulder (shift masked by adjacent band).

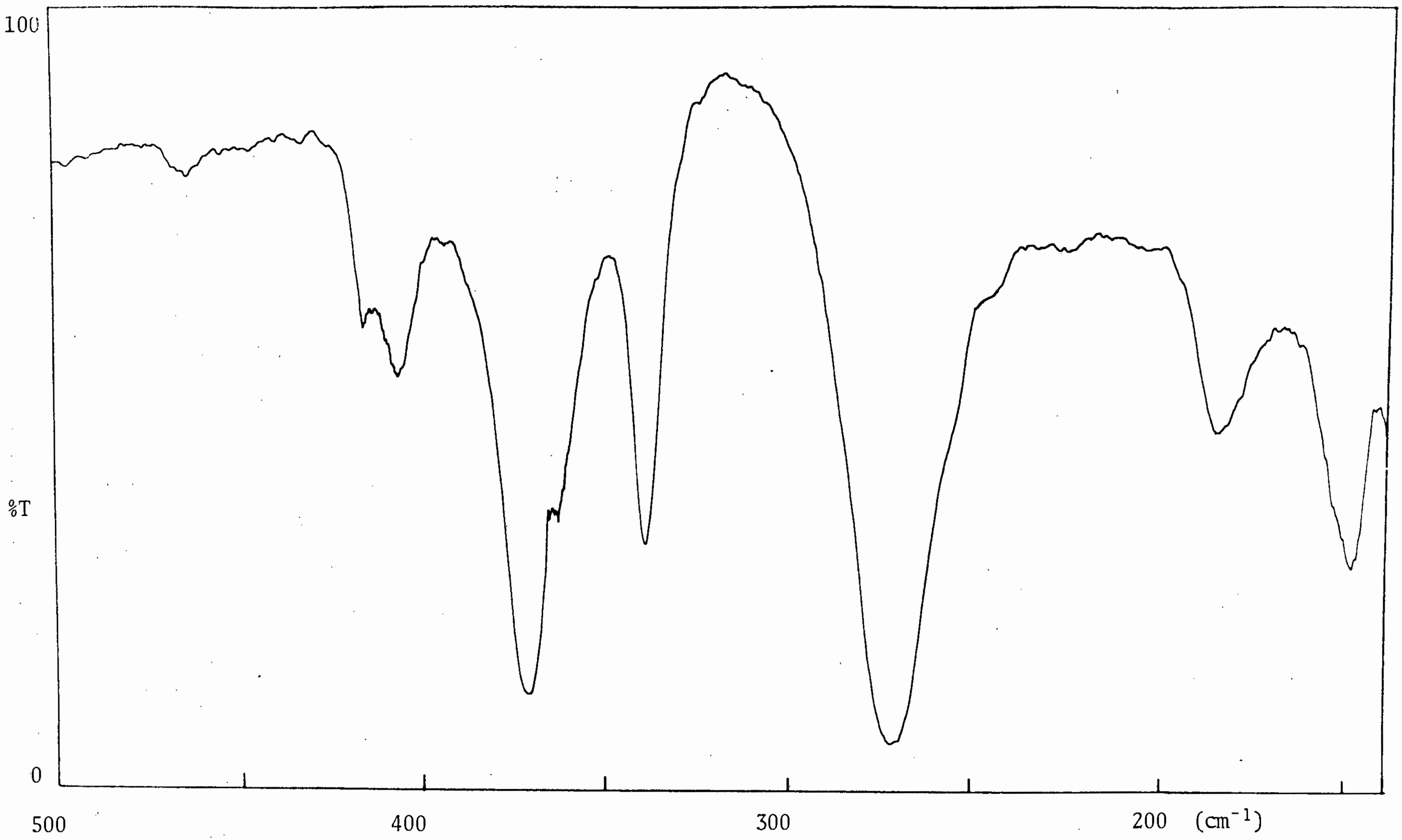


Figure 18. Infrared spectrum of $[Ni(phth)_2(n\text{-}C_3H_7NH_2)_2]$.

IV DISCUSSION

1. INFRARED SPECTRA OF COBALOXIMES

1.1 Infrared spectra of dimethylglyoxime

In a recent paper by Keresztury and Holly [39], the vibrational spectrum of pure dimethylglyoxime was investigated. The internal vibrations were assigned on the basis of polarisation angles and ^{2}H-induced shifts. The molecular structure and hydrogen bonding in crystalline dimethylglyoxime, determined by a combined X-ray and neutron diffraction experiment [69], is illustrated in Fig. 19. The unit cell and molecule have a common centre of symmetry.

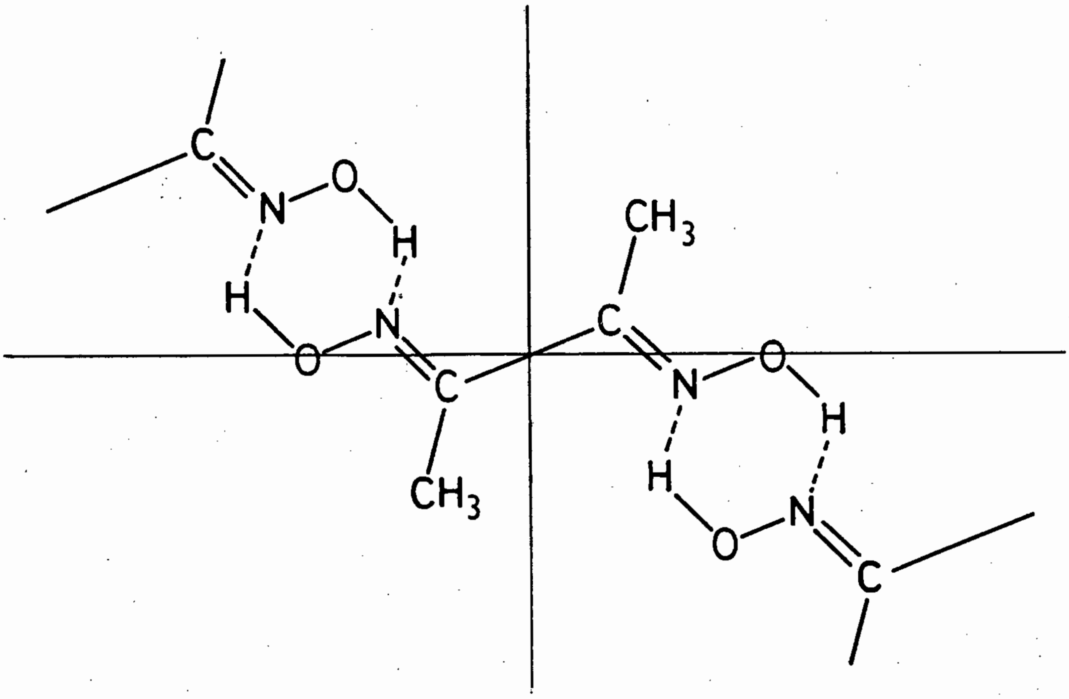


Figure 19. Molecular structure and hydrogen bonding in crystalline dimethylglyoxime.

In this work the infrared spectra of dimethylglyoxime, dimethylglyoxime-$^{15}N_2$ and dimethylglyoxime-d_2 were investigated in the region 1700 - 140 cm^{-1}. The spectrum of the unlabelled dimethylglyoxime is reproduced in Fig. 5. The effects of the various types of labelling on the spectrum of dimethylglyoxime may be seen in Table 9, where the band frequencies and isotopic shifts are reported. The environment of the dimethylglyoxime is very different from that of the coordinated dimethylglyoximate anion in cobaloximes. It is therefore not surprising to observe considerable differences in the absorption frequencies of similar vibrations in the two species.

The effects of deuteration on the vibrational modes of the hydrogen bonded OH group are clearly seen. The νO-H at 3200 cm^{-1} is replaced by νO-D near 2400 cm^{-1}, and the in-plane bending mode is shifted from 1142 to 1100 cm^{-1}. The two intense bands at 1364 and 1440 cm^{-1} (neither of which is sensitive to labelling) are the CH_3 symmetric and antisymmetric deformations, respectively. It is interesting to note that the infrared-active pair of the C=N stretching vibrations is too weak to be observed in the spectrum of the unlabelled compound. However, on labelling, a medium intensity band appears at 612 cm^{-1} in the spectrum of D-d_2 and at 690 cm^{-1} in the spectrum of DH_2-$^{15}N_2$. This lowering of νC=N on deuteration supports the suggestion [39] that it is coupled with δO-H. The N-O vibrations are expected to be sensitive to both forms of labelling. Two bands (at 977 and 902 cm^{-1}) satisfy these criteria. Both are assigned to νN-O. The vibration of lower frequency, which is more sensitive to labelling is the principal band. Low intensity bands at 468 and 372 cm^{-1}, which exhibit sensitivity to both d_2- and ^{15}N-labelling are assigned to out-of-plane N-O-H bending modes.

1.2 Infrared spectra of the complexes [CoX(DH)$_2$py]

The effects of the various types of labelling on the spectrum of [CoCl(DH)$_2$py] are depicted in Fig. 20. The spectra of the ligands and unlabelled complexes [CoX(DH)$_2$py] are shown in Fig. 21. The band frequencies and isotopically-induced shifts are reported in Table 10. In the ensuing discussion, the bands which shift on ^{15}N-labelling of the pyridine and dimethylglyoximate nitrogens are referred to as ^{15}N(py)- and ^{15}N(DH)-sensitive bands, respectively. Those which move on deuteration of the pyridine ring are termed py-d_5-sensitive and those affected by X-substitution are termed X-sensitive.

Internal vibrations of coordinated pyridine

Over the range 1700 - 150 cm^{-1}, 27 bands are observed within the spectrum of each complex and a band-for-band correspondence exists between the spectra of the four complexes with differing X-substituents. The pyridine ligand vibrations are identified as those bands which are sensitive to both ^{15}N(py) and py-d_5 labelling. Deuteration of the pyridine complexes leads to large shifts in the internal ligand modes. The C-H bending modes characteristically shift between 100 and 350 cm^{-1} to lower frequency while the ring stretching vibrations are less affected. This causes some C-H modes to cross over ring modes in the spectra of the deuterated complexes leading to some degree of uncertainty as to which band in the deuterated spectrum corresponds with a particular band in the undeuterated spectrum. Although most of these uncertainties are removed by earlier studies on the spectra of pyridine [70] and [Zn(py)$_2$Cl$_2$] [13], ^{15}N-labelling of the pyridine nitrogen atom provides a check on the assignments resulting from pyridine deuteration.

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A rule-of-thumb distinction between the ring stretching and C-H bending vibrations of pyridine is provided by an earlier isotopic labelling study of

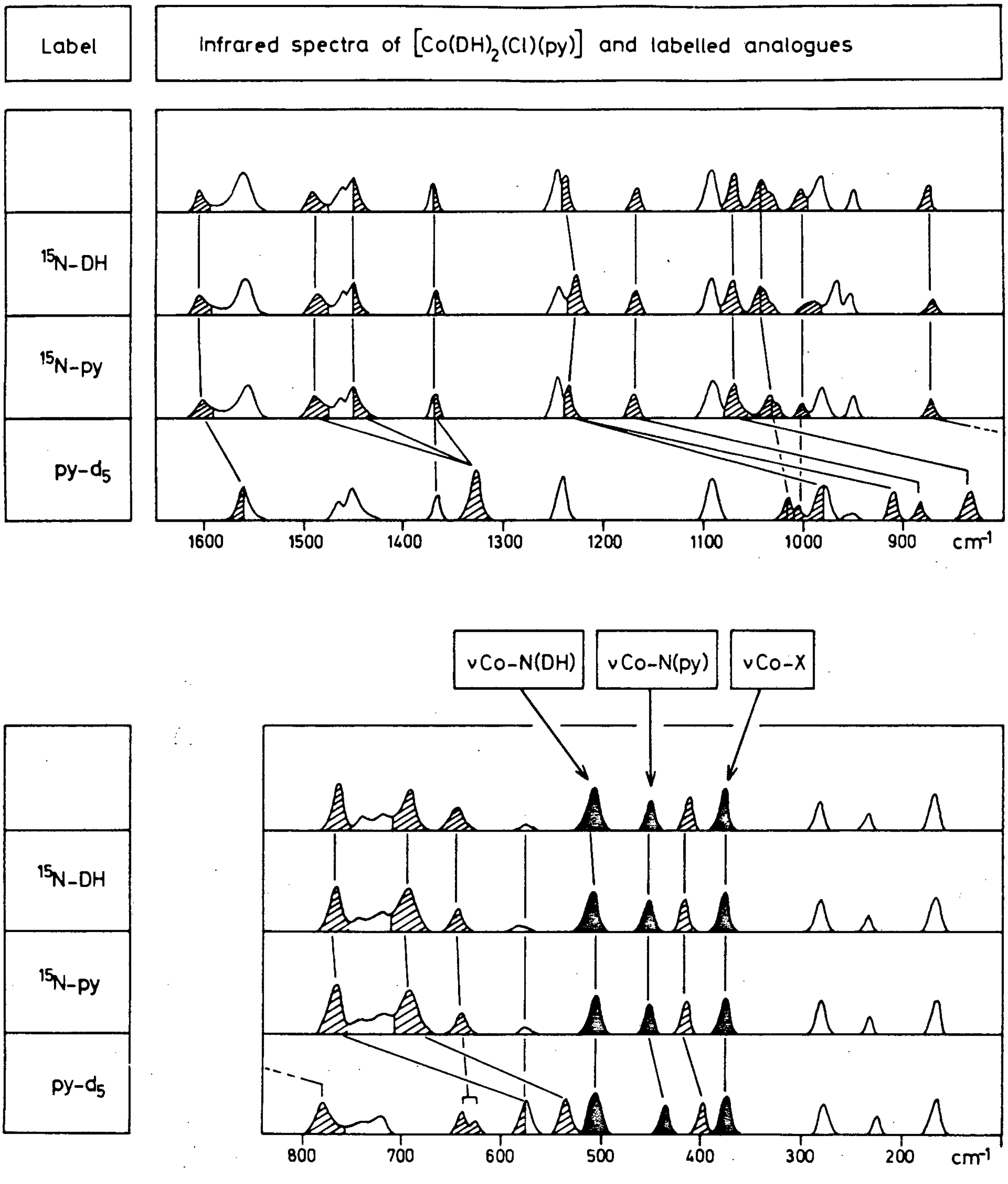

Figure 20. The infrared spectra of [CoCl(DH)$_2$py] and labelled analogues.

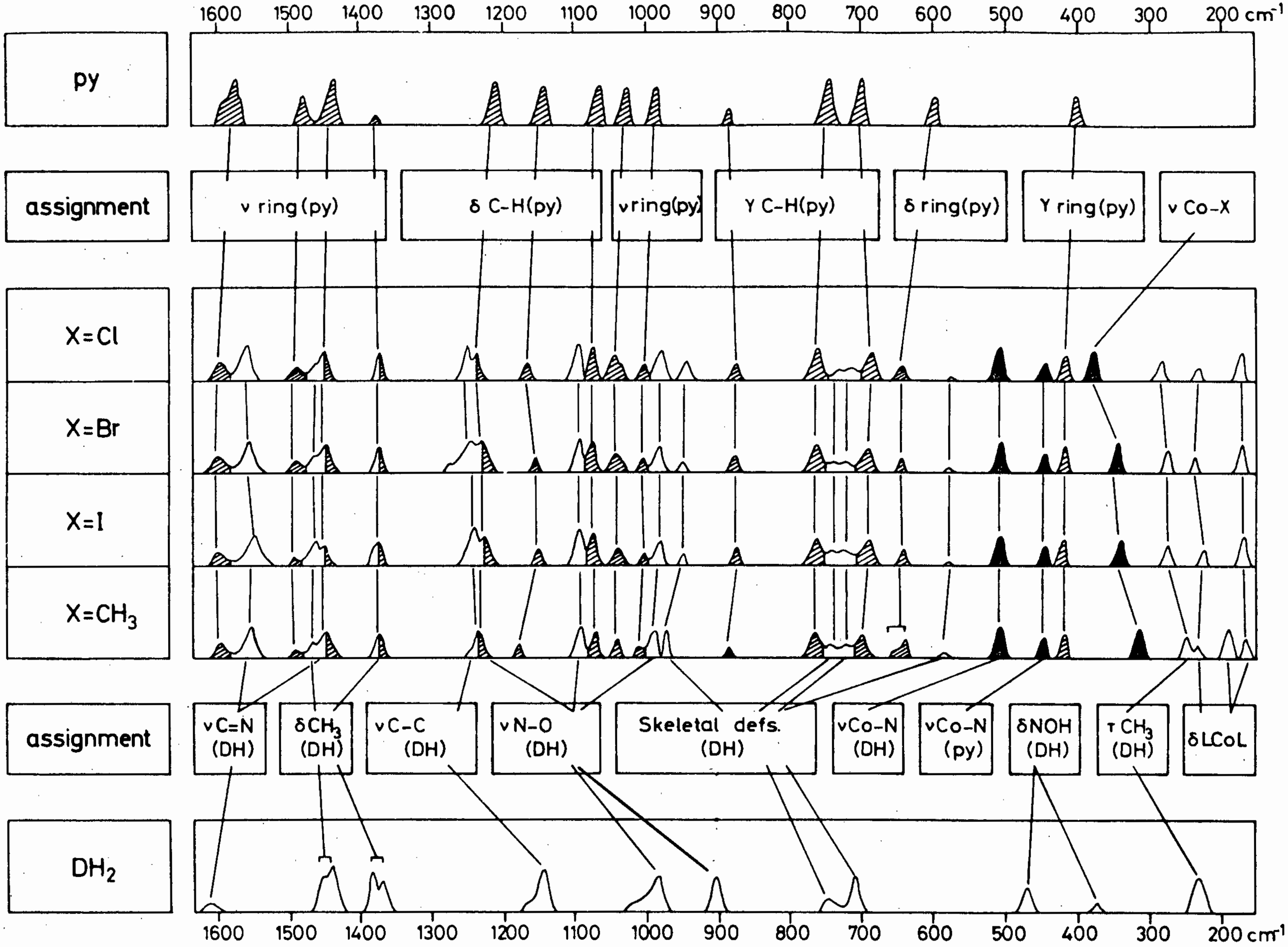

Figure 21. The infrared spectra of the ligands and unlabelled complexes of [CoX(DH)$_2$py].

free and complexed pyridine [13] which indicated that, in the spectra of both pyridine and the complex [Zn(py)$_2$Cl$_2$], the ratio between the frequencies of the deuterated and undeuterated species is ~0.95 for the ring stretching modes and ~0.75 for the C-H bending modes. These ratios serve very well for the cobaloxime complexes also. The final criterion used to identify the pyridine bands in the present work is absence of ^{15}N-DH sensitivity. The procedures indicated above enable each band in the spectrum of pyridine to be assigned in the spectra of the complexes.

Skeletal vibrations of the chelated dimethylglyoximate anion

Without ^{15}N(DH) labelling, reliable assignments for the skeletal DH- vibrations would not be possible. The spectrum of dimethylglyoxime (DH$_2$) is not very helpful for empirical assignment of the coordinated dimethylglyoximate bands since the free ligand is in a very different environment from the chelated ligand [39]. This is particularly true of the oximino groups.

^{15}N(DH)-Labelling unambiguously identifies the vibrations involving the oximino nitrogen atoms. Earlier proposals [31,71] that the band near 1560 cm^{-1} originates in the νC=N mode are confirmed by its high ^{15}N(DH)-sensitivity and the fact that it is unaffected by pyridine labelling. The corresponding band in the spectrum of uncoordinated DH$_2$ occurs [39] at 1620 cm^{-1} and the shift of 60 cm^{-1} on complexation is reasonable for coordination via the oximino nitrogen atom.

In previous work [31,32,71], the νN-O band has been empirically identified near 1100 cm^{-1}. The assignment is supported here by its ^{15}N(DH)-sensitivity and absence of any shift on pyridine labelling. A second νN-O band has been empirically assigned near 1240 cm^{-1} [31,32,71]. This band is principally a pyridine δC-H mode since it shifts substantially on both ^{15}N(py) and py-d_5

labelling. However, it also moves on ^{15}N-DH labelling and therefore probably comprises some coupling with νN-O. An uncoupled νN-O band occurs neat 980 cm^{-1}, this band is only sensitive to ^{15}N(DH) labelling.

A band near 950 cm^{-1} is insensitive to all modes of labelling: it is probably a CCC deformation of the DH group. Bands near 735 and 720 cm^{-1} are too broad for their ^{15}N-sensitivity to be determined. Since they are not substantially affected by pyridine deuteration, they are likely to originate in skeletal vibrations of the coordinated dimethylglyoximate ion.

Cobalt-ligand vibrations

The above discussion has yielded assignments for all bands with a frequency exceeding 550 cm^{-1}. The metal-ligand stretching frequencies in cobaloximes, νCo-N(DH) and νCo-N(py), are expected [72] to occur towards the high frequency limit of the range of νM-N in complexes of first transition series ions because of the very high ligand field strength associated with the spin-paired $3d^6$ configuration of Co(III).

The strong band near 510 cm^{-1} has been generally recognised as the νCo-N(DH) band although the earlier empirical studies failed reliably to differentiate it from the νCo-N(py) band [31,32,71]. The 510 cm^{-1} band is now firmly established as νCo-N(DH) by its sensitivity to ^{15}N(DH) labelling. Absence of any coupling with a pyridine ligand mode or with νCo-N(py) is confirmed by lack of any sensitivity to ^{15}N(py) or py-d_5 labelling.

The out-of-plane pyridine ring vibration at 405 cm^{-1} in the ligand spectrum characteristically appears near 425 cm^{-1} in pyridine complex spectra [13]. Hence, of the two bands near 420 and 450 cm^{-1} in the spectra of the cobaloxime complexes (both of which move on ^{15}N(py) and py-d_5 labelling) that of lower frequency is assigned to the γ ring(py) mode. There is probably some coupling with νCo-N(DH) since it exhibits a small but finite ^{15}N(DH)-sensitivity. That the 450 cm^{-1} band is correctly assigned to νCo-N(py) is confirmed by its sensitivity to ^{15}N(py) and py-d_5 labelling and insensitivity to ^{15}N(DH)-labelling. This band has been formerly assigned to νCo-N(DH) [31].

The νCo-X band is reliably identified as the only band in the spectra of these complexes to exhibit significant X-sensitivity. It occurs within the range 300 - 400 cm^{-1}. The assignment is confirmed by complete insensitivity to any mode of labelling. Bands near 230 - 170 cm^{-1} are likely to originate in L-Co-L bending modes.

1.3 Infrared spectra of the linkage isomers [Co(CNS)(DH)$_2$py]

The multiple labelling technique employed here again enables distinction between bands arising from vibrations of the different ligands. The pyridine ring vibrations are assigned on the basis of their sensitivity to ^{15}N-labelling of the pyridine nitrogen and d-labelling of pyridine hydrogen atoms. Vibrations associated with the thiocyanato and isothiocyanato ligands are assigned mainly on the basis of their sensitivity to ^{15}NCS-labelling. However, ^{15}NCS-labelling does not always induce significant shifts in metal-ligand vibrations. There are two reasons for this. Firstly, the expected isotopic shifts are small because the small increase in mass with respect to the unlabelled thiocyanate ion yields an unfavourable mass ratio μ/μ^{i}. Secondly where M-SCN bonding occurs the labelled nitrogen atom is too far removed from the metal to induce significant isotopic shift. In previous work employing ^{15}NCS-labelling [73-75], shifts of only 1-4 cm^{-1} were obtained for M-SCN and M-NCS vibrations. Thus empirical methods are relied upon considerably in assigning the M-CNS vibrations. The skeletal vibrations of the chelated dimethylglyoximate anion were based upon earlier assignments made for the cobaloximes with axially coordinated pyridine and halide ligands. In the ensuing discussion, M-NCS and M-SCN represent N- and S-bonded thiocyanato groups, respectively, while M-CNS indicates that the mode of thiocyanato coordination is unspecified. The effects of the various forms of labelling on the spectra of $[Co(CNS)(DH)_2py]$ complexes are depicted in Fig. 22. The band frequencies and isotopic shifts are displayed in Table 11. The spectra of the unlabelled complexes are reproduced in Figs. 10 and 11.

Internal vibrations of coordinated pyridine

The pyridine ligand vibrations are identified on the basis of their sensitivity to ^{15}N(py) and py-d_5 labelling. As expected, these vibrations do not differ considerably from those observed in the earlier spectra of cobaloximes with axially coordinated pyridine and halide ligands. Furthermore there is little difference between the pyridine vibrations of the M-SCN and M-NCS complexes. One exception is the py-d_5-sensitive band near 957 cm^{-1} in the spectrum of $[Co(SCN)(DH)_2py]$. This band, which is absent from the spectrum of the M-NCS isomer, is ascribed to a pyridine ring vibration. The out-of-plane bending mode of the pyridine ring at 404 cm^{-1} is observed characteristically at higher frequency in the spectra of the complexes. In the thiocyanato complex it occurs at 424 cm^{-1} and masks a δNCS vibration which is revealed in the py-d_5 spectrum where the pyridine vibration is shifted to 403 cm^{-1} (Fig. 22). In the isothiocyanato complex the γ ring(py) appears as a broad py-d_5-sensitive band between 423 and 412 cm^{-1}.

Ligand vibrations associated with the thiocyanato and isothiocyanato groups

The spectrum of NaNCS (Fig. 22) yields only four bands in the range 4000 - 140 cm^{-1}. Each of these bands exhibits significant ^{15}N-sensitivity. The

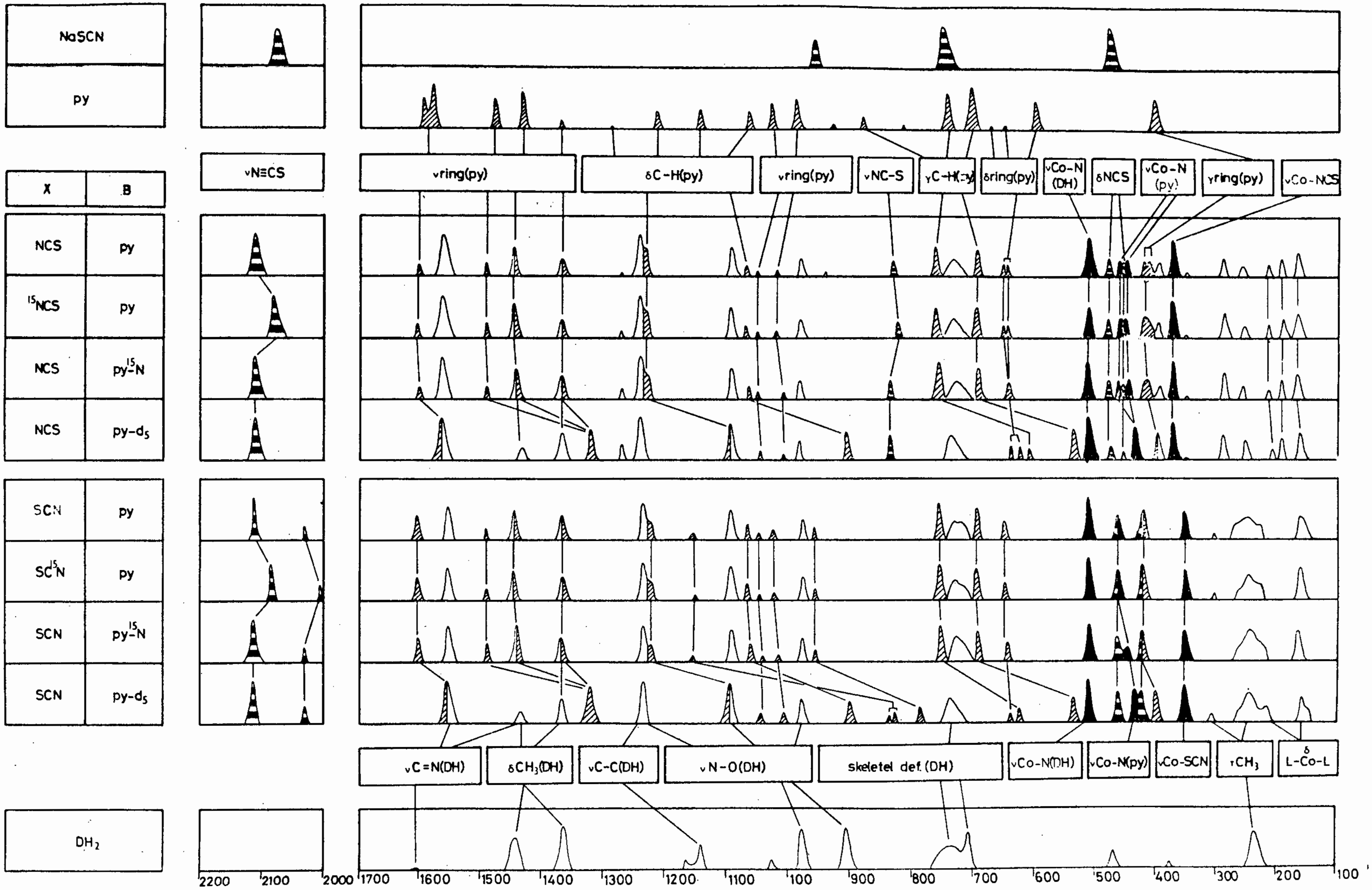

Figure 22. The infrared spectra of the ligands amd linkage isomers of [Co(CNS)(DH)$_2$py] and their labelled analogues.

band at 2074 cm^{-1}, assigned to νN-CS appears as a relatively broad band at 2122 cm^{-1} in the spectrum of the isothiocyanato complex and exhibits a large ^{15}NCS-induced shift (30 cm^{-1}). In the thiocyanato complex νN-CS is split into two bands occurring at 2112 and 2028 cm^{-1}. Their ^{15}NCS-sensitivities are 29 and 26 cm^{-1}, respectively. The former band is much sharper than its counterpart in the spectrum of the [Co(NCS)(DH)$_2$py] complex. This is in agreement with earlier observations by Pecile [86] regarding the integrated intensities of νC-NS in thiocyanates and isothiocyanates, and has previously been used [40] as a diagnostic criterion for differentiating between the two linkage isomers.

The νNC-S band, which occurs at 757 cm^{-1} in the spectrum of NaNCS, is shifted 10 cm^{-1} by ^{15}NCS-labelling. In the isothiocyanato complex νNC-S appears at 833 cm^{-1} (characteristic of M-NCS coordination) and exhibits a ^{15}NCS-sensitivity of 9 cm^{-1}. It is absent from the spectra of the thiocyanato complex, where it is probably obscured by the broad skeletal deformation of the dimethylglyoximate ion around 730 cm^{-1}. The NC-S stretching mode in this complex is expected to occur between 690 and 720 cm^{-1} [76].

The bending vibration (δNCS) occurring at 481 cm^{-1} in the spectrum of NaNCS, is split in the spectra of the complexes, where it appears as two bands. Although the ^{15}NCS-sensitivity of these two bands cannot be considered significant, they are assigned as δNCS on the basis of comparison with the [CoX(DH)$_2$py] and NaNCS spectra. The overtone of the δNCS vibration (2δNCS) at 960 cm^{-1} in the spectrum of NaNCS is absent from the spectra of the complexes. A similar occurrence was noted [73] in the spectra of *bis*-(aniline)metal(II) isothiocyanato complexes.

Skeletal vibrations of the chelated dimethylglyoximate anion

Because of the similarity between DH vibrations of [Co(CNS)(DH)$_2$py] and

$[CoX(DH)_2py]$ and the expense of labelled dimethylglyoxime it was not considered desirable to examine the spectra of the (DH-^{15}N)-complexes. All assignments could be made by simple comparison between the spectra. There is a band-for-band correspondence in the DH-vibrations of the two linkage isomers and generally they appear at similar frequencies. One exception, the band at 1273 cm^{-1} in the spectrum of the isothiocyanato complex, which is insensitive to all forms of labelling and absent from the spectrum of the thiocyanato complex, is assigned to a νC-C of dimethylglyoxime. The bands near 1240 cm^{-1} assigned by Norbury *et al.* [40] to a pyridine ring vibration are shown here, by their insensitivity to either form of labelling, to be due to νC-C of the dimethylglyoximate anion.

Metal-ligand vibrations

The metal-ligand stretching vibrations: νCo-N(DH) and νCo-N(py), being relatively insensitive to variation of the axial ligand, are expected to occur at frequencies similar to those experienced by the cobaloximes with the halide ligands. The strong band near 513 cm^{-1} is confirmed as νCo-N(DH) by its lack of sensitivity to either form of labelling. In the isothiocyanato complexes, the split band near 460 cm^{-1} is assigned as νCo-N(py). Both components are sensitive to labelling of the pyridine ligand. In the thiocyanato complex νCo-N(py) occurs at 464 cm^{-1} as a single band masking a δNCS vibration. It is sensitive to both ^{15}N(py) and py-d_5 labelling; whereupon it shifts to lower frequency, revealing the δNCS band which remains insensitive to labelling. As expected νCo-CNS is considerably sensitive to the mode of coordination of the thiocyanato ligand. The bands occurring at 376 cm^{-1} in the spectrum of the isothiocyanato complex and at 356 cm^{-1} in the spectrum of the thiocyanato complex, are assigned to νCo-NCS and νCo-SCN, respectively. Although neither of these bands exhibits sensitivity to ^{15}NCS labelling, they are the only vibrations sufficiently sensitive to change of the bonding mode in the isomers to be assigned to νCo-CNS. Furthermore they occur in the same region of the spectrum as νCo-X in the complexes [CoX(DH)$_2$py]. The assignment of νCo-CNS thus being established, it now provides a useful diagnostic criterion for differentiation between the two isomers. The low frequency bands between 160 and 220 cm^{-1} are likely to originate in L-Co-L bending modes.

2 INFRARED SPECTRA OF BASE ADDUCTS OF VANADYL ACETYLACETONATE

The method used for assignment of the infrared spectra of the $VO(acac)_2B$ complexes was as follows: assignments of vibrations of the uncoordinated bases were made according to the magnitude of the isotopically induced shifts in conjunction with earlier assignments in the literature. These ligand bands, which retained their isotopic sensitivity, were traced in the spectra of the adducts and assigned accordingly. Vibrations originating in the acetylacetonate moiety are expected to be insensitive to labelling and only mildly sensitive to variation of the base. Metal-oxygen vibrations of $VO(acac)_2$ which normally occur below 600 cm^{-1}, should be reduced in frequency on adduct formation and be sensitive to variation of the amine. Figures 12 - 16 contain the infrared spectra of the unlabelled $VO(acac)_2$, $VO(acac)_2py$, $VO(acac)_2pyO$, $VO(acac)_2Him$ and $VO(acac)_2quin$ complexes in the range 1700 - 140 cm^{-1}. Frequency data are recorded in Tables 12 - 15. In Figures 23 - 26, the spectra of the base adducts and labelled analogues are compared with the parent $VO(acac)_2$ complex and uncoordinated base, while the low frequency spectra of the various base adducts are compared in Figure 27.

Vibrations of the uncoordinated bases

Deuteration of the heterocyclic bases leads to large shifts of the internal vibrational modes. It has been found, however, that the C-H bending modes characteristically shift between 100 and 350 cm^{-1} to lower frequency while the ring stretching vibrations are less affected. Distinction between these modes is made possible by the method discussed in Chapter IV. The ratio ν^i/ν for the frequencies of the labelled and unlabelled species respectively is ~0.75 for the C-H bending modes and ~0.95 for the ring stretching modes [13]. This rule for assigning the

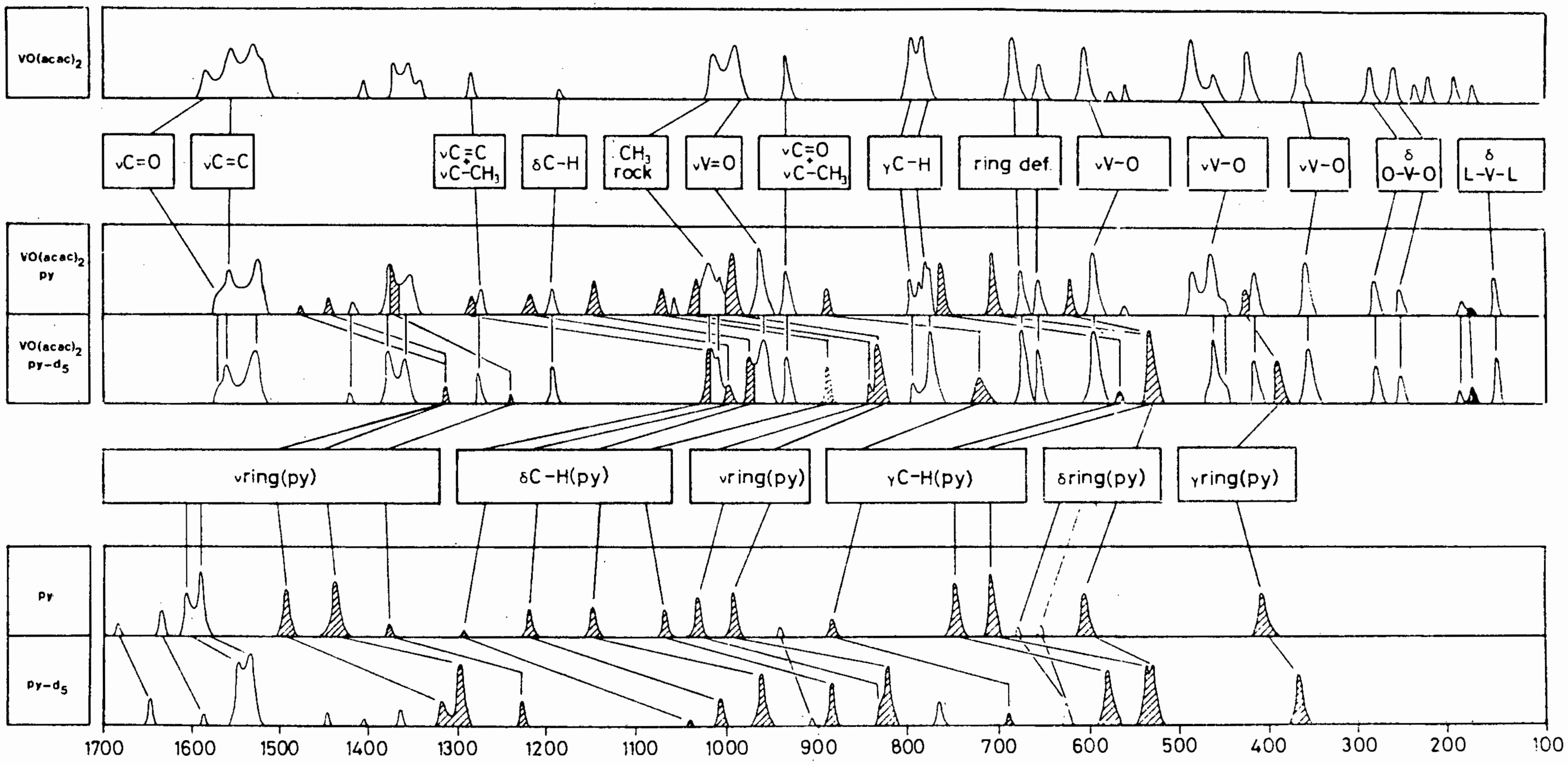

Figure 23. Infrared spectra of the ligands and complex VO(acac)$_2$py and their labelled analogues.

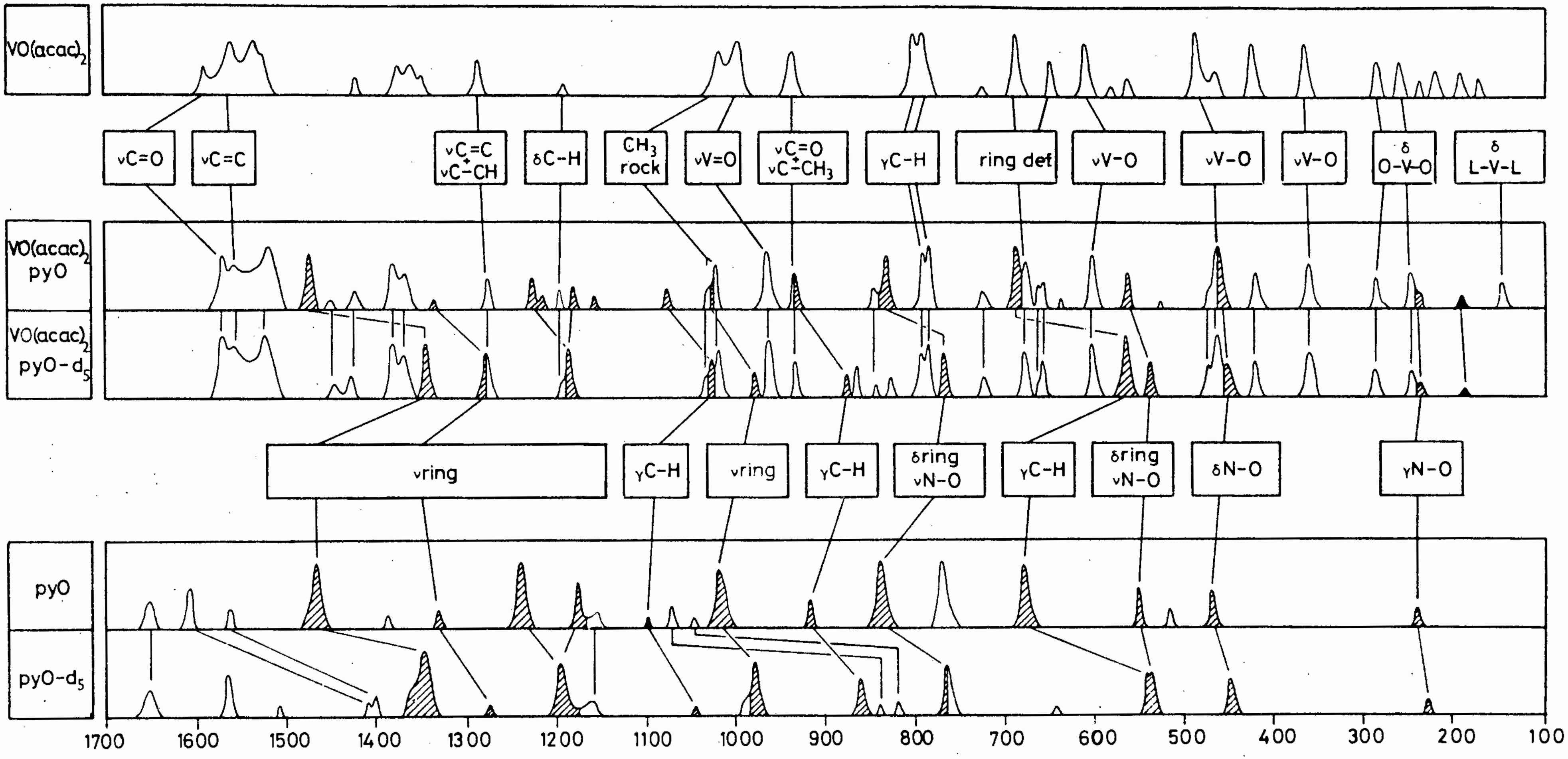

Figure 24. Infrared spectra of the ligands and complex VO(acac)$_2$pyO and their labelled analogues.

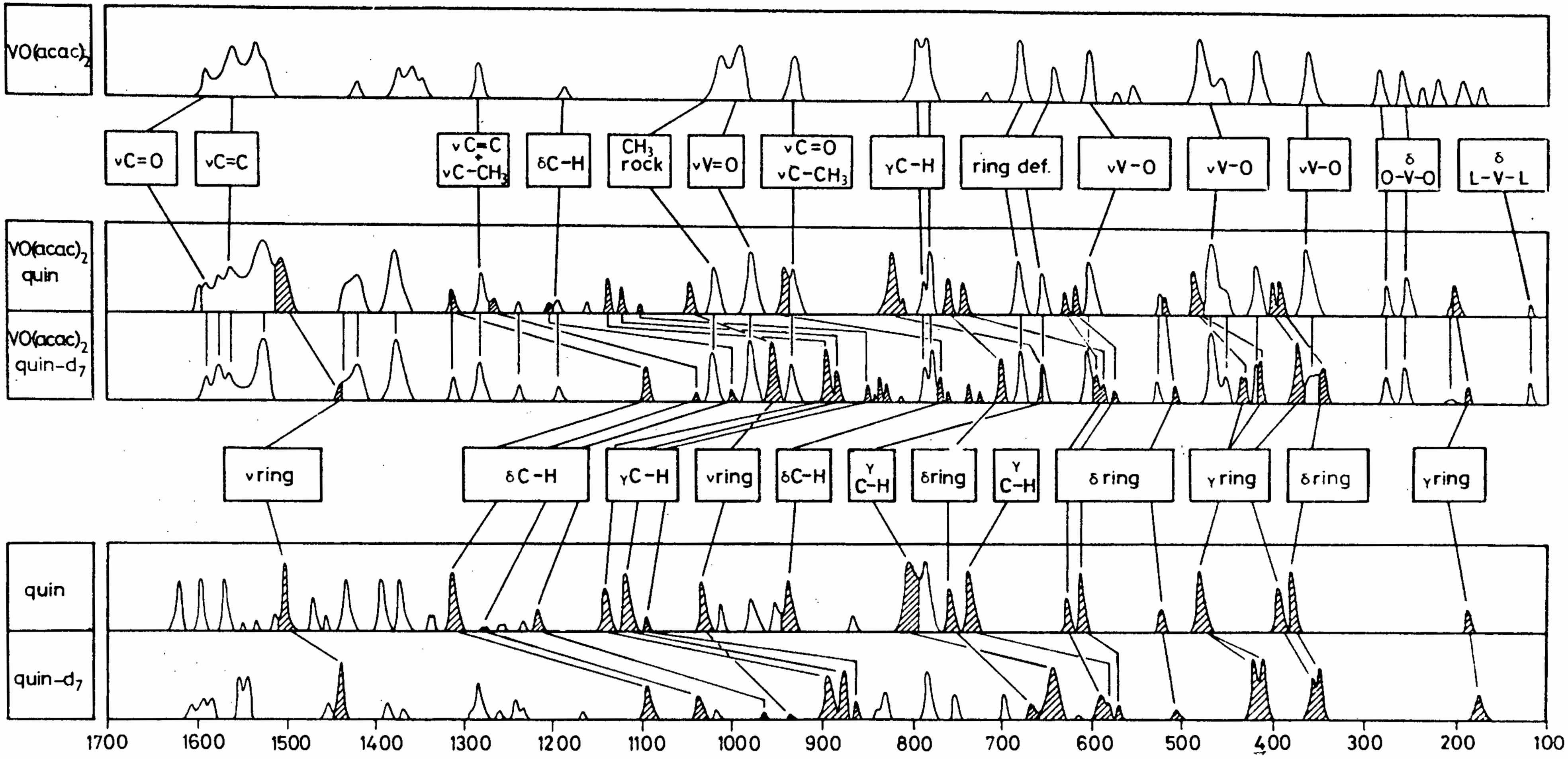

Figure 25. Infrared spectra of the ligands and complex VO(acac)$_2$quin and their labelled analogues.

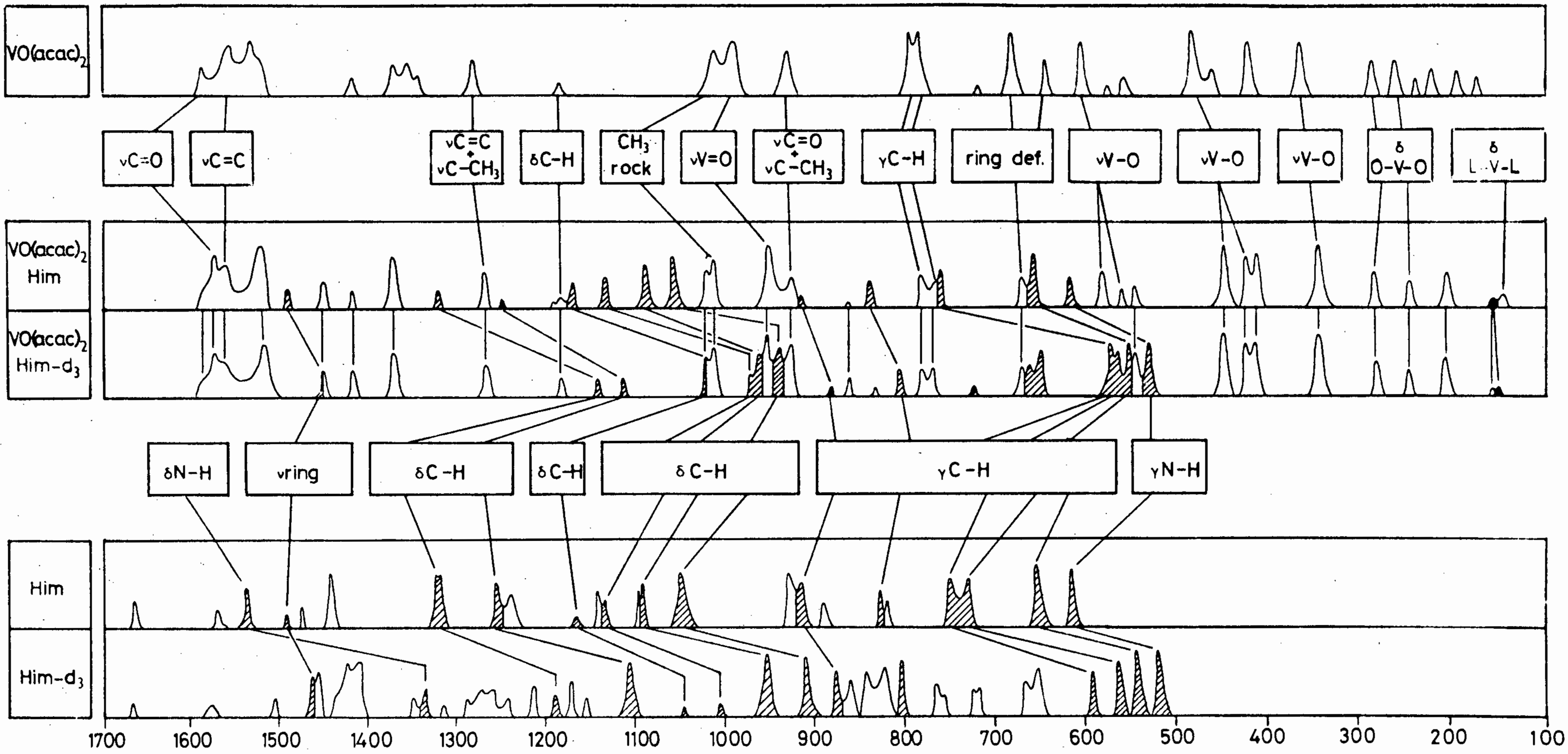

Figure 26. Infrared spectra of the ligands and complex VO(acac)$_2$Him and their labelled analogues.

ligand vibrations was applied to all the bases investigated here. A number of studies on the infrared spectra of these bases have previously been carried out. These include normal coordinate analyses of pyridine [77], pyridine *N*-oxide [78], quinoline [79] and imidazole [80], as well as isotopic labelling studies of pyridine [70], imidazole [80-82] and quinoline [83]. These studies were used in this work to confirm assignments of the ligand spectra based upon the shifts obtained on deuteration. Generally good agreement between the assignments by the various techniques was obtained. In the spectra of the complexes the ligand vibrations are not all observed. Those which are, usually appear at a slightly higher frequency than in the spectra of the uncoordinated species and are easily identified and assigned by their isoptopic sensitivities (see Figs. 23-27).

Vibrations associated with the acetylacetonate moiety

Vibrations originating in the acetylacetonate ligand were identified by virtue of their insensitivity to deuteration of the base. They were generally lowered in frequency by adduct formation. The broad, complex absorption near 1550 cm^{-1} contains the C=O, C=C and C=N stretching vibrations of the acetylacetonate and base ligands. The νC=O band which occurs at 1587 cm^{-1} in the spectrum of $VO(acac)_2$ is lowered in frequency to between 1569 and 1575 cm^{-1} in the spectra of the adducts. The remaining assignments of the acetylacetonate vibrations are in agreement with the proposals of Haigh [50] who based his assignments of acetylacetonate bands in a series of variously substituted pyridine adducts of $VO(acac)_2$, on their insensitivty to variation of the pyridine substituents.

Metal-ligand vibrations

There are four principal V-O stretching modes observed in the spectra of the adducts. These are all unaffected by deuteration of the base, have their frequencies lowered (with respect to VO(acac)$_2$) by adduct formation and are sensitive to variation of the base. The band at 996 cm^{-1} in the spectrum of VO(acac)$_2$ has been firmly established as νV=O [84]. In the spectra of the pyridine, pyridine *N*-oxide, quinoline and imidazole adducts of vanadyl acetylacetonate this band is reduced in frequency by 32, 34, 17 and 42 cm^{-1}, respectively (Table 16). Bands at 608, 484 and 364 cm^{-1} in the spectrum of VO(acac)$_2$ are assigned to νV-O. Their frequencies are lowered by adduct formation by between 3 and 34 cm^{-1}, they are insensitive to deuteration of the base and retain their sensitivity to variation of the base. The bands near 608 and 484 cm^{-1} are split in the spectrum of VO(acac)$_2$Him, displaying additional peaks at 563 and 348 cm^{-1}. The assignments made here are in general agreement with those of previous studies [48,53] on adducts of vanadyl acetylacetonate.

If the infrared criteria employed by Caira *et al.* [48], in assigning the geometric configuration of substituted pyridine adduts of vanadyl acetylacetonate, are applied to the VO(acac)$_2$B complexes, they suggest that VO(acac)$_2$Him has a *cis*-configuration while VO(acac)$_2$py, VO(acac)$_2$pyO and VO(acac)$_2$quin have *trans*-configurations. There are two reasons for reaching this conclusion. Firstly: the reductions in frequency on adduct formation of the νV=O and νV-O bands of the VO(acac)$_2$Him complex are all considerably larger than those observed for the other three adducts. Secondly the νV-O bands at 586 and 450 cm^{-1} in the spectrum of VO(acac)$_2$Him are split while those of the remaining adducts are not.

Two bands, at 286 and 260 cm^{-1} in the spectrum of VO(acac)$_2$, appear in the spectra of the adducts near 283 and 249 cm^{-1}. They do not shift on deuteration of the base but do exhibit some sensitivity to variation of the base. They are thus assigned to O-V-O bending modes. The weak bands, occurring between 159 and 189 cm^{-1} in the spectra of the pyridine, pyridine *N*-oxide and imidazole adducts, which shift 4 - 5 cm^{-1} to lower frequency

TABLE 16. Frequencies and shifts of V-O stretching vibrations of $VO(acac)_2B$ complexes on adduct formation*.

Complex	$\nu(cm^{-1})$					
	$\nu V{=}O$	$\nu V\text{-}O$		$\nu V\text{-}O$		$\nu V\text{-}O$
$VO(acac)_2$	996	608		484		364
$VO(acac)_2$ py	964(32)	598(10)	-	463(21)	-	360(4)
$VO(acac)_2$ pyO	962(34)	600(8)	-	460(24)	-	359(5)
$VO(acac)_2$ quin	979(17)	604(4)	-	467(17)	-	361(3)
$VO(acac)_2$ Him	954(42)	586(22)	563(45)	450(34)	427(57)	348(16)

* Shifts to lower frequency on adduct formation in parentheses.

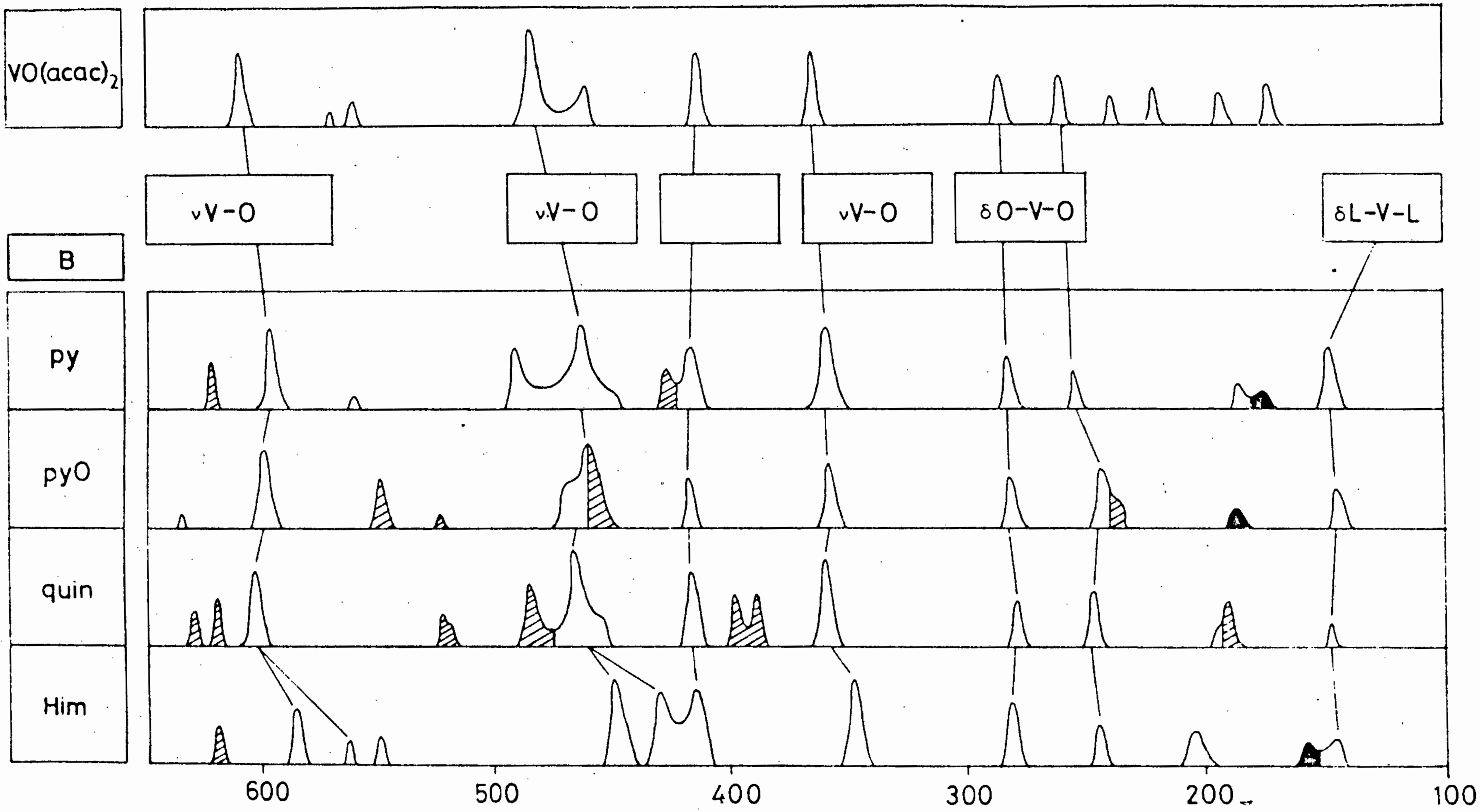

Figure 27. Infrared spectra of the unlabelled complexes of VO(acac)$_2$B.

on deuteration, are assigned to νV-N(py), νV-O(pyO) and νV-N(Him), in order of decreasing frequency. In recent work [85] on pyridine adducts of nickel(II) acetylacetonate, νNi-N was identified at 186 and 197 cm^{-1}. The equivalent νV-N band is not observed in the spectrum of the quinoline adduct and probably occurs in the region below 140 cm^{-1}. This is suggested since the relatively large molecular mass of the quinoline ligand contributes to the reduction in frequency of νV-N. Also, the relatively poor donor capacity of the quinoline ligand (which is reflected by the small reduction in frequency of νV=O on adduct formation) results in a weak V-N bond.

3. INFRARED SPECTRA OF ALKYLAMINE COMPLEXES OF COPPER(II) AND NICKEL(II) PHTHALIMIDE

The far-infrared spectra (500 - 140 cm^{-1}) of the series of complexes [M(phth)$_2$(RNH$_2$)$_2$] (M = Cu; R = *cy*-C_6H_{11}, *n*-C_4H_9, *sec*-C_4H_9, *iso*-C_4H_9, *ter*-C_4H_9, *n*-C_3H_7, ϕCH_2CH_2, ϕCH_2 and M = Ni; R = *cy*-C_6H_{11}, *n*-C_4H_9, *n*-C_3H_7, ϕCH_2) as well as their phthalimide-^{15}N and amino deuterated analogues were taken. Some typical examples of the spectra of the unlabelled complexes are shown in Figs. 17 and 18, while their frequencies and isotopic shifts are displayed in Tables 16 and 17. The correlation diagrams (Figs. 28 and 29) illustrate a comparison of the spectra of the unlabelled complexes.

While independent labelling of, on the one hand, the phthalimide nitrogen with the ^{15}N-isotope and, on the other, the amino hydrogens with deuterium, enables a distinction to be made between vibrations of the two species of ligand, it does not facilitate differentiation between internal ligand and metal-ligand vibrations. Since several bands originating in the vibrations of uncoordinated phthalimide and amine ligands appear in the spectral region below 500 cm^{-1}, assignment of metal-ligand stretching frequencies is not completely straightforward. On coordination, shifts in the frequencies of these ligand vibrations, changes of intensity and the strong possiblity of coupling with lower frequency metal-ligand vibrations, further tend to complicate the final spectra of the complexes. Coupled with the uncertainties regarding the structure of the complexes, this produces difficulties in the absolute assignment of every band in the spectra. However, a comparison of the spectra of a series of complexes does reveal a general pattern which has a degree of regularity. Utilizing this and the isotopic shifts produced, a satisfactory interpretation of the spectra may be achieved. A comparison of the spectra of copper and nickel complexes in Figs. 28 and 29 shows a considerable dissimilarity in their band patterns. This is indicative of structural differences. For this reason the spectra of the complexes of the two metals will be discussed separately.

Copper complexes

The correlation diagram in Fig. 28 reflects a comparison between the spectra of the uncoordinated phthalimide ligand and phthalimide complexes of copper(II) with various aliphatic amines.

Over the range 500 - 420 cm^{-1}, the spectra of the complexes differ considerably in both the number and positions of absorptions, and almost all of these bands exhibit some sensitivity to am-d_2 labelling (shifting to lower frequency by between 3 and 26 cm^{-1}). Furthermore,they occur in a region of amine absorption and are attributed mainly to amine ligand vibrations. Because of the considerable differences in mass and donor capacities of the various amines,correspondence between the positions of the νCu-N(am) bands through the series is not anticipated. Although it is quite reasonable to expect νCu-N(am) to occur in this region, completely unambiguous assignments are not achieved.

Between 420 and 150 cm^{-1}, there is a band-for-band correspondence between the spectra of the series. This reflects the isostructural nature of these complexes. The six bands occurring in this region (ν_1-ν_6) are ascribed mainly to phthalimide ligand vibrations. The bands ν_1, ν_2 and ν_6 coincide with the phthalimide vibrations at 408, 360 and 198 cm^{-1}, respectively and occur regularly throughout the series. They are insensitive to labelling or variation of the amine and are thus assigned as phthalimide ring vibrations. The band ν_3, occurring between 292 and 299 cm^{-1}, is in a region free from ligand absorption. It shifts 5 cm^{-1} to lower wavenumber on phth-^{15}N labelling and is insensitive to am-d_2 labelling. It is thus assign-

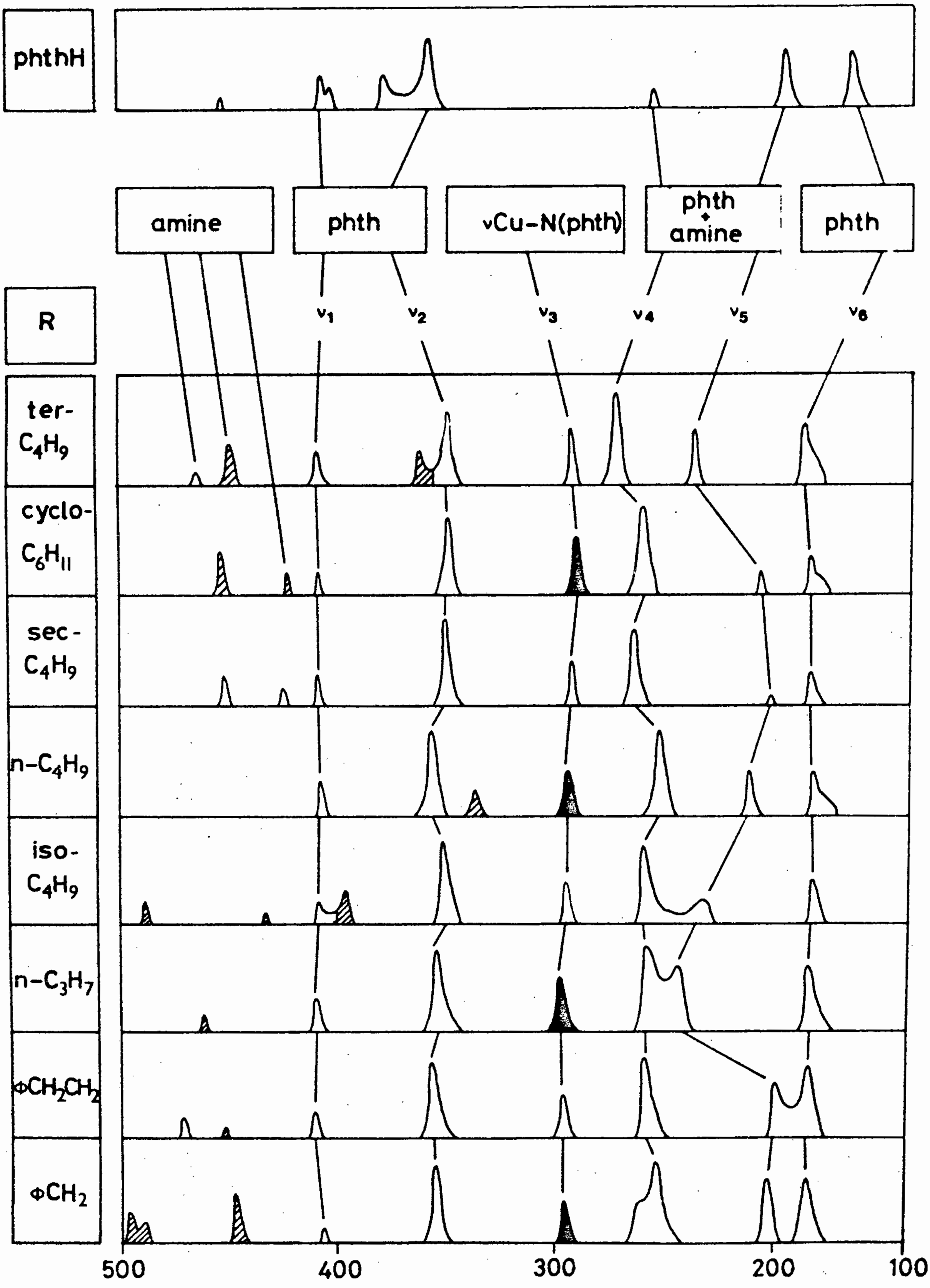

Figure 28. Infrared spectra of the unlabelled complexes $[Cu(phth)_2(RNH_2)_2]$.

ed to a vibrationally pure νCu-N(phth). This assignment confirms earlier suggestions [59] regarding the coordination site of phthalimide, namely, that coordination to copper occurs via the imide nitrogen and not the carbonyl oxygen. The remaining two bands (ν_4 and ν_5) are both insensitive to labelling but strongly sensitive to variation of the amine. However, they occur in a region where phthalimide absorbs and the amines do not. They are therefore considered to be due to a phthalimide ring mode coupled with an amine vibration.

Nickel complexes

It can be seen from the correlation diagram of the spectra of the nickel complexes (Fig. 29) that both band patterns and isotopic sensitivities differ considerably from those observed for the copper complexes. This is a clear indication that there are structural differences between the complexes of these two metals. Whether these differences take the form of the mode of bonding of the phthalimide ligand, the type of intermolecular hydrogen bonding or actual molecular symmetry cannot with present results be predicted. From a purely structural point of view, numerous alternatives do exist [63] including the possibility of polymer formation. In this respect, a crystal structure determination would be extremely useful if suitable crystals could be obtained.

In the region 500 - 420 cm^{-1}, the spectra are similar to those of the copper complexes. There is no band correspondence through the series; some of the bands exhibit am-d_2-sensitivity and they occur in a region of amine absorption. They can therefore be ascribed to amine ligand vibrations.

In the region 420 - 140 cm^{-1}, there is a general band pattern throughout the series with six major bands (ν_1'-ν_6') occurring. ν_1' and ν_6', near 410 and 185 cm^{-1}, correspond with the equivalent bands in the copper complexes.

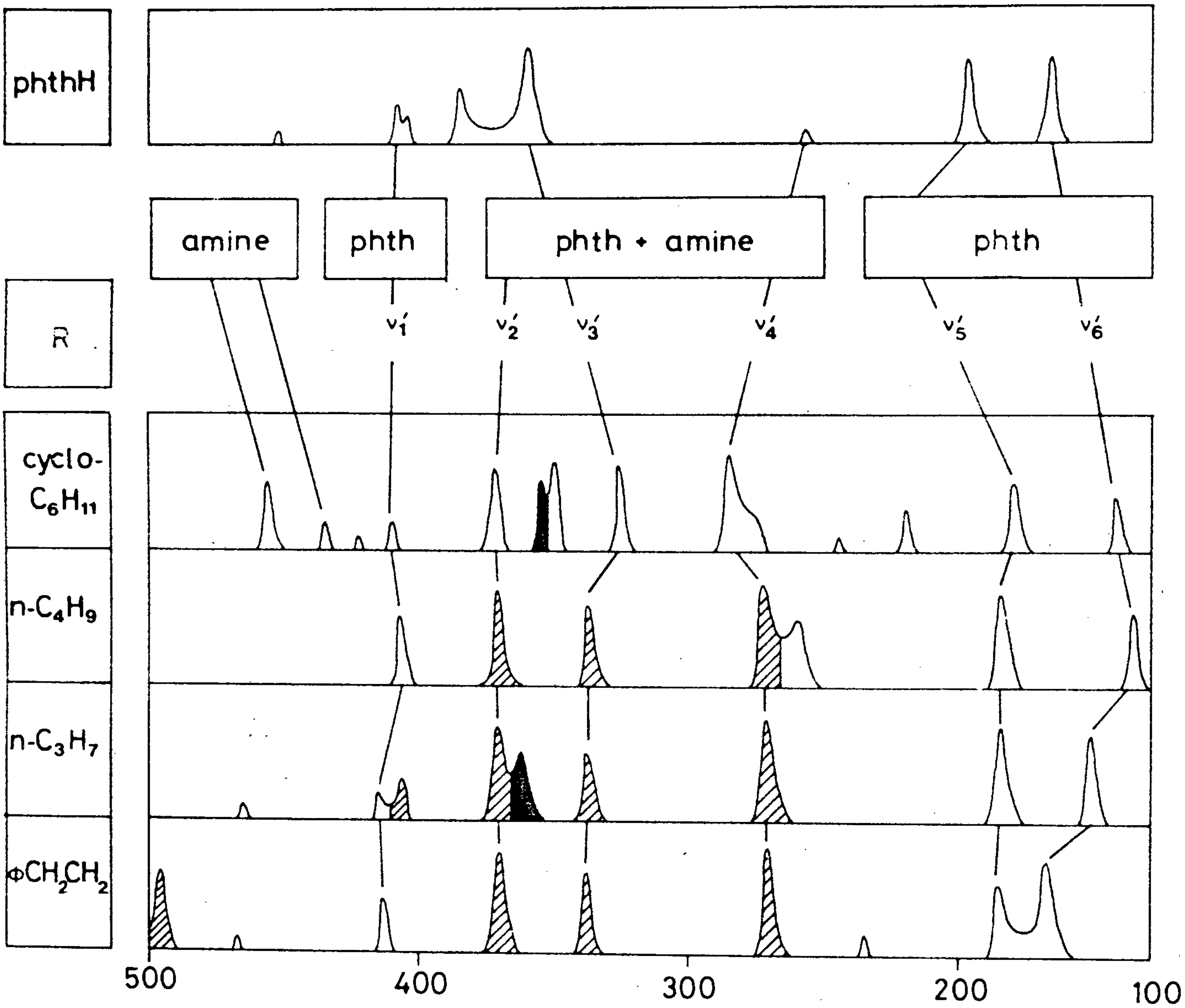

Figure 29. Infrared spectra of the unlabelled complexes $[Ni(phth)_2(RNH_2)_2]$.

This supports their assignment to phthalimide vibrations. The three bands ν_2', ν_3' and ν_4', all occur regularly through the series, ν_3' being unique to the spectra of the nickel complexes. They each exhibit strong sensitivity to deuteration but exhibit little or no sensitivity to variation of the amine. Furthermore,they occur in a region where phthalimide absorbs and the amine does not. Hence they cannot be assigned to vibrationally pure νNi-N(am) but more probably originate in a phthalimide ligand vibration coupled with an amine mode. In only two of the five nickel complexes were any bands observed which are sensitive to phth-^{15}N labelling *viz.* $[Ni(phth)_2(\mathit{cy}\text{-}C_6H_{11}NH_2)_2]$ (at 355 cm^{-1}) and $[Ni(phth)_2=(\mathit{n}\text{-}C_3H_7NH_2)_2]$ (at 362 cm^{-1}). These two bands which both shift 4 cm^{-1} and are unique to spectra of those complexes,are assigned to νNi-N(phth). The fact that these bands are not observed in the spectra of the remaining complexes may arise, either because they are obscured by adjacent phthalimide vibrations or, because nickel does not coordinate through the phthalimide nitrogen atom.

The considerable difference between the spectra of the copper(II) and nickel(II) complexes strongly suggests the possibility of structural differences between the complexes of these two metal ions. While the unambiguous assignment of νCu-N(phth) confirms the mode of bonding of the phthalimide ligand in the copper complexes, uncertainty remains with respect to the structure and mode of bonding in the nickel complexes.

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