ISOTOPIC LABELLING APPLIED TO THE INFRARED SPECTRA OF METAL COMPLEXES

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CONTENTS

SUMMARY

The infrared spectra of pyridine adducts of first transition series metal(II) acetylacetonates are discussed in relation to the band shifts induced by ^{15}N-labelling and deuteration of the pyridine ring and by metal ion substitution. ^{15}N-Labelling aids in establishing the pyridine ring vibrations, while deuteration and metal substitution are more useful in assigning the νM-L frequencies. Results of the isotopic labelling study lead to a revision of previously-reported νM-O and νC...O frequencies. This technique also facilitates assignment of the νM-N vibrations, observed in the region below 200 cm^{-1}. The occurrence of these bands in this spectral region was expected because of the known relative weakness of the M-N bond strength in pyridine adducts. The effects on the spectra resulting from introduction of a variety of substituents into the pyridine ring are discussed on the basis of the electronic effects of the substituents. After allowing for mass effects, electron-withdrawing substituents are found to decrease νNi-N frequencies while electron-releasing substituents exert negligible effect on the νNi-N bands. An opposite trend is, however, observed for the νNi-O bands and is explained.

An investigation of a series of aniline and *p*-toluidine complexes of first transition metal(II) isothiocyanates is reported. Independent ^{15}N-labelling of the amino and isothiocyanato groups yields unambiguous assignments for the internal vibrations of both ligands. The technique also permits differentiation between the two species of metal-nitrogen stretching vibrations, *viz.* νM-NH_2 and νM-NCS. Both

$\nu M\text{-}NH_2$ and $\nu M\text{-}NCS$ are metal ion dependent in the Irving-Williams sequence, supporting their assignment to metal-ligand bands. Magnetic moment determinations serve to confirm polymeric octahedral co-ordination for the aniline and *p*-toluidine complexes of Co(II) and Ni(II), this structure also being suggested by their infrared spectra. The aniline complex of zinc(II) is assigned polymeric octahedral structure on the basis of its infrared band pattern. The spectrum of the corresponding *p*-toluidine complex, however, exhibits unique features which strongly suggest tetrahedral coordination. Crystallographic determination of the structure of this complex has since confirmed tetrahedral coordination and also reveals that the NCS group is bonded to the Zn(II) ion through the nitrogen atom. The spectrum of the complex $[Co(NCS)_4Hg]$ has been studied in view of its unusual polymeric tetrahedral structure. Isotopic labelling of the NCS ligand results in the assignment of the two species of metal-ligand vibrations, *viz.* $\nu Co\text{-}N$ and $\nu Hg\text{-}S$. The internal vibrations of the NCS group are clearly identified from the ^{15}N-induced shifts and occur in the regions previously reported for bridged NCS complexes.

In a study of the infrared spectra of pyridine complexes of first transition series metal(II) isothiocyanates, deuteration of the pyridine ring and ^{15}N-labelling of the NCS ligand areused in the assignment of metal-ligand vibrations. The $\nu M\text{-}py$ and $\nu M\text{-}NCS$ bands are assigned by observing the isotopically-induced shifts and also by comparing the spectra with those of the previously-studied complexes : $[M(py)_2Cl_2]$. Metal substitution causes the $\nu M\text{-}L$ bands to shift in parallel with the crystal field stabilization energies of the respective metal ions. The two species of metal-ligand stretching bands occur within a rather

narrow frequency range and there is evidence of vibrational coupling between νM-py and νM-NCS. The results lead to a revision of some earlier assignments of νM-L frequencies for both the bis(pyridine) and tetrakis(pyridine) isothiocyanate complexes. A study of the spectra of the complexes: *trans*-$[Fe(py)_4(NCS)_2]$, its oxidation product and the complex *cis*-$[Fe(py)_3(NCS)_3]$, leads to the suggestion that the oxidation reaction involves the transformation of *trans*-$[Fe(py)_4(NCS)_2]$ into *cis*-$[Fe(py)_3(NCS)_3]$.

An investigation of the infrared spectra of a series of square planar bis(pyridine) complexes of platinum(II) halides and thiocyanates reveals characteristic differences between the *cis*- and *trans*-isomers. A crystallographic study of the complex *trans*-$[Pt(py)_2(SCN)_2]$ has shown square planar coordination of the Pt(II) ion and confirmed the infrared results with respect to S-bonding of the NCS ligands. Assignment of the νPt-N and νPt-X frequencies is based on ^{15}N-labelling and deuteration of the pyridine ring and also on halogen substitution. The number of νPt-N and νPt-X bands observed satisfies the selection rule for C_{2v} and D_{2h} site-symmetry for the *cis*- and *trans*-isomers, respectively, except for the appearance of additional bands in the spectra of the *trans*-isomers, a feature which is ascribed to coupling between νPt-N and νPt-X. Substitution of chloride in both the *cis*- and *trans*-isomers by bromide and iodide, respectively, causes the νPt-X bands to shift to lower frequencies in accordance with the increased mass of the halide.

Previous work on the infrared spectra of *m*- and *p*-toluidine complexes of metal(II) chlorides is extended here to the *o*-toluidine complexes of metal(II) halides. ^{15}N-Labelling of the *o*-toluidine ligand facilitates assignment of the various stretching and bending vibrations of the amino-group and yields unambiguous assignments for the important νM-N and νM-X vibrations. The effects of metal ion substitution support the results obtained from isotopic labelling: both νM-N and νM-X bands follow the sequence Co > Ni < Cu > Zn (a deranged Irving-Williams stability sequence) which is in accordance with the proposed structures of the complexes. For the Ni(II) and Cu(II) complexes (which are assigned polymeric octahedral and polymeric tetragonal structure, respectively) one band for each of the vibrations νM-N and νM-X, is observed. This is in agreement with the number of infrared-active bands expected for their C_i site-symmetry. In the spectra of the tetrahedral Co(II) and Zn(II) complexes, two νM-N and two νM-X bands are observed as required by the C_{2v} site-symmetry of these complexes. The effects of halogen substitution lend further support to the assignments made.

PUBLICATIONS

Parts of this work have been published as follows:

1. CAROLA ENGELTER and DAVID A. THORNTON, J. Mol. Structure, 33 (1976) 119.
   Infrared Spectra of Bis(Aniline) and Bis(*p*-Toluidine) Metal(II) Isothiocyanate Complexes.

2. CAROLA ENGELTER and DAVID A. THORNTON, J. Mol. Structure, (in press).
   The Far Infrared Spectra of Pyridine Adducts of Nickel(II) Acetylacetonate.

3. CAROLA ENGELTER and DAVID A. THORNTON, J. Mol. Structure, (in press).
   The Far Infrared Spectra of Pyridine Complexes of Transition Metal(II) Isothiocyanates.

4. CAROLA ENGELTER, ALAN T. HUTTON and DAVID A. THORNTON, J. Mol. Structure (submitted for publication).
   The Infrared Spectra (500 - 150 cm^{-1}) of the Complexes *cis*- and *trans*-$[Pt(pyridine)_2X_2]$ (X = Cl, Br, I, SCN).

ABBREVIATIONS

AA	acetylacetonate anion
an	aniline
CFT	crystal field theory
CFSE	crystal field stabilization energy
IR	infrared
LFT	ligand field theory
L	generalized ligand
M	central metal ion
py	pyridine
R	generalized substituent
X	generalized halide
o-tol	*o*-toluidine
m-tol	*m*-toluidine
p-tol	*p*-toluidine
ν	infrared stretching mode
γ	infrared bending mode : out-of-plane
δ	infrared bending mode : in-plane

I. INTRODUCTION

1. CRYSTAL FIELD ASPECTS OF INFRARED SPECTRA

Theoretical treatment of bonding in coordination compounds has led to the development of crystal field theory (CFT) and ligand field theory (LFT). In CFT the approach is entirely electrostatic, whereas in LFT (effectively molecular orbital theory combined with CFT) covalent interactions between the metal ion and its ligands are taken into account. When applied to transition metal chemistry, LFT and CFT lead to similar conclusions but LFT accounts for additional effects, such as π-bonding. CFT, although based on a simplified model of the coordination compound, can nevertheless explain many of the known properties of transition metal complexes. This applies in particular to their electronic and vibrational spectra, their magnetic properties and to certain thermodynamic constants such as lattice energies, heats of ligation and heats of hydration.

In the process of complex formation, the approach of ligands, creating an electrostatic field akin to a set of negative point charges, causes repulsion of the degenerate *d*- (or *f*-) orbitals of the metal ion. Because of different spatial orientation of these orbitals, the repulsion suffered does not affect them equally. This leads to the removal of degeneracy of the *d*- (or, to a much smaller extent) *f*-orbitals.

In an octahedral environment this phenomenon (crystal field splitting) causes a splitting of the five *d*-orbitals into two sets of degenerate orbitals, the three t_{2g}-orbitals being stabilized by $4Dq$ and the two e_g-orbitals being destabilized by $6Dq$. The total energy

difference between them, $10Dq$, is proportional to the field strength of the ligands present. The electronic occupation of the split orbitals is one of the factors which determines the stability of the metal complex, *i.e.* the metal-ligand bond strength. In all configurations other than d^0, d^5 (high spin) and d^{10}, where the destabilization due to electrons in e_g-orbitals is just balanced by the stabilization due to electrons in t_{2g}-orbitals, the CF splitting lowers the total energy of the coordination compound. The crystal field stabilization energy (CFSE) of any transition metal ion in an octahedral environment can be expressed as[1]

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

where $n_{t_{2g}}$ and n_{e_g} are the numbers of electrons in the t_{2g} and e_g-orbitals, respectively.

$10Dq$ has been factorized by Jorgensen[2] into its ligand (f) and metal ion (g) components:

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

where f is the CF splitting power of the ligand relative to that of water ($f = 1$) and g is the spectroscopically-determined magnitude of $10Dq$ for the octahedrally-hydrated metal ion. From this relationship $10Dq$ may be estimated for ions where experimental values are not available. From examples where $10Dq$ has been empirically determined, f values for a variety of ligands have been obtained. These data are valuable since they provide an index of the relative CF splitting powers of various ligands.

In tetrahedral complexes, where the four ligand molecules are placed

between x, y and z axes, a situation opposite to that found in octahedral environments, arises. The e -orbitals are stabilized by $6Dq$ whereas the t_2 -orbitals are destabilized by $4Dq$, hence:

$$\text{CFSE} = -(0.6n_e - 0.4n_{t_2})10Dq \qquad (3)$$

The value of $10Dq$ being only about one half of that for octahedral environments, has the effect of inducing high spin configuration in all tetrahedral complexes.

In the case of tetragonally-distorted compounds, the increased axial metal-ligand distance removes the degeneracy of both the e_g and t_{2g}-orbitals. The d—orbitals are split into four different energy levels, the separation energy between the highest and lowest levels being greater than the $10Dq$ value in an octahedral environment. A similar situation exists in a square planar configuration, which may be considered as the extreme case of tetragonal distortion in which both ligands along the z—axis are removed to infinity.

CFSE represents only a minor part of the energy changes taking place during complex formation. The total bonding energy depends principally on other factors, such as the attraction between the metal ion and the ligands and on interelectronic repulsion between ligand electrons and s- and p- electrons of the metal[3]. In a series of isostructural and isovalent transition metal complexes, properties such as ionic radii and masses vary smoothly through the series, *i.e.* smoothly increasing or decreasing with d-orbital population. The variation of CFSE superimposed on these effects, is therefore expected to be similar to the variation with d-orbital population shown by CFSE alone. Investigations of such series of complexes with constant ligand combination,

have shown a direct correlation between CFSE and various thermodynamic properties, such as lattice energies, heats of ligation, and M-L bond distances[1,3]. Since the variation in CFSE influences the M-L bond strength and hence the M-L force constants, it could be expected that in the absence of significant mass effects the M-L stretching frequencies of such a series of complexes would vary in parallel with their CFSE's.

Thornton and co-workers[4-17] have investigated the IR spectra of an extensive range of first and second transition metal systems. Their results provide convincing evidence for the existence of such correlations of νM-L with *d*-orbital population. Variations of νM-O have been shown to correlate with the relative CFSE values for β-keto-enolates of trivalent first transition series metal ions[4]. Similar correlations have been obtained for νM-L in several series of metal(II) and metal(III) tropolonate complexes[5], in divalent metal acetylacetonates and their nitrogen base adducts[6], metal(II) 2,2'-bipyridyl and 1,10-phenanthroline complexes[7], 2-thenoyltrifluoroacetonates[8]. metal(II) anthranilates[9], the di- and trivalent γ-substituted acetylacetonates[10], a large series of complexes with nitrogen donor ligands[11] and in the metal(III) oxalate and cyanide complexes[12]. These studies have been extended to the second transition series metal acetylacetonates[12] and the tris- and tetrakis- lanthanide(III) tropolonate chelates[13,14]. These latter complexes involve splitting of the 4*f*-orbitals, where CFS effects are smaller by a factor of ten than those occurring for the 3*d*-orbitals.

The correlation of νM-L with CFSE has been found of value in the assignment of this vibration for a number of metal(II) salicylaldimine complexes[15-17].

In order to isolate the crystal field contribution to the M-L stretching frequency, the following method has been found valuable. By plotting νM-L versus *d*-orbital population, an interpolation line is drawn through the points for the d^0, d^5 (high spin) and d^{10} (or f^0, f^7 and f^{14}) ions. Since their CFSE is zero, their νM-L frequencies are determined only by factors other than CF effects, thus providing a standard of comparison for the other ions of the series. The contribution of the CFSE to νM-L for a particular ion is represented by the difference between the observed frequency ν and the frequency ν_0 given by the appropriate point on the interpolation line.

Graphical determinations of $(\nu - \nu_0)$ have been shown to yield good qualitative agreement with calculated CFSE values.

2. SUBSTITUENT CONSTANTS

One of the earliest (quantitative) expressions relating the effect of a substituent R to the reactivity of a chemical reaction taking place on the side chain of an aromatic system was found by Hammett[18]

$$\log (k/k_0) = \sigma\rho \qquad (4)$$

where k and k_0 are the rate or equilibrium constants for the reactions of the substituted and unsubstituted compounds, respectively, σ is the substituent constant, depending solely on the nature and position of the substituent and ρ is the reaction constant, depending on the type of reaction, its conditions and the nature of the side chain. Thus ρ will be constant for a given reaction under a given set of conditions.

One of the first series of reactions to be investigated was the dissociation of *m*- and *p*-substituted benzoic acids (in water at 25°C) for which ρ has been defined as unity, so that σ_m and σ_p values could be calculated from the dissociation constants of the substituted and unsubstituted benzoic acids, respectively.

The reaction constant ρ is a measure of the sensitivity of a particular reaction to ring substitution. The substituent parameter σ represents the ability of a substituent to attract or release electrons, combining the inductive (field) and mesomeric (resonance) effects. A positive σ denotes an electron-withdrawing substituent which influences the reaction *via* a decrease of electron density at the reaction centre, facilitating a nucleophilic reaction. An electron-releasing substituent, characterised by a negative σ will increase the electron density at the reaction site, thus facilitating an electrophilic reaction.

The Hammett equation has been successfully applied to a wide variety of reactions of *m*- and *p*-substituted benzenes. For *ortho*-substituents however, no straight line is obtained if log k/k_0 is plotted against σ; *i.e.* the Hammett equation does not yield reliable substituent constants. This is due to steric interference of the substituent with the reaction centre. Deviations have also been found for substituents which exhibit a direct resonance effect on the reaction centre, *e.g.* *p*-NO_2 or *p*-CN. These groups increase, for instance, the acidity of phenols, to a higher degree than is expected from their σ value by virtue of resonance stabilization of the phenolate anion. In these cases, effective substituent constants, $\bar{\sigma}$, have to be used for that particular reaction; $\bar{\sigma}$ is determined empirically.

Jaffé, in a comprehensive review[19], has recalculated all Hammett's original σ values, using the latest values for the ionization and rate or equilibrium constants. These Jaffé values are used throughout this thesis.

A systematic study of the effect of substitution on the reactions of the pyridine system where the nitrogen atom is the reactive centre has been carried out by Fisher *et al*[20]. It was suggested that these reactions would be especially sensitive to substitution as the reaction centre is within the heterocyclic nucleus. Effective substituent constants, $\bar{\sigma}$, were calculated from the acid dissociation constants of a wide range of substituted pyridines. These $\bar{\sigma}$ values are applicable to substituted pyridines only. Although in most cases the difference between $\bar{\sigma}$ and σ values is insignificant, a few $\bar{\sigma}$ values deviate considerably from the original Hammett or Jaffé substituent parameters.

Since both σ and $\bar{\sigma}$ values represent a combination of inductive and mesomeric effects, they cannot be used for aliphatic systems. Ingold[21] proposed a method for measuring purely polar (inductive) effects in aliphatic molecules. Following Ingold's proposal, Taft[22] derived a new set of substituent constants σ^* which in contrast to the original σ values, depend only upon the net polar effect of the substituent R relative to that of a reference substituent (R = CH_3).

An extensive study aimed at separating the electronic effects of all existing sets of substituent constants into their pure field (F) and resonance (R) components has been reported by Swain and Lupton[23]. The field and resonance constants which they derived are independent of the position of the substituent. They showed that the resonance effect (%R) made a 2.5 times greater combination to σ_p than to σ_m.

Infrared spectroscopy has been widely applied to substituted aromatic, heterocyclic and aliphatic compounds. Correlations between the frequencies of various ligand and metal-ligand vibrations and the substituent constants have been found to exist. The symmetric and antisymmetric νN-H frequencies of anilines[24] and aliphatic amines[25], νO-H of phenols[26] and νC=O of a series of aliphatic ketones[27] have been shown to vary linearly with σ or σ^*. In the field of coordination chemistry, Thornton and co-workers have established similar correlations between substituent constants and νC=O and νM-O in alkylamine, aniline and pyridine adducts of metal(II) acetylacetonates[28,29], νC=O in alkylamine complexes of copper(II) and nickel(II) imides[30], νU=O in alkylamine adducts of uranyl dibenzoylmethanate[31] and pyridine adducts of uranyl acetylacetonate[32], νM-L in metal(II) salicylaldimine complexes[15,16,17], νM-L in metal(II) anthranilates[9] and 8-hydroxyquinolates[33], and νCo-N in *trans*-nitro-bis(acetylacetonato)mono(amine)

cobalt(III) complexes[34,35].

Nuclear magnetic resonance (N.M.R.) has also been used to study the effect of ring substitution in various aromatic systems. A linear relationship between the chemical shifts of the amino protons and the substituent constants was found by Dyall for substituted anilines[36]. Similar correlations have been observed for the carboxylic protons of mono-substituted benzoic acids[37] and for the ring protons of various substituted pyridines[38].

3. METHODS USED TO ASSIGN METAL-LIGAND VIBRATIONS IN THE IR SPECTRA OF TRANSITION METAL COMPLEXES

In the infrared spectra of metal complexes, the metal-ligand vibrations are of greatest interest to an inorganic chemist since they provide direct information about the nature of the metal-ligand bond and the structure of the complex. These vibrations generally appear towards low frequencies (< 600 cm^{-1}) because of the high mass of the metal ion and the comparatively small force constants of the M-L bonds. Assignment of νM-L may be complicated by intermolecular interactions, such as hydrogen bonding, lattice modes, activation of ligand vibrations by complex formation and, in particular, by vibrational coupling between bands of similar vibrational frequency[39].

M-L vibrations have been assigned by the following methods:

1. One of the simplest techniques involves comparison of the spectrum of the free ligand with that of its metal complex. As M-L vibrations are absent from the ligand spectrum, a band occurring in the complex spectrum in a region free from ligand absorption may be assigned to νM-L. This method is, however, prone to yield erroneous assignments because some ligand vibrations, activated by complex formation, may appear in the same region as the νM-L vibrations[40].

2. For complexes of identical metal ions with a series of similarly substituted ligands, M-L vibrations are expected to appear within a relatively narrow frequency range. This method has been used to assign νCu-N in the compounds CuX_2L_2[41] (X = Cl, Br; L = substituted pyridine), νNi-O in substituted pyridine adducts of

Ni(II) acetylacetonate[28] and νM-O in metal β-ketoenolates[42].

3. If, in a series of isostructural, isovalent transition metal complexes of a common ligand, the metal ion is varied through the transition series, the νM-L vibrations are expected to follow the CFSE's of the respective metal ions. Such metal-sensitive IR bands can therefore be attributed to νM-L.

4. Theoretical evaluation such as normal coordinate analysis, usually based on a simplified model of the coordination compound, has been used to calculate frequencies of metal-ligand and other vibrations. Assignments of vibrations in acetylacetonate complexes have been made in this manner. This method is, however, prone to yield assignments which disagree with those obtained by other procedures for molecules with even a small degree of complexity. Certain earlier assignments based on normal coordinate analysis have had to be withdrawn or revised by the original authors[43].

5. Since stretching frequency of a vibration is a function of the masses of the vibrating atoms, isotopic labelling of a particular atom in a metal complex results in an IR spectrum which differs distinctly from that of the unlabelled compound. The observed shifts in the spectra depend on the ratio of the masses of labelled and unlabelled atoms, *i.e.*, the larger the mass difference the greater the isotopic shifts of the respective bands. The biggest shifts are observed for tritiated and deuterated molecules, up to 1300 and 1000 cm^{-1}, respectively[44]. For labelled atoms other than hydrogen, where the mass advantage is much smaller, shifts

Isotopic labelling of coordination compounds as a means of assigning metal-ligand vibrations may be approached in two ways, either the metal ion is replaced by a heavier isotope or the ligand donor atom is labelled.

Labelling of the metal ion has the obvious advantage of causing significant shifts only in metal-ligand vibrations, thus facilitating unambiguous assignments of νM-L. However, the isotopic shifts to be measured may be very small due to an unfavourable mass ratio between the labelled and unlabelled metal ion. Secondly, the method is rather costly and limited by the availability of the appropriate (preferably stable) metal isotope. Thirdly, the method fails to distinguish between the metal-ligand vibrations in complexes with different donors, *e.g.* between νM-N and νM-Cl in $[M(py)_2Cl_2]$ complexes. Labelling of the metal ion has been widely used by Nakamoto and co-workers. In a comprehensive review[45], the use of heavy isotopes of various transition metals for the assignment of metal-ligand vibrations has been discussed. Metal labelling has been applied to a variety of coordination compounds such as phosphines, α-diimines, acetylacetonates, triarylphosphine complexes of nickel and palladium, quinolinate complexes of nickel, copper and zinc, tris-(bipyridyl) complexes of the first transition series metal(II) ions, amine complexes of zinc iodide and pyridine complexes of zinc(II) and tin(IV) halides. The technique has also been recently applied by Lever and co-workers to diamine complexes and amino acid complexes[46,47] and by Hutchinson[48] to tropolonate complexes. The alternative labelling technique, *viz.* labelling of the ligand donor atom generally produces larger shifts because of a greater mass ratio μ/μ_i. There is a

limited number of commercially-available ligands with labelled donor atoms of high isotopic purity. The most commonly employed stable isotopes are ^{2}H, ^{18}O, ^{13}C and ^{15}N. In ^{15}N species, the largest shifts have been observed for $^{15}N-H$, $C=^{15}N$, $^{15}N=O$ and $C\equiv^{15}N$ stretching vibrations but significant shifts are also observed for $^{15}N-H$ bending and $C-^{15}N$ and $M-^{15}N$ stretching frequencies[44]. The shifts reported on ^{18}O-labelling are on various $X=^{18}O$ stretching vibrations where X is C, N, P, As, S, V or U but significant shifts have also been found for $^{18}O-H$, $C-^{18}O$ and $M-^{18}O$ stretching vibrations. ^{13}C-labelling has also been used in a wide variety of compounds and significant shifts have been reported. In metal(II) acetylacetonates, the metal-ligand and other vibrations were assigned by using multiple labelling, *i.e.* replacing the ^{1}H, ^{12}C and ^{16}O atoms of the ligand by their respective heavy isotopes ^{2}H, ^{13}C, ^{18}O.

A disadvantage of the ligand labelling technique is that bands originating in ligand vibrations involving the donor atom but not the metal ion may be incorrectly assigned to νM-L. Confusion from this source does not often arise, however, because of the different spectral regions in which νM-L and internal ligand vibrations generally occur. Labelling of the ligand donor atom has been used, for example, to assign νM-L in salicylaldimine complexes[49,50], acetylacetonate complexes[51-53], anthranilate complexes[54] and tropolonate complexes[55].

More recently the technique has been applied to IR spectra of trans-nitro-bis(acetylacetonato)mono(amine) cobalt(III) complexes[34,35], vanadyl complexes of *N*-salicylideneglycinate and

N-salicylideneamino acids[58,59] and *N*-salicylideneglycinate complexes of Co(II) and Ni(II)[60,61]. Finally, assignments of νM-L and other vibrations of the glycine complexes of Cu(II) and Ni(II) and of the L- and β-alanine complexes of Cu(II) and Ni(II) have been achieved by multiple labelling[62,63,64].

4. PYRIDINE ADDUCTS OF METAL(II) ACETYLACETONATES

The chemistry of metal β-ketoenolates has been studied extensively during the past decade. I.R. spectra of transition metal acetylacetonates have been investigated by several groups of workers. In these studies, attention has been focussed mainly on the assignment of the νC...O and νC...C stretching vibrations of the chelate ring. In this laboratory the spectroscopic properties of a great variety of metal β-ketoenolates have been studied[8,56,57]. More recently, work has been extended to adducts formed by first transition series metal(II) acetylacetonates with monodentate nitrogen donor ligands such as alkylamines, anilines, pyridines[28,29] and to adducts of bidentate ligands such as 1,10-phenanthroline, 2,2'-bipyridine and 2,2-biquinoline[7]. In most of these adducts, the coordination number of the metal ion is raised from four to six on reaction with either 2 moles of a monodentate ligand or one mole of a chelating bidentate ligand. Generally, the higher ligand field strength of the amines compared with that of water in the aquo complexes, causes a colour change from blue to green in the base adducts of Ni(II) acetylacetonate.

The I.R. studies of base adducts of first transition metal acetylacetonates by Thornton and co-workers were essentially concerned with establishing assignments for the metal to oxygen stretching frequencies and the various vibrations of the chelate ring. Furthermore, the influence of various substituents on the νC...O and νM-O frequencies of aniline and pyridine adducts of Ni(II) acetylacetonate has been investigated and shown to correlate with the Hammett σ-values of the substituents.[28] Electron-withdrawing substituents were found to

increase νNi-O whereas electron-releasing substituents caused these frequencies to decrease. The bond strength of the M-N bond, however, has been considered to be comparatively weak on the basis of non-formation of adducts with anilines bearing strongly electron-withdrawing substituents. The νM-N frequencies were therefore expected to occur beyond the range of measurement possible in earlier work, *i.e.* below 250 cm^{-1} [28]. Subsequent I.R. studies by Rüede and Thornton[65] have proved that this is the case for νNi-N in the complex $[Ni(py)_2Cl_2]$.

The far-infrared spectra of the pyridine adducts are of interest for several reasons. Firstly, present facilities enable the spectra to be extended from 250 to 150 cm^{-1} where νNi-N is expected to occur. Secondly, deuteration and ^{15}N-labelling of pyridine enables unambiguous identification of the νNi-N and pyridine ligand vibrations to be made. Thirdly, substitution of Ni(II) by Co(II) and Zn(II) may be used to corroborate the assignments based on the deuteration study. Fourthly, the effects of varying the pyridine substituents enable the hypothesis[28] that electron-withdrawing groups will shift νNi-O and νNi-N in opposite directions to be tested. Finally, assignments resulting from a metal ion labelling study[66] of the nickel complex may be examined in the light of these results.

5. BIS(ANILINE) AND BIS(*p*-TOLUIDINE) METAL(II) ISOTHIOCYANATE COMPLEXES

The IR spectra of metal complexes of aromatic amines have received considerably less attention than those of heterocyclic amines. Ahuja and co-workers reported on the spectroscopic properties of complexes of first transition series metal(II) halides with aniline and substituted anilines[67].

Jungbauer and Curran[68], investigating the IR spectra of complexes of metal(II) halides with aniline, used deuteration of the amino group to aid assignment of the fundamental vibrations of the amino group. In both of these studies, no definite conclusions on the assignment of the metal - nitrogen vibrations were reached.

Johnson and Thornton[69] studied the IR spectra of *p*-toluidine complexes of metal(II) chlorides $[M(p\text{-tol})_2Cl_2]$ with M = Co, Ni, Cu, Zn. They firmly assigned the metal - nitrogen stretching frequencies by observing the shifts induced, firstly, by ^{15}N-labelling of the aromatic amine and, secondly, by metal ion substitution. ^{15}N-labelling also yielded assignments of the various internal vibrations of the amine which recur in the spectra of the complexes.

No systematic study of the IR spectra of the complexes $[ML_2(NCS)_2]$ (where M = Co, Ni, Cu, Zn and L = aniline, *p*-toluidine) has previously been reported. Such studies are of particular interest with regard to the nature of the bonding between the metal and the NCS-group. The thiocyanate ligand may coordinate through the nitrogen atom, through the sulphur atom, or through both nitrogen and sulphur by acting as a bridging ligand. The fundamental vibrations of the NCS group and their position in the IR spectra of the metal complexes have been

found valuable in distinguishing between the different types of bonding[70]. Turco and Pecile[71] have reported on the position of the two fundamental stretching vibrations of the NCS-group (νN-CS and νNC-S) in various transition metal thiocyanate complexes. Their results confirm that the νNC-S stretching frequencies occur at considerably higher frequencies in isothiocyanates than in thiocyanates. Unfortunately the νNC-S absorptions are generally not very intense and are masked in some complexes by other absorptions in that region. The position of the NCS-bending frequency (δNCS) is therefore considered a more reliable indication of the nature of coordination of the NCS group in a metal complex[70]. Bonding through the nitrogen is generally expected with the hard (class A) metal ions while S-bonding should take place with those of the soft (class B) category[72]. Results indicate, however[71], that in complexes where the NCS-group is not the only ligand present, the type of coordination may depend on the nature of the second ligand.

Except for the zinc complex $[Zn(NCS)_2(p\text{-tol})_2]$, the structure of which was determined during the course of this work, no crystallographic studies have been reported on these complexes.

In a study of the IR spectra, empirical assignments of the metal-ligand stretching vibrations would necessarily lead to conjecture in view of the presence of two species of metal-nitrogen bonds. Therefore, in this work, each species of nitrogen donor has been independently labelled by using either ^{15}N-labelled thiocyanate or the appropriate ^{15}N-labelled aromatic amine in the preparation of the complexes. The observed shifts in the IR spectra facilitate firm assignments of the two types of metal-nitrogen stretching vibrations. Furthermore, this technique enables the internal vibrations of the amino and isothiocyanate groups to

be distinguished from each other. The effects of metal ion substitution in relation to the structure of the complexes confirm the results obtained from the labelling technique.

6. PYRIDINE COMPLEXES OF FIRST TRANSITION SERIES METAL(II) ISOTHIOCYANATES

The infrared spectra of pyridine complexes of first transition series metal(II) isothiocyanates have received much less attention than those of metal(II) halides. Infrared studies of isothiocyanate complexes have been reported by Clark and Williams[73] and Frank and Rodgers[74] (both in 1966). Investigations by the latter workers have been extended to 150 cm^{-1}. They have also reported on the mono- and di-substituted pyridine complexes of Cu(II) chloride and the quinoline complexes of transition metal(II) chlorides.

In these studies, the isotopic labelling technique for the assignment of metal-ligand bands was not employed. In a recent study by Rüede and Thornton of the IR spectra of pyridine complexes of metal(II) chlorides[65], deuteration of the pyridine ring has been successfully used to assign the νM-py bands. Furthermore, isotopic labelling has been used to obtain unambiguous assignments for the two species of νM-N bands in the spectra of the complexes $[ML_2(NCS)_2]$ (M = Co, Ni, Cu, Zn; L = aniline, *p*-toluidine). Assignments have been achieved by independently labelling the two different nitrogen donor atoms (see Chapter IV.2). The technique has now been applied to the complexes $[M(py)_2^2(NCS)_2]$ (M = Mn, Co, Ni, Cu, Zn) and to the complexes $[M(py)_4(NCS)_2]$ (M = Mn, Fe, Co, Ni). Comparison with the results reported in the two earlier studies[73,74] shows that assignments of the νM-py bands require revision.

An explanation of the structural changes accompanying the oxidation of the yellow iron complex $[Fe(py)_4(NCS)_2]$ is provided.

7. BIS(PYRIDINE) COMPLEXES OF PLATINUM(II) HALIDES AND THIOCYANATES

Amine complexes of platinum(II) chlorides have been known for many years[75]. A more recent review of the chemical properties of these compounds was published in 1974 by Beaumont and McAuliffe[76].

Since the discovery made in 1969 that the *cis*-isomer of $[Pt(NH_3)_2Cl_2]$ is particularly active in cancer chemotherapy[77,78], these complexes have received considerable attention. Consequent to their proven chemotherapeutic value, a large variety[78] of structurally analogous platinum(II) complexes have been synthesized and tested for their antitumour activity.

Some of the complexes prepared during the course of the work reported in this thesis have been submitted for screening tests. The details are reported in Chapter IV.4.

Numerous reports on the IR spectra of *cis*- and *trans*-$[Pt(py)_2X_2]$ (X = Cl, Br, I) have been published during the past decade[79-84]. In the study by Adams *et al.*[80], attention was focussed on the assignment of the νPt-X frequencies in the complexes $[ML_2X_2]$. In particular, the influence of incorporating a variety of neutral ligands, L, on the νPt-Cl and νPt-Br frequencies in both the *cis*- and *trans*-isomers, was studied. The νPt-X frequencies were found to depend considerably on the nature of L in the *cis*-isomers, whereas, in the *trans*-complexes, νPt-X was observed to be practically independent of the nature of L.

Durig and co-workers[83] have reported an extensive study of the IR spectra of the complexes *cis*- and *trans*-$[M(py)_2X_2]$ (M = Pt, Pd; X = Cl, Br, I). Although definite assignments of the metal-nitrogen

stretching frequencies were not made, the authors suggested that low frequency bands (near 250 cm^{-1}) were probably νM-N bands. Other workers[79], however, assigned bands near 500 cm^{-1} to νM-N. There is therefore no unanimity of opinion on the metal-ligand band assignments in these complexes.

For the complexes *cis*-$[PtL_2X_2]$ (C_{2v} site symmetry) two IR-active bands for each of the stretching vibrations, νM-L and νM-X, are expected. For the corresponding *trans*-isomers (D_{2h} symmetry) only one band is required for each vibration.

Durig *et al.* and Herbelin and co-workers[83,82] have failed either to observe or to assign the second νPt-N band expected for the *cis*-isomers. Further difficulties have arisen from the observation of far-infrared bands in excess of the number expected from symmetry considerations for the *trans*-isomers.

In this thesis, the spectra of these complexes are re-examined. Assignments are based on labelling of the pyridine ring (^{15}N-labelling and deuteration).

As discussed in connection with the pyridine adducts of metal(II) acetylacetonates in Chapter IV.1, ^{15}N-labelling has been found to be a particularly useful technique for the assignment of internal pyridine vibrations. Since the shifts in internal ligand vibrations are much smaller than those resulting from deuteration, there is less confusion as to which band in the labelled spectrum corresponds with a particular band in the unlabelled spectrum. On the other hand, assignment of metal-ligand vibrations are more readily made by pyridine deuteration.

The effect of halogen substitution supports the assignments based on labelling and therefore serves to confirm the assignment of metal-halogen bands.

This thesis reports the first IR study of the complexes *cis*- and *trans*-$[Pt(py)_2(SCN)_2]$, the νPt-N and νPt-S bands being distinguished by labelling of the pyridine and thiocyanate ligands.

8. THE BIS(*o*-TOLUIDINE) COMPLEXES OF METAL(II) HALIDES

Compared with the numerous published reports on the infrared spectra of pyridine complexes, very little attention has been paid to the corresponding substituted aniline complexes.

In 1965 Ahuja and colleagues[67] published an extensive investigation of the complexes of *o*-, *m*- and *p*-toluidine and various xylidines with metal(II) halides. The study presents data on the ultra-violet, visible and IR spectra of a large variety of these complexes. Unambiguous assignments of the metal-halogen frequencies were, however, not achieved and no attempt was made to assign the metal-nitrogen stretching vibrations.

Johnson and Thornton[69] in 1974 re-investigated the IR spectra of the complexes $[M(p\text{-tol})_2Cl_2]$ (M = Co, Ni, Cu, Zn). They firmly established the νM-N frequencies on the basis of the shifts induced by ^{15}N-labelling of *p*-toluidine and by observing the effects of metal ion substitution. The same technique was used recently in this laboratory in a study of the *m*-toluidine complexes of metal(II) halides[85].

The present investigation reports on the IR spectra of the complexes $[M(o\text{-tol})_2X_2]$ (M = Co, Ni, Cu; X = Cl, Br; M = Zn; X = Cl,Br,I). ^{15}N-Labelling of the *o*-toluidine ligand facilitated the assignment of the metal-ligand frequencies. This technique also aided in establishing the internal vibrations of the amino group.

The effects of metal ion substitution in relation to the structures of the complexes supports the results obtained from ^{15}N-labelling. Halogen substitution lends further support to the assignments made.

II EXPERIMENTAL

1. PHYSICAL METHODS

1.1 Infrared Spectra

IR spectra were obtained from Nujol mulls between caesium iodide plates on a Beckman IR-12 spectrophotometer and from Nujol mulls between polyethylene plates on a Perkin-Elmer 180 spectrophotometer. IR spectra of liquid heterocyclic amine ligands were determined as liquid films using the same window material. The Perkin-Elmer spectrophotometer was used mainly for the lower frequency region (250 - 140 cm^{-1}) whereas the Beckman IR-12 was used for the range 4000 - 250 cm^{-1}. The wavenumber precision of the latter instrument is quoted by the manufacturers as 0.2 cm^{-1} at 200 cm^{-1}, 0.3 cm^{-1} at 400 cm^{-1}, 0.4 cm^{-1} at 740 cm^{-1}, 0.6 cm^{-1} at 1330 cm^{-1} and 0.7 cm^{-1} at 2220 cm^{-1}. The wavenumber repeatability of the spectrophotometer is given by the manufacturers as 0.1 cm^{-1} at 200 cm^{-1}, 0.15 cm^{-1} at 400 cm^{-1}, 0.2 cm^{-1} at 740 cm^{-1}, 0.3 cm^{-1} at 1330 cm^{-1} and 0.35 cm^{-1} at 2220 cm^{-1}.

For maximum precision the frequencies were read directly from the wavenumber drum, not from the chart paper. Principal bands in the spectra of labelled compounds and their unlabelled analogues were repeated at least five times. Reproducibility of quoted frequencies is better than 0.5 cm^{-1}.

1.2 Magnetic Measurements

Magnetic susceptibilities were determined at room temperature on a Newport-Stanton Gouy magnetic balance. The instrument was calibrated with mercury(II) tetrathiocyanatocobaltate.

1.3 Microanalyses

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

2. PREPARATION OF COMPOUNDS

2.1 The Pyridine Adducts of Metal(II) Acetylacetonates $[M(AA)_2(py)_n]$ (n = 2, M = Co, Ni; n = 1, M = Zn)

The adducts precipitated from hot ethanolic solutions of the bis-aquo complexes of the metal(II) acetylacetonates on addition of ethanolic pyridine as described in the literature[28,29].

For nickel and zinc, this method yields well-crystallized compounds which are dark green and colourless, respectively. The cobalt adduct, however, could not be obtained by this procedure. It was prepared by recrystallizing the bis-aquo complex from pyridine. Precipitation of the adduct occurred on slow evaporation of the pyridine at room temperature. The deep orange crystals were filtered, washed with ethanol followed by petroleum ether (b.r. 60 - 80°C) and dried under reduced pressure.

Preparation of the substituted pyridine adducts of Ni(II) acetylacetonates followed the same procedure as described for the adducts of pyridine itself. The deuterated and ^{15}N-labelled adducts were similarly prepared from pyridine-d_5 of 99% isotopic purity (British Oxygen Co., Prochem Division) or from ^{15}N-pyridine of 95% isotopic purity (Merck, Sharp and Dohme, Canada, Ltd.).

Since the ^{15}N-labelled cobalt complex would be extremely costly to synthesize, only the adducts of nickel and zinc were prepared.

2.2 The Bis(Aniline) and Bis(*p*-Toluidine) Complexes of Metal(II) Isothiocyanates $[ML_2(NCS)_2]$ (M = Co, Ni, Cu, Zn; L = aniline, *p*-toluidine)

The aniline and *p*-toluidine complexes were prepared by slow addition of the amine (0.0022 mole) in ethanol to an aqueous solution of the metal sulphate (0.001 mole) and sodium thiocyanate (0.002 mole). Except for copper, where precipitation occurs rapidly, the total volume of solution was maintained at approximately 20 ml in order to achieve precipitation of the complexes. The compounds were collected by filtration and washed with water, followed by ethanol.

Since the zinc complexes are soluble in ethanol, they were washed with water only. All compounds were dried under reduced pressure over silica gel. The labelled complexes were similarly prepared from ^{15}N-aniline or ^{15}N-*p*-toluidine of 96 atom % isotopic purity (British Oxygen Co., Prochem Division) and ^{15}N-sodium thiocyanate of 97 atom % isotopic purity (Merck, Sharp and Dohme, Canada, Ltd.)

2.3 The Pyridine Complexes of Metal(II) Isothiocyanates $[M(py)_n(NCS)_2]$ (n = 4, M = Mn, Fe, Co, Ni; n = 2, M = Mn, Co, Ni, Cu, Zn)

These complexes have been known for many years and have been widely used in the quantitative analysis of first transition series metal(II) ions.

The preparation of these compounds follows the original method of Spacu and Dick[86,87] which was re-examined and summarized by Kauffman and co-workers[88]. Several modifications have been found necessary in

order to obtain pure, well-crystallized compounds.

The tetrakis(pyridine) complexes and the bis(pyridine) zinc complex were prepared as follows. To an aqueous solution containing 0.001 mole of the metal(II) sulphate and 0.002 moles of sodium or potassium thiocyanate an excess of aqueous pyridine was slowly added.

In the preparation of the bis(pyridine) copper complex it was found preferable to reverse the sequence of addition of the starting materials in order to prevent initial precipitation of copper thiocyanate. The aqueous NaSCN was therefore introduced dropwise to the deep blue solution of $CuSO_4$ and pyridine, forming the soluble complex $[Cu(py)_4]SO_4$. The complexes of manganese, copper and zinc were prepared at room temperature, whereas the cobalt and nickel complexes were found to yield more crystalline products if prepared from hot solutions (about 90°C) which were then left to cool until precipitation was complete.

The yellow iron complex was prepared from Fe(II) chloride instead of the sulphate. A trace of ascorbic acid was added to prevent oxidation[88]. The precipitated complex was filtered rapidly and dried in an atmosphere of nitrogen. It was subsequently stored in nitrogen-filled containers in order to exclude atmospheric oxygen as far as possible. The violet iron compound is obtained by re-crystallization of the yellow complex from chloroform.

The complex $[Fe(py)_3(NCS)_3]$ was prepared according to the method of Burbridge *et al.*[89]. The dried compound is comprised of dark violet crystals with a green surface iridescence.

All complexes were collected by filtration and washed thoroughly with water followed by ethanol (each containing about 5-10 v/v % of pyridine). Finally, they were washed with small amounts of ether and dried under reduced pressure over silica gel.

Attempts to prepare the tetrakis(pyridine) isothiocyanate complexes of copper and zinc resulted in well-crystallized compounds which were dark green and colourless, respectively. Since both of these compounds decompose in the atmosphere to yield the bis(pyridine) complexes, they were not obtained analytically-pure.

Features in the IR spectrum of the comparatively stable tetrakis(pyridine) zinc complex strongly indicated the presence of a mixture of two compounds with different structures.

The bis(pyridine) isothiocyanate complexes of manganese, cobalt and nickel were prepared by thermal decomposition of the tetrakis(pyridine) complexes following the method of Schutte[90].

The loss of pyridine which accompanies the structural change is indicated by a colour change for the cobalt and nickel complexes. The process of decomposition was further controlled by weighing the sample after each period of heating. The procedure was continued until the calculated mass loss was achieved and the colour change complete. The most favourable conditions applied to the preparation of pure bis(pyridine) complexes are as follows:

M	Temperature	Time	Colour change
	°C	min.	
Mn	100	120	white → white
Co	104	60	pink → mauve
Ni	110	90	blue → green

The ^{15}N-labelled compounds were similarly prepared from ^{15}N-pyridine (95% isotopic purity), or ^{15}NCS-sodium thiocyanate (97% isotopic purity). Deuterated pyridine complexes were synthesized from pyridine-d_5 (99% isotopic purity) as described for the undeuterated compounds.

2.4 The Bis(Pyridine) Complexes of Platinum(II) Halides and Thiocyanates $[Pt(py)_2X_2]$ (X = Cl, Br, I, SCN)

2.4.1 The Complexes $[(Pt(py)_2X_2]$ (X = Cl, Br, I)

The *cis*- and *trans*-isomers of the chloro complex were prepared according to previously-reported methods[91]. They are both microcrystalline powders of pale yellow colour.

Preparation of the corresponding *cis*-bromo complex in a similar manner from aqueous K_2PtCl_4 containing an excess of potassium bromide and diluted pyridine failed to produce the analytically pure compound. Analysis results and IR spectra of the yellow compounds suggested the formation of a mixed bromo-chloro complex, *viz.* $[Pt(py)_2BrCl]$ or a mixture of $[Pt(py)_2Br_2]$ and $[Pt(py)_2Cl_2]$.

The pure bromo complex was prepared according to an earlier method reported by Biilmann and Andersen[93].

This method is based on the reduction of potassium hexabromoplatinum(IV) to potassium tetrabromoplatinum(II) with potassium oxalate. The preparative procedure was as follows. K_2PtBr_6, suspended in water, was heated on a water bath with several portions (exceeding the stoichiometric amount) of potassium oxalate. Reduction is indicated by the

formation of carbon dioxide. The insoluble potassium hexabromoplatinum(IV) (bright red) disappeared during the course of the reaction and a dark brown solution of potassium tetrabromoplatinum(II) (K_2PtBr_4) was formed. This solution was heated gently for another hour and left to stand overnight. After decanting, slow addition of aqueous pyridine to the solution immediately precipitated a yellow complex, which proved to be the desired *cis*-$[Pt(py)_2Br_2]$. It was filtered off, washed with water to remove potassium bromide and dried under reduced pressure over silica gel.

The complex *trans*-$[Pt(py)_2Br_2]$ was prepared from the *cis*-isomer as follows:

A small sealed ampoule containing the *cis*-isomer and a slight excess of aqueous pyridine (diluted 1:2.5) was placed in an oven for 90 minutes at 110°C. The resulting solution containing the water-soluble complex $[Pt(py)_4]Br_2$ was evaporated to dryness. This colourless complex was covered with aqueous HBr (47 v/v %) and heated on a water bath. This process was repeated and resulted in the yellow *trans*-complex which was filtered, washed with water and dried at 90°C.

The complex *cis*-$[Pt(py)_2I_2]$ was prepared as described by Durig and co-workers[83] from K_2PtCl_4, KI and pyridine. The *trans*-isomer was synthesized in the same manner as the corresponding bromo complex, except that the concentration of pyridine was increased to 1:1 and the sealed container heated at 150°C overnight.

These comparatively drastic conditions were found necessary in order to form the soluble (tetrakis)pyridine complex $[Pt(py)_4]I_2$. In comparison with the chloro and bromo complexes the introduction of two extra pyridine molecules into the complex *cis*-$[Pt(py)_2I_2]$ is hindered by the stronger *trans*-effect of the iodide ligands.

The ^{15}N-labelled complexes were synthesized by identical methods using ^{15}N-pyridine and pyridine-d_5.

2.4.2 The Complexes $[Pt(py)_2(SCN)_2]$

The preparation of the *cis*-isomer follows the method described by Grünberg[92] in 1926 for the corresponding bis(ammonia) platinum(II) complex.

An aqueous solution of $K_2[Pt(SCN)_4]$ was prepared by heating 0.5 mMole of K_2PtCl_4 with 2 mMole of NaSCN in water for a few minutes on a water bath. Slow addition of aqueous pyridine (diluted about 1:10) to the cooled solution caused the yellow compound to precipitate. It was collected by filtration, washed with water followed by ethanol and dried under reduced pressure.

The complex *trans*-$[Pt(py)_2(SCN)_2]$ was prepared by recrystallization of the *cis*-isomer from acetone containing a small amount of pyridine. The compound precipitated overnight as large yellow needles.

The ^{15}N-labelled analogues were synthesized by the same method using ^{15}NCS-labelled sodium thiocyanate and ^{15}N-pyridine, respectively. The deuterated compounds were similarly prepared from pyridine-d_5.

2.5 The Bis(*o*-Toluidine) Complexes of Metal(II) Halides $[M(o\text{-tol})_2X_2]$ (M = Co, Ni, Cu; X = Cl, Br M = Zn; X = Cl, Br, I).

The complexes were precipitated from ethanolic solutions containing stoichiometric amounts of the metal halides and *o*-toluidine as described by Ahuja and co-workers[67].

The chloro and bromo complexes of nickel precipitated only if ethanolic solutions were left to evaporate at room temperature overnight. They comprise blue-green crystals which analyze for bis(aquo) hemihydrates (X = Cl) and bis(aquo) monohydrates (X = Br), respectively. Attempts to dry these compounds at room temperature under reduced pressure (~2 mm Hg) failed to produce the anhydrous complexes. If, however, the temperature is raised to 35-40°C in this procedure, both complexes changed their colour from green to yellow, the bromo complex being slightly more stable than the corresponding yellow chloro complex.

Preparation of the anhydrous complex $[Ni(o\text{-tol})_2Br_2]$ by heating the metal bromide in *o*-toluidine as suggested by Ahuja and colleagues[67] also failed to produce the analytically-pure complex. The analysis of the greenish yellow compound which precipitated from the *o*-toluidine, showed surprisingly high C, H and N values compared with those obtained for the green compound prepared from diluted amine solutions. It is suggested that, in the presence of excess amine, the formation of a dinuclear complex, $[Ni_2(o\text{-tol})_6Br_4]$ (in which two terminal halogens are replaced by *o*-toluidine) is favoured. Analysis results agree reasonably well with this formula. The green compound turned yellow, however, if washed with dry ether.

The colour change taking place on drying the nickel complexes (X = Cl, Br) indicates a change of structure (possibly to square planar) resulting from simultaneous loss of crystal water and *o*-toluidine.

The bromo complexes of cobalt and copper, prepared according to the methods[67] mentioned above, analysed unsatisfactorily (about 2% high on carbon). They were successfully prepared in the following manner. 1 mMole of the metal bromide was suspended in a solution of *o*-toluidine (approximately fivefold molar excess) in ether. Stirring for two to three hours at room temperature resulted in a thickening of the reaction mixture, indicating complex formation. The complexes (blue for cobalt and dark brown for copper) were collected by filtration, washed with ether and dried under reduced pressure. This method was particularly useful for the preparation of the ^{15}N-labelled bromo complexes.

The ^{15}N-labelled compounds were prepared by the above methods using ^{15}N-labelled *o*-toluidine of 96% isotopic purity (British Oxygen Co., Prochem Division).

The chloro and bromo complexes of copper proved to be comparatively unstable when stored for longer periods. IR spectra indicated decomposition of the compounds, which was accompanied by a colour change from dark brown to black. Thus, all copper complexes were re-prepared and their IR spectra recorded within a few hours after preparation. The spectrum of the ^{15}N-labelled bromo complex, however, remained

unsatisfactory, so that frequencies of bands could not be determined with certainty.

No ^{15}N-labelling was applied to the nickel complexes (X = Cl, Br) because the synthesis requires extravagant use of the costly labelled ligand.

III. RESULTS

1. ANALYSES OF COMPOUNDS

TABLE 1

Analytical data on the pyridine adducts of metal(II) acetylacetonates and their deuterated and ^{15}N-labelled analogues.

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Co(AA)_2(py)_2]$	57.8	5.8	6.8	57.6	6.0	6.6
$[Co(AA)_2(d_5\text{-py})_2]$	56.5	5.7	6.6	56.2	5.8	6.3
$[Ni(AA)_2(py)_2]$	57.9	5.8	6.8	57.7	5.9	6.7
$[Ni(AA)_2(d_5\text{-py})_2]$	56.5	5.7	6.6	56.4	5.8	6.5
$[Zn(AA)_2(py)\ ]$	52.6	5.6	4.1	52.3	5.6	4.0
$[Zn(AA)_2(d_5\text{-py})\ ]$	51.8	5.5	4.0	51.2	5.5	3.9
$[Ni(AA)_2(^{15}N\text{-py})_2]$	57.6	5.8	6.7	57.7	5.9	6.6
$[Zn(AA)_2(^{15}N\text{-py})]$	52.4	5.6	4.1	51.7	5.6	4.0

TABLE 2

Analytical data on the substituted pyridine adducts of Ni(II) acetylacetonate $[Ni(AA)_2(R\text{-}C_5H_4N)_2]$

R	Calculated			Found		
	%C	%H	%N	%C	%H	%N
4-CN	56.8	4.8	12.1	56.8	4.8	12.1
$4\text{-}COCH_3$	57.7	5.7	5.6	57.5	5.7	5.7
$3\text{-}CO_2CH_3$	54.3	5.3	5.3	53.5	5.2	5.2
$3\text{-}CH_3$	59.6	6.4	6.3	59.6	6.5	6.4
$3,5\text{-di-}CH_3$	61.2	6.9	6.0	61.1	6.9	5.9
$4\text{-}C_2H_5$	61.2	6.9	6.0	60.8	6.7	5.9
$4\text{-}CH_3$	59.6	6.4	6.3	59.7	6.5	6.3
$4\text{-}t\text{-}C_4H_9$	63.8	7.7	5.3	63.8	7.8	5.3
$3,4\text{-di-}CH_3$	61.2	6.9	6.0	60.9	6.8	6.0
$4\text{-}N(CH_3)_2$	57.5	6.8	11.2	57.3	6.8	11.0

TABLE 3

Analytical data on the complexes $[ML_2(NCS)_2]$ (L = aniline; *p*-toluidine) and their ^{15}N-labelled analogues.

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Co(an)_2(NCS)_2]$	46.5	3.9	15.5	46.5	3.9	15.6
$[Ni(an)_2(NCS)_2]$	46.5	3.9	15.5	46.5	3.9	15.6
$[Cu(an)_2(NCS)_2]$	46.0	3.9	15.3	45.9	3.8	15.5
$[Zn(an)_2(NCS)_2]$	45.7	3.8	15.2	45.5	3.7	15.1
$[Co(p\text{-tol})_2(NCS)_2]$	49.4	4.7	14.4	49.4	4.6	14.3
$[Ni(p\text{-tol})_2(NCS)_2]$	49.4	4.7	14.4	49.2	4.5	14.1
$[Cu(p\text{-tol})_2(NCS)_2]$	48.8	4.6	14.2	48.4	4.4	14.0
$[Zn(p\text{-tol})_2(NCS)_2]$	48.5	4.6	14.2	48.0	4.5	13.9
$[Co(^{15}N\text{-an})_2(NCS)_2]$	46.3	3.9	15.4	46.2	3.8	15.5
$[Ni(^{15}N\text{-an})_2(NCS)_2]$	46.3	3.9	15.4	46.2	3.8	15.3
$[Cu(^{15}N\text{-an})_2(NCS)_2]$	45.7	3.8	15.2	45.6	3.8	14.6
$[Zn(^{15}N\text{-an})_2(NCS)_2]$	45.5	3.8	15.2	44.8	3.8	15.2
$[Co(an)_2(^{15}NCS)_2]$	46.3	3.9	15.4	46.2	3.8	15.4
$[Ni(an)_2(^{15}NCS)_2]$	46.3	3.9	15.4	46.5	3.9	15.4
$[Cu(an)_2(^{15}NCS)_2]$	45.7	3.8	15.2	45.4	3.8	15.2
$[Zn(an)_2(^{15}NCS)_2]$	45.5	3.8	15.2	45.3	3.8	15.1
$[Co(^{15}N\text{-}p\text{-tol})_2(NCS)_2]$	49.1	4.6	14.3	49.0	4.6	14.4
$[Ni(^{15}N\text{-}p\text{-tol})_2(NCS)_2]$	49.1	4.6	14.3	49.2	4.8	14.5
$[Cu(^{15}N\text{-}p\text{-tol})_2(NCS)_2]$	48.5	4.6	14.2	47.9	4.5	14.2
$[Zn(^{15}N\text{-}p\text{-tol})_2)NCS)_2]$	48.3	4.6	14.1	47.7	4.5	13.5
$[Co(p\text{-tol})_2(^{15}NCS)_2]$	49.1	4.6	14.3	49.0	4.5	14.4
$[Ni(p\text{-tol})_2(^{15}NCS)_2]$	49.1	4.6	14.3	49.0	4.6	14.2
$[Cu(p\text{-tol})_2(^{15}NCS)_2]$	48.5	4.6	14.2	46.6	4.3	14.2
$[Zn(p\text{-tol})_2(^{15}NCS)_2]$	48.3	4.6	14.1	47.3	4.4	13.7

TABLE 4

Analytical data on the pyridine complexes of metal(II) isothiocyanates and their deuterated and ^{15}N-labelled analogues.

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Mn(py)_4(NCS)_2]$	54.2	4.1	17.2	54.1	4.0	17.2
$[Fe(py)_4(NCS)_2]$	54.1	4.1	17.2	53.9	4.1	17.2
$[Co(py)_4(NCS)_2]$	53.8	4.1	17.1	53.6	4.0	16.6
$[Ni(py)_4(NCS)_2]$	53.8	4.1	17.1	53.8	4.0	16.9
$[Mn(py)_4(^{15}NCS)_2]$	54.0	4.1	17.1	53.3	4.2	17.0
$[Fe(py)_4(^{15}NCS)_2]$	53.9	4.1	17.1	53.7	3.8	17.2
$[Co(py)_4(^{15}NCS)_2]$	53.5	4.1	17.0	53.1	4.0	17.0
$[Ni(py)_4(^{15}NCS)_2]$	53.6	4.1	17.0	54.4	4.0	17.0
$[Mn(py\text{-}^{15}N)_4(NCS)_2]$	53.8	4.1	17.1	53.4	4.1	17.2
$[Fe(py\text{-}^{15}N)_4(NCS)_2]$	-	-	-	-	-	-
$[Co(py\text{-}^{15}N)_4(NCS)_2]$	53.3	4.1	17.0	53.3	4.0	17.2
$[Ni(py\text{-}^{15}N)_4(NCS)_2]$	53.4	4.1	17.0	53.2	4.0	17.2
$[Mn(d_5\text{-}py)_4(NCS)_2]$	52.1	4.0	16.6	51.3	4.0	16.8
$[Fe(d_5\text{-}py)_4(NCS)_2]$	52.0	4.0	16.5	51.5	3.9	16.5
$[Co(d_5\text{-}py)_4(NCS)_2]$	51.6	3.9	16.4	51.3	4.0	16.7
$[Ni(d_5\text{-}py)_4(NCS)_2]$	51.6	3.9	16.4	51.7	4.0	16.5
$[Fe(py)_3(NCS)_3]$	46.3	3.2	18.0	44.1	3.2	18.0
$[Mn(py)_2(NCS)_2]$	43.8	3.1	17.0	43.4	2.9	17.0
$[Co(py)_2(NCS)_2]$	43.2	3.0	16.8	42.8	2.9	16.8
$[Ni(py)_2(NCS)_2]$	43.3	3.0	16.8	43.0	2.9	16.9
$[Cu(py)_2(NCS)_2]$	42.7	3.0	16.6	42.6	2.9	16.5
$[Zn(py)_2(NCS)_2]$	42.4	3.0	16.5	42.4	2.9	16.4

TABLE 4 (CONTD.)

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Mn(py)_2(^{15}NCS)_2]$	43.5	3.0	16.9	42.0	3.0	16.9
$[Co(py)_2(^{15}NCS)_2]$	43.0	3.0	16.7	41.9	2.8	16.7
$[Ni(py)_2(^{15}NCS)_2]$	43.0	3.0	16.7	42.9	3.0	17.0
$[Cu(py)_2(^{15}NCS)_2]$	42.4	3.0	16.5	42.0	2.9	16.5
$[Zn(py)_2(^{15}NCS)_2]$	42.2	3.0	16.4	42.0	2.9	16.4
$[Mn(d_5\text{-}py)_2(NCS)_2]$	42.5	3.0	16.5	42.0	3.1	16.4
$[Co(d_5\text{-}py)_2(NCS)_2]$	42.0	2.9	16.3	41.6	3.0	16.4
$[Ni(d_5\text{-}py)_2(NCS)_2]$	42.0	2.9	16.3	42.0	3.0	16.5
$[Cu(d_5\text{-}py)_2(NCS)_2]$	41.4	2.9	16.1	41.4	3.0	16.2
$[Zn(d_5\text{-}py)_2(NCS)_2]$	41.2	2.9	16.0	41.0	2.9	16.1

TABLE 5

Analytical data on the pyridine complexes of platinum(II) halides and their deuterated and ^{15}N labelled analogues.

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
cis - $[Pt(py)_2Cl_2]$	28.3	2.4	6.6	28.3	2.4	6.7
cis - $[Pt(d_5\text{-py})_2Cl_2]$	27.7	2.3	6.5	27.6	2.4	6.5
cis - $[Pt(py)_2Br_2]$	23.4	2.0	5.5	23.2	2.0	5.5
cis - $[Pt(d_5\text{-py})_2Br_2]$	23.0	1.9	5.4	22.9	1.9	5.3
cis - $[Pt(py)_2I_2]$	19.8	1.7	4.6	19.7	1.7	4.6
trans - $[Pt(py)_2Cl_2]$	28.3	2.4	6.6	28.4	2.4	6.7
trans - $[Pt(d_5\text{-py})_2Cl_2]$	27.7	2.3	6.5	27.6	2.4	6.6
trans - $[Pt(py)_2Br_2]$	23.4	2.0	5.5	23.1	1.9	5.4
trans - $[Pt(d_5\text{-py})_2Br_2]$	23.0	1.9	5.4	22.7	2.0	5.3
trans - $[Pt(py)_2I_2]$	19.8	1.7	4.6	19.9	1.7	4.7
cis - $Pt(py)_2(SCN)_2$	30.7	2.2	11.9	30.0	2.1	11.7
cis - $Pt(d_5\text{-py})_2(SCN)_2$	30.1	2.1	11.7	29.6	2.1	11.6
cis - $Pt(py)_2(SC^{15}N)_2$	30.6	2.1	11.8	30.1	2.2	11.8
trans - $Pt(py)_2(SCN)_2$	30.7	2.2	11.9	30.5	2.1	11.9
trans - $Pt(d_5\text{-py})_2(SCN)_2$	30.1	2.1	11.7	30.1	2.1	11.7
trans - $Pt(py)_2(SC^{15}N)_2$	30.6	2.1	11.8	30.5	2.1	11.9

TABLE 6

Analytical data on the bis(*o*-toluidine) complexes of metal(II) halides.

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Co(o\text{-tol})_2Cl_2]$	48.8	5.3	8.1	48.3	5.3	8.2
$Ni(o\text{-tol})_2Cl_2.2\frac{1}{2}H_2O$[a]	43.2	6.0	7.2	43.4	5.9	7.3
$[Cu(o\text{-tol})_2Cl_2]$	48.2	5.2	8.0	47.9	5.2	8.0
$[Zn(o\text{-tol})_2Cl_2]$	48.0	5.2	8.0	47.9	5.2	8.1
$[Co(o\text{-tol})_2Br_2]$	38.8	4.2	6.5	38.6	4.3	6.5
$Ni(o\text{-tol})_2Br_2.3H_2O$[a]	34.5	5.0	5.8	34.2	5.2	4.9
$[Cu(o\text{-tol})_2Br_2]$	38.4	4.1	6.4	38.3	4.2	6.3
$[Zn(o\text{-tol})_2Br_2]$	38.3	4.1	6.4	38.2	4.2	6.3
$[Zn(o\text{-tol})_2I_2]$	31.5	3.4	5.3	31.5	3.4	5.5

[a] Green aquo complexes.

2. INFRARED RESULTS

TABLE 7

Vibrational frequencies of the complexes $[M(AA)_2(py)_2]$ in the regions 1610 - 1500 cm^{-1} and 1260 - 150 cm^{-1}. [a]

Co	Ni	Zn[b]	Assignment[c]
1597(38)	1600(40;4)	1607(42;2)	py, νring
1589(2)	1590(1;0)	1586(2;0)	ν C···O
1519(1)	1520(1;0)	1525(0;0)	ν C···O
1256	1250	1265	ν C=C + ν C-CH_3
1215	1215 (1)	1220 (0)	py, δC-H
1199	1200	1198	δ C-C-H, chelate ring
1149	1151 (1)	1163 (1)	py, δC-H
1075	1076 (0)	1078 (3)	py, δC-H
1058	1059 (3)	1065 (2)	
1035	1038 (6)	1046 (9)	py, νring
		1023 (1)	py, νring
1010	1013 (11)	1016 (8)	
921	922	929	ν C=O + ν C-CH_3
881	881 (0)	886 (0)	py, γC-H
		787 (0)	γC-C-H, chelate ring
769	768 (0)	775 (0)	
758	760 (3)	762 (3)	py, γC-H
702	702 (3)	706 (3)	py, γC-H
		669 (3)	chelate ring def.
654(+1)	658(2;0)	656(0;0)	
626(25)	631(26;7)	640(26;6)	py, δring
559(1)	575(0;0)	558(1;0)	coupled ν Ni-O
432(39)	438(40;0)	425[d](39:4)	py, γring
413(1)	420(0;0)		coupled ν Ni-O
263(0)	269(0;0)	216(0;0)	ν Ni-O
227(0)	244(0;0)	188(0;0)	ν Ni-O
	197(4;1)		ν Ni-N
181(7)	186(8;0)	164(4;0)	

[a] Figures in parentheses are the shifts induced by d_5-labelling (regions determined : 1610 - 1500 cm^{-1} and 660 - 150 cm^{-1}) followed by ^{15}N-induced shifts where applicable (region 1610 - 150 cm^{-1}; M = Ni, Zn). Only shifts ≥ 1 are considered significant. They are reported to the nearest integral values and are to lower frequencies unless otherwise stated.

[b] Mono-pyridine adduct.

[c] Based on the paper by Akyüz *et al.*[94].

[d] The band represents both vibrations; resolution into separate bands is observed in the deuterated spectrum (Fig. 1).

TABLE 8

Vibrational frequencies of substituted pyridine adducts $[Ni(AA)_2(R\text{-}C_5H_4N)_2]$ (1600-1580; 800-150 cm^{-1})

R	4-CN	4-$COCH_3$	3-CO_2CH_3	3-CH_3	3,5-di-CH_3	Assignment
σ	+0.63	+0.52	+0.32	-0.07	-0.17	
	1595	1592	1594	1596	1597	νC...O
	800			794[a,b]		
	779[b]	768	769	761	760	
		748[b]	749[b]		755[b]	
	728	725		724[b]	727[b]	
			706[b]	705	704	
	674[b]		698	670	670	
	658	660	659	653	655	ring def.
		596[a,b]	647[b]			
	574	580	578	575	573	coupled νNi-O
	564[b]			539[b]	542[b]	
	479[b]	451[b]		497[b]		
			485[b]	479[b]		
			461[b]			
	422	420	420	415[b]	415	coupled νNi-O
	379[b]	386[b]	351[b]			
	275[a]	278	272[a,b]	269	268[b])	νNi-O
	244[b]	241[a,b]	242[a,b]	244	244[b])	
	206[b]		208[a,b]		204[b]	
	193[b]		169	181	171)	νNi-N
	145	156	164	168	161)	

[a] Mean of doublet.

[b] Bands occurring near regions of absorption in the free ligands.

[c] Masked by neighbouring bands.

TABLE 8 (CONTD.)

R σ	4-C_2H_5 -0.15	4-CH_3 -0.17	4-t-C_4H_9 -0.20	3,4-di-CH_3 -0.24	4-$N(CH_3)_2$ -0.60	Assignment
	1597	1593	1600	1595	1597	νC...O
	786[b]					
	759[b]	762	760[b]	760[b]	756[b]	
	726[b]	725[b]	724[b]	723[b]	725[b]	
	670	670	670	671	667	
	656	655	655	656	655	ring def.
				612[b]		
	576[b]	575	575[b]	576	574	coupled νNi-O
		565[b]			565[b]	
	507[b]	540[b]	543[b]	539[b]	533[b]	
		496[b]		522[b]	487[b]	
				427[b]		
	417	418	417[b]	415	414[b])	coupled
				400[b]	)	νNi-O
		282[b]	333[b]	291[b]	303[b]	
	269[a]	b	266[b]	264[b]	c)	
	243[a]	243[a]	245[a]	240[a]	241[a])	νNi-O
		182	175	174	168)	
	168	162	156	163	160)	νNi-N

[a] Mean of doublet.

[b] Bands occurring near regions of absorption in the free ligands.

[c] Masked by neighbouring band.

TABLE 9. Vibrational frequencies and ^{15}N-induced shifts of the complexes $[M(an)_2(NCS)_2]$[a] in the regions 3500 - 3100 cm^{-1}; 2200 - 2000 cm^{-1}; 1600 - 150 cm^{-1}.

Ligand						
NaNCS	aniline[b]	Co	Ni	Cu	Zn	Assignment
	3481(10)	3324(0;9)	3325(0;9)	3300(0;9)	3279(0;6)	νN-H asym.
	3395(5)	3252(2;8)	3254(0;6)	3218(3;8)	3235(0;6)	νN-H sym.
		3153(0;8)		3128(0;8)	3138(0;6)	νN-H---S
2074(26)		2123(29;2)	2131(27;0)	2118(28;2)	2100(29;0)	νN-CS[c]
		1602(0;0)	1603(0;0)	1601(0;0)	1604(0;0)	
	1619(6)	1589(0;5)	1590(0;4)	1578(0;4)	1591(0;3)	NH_2 scissor
		1494(2;2)	1494(0;2)	1495(0;0)	1495(0;0)	
		1248(0;2)	1238		1239(0;0)	
	1276(5)	1234(0;4)	1238(3;8)	1232(0;5)	1223(0;4)	νC-N
		1174(0;0)	1174(0;0)	1175(0;0)	1172(0;0)	
		1158(0;0)	1158(0;0)		1142(0;2)	
	1115(2)	1043(0;2)	1051(0;4)	1077(0;6)	1050(0;4)	NH_2 twist
		1000(0;0)	1001(0;0)	1003(0;0)	1000(0;0)	
		966(0;0)	965(0;0)	970(0;0)		
960(7)		922(7;0)			948(7;0)	2 δNCS
		896(0;0)	895(0;0)	900(0;0)	895(0;0)	
		839(0;2)	839(0;0)	840(0;1)	832(0;1)	
		825(0;2)	826(0;2)	828(2;2)	815(0;0)	
	884(2)	805(0;7)	806(0;6)	808(6;6)	798(0;6)	NH_2 wag

TABLE 9 (Continued)

Ligand						
NaNCS	aniline[b]	Co	Ni	Cu	Zn	Assignment
756(10)		784(11;0)	779(8;0)	815(5;0)	833(11;0)	νNC-S
		761(0;0)	762(0;0)	764(0;0)	756(0;0)	
		692(0;0)	693(0;0)	692(0;0)	691(0;0)	
		588(0;5)	602(0;5)	638(0;7)	648(0;6)	NH_2 rock
		541(0;6)	544(0;5)	550(0;6)	534(0;6)	νM-NH_2 + ligand
	529(6)	520(0;2)	523(0;2)	532(0;4)	520(0;3)	
481(4)		471(4;0)	471(4;0)	465(3;0)	470(4;0)	δNCS
		461(3;0)	460(4;0)			
		376(0;4)	380(0;4)	403(0;6)	390(0;6)	νM-NH_2
	382(0)[i]	361(0;8)	361(0;4)	370(0;3)	367(0;3)	νM-NH_2 + ligand
		273(0;0)	284(0;0)	314(0;0)	275(0;0)	νM-NCS?
	230(4)	210(1;0)			212(0;0)	ligand, γring
		186(4;0)	227(2;0)	231(2:0)	167(4:0)	νM-NCS
			160(1;0)	175[h]		δNMN

[a] Frequencies are followed by ^{15}N-induced shifts in parentheses in the order (^{15}NCS shift, $^{15}NH_2$ shift). Shifts < 1 cm^{-1} are not considered significant and are cited as zero shifts. All shifts are reported to the nearest integral values and are to lower frequencies unless otherwise indicated.

[b] Frequencies > 1000 cm^{-1} from spectra of 0.05 M CCl_4 solutions. Frequencies ≷ 1000 cm^{-1} from liquid film (aniline) or Nujol mull (*p*-toluidine) except band at 812 cm^{-1} in *p*-toluidine spectrum (taken in 0.05 M cyclohexane).

[c] Sharp shoulders on these bands are omitted.

TABLE 9 (Continued)

[d] Band disappears on ^{15}NCS-labelling.

[e] Shift towards higher frequency.

[f] Mean of doublet.

[g] No ^{15}NCS-sensitive band observed in this region.

[h] Broad or weak band; frequency and shift cannot be determined precisely.

[i] Band has not been observed in freshly-distilled aniline but is present in the spectrum a few hours after distillation.

TABLE 10. Vibrational frequencies and ^{15}N-induced shifts of the complexes $[M(p\text{-tol})_2(NCS)_2]$[a] (regions as for aniline complexes).

Ligand						
NaNCS	*p*-tol[b]	Co	Ni	Cu	Zn	Assignment
	3486(8)	3318(0;7)	3320(0;8)	3292(0;3)	3260(1[e];7)	νN-H asym
	3399(4)	3254(0;6)	3256(0;4)	3224(0;6)	3209(0;8)	νN-H sym
2074(26)		3152(0;8)		3130(0;9)	3127(0;6)	νN-H---S
		2124(27;0)	2135(28;0)	2124(29;0)	2100(30;0)	νN-CS[c]
		1615(0;0)	1616(0;0)	1615(0;0)	1618(0;0)	
	1628(2)	1585(0;3)	1588(1;5)	1577(0;4)	1585(0;4)	NH_2 scissor
		1514(0;0)	1514(0;0)	1514(0;0)	1513(0;0)	νC-C ring
	1275(4)	1244(0;10)	1246(0;7)	1247(0;3)	1222(0;3)	νC-N
				1229(0;2)	1214(0;2)	
		1104(0;0)	1103(0;0)	1105(0;0)		
	1126(1)	1036(0;4)	1044(0;5)	1069(0;4)	1110(0;7)	NH_2 twist
					1075(0;6)	
		1015(0;0)	1017(0;0)			
		931(0;0)	935(0;3)	934(0;0)	935(0;0)	
		813(0;0)	815(0;0)		816[f](0;0)	
756(10)		784(11;0)	781(10;0)	817(13;0)	g	νNC-S
	812(1)	739(0;6)	740(0;6)	744(0;5)	737(0;6)	NH_2 wag
		706(0;0)	707(0;0)	708(0;0)	707(0;0)	
		647(0;1)	647(0;1[e])			

TABLE 10 (Continued)

Ligand						
NaNCS	*p*-tol[b]	Co	Ni	Cu	Zn	Assignment
		580(0;4)	598(0;4)	653(0;4)	664(0;5)	
				623(0;4)	653(0;3)	NH_2 rock
					630(0;3)	
	505(1)	521(0;1)	526(0;2)	532(0;3)	529(0;3)	$\nu M\text{-}NH_2$ + ligand
					520(0;2)	
481(4)		470(4;0)	471(4;0)	463(4;0)	479(4;0)	δNCS
		455(4;0)	453(4;0)			
		402(0;3)	407(0;3)	425(0;6)	471(0;3)	$\nu M\text{-}NH_2$
					414(0;2)	
	380(0)	381(0;3)	385(0;1)	391(0;0)	394(0;0)	$\nu M\text{-}NH_2$ + ligand
	338[h]	307(0;2)	309(0;2)	313(0;0)	316(0;0)	ligand
	315[h]	270(1;0)	281(0;0)	295[h]		
		190(3;0)	212(4;0)	234(4;0)	265(3;0)	νM-NCS
					162(3;0)	
		154[h]	169(0;0)	173[h]		δNMN

[a] Frequencies are followed by ^{15}N-induced shifts in parentheses in the order (^{15}NCS shift, $^{15}NH_2$ shift). Shifts < 1 cm^{-1} are not considered significant and are cited as zero shifts. All shifts are reported to the nearest integral values and are to lower frequencies unless otherwise indicated.

[b] Frequencies > 1000 cm^{-1} from spectra of 0.05 M CCl_4 solutions. Frequencies $\geq$1000 cm^{-1} from liquid film (aniline) or Nujol mull (*p*-toluidine) except band at 812 cm^{-1} in *p*-toluidine spectrum (taken in 0.05 M cyclohexane).

TABLE 10 (Continued)

[c] Sharp shoulders on these bands are omitted.

[d] Band disappears on ^{15}NCS-labelling.

[e] Shift towards higher frequency.

[f] Mean of doublet.

[g] No ^{15}NCS-sensitive band observed in this region.

[h] Broad or weak band; frequency and shift cannot be determined precisely.

TABLE 11. Vibrational frequencies of the bis(pyridine) complexes $[M(py)_2(NCS)_2]$ in the region 2200 - 2000 and 1650 - 145 cm^{-1}. [a]

Mn	Co	Ni	Cu	Zn	Assignment
2094[b](28;1)	2102[b](27;0)	2114[b](29;0)	2098[b](30;1)	2100(29;0) 2081(29;0)	νN-CS
1604	1605	1606	1607	1605[c]	py, νring
1580	1578	1576	1575	1573	
1491	1491	1493	1491	1493	py, νring
			1242	1249	δC-H
1221	1220	1220	1217	1217	
1154	1154	1153	1156	1156	δC-H
1074	1075	1076	1073	1072	
1041	1042	1044	1045	1050	py, νring
1011	1012	1014	1017	1020[c]	
				973(7;d)	2 δNCS
957(6;1)	955(t.b.)	959(6;0)	962(3;0)	962(t.b.)	
940(3;0)	945(t.b.)	944(0;0)	945(0;0)	953(0;d)	2 δNCS
879(1;193)	875(0;190)	873(0;191)	874(0;d)	877(0;191)	py, γC-H
788(10;0)	790(11;0)	784(10;0)	826(12;+1)	848(12;0)	νNC-S
754(0;200)	755(0;201)	756(1;201)	757(0;200)	756[c](0;195)	py, γC-H
				701(0;162)	py, γC-H
696(0;166)	696(0;167)	695(0;166)	693(0;159)	693(1;162)	
626(0;24)	630(0;25)	631(0;25)	639(0;25)	645(0;29)	py, δring
476(3;1)	475(3;0)	477(0;1)	478(4;0)	486(3;0)	δNCS
470(4;0)	470(t.b.)	469(4;0)	469(3;0)	481(3;0)	
418(0;40)	426(0;40)	433(0;40)	434(0;40)	426(0;39)	py, γring
				414(0;39)	
258(1;0)	270(0;0)	285(2;0)	324(1;3)	315(1:1)	νM-NCS
196(0;2)[e]	208(2;2)[e]	226(2;4)[e]	257(1;0)	270(0;2)	
164(1;4)	185(1;3)	206(1;9)	225(0;5)	232(0;4)	νM-py
				207(0;5)	
153(t.b.)	162(1;3)	179(0;3)	212(1;5)	162((4;5)	δNMN
b.r.	145(0;3)	155(1;4)	193(0;8)	b.r.	

TABLE 11 (Continued)

[a] Abbreviations: b.r. = beyond range of measurement, t.b. = too broad for determination of shift. Figures in parentheses following the frequencies are the shifts (nearest integral values in cm^{-1}) towards lower frequency induced by ^{15}NCS-labelling (first figure) and pyridine deuteration (second figure). Shifts < 1 cm^{-1} are not regarded as significant and are reported as zero shifts.

[b] Sharp shoulders on νN-CS bands ignored (see Fig. 5).

[c] Mean of doublet.

[d] Bands do not recur in the deuterated spectra.

[e] Some *d*-sensitivity in these bands indicates coupling with νM-py.

TABLE 12. Vibrational frequencies of the tetrakis (pyridine) complexes $[M(py)_4(NCS)_2]$ in the region 2200 - 2000 cm^{-1} and 1650 - 145 cm^{-1}.[a]

Mn	Fe	Co	Ni	Assignment
2062[b](27;1)	2066(29;0)	2074[b](27;1)	2084[b](27;0)	νN-CS
1632	1639	1636	1635	
1598	1603	1598	1598	py, νring
1570	1575	1571	1570	py, νring
1486	1489	1486		
1236	1237	1235	1233	δC-H
1214	1217[c]	1212	1211	py, δC-H
1148	1150	1148	1148	
1069	1071	1069	1069	py, δC-H
1038[c]	1041[c]	1040[c]	1041[c]	py, νring
1005	1007	1006	1007	py, νring
967(9;0)	972(10;0)	970(9;+2)	971(9;0)	2 δNCS
961(8;0)	963(8;0)	962(t.b.)	962(t.b.)	
948(1;d)	949(1;d)	952(+1;d)	952(2;d)	2 δNCS
887(0;d)	887(0;d)	885(1;d)	885(1;d)	py, γC-H
798(11;0)	806(11;1)	802(11;0)	801(11;0)	νNC-S
765(0;d)	765(0;d)	767(0;d)	768(0;d)	py, γC-H
755(0;d)	755(0;d)	757(0;d)	758(0;d)	
713(0;166)	712(0;165)	713(0;165)	714(0;166)	py, γC-H
701(0;168)	701(0;167)	702(0;168)	702(0;167)	
653(0;28)	653(0;27)	654(0;28)	654(0;28)	py
624(0;24)	624(0;24)	625(0;24)	626(0;24)	py, δring
481(3;0)	483(3;0)	482(3;0)	483(3;0)	δNCS
422(0;40)	428(0;38)	431(0;40)	437(0;38)	py, γring
414(0;40)	420(0;38)	423(0;39)	430(0;38)	
256(0;0)	271(1;0)	272(0;0)	287(0;0)	νM-NCS
188(0;0)	201(0;3)	212(2;0)	230(0;2)	νM-py + νM-NCS
174(1;3)	193(0;4)	202(2;4)	220(0;4)	νM-py
b.r.	163(0;2)	165(t.b.)	172(1;3)	δNMN
b.r.	b.r.	b.r.	160(1;7)	

TABLE 12 (Continued)

[a] Abbreviations: b.r. = beyond range of measurement, t.b. = too broad for determination of shift. Figures in parentheses following the frequencies are the shifts (nearest integral values in cm^{-1}) towards lower frequency induced by ^{15}NCS-labelling (first figure) and pyridine deuteration (second figure). Shifts $< 1\ cm^{-1}$ are not regarded as significant and are reported as zero shifts.

[b] Sharp shoulders on νN-CS bands ignored (see Fig. 5).

[c] Mean of doublet.

[d] Bands do not recur in the deuterated spectra.

[e] Some *d*-sensitivity in these bands indicates coupling with νM-py.

TABLE 13

Vibrational frequencies of the pyridine complexes of Fe(II) and Fe(III) in the regions 2200 - 2000 cm^{-1} and 850 - 150 cm^{-1} [a]

trans-$[Fe(py)_4(NCS)_2]$	Oxidation product	*cis*-$[Fe(py)_3(NCS)_3]$	Assignment
2066(29;0)	2065	2043	νN-CS
806(11;1)	807	853	νNC-S
765(0;b)	766	766	py, γCH
755(0;b)	756	755	
	747	745	py
712(0;165)	712		py, γCH
701(0;167)	702	698	
	674	673	py
653(0;27)	654	652	py
	639	638	py
624(0;24)	625		py, δring
483(3;0)	483	489	δNCS
428(0;38)	429	429	py, γring
420(0;38)	422	413	
	313	319	νM-NCS
	296	300	
271(1;0)	271		νM-NCS
201(0;3)	201		νM-py+ M-NCS
	247	247	νM-py
193(0;4)	192	212	
163(0;2)	160	189	δNMN

[a] Figures in parentheses are the shifts (nearest integral values) towards lower frequencies induced by ^{15}NCS-labelling (first figure) and pyridine deuteration (second figure). Shifts < 1 cm^{-1} are not regarded as significant and are reported as zero shifts.

[b] Bands do not recur in the deuterated spectra.

TABLE 14. Vibrational frequencies and ^{15}N-induced shifts for the complexes *cis*- and *trans*-$[Pt(py)_2Cl_2]$ in the regions 1650 -1450 cm^{-1} and 1250 - 150 cm^{-1}

cis-$[Pt(py)_2Cl_2]$		*trans*-$[Pt(py)_2Cl_2]$		Assignment[b]
Frequency	Shift ($\Delta\nu$)[a]	Frequency	Shift ($\Delta\nu$)[a]	
1606	3	1608[d]	4	py, γring
1570	5	1572[d]		
1481	2	1476	2	
1242	12	1249	13	py; δC-H?
1207	1	1205	2	py, δC-H
1156	0	1151	0	
1071	7	1072[c]	5	
1052	3			py, γring
1020	4	1020	5	
948	4	945	3	py, γC-H
885	0	874	0	py, γC-H
875	0			
774	3	772	5	py, γC-H
763	3			
726[d]		730[d]		
699	3	694	3	py, γC-H
692	1			
664	6	659	5	py, δring
647	2			
471	8	482	8	νpy + νPt-N
457	7			
345	0	344	0	νPt-Cl
331	0			
256	2	285	3	νPt-N
232	2			
		254	1	νPt-N + νPt-Cl
		230	1	
160	0	165	0	δClPtCl

[a] Shifts (cm^{-1}) are reported to the nearest integral values and are to lower frequencies.

[b] Based on paper by Akyüz *et al.*[94]

[c] Mean of doublet.

[d] Broad and weak band; frequency and shift cannot be determined precisely.

TABLE 15. Vibrational frequencies of the complexes *cis*-$[Pt(py)_2X_2]$ (X = Cl, Br, I) in the region 900 - 150 cm^{-1}

$[Pt(py)_2Cl_2]$	$[Pt(py)_2Br_2]$	$[Pt(py)_2I_2]$	Assignment
885	881	884	py, γC-H
875	874	877	
774	770	766	py, γC-H
763	762	760[a]	
726[a]	726[a]	725[a]	
699			py, γC-H
692	693	692	
664	661	657	py, δring
647			
471	467	460	νpy + νPt-N
457	452	446	
345			νPt-Cl
331			
256	259	244	νPt-N
232	230	220	
	216		νPt-Br + νPt-N
	208		νPt-Br
		175	νPt-I
		165	
160			δClPtCl

[a] Broad and weak band; frequency cannot be determined precisely.

TABLE 16. Vibrational frequencies of the complexes *trans*-$[Pt(py)_2X_2]$ (X = Cl, Br, I) in the region 900 - 150 cm^{-1}

$[Pt(py)_2Cl_2]$	$[Pt(py)_2Br_2]$	$[Pt(py)_2I_2]$	Assignment
874		886	py, γC-H
772	770	772	
	757		
730[a]	724[a]	725[a]	
694	691	695	py, γC-H
659	658	650	py, δring
482	479	476	νpy + νPt-N
344			νPt-Cl
285	296	290	νPt-N
254			νPt-N + νPt-Cl
230			
	247		νPt-N + νPt-Br
	212		νPt-Br + νPt-N
		179	νPt-I
165			δClPtCl

[a] Broad and weak band; frequency cannot be determined precisely.

TABLE 17. Vibrational frequencies and isotopic shifts of the complexes *cis*- and *trans*-$[Pt(py)_2(SCN)_2]$ in the regions 2200 - 2000 cm^{-1} and 1650 - 150 cm^{-1}

cis-$[Pt(py)_2(SCN)_2]$				*trans*-$[Pt(py)_2(SCN)_2]$				
Frequency	Shift ($\Delta\nu$)[a]			Frequency	Shift ($\Delta\nu$)[a]			Assignment[b]
	^{15}N	d_5	^{15}NCS		^{15}N	d_5	^{15}NCS	
2124	0		28	2119	0		28	νN-CS[c]
1606	4		0	1608	3		0	py, νring
1571	3		0	1573	3		0	py, νring
								Nujol-masked
1354	1		0	1347	1		0	py, νring
1242[e]	12		0	1244	10		d	py, δC-H?
1208[e]	1		0	1205	0		+1	
1157	0		d	1147	d		1	
				1093	1		0	py, δC-H
1072	n.o.		0	1077	9		1	
1069	7		0	1063	4		0	
1018	4		1	1019	3		0	py, νring
944	0		0	946	1		0	py, γC-H
878[d]	1		0	884	0		0	py, γC-H
851[d]	0	0	2	856	0	0	11	2δNCS
764	6	202	0	769	5	206	0	
696	3	160	0					py, γC-H
692	4	160	n.o.	691	4	158	0	
659	6	29	0					
656	7	35	0	647	n.o.	27	0	py, δring
480	4	59	0	480	5	46	0	νpy + νPt-N
462	0	0	2					δSCN
447	6	39	0					νpy + νPt-N
423	0	2	3	427	0	0	3	δSCN
321	0	2	1					
311	0	1	0	292	0	0	0	νPt-S
244	2	11	0					
231	1	9	0	288	3	15	0	νPt-N
				263	0	4	0	
				224	2	14	0	νPt-N + νPt-S
151	0	0	0	158	1	0	2	δSPtS

TABLE 17 (Continued).

[a] Shifts (cm^{-1}) are reported to the nearest integral values and are to lower frequencies unless otherwise stated; shifts on deuteration were determined in the region 850 - 150 cm^{-1}.

[b] Based on papers by Akyüz *et al.*[94] and Hutton and Thornton[95].

[c] Sharp shoulders on νN-CS bands ignored.

[d] Broad or weak band; frequency and/or shift cannot be determined precisely.

[e] Mean of doublet.

[f] Abbreviation: n.o. = not observed; the respective band does not recur in the labelled spectrum.

TABLE 18. Vibrational frequencies and ^{15}N-induced shifts[a] of the complexes $[M(o\text{-tol})_2Cl_2]$ in the regions 3400-3100 cm^{-1}; 1700-1500 cm^{-1}; 1300-145 cm^{-1}.

Ligand[b]	Co	Ni	Cu	Zn	Assignment
3458(6)	3286(7)	3350[c]	3264(8)	3296(10)	νN-H antisym.
3376(7)	3242(4)	3330[c]	3217(6)	3247(4)	νN-H sym.
3214(4)	3132(4)	3277	3134(5)	3138(8)	νN-H...Cl(N)
1624(4)	1578(3)	1583	1588(2)	1580(3)	NH_2 scissor
1586(0)	1594(0)	1616[b]	1621(2)	1595(1)	νC...C ring
		1592			
1304(2)	1294(0)	1302	1303(0)	1294(1)	
		1273	1274(4)		νC-N
1274(4)	1235(2)	1243	1235(2)	1235(3)	
1205(0)	1195(3)	1202	1200(1)	1192(0)	
1157(1)	1157(0)	1170			
	1151(0)		1154(+1)	1158(0)	
1145(2)		1089	1095(5)		NH_2 twist
	1076(7)	1057	1077(4)	1077(2)	
1067(3)	1043(0)	1042	1044(0)	1043(0)	
1036(0)	1035(0)		1036(0)	1035(0)	
988(0)	994(0)	994	991(0)	993(0)	
929(0)	938(0)	937	937[d](0)	938(0)	
	856(0)	862[d]	857(0)	856(0)	
847(2)	835(4)	837	835(3)	834(3)	NH_2 wag
	743(4)	749	746(1)	743(5)	
753(0)	760(0)	760		760(0)	ligand
716(0)	712(0)	712	713(0)	713(0)	ligand
	642(4)	599		650(7)	NH_2 rock
586(2)	585(2)	582	586(2)	586(3)	
539(0)	545(2)	555	548(2)	546(2)	ligand
518(5)	520(3)	519	518(3)	519(3)	
		480			
441(0)	455(2)	454	453(3)	453(0)	ligand
	418(4)			415(3)	νM-NH_2
	404(5)	408	419(4)	396(6)	
		364	345(3)	331(3)	
		325			
	328(0)	247	302(0)	309(0)	νM-Cl
	297(0)	208	253(0)	294(0)	
272(0)	265(0)	260	267(0)	262(0)	ligand + νM-Cl
	188(0)	171	165(0)	185(0)	δClMCl
		151	145(1)		

TABLE 18 (Continued)

[a] Frequencies are followed by ^{15}N-induced shifts in parentheses. Shifts <1 cm^{-1} are not regarded as significant and are cited as zero shifts. All shifts are to lower frequencies unless otherwise indicated.

[b] Frequencies are from liquid film spectra of *o*-toluidine and ^{15}N-labelled *o*-toluidine.

[c] Broad or weak band; frequency and shift cannot be determined precisely.

[d] Mean of doublet.

TABLE 19. Vibrational frequencies and ^{15}N-induced shifts[a] of the complexes $[M(o\text{-tol})_2Br_2]$ in the regions 3400-3100 cm^{-1}; 1700-1500 cm^{-1}; 1300-145 cm^{-1}.

Ligand[b]	Co	Ni	Cu	Zn	Assignment
3458(6)	3278(6)	3310	3258	3289(8)	νN-H antisym.
		3278			
3376(7)	3234(5)	3249	3208	3240(5)	νN-H sym.
		3221			
3214(4)	3121(5)	3119	3127	3127(7)	νN-H...Br(N)
1624(4)	1571(1)	1570	1585	1575(3)	NH_2 scissor
1586(0)	1611(0)	1605	1610		νC...C ring
	1591(0)	1592	1590	1593	
1304(2)	1294(0)	1303			
		1273	1273[c]		νC-N
1274(4)	1234(2)	1238	1233	1235(3)	
1205(0)	1192(3)	1202	1198	1195(4)	
1157(1)		1163[d]	1159	1156(+1)	
1145(2)	1076(4)	1089	1088	1077(5)	NH_2 twist
1067(3)	1043(0)	1045	1044	1044(0)	
1036(0)	1036(0)	1032	1040	1036(0)	
988(0)	994(0)	988	994	994(+1)	
929(0)	939(0)	936	938	938(0)	
	859(0)	862	857	857(0)	
847(2)	830(4)	832	835	833(3)	NH_2 wag
	743(5)	745	746	743(4)	
753(0)	759[d](0)	765		759[d](0)	ligand
716(0)	712(0)	715	712	713(0)	ligand
	636(5)	629		642(5)	NH_2 rock
		604			
586(2)	585(2)	585	585	585(2)	
539(0)	545(3)	548	547	546(3)	ligand
518(5)	521(3)	515	517	519(3)	
441(0)	454(0)	452	455	453(1)	ligand
	415(4)			412(2)	νM-NH_2
	402(4)	413	419	390(5)	
		368			
		338	340[c]		
272(0)	261(0)	241	243	255(1)	ligand
				246(0)	
	246(0)	192	224	227(0)	νM-Br
	202(0)	162	169	195(0)	

TABLE 19 ((Continued)

[a] Frequencies are followed by ^{15}N-induced shifts in parentheses. Shifts <1 cm^{-1} are not regarded as significant and are cited as zero shifts. All shifts are to lower frequencies unless otherwise indicated.

[b] Frequencies are from liquid film spectra of *o*-toluidine and ^{15}N-labelled *o*-toluidine.

[c] Broad or weak band; frequency and shift cannot be determined precisely.

[d] Mean of doublet.

TABLE 20. Vibrational frequencies and ^{15}N-induced shifts[a] of the complex $[Zn(o\text{-tol})_2I_2]$ in the regions 3400-3100 cm^{-1}; 1700-1500 cm^{-1}; 1300-145 cm^{-1}.

Ligand[b]	$[Zn(o\text{-tol})_2I_2]$	Assignment
3458(6)	3285(7)	νN-H antisym.
3376(7)	3233(5)	νN-H sym.
3214(4)	3114(4)	νN-H...I(N)
	1610(0)	
1624(4)	1567(1)	NH_2 scissor
1586(0)	1610(0) }	νC...C ring
	1590(1) }	
1274(2)	1232(0)	νC-N
1205(0)	1190(1)	
1157(1)	1164[c]	
	1156[c]	
1145(2)	1076(2)	NH_2 twist
1067(3)	1044(0)	
1036(0)	1034(0)	
988(0)	993(2)	
929(0)	934(0)	
	858[d](0)	
847(2)	831(3) }	
	759(3) }	NH_2 wag
	740(4) }	
753(0)	762(0)	
716(0)	713(0)	ligand
	636(6) }	
	619(5) }	NH_2 rock
586(2)	583(2) }	
539(0)	545(2) }	ligand
518(5)	517(3) }	
441(0)	453(0)	ligand
	410(2) }	νM-NH_2
	380(3) }	
272(0)	250(0) }	ligand
	241(0) }	
	191(0) }	νZn-I
	156(1) }	

TABLE 20 (Continued)

[a] Frequencies are followed by ^{15}N-induced shifts in parentheses. Shifts <1 cm^{-1} are not regarded as significant and are cited as zero shifts. All shifts are to lower frequencies unless otherwise indicated.

[b] Frequencies are from liquid film spectra of *o*-toluidine and ^{15}N-labelled *o*-toluidine.

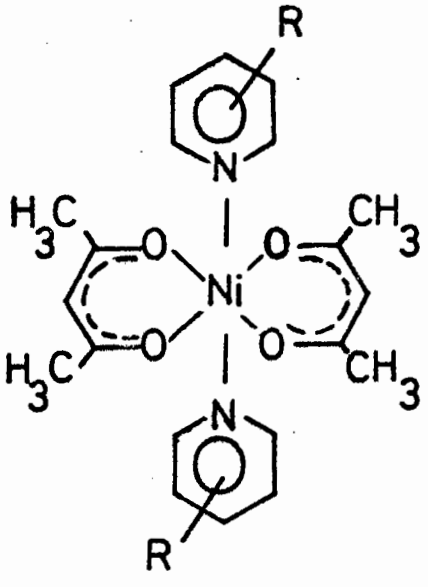
[c] Broad or weak band; frequency and shift cannot be determined precisely.

[d] Mean of doublet.

IV. DISCUSSION

1. INFRARED SPECTRA OF PYRIDINE ADDUCTS OF METAL(II) ACETYLACETONATES

The far-infrared spectra of the pyridine and pyridine-d_5 adducts of Co(II), Ni(II) and Zn(II) bis(acetylacetonate) complexes are shown in Figure 1. *Trans*-octahedral configuration has been established by X-ray crystallographic methods for the bis(pyridine) adducts (I) of cobalt(II) and nickel(II)[96,97]. Different orientation of the *trans*-pyridine rings (eclipsed in the nickel and staggered in the cobalt complex) has been established by Elder[97] in 1968. This may well account for the slight differences in the far I.R. spectra of the two complexes (below 200 cm^{-1}). The Zn(II) complex is uniquely 5-coordinate and probably has square pyramidal structure by analogy[98] with $[Zn(AA)_2(H_2O)]$. Spectra of the substituted pyridine adducts are depicted in Figure 2. Bands shifted by metal ion labelling are termed ^{i}M-sensitive bands; those shifted by metal ion substitution are called M-sensitive bands; those affected by deuteration of the pyridine ring are referred to as *d*-sensitive bands and those which move on varying the pyridine substituents are termed R-sensitive bands.



I. Formula of pyridine adducts of Ni(II) acetylacetonate.

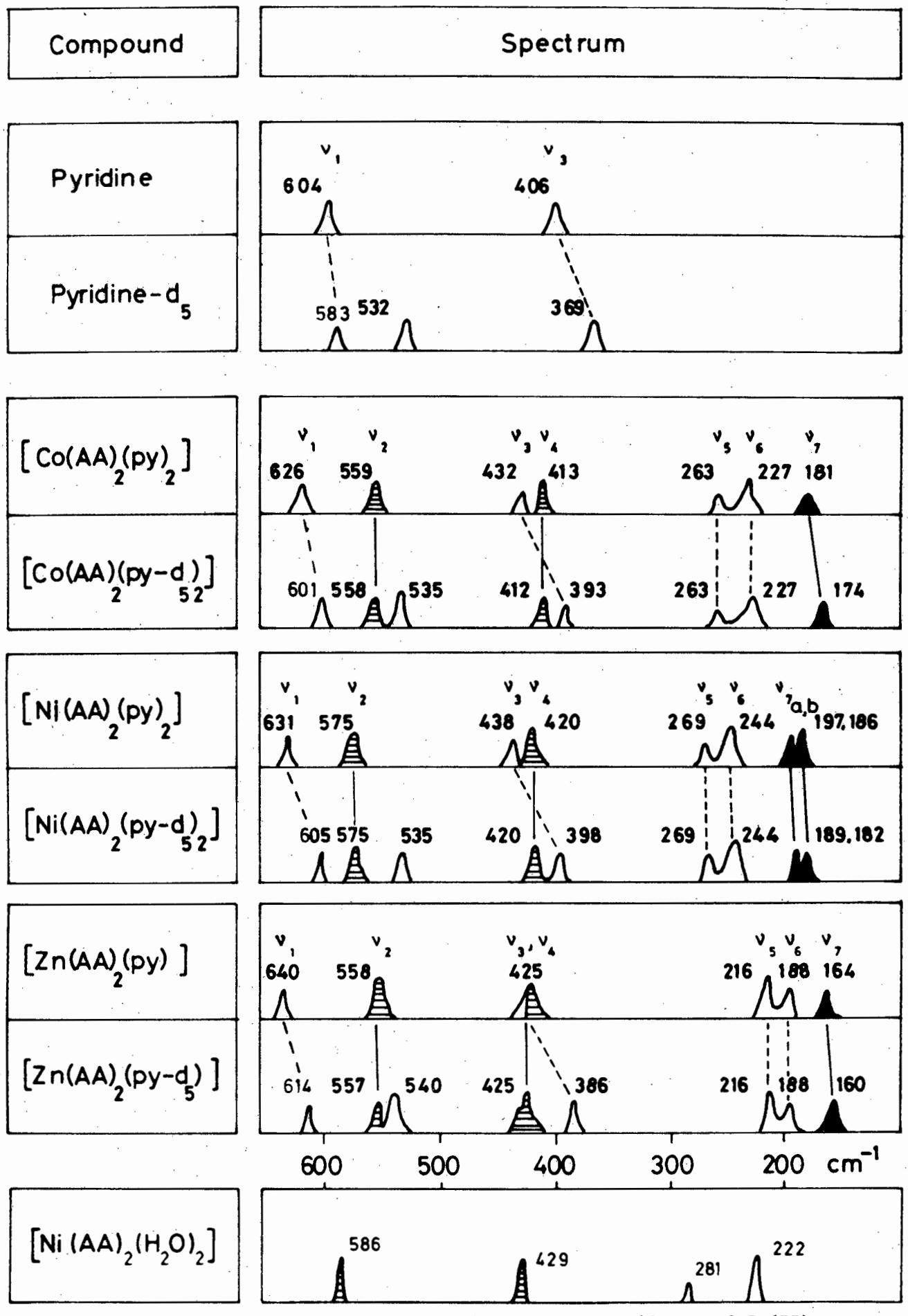


Fig. 1. Infrared spectra of pyridine and pyridine-d_5 adducts of Co(II), Ni(II) and Zn(II) bis(acetylacetonates). ν_1 and ν_3 are pyridine bands; ν_2 and ν_4 (shaded) are coupled νM-O bands; ν_5 and ν_6 are pure νM-O bands; ν_7 (solid) is the νM-N band.

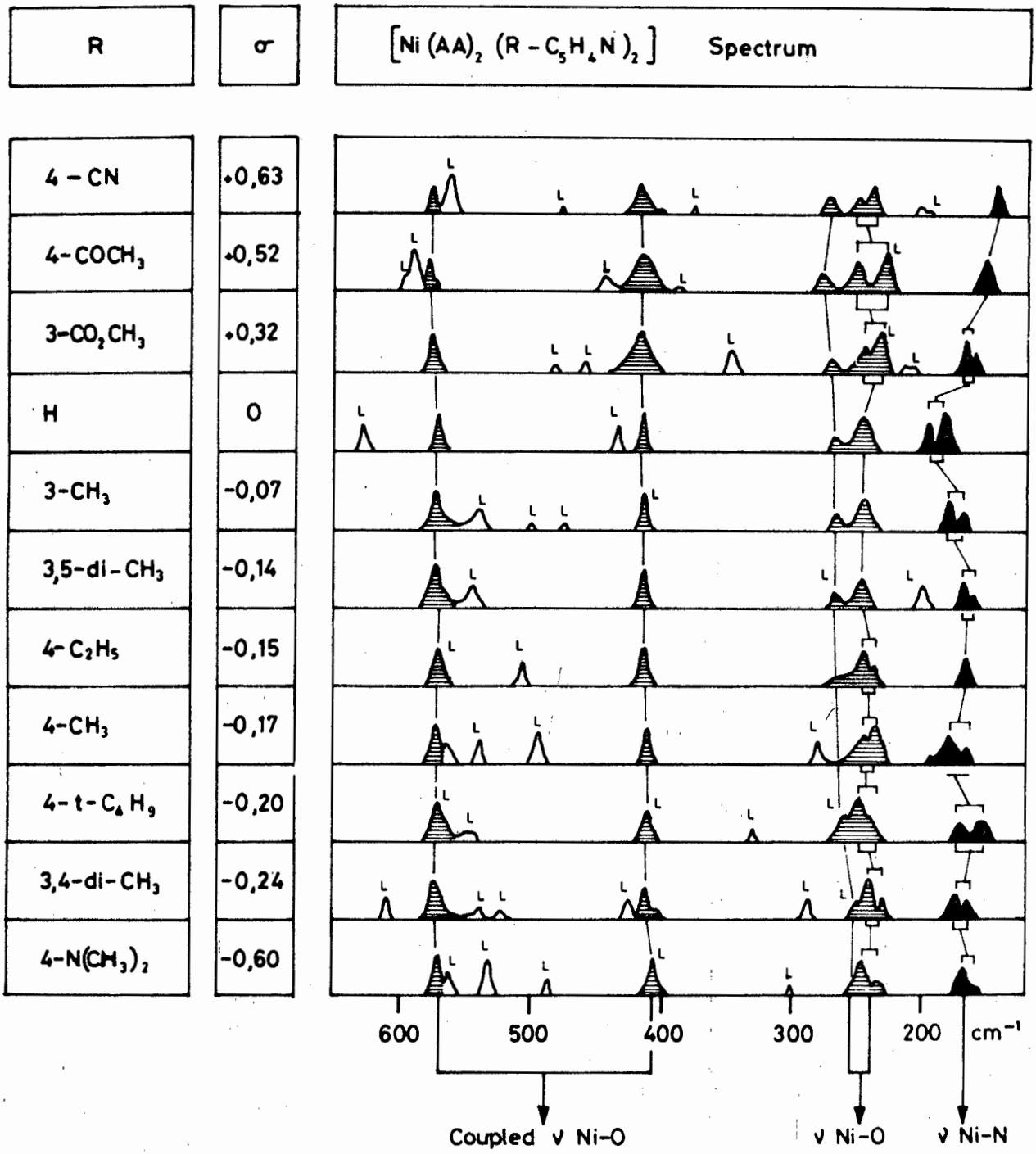


Fig. 2. Infrared spectra of substituted pyridine adducts. Shaded peaks : νNi-O, solid peaks : νNi-N, L = bands occurring at or near regions of absorption in the spectra of the free pyridines.

TABLE 21

Frequencies (cm^{-1}) of far-infrared bands in $[Ni(AA)_2(py)_2]$ and their ^{i}M-, *d*- and M-sensitivities

Band No.	Frequency cm^{-1}	^{i}M-sensitivity[66a] cm^{-1}	*d*-sensitivity[b] cm^{-1}	M-sensitivity[c] Co cm^{-1}	Zn cm^{-1}	Previous assignment[66]	Present assignment
ν_1	631	0.5	26	5	-9	$\pi(CH_3)CCO$	νpy[d]
ν_2	575	0.8	0	16	17	νNi-O+ring[e]	coupled ν(Ni-O)
ν_3	438	0.8	40	6	13	νNi-O+νC-CH_3	νpy[f]
ν_4	420	0.4	0	7	-5	ring[g]	coupled ν(Ni-O)
ν_5	269	5.4	0	6	53	νNi-O	νNi-O
ν_6	244	3.8	0	17	56	νNi-N	νNi-O
ν_{7a}	197[h]	n.o.[i]	8	(11[j]	(28[j]	n.o.[i]	(
ν_{7b}	186	n.r.[k]	4	(	(	ring	(νNi-N

a ^{i}M-sensitivity = {frequency for $[^{58}Ni(AA)_2(py)_2]$}-{frequency for $[^{62}Ni(AA)_2(py)_2]$}

b *d*-sensitivity = {frequency for $[Ni(AA)_2(py)_2]$}-{frequency for $[Ni(AA)_2(py\text{-}d_5)_2]$}

c M-sensitivity(Co) = {frequency for $[Ni(AA)_2(py)_2]$}-{frequency for $[Co(AA)_2(py)_2]$}

M-sensitivity(Zn) = {frequency for $[Ni(AA)_2(py)_2]$}-{frequency for $[Zn(AA)_2(py)]$}

d A_1 mode, δring

e Independently assigned to νNi-O[28]

f B_2 mode, γring

g Independently assigned to νNi-O[28]

h Shoulder

i n.o. = shoulder not observed[66]

j νNi-N taken as mean of 197, 186 cm^{-1} bands

k n.r. = shift not reported[66]

1.1 Infrared Spectrum of $[Ni(AA)_2(py)_2]$

The ^{i}M-, M- and *d*- sensitivities of the bands in the spectrum of this complex are compared in Table 21. Based on the results of normal coordinate analyses of metal acetylacetonates and in view of its small ^{i}M-sensitivity, ν_1 has been assigned[66] to the $\pi(CH_3)CCO$ vibration. This assignment is now discounted by its *d*-sensitivity ($\Delta\nu$ = 26 cm^{-1}) which is similar in magnitude to that exhibited (Fig. 1) by the 604 cm^{-1} ligand band in pyridine ($\Delta\nu$ = 21 cm^{-1}) and by the 635 cm^{-1} band[65] in $[Ni(py)_2Cl_2]$ ($\Delta\nu$ = 25 cm^{-1}). Under these circumstances, ν_1 is firmly assigned to the pyridine vibration.

ν_2 has a significantly greater ^{i}M-sensitivity than ν_1. This has led[66] to its assignment to a coupled νNi-O band. Its R-sensitivity has also been cited[28] as support for this assignment. In the present work ν_2 is observed to be significantly M-sensitive and completely unaffected by pyridine deuteration. The combined evidence supports its assignment to a νNi-O band.

That ν_3 has an ^{i}M-sensitivity comparable with ν_2 has led[66] to its assignment as a second coupled νNi-O band. This assignment is discounted by the present work since its substantial *d*-sensitivity ($\Delta\nu$ = 40 cm^{-1}) is similar to the *d*-sensitivity ($\Delta\nu$ = 37 cm^{-1}) of the 406 cm^{-1} ligand band in the spectrum of pyridine and its position (438 cm^{-1}) is practically identical with that[65] of the pyridine vibration (440 cm^{-1}) in $[Ni(py)_2Cl_2]$. Hence ν_3 is firmly assigned as the pyridine vibration of lowest frequency.

The weak ^{i}M-sensitivity of ν_4 has led to its assignment to an (unspecified)

chelate ring vibration[66]. It has also been assigned[28] to νNi-O on the grounds of its R-sensitivity and the fact that its position (420 cm^{-1}) is close to that of a strong band at 429 cm^{-1}, assigned to νNi-O in the spectrum of $[Ni(AA)_2(H_2O)_2]$. The present finding that the band is moderately M-sensitive but completely insensitive to pyridine deuteration is consistent with its assignment to νNi-O.

Although ^{18}O-labelling has not been applied to the compound $[Ni(AA)_2(py)_2]$, this technique has been used[53] to assign νM-O in certain simple metal acetylacetonates such as $[Cr(AA)_3]$. In these compounds, the significant ^{18}O-sensitivity of bands near 590 and 420 cm^{-1} has led to their assignment to νM-O. That the positions of these bands are very similar to those of ν_2 and ν_4 in the spectrum of $[Ni(AA)_2(py)_2]$, supports our assignment of these bands to νNi-O. However, these bands are unlikely to originate in pure (uncoupled) νNi-O modes because of their small ^{i}M-, M- and R-sensitivities relative to ν_5 and ν_6 (see below).

That ν_5 (at 269 cm^{-1}) is the most strongly ^{i}M-sensitive band in the spectrum of $[Ni(AA)_2(py)_2]$ has led[66] to its assignment as a pure νNi-O band. This assignment is supported here by its substantial M- and R-sensitivity and its complete absence of *d*-sensitivity. Furthermore, the spectrum of $[Ni(AA)_2(H_2O)_2]$ exhibits a band at 281 cm^{-1} which undoubtedly has the same origin and excludes the possibility that ν_5 is associated with coordinated pyridine. Entirely similar observations pertain to ν_6 (at 244 cm^{-1}). Its earlier assignment[66] to νNi-N on the grounds of its substantial ^{i}M-sensitivity is definitely discounted by complete absence of *d*-sensitivity and the occurrence of a corresponding band at 222 cm^{-1} in the spectrum of $[Ni(AA)_2(H_2O)_2]$. All the available

evidence suggests that ν_6 is a second, pure νNi-O band.

Below 200 cm^{-1}, the spectrum of $[Ni(AA)_2(py)_2]$ comprises a shoulder at 197 cm^{-1} (ν_{7a}) and a peak at 186 cm^{-1} (ν_{7b}). These are the most strongly M-sensitive bands in the spectrum and are the only bands below 400 cm^{-1} to exhibit any *d*-sensitivity. Furthermore, these bands shift on varying the pyridine substituent, R, in the opposite direction to νNi-O (Fig. 2) and they occur in a region free from absorption in the spectrum of $[Ni(AA)_2(H_2O)_2]$. All of these observations support their assignment to νNi-N modes and an earlier assignment[66] to a chelate ring mode is definitely discounted.

1.2 M-Sensitivity of Bands in Pyridine Adducts of Co(II), Ni(II) and Zn(II) Acetylacetonates.

The vibrational frequencies and isotopic shifts are listed in Table 7. Earlier work[11] has shown that metal-ligand vibrations are in the sequence Co<Ni>Zn for a series of octahedral complexes comprising these metal(II) ions bound within the same ligand system. In the adducts studied here, the Zn(II) complex is uniquely 5-coordinate. Relative to the Ni(II) complex, the lower coordination number of Zn(II) will serve[99] to raise the frequencies of the zinc-ligand vibrations while the zero crystal field stabilization energy (CFSE) of Zn(II) will serve to lower the zinc-ligand frequencies. Thus the observed order of metal-ligand frequencies may be Co<Ni>Zn or Co<Ni<Zn depending on whether the position of Zn(II) is determined primarily by coordination number or CFSE effects. In the present work it is observed that the sequence Co<Ni>Zn obtains for the principal νM-O and νM-N bands. Hence, the CFSE effect overrides the coordination number effect in determining the zinc-ligand frequencies.

1.3 Infrared Spectra of ^{15}N-labelled Pyridine Adducts $[Ni(AA)_2(^{15}N\text{-}py)_2]$ and $[Zn(AA)_2(^{15}N\text{-}py)]$

As has been mentioned in the Experimental Section, the ^{15}N-labelled adduct of Co(II) acetylacetonate has not been synthesized because its preparation is too extravagant in terms of usage of the expensive labelled amine (it requires recrystallization from the 'neat' amine). The ^{15}N-induced shifts in the spectra of the nickel and zinc complexes are included in Table 7. As can be seen from the Table, the shifts measured in the far I.R. region (400-150 cm^{-1}) where the uncoupled νM-O and νM-N vibrations are to be found, are often close to the instrumental limits of error. They therefore did not facilitate the attainment of unambiguous assignments for these vibrations. Deuteration of the pyridine ring, with its five-fold mass advantage yielded considerably bigger shifts and was therefore the preferred technique in this work.

Nevertheless, for bands associated with the fundamental vibrations of the pyridine molecule, shifts induced by ^{15}N-labelling are found to have values between 2 and 10 cm^{-1}. Shifts of this magnitude prove to be most convenient for assignment of the pyridine modes in the spectra of the complexes. These assignments are complicated by the large shifts which occur on deuteration, the difficulty being to find which band in the deuterated spectrum corresponds with a specific band in the undeuterated spectrum. The two bands near 400 cm^{-1} and 570 cm^{-1} in each spectrum (assigned to coupled νM-O vibrations on the grounds of deuteration and M-sensitivity) do not show any ^{15}N-sensitivity in

the nickel complex, thus supporting the assignments made. In the zinc complex, the band at 425 cm^{-1} shifts 4 cm^{-1} towards lower frequency, indicating that this band represents two vibrations: the coupled νM-O vibration and the pyridine γring mode. This confirms the results obtained on d_5-labelling (see Fig.1) where the 425 cm^{-1} band actually becomes resolved into two bands in the deuterated spectrum.

Above 600 cm^{-1} the δring vibration of pyridine[94] is readily identified in the spectra of the nickel and zinc complexes by ^{15}N-induced shifts of 7 and 6 cm^{-1} respectively. This latter vibration and also the γring mode (found at 407 cm^{-1} in pyridine itself) usually shift between 25 and 35 cm^{-1} towards higher frequency on complexation. This has been observed in the pyridine complexes of the first transition series metal(II) isothiocyanates (see Section 3) and in the pyridine complexes of first transition metal(II) halides[65]. The most strongly ^{15}N-sensitive band in the spectra of the complexes is a νring band (occurring at 991 cm^{-1} in pyridine, with a shift of 13 cm^{-1} on labelling) found at 1013 and 1016 cm^{-1} in the nickel and zinc complexes, respectively.

The two strong bands occurring in the spectra of each of the complexes (M = Co, Ni, Zn) at approximately 1600 cm^{-1} warrant some discussion. In the nickel complex, the bands occur at 1590 and 1600 cm^{-1}. Of these, only the band of higher frequency shifts significantly on ^{15}N-labelling. Similar observations pertain to the corresponding bands in the zinc complex. The band of higher frequency has been empirically assigned by Haigh and co-workers[28] to the carbonyl stretching vibration νC⋯O of the β-ketoenolate ring. This assignment is now discounted

on the basis of the ^{15}N-induced shift of 4 cm^{-1} for the nickel complex. The same band shifts 40 cm^{-1} on deuteration and is therefore almost certainly associated with a pyridine ring vibration occurring at 1582 cm^{-1} in the pyridine[94] molecule (in the free ligand a shift of 12 cm^{-1} occurs on ^{15}N-labelling). The lower frequency band at 1590 cm^{-1} in the nickel complex (corresponding bands occur at 1589 cm^{-1} in the Co complex and at 1586 cm^{-1} in the Zn complex) exhibits no ^{15}N-sensitivity and insignificant *d*-sensitivity. On these grounds, these bands are firmly assigned to the $\nu C\cdots O$ vibration, an assignment which has long been a matter of controversy in I.R. studies of transition metal acetylacetonates.

It is noteworthy that, without exception, the bands associated with the pyridine modes occur at higher frequencies in the spectrum of the Zn complex than in those of the Ni and Co complexes. This is undoubtedly due to the unique structure of the zinc adduct, which is five-coordinate compared to six-coordination in the *trans*-octahedral complexes of cobalt and nickel.

1.4 Effects of Substitution in the Pyridine Ring

Figure 2 illustrates the spectra of variously-substituted pyridine adducts of Ni(II) acetylacetonate. In an earlier paper[28] it was shown that ν_2 and ν_4 (coupled νNi-O bands) are shifted to higher frequency by electron-withdrawing substituents. The present work confirms this trend for the pure νNi-O band, ν_5, and also probably for ν_6, although the appearance of shoulders on ν_6 in the spectra of complexes with electron-releasing substituents introduces difficulties in determining precise frequencies in this region. The correlation previously found between the νC$\cdots$O frequencies and the Hammett substituent parameters, σ, had been based on an erroneous assignment of νC$\cdots$O[28]. The present study clearly shows that no specific trend is noticeable in the variation of the νC$\cdots$O frequencies of the variously-substituted pyridine adducts of Ni(II) acetylacetonate.

So far as the R-sensitivity of νNi-N is concerned, it is clear that electron-withdrawing substituents cause a substantial shift of ν_7 towards lower frequency, *i.e.* the opposite trend shown by νNi-O. Thus, an earlier prediction[28] that the electronic effects of pyridine substituents would cause νNi-O and νNi-N to shift in opposite directions, is now confirmed. The effect of electron-releasing substituents is much smaller and νNi-N remains approximately constant for $\sigma<0$.

In order to confirm that the shift of νNi-N towards lower frequency caused by electron-withdrawing substituents does not originate solely in the mass effects of R, allowance was made for the mass effects by assuming that the pyridine ring is vibrating against the mass of the

remainder of the molecule during the Ni-N stretching vibration. The νNi-N values calculated to arise from the mass effects of R are given by the relationship[100]

$$\nu_i = \nu_7[\{m_1m_2/(m_1 + m_2)\}\{(M_1 + M_2)/M_1M_2\}]^{\frac{1}{2}} \qquad (7)$$

where m_1 = mass of pyridine; m_2 = mass of species $[Ni(AA)_2(py)]$; M_1 = mass of substituted pyridine; M_2 = mass of species $[Ni(AA)_2(R\text{-}C_5H_4N)]$; and ν_7 is the mean frequency (191.5 cm^{-1}) of the principal νNi-N bands in the pyridine complex (R=H). The difference:

$$\Delta\nu = \nu_7 - \nu_i \qquad (8)$$

gives the shift in νNi-N arising from the mass effect of R, while ν_{corr}Ni-N, defined by:

$$\nu_{corr}\text{Ni-N} = \nu\text{Ni-N} + \Delta\nu \qquad (9)$$

is the value of νNi-N corrected for the mass effect. The difference between the observed and corrected νNi-N values is attributed to the electronic effects of R.

From the ν_{corr}Ni-N values in Table 22, it is clear that the tendency for electron-withdrawing substituents to decrease νNi-N (which was observed before taking the mass effect into account) retains its direction and significance after allowing for the mass effects of R. The effect of electron-releasing substituents, on the other hand, is negligible, the ν_{corr}Ni-N values remaining within a relatively narrow range of values above and below the νNi-N value of the pyridine adduct.

TABLE 22

Frequencies of principal νNi-O and νNi-N bands and νNi-N corrected for mass effects of R in $[Ni(AA)_2(R\text{-}C_5H_4N)_2]$

R	σ	ν_i (eqn.7) cm^{-1}	Δν (eqn.8) cm^{-1}	ν_{corr}Ni-N (eqn.9) cm^{-1}	νNi-N observed cm^{-1}	νNi-O cm^{-1}
4-CN	+0.63	170.5	21	166	145	275,244[a]
4-$COCH_3$	+0.52	160	31.5	187.5	156	278,241[a]
3-CO_2CH_3	+0.32	152	39.5	206	166.5[a]	272,242[a]
H	0	-	-	(191.5)	191.5[a]	269,244
3-CH_3	-0.07	178.5	13	188	175[a]	269,244
3,5-di-CH_3	-0.14	168.5	23	189	166[a]	268,244
4-C_2H_5	-0.15	168.5	23	191	168	269,243[a]
4-CH_3	-0.17	178.5	13	185	172[a]	—[b],243[a]
4-*t*-C_4H_9	-0.20	153	38.5	204	165.5[a]	266,245[a]
3,4-di-CH_3	-0.24	168.5	23	191.5	168.5[a]	264,240[a]
4-$N(CH_3)_2$	-0.60	159.5	32	196	164[a]	—[b],241[a]
py-d_5	0	186.5	5	190.5	185.5[a]	269,244

[a] Mean of doublet.

[b] Masked by neighbouring band.

2. INFRARED SPECTRA OF COMPLEXES OF ANILINE AND *p*-TOLUIDINE WITH METAL(II) ISOTHIOCYANATES

No crystallographic studies of the complexes $[ML_2(NCS)_2]$ (where M = Co, Ni, Cu, Zn and L = aniline, *p*-toluidine) have previously been reported. However, the structures of similar complexes $[M(py)_2(NCS)_2]$ have been investigated and were shown to be polymeric octahedral for M = Co and Cu[101]. The NCS-groups are bonded to the metal ions through both the nitrogen and the sulphur atoms, thus acting as bridging ligands.

Electronic spectra, magnetic moments and X-ray data of complexes containing either an aromatic amine or the thiocyanate ion, such as $[Zn(py)_2(NCS)_2]$, $[M(aniline)_2Cl_2]$ and $[M(p\text{-tol})_2Cl_2]$ have been reported[73,67,102,103]. They suggest that the complex $[Zn(py)_2(NCS)_2]$ and the aniline and *p*-toluidine complexes are tetrahedral for M = Co, Zn, polymeric octahedral for M = Ni and polymeric tetragonal for M = Cu.

The infrared spectra of the Co(II) and Ni(II) complexes of both aniline and *p*-toluidine show a band-for-band correspondence which suggests that they are isostructural. Their magnetic moments have been determined and the values obtained are consistent with octahedral coordination[104,105]. Their colours (pink for the Co(II) and green for the Ni(II) complex) also indicate that these compounds are octahedral. The IR spectra of the Cu(II) complexes show a band pattern similar to those of the Co(II) and Ni(II) complexes but both the metal-nitrogen stretching frequencies ($\nu M\text{-}NH_2$ and $\nu M\text{-}NCS$) follow the Irving-Williams stability sequence[106]. *i.e.* Co<Ni<Cu>Zn. As this sequence is based on tetragonally-distorted

TABLE 23

Magnetic moment determinations for the complexes $[M(aniline)_2(NCS)_2]$ and $[M(p\text{-toluidine})_2(NCS)_2]$

Complex	μ_{eff} at 296 K
	B.M.
$[Co(aniline)_2(NCS)_2]$	4.95
$[Ni(aniline)_2(NCS)_2]$	3.40
$[Co(p\text{-toluidine})_2(NCS)_2]$	5.13
$[Ni(p\text{-toluidine})_2(NCS)_2]$	3.19

Cu(II), the Cu(II) complexes are assigned polymeric tetragonal structure. The IR band pattern of the Zn(II) aniline complex resembles that of the other aniline complexes, suggesting that it also has polymeric octahedral structure. The Zn(II) *p*-toluidine complex, however, is distinguished from all the other complexes by some unique features in the IR band pattern, which points to tetrahedral coordination.

In the following discussion, the two species of metal-nitrogen stretching vibrations will be distinguished by the notation νM-NH_2 and νM-NCS and the two types of labelling will be differentiated by $^{15}NH_2$ and ^{15}NCS. Bands shifted by ^{15}N-labelling are termed ^{15}N-sensitive and those shifted by metal ion substitution are termed M-sensitive. All ^{15}N-induced shifts are towards lower frequencies. The two species of C-N stretching vibrations are distinguished by the notation νC-N (where C is the carbon atom of the aromatic amine and N is the amine nitrogen atom) and νN-CS where N and C are atoms of the isothiocyanate group.

Spectra of the complexes and of the ligands aniline and *p*-toluidine and the spectrum of sodium thiocyanate are shown in Fig. 3. The frequencies and shifts are given in Tables 9 and 10.

2.1 Ligand Vibrations Associated with the Amino Group

The stretching and bending vibrations of the amino group are readily identified by $^{15}NH_2$-labelling of the ligands aniline and *p*-toluidine and their complexes. The antisymmetric and symmetric N-H stretching bands in the spectra of the complexes occur at frequencies which are

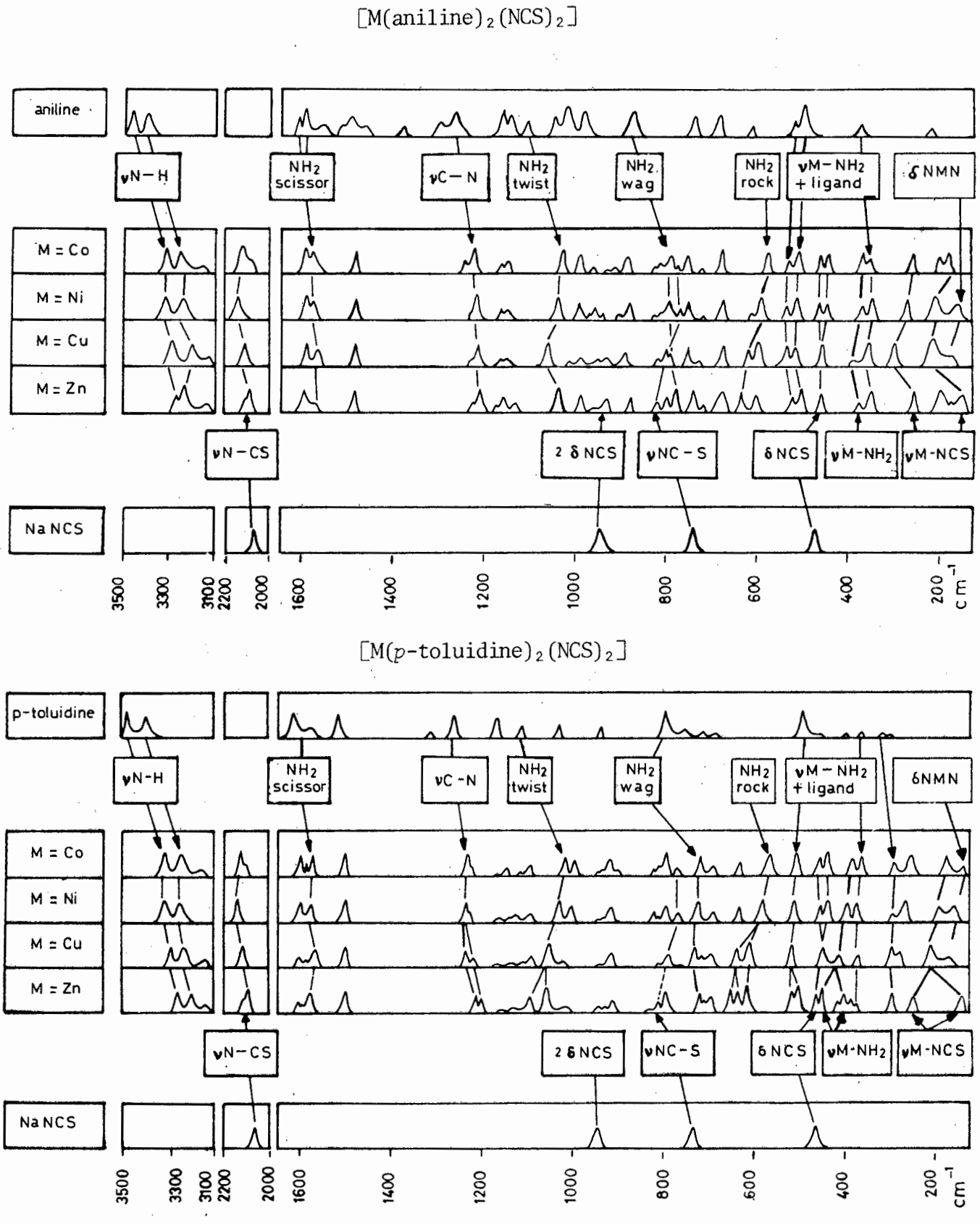


Fig. 3. Infrared spectra of complexes $[ML_2(NCS)_2]$ (L = aniline, *p*-toluidine).

between 70 and 200 cm^{-1} lower than the corresponding bands in the ligand spectra. $^{15}NH_2$-labelling induces low frequency shifts of between 4 and 10 cm^{-1} in both bands in the ligands and their complexes. A third $^{15}NH_2$-sensitive band near 3140 cm^{-1} is observed in the spectra of most of the complexes and is assigned to hydrogen-bonded νN-H...N on the basis of earlier hydrogen bonding studies[107,108] on the IR spectra of amines and their complexes. The spectrum of the complex $[Zn(p\text{-tol})_2(NCS)_2]$ exhibits a weak band at 3127 cm^{-1} which is markedly $^{15}NH_2$-sensitive. The crystallographic investigation of this complex which has recently been reported[109], reveals the existence of intermolecular N-H...S bonds between sulphur atoms and amino hydrogens with H-S distances between 2.4 and 2.8 Å. The band at 3127 cm^{-1} is therefore assigned to the νN-H...S vibration.

Absorption within the range 1570 - 1620 cm^{-1} in the spectra of the complexes comprises two bands (aniline series) or three bands (*p*-toluidine series). Only the component of lowest frequency exhibits $^{15}NH_2$-sensitivity. This component corresponds with the $^{15}NH_2$-sensitive band near 1620 cm^{-1} assigned[35] to the NH_2 scissoring vibration in the ligand spectra. The NH_2 twisting modes have been assigned[35] to $^{15}NH_2$-sensitive bands in the ligand spectra near 1120 cm^{-1}. The corresponding bands in the spectra of the complexes occur near 1050 cm^{-1}. The NH_2 wagging mode yields $^{15}NH_2$-sensitive bands at 884 and 812 cm^{-1} in aniline and *p*-toluidine, respectively[35]. Coordination induces a low frequency shift of approximately 70 cm^{-1} in each band. The NH_2 rocking frequencies of the complexes occur near 600 cm^{-1}.

With one exception, all the $^{15}NH_2$-sensitive bands with frequencies exceeding 580 cm^{-1} are accounted for by the assignments given above.

The exception is a strong band near 1230 cm^{-1} in the spectra of the complexes which corresponds with the $^{15}NH_2$-sensitive ligand band at 1275 cm^{-1}. This is assigned to νC-N, occurring in the region previously reported[68 69,110,111] for this vibration.

Each vibration of the amino group is sensitive to the nature of the coordinated metal ion. The νN-H and νC-N bands generally follow the frequency sequence Co<Ni>Cu>Zn which is the inverse order of the masses of the metal ions.

2.2 Ligand Vibrations Associated with the Isothiocyanate Group

The spectrum of NaNCS (Fig. 3) yields only four bands (each of which exhibits significant ^{15}NCS-sensitivity) within the range 4000 - 200 cm^{-1}. The band at 2074 cm^{-1}, assigned to νN-CS, appears within the range 2100 - 2135 cm^{-1} in the complexes. Its position is similar to that reported[73] for the isothiocyanate complexes $[M(py)_2(NCS)_2]$. This band exhibits large ^{15}NCS-induced shifts (26 - 30 cm^{-1}) in both NaNCS and in the isothiocyanate complexes. Some very sharp shoulders are observed in the νN-CS bands of the complexes. This splitting is considered[73] to be diagnostic of either polymeric octahedral or tetrahedral structure (it is not observed in the spectra of mononuclear octahedral isothiocyanate complexes).

The νNC-S vibration occurs at 757 cm^{-1} in the spectrum of NaNCS. A surprisingly large shift (10 cm^{-1}) is induced by ^{15}NCS-labelling. The band is increased in frequency and reduced in intensity in the isothiocyanate complexes but retains considerable ^{15}NCS-sensitivity.

The bending vibration of the isothiocyanate group (δNCS) occurring at 481 cm^{-1} in the spectrum of NaNCS, is observed near 470 cm^{-1} in the isothiocyanate complexes. It is split into a doublet in the isostructural

Co(II) and Ni(II) complexes, each component exhibiting similar ^{15}NCS-sensitivity. The overtone of this vibration (2δNCS) at 960 cm^{-1}, surprisingly strong in the spectrum of NaNCS, is observed in only two of the complex spectra where it is considerably reduced in intensity.

Both internal stretching vibrations of the isothiocyanate group (νN-CS and νNC-S) exhibit significant sensitivity to the metal ion. Like νN-H and νC-N, νN-CS is inversely related to the masses of the co-ordinated ions while (as may be expected for constancy of bond order summation about the carbon atom) the M-sensitivity of νN-CS (Co<Ni>Cu>Zn) is the inverse of the M-sensitivity of νNC-S (Co>Ni<Cu<Zn).

2.3 Metal-ligand Vibrations

The metal-ligand stretching vibrations (νM-NH_2 and νM-NCS) are expected[112] to have frequencies below 600 cm^{-1}. A $^{15}NH_2$-labelling study[69] of the IR spectra of the complexes $[M(p\text{-tol})_2Cl_2]$ (M = Co, Ni, Cu, Zn) yielded $^{15}NH_2$-sensitive bands near 525, 475 and 425 cm^{-1} of which the first two were assigned to ligand vibrations shifted by coupling with νM-NH_2 while the band near 425 cm^{-1} (occurring in a region free from ligand absorption) was assigned to vibrationally pure (uncoupled) νM-NH_2. Support for the assignment was provided by the observation that this band is M-sensitive in the sequence of crystal field stabilization energies (CFSE's) of the complexes: Co>Ni<Cu>Zn.

In the metal-isothiocyanate complexes studied here, the following criteria were used to establish the νM-NH_2 assignments: presence of $^{15}NH_2$-sensitivity, absence of ^{15}NCS-sensitivity, occurrence of

νM-NH_2 in a region free from $^{15}NH_2$-sensitive ligand bands and M-sensitivity in the CFSE sequence Co<Ni<Cu>Zn (*i.e.* the Irving-Williams sequence) determined[11] on the basis of octahedral Co(II) and some tetragonal distortion in the Cu(II) complexes. It is worth emphasizing that the expected M-sensitivity of νM-NH_2 in the complexes $[M(p\text{-tol})_2Cl_2]$ differs from that of the complexes $[ML_2(NCS)_2]$ (L = aniline, *p*-toluidine) due to the different structures of the Co(II) complexes in the two series (tetrahedral in the former, octahedral in the latter).

Tables 9,10 show that, below 600 cm^{-1}, two regions of $^{15}NH_2$-sensitive bands occur: 520 - 550 cm^{-1} and 360 - 425 cm^{-1}. None of the $^{15}NH_2$- sensitive bands exhibits any ^{15}NCS-sensitivity, indicating that little, if any, coupling between νM-NH_2 and νM-NCS occurs. Since a strong $^{15}NH_2$-sensitive ligand band is present near 515 cm^{-1} in the spectra of aniline and *p*-toluidine and since this band does not recur in the spectra of the complexes, the bands within the range 520 - 550 cm^{-1} are considered to originate in the ligand vibration near 515 cm^{-1} shifted to higher frequency by coordination and becoming M-sensitive in the Irving-Williams sequence by coupling with νM-NH_2.

Within the range 360 - 425 cm^{-1}, there are generally two $^{15}NH_2$-sensitive bands in the spectrum of each complex (exceptionally, the copper *p*-toluidine complex has only one $^{15}NH_2$-sensitive band in this region). It is possible that one component of each pair of bands in this region is associated with the very weak and $^{15}NH_2$-insensitive ligand bands observed near 380 cm^{-1}; the other component satisfies all the criteria listed above for a band assigned to uncoupled νM-NH_2. In the six-coordinate complexes (*i.e.* except for

tetrahedral $[Zn(p\text{-tol})_2(NCS)_2]$ this band exhibits M-sensitivity in the Irving-Williams sequence, supporting the assignment.

Observation of a single uncoupled $\nu M\text{-}NH_2$ band in the isothiocyanate complexes satisfies the C_i symmetry requirement[113] of one IR-active normal $\nu M\text{-}L$ mode in polymeric octahedral complexes of general formula $[ML_2X_2]$. In tetrahedral complexes $[ML_2X_2]$, C_{2v} symmetry requires two IR-active $\nu M\text{-}L$ modes. In the spectrum of $[Zn(p\text{-tol})_2(NCS)_2]$, clearly observable splitting of several bands yields additional $^{15}NH_2$-sensitive bands of which that at 414 cm^{-1} is assigned to the second $\nu M\text{-}NH_2$ band expected in C_{2v} symmetry. For this reason, this complex is uniquely assigned tetrahedral structure.

The study of the crystal structure of the $[Zn(p\text{-tol})_2(NCS)_2]$ complex which has been mentioned earlier, confirms that the coordination is tetrahedral[109]. The isothiocyanate groups are linear and are co-ordinated to the metal ion through the nitrogen atoms.

Assignment of $\nu M\text{-}NCS$ is readily achieved by ^{15}NCS-labelling. Bands near 200 cm^{-1} are ^{15}NCS-sensitive and occur in a region free from absorption in the spectrum of NaNCS. The complete absence of $^{15}NH_2$-sensitivity supports their assignment to uncoupled $\nu M\text{-}NCS$ vibrations. Both C_i and C_{2v} symmetries require two IR-active $\nu M\text{-}NCS$ modes. Two bands are observed near 200 cm^{-1} in the spectrum of each complex. Significant ^{15}NCS-sensitivity is observed for both bands only in the Zn(II) *p*-toluidine complex (which has been assigned tetrahedral structure). The unique structure of this complex is further demonstrated by the wide separation (100 cm^{-1}) between its two ^{15}NCS-sensitive bands and doubling of several of the ligand vibrations. Apart from the spectrum of this complex, the $\nu M\text{-}NCS$ frequencies resemble the $\nu M\text{-}NH_2$ frequencies in exhibiting a marked M-sensitivity in the Irving-Williams sequence.

Failure to observe the second νM-Cl band expected for C_i symmetry in the spectra of polymeric octahedral complexes $[M(py)_2Cl_2]$ (M = Co, Ni) has previously been reported[114].

The aniline complexes exhibit remarkably strong bands in the region 270 - 320 cm^{-1}. These bands are substantially metal-sensitive in the Irving-Williams sequence Co<Ni<Cu>Zn. They appear in a region free from ligand absorption but do not show any significant ^{15}NCS- or $^{15}NH_2$-sensitivity.

In the IR study of the complexes $[M(py)_2(NCS)_2]$ (M = Mn, Co, Ni, Cu, Zn; see Section 3) bands of similar intensity have been observed in the same region. They have been assigned to the second νM-NCS vibration in spite of the fact that shifts induced by ^{15}NCS-labelling were in some cases insignificant or close to the instrumental limit of error. It would therefore seem reasonable to assign these bands in the aniline complexes to the same vibration. Results obtained by ^{15}NCS-labelling, however, have shown shifts between 2 and 4 cm^{-1} for the bands assigned to the νM-NCS vibrations in the region 160 - 230 cm^{-1}. Therefore, only a tentative assignment of the bands in question to a second νM-NCS vibration is justified.

The other alternative would be to assign these bands to a νM-SCN vibration. However, comparatively large interatomic M-S distances have been found for the polymeric actahedral pyridine complexes $[Co(py)_2(NCS)_2]$ and $[Cu(py)_2(NCS)_2]$ (2.6 and 3.0 Å, respectively)[101]. These distances are larger than the maximum values determined for (mononuclear) cobalt and copper complexes previously investigated[115]. This suggests a rather weak M-S bond, especially in comparison with the M-N bond strength. For

these reasons the assignment of bands occurring between 60 and 100 cm^{-1} higher than the νM-NCS vibrations to a νM-SCN mode cannot be considered reasonable.

Similar considerations apply to bands observed in the *p*-toluidine complexes in the same region. For M = Co, Ni, Cu, doublets are observed of which only the lower frequency component exhibits substantial M-sensitivity in the order Co<Ni<Cu. In the zinc complex only one band is found at 316 cm^{-1}. The position of this band corresponds with the higher frequency component of the doublet in the other complexes. None of these bands shows significant ^{15}NCS-sensitivity. The bands at 307 and 309 cm^{-1} in the complexes of Co and Ni, respectively, are $^{15}NH_2$-sensitive. The bands in the region 307 - 316 cm^{-1} in the *p*-toluidine complexes could originate in a weak ligand vibration, increased in intensity by complexation.

2.4 IR Spectra of the Complex $[Co(NCS)_4Hg]$ and its ^{15}NCS-Labelled Analogue

In general, there is not much information on the relative positions of the νM-NCS and νM-SCN vibrations in the IR spectra of complexes involving bridging NCS-groups[70]. Tentative assignments of the νM-NCS and νM-SCN frequencies have been made by Foster and Goodgame[116] for a few bridged NCS— complexes of the type $[M(NCS)_4Hg]$ (M = Mn, Fe, Co, Ni, Cu, Zn). The νM-NCS values cited are between 250 and 320 cm^{-1}, whereas νM-SCN frequencies are reported to occur at about 215 cm^{-1}, *i.e.* approximately 90 cm^{-1} to lower frequency. As these assignments appear to have been made on an empirical basis, the cobalt complex $[Co(NCS)_4Hg]$ has been prepared together with its ^{15}NCS-labelled analogue. ^{15}NCS-labelling was employed in order to ascertain

assignments of νM-NCS and νM-SCN bands for this complex and also to assist in obtaining assignments for other complexes involving bridging NCS-groups. A detailed crystallographic study of $[Co(NCS)_4Hg]$ shows[117] that both metals are tetrahedrally coordinated. The cobalt is bound to the nitrogen, whereas the mercury is coordinated to the sulphur atom of the NCS-group. From a crystallographic point of view, the combination of these two interlinked metals has produced a most unusual arrangement in which Hg and Co atoms are held apart by four spirals, each containing four NCS-bridges.

The spectrum of the complex together with the shifts induced by ^{15}NCS-labelling is shown in Fig.4.

The notable simplicity of the spectrum is to be expected in view of the presence of only one ligand species.

The internal vibrations of the NCS-group are readily identified by the substantial shifts which occur on labelling. The νN-CS vibration is found at 2144 cm^{-1} (comprising two well-defined shoulders on the lower-frequency side which are not present in the labelled spectrum). It shifts 29 cm^{-1} on labelling. The position of this band agrees well with that reported by Nakamoto and co-workers[118] and is consistent with the general finding that, in bridged complexes, this vibration occurs at considerably higher frequencies than in complexes with terminal NCS-groups (see Section 3). The νNC-S band occurs at 792 cm^{-1} and shifts 11 cm^{-1} on labelling. A shift of this size has been observed for this vibration in most NCS-complexes reported in this thesis. A broad band of lower intensity at about 740 cm^{-1} is unique to this particular complex and may be associated with a bending

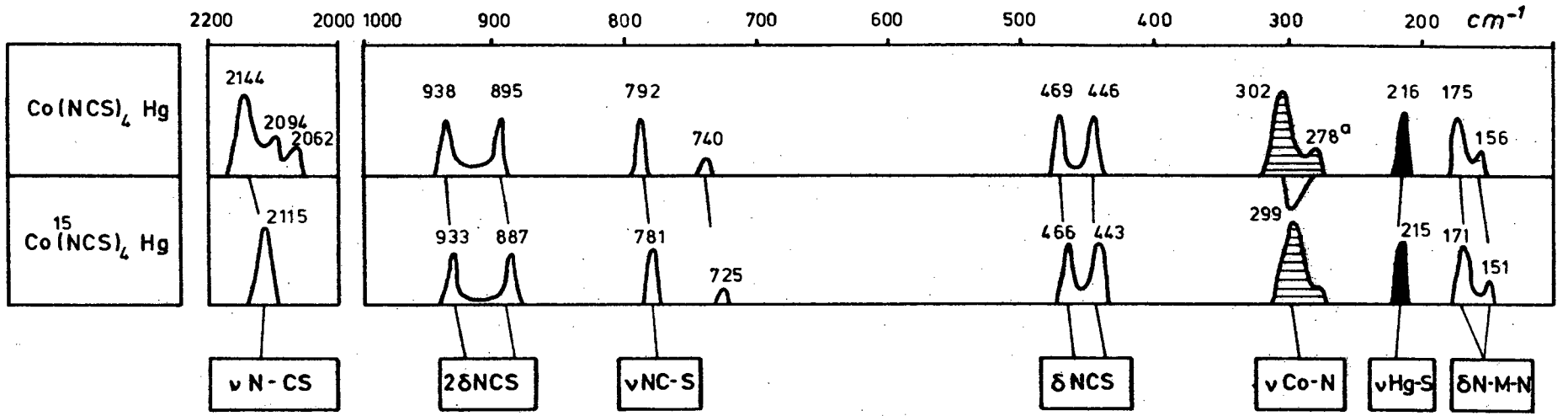


Fig. 4. Infrared spectra of $[Co(NCS)_4Hg]$ and its ^{15}N-labelled analogue.

[a] Broad band; position and shift cannot be determined precisely.

vibration of the four interlinked NCS-groups forming part of each spiral of this particular polymeric tetrahedral structure. The δNCS vibration is represented by two strong bands at 469 and 446 cm^{-1}, both shifting 3 cm^{-1} on labelling. The finding that the δNCS vibration yields two bands in complexes of tetrahedral or polymeric octahedral symmetry is consistent with similar observations for the pyridine complexes of first transition metal isothiocyanates $[M(py)_2(NCS)_2]$ (see Section 3). The overtones of the bending vibrations (2δNCS) are found at 938 and 895 cm^{-1} and shift 5 and 8 cm^{-1}, respectively. In this complex, the 2δNCS vibration exhibits an unusually high intensity relative to other NCS-complexes studied in this thesis.

In the region 300 - 150 cm^{-1}, the spectrum comprises five bands, three of which are substantially shifted by ^{15}NCS-labelling. The strong doublet at 301, 278 cm^{-1} is assigned to the νCo-NCS vibration on the basis of its shift of 3 cm^{-1} for the main band. The frequencies observed for this vibration are in good agreement with those reported by Foster and Goodgame[116]. Comparing the two complexes $[Zn(p\text{-tol})_2(NCS)_2]$ and $[Co(NCS)_4Hg]$, it is understandable that the νM-NCS vibrations occur at considerably higher frequencies in the latter complex. In both complexes the metal ions are tetrahedrally coordinated, but whereas the Co complex is strongly stabilized by the crystal field (CFSE = 12*Dq*), the Zn complex is not (CFSE = 0)[11]. The same trend has been observed for the νM-N and νM-Cl frequencies in the tetrahedral complexes $[Co(py)_2Cl_2]$ and $[Zn(py)_2Cl_2]$[65].

The sharp band at 216 cm^{-1} (shift =-1 cm^{-1}) is attributed to the νHg-SCN vibration since this vibration is expected to be less influenced than

the νCo-NCS by the mass increase arising from labelling. In the isomorphous complex $[Zn(NCS)_4Hg]$, the νHg-SCN frequency has been tentatively assigned to a band at 217 cm^{-1}[116]. Bands of similar intensity have been reported for the complexes $[Mn(NCS)_4Hg]$ and $[Fe(NCS)_4Hg]$ at 213 and 216 cm^{-1}, respectively[119]. The occurrence of the νHg-SCN frequency in such a narrow range of the spectrum supports the suggestion[116] that these complexes have similar structures.

Below 200 cm^{-1}, two bands are observed (at 175 and 156 cm^{-1}). Since both bands shift significantly on labelling, they are assigned to a bending vibration of the type δNCoN. Since symmetry considerations require only one vending vibration for a tetrahedral molecule MX_4 (T_d symmetry) it is possible, that the lower frequency band originates in a bending mode of the δSHgS kind. The shift of 5 cm^{-1}, however, is surprisingly high for such a vibration.

3. INFRARED SPECTRA OF THE PYRIDINE COMPLEXES OF METAL(II) ISOTHIOCYANATES

The spectra are shown in Fig. 5 and the frequency data are recorded in Tables 11, 12 and 13.

In the labelling study of the complexes $[M(an)_2(NCS)_2]$ and $[M(p\text{-tol})_2(NCS)_2]$ (see Section 2) the two species of metal-nitrogen bands ($\nu M\text{-}NH_2$ and $\nu M\text{-}NCS$) could be clearly distinguished by ^{15}N-labelling of each nitrogen donor. The success of the technique was aided by the wide frequency separation between the two vibrations, $\nu M\text{-}NH_2$ (~ 400 cm^{-1}) and $\nu M\text{-}NCS$ (~ 200 cm^{-1}). Under these circumstances, very little vibrational coupling is expected to occur. Thus, none of the ^{15}NCS-sensitive bands exhibited any $^{15}NH_2$-sensitivity and none of the $^{15}NH_2$-sensitive bands was shifted by ^{15}NCS-labelling. Furthermore, the magnitude of the shifts induced by donor atom labelling lay well outside the limits of experimental error which are determined by the reproducibility of the absorption maxima in replicate spectral determinations.

In the infrared study of the complexes $[M(py)_2Cl_2]$, the $\nu M\text{-}py$ frequencies have been assigned to bands at about 200 cm^{-1}.[65] Since the $\nu M\text{-}NCS$ frequencies appear in the same spectral region, some vibrational coupling between these two modes in the complexes $[M(py)_n(NCS)_2]$ is expected to occur. Such coupling has two ramifications with respect to the isotopic assignment technique. Firstly, the coupled bands are expected to shift on both ^{15}NCS- and pyridine-labelling. Secondly, the magnitude of the shift of a coupled band will be smaller than that of a vibrationally pure band. Both effects are observed in the spectra of the pyridine-isothiocyanate complexes. The existence of bands sensitive to labelling

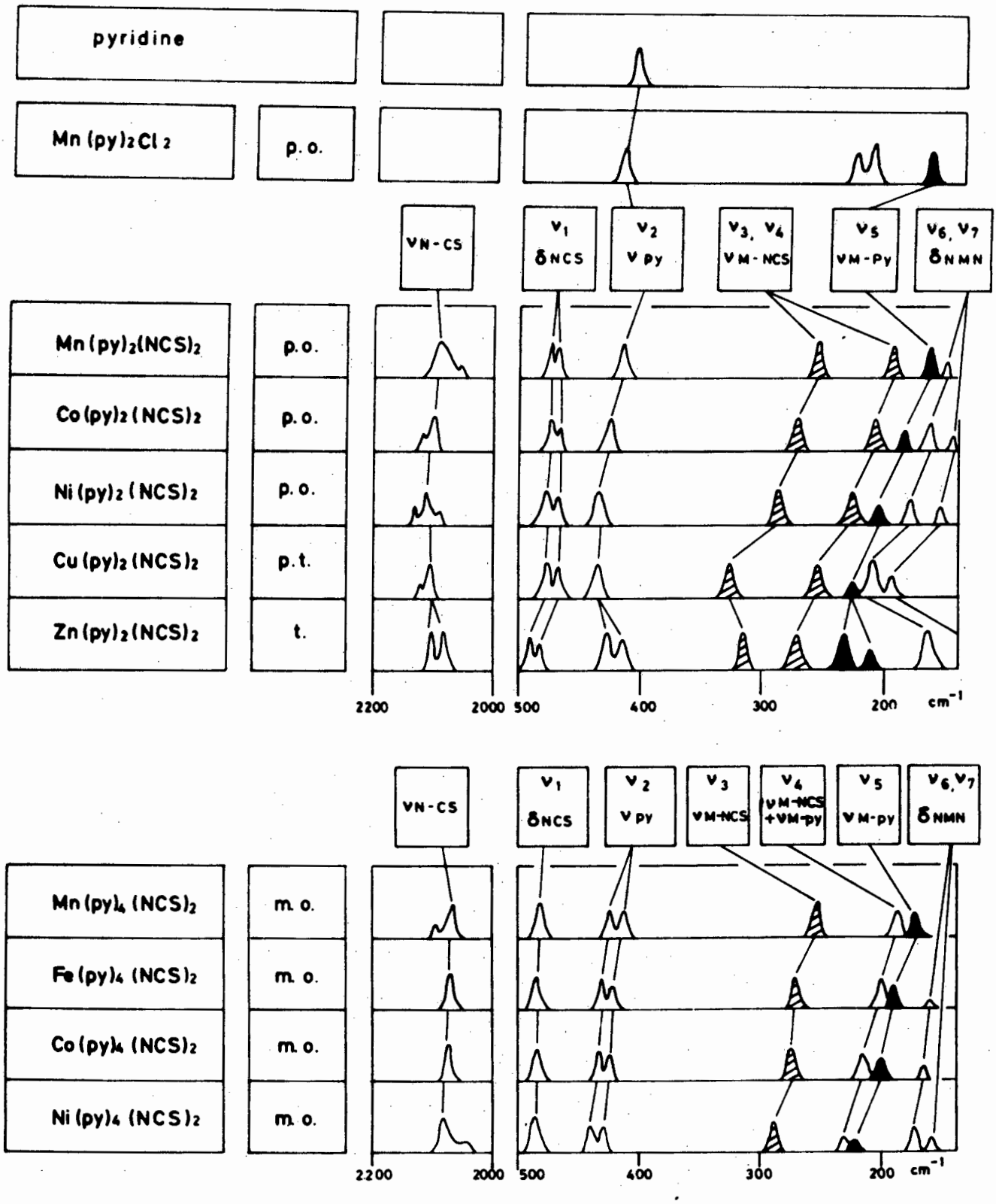


Fig. 5. Infrared spectra of $[M(py)_n(NCS)_2]$ (n = 2,4). The spectra of pyridine and $[Mn(py)_2Cl_2]$ are included for comparison. Abbreviations : p.o. = polymeric octahedral, p.t. = polymeric tetragonal, t = tetrahedral, m.o. = monomeric octahedral.

of both species of nitrogen donors provides evidence for some coupling between νM-py and νM-NCS. The small shifts which were observed initially on employing pyridine-^{15}N as the labelled source of pyridine were improved by substituting pyridine-^{15}N by pyridine-d_5 with its considerable mass advantage. The problem of the small shifts induced by ^{15}NCS-labelling (frequently on the borderline of significance) was overcome by comparing the spectra of the complexes $[M(py)_2(NCS)_2]$ with the structurally analogous $[M(py)_2Cl_2]$ in the expectation that substitution of chloride by isothiocyanate would cause significant shifts in νM-X (X = Cl, NCS) but relatively small shifts in νM-py.

3.1 The Bis(Pyridine) Complexes $[M(py)_2(NCS)_2]$ (M = Mn, Co, Ni)

The structure of the Co(II) complex has been shown to be polymeric octahedral with bridging NCS— units[101]. Since the spectra of the Mn(II) and Ni(II) complexes exhibit a band-for-band correspondence with that of Co(II), including the feature diagnostic[72] of NCS bridging (doubling of the 470 cm^{-1} δNCS band) they are also considered to be octahedral polymers.

Above 500 cm^{-1} the most important internal vibrations of the NCS-group are the two stretching vibrations, νN-CS and νNC-S both of which are substantially ^{15}NCS-sensitive. The νN-CS frequencies in the complexes of Mn, Co and Ni occur at approximately 2100 cm^{-1} which agrees well with the values reported by Clark and Williams[73]. They shift approximately 30 cm^{-1} to lower frequencies on ^{15}NCS-labelling. Shifts of this magnitude have been observed for the νN-CS vibrations in most isothiocyanate complexes studied in this thesis. The νNC-S frequencies are assigned to sharp bands of medium intensity occurring at about 790 cm^{-1}.

Their position and shift (~10 cm^{-1}) are consistent with results obtained for the complexes $[ML_2(NCS)_2]$ (L = aniline, *p*-toluidine).

In the lower wavenumber region (500 - 140 cm^{-1}) the spectrum of each of these complexes has seven bands (the band of lowest frequency for the Mn(II) complex lies beyond the low frequency limit of measurement).

Following the numbering system depicted in Fig. 5, ν_1 is firmly assigned to the δNCS vibration by virtue of its position[70,72], its ^{15}NCS-sensitivity and its doublet nature which is characteristic[72] of bridging NCS-units (see Section 2). ν_2 is the 406 cm^{-1} out-of-plane ring vibration of pyridine, raised some 20 to 30 cm^{-1} by coordination. The origin of this band is clear from its high *d*-sensitivity: it undergoes a 40 cm^{-1} shift towards lower frequency on deuteration of pyridine. This shift is similar to that observed[65] for the corresponding band in the spectra of the complexes $[M(py)_2Cl_2]$.

Since neither pyridine nor the isothiocyanate ion absorbs below 400 cm^{-1}, all subsequent bands must originate in metal-ligand modes. Although the ^{15}NCS-sensitivity of ν_3 is not significant (< 1 cm^{-1}) it is nevertheless assigned to a νM-NCS vibration since it disappears on replacing isothiocyanate by chloride. The only other possible assignment for a band which is both ^{15}NCS- and *d*-insensitive is νM-S. This possibility is ruled out by recurrence of the band in the spectra of monomeric $[M(py)_4(NCS)_2]$ complexes at a practically identical position. These complexes, comprising only terminal NCS-groups, have no M-S bonds. Moreover, crystallographic data for the polymeric octahedral complexes of Co(II) and Cu(II) suggest that the M-SCN bonds are weaker than the M-NCS bonds[101](see Section 2). ν_4 is a second νM-NCS band which exhibits ^{15}NCS-sensitivity in the Co(II) and Ni(II) complexes but

also slight *d*-sensitivity, indicating that it is not entirely free from coupling with νM-py.

ν_5 is firmly assigned to νM-py since it has the highest *d*-sensitivity of the bands below 400 cm^{-1} (the shifts are within the range 3 to 9 cm^{-1}) and it is very close to the position of νM-py[65] in the structurally-analogous $[M(py)_2Cl_2]$ complexes. Since the existence of two νM-NCS and one νM-py bands satisfies the requirements of C_i symmetry[113] for the complexes $[M(py)_2(NCS)_2]$, ν_6 and ν_7, which exhibit some *d*-sensitivity, are assigned to the δNMN modes. Their frequencies are similar to those of the δNMN bands in the complexes $[M(py)_2Cl_2]$[65].

3.2 The Bis(Pyridine) Complexes $[M(py)_2(NCS)_2]$ (M = Cu, Zn)

These complexes differ structurally from those of Mn(II), Co(II) and Ni(II). The Cu(II) complex is polymeric tetragonal with bridging NCS- groups in which the M-S bonds (3.0Å) are considerably longer than those of the Co(II) complex ~2.6Å)[101]. The band pattern expected for the Cu complex is identical since all four Cu-N bonds are *trans*-co-planar. On the other hand, both the Cu-NCS and Cu-py stretching frequencies are expected to be higher than the corresponding values for the Ni(II) complex due to the shortening of the Cu-N bonds which accompanies tetragonal distortion. The sequence Cu>Ni is observed for both the νM-NCS and νM-py vibrations.

For the tetrahedral Zn(II) complex[73], C_{2v} symmetry requires two νM-NCS and two νM-py bands and two of each are observed.

Both the νM-NCS and νM-py frequencies follow the Irving-Williams[106] stability sequence Mn < Co < Ni < Cu. It is now well-established[11]

that the metal-ligand stretching frequencies for a series of octahedral complexes containing successive metal(II) ions of the first transition series invariably follow this stability sequence (if the Cu(II) complex is tetragonally-distorted). In the series of complexes $[M(py)_2(NCS)_2]$, the Zn(II) compound is tetrahedral so that the bonding capacity of the metal ion is distributed over four bonds rather than six. This will tend to raise the metal-ligand frequencies relative to the octahedral complexes. On the other hand, the Zn(II) complex is not stabilized by crystal field effects and this will tend to reduce the metal-ligand frequencies relative to the octahedral Co(II), Ni(II) and Cu(II) complexes. Thus, it is not surprising to observe from Fig. 5 that one component of each pair of νM-NCS (or νM-py) bands is raised in frequency (while the other is lowered) relative to the Cu(II) complex.

It is noteworthy that the out-of-plane ring vibration of the pyridine ligand (ν_2) is represented by a single band (region 415 - 435 cm^{-1}) in the polymeric octahedral and polymeric tetragonal complexes; whereas in the monomeric octahedral and tetrahedral complexes (terminal NCS^- groups)this vibration invariably comprises a doublet in the same spectral region. Similar observations have been made for the IR spectra of bis(pyridine) and tetrakis(pyridine) complexes of metal(II) chlorides and nitrates[74]. Exceptions to this generalization are the tetrahedral complexes $[Co(py)_2Cl_2]$ and $[Zn(py)_2Cl_2]$ which exhibit only one band in this region[65].

The νNC-S vibrations occurring at 826 and 848 cm^{-1} respectively, in the Cu and Zn complexes, exhibit substantial ^{15}NCS-sensitivity ($\Delta\nu$ = 12 cm^{-1}).

Their position agrees well with that found by Clark and Williams[73]. These workers also noticed that this vibration occurs at considerably higher frequencies for tetrahedral complexes than for monomeric or polymeric octahedral complexes.

3.3 The Tetrakis(Pyridine) Complexes $[M(py)_4(NCS)_2]$ (M = Mn, Fe, Co, Ni)

The structures of the Co(II) and Ni(II) complexes were investigated in 1958[120] and were found to be *trans*-octahedral. The NCS-groups are linear and are bound to the metal *via* the nitrogen atom. Octahedral coordination has been confirmed by magnetic measurements. Both compounds are paramagnetic and their μ_{eff} values correspond to three and two unpaired electrons for the Co(II) and Ni(II) complexes, respectively. The band-for-band correspondence of the Mn(II) and Fe(II) complexes suggests that they are structurally analogous.

The νN-CS vibrations occur at lower frequencies in the monomeric octahedral complexes relative to the polymeric octahedral bis(pyridine) complexes. The values are generally in good agreement with those found by Clark and Williams[73]. The shifts observed on ^{15}NCS-labelling ($\Delta\nu$ between 27 and 29 cm^{-1} to lower frequencies) are consistent with those found for the νN-CS vibrations in the aniline and *p*-toluidine complexes of metal(II) isothiocyanates (see Section 2).

Following the numbering system in Fig. 5, ν_1 is a singlet and is assigned to the δNCS vibration. On ^{15}NCS-labelling the band shifts 3 cm^{-1} to lower frequency. The lowest pyridine vibration (ν_2) comprises two bands in monomeric complexes as has been previously discussed. Both features are diagnostic[72] of terminal N-bonded NCS-groups. ν_3 (νM-NCS) occurs at practically identical positions

to ν_3 of the bis(pyridine) complexes. The symmetry requirements for the complexes *trans*-ML_4X_2 (D_{4h} symmetry) are one infrared-active νM-L and one infrared-active νM-X vibration[113]. Thus, ν_4 in these complexes is assigned to the coupled vibration, νM-py + νM-NCS. ν_5 is the single νM-py vibration expected and is, accordingly, significantly *d*-sensitive (the observed shifts are between 3 and 4 cm^{-1} to lower frequencies). The selection rules for D_{4h} *trans*-octahedral ML_4X_2 complexes require three infrared-active bending vibrations, (two e_u and one a_{2u}) for each complex[121]. These bands probably occur beyond the limit of measurement in the Mn(II) complex. In the Fe(II) and Co(II) complexes, one fairly weak band is observed below 170 cm^{-1} in each complex. In the Ni(II) complex, however, two relatively intense bands, which are strongly d_5-sensitive but only slightly ^{15}NCS-sensitive, are observed. On these grounds, they are assigned to δNMN modes.

The fact that the νM-py values of the monomeric octahedral complexes are somewhat higher than those of their polymeric octahedral analogues is consistent with the shorter metal-pyridine bond lengths[101,120] in the former.

3.4 Structural Implications of the Spectra of $[Fe(py)_4(NCS)_2]$ and its Oxidation Product

The complex $[Fe(py)_4(NCS)_2]$ deserves special mention because of earlier confusion concerning its identity. Depending on the method of preparation, the complex is obtained in either a light yellow or (so-called) black form. The latter is actually deep violet in transmitted light. Originally, these two compounds were thought[122,123] to be geometrical

isomers, *viz.* *cis*- and *trans*-$[Fe(py)_4(NCS)_2]$, respectively.

A study of these presumed isomers by Spacu and co-workers[124] in 1964 referred to their chemical reactivity with certain bidentate heterocyclic amines. Data on their infrared and visible absorption spectra as well as magnetic moments were included. The whole study is, however, based on the erroneous assumption of *cis-trans* isomerism. The authors ultimately concluded that the yellow complex is the *cis*-isomer and the violet compound is the *trans*-isomer.

In 1966, the two complexes were re-examined by two groups of workers[89,125] who considered the possibility of oxidation of the Fe(II) complex to an Fe(III) complex accompanied by a colour change. The chemical reactivity of the two complexes towards oxidizing and reducing agents was thoroughly investigated. The examination of chemical properties established beyond reasonable doubt that the different colours do not arise from a difference in structure but result from contamination of the normal yellow isomer with a violet Fe(III) complex, most probably $[Fe(py)_3(NCS)_3]$[89]. The amount of the violet Fe(III) complex was estimated as 0.02% in the normal yellow *trans*-$[Fe(py)_4(NCS)_2]$ and as 0.4-1.6% in the violet oxidation product[125], the latter value depending on the method of preparation.

Data on the Mössbauer, esr, electronic and infrared spectra of the two complexes were also reported in these studies. The infrared spectra were not extended below 200 cm^{-1} but showed identical frequencies for the νN-CS and νNC-S bands[89].

Reflectance spectra in the region 20 000 - 7 000 cm^{-1} revealed significant differences between the two complexes. The extremely strong band at about 19 000 cm^{-1} in the spectrum of the violet complex (probably a

thiocyanate-Fe(III) electron transfer band) was considered responsible for the dark colour of the complex[89]. X-ray powder photographs yielded identical patterns[125]. It was therefore reasonably concluded that the yellow form has *trans*-octahedral configuration like the analogous complexes of nickel and cobalt. The violet form is merely the yellow form contaminated with traces of an Fe(III) complex, presumably $[Fe(py)_3(NCS)_3]$.

The infrared results show (see Fig. 5) that the yellow Fe(II) complex is undoubtedly *trans*-$[Fe(py)_4(NCS)_2]$ since its spectrum is identical with the other $[M(py)_4(NCS)_2]$ complexes, for two of which *trans*-configuration has been crystallographically established[120]. Furthermore, the spectrum yields one νM-py and one νM-NCS band as required for the *trans*-ML_4X_2 isomer (D_{4h} symmetry) whereas the *cis*-isomer (C_{2v} symmetry) would require four νM-py and two νM-NCS bands[121].

A sample of the violet oxidation product, obtained by recrystallization of yellow *trans*-$[Fe(py)_4(NCS)_2]$ from chloroform, yields an infrared spectrum (Fig.6) which comprises bands corresponding in position with those of the yellow Fe(II) complex and additional bands at higher frequencies, especially below 400 cm^{-1}. These high frequency shifts of metal-ligand bands are expected[99] to accompany the increase in oxidation state Fe(II) → Fe(III) while the coordination number remains constant. Thus, in addition to the band at 271 cm^{-1} in the Fe(II) spectrum (assigned to the νM-NCS vibration) a doublet (313, 296 cm^{-1}) is observed in the spectrum of the oxidation product. Similarly, the coupled (νM-py + νM-NCS) band at 201 cm^{-1}, with its vibrationally-pure νM-py shoulder at 193 cm^{-1} in the yellow Fe(II) complex becomes resolved into two widely separated bands at 247 and 201 cm^{-1} in the violet complex.

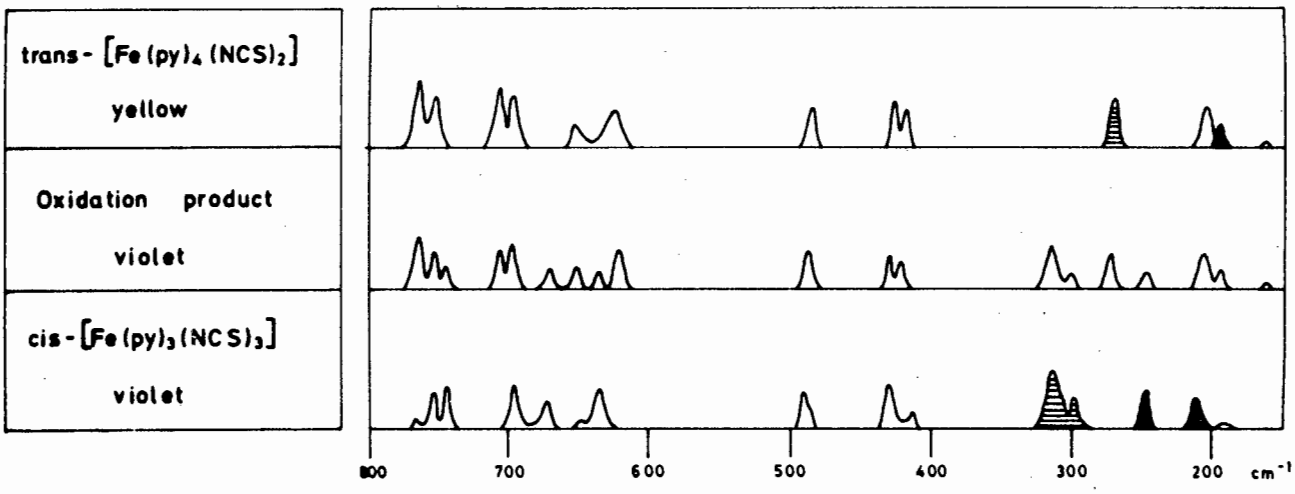


Fig. 6. Infrared spectra of *trans*-$[Fe(py)_4(NCS)_2]$, its oxidation product and *cis*-$[Fe(py)_3(NCS)_3]$. Shaded bands : νFe-NCS, Solid bands : νFe-py.

These features (two νM-NCS and two νM-py bands) satisfy the symmetry requirements for the C_{3v} complex *cis*-$[Fe(py)_3(NCS)_3]$. For the *trans*-isomer (C_{2v} symmetry) three of each species of metal-ligand stretching bands would be expected[121]. It is concluded, therefore, that the contamination of the yellow Fe(II) complex arises from traces of *cis*-$[Fe(py)_3(NCS)_3]$.

The fact that all bands which occur in the Fe(II) complex are repeated in the spectrum of the oxidation product, provides convincing evidence that it is not simply an isomer of the yellow compound. This supports the conclusions of Burbridge and co-workers[89] and contradicts those of earlier workers[124].

In order to confirm the identity of the oxidation product, a sample of *cis*-$[Fe(py)_3(NCS)_3]$ was prepared from ferric thiocyanate and pyridine[89]. The spectrum of this compound contains bands which correspond precisely, in position, with the additional bands in the spectrum of the oxidation product. The oxidation of the yellow Fe(II) complex is therefore considered to involve the transformation : *trans*-$[Fe(py)_4(NCS)_2] \rightarrow$ *cis*-$[Fe(py)_3(NCS)_3]$.

Comparing the spectra of the three iron complexes in the region 800 - 600 cm^{-1}, it is noteworthy that three bands observed in the oxidation product at 747, 674 and 639 cm^{-1} do not occur in the yellow Fe(II) complex. These bands correspond, both in position and intensity, with bands occurring in the spectrum of the Fe(III) compound. Since no internal vibrations of the NCS— group occur in this spectral region these bands may be pyridine bands associated with the C_{3v} site-symmetry of the complex *cis*-$[Fe(py)_3(NCS)_3]$.

3.5 Comparison of Present Assignments with those Previously Reported

Table 24 lists, for comparison with the present work, the assignments which result from the two principal earlier studies[73,74] on pyridine-isothiocyanate complexes. Generally, the agreement between the frequencies is good. There is essentially little difference between the earlier and present assignments for νN-CS, ν_1, ν_2 and ν_3. ν_4 is now preferentially assigned to νM-NCS rather than νM-py although the observed *d*-sensitivity of this band clearly indicates that some coupling with νM-py occurs in several of the complexes. ν_5 is now regarded as the principal νM-py band since it has a higher *d*-sensitivity than ν_4. The νM-py values are now consistent with the range of νM-py in the complexes $[M(py)_2Cl_2]$ for which erroneously high values of νM-py had also previously been reported[65]. In the earlier reports[73,74] on the spectra of the pyridine-isothiocyanate complexes, ν_5 was either beyond the range of measurement or, if observed, was not assigned. A single exception is the complex $[Co(py)_4(NCS)_2]$ in which ν_5 was assigned to νCo-py, in agreement with the present work. In earlier studies, ν_6 and ν_7 were generally unobserved or unassigned.

TABLE 24

Vibrational frequencies, isotopic shifts (cm^{-1}) and band assignments for complexes $[M(py)_n(NCS)_2]$[a] in comparison with those previously reported.

Band	Reference	$[Mn(py)_2(NCS)_2]$		$[Co(py)_2(NCS)_2]$		$[Ni(py)_2(NCS)_2]$		$[Cu(py)_2(NCS)_2]$		$[Zn(py)_2(NCS)_2]$	
	this work	2094[b](28;1)	νN-CS	2102[b](27;0)	νN-CS	2114[b](29;0)	νN-CS	2098[b](30;1)	νN-CS	2100(29;0)	νN-CS
										2081(29;0)	νN-CS
	73	2095	νN-CS	2099	νN-CS	2100	νN-CS	2085	νN-CS	2100	νN-CS
										2075	νN-CS
ν_1	this work	476(3;1)	δNCS	475(3;0)	δNCS	477(0;1)	δNCS	478(4;0)	δNCS	486(3;0)	δNCS
		470(4;0)	δNCS	470(t.b.)	δNCS	469(4;0)	δNCS	469(3;0)	δNCS	481(3;0)	δNCS
	73	475	δNCS	472	δNCS	474	δNCS	477	δNCS	484	δNCS
		468	δNCS	468	δNCS	466	δNCS	468	δNCS	478	δNCS
	74	475	δNCS	473	δNCS	477	δNCS	478	δNCS	486	δNCS
		468	δNCS			469	δNCS	468	δNCS		
ν_2	this work	418(0;40)	νpy	426(0;40)	νpy	433(0;40)	νpy	434(0;40)	νpy	426(0;39)	νpy
										414(0;39)	νpy
	73	417	νpy	422	νpy	429	νpy	431	νpy	n.r.	
	74	417	νpy	425	νpy	432	νpy	435	νpy	427	νpy
										414	νpy
ν_3	this work	258(1;0)	νM-NCS	270(0;0)	νM-NCS	285(2;0)	νM-NCS	324(1;3)	νM-NCS	315(1;1)	νM-NCS
	73	254	νM-NCS	268	νM-NCS	280	νM-NCS	319	νM-NCS	312	νM-NCS
	74	256	νM-NCS	270	νM-NCS	283	νM-NCS	324	νM-NCS	313	νM-NCS
ν_4	this work	196(0;2)	νM-NCS[c]	208(2;2)	νM-NCS[c]	226(2-4)	νM-NCS[c]	257(1;0)	νM-NCS	270(0;2)	νM-NCS
	73	b.r.		213	νM-py	229	νM-py	256	νM-py	268	νM-py
	74	201	νM-py	211	νM-py	230	νM-py	256	νM-py	268	νM-py
ν_5	this work	164(1;4)	νM-py	185(1;3)	νM-py	206(1;9)	νM-py	225(0;5)	νM-py	232(0;4)	νM-py
										207(0;5)	νM-py
	73	b.r.		b.r.		b.r.		n.r.		215	νM-py
	74	168	n.a.	n.r.		n.r.		218	n.a.	231	n.a.
ν_6	this work	153(t.b.)	δNMN	162(1;3)	δNMN	179(0;3)	δNMN	212(1;5)	δNMN	162(4;5)	δNMN
	73	b.r.		b.r.		b.r.		214	νM-py	b.r.	
	74	155	n.a.	165	n.a.	n.r.		218	n.a.	166	n.a.

TABLE 24 (CONTINUED)

Band	Reference	$[Mn(py)_2(NCS)_2]$	$[Co(py)_2(NCS)_2]$	$[Ni(py)_2(NCS)_2]$	$[Cu(py)_2(NCS)_2]$	$[Zn(py)_2(NCS)_2]$
ν_7	this work	b.r.	145(0;3) δNMN	155(1;4) δNMN	193(0;8) δNMN	b.r.
	73	b.r.	b.r.	b.r.	b.r.	b.r.
	74	b.r.	b.r.	158 n.a.	197 n.a.	b.r.

TABLE 24 (CONTINUED)

Band	Reference	$[Mn(py)_4(NCS)_2]$		$[Fe(py)_4(NCS)_2]$		$[Co(py)_4(NCS)_2]$		$[Ni(py)_4(NCS)_2]$	
	this work	2062[b](27;1)	νN-CS	2066(29;0)	νN-CS	2074[b](27;1)	νN-CS	2084[b](27;0)	νN-CS
	73	2066	νN-CS	2070[g]	νN-CS	2072	νN-CS	2079	νN-CS
ν_1	this work	481(3;0)	δNCS	483(3;0)	δNCS	482(3;0)	δNCS	483(3;0)	δNCS
	73	482[d]	δNCS	482[dg]	δNCS	481[d]	δNCS	483[d]	δNCS
	74	482	δNCS	h		483	δNCS	482	δNCS
ν_2	this work	422(0;40)	νpy	428(0;38)	νpy	431(0;40)	νpy	437(0;38)	νpy
		414(0;40)	νpy	420(0;38)	νpy	423(0;39)	νpy	430(0;38)	νpy
	73	420	νpy	424[g]	νpy	426	νpy	434	νpy
		414	νpy	420[g]	νpy	420	νpy	429	νpy
	74	422[e]	νpy	h		433[e]	νpy	438[e]	νpy
		415	νpy			423	νpy	432	νpy
ν_3	this work	256(0;0)	νM-NCS	271(1;0)	νM-NCS	272(0;0)	νM-NCS	287(0;0)	νM-NCS
	73	254	νM-NCS	266[g]	νM-NCS	268	νM-NCS	280	νM-NCS
	74	259	νM-NCS	h		272	νM-NCS	287	νM-NCS
ν_4	This work	188(0;0)	νM-py[f]	201(0;3)	νM-py +νM-NCS	212(2;0)	νM-py +νM-NCS	230(0;2)	νM-py +νM-NCS
	73	b.r.		203[g]	νM-py	215	νM-py	233	νM-py
	74	195	νM-py	h		212	νM-py	232	νM-py
ν_5	this work	174(1;3)	νM-py	193(0;4)	νM-py	202(2;4)	νM-py	220(0;4)	νM-py
	73	b.r.		b.r.		205	νM-py	n.r.	
	74	172	n.a.	h		204	n.a.	n.r.	

TABLE 24 (CONTINUED)

Band	Reference	$[Mn(py)_4(NCS)_2]$	$[Fe(py)_4(NCS)_2]$	$[Co(py)_4(NCS)_2]$	$[Ni(py)_4(NCS)_2]$
ν_6	this work	b.r.	163(0;2) δNMN	165(t.b.) δNMN	172(1;3) δNMN
	73	b.r.	b.r.	b.r.	b.r.
	74	b.r.	h	170 n.a.	174 n.a.
ν_7	this work	b.r.	b.r.	b.r.	160(1;7) δNMN
	73	b.r.	b.r.	b.r.	b.r.
	74	b.r.	h	b.r.	164 n.a.

[a] Abbreviations : b.r. = beyond range of measurement, n.a. = not assigned, n.r. = not reported, t.b. = too broad for determination of shift. Figures in parentheses following the frequencies are the shifts (nearest integral values in cm^{-1}) towards lower frequency induced by ^{15}NCS-labelling (first figure) and pyridine deuteration (second figure). Shifts < 1 cm^{-1} are not regarded as significant and are reported as zero shifts.

[b] Sharp shoulders on νN-CS bands ignored (see Fig. 5).

[c] Some *d*-sensitivity in these bands indicates coupling with νM-py.

[d] Shoulders reported to precede these bands by approximately 2 cm^{-1} were not observed in this work.

[e] Additional bands reported near 400 cm^{-1} (not observed in present work nor cited in reference 73).

[f] Coupled with νM-NCS.

[g] Compound incorrectly formulated as *cis*-isomer.

[h] Compound not studied.

4. IR SPECTRA OF THE PYRIDINE COMPLEXES OF PLATINUM(II) HALIDES AND THIOCYANATES

The spectra are depicted in Fig. 7 and the frequencies are reported in Tables 14-17 (Chap. III). In Table 25 band frequencies, their isotopic shifts and the assignments based on these shifts are compared with those reported by earlier workers.

4.1 Spectra of *cis*- and *trans*-$[Pt(py)_2Cl_2]$

The structure of these complexes was investigated recently[126] by Colamarino and colleagues. Results show the usual square planar coordination for platinum(II), the Pt-N and Pt-Cl bond distances being almost identical for the *cis*- and *trans*-isomers (2.0 and 2.3 Å, respectively). The pyridine rings are rotated with respect to the coordination plane in order to minimize intermolecular repulsions. Since the bond angles about the Pt(II) ion are very nearly 90° the selection rules for C_{2v} (*cis* complex) and D_{2h} (*trans* complex) may reasonably be expected to apply. Therefore, we expect two νPt-N and two νPt-Cl infrared-active bands for the *cis*-isomer and one of each for the *trans*-isomer.

In the region 1600 - 800 cm^{-1} the spectra of the two isomers resemble each other closely. The band frequencies generally agree well with those reported[127] for these complexes by Adams in 1967. Their assignment to the various internal pyridine vibrations is supported here on the basis of the observed ^{15}N-induced shifts which are generally between 2 and 8 cm^{-1} to lower frequencies. In the region below 800 cm^{-1} several of the pyridine bands (see Table 14)

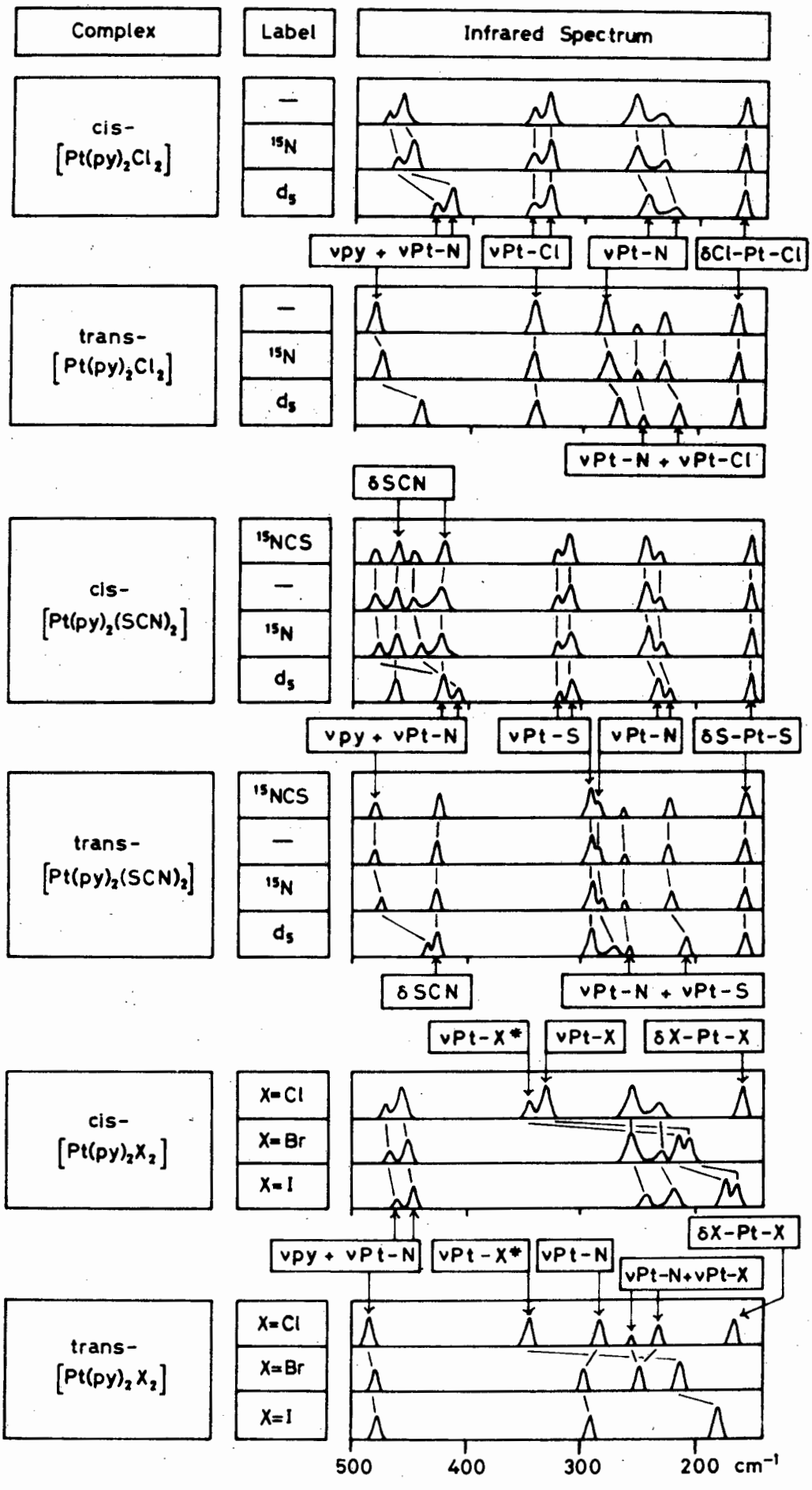


Fig. 7. Infrared spectra of pyridine complexes of Pt(II) halides and thiocyanates.

* coupled with νPt-N in the bromo complexes.

TABLE 25. Frequencies, isotopic shifts (cm^{-1}) and assignments for complexes $[Pt(py)_2X_2]$ (X = Cl, Br, I)

Frequency	Shift ($\Delta\nu$)[a] ^{15}N	d_5	Assignment	Previously reported frequencies and assignments[b]
cis-$[Pt(py)_2Cl_2]$				
471	8	42	νpy + νPt-N	467 νPt-N(79), 466 n.a.(82), 467 νpy(83)
457	7	42	νpy + νPt-N	454 νPt-N(79), 456 n.a.(80), 454 n.a.(82), 456 n.a.(83), 455 n.a.(84)
345	0	0	νPt - X	344 νPt-X(79), 343 νPt-X(80), 342 νPt-X(82), 343 νPt-X(83), 342 νPt-X(84)
331	0	1	νPt - X	330 νPt-X(79), 328 νPt-X(80), 328 νPt-X(82), 329 νPt-X(83), 330 νPt-X(84)
256	2	12	νPt - N	260 n.a.(80), 260 n.a.(82), 260 νPt-N(83)
232	2	12	νPt - N	233 n.a.(80), 235 n.a.(83)
160	0	0	δXPtX	163 δPt-X(83)
cis-$[Pt(py)_2Br_2]$				
467		42	νpy + νPt-N	464 νpy(83)
452		41	νpy + νPt-N	452 n.a.(80), 448 νpy(81), 451 n.a.(83)
259		9	νPt - N	254 n.a.(80), 260 νPt-N(81), 262 νPt-N(83)
230		9	νPt - N	234 n.a.(80), 234 νPt-N(81), 235 νPt-X(83)
216		7	νPt - X + Pt-N	219 νPt-X(80), 218 νPt-X(81), 216 n.a.(83)
208		c	νPt - X	211 νPt-X(80), 209 νPt-X(81)
cis-$[Pt(py)_2I_2]$[d]				
460			νpy + νPt-N	460 νpy(83)
446			νpy + νPt-N	447 n.a.(83)
244			νPt - N	246 νPt-N(83)
220			νPt - N	
175			νPt - X	178 νPt-X(83)
165			νPt - X	167 νPt-X(83)

TABLE 25 (Continued)

Frequency	Shift ($\Delta\nu$)[a]		Assignment	Previously reported frequencies and assignments[b]
	^{15}N	d_5		
trans-$[Pt(py)_2Cl_2]$				
482	8	41	νpy + νPt - N	480 νPt-N(79), 479 νpy(81), 478 n.a.(82), 481 νpy(83)
344	0	3	νPt - X	343 νPt-X(79), 343 νPt-X(80), 341 νPt-X(81), 342 νPt-X(82), 342 νPt-X(83)
285	3	14	νPt - N	283 n.a.(80), 282 νPt-N(81), 279 νPt-N(82), 284 νPt-N(83)
254	1	7	νPt - N + νPt - X	256 n.a.(80), 242 n.a.(80), 256 n.a.(83)
230	1	14	νPt - N + νPt - X	232 n.a.(80), 233 n.a.(81), 235 n.a.(83)
165	0	0	δXPtX	167 δPt-X(83)
trans-$[Pt(py)_2Br_2]$				
479		41	νpy + νPt - N	476 νpy(81), 478 νpy(83)
296		12	νPt - N	298 n.a.(80), 297 νPt-N(81), 300 νPt-N(83)
247		9	νPt - N + νPt - X	251 νPt-X(80), 249 νPt-X(81), 252 νPt-X(83)
212		9	νPt - X + νPt - N	216 n.a.(80), 214 n.a.(81), 215 n.a.(83)
trans-$[Pt(py)_2I_2]$[d]				
476			νpy + νPt - N	475 νpy(83)
290			νPt - N	293 νPt-N(83)
179			νPt - X	183 νPt-X(83)

TABLE 25 (Continued)

[a] Shifts are reported to the nearest integral values and are to lower frequencies. Shifts <1 cm^{-1} are not considered significant and are reported as zero shifts.

[b] Figures in parentheses are the reference numbers (n.a. = not assigned).

[c] Band disappeared on deuteration.

[d] No labelling was applied to the iodo complexes.

in the spectrum of the *cis*-isomer show a characteristic splitting as compared with the *trans* spectrum. This feature is also observed in the spectra of the complexes *cis*- and *trans*-$[Pt(py)_2(SCN)_2]$.

The spectral region 500 - 400 cm^{-1} exhibits two bands for the complex *cis*-$[Pt(py)_2Cl_2]$ and one band for the corresponding *trans* complex. The fact that these bands are strongly *d*-sensitive (shifts observed are $\sim$40 cm^{-1} to lower frequencies) and ^{15}N-sensitive (shifts are about 8 cm^{-1}) rules out an earlier suggestion[79] that they are pure νPt-N bands. The latter assignment has been questioned[128] on other grounds, principally the fact that this would place νPt-N frequencies too close to those observed for Pt(II)-ammine complexes. Since the *d*-sensitivities of these bands are very similar to the *d*-sensitivity ($\Delta\nu$ = 37 cm^{-1}) of the γring vibration of pyridine occurring at 406 cm^{-1} (see Sections 1 and 3), the bands near 470 cm^{-1} in the spectra of the complexes are almost certainly associated with this vibration.

It is well known[129] that the frequency of the γring pyridine vibration is increased by complex formation, the shift to higher frequencies being proportional to the CFSE in the pyridine complexes of first transition series metal(II) halides[65]. In view of its CFSE dependence it is not surprising to find that, in the spectra of the Pt(II) complexes, this band is observed some 30 to 40 cm^{-1} higher compared with the pyridine complexes of first transition metal(II) isothiocyanates (see Section 3). This marked CFSE-dependence has, amongst other factors, led to the suggestion[65,94,130,131] that these bands are coupled νpy + νM-N bands. This assignment is certainly consistent with the appearance of two bands in the spectra of the *cis* and one band

in the *trans* complexes, a feature which has also been observed for the corresponding bromo and iodo complexes of Pt(II). The assignment of these bands to νpy + νM-N is therefore adopted here.

In the region 400 - 300 cm^{-1}, two intense bands are observed at 345 and 331 cm^{-1} for the *cis*-isomer and one equally strong band at 344 cm^{-1} for the *trans*-isomer. There is general agreement[79-84] that these are the Pt-Cl stretching vibrations, the assignment being based on their marked halogen-sensitivities in the sequence νPt-Cl > νPt-Br > νPt-I. The finding that these bands are almost insensitive to both ^{15}N-labelling and deuteration of the pyridine ring supports this assignment.

Between 300 and 200 cm^{-1}, two bands are observed in the spectrum of *cis*-$[Pt(py)_2Cl_2]$. Their substantial ^{15}N- and *d*-sensitivities (2 and 12 cm^{-1}, respectively) suggest their assignment to νPt-N bands. For the *trans*-isomer, the selection rules require one infrared-active νPt-N band but three are observed in this region. The band at 285 cm^{-1} exhibits the greatest ^{15}N- and *d*-sensitivity (3 and 14 cm^{-1}, respectively) and is therefore assigned to νPt-N. The origin of the other bands warrants discussion since they have been observed but remained unassigned in earlier reports[80,81,83]. Since they correspond almost precisely in position and isotopic sensitivity with the two νPt-N bands in the *cis* complex, one may be tempted to ascribe them to contamination of the *trans* complex by some of the *cis*-isomer. This is firmly discounted by the fact that no other *cis*-isomer bands recur in the spectrum of the *trans* complex and by the differing intensities of these bands in the two spectra. Of the two bands observed at 256 and 232 cm^{-1} in the spectrum of the *cis* complex, the higher frequency band

is more intense, whereas in the *trans*-isomer the intensity order for the bands in question is reversed. These bands originate most probably in vibrational coupling between νPt-N and νPt-Cl. That such coupling should preferentially occur in the *trans* complex is consistent with the smaller frequency gap between the νPt-N and νPt-Cl bands in this isomer. This indicates that the force constants of the Pt-N and Pt-Cl bonds are more comparable in the *trans* than in the *cis* complex, thereby enhancing the opportunity for vibrational coupling.

The bands of lowest frequency are observed at 160 and 165 cm^{-1} for the *cis*- and *trans*-isomers, respectively. They are completely unaffected by pyridine labelling and are accordingly assigned to a bending mode which does not involve the nitrogen atom, *viz.* δ ClPtCl.

4.2 Spectra of *cis*- and *trans*-$[Pt(py)_2X_2]$ (X = Br, I).

In agreement with symmetry considerations two νPt-X and two νPt-N bands (each) are observed for the *cis* bromides and iodides and one band (each) for the corresponding *trans* complexes.

Halogen substitution is expected to yield large shifts in the νPt-X frequencies in the order νPt-Cl > νPt-Br > νPt-I. On the other hand, νPt-N bands are expected to be relatively unaffected by the change of halogen. On this basis, the spectra of the bromo and iodo complexes are readily interpreted.

The very intense bands near 340 cm^{-1} assigned to νPt-Cl in the *cis*- and *trans*-chloro complexes move to the 210 cm^{-1} region in the bromo and to the 170 cm^{-1} region in the iodo complexes. The ratios

νPt-Br/νPt-Cl ~ 0.63 and νPt-I/νPt-Cl ~ 0.50 in both the *cis*- and *trans*-isomers are consistent with those observed[132] for the square planar ions $[PtX_4]^{2-}$ (X = Cl, Br, I). The labelling study reveals that the νPt-Br bands in the bromo complexes are significantly more *d*-sensitive than the νPt-Cl bands in the chloro complexes. Strong coupling of νPt-Br with νPt-N is indicated. This is consistent with the increased covalency of the νPt-X bonds in the sequence Cl < Br < I.

In the *cis*-bromo complexes the bands at 259 and 230 cm^{-1} exhibit the strongest *d*-sensitivity (shifts of 9 cm^{-1} are observed) of the four bands occurring in the region 260 - 150 cm^{-1}. They are assigned to νPt-N bands. The corresponding band in the *trans*-bromo complex occurs at 296 cm^{-1} and shifts 12 cm^{-1} to lower frequency on deuteration. The third band occurring between 300 and 200 cm^{-1} in the spectrum of this complex is assigned to νPt-N + νPt-Br in accordance with the assignment for the two similarly *d*-sensitive bands observed in this region for the *trans*-chloro complex. In the spectrum of the *trans*-iodo complex no extra band exceeding the number expected for D_{2h} symmetry is observed. The large frequency gap between νPt-N and νPt-I bands (about 110 cm^{-1}) suggests greater differences in the force constants of these bonds, so that vibrational coupling is less favoured.

4.3 Spectra of *cis*- and *trans*-$[Pt(py)_2(SCN)_2]$

The spectra of these complexes have not previously been reported. Crystal structure determination[133] of the *trans*-isomer has been reported during the course of this thesis. The Pt(II) ion showed

the usual square planar coordination with S-bonded thiocyanate groups, the bond angles N-Pt-N and S-Pt-S being precisely 180°. The observed Pt-N and Pt-S bond lengths (2.0 and 2.3 Å, respectively) are comparable with those found[133] in other Pt(II) complexes.

The infrared spectra lend support[70] to S-bonding of the NCS- groups in both *cis*- and *trans*-isomers since relatively high values for the νN-CS vibration are observed: 2124 cm^{-1} for the *cis*- and 2119 cm^{-1} for the *trans*-isomer. Both bands shift 28 cm^{-1} to lower frequencies on ^{15}NCS-labelling. Shifts of similar magnitude were observed for the aniline and pyridine complexes of first transition metal(II) isothiocyanates (see Sections 2 and 3).

In the region 1600 - 900 cm^{-1} the spectra of the *cis*- and *trans*-isomers resemble each other closely, the band pattern being similar to that observed for the corresponding chloro complexes. Generally, the bands are only slightly ^{15}NCS-sensitive but significantly ^{15}N-sensitive and are accordingly assigned to the respective internal vibrations of the pyridine molecule (see Table 17).

The νNC-S vibrations for thiocyanate complexes are expected to occur[118] between 720 and 690 cm^{-1}, whereas for isothiocyanates this vibration is normally shifted to higher frequencies, (*i.e.* 860 - 780 cm^{-1}). Since, in the lower frequency region, no significantly ^{15}NCS-sensitive bands are observed, the νNC-S vibration for the complexes *cis*- and *trans*-$[Pt(py)_2(SCN)_2]$ is most probably masked by the very intense bands associated with pyridine modes occurring in this region.

The relatively weak bands near 850 cm^{-1} observed in the spectrum of

both isomers exhibit moderate to strong ^{15}NCS-sensitivity, suggesting their assignment to νNC-S bands. However, these frequencies are some 30 - 40 cm^{-1} higher than those observed for νNC-S vibrations in all isothiocyanate complexes studied in this thesis (see Sections 2 and 3). Since the frequencies of the bands near 850 cm^{-1} are almost precisely double the observed values for the δNCS modes (near 425 cm^{-1}), these bands are assigned to the first overtone of this vibration, *viz.* 2δNCS (a characteristically intense overtone). The spectral region 500 - 400 cm^{-1} comprises two bands for the *trans*- and four bands for the *cis*-isomer. Of the two bands in the *trans* spectrum, that of higher frequency (at 480 cm^{-1}) is substantially ^{15}N-sensitive ($\Delta\nu$ = 5 cm^{-1}) and *d*-sensitive ($\Delta\nu$ = 44 cm^{-1}) but completely unaffected by ^{15}NCS-labelling. It occurs at almost precisely the same frequency as the band assigned to the coupled vibration νpy + νPt-N in *trans*-$[Pt(py)_2Cl_2]$. An identical assignment is therefore indicated. The second band in the *trans* spectrum at 427 cm^{-1} shifts 3 cm^{-1} to lower frequencies on ^{15}NCS-labelling but exhibits no ^{15}N- or *d*-sensitivity. It is firmly assigned to the δNCS vibration expected to occur near this frequency in terminal S-bonded thiocyanate complexes[70].

The assignments for the four bands observed in the spectrum of the *cis*-isomer are readily achieved by the isotopic labelling technique. In order of decreasing frequency the first and third bands are sensitive only to pyridine labelling, indicating their assignment to the γring pyridine vibration (coupled with νPt-N), while the second and fourth bands are significantly sensitive only to ^{15}NCS-labelling, supporting their assignment to the δNCS vibration.

The spectral region 350 - 270 cm^{-1} comprises two bands of moderate to strong intensity for the *cis*-isomer and one strong band with a shoulder for the *trans*-isomer. Except for the shoulder (which shifts significantly on pyridine labelling) these bands are insensitive towards any of the three kinds of isotopic labelling, suggesting their assignment to Pt-S stretching frequencies. ^{15}N-Labelling of S-bonded thiocynate groups is not expected to induce significant shifts in νM-S bands since even N-bonded NCS-groups have been found to undergo relatively small shifts, characteristically about 3 cm^{-1}, on ^{15}NCS-labelling (see Section 2). The shoulder on the νPt-S band in the *trans*-isomer is insensitive to ^{15}NCS-labelling. It is assigned to νPt-N on the basis of its shift of 3 and 15 cm^{-1} to lower frequencies on ^{15}N-labelling and deuteration, respectively. The position of this band and its sensitivity towards labelling of the pyridine ring are practically identical with the νPt-N band in the corresponding *trans*-chloro complex.

Between 270 and 200 cm^{-1}, two bands are observed for the *cis*-isomer. They are insensitive towards ^{15}NCS-labelling but equally ^{15}N- and *d*-sensitive and are therefore assigned to the two νPt-N bands expected for C_{2v} site symmetry. Their positions are very similar to the νPt-N bands of the analogous *cis*-chloro complex.

In the *trans*-thiocyanate, two bands, which are ^{15}NCS-insensitive but ^{15}N- and *d*-sensitive, occur at 263 and 224 cm^{-1}. Since the one νPt-N band required for D_{2h} symmetry has been accounted for and since the ^{15}N- and *d*-sensitivities are smaller for these two bands, they are assigned to the coupled vibration νPt-N + νPt-S. Their frequencies

are similar to the bands assigned to the coupled vibration νPt-N + νPt-Cl in the complex *trans*-$[Pt(py)_2Cl_2]$[65].

The spectral region 200 - 150 cm^{-1} exhibits one band each for the *cis*- and *trans*-isomers. These bands are almost completely insensitive to labelling of either the pyridine or the NCS-group and are therefore assigned to a bending mode which does not involve the nitrogen, *viz.* δSPtS.

4.4 Anti-Cancer Activity of Platinum(II) Complexes.

Systematic investigation of the anti-cancer activity of metal complexes commenced in 1969 following reports on the anti-tumour properties of *cis*-$[Pt(NH_3)_2Cl_2]$. The field has been extensively reviewed by Williams[77] and Cleare[78]. While the mechanism of the activity is by no means firmly established, certain Pt(II) complexes are known to exhibit particularly high activity, for instance, the complex *cis*-$[PtL_2Cl_2]$ (L = NH_3 or RNH_2). The *trans*-forms are inactive. Systematic testing of compounds of this type has revealed that the following properties enhance the activity: (a) *cis*-configuration, (b) *cis*-leaving groups of intermediate lability, (c) L = alicyclic amine, (d) X = chloride. It has been suggested that a possible mode of action involves selective attack on DNA synthesis by chelate ring formation. This possibly occurs by initial loss of the two halide ions followed by formation of a purine-Pt-purine cross-link *via* the nitrogens of two neighbouring purines. Complexes of several other metal ions, particularly those of the heavier transition metal ions, are now known to have anti-tumour activity[78]. The observation that certain

complexes of rhodium(III), *i.e.* the octahedral complex $[Rh(NH_3)_3Cl_3]$, are active anti-cancer drugs[78], shows that anti-tumour activity is not limited to compounds of square planar stereochemistry. Progress in the field is such that the intelligent design of potential anti-cancer drugs is now possible.

Several of the Pt(II) complexes synthesized during the course of this thesis contain the ligands and structural features desirable for an active anti-cancer drug. Three of these complexes were submitted to the National Cancer Institute (U.S.A.) which has initiated a mass screening programme in the search for new compounds as potential anti-cancer agents.

Mouse tumours are the most popular for primary screens and the most successful tumour, used as a universal primary screen to detect useful drugs, is Lymphoid Leukemia L1210[78]. The results of primary screens for testing against Lymphoid Leukemia L1210 are listed in Table 26. The amount of inhibition obtained for a particular dose expressed as mg drug administered per kg of mouse per injection (usually three injections are administered) is listed as (T/C)% which is the ratio of test (T) evaluation to control (C) evaluation expressed as a percentage.

TABLE 26. Anti-cancer activity of Pt(II) complexes

Complex	Dose	(T/C)%
cis-$[Pt(PNA)_2Cl_2]$[a]	200	113
cis-$[Pt(py)_2Cl_2]$	100	118
cis-$[Pt(an)_2Cl_2]$	100	86

[a] PNA = *p*-nitroaniline

5. IR SPECTRA OF COMPLEXES OF *o*-TOLUIDINE WITH METAL(II) HALIDES.

The IR spectra of *o*-toluidine and its metal(II) halide complexes are shown in Fig. 8. Vibrational frequencies and shifts are listed in Tables 18 - 20.

In the following discussion, bands which shift on ^{15}N-labelling are termed ^{15}N-sensitive while bands which shift on substitution of the metal or halogen ion are termed M-sensitive and X-sensitive, respectively.

No crystallographic investigations of the complexes studied here have been reported. However, structural information on the corresponding complexes of aniline and *p*-toluidine with metal(II) chlorides[67,102,103] is available. X-ray data and electronic spectra indicate a tetrahedral environment for the cobalt and zinc complexes and polymeric octahedral and polymeric tetragonal coordination for the nickel and copper complexes, respectively. In a detailed study of the IR spectra of a series of *p*-toluidine complexes[69], $[M(p\text{-tol})_2Cl_2]$ (M = Co, Ni, Cu, Zn) the structures proposed on the basis of the electronic spectra are supported.

Ahuja *et al.*[67] reported on the spectroscopic properties of a number of substituted aniline complexes of metal(II) halides. On the basis of their electronic spectra, they suggested that the *o*-toluidine complexes of cobalt and zinc are tetrahedral, the nickel complexes are polymeric octahedral and the copper complexes are probably polymeric tetragonal. The blue colour of the Co(II) complexes of *o*-toluidine (X = Cl, Br) is consistent with tetrahedral coordination.

The nickel complexes deserve special mention, firstly, because of their

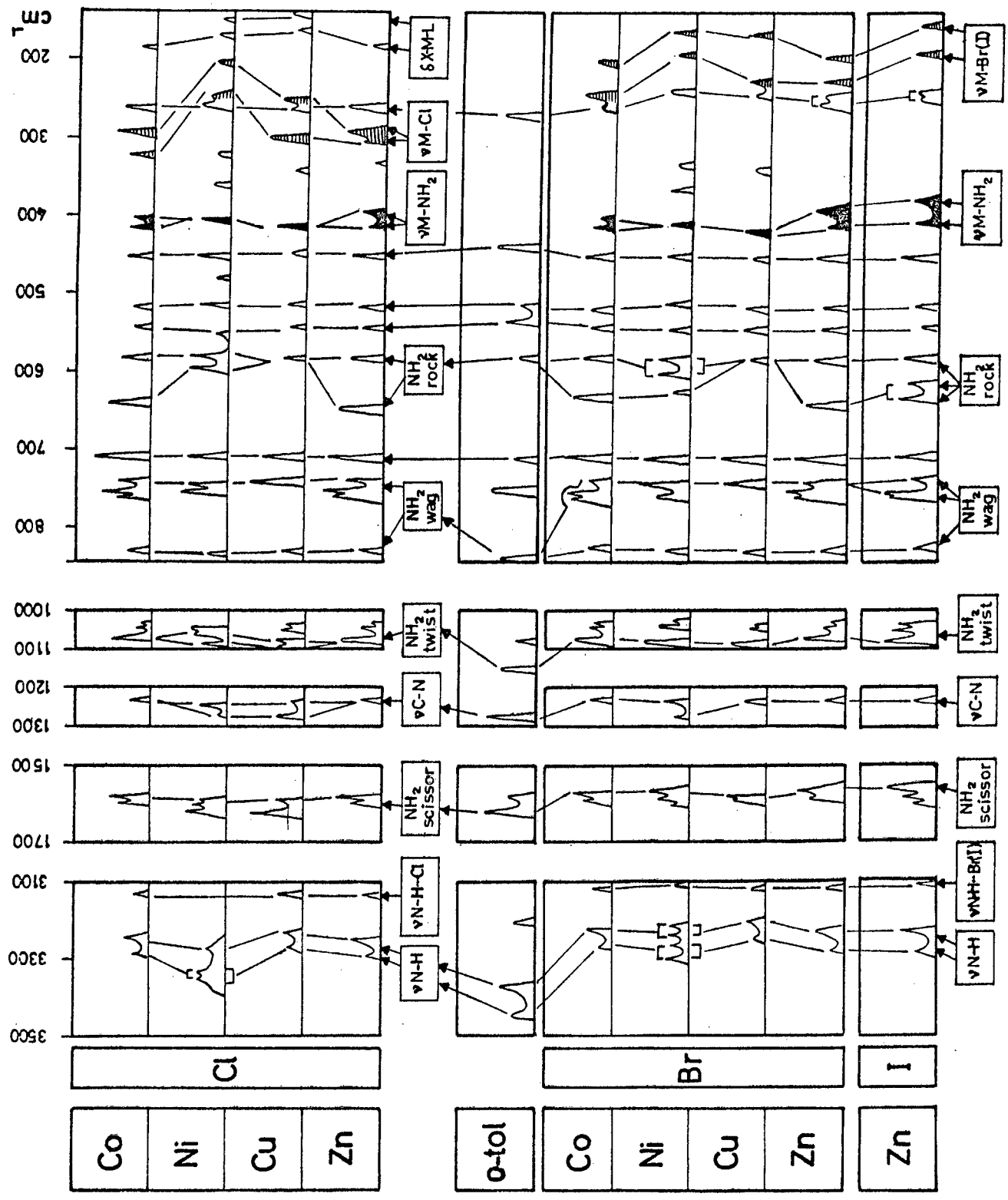


Fig. 8 Infrared spectra of *o*-toluidine complexes of metal(II) halides.

unique composition (hydrates are obtained) and, secondly, because of the existence of a second unstable form of unknown structure, which is distinguished from the green hydrate by its yellow colour.

The green colour of the hydrated compounds (X = Cl, Br) suggests octahedral coordination. Six-coordination may be achieved by two of the water molecules entering the primary coordination sphere of the nickel(II) ion, thus forming a monomeric octahedral complex with terminal halide ligands. Alternatively, octahedral coordination may be achieved by polymer formation in which bridging halides serve to link the monomeric units.

In a similar series of metal(II) pyridine complexes investigated recently[65], the νM-X frequencies were found at considerably higher frequencies in complexes with terminal halides than in complexes with bridging halides. The νM-Cl frequencies of the tetrahedral bis(pyridine) cobalt complex $[Co(py)_2Cl_2]$ (observed at 346 and 307 cm^{-1}) shift 82 and 71 cm^{-1}, respectively, to lower frequencies on substitution of Co(II) by Ni(II), the Ni(II) complex having polymeric octahedral structure[65]. In the *o*-toluidine complexes of cobalt and nickel, the corresponding M-sensitivities of the two bands assigned to νM-Cl in each complex are 81 and 89 cm^{-1}, respectively. That these shifts are similar to those observed for the pyridine complexes indicates that the hydrated nickel complexes of *o*-toluidine also be assigned polymeric octahedral structure.

The yellow colour of the unstable nickel complexes (obtained by drying the green hydrated complexes; see Experimental Chapter) points to square planar coordination. However, microanalysis shows that these compounds are not the pure anhydrous compounds $[Ni(o\text{-tol})_2X_2]$ (X = Cl, Br)

but are more probably partially decomposed hydrates, the decomposition involving simultaneous loss of crystal water and *o*-toluidine. The analysis results suggest that dinuclear square planar nickel complexes with bridging halogens, *viz.* $[Ni_2(o\text{-tol})_2X_4]$ may be partially formed although the IR spectra of the yellow compounds resemble those of the green nickel complexes rather closely.

The Cu(II) complexes most probably have the polymeric tetragonal structure with weak axial Cu-X bonds crystallographically established[134] for the pyridine complex $[Cu(py)_2Cl_2]$. The Zn(II) complexes almost certainly have the tetrahedral structure established for the corresponding *p*-toluidine complex[69], $[Zn(p\text{-tol})_2Cl_2]$, and the isothiocyanate complex[109] $[Zn(p\text{-tol})_2(NCS)_2]$ discussed in Section 2.

5.1 Metal-Nitrogen Vibrations

In a series of complexes with the above-mentioned structures, the Irving-Williams stability sequence Co < Ni < Cu > Zn becomes deranged[11] to Co > Ni < Cu > Zn. The difference arises from the fact that the Irving-Williams sequence is based on octahedral Co(II) and Ni(II) and tetragonal Cu(II). In the complexes of *o*-toluidine, however, the presence of 4-coordinate Co(II) implies that greater stability for each cobalt-ligand bond is achieved compared with a 6-coordinate octahedral complex. It is now well-established[5,11] that metal-ligand stretching frequencies follow the order of metal-ligand bond stabilities in a series of first transition metal(II) complexes. The metal-ligand bands in the *o*-toluidine complexes are therefore expected to be M-sensitive in the order Co > Ni < Cu > Zn. Furthermore, we expect to observe substantial ^{15}N-sensitivity for νM-N bands and insignificant or no ^{15}N-sensitivity for bands assigned to νM-X frequencies. The

latter bands should also shift on halogen substitution in the order νM-Cl > νM-Br > νM-I, *i.e.* according to the increasing mass of the halide ligand. Finally, the number of IR-active metal-ligand stretching frequencies in a series of complexes possessing the structures proposed is determined by their respective site symmetries. Thus, two νM-N bands each are required for the complexes of cobalt and zinc (C_{2v} symmetry) and one νM-N band for the complexes of nickel and copper (C_i symmetry)[113].

In the series of chloro complexes, two ^{15}N-sensitive bands each are observed for the cobalt and zinc complexes in the region 420-390 cm^{-1} whereas only one such band is found in the complexes of nickel and copper. They appear in a region free from ligand absorption and their frequencies follow the order Co > Ni < Cu > Zn expected from the arguments put forward in the previous paragraph. These bands are therefore firmly assigned to the metal-nitrogen stretching frequencies.

The shifts induced by ^{15}N-labelling are between 3 and 6 cm^{-1} towards lower frequencies. Similar shifts have been observed for νM-N frequencies in the aniline and *p*-toluidine isothiocyanate complexes, $[ML_2(NCS)_2]$ (see Section 2) and in the metal(II) halide complexes of *m*-toluidine[85], $[M(m\text{-tol})_2X_2]$.

In the bromo series, two ^{15}N-sensitive bands (each) for the cobalt and zinc complexes and one band (each) for the complexes of nickel and copper are again observed at positions almost identical to the corresponding bands in the chloro complexes. Their frequencies also follow the sequence Co > Ni < Cu > Zn and their ^{15}N-sensitivities are between 2 and 5 cm^{-1}. These bands are therefore assigned to the νM-N modes.

In the tetrahedral iodo complex, $[Zn(o\text{-tol})_2I_2]$, the two ^{15}N-sensitive

bands occurring at 410 and 380 cm^{-1} are assigned to the νM-N modes. Similar bands have been observed at 412 and 385 cm^{-1} in the corresponding *m*-toluidine complex[85].

As mentioned in the Experimental Chapter (see Chapter II.2), no ^{15}N-labelling was used for the nickel complexes (X = Cl, Br). The ^{15}N-labelled bromo complex of copper was synthesized but found to be too unstable for its IR spectrum to be determined. It seems that the bromo complexes and, to some extent, also the chloro complexes of copper are susceptible to decomposition (possibly reduction to Cu(I)), this feature being noticeable from a colour change of the complexes from brown to black. Comparing these complexes with those of *m*-toluidine, no such difficulties were experienced[85]. Analytically-pure, anhydrous nickel complexes were obtained and no decomposition of the copper compounds was observed. The reason for these differences is almost certainly associated with the steric effect imposed by the bulky methyl group in *ortho*-position to the amino group.

5.2 Metal-Halogen Vibrations

In comparison with the νM-N region, the band pattern in the spectral region below 330 cm^{-1} exhibits a higher degree of complexity, especially in the spectra of the chloro complexes (see Fig. 8). Between 330 and 200 cm^{-1}, three or four bands are observed in each chloro complex. None of these bands shifts significantly on ^{15}N-labelling, as may be expected for bands associated with νM-X stretching vibrations. Also, marked metal-sensitivity is expected for νM-X frequencies in the order Co > Ni < Cu > Zn. Furthermore, symmetry considerations require two νM-X bands for complexes with C_{2v} site symmetry (cobalt and zinc) and

two νM-X bands for complexes with C_i symmetry (nickel and copper). In order to assign νM-X vibrations in the complexes of *o*-toluidine we seek bands which satisfy these criteria. The two bands occurring in the region 330-250 cm^{-1} for the complexes of cobalt, copper and zinc and at 247 and 208 cm^{-1} in the nickel complex satisfy these criteria and are therefore firmly assigned to the νM-Cl vibrations.

Comparing the complexes of cobalt and nickel, a considerable shift to lower frequencies ($\sim$80 cm^{-1}) is observed for νM-Cl. A shift of this magnitude is expected from the change in structure (*i.e.* tetrahedral coordination with terminal halogens and polymeric octahedral coordination with bridging halogens for cobalt and nickel, respectively) and has been previously observed in a series of pyridine complexes[65].

In the region of the νM-Cl bands, a third strong band which shows no ^{15}N-sensitivity is observed in the spectra of each of the complexes. These bands occur at about 260 cm^{-1} in the chloro complexes and are metal-sensitive in the order Co > Ni < Cu > Zn. Since their metal-sensitivity is much smaller than that of the νM-Cl bands, they are almost certainly associated with the ligand vibration occurring at 272 cm^{-1} in *o*-toluidine, probably a γ ring vibration[95]. However, since the metal-sensitivity follows the stability sequence cited, coupling with the νM-Cl bands probably occurs.

The νM-Cl assignments for the cobalt and zinc complexes agree well with those made previously[67] by Ahuja *et al.* These workers failed, however, to observe the second νM-Cl band in the nickel complex and assigned three bands to νM-Cl in the copper complex. The third band, occurring in the νM-Cl region, was observed[67] at about 255 cm^{-1}, but no assignment

was given.

The bands below 200 cm^{-1} in the chloro complexes (one band each for cobalt and zinc and two bands each for nickel and copper) do not shift on ^{15}N-labelling. They are tentatively assigned to a bending mode of the type δXMX.

In order to assign the $\nu M-X$ frequencies in the bromo complexes, bands which satisfy the same criteria as for the $\nu M-Cl$ vibrations are sought. Additionally, the $\nu M-Br$ vibrations are expected at considerably lower frequencies in accordance with the increased mass of the halogen.

The bands in the region 250-160 cm^{-1} are assigned to the $\nu M-Br$ vibrations. They are insensitive to ^{15}N-labelling and their frequencies follow the stability order Co > Ni < Cu > Zn. The $\nu M-Br$ bands in the nickel complex are shifted about 50 cm^{-1} towards lower frequencies compared with the cobalt complex.

It is interesting to note that the $\nu M-X$ frequencies in the cobalt complexes are higher than in the corresponding zinc complexes. Both complexes are tetrahedral but, whereas the Co(II) complexes are strongly stabilized by the crystal field, the CFSE for Zn(II) is zero. Their metal-ligand frequencies would therefore be expected to have the order Co > Zn. This effect is less pronounced in the $\nu M-N$ frequencies of the cobalt and zinc complexes.

The bands associated with the ring vibration of the ligand occur between 260 and 240 cm^{-1} and show no ^{15}N-sensitivity. In the earlier study of the *o*-toluidine complexes[67], assignments of $\nu M-X$ in the bromo complexes are incomplete, possibly due to their occurrence below 200 cm^{-1}. However, bands in similar positions have been found for the $\nu M-Br$ vibrations in the complexes of *m*-toluidine[85].

TABLE 27. Comparison of the νM-X frequencies (cm^{-1}) for the complexes $[M(o\text{-tol})_2X_2]$.

M	νM-Cl observed	νM-Br calc.[a]	νM-Br observed	(νM-Br)/(νM-Cl) observed
Co	328	265	246	0.75
	297	240	202	0.68
Ni	247	200	192	0.78
	208	168	162	0.78
Cu	302	242	224	0.74
	253	203	169	0.67
Zn	309	247	227	0.73
	294	235	195	0.66

M	νM-Cl observed	νM-I calc.	νM-I observed	(νM-I)/(νM-Cl) observed
Zn	309	226	191	0.62
	294	215	156	0.53

[a] Frequencies were calculated from equation 6; see Chapter I.3.

In the complex $[Zn(o\text{-tol})_2I_2]$, the νM-X frequencies are assigned to two ^{15}N-insensitive bands at 191 and 156 cm^{-1}. Compared to the corresponding chloro complex, the shifts to lower frequencies are between 40 and 60 cm^{-1} larger than the shifts calculated on the basis of the mass increase of the halogen (see Table 27).

The two bands at 410 and 380 cm^{-1}, which shift about 3 cm^{-1} on ^{15}N-labelling, are assigned to the metal-nitrogen stretching frequencies.

5.3 Ligand Vibrations Associated with the Amino Group

The fundamental stretching and bending vibrations of the amino group are readily identified by ^{15}N-labelling of *o*-toluidine and by comparison with the spectra of *p*-toluidine and *m*-toluidine complexes of similar structure[69,85].

In the *o*-toluidine complexes, the ^{15}N-sensitive bands in the range 3400-3200 cm^{-1} are assigned to the antisymmetric and symmetric N-H stretching modes. They correspond with two νN-H bands in the free ligand, shifted between 100 and 200 cm^{-1} to lower frequencies by coordination. A third ^{15}N-sensitive band near 3135 cm^{-1} is observed in both the chloro and bromo complexes. This band corresponds with the ligand band at 3214 cm^{-1} and is associated with the hydrogen bonded νN-H...X vibration (X = Cl, Br, I for the complexes; X = N for *o*-toluidine). The fact that this band is sensitive to both ^{15}N-labelling and halogen substitution, supports the assignment.

In the chloro complex of nickel, the νN-H bands occur at considerably higher frequencies and are not very well defined (see Fig.8). Broadening of these bands is attributed to strong hydrogen bonding

between the amino hydrogens and the water present only in the complexes of nickel. Also, the absence of a third ^{15}N-sensitive band at about 3100 cm^{-1}, assigned to the νN-H...X vibrations in the other complexes, strongly suggests the preference of hydrogen bonding to water rather than halogen, *i.e.* the species N-H...X does not exist in the complex $[Ni(o\text{-tol})_2Cl_2]$.

The νN-H and νN-H...X bands shift between 4 and 10 cm^{-1} to lower frequencies on ^{15}N-labelling. Shifts of this magnitude have been observed for the corresponding bands in halide complexes of *m*- and *p*-toluidine[69,85] and in the isothiocyanate complexes of aniline and *p*-toluidine (see Section 2).

From previous work on similar complexes[69,85] the NH_2 scissoring vibration is expected at about 1600 cm^{-1}. This vibration is represented by strong bands at about 1580 cm^{-1} in the *o*-toluidine complexes, ^{15}N-induced shifts being about 3 cm^{-1}. The corresponding vibration in the ligand occurs some 40 cm^{-1} towards higher frequencies.

The νC-N mode in the *o*-toluidine complexes is assigned to ^{15}N-sensitive bands in the region 1270-1230 cm^{-1}. The position of these bands and the shifts which they undergo are similar to those observed for the corresponding *p*-toluidine complexes of metal(II) halides[69].

In the region 1100-1000 cm^{-1} three or four bands are observed, of which only those of higher frequency, *i.e.* two bands (each) in the chloro complexes of nickel and copper and one band (each) for cobalt and zinc, are ^{15}N-sensitive. They are assigned to the NH_2 twisting mode previously reported[69] to absorb in this region. The corresponding ligand band occurs at 1145 cm^{-1} which is some 20 cm^{-1} higher than the frequency of

NH_2 twisting bands in aniline and *p*-toluidine.

The NH_2 wagging mode, normally observed[69] between 750 and 700 cm^{-1}, is represented by two bands in each of the *o*-toluidine complexes (three bands in the complex $[Zn(o\text{-tol})_2I_2]$). The bands observed at about 830 and 750 cm^{-1} are ^{15}N-sensitive, whereas bands occurring between those limits do not shift on labelling and are associated with the ^{15}N-insensitive ligand band at 753 cm^{-1}.

Among the NH_2 bending modes which are expected to occur in complexes of heterocyclic amines, the NH_2 rocking vibrations normally have the lowest frequency. Generally, they occur between 700 and 600 cm^{-1} and are substantially ^{15}N-sensitive[69,85]. For the *p*-toluidine complexes of metal(II) halides, this vibration has been found to be particularly metal-sensitive[69]. In the *o*-toluidine complexes the NH_2 rocking vibrations occur at slightly lower frequencies compared to the *para*-isomer. Generally, two bands are observed between 650 and 580 cm^{-1}, both of which exhibit substantial shifts (between 7 and 2 cm^{-1}) on ^{15}N-labelling. Their metal-sensitivities are less pronounced than those observed for the NH_2 rocking vibration in the *p*-toluidine complexes.

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THE FAR INFRARED SPECTRA OF PYRIDINE COMPLEXES OF TRANSITION METAL(II) ISOTHIOCYANATES

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ABSTRACT

The infrared spectra (500 - 140 cm^{-1}) of the complexes $[M(pyridine)_n(NCS)_2]$(n = 2, M = Mn, Co, Ni, Cu, Zn; n = 4, M = Mn, Fe, Co, Ni) are discussed. The νM-pyridine and νM-NCS bands are assigned by observing the band shifts induced by isotopic labelling of the coordinated pyridine and isothiocyanate, by comparing the spectra with those of the $[M(pyridine)_2Cl_2]$ complexes and from symmetry considerations based on their known structures. The two species of metal-ligand stretching bands occur within a rather narrow frequency range and there is evidence of some vibrational coupling between these two modes. Some earlier assignments of νM-pyridine bands require revision. The spectra of the yellow $[Fe(py)_4(NCS)_2]$ complex and its violet oxidation product suggest that the oxidation reaction involves the transformation of *trans*-$[Fe(py)_4(NCS)_2]$ into *cis*-$[Fe(py)_3(NCS)_3]$.

INTRODUCTION

The infrared spectra of pyridine (py) complexes of metal(II) isothiocyanates have received considerably less attention than those of metal(II) halides. A review [1] and the more recent literature reveal that no attempts have been made to use the isotopic labelling technique for the assignment of metal-ligand bands in these complexes. We have now applied the technique [2] of independent labelling of of the two species of nitrogen donors to the spectra of the complexes $[M(py)_n(NCS)_2]$ (n = 2,4).

EXPERIMENTAL

The complexes, *trans*-$[M(py)_4(NCS)_2]$ (M = Mn, Fe, Co, Ni) and $[M(py)_2(NCS)_2]$ (M = Cu, Zn) were synthesized by the reported methods [3]. The labelled complexes were similarly prepared from pyridine- of 99% isotopic purity (Merck) and sodium thiocyanate-^{15}N of 96% isotopic purity (Merck, Sharp and Dohme, Canada). The unlabelled and labelled complexes $[M(py)_2(NCS)_2]$ (M = Mn, Co, Ni) were obtained by thermal decomposition of the analogous $[M(py)_4(NCS)_2]$ compounds. Composition and purity of the complexes were established by micro-analysis.

Infrared spectra were observed from Nujol mulls between caesium iodide plates on a Beckman IR-12 spectrophotometer (2200 - 250 cm^{-1}) and from Nujol mulls between polyethylene film on a Perkin-Elmer 180 spectrophotometer (250 - 140 cm^{-1}).

RESULTS AND DISCUSSION

The spectra are depicted in Fig. 1 and the frequency data are recorded in Table 1. Bands shifted by ^{15}NCS-labelling are termed ^{15}NCS-sensitive bands while those shifted by pyridine deuteration are termed *d*-sensitive bands.

In a previous paper [2], a clear distinction between the two species of metal-ligand stretching bands (νM-NH_2 and νM-NCS) in the complexes $[M(an)_2(NCS)_2]$ (an = aniline) was achieved by observing the band shifts induced by ^{15}N-labelling of each nitrogen donor. The success of the technique was aided by the wide frequency separation between the νM-NH_2 (~400 cm^{-1}) and νM-NCS (~200 cm^{-1}) bands. Under these circumstances, very little vibrational coupling is expected to occur. Thus, none of the ^{15}NCS-sensitive bands exhibited any $^{15}NH_2$-sensitivity and none of the $^{15}NH_2$-sensitive bands was shifted by ^{15}NCS-labelling. Furthermore, the magnitude of the shifts induced by donor atom labelling lay well outside the limits of experimental error which are determined by the reproducibility of the absorption maxima in replicate spectral determinations.

In a subsequent infrared study [4] of the complexes $[M(py)_2Cl_2]$, the νM-py bands were assigned by observing the band shifts induced by labelling of the pyridine ring. Since the νM-py frequencies (~200 cm^{-1}) are similar to those characteristic of νM-NCS, some vibrational coupling between these two modes in the complexes $[M(py)_n(NCS)_2]$ is expected to occur. Such coupling has two ramifications with respect to the isotopic assignment technique. Firstly, the coupled bands are expected to shift on both ^{15}NCS- and pyridine-labelling. Secondly, the magnitude of the shift of a coupled band will be smaller than that of a vibrationally-pure band. Both effects are observed in the spectra of the pyridine-

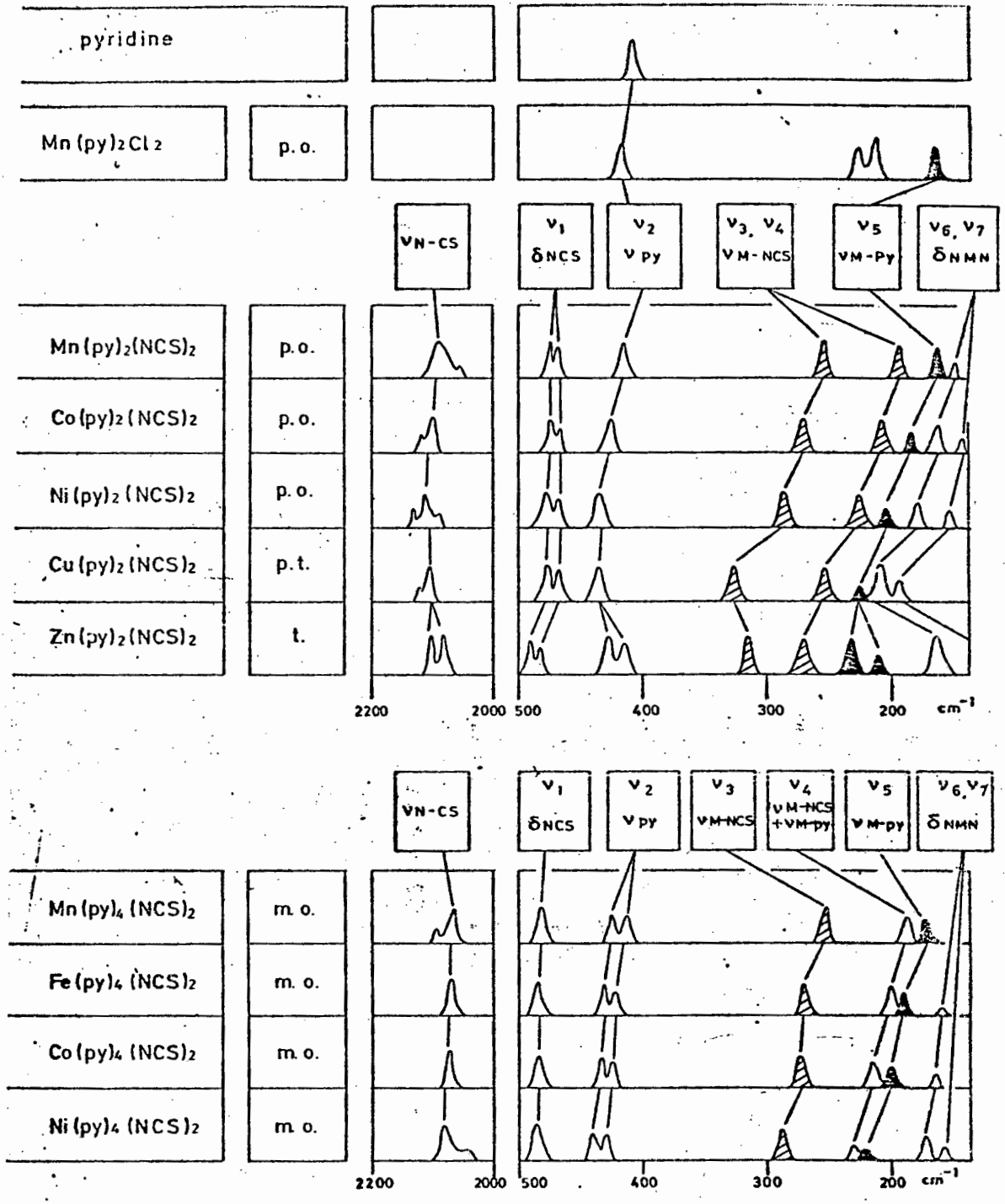

Fig. 1 Infrared spectra of $[M(py)_n(NCS)_2]$ (n = 2,4). The spectra of pyridine and $[Mn(py)_2Cl_2]$ are included for comparison. Abbreviations : p.o. polymeric octahedral, p.t. = polymeric tetragonal, t = tetrahedral, m.o. = monomeric octahedral.

TABLE 1

Frequencies, isotopic shifts (cm^{-1}) and band assignments for complexes $[M(py)_n(NCS)_2]$[a]

Band	Reference	$[Mn(py)_2(NCS)_2]$		$[Co(py)_2(NCS)_2]$		$[Ni(py)_2(NCS)_2]$	
	this work	2094[b](28,1)	νN-CS	2102[b](27,0)	νN-CS	2114[b](29,0)	νN-CS
	5	2095	νN-CS	2099	νN-CS	2100	νN-CS
ν_1	this work	476(3,1)	δNCS	475(3,0)	δNCS	477(0,1)	δNCS
		470(4,0)	δNCS	470(t.b.)	δNCS	469(4,0)	δNCS
	5	475	δNCS	472	δNCS	474	δNCS
		468	δNCS	468	δNCS	466	δNCS
	6	475	δNCS	473	δNCS	477	δNCS
		468	δNCS			469	δNCS
ν_2	this work	418(0,40)	νpy	426(0,40)	νpy	433(0,40)	νpy
	5	417	νpy	422	νpy	429	νpy
	6	417	νpy	425	νpy	432	νpy
ν_3	this work	258(1,0)	νM-NCS	270(0,0)	νM-NCS	285(2,0)	νM-NCS
	5	254	νM-NCS	268	νM-NCS	280	νM-NCS
	6	256	νM-NCS	270	νM-NCS	283	νM-NCS
ν_4	this work	196(0,2)	νM-NCS[c]	208(2,2)	νM-NCS[c]	226(2,4)	νM-NCS[c]
	5	b.r.		213	νM-py	229	νM-py
	6	201	νM-py	211	νM-py	230	νM-py
ν_5	this work	164(1,4)	νM-py	185(1,3)	νM-py	206(1,9)	νM-py
	5	b.r.		b.r.		b.r.	
	6	168	n.a.	n.r.		n.r.	
ν_6	this work	153(t.b.)	δNMN	162(1,3)	δNMN	179(0,3)	δNMN
	5	b.r.		b.r.		b.r.	
	6	155	n.a.	165	n.a.	n.r.	
ν_7	this work	b.r.		145(0,3)	δNMN	155(1,4)	δNMN
	5	b.r.		b.r.		b.r.	
	6	b.r.		b.r.		158	n.a.

Band	Reference	$[Fe(py)_4(NCS)_2]$		$[Co(py)_4(NCS)_2]$		$[Ni(py)_4(NCS)_2]$	
	this work	2066(29,0)	νN-CS	2074[b](27,1)	νN-CS	2084[b](27,0)	νN-CS
	5	2070[g]	νN-CS	2072	νN-CS	2079	νN-CS
ν_1	this work	483(3,0)	δNCS	482(3,0)	δNCS	483(3,0)	δNCS
	5	482[dg]	δNCS	481[d]	δNCS	483[d]	δNCS
	6	-h		483	δNCS	482	δNCS
ν_2	this work	428(0,38)	νpy	431(0,40)	νpy	437(0,38)	νpy
		420(0,38)	νpy	423(0,39)	νpy	430(0,38)	νpy
	5	424[g]	νpy	426	νpy	434	νpy
		420[g]	νpy	420	νpy	429	νpy
	6	-h		433	νpy	438	νpy
				423[e]	νpy	432[e]	νpy
ν_3	this work	271(1,0)	νM-NCS	272(0,0)	νM-NCS	287(0,0)	νM-NCS
	5	266[g]	νM-NCS	268	νM-NCS	280	νM-NCS
	6	-h		272	νM-NCS	287	νM-NCS
ν_4	this work	201(0,3)	νM-py +νM-NCS	212(2,0)	νM-py +νM-NCS	230(0,2)	νM-py +νM-NCS
	5	203[g]	νM-py	215	νM-py	233	νM-py
	6	-h		212	νM-py	232	νM-py
ν_5	this work	193(0,4)	νM-py	202(2,4)	νM-py	220(0,4)	νM-py
	5	b.r.		205	νM-py	n.r.	
	6	-h		204	n.a.	n.r.	
ν_6	this work	163(0,2)	δNMN	165(t.b.)	δNMN	172(1,3)	δNMN
	5	b.r.		b.r.		b.r.	
	6	-h		170	n.a.	174	n.a.
ν_7	this work	b.r.		b.r.		160(1,7)	δNMN
	5	b.r.		b.r.		b.r.	
	6	-h		b.r.		164	n.a.

[a]Abbreviations : b.r. = beyond range of measurement, n.a. = not assigned, n.r. = not reported, t.b. = too broad for determination of shift. Figures in parentheses following the frequencies are the shifts (nearest integral values in cm^{-1}) towards lower frequency induced by ^{15}NCS-labelling (first figure) and pyridine deuteration (second figure). Shifts < 1 cm^{-1} are not regarded as significant and are reported as zero shifts.

[b] Sharp shoulders on νN-CS bands ignored (see Fig. 1).

[c] Some *d*-sensitivity in these bands indicates coupling with νM-py.

[d] Shoulders reported to precede these bands by approximately 2 cm^{-1} were not observed in this work.

[e] Additional bands reported near 400 cm^{-1} (not observed in present work nor cited in reference 5).

[f] Coupled with νM-NCS.

[g] Compound incorrectly formulated as *cis*-isomer.

[h] Compound not studied.

isothiocyanate complexes. The existence of bands sensitive to labelling of both species of nitrogen donors provides evidence for some coupling between νM-py and νM-NCS. The problem of the small shifts induced by ^{15}NCS-labelling (frequently on the borderline of significance) was overcome by comparing the spectra of the complexes $[M(py)_2(NCS)_2]$ with the structurally analogous $[M(py)_2Cl_2]$ in the expectation that substitution of chloride by isothiocyanate would cause significant shifts in νM-X (X = Cl, NCS) but relatively small shifts in νM-py.

The bis*(pyridine) complexes* $[M(py)_2(NCS)_2]$ *(M = Mn, Co, Ni)*

The Co^{II} complex has polymeric octahedral structure with bridging -NCS- units [7]. Since the spectra of the Mn^{II} and Ni^{II} complexes exhibit a band-for-band correspondence with that of Co^{II}, including the feature diagnostic [1] of NCS bridging (doubling of the 470 cm^{-1} δNCS band) they are also considered to be octahedral polymers. The spectrum of each of these complexes has seven bands within the range 500 - 140 cm^{-1} (the band of lowest frequency for the Mn^{II} complex lies beyond the low frequency limit of measurement).

Following the numbering system depicted in Fig. 1, ν_1 is firmly assigned to the δNCS vibration by virtue of its position [1], its ^{15}NCS-sensitivity and its doublet nature which is characteristic [1] of bridging -NCS- units. ν_2 is the 406 cm^{-1} out-of-plane ring vibration of pyridine, raised some 20 to 30 cm^{-1} by coordination. The origin of this band is clear from its high *d*-sensitivity : it undergoes a 40 cm^{-1} shift towards lower frequency on deuteration of pyridine [4].

Since neither pyridine nor the isothiocyanate ion absorbs below 400 cm^{-1}, all lower frequency bands originate in metal-ligand modes. Although the ^{15}NCS-sensitivity of ν_3 is not significant (< 1 cm^{-1}) it is assigned to a νM-NCS vibration since it disappears on replacing isothiocyanate by chloride. An alternative assignment (νM-S) for a band which is both ^{15}NCS- and *d*-sensitive is ruled out by recurrence of the band in the spectra of the monomeric $[M(py)_4(NCS)_2]$ complexes (in which there is no M-S bonding) at a practically identical position. Moreover, the crystallographic data [7] for the polymeric octahedral complexes of Co^{II} and Cu^{II} suggest that the M-SCN bonds are weaker than the M-NCS bonds since the M-S distances (~2.8 Å) are well in excess of those observed in monomeric thiocyanate complexes whereas the M-N distances are similar to those observed in monomeric isothiocyanate complexes. ν_4 is a second νM-NCS band which exhibits measurable ^{15}NCS-sensitivity in the Co^{II} and Ni^{II} complexes but also slight *d*-sensitivity, indicating that it is not entirely free from coupling with νM-py.

ν_5 is firmly assigned to νM-py since it has the highest *d*-sensitivity of the bands below 400 cm^{-1} and it is very close to the position of νM-py [4] in the structurally-analogous $[M(py)_2Cl_2]$ complexes. Since the existence of two νM-NCS and one νM-py band satisfies the requirements [8] of C_s symmetry for the complexes $[M(py)_2(NCS)_2]$, ν_6 and ν_7, which exhibit some *d*-sensitivity, are assigned to the δNMN modes.

The bis*(pyridine) complexes* $[M(py)_2(NCS)_2]$ *(M = Cu, Zn)*

These complexes differ structurally from those of Mn^{II}, Co^{II} and Ni^{II}. The Cu^{II} complex is polymeric tetragonal with bridging NCS

Structural implications of the spectra of $[Fe(py)_4(NCS)_2]$ *and its oxidation product*

The complex $[Fe(py)_4(NCS)_2]$ deserves special mention because of earlier confusion concerning its identity [10]. As synthesized, the complex is yellow but slowly darkens in air, yielding the so-called black form (actually deep violet in transmitted light). Originally, the yellow and violet compounds were thought [11] to be *cis*- and *trans*-$[Fe(py)_4(NCS)_2]$, respectively. More recent examination of their Mössbauer, esr, electronic and infrared spectra, X-ray powder patterns, magnetic moments and chemical properties [10] has established beyond reasonable doubt that the violet form is the normal yellow *trans*-$[Fe(py)_4(NCS)_2]$ isomer contaminated with a violet Fe^{III} oxidation product, most probably $[Fe(py)_3(NCS)_3]$. The infrared measurements were not extended below 200 cm^{-1} and it could not be established with certainty which isomer of the Fe^{III} compound resulted from the oxidation.

The yellow Fe^{II} complex is undoubtedly *trans*-$[Fe(py)_4(NCS)_2]$ since its spectrum (Fig. 1) is identical with the other $[M(py)_4(NCS)_2]$ complexes for two of which *trans*-configuration has been crystallographically established [9]. Furthermore, the spectrum yields one νM-py and one νM-NCS band as required for the *trans* (D_{4h}) isomer whereas the *cis* (C_{2v}) isomer would require four νM-py and two νM-NCS bands.

A sample of the violet oxidation product, obtained by recrystallization of yellow *trans*-$[Fe(py)_4(NCS)_2]$ from chloroform, yields an infrared spectrum (Fig. 2) comprising bands which correspond in position with those of the yellow Fe^{II} complex and additional bands at higher frequencies. These high-frequency shifts of metal-ligand bands are expected [12] to accompany the increase in oxidation state $Fe^{II} \rightarrow Fe^{III}$ while the coordination number remains constant. Thus, the νM-NCS band (ν_3) at 271 cm^{-1} in the Fe^{II} spectrum becomes a doublet in the spectrum of the oxidation product with peaks at 313 and 296 cm^{-1}. Similarly,

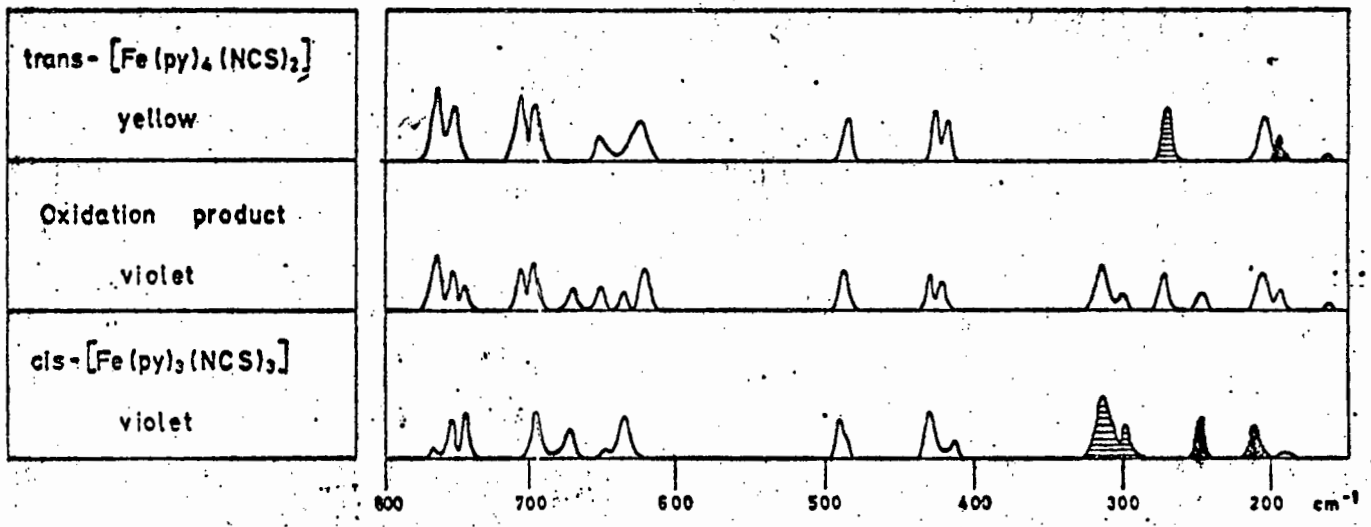

Fig. 2. Infrared spectra of *trans*-$[Fe(py)_4(NCS)_2]$, its oxidation product and *cis*-$[Fe(py)_3(NCS)_3]$. Shaded bands : νFe-NCS, Solid bands : νFe-py.

the coupled (νM-py + νM-NCS) band at 201 cm^{-1}, with its vibrationally-pure νM-py shoulder at 193 cm^{-1}, is resolved into two widely-separated bands at 253 and 219 cm^{-1} in the spectrum of the oxidation product suggesting that the latter contains *cis*-$[Fe(py)_3(NCS)_3]$. The C_{3v} symmetry of this complex requires two νM-NCS and two νM-py infrared-active modes whereas the *trans*-$[Fe(py)_3(NCS)_3]$ isomer (C_{2v} symmetry) would require three of each. The oxidation of the yellow Fe^{II} complex is therefore considered to involve the transformation: *trans*-$[Fe(py)_4(NCS)_2] \rightarrow$ *cis*-$[Fe(py)_3(NCS)_3]$.

In order to confirm the identity of the oxidation product, a sample of *cis*-$[Fe(py)_3(NCS)_3]$ was prepared from ferric thiocyanate and pyridine [9]. The spectrum of this compound contains bands which correspond precisely, in position, with the additional bands in the spectrum of the oxidation product.

Comparison of present assignments with those previously reported

Table 1 lists, for comparison with the present work, the assignments which result from the two principal ealier studies [5,6] on pyridine-isothiocyanate complexes. There is essentially little difference between the earlier and present assignments for νN-CS, ν_1, ν_2 and ν_3. ν_4 is now preferentially assigned to νM-NCS rather than νM-py although the observed *d*-sensitivity of this band clearly indicates that some coupling with νM-py occurs in several of the complexes. ν_5 is now regarded as the principal νM-py band since it has a higher *d*-sensitivity than ν_4. The νM-py values are now consistent with the range of νM-py in the complexes $[M(py)_2Cl_2]$ for which erroneously high values of νM-py had also previously been reported [4]. In the earlier reports [5,6] on the spectra of the pyridine-isothiocyanate complexes, ν_5 was either beyond the range of measurement or, if observed, was not assigned. A single exception is the complex $[Co(py)_4(NCS)_2]$ in which ν_5 was assigned to νCo-py, in agreement with the

present work. In earlier studies, ν_6 and ν_7 were generally unobserved or unassigned.

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THE FAR INFRARED SPECTRA OF PYRIDINE ADDUCTS OF NICKEL(II) ACETYLACETONATE

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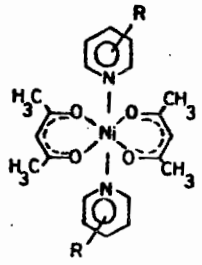
ABSTRACT

The infrared spectrum (650—150 cm^{-1}) of *trans*-$[Ni(AA)_2(py)_2]$ (where AA = acetylacetonate anion and py = pyridine) is discussed in relation to the band shifts induced by deuteration of the pyridine ring and substitution of the Ni^{II} ion by Co^{II} and Zn^{II}. The results lead to a revision of some previously-proposed assignments based on isotopic labelling of the metal ion. The effects on the spectra which result from introducing a variety of substituents into the pyridine ring are discussed. After allowing for mass effects, electron-withdrawing pyridine substituents are found to decrease ν(Ni—N). An opposite trend is exhibited by ν(Ni—O).

INTRODUCTION

In a previous paper [1], the infrared spectra (in the caesium bromide region) of a series of variously-substituted *trans*-pyridine adducts of Ni^{II} acetylacetonate (formula I) were discussed. Empirical assignments of the carbonyl and nickel—oxygen stretching bands, ν(C—O) and ν(Ni—O), were made and their frequencies were found to correlate with the Hammett σ-values of the substituents. Electron-withdrawing substituents were found to increase ν(Ni—O) and were assumed to decrease ν(Ni—N). The effect on ν(Ni—N) remains unsubstantiated because this band was considered to lie beyond the range of measurement (below 250 cm^{-1}). Subsequent work [2] in this laboratory has shown that ν(Ni—N) in $[NI(py)_2Cl_2]$ occurs at 190 cm^{-1}.

The far-infrared spectra of the adducts (I) are of interest for several reasons. Firstly, present facilities enable the spectra to be extended from 250 to 150 cm^{-1} where ν(Ni—N) is expected to occur. Secondly, deuteration of pyridine enables unambiguous identification of the ν(Ni—N) and pyridine ligand vibrations to be made. Thirdly, substitution of Ni^{II} and Co^{II}



(I)

and Zn^{II} may be used to corroborate the assignments based on the deuteration study. Fourthly, the effects of varying the pyridine substituents enable the hypothesis [1] that electron-withdrawing groups will shift ν(Ni—O) and ν(Ni—N) in opposite directions to be tested. Finally, assignments resulting from a metal ion labelling study [3] of the pyridine complex (I, R=H) may be examined in the light of these results.

EXPERIMENTAL WORK, RESULTS AND DISCUSSION

Compounds were prepared by reported methods [1]. Purity and composition were determined by microanalysis (C, H and N). Pyridine-d_5 of 99% isotopic purity was supplied by Prochem BOC Ltd. Infrared spectra were determined on Nujol mulls between caesium iodide plates on a Beckman IR-12 spectrophotometer (650—250 cm^{-1}) and between polyethylene plates on a Perkin—Elmer 180 spectrophotometer (250—150 cm^{-1}). Replicate determination of band frequencies yielded a reproducibility within 0.5 cm^{-1}.

The far-infrared spectra of the pyridine and pyridine-d_5 adducts of Co^{II}, Ni^{II} and Zn^{II} bis(acetylacetonate) complexes are shown in Fig. 1. The Zn^{II} complex is uniquely 5-coordinate and probably has square pyramidal structure by analogy [4] with $[Zn(AA)_2(H_2O)]$. Spectra of the substituted pyridine adducts are depicted in Fig. 2. Bands shifted by metal ion labelling are termed ^{1}M-sensitive bands; those shifted by metal ion substitution are called M-sensitive bands; those affected by deuteration of the pyridine ring are referred to as *d*-sensitive bands and those which move on varying the pyridine substituents are termed R-sensitive bands.

Infrared spectrum of $[Ni(AA)_2(py)_2]$

The ^{1}M-, M- and *d*-sensitivities of the bands in the spectrum of this complex are compared in Table 1. Based on the results of normal coordinate analyses of metal acetylacetonates and in view of its small ^{1}M-sensitivity, ν_1 has been assigned [3] to the $\pi[(CH_3)CCO]$ vibration. This assignment is now discounted by its high *d*-sensitivity ($\Delta\nu$ = 96 cm^{-1}) which is similar in magnitude to that exhibited (Fig. 1) by the 604 cm^{-1} ligand band in pyridine

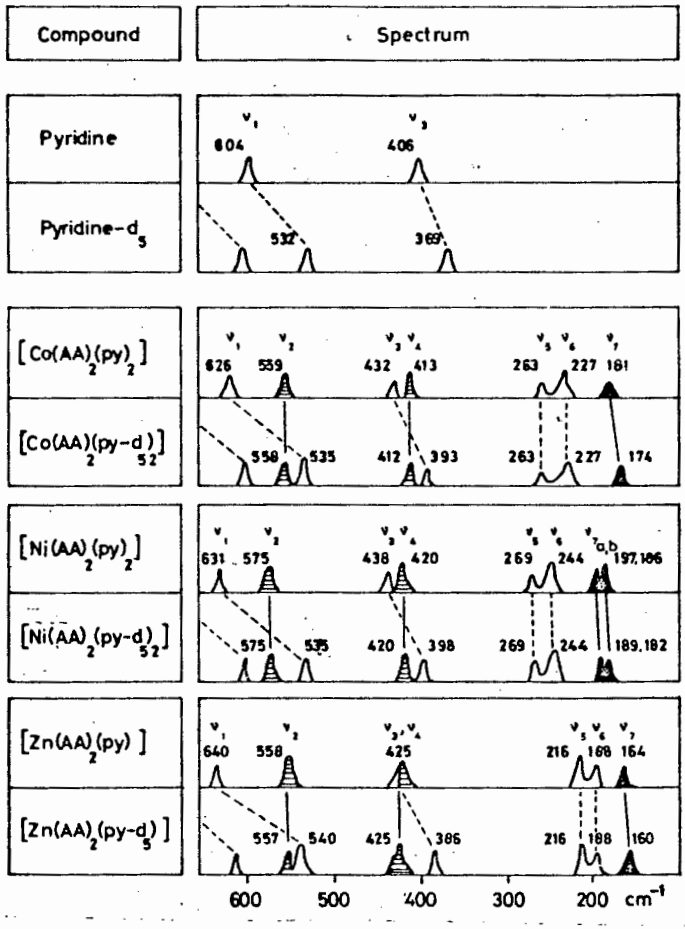


Fig. 1. Infrared spectra (650—150 cm^{-1}) of pyridine and pyridine-d_5 adducts of Co^{II}, Ni^{II} and Zn^{II} bis (acetylacetonates). ν_1 and ν_3 are pyridine bands; ν_2 and ν_4 (shaded) are coupled ν(M—O) bands; ν_5 and ν_6 are pure ν(M—O) bands; ν_7 (solid) is the ν(M—N) band.

($\Delta\nu$ = 72 cm^{-1}) and by the 635 cm^{-1} band [2] in $[Ni(py)_2Cl_2]$ ($\Delta\nu$ = 99 cm^{-1}). Under these circumstances, ν_1 is firmly assigned to the pyridine vibration.

ν_2 has a significantly greater ^{i}M-sensitivity than ν_1. This has led [3] to its assignment to a coupled ν(Ni—O) band. Its R-sensitivity has also been cited [1] as support for this assignment. In the present work ν_2 is observed to be significantly M-sensitive and completely unaffected by pyridine deuteration. The combined evidence supports its assignment to a ν(Ni—O) band.

That ν_3 has an ^{i}M-sensitivity comparable with ν_2 has led [3] to its assignment as a second coupled ν(Ni—O) band. This assignment is discounted by the present work since its substantial *d*-sensitivity ($\Delta\nu$ = 40 cm^{-1}) is similar to the *d*-sensitivity ($\Delta\nu$ = 37 cm^{-1}) of the 406 cm^{-1} ligand band in the spectrum of pyridine and its position (438 cm^{-1}) is practically identical with that [2] of the pyridine vibration (440 cm^{-1}) in $[Ni(py)_2Cl_2]$. Hence ν_3 is firmly assigned as the pyridine vibration of lowest frequency.

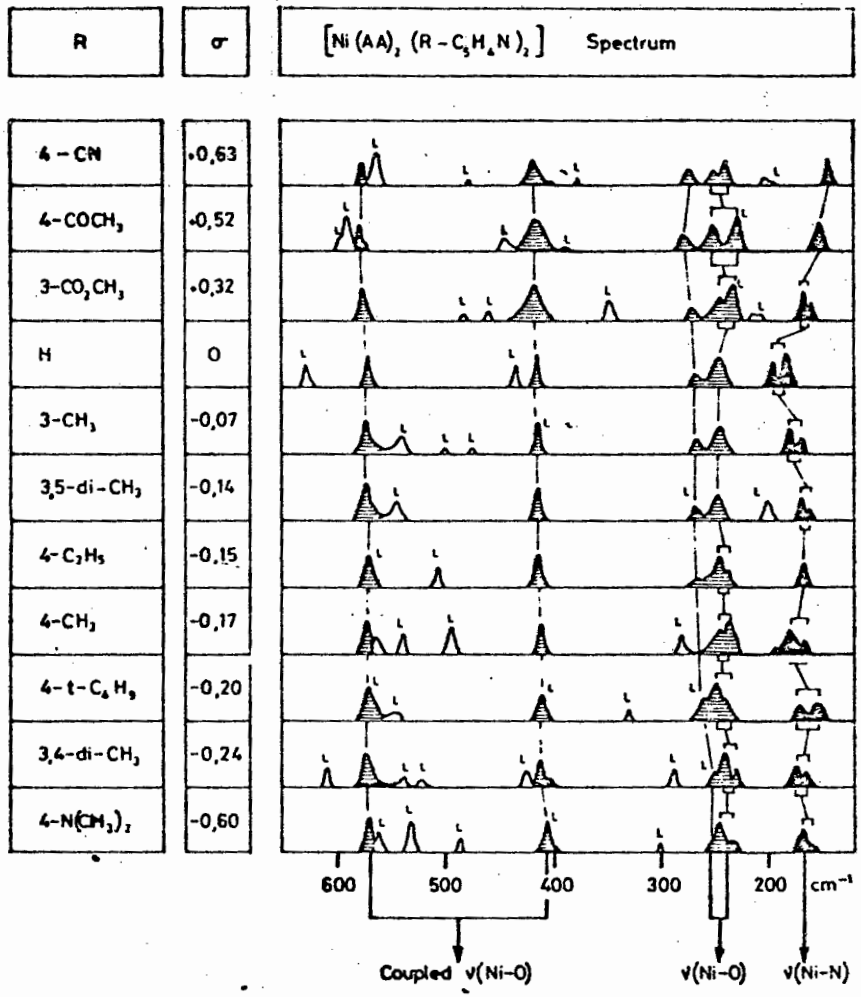


Fig. 2. Infrared spectra of substituted pyridine adducts. Shaded peaks: ν(Ni—O), solid peaks: ν(Ni—N), L = bands occurring at or near regions of absorption in the spectra of the free pyridines.

The weak ^{1}M-sensitivity of ν_4 has led [3] to its assignment to an (unspecified) chelate ring vibration. It has also been assigned [1] to ν(Ni—O) on the grounds of its R-sensitivity and the fact that its position (420 cm^{-1}) is close to that of a strong band at 429 cm^{-1}, assigned to ν(Ni—O) in the spectrum of $[Ni(AA)_2(H_2O)_2]$. Our present finding that the band is moderately M-sensitive but completely insensitive to pyridine deuteration is consistent with its assignment to ν(Ni—O).

Although ^{18}O-labelling has not been applied to the compound $[Ni(AA)_2(py)_2]$, this technique has been used [6] to assign ν(M—O) in certain simple metal acetylacetonates such as $[Cr(AA)_3]$. In these compounds, the significant

TABLE 1

Frequencies (cm^{-1}) of far-infrared bands in $[Ni(AA)_2(py)_2]$ and their ^{i}M-, *d*- and M-sensitivities in cm^{-1}

Band no.	Frequency	^{i}M-sensitivity [3][a]	*d*-sensitivity[b]	M-sensitivity[c] Co	M-sensitivity[c] Zn	Previous assignment [3]	Present assignment
ν_1	631	0.5	96	5	−9	$\pi((CH_3)CCO)$	ν(py)[d]
ν_2	575	0.8	0	16	17	ν(Ni—O) + ring[e]	coupled ν(Ni—O)
ν_3	438	0.8	40	6	13	ν(Ni—O) + ν(C—CH_3)	ν(py)[f]
ν_4	420	0.4	0	7	−5	ring[g]	coupled ν(Ni—O)
ν_5	269	5.4	0	6	53	ν(Ni—O)	ν(Ni—O)
ν_6	244	3.8	0	17	56	ν(Ni—N)	ν(Ni—O)
ν_{7a}	197[h]	n.o.[i]	8	11[j]	28[j]	n.o.[i]	ν(Ni—N)
ν_{7b}	186	n.r.[k]	4			ring	

[a] ^{i}M-sensitivity = {frequency for $[^{58}Ni(AA)_2(py)_2]$} − {frequency for $[^{62}Ni(AA)_2(py)_2]$}.
[b] *d*-sensitivity = {frequency for $[Ni(AA)_2(py)_2]$} − {frequency for $[Ni(AA)_2(py\text{-}d_5)_2]$}.
[c] M-sensitivity(Co) = {frequency for $[Ni(AA)_2(py)_2]$} − {frequency for $[Co(AA)_2(py)_2]$}.
M-sensitivity(Zn) = {frequency for $[Ni(AA)_2(py)_2]$} − {frequency for $[Zn(AA)_2(py)_2]$}.
[d] A_1 mode, δ(ring) [5]. [e] Independently assigned to ν(Ni—O) [1]. [f] B_1 mode, γ(ring) [5].
[g] Independently assigned to ν(Ni—O) [1]. [h] Shoulder. [i] n.o. = shoulder not observed [3].
[j] ν(Ni—N) taken as mean of 197, 186 cm^{-1} bands. [k] n.r. = shift not reported [3].

^{18}O-sensitivity of bands near 590 and 420 cm^{-1} has led to their assignment to ν(M—O). That the positions of these bands are very similar to those of ν_2 and ν_4 in the spectrum of $[Ni(AA)_2(py)_2]$, supports our assignment of these bands to ν(Ni—O). However, these bands are unlikely to originate in pure (uncoupled) ν(Ni—O) modes because of their small ^{i}M-, M- and R-sensitivities relative to ν_5 and ν_6 (see below).

That ν_5 (at 269 cm^{-1}) is the most strongly ^{i}M-sensitive band in the spectrum of $[Ni(AA)_2(py)_2]$ has led [3] to its assignment as a pure ν(Ni—O) band. This assignment is supported here by its substantial M- and R-sensitivity and its complete absence of *d*-sensitivity. Furthermore, the spectrum of $[Ni(AA)_2(H_2O)_2]$ exhibits a band at 281 cm^{-1} which undoubtedly has the same origin and excludes the possibility that ν_5 is associated with coordinated pyridine. Entirely similar observations pertain to ν_6 (at 244 cm^{-1}). Its earlier assignment [3] to ν(Ni—N) on the grounds of its substantial ^{i}M-sensitivity is definitely discounted by complete absence of *d*-sensitivity and the occurrence of a corresponding band at 222 cm^{-1} in the spectrum of $[Ni(AA)_2(H_2O)_2]$. All the available evidence suggests that ν_6 is a second, pure ν(Ni—O) band.

Below 200 cm^{-1}, the spectrum of $[Ni(AA)_2(py)_2]$ comprises a shoulder at 197 cm^{-1} (ν_{7a}) and a peak at 186 cm^{-1} (ν_{7b}). These are the most strongly M-sensitive bands in the spectrum and are the only bands below 400 cm^{-1} to exhibit any *d*-sensitivity. Furthermore, these bands shift on varying the pyridine substituent, R, in the opposite direction to ν(Ni—O) (Fig. 2) and they occur in a region free from absorption in the spectrum of $[Ni(AA)_2(H_2O_2)]$.

All of these observations support their assignment to ν(Ni—N) modes and an earlier assignment [3] to a chelate ring mode is definitely discounted.

M-sensitivity of bands in pyridine adducts of Co^{II}, Ni^{II} and Zn^{II} acetylacetonates

Earlier work [7] has shown that metal—ligand vibrations are in the sequence Co < Ni > Zn for a series of octahedral complexes comprising these metal(II) ions bound within the same ligand system. In the adducts studied here, the Zn^{II} complex is uniquely 5-coordinate. Relative to the Ni^{II} complex, the lower coordination number of Zn^{II} will serve [8] to raise the frequencies of the zinc—ligand vibrations while the zero crystal field stabilization energy (CFSE) of Zn^{II} will serve to lower the zinc—ligand frequencies. Thus the observed order of metal—ligand frequencies may be Co < Ni > Zn or Co < Ni < Zn depending on whether the position of Zn^{II} is determined primarily by coordination number of CFSE effects. In the present work it is observed that the sequence Co < Ni > Zn obtains for the principal ν(M—O) and ν(M—N) bands. Hence, the CFSE effect overrides the coordination number effect in determining the zinc—ligand frequencies.

Effects of substitution in the pyridine ring

Figure 2 illustrates the spectra of variously-substituted pyridine adducts of Ni^{II} acetylacetonate. In an earlier paper [1] it was shown that ν_2 and ν_4 (coupled ν(Ni—O) bands) are shifted to higher frequency by electron-withdrawing substituents. The present work confirms this trend for the pure ν(Ni—O) band, ν_5, and also probably for ν_6, although the appearance of shoulders on ν_6 in the spectra of complexes with electron-releasing substituents introduces difficulties in determining precise frequencies in this region.

So far as the R-sensitivity of ν(Ni—N) is concerned, it is clear that electron-withdrawing substituents cause a substantial shift of ν_7 towards lower frequency, i.e. the opposite trend shown by ν(Ni—O). Thus, an earlier prediction [1] that the electronic effects of pyridine substituents would cause ν(Ni—O) and ν(Ni—N) to shift in opposite directions is now confirmed. The effect of electron-releasing substituents is much smaller and ν(Ni—N) remains approximately constant for $\sigma < 0$.

In order to confirm that the shift of ν(Ni—N) towards lower frequency caused by electron-withdrawing substituents does not originate solely in the mass effects of R, allowance was made for the mass effects by assuming that the pyridine ring is vibrating against the mass of the remainder of the molecule during the Ni—N stretching vibration. The ν(Ni—N) values calculated to arise from the mass effects of R are given by the well-known relationship [9]

$$\nu_1 = \nu_7 [\{m_1 m_2/(m_1 + m_2)\}\{(M_1 + M_2)/M_1 M_2\}]^{\frac{1}{2}} \quad (1)$$

where m_1 = mass of pyridine; m_2 = mass of species $[Ni(AA)_2(py)]$; M_1 = mass of substituted pyridine; M_2 = mass of species $[Ni(AA)_2(R{-}C_5H_4N)]$; and ν_7 is the mean frequency (191.5 cm^{-1}) of the principal ν(Ni—N) bands in the pyridine complex (R=H). The difference

$$\Delta\nu = \nu_7 - \nu_1 \qquad (2)$$

gives the shift in ν(Ni—N) arising from the mass effect of R, while $\nu(Ni{-}N)_{corr}$, defined by

$$\nu(Ni{-}N)_{corr} = \nu(Ni{-}N) + \Delta\nu \qquad (3)$$

is the value of ν(Ni—N) corrected for the mass effect. The difference between the observed and corrected ν(Ni—N) values is attributed to the electronic effects of R.

From the $\nu(Ni{-}N)_{corr}$ values in Table 2, it is clear that the tendency for electron-withdrawing substituents to decrease ν(Ni—N) (which was observed before taking the mass effect into account) retains its direction and significance after allowing for the mass effects of R. The effect of electron-releasing substituents, on the other hand, is negligible, the $\nu(Ni{-}N)_{corr}$ values remaining within a relatively narrow range of values above and below the ν(Ni—N) value of the pyridine adduct.

TABLE 2

Frequencies of principal νNi—O) and ν(Ni—N) bands and ν(Ni—N) corrected for mass effect of R in $[Ni(AA)_2(R\text{-}C_5H_4N)_2]$; units are cm^{-1}

R	σ	ν_1 (eqn. 1)	$\Delta\nu$ (eqn. 2)	$\nu(Ni{-}N)_{corr}$ (eqn. 3)	ν(Ni—O) (observed)	ν(Ni—O)
4-CN	+0.63	170.5	21	166	145	275,244[a]
4-$COCH_3$	+0.52	160	31.5	187.5	156	278,241[a]
3-CO_2CH_3	+0.32	152	39.5	206	166.5[a]	272,242[a]
H	0	—	—	(191.5)	191.5[a]	269,244
3-CH_3	−0.07	178.5	13	188	175[a]	269,244
3,5-di-CH_3	−0.14	168.5	23	189	166[a]	268,244
4-C_2H_5	−0.15	168.5	23	191	168	269,243[a]
4-CH_3	−0.17	178.5	13	185	172[a]	—[b], 243[a]
4-*t*-C_4H_9	−0.20	153	38.5	204	165.5[a]	266,245[a]
3,4-di-CH_3	−0.24	168.5	23	191.5	168.5[a]	264,240[a]
4-$N(CH_3)_2$	−0.60	159.5	32	196	164[a]	—[b], 241[a]
py-d_5	0	186.5	5	190.5	185.5[a]	269,244

[a]Mean of doublet.
[b]Masked by neighbouring band.

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INFRARED SPECTRA OF BIS(ANILINE) AND BIS (*p*-TOLUIDINE) METAL(II) ISOTHIOCYANATE COMPLEXES

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ABSTRACT

The infrared spectra of eight complexes of general formula $[ML_2(NCS)_2]$ (M = Co, Ni, Cu, Zn; L = aniline or *p*-toluidine) have been determined over the range 4000—150 cm^{-1}. Colour, magnetic moments and IR spectra are consistent with polymeric octahedral coordination in the Co(II) and Ni(II) complexes and polymeric tetragonal coordination in the Cu(II) complexes, while the Zn(II) complexes are assigned polymeric octahedral (L = aniline) and tetrahedral (L = *p*-toluidine) structure on the basis of their IR spectra. Independent ^{15}N-labelling of the nitrogen atoms of the amino and isothiocyanate groups yields assignments for the internal vibrations of both groups and enables the metal—amine and metal—isothiocyanate stretching vibrations ($\nu M—NH_2$ and $\nu M—NCS$) to be distinguished. Both $\nu M—NH_2$ and $\nu M—NCS$ are metal ion dependent in the Irving—Williams sequence (Co < Ni < Cu > Zn) expected from their proposed structures while the $\nu N—H$ and $\nu N—CS$ vibrations are inversely related to the masses of the coordinated metal ions.

INTRODUCTION

No systematic study of the IR spectra of metal complexes of general formula $[ML_2(NCS)_2]$ (where L is an aromatic amine) has been reported. Since an empirical approach to the assignment problem in the spectra of these complexes would necessarily be subject to conjecture in view of the presence of two species of metal—nitrogen bond (distinguished in this paper as $M—NH_2$ and M—NCS), we have approached this problem by observing the effects on the spectra of independent ^{15}N-labelling of each species of nitrogen donor and by observing the effects of metal ion substitution in relation to the structures of the complexes. The results enable a clear distinction to be made between the internal vibrations of the amino and isothiocyanate groups and between the two types of metal—ligand stretching vibration

EXPERIMENTAL

The complexes were prepared by slow addition of the amine (0.0022 mole) in ethanol to an aqueous solution of the metal sulphate (0.001 mole) and sodium thiocyanate (0.002 mole), restricting the total volume to

approximately 20 ml. The precipitated complexes were collected by filtration, washed successively with water and ethanol (water only for zinc complexes) and dried under reduced pressure over silica gel. The labelled complexes were similarly prepared from ^{15}N-aniline or ^{15}N-*p*-toluidine of 96 atom-% isotopic purity (British Oxygen Co., Prochem Division) and ^{15}N-sodium thiocyanate of 97 atom-% isotopic purity (Merck, Sharp and Dohme, Canada, Ltd.). Composition and purity of the complexes were established by microanalysis.

Infrared spectra were obtained from Nujol mulls between caesium iodide plates on a Beckman IR-12 spectrophotometer (4000—250 cm^{-1}) and from Nujol mulls between polyethylene film (thickness approximately 1 mm) on a Perkin—Elmer 180 spectrophotometer (250—150 cm^{-1}). Replicate spectra of principal bands yielded a reproducibility of better than 0.4 cm^{-1}.

Room temperature magnetic moments (determined on a Newport—Stanton Gouy balance) yielded the following results: $[Co(aniline)_2(NCS)_2]$, μ = 4.95 BM; $[Ni(aniline)_2(NCS)_2]$, μ = 3.40 BM; $[Co(p\text{-toluidine})_2(NCS)_2]$, μ = 5.13 BM; $[Ni(p\text{-toluidine})_2(NCS)_2]$, μ = 3.19 BM.

RESULTS AND DISCUSSION

No crystallographic studies of the complexes studied here have been reported but information is available on the structures of complexes containing either an aromatic amine or the isothiocyanate ion; thus, X-ray data, electronic spectra and magnetic moments [1—4] indicate that the complexes $[Zn(py)_2(NCS)_2]$, $[M(aniline)_2Cl_2]$ and $[M(p\text{-toluidine})_2Cl_2]$ are tetrahedral (M = Co, Zn), polymeric octahedral (M = Ni) or polymeric tetragonal (M = Cu) while a pink octahedral isomer of $[Co(aniline)_2Cl_2]$ is also known.

The colours of the Co(II) and Ni(II) complexes studied here (pink and green, respectively) and their magnetic moments are consistent [5] with polymeric octahedral coordination while the band-for-band correspondence of their far-IR spectra also suggests that they are isostructural. The Cu(II) complexes exhibit band patterns similar to those of the Co(II) and Ni(II) complexes but the metal ion dependence of both the νM—NH_2 and νM—NCS vibrations viz. Co < Ni < Cu > Zn (the Irving—Williams [6] stability sequence) implies [7] that the Cu(II) complexes have polymeric tetragonal structure. The band pattern of the Zn(II) aniline complex resembles that of the other aniline complexes suggesting that it also has polymeric octahedral structure while the spectrum of the Zn(II) *p*-toluidine complex has features which (as subsequent discussion will show) point to tetrahedral coordination.

Infrared Spectra

In the ensuing discussion, labelling of the amino and isothiocyanate nitrogen atoms will be distinguished by the notation $^{15}NH_2$ and ^{15}NCS. Bands shifted by ^{15}N-labelling are termed ^{15}N-sensitive and those shifted by

metal ion substitution are termed M-sensitive. All ^{15}N-induced shifts quoted are towards lower frequencies. The two species of C—N stretching vibration are distinguished by the notation νC—N (where C is the carbon atom of the aromatic ring and N is the amino nitrogen atom) and νN—CS where N and C are atoms of the isothiocyanate group. Spectra of the ligands and complexes are shown in Fig. 1 and the frequencies and shifts are given in Table 1.

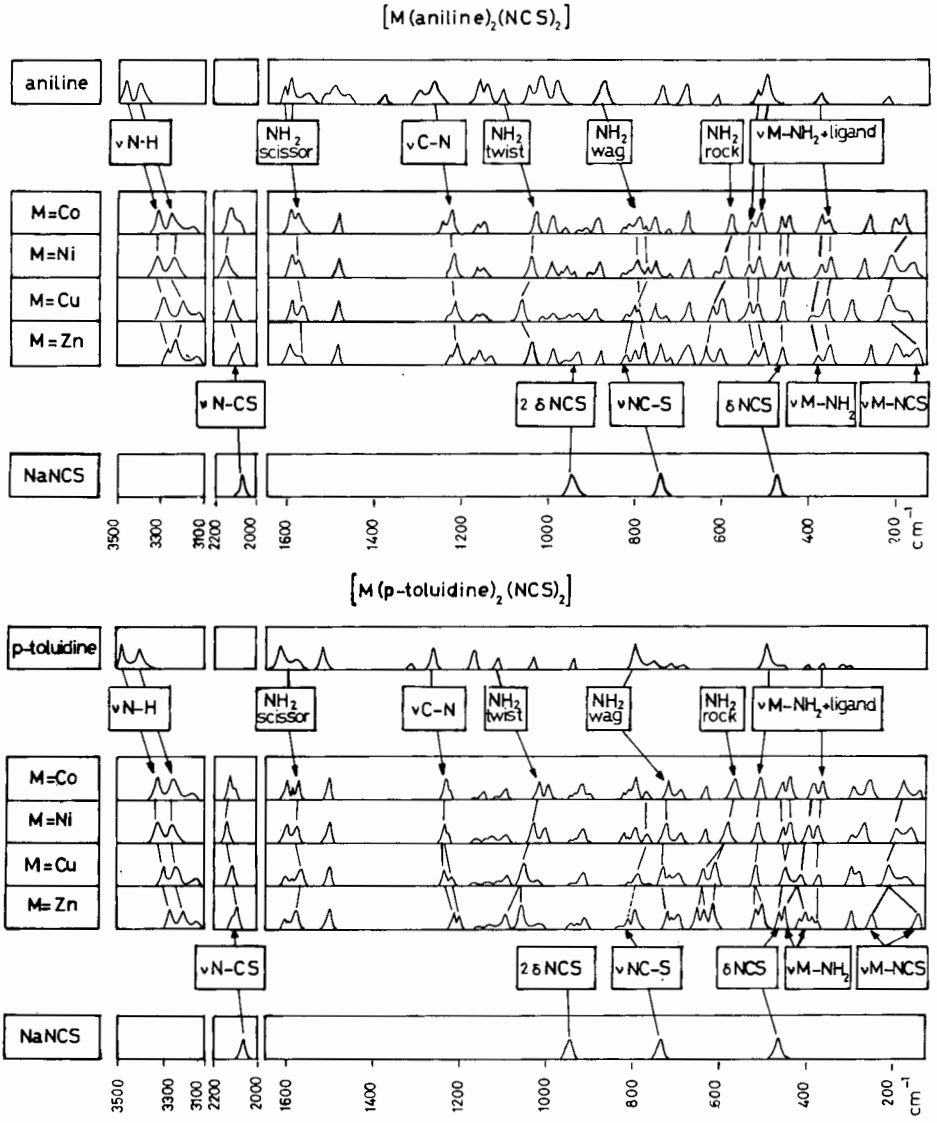

Fig. 1. Infrared spectra of complexes $[ML_2(NCS)_2]$ (L = aniline, *p*-toluidine).

TABLE 1

Infrared frequencies (cm^{-1}) of complexes $[ML_2(NCS)_2]$ (L = aniline, *p*-toluidine)[a]

Vibration	Ligand		M = Co	M = Ni	M = Cu	M = Zn
	NaNCS	Amine[b]				
Aniline complexes						
νN—H asym		3481(10)	3324(0,9)	3325(0,9)	3300(0,9)	3279(0,6)
νN—H sym		3395(5)	3252(2,8)	3254(0,6)	3218(3,8)	3235(0,6)
νN—H···N			3153(0,8)		3128(0,8)	3138(0,6)
νN—CS[c]	2074(26)		2123(29,2)	2131(27,0)	2118(28,2)	2100(29,0)
NH_2 scissor		1619(6)	1589(0,5)	1590(0,4)	1578(0,4)	1591(0,3)
νC—N		1276(5)	1234(0,4)	1238(3,8)	1232(0,5)	1223(0,4)
NH_2 twist		1115(2)	1043(0,2)	1051(0,4)	1077(0,6)	1050(0,4)
2δ NCS	960(7)		922(7,0)			948(7,0)
NH_2 wag		884(2)	805(0,7)	806(0,6)	808(6,6)	798(0,6)
νNC—S	756(10)		784(11,0)	779([d],0)	815(5,0)	833(11,0)
NH_2 rock			588(0,5)	602(0,5)	638(0,7)	648(0,6)
νM—NH_2 + ligand			541(0,6)	544(0,5)	550(0,6)	534(0,6)
		529(6)	520(0,2)	523(0,2)	532(0,4)	520(0,3)
		382(0)	361(0,8)	361(0,4)	370(0,3)	367(0,3)
νM—NH_2			376(0,4)	380(0,4)	403(0,6)	390(0,6)
δ NCS	481(4)		471(4,0)	471(4,0)	465(3,0)	470(4,0)
			461(3,0)	460(4,0)		
νM—NCS			186(4,0)	227(2,0)	231(2,0)	167(4,0)
p-Toluidine complexes						
νN—H asym		3486(8)	3318(0,7)	3320(0,8)	3292(0,3)	3260(1[e],7)
νN—H sym		3399(4)	3254(0,6)	3256(0,4)	3224(0,6)	3209(0,8)
νN—H···N			3152(0,8)		3130(0,9)	3127(0,6)
νN—CS[c]	2074(26)		2124(27,0)	2135(28,0)	2124(29,0)	2100(30,0)
NH_2 scissor		1628(2)	1585(0,3)	1588(1,5)	1577(0,4)	1585(0,4)
νC—N		1275(4)	1244(0,10)	1246(0,7)	1247(0,3)	1222(0,3)
					1229(0,2)	1214(0,2)
NH_2 twist		1126(1)	1036(0,4)	1044(0,5)	1069(0,4)	1110(0,7)
						1075(0,6)
NH_2 wag		812(1)	739(0,6)	740(0,6)	744(0,5)	737(0,6)
νNC—S	756(10)		784(11,0)	781(10,0)	817(13,0)	[f]
NH_2 rock			580(0,4)	598(0,4)	653(0,4)	664(0,5)
					623(0,4)	653(0,3)
						630(0,3)
νM—NH_2 + ligand		505(1)	521(0,1)	526(0,2)	532(0,3)	529(0,3)
						520(0,2)
		380(0)	381(0,3)	385(0,1)	391(0,0)	394(0,0)
νM—NH_2			402(0,3)	407(0,3)	425(0,6)	471(0,3)
						414(0,2)
δ NCS	481(4)		470(4,0)	471(4,0)	463(4,0)	479(4,0)
			455(4,0)	453(4,0)		
νM—NCS			190(3,0)	212(4,0)	234(4,0)	265(3,0)
						162(3,0)

Ligand vibrations associated with the amino group

The stretching and bending vibrations of the amino group are readily identified by $^{15}NH_2$-labelling of the ligands aniline and *p*-toluidine and their complexes. The antisymmetric and symmetric N—H stretching bands in the spectra of the complexes occur at frequencies which are between 70 and 200 cm^{-1} lower than the corresponding bands in the ligand spectra. $^{15}NH_2$-labelling induces low frequency shifts of between 4 and 10 cm^{-1} in both bands in the ligands and their complexes. A third $^{15}NH_2$-sensitive band near 3140 cm^{-1} is observed in the spectra of most of the complexes and is assigned to hydrogen-bonded νN—H---N on the basis of earlier hydrogen bonding studies [10, 11] on the IR spectra of amines and their complexes.

Absorption within the range 1570—1620 cm^{-1} in the spectra of the complexes comprises two bands (aniline series) or three bands (*p*-toluidine series). Only the component of lowest frequency exhibits $^{15}NH_2$-sensitivity. This component corresponds with the $^{15}NH_2$-sensitive band near 1620 cm^{-1} assigned [12] to the NH_2 scissoring vibration in the ligand spectra. The NH_2 twisting modes have been assigned [12] to $^{15}NH_2$-sensitive bands in the ligand spectra near 1120 cm^{-1}. The corresponding bands in the spectra of the complexes occur near 1050 cm^{-1}. The NH_2 wagging mode yields $^{15}NH_2$-sensitive bands at 884 and 812 cm^{-1} in aniline and *p*-toluidine, respectively [12]. Coordination induces a low frequency shift of approximately 70 cm^{-1} in each band. The NH_2 rocking frequencies of the complexes occur near 600 cm^{-1}.

With one exception, all the $^{15}NH_2$-sensitive bands with frequencies exceeding 580 cm^{-1} are accounted for by the assignments given above. The exception is a strong band near 1230 cm^{-1} in the spectra of the complexes which corresponds with the $^{15}NH_2$-sensitive ligand band at 1275 cm^{-1}. This is assigned to νC—N, occurring in the region previously reported [8, 9, 13, 14] for this vibration

Each vibration of the amino group is sensitive to the nature of the co-ordinated metal ion. The νN—H and νC—N bands generally follow the frequency sequence Co < Ni > Cu > Zn which is the inverse order of the masses of the metal ions.

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[a] Frequencies are followed by ^{15}N-induced shifts in parentheses in the order (^{15}NCS shift, $^{15}NH_2$ shift). Shifts < 1 cm^{-1} are not considered significant and are cited as zero shifts. All shifts are reported to the nearest integral values and are to lower frequencies unless otherwise indicated.

[b] Frequencies > 1000 cm^{-1} from spectra of 0.05 M CCl_4 solutions. Frequencies < 1000 cm^{-1} from liquid film (aniline) or Nujol mull (*p*-toluidine) except band at 812 cm^{-1} in *p*-toluidine spectrum (taken in 0.05 M cyclohexane) [8, 9].

[c] Sharp shoulders on these bands are omitted.

[d] Band disappears on ^{15}NCS-labelling.

[e] Shift towards higher frequency.

[f] No ^{15}NCS-sensitive band observed in this region.

Ligand vibrations associated with the isothiocyanate group

The spectrum of NaNCS (Fig. 1) yields only four bands (each of which exhibits significant ^{15}NCS-sensitivity) within the range 200—4000 cm^{-1}. The band at 2074 cm^{-1}, assigned to νN—CS, appears within the range 2100—2135 cm^{-1} in the complexes. Its position is similar to that reported [1] for the isothiocyanate complexes $[M(py)_2(NCS)_2]$. This band exhibits large ^{15}NCS-induced shifts (26—30 cm^{-1}) in both NaNCS and in the isothiocyanate complexes. Some very sharp shoulders are observed in the νN—CS bands of the complexes. This splitting is considered [1] to be diagnostic of either polymeric octahedral or tetrahedral structure (it is not observed in the spectra of mononuclear octahedral isothiocyanate complexes).

The νNC—S vibration occurs at 757 cm^{-1} in the spectrum of NaNCS. A surprisingly large shift (10 cm^{-1}) is induced by ^{15}NCS-labelling. The band is increased in frequency and reduced in intensity in the isothiocyanate complexes but retains considerable ^{15}NCS-sensitivity.

The bending vibration of the isothiocyanate group (δNCS) occurring at 481 cm^{-1} in the spectrum of NaNCS, is observed near 470 cm^{-1} in the isothiocyanate complexes. It is split into a doublet in the isostructural Co(II) and Ni(II) complexes, each component exhibiting similar ^{15}NCS-sensitivity. The overtone of this vibration (2δNCS) at 960 cm^{-1}, surprisingly strong in the spectrum of NaNCS, is observed in only two of the complex spectra where it is considerably reduced in intensity.

Both internal stretching vibrations of the isothiocyanate group (νN—CS and νNC—S) exhibit significant sensitivity to the metal ion. Like νN—H and νC—N, νN—CS is inversely related to the masses of the coordinated ions while (as may be expected for constancy of bond order summation about the carbon atom) the M-sensitivity of νN—CS (Co < Ni > Cu > Zn) is the inverse of the M-sensitivity of νNC—S (Co > Ni < Cu < Zn).

Metal—ligand vibrations

The metal—ligand stretching vibrations (νM—NH$_2$ and νM—NCS) are expected [15] to have frequencies below 600 cm^{-1}. A ^{15}NH$_2$-labelling study [8] of the IR spectra of the complexes $[M(p\text{-toluidine})_2Cl_2]$ (M = Co, Ni, Cu, Zn) yielded ^{15}NH$_2$-sensitive bands near 525, 475 and 425 cm^{-1} of which the first two were assigned to ligand vibrations shifted by coupling with νM—NH$_2$ while the band near 425 cm^{-1} (occurring in a region free from ligand absorption) was assigned to vibrationally pure (uncoupled) νM—NH$_2$. Support for the assignment was provided by the observation that this band is M-sensitive in the sequence of crystal field stabilization energies (CFSE's) of the complexes: Co > Ni < Cu > Zn.

In the metal—isothiocyanate complexes studied here, the following criteria were used to establish the νM—NH$_2$ assignments: presence of ^{15}NH$_2$-sensitivity, absence of ^{15}NCS-sensitivity, occurrence of νM—NH$_2$ in a region free from

$^{15}NH_2$-sensitive ligand bands and M-sensitivity in the CFSE sequence Co < Ni < Cu > Zn (i.e. the Irving—Williams sequence) determined [7] on the basis of octahedral Co(II) and some tetragonal distortion in the Cu(II) complexes. It is worth emphasizing that the expected M-sensitivity of the νM—NH_2 in the complexes [M(*p*-toluidine)$_2$Cl$_2$] differs from that of the complexes [ML$_2$(NCS)$_2$] (L = aniline, *p*-toluidine) due to the different structures of the Co(II) complexes in the two series (tetrahedral in the former, octahedral in the latter).

The spectra (Fig. 1) show that (below 600 cm^{-1}) two regions of $^{15}NH_2$-sensitive bands occur: 520—550 cm^{-1} and 360—425 cm^{-1}. None of the $^{15}NH_2$-sensitive bands exhibits any ^{15}NCS-sensitivity, indicating that little, if any, coupling between νM—NH_2 and νM—NCS occurs. Since a strong $^{15}NH_2$-sensitive ligand band is present near 515 cm^{-1} in the spectra of aniline and *p*-toluidine and since this band does not recur in the spectra of the complexes, the bands within the range 520—550 cm^{-1} are considered to originate in the ligand vibration near 515 cm^{-1} shifted to higher frequency by coordination and becoming M-sensitive in the Irving—Williams sequence by coupling with νM—NH_2.

Within the range 360—425 cm^{-1}, there are generally two $^{15}NH_2$-sensitive bands in the spectrum of each complex (exceptionally, the copper *p*-toluidine complex has only one $^{15}NH_2$-sensitive band in this region). It is possible that one component of each pair of bands in this region is associated with the very weak and $^{15}NH_2$-insensitive ligand bands observed near 380 cm^{-1}; the other component satisfies all the criteria listed above for a band assigned to uncoupled νM—NH_2. In the six-coordinate complexes (i.e. except for tetrahedral [Zn(*p*-toluidine)$_2$(NCS)$_2$]) this band exhibits M-sensitivity in the Irving—Williams sequence, supporting the assignment.

Observation of a single uncoupled νM—NH_2 band in the isothiocyanate complexes satisfies the C_i symmetry requirement [16] of one IR-active normal νM—L mode in polymeric octahedral complexes of general formula [ML$_2$X$_2$]. In tetrahedral complexes [ML$_2$X$_2$], C_{2v} symmetry requires two IR-active νM—L modes. In the spectrum of [Zn(*p*-toluidine)$_2$(NCS)$_2$] clearly observable splitting of several bands yields additional $^{15}NH_2$-sensitive bands of which that at 414 cm^{-1} is assigned to the second νM—NH_2 band expected in C_{2v} symmetry. For this reason, this complex is uniquely assigned tetrahedral structure.

Assignment of νM—NCS is readily achieved by ^{15}NCS-labelling. Bands near 200 cm^{-1} are ^{15}NCS-sensitive and occur in a region free from absorption in the spectrum of NaNCS. The complete absence of $^{15}NH_2$-sensitivity supports their assignment to uncoupled νM—NCS vibrations. Both C_i and C_{2v} symmetries require two IR-active νM—NCS modes. Two bands are observed near 200 cm^{-1} in the spectrum of each complex. Significant ^{15}NCS-sensitivity is observed for both bands only in the Zn(II) *p*-toluidine complex which has been assigned tetrahedral structure. Failure to observe the second νM—X band expected for C_i symmetry in the spectra of polymeric octahedral

complexes $[Mpy_2X_2]$ (M = Co, Ni; X = Cl) has been reported previously [17].

Among the isothiocyanate complexes discussed here, the unique tetrahedral structure of $[Zn(p\text{-toluidine})_2(NCS)_2]$ is further demonstrated by the wide separation (100 cm^{-1}) between its two ^{15}NCS-sensitive bands and doubling of several of the ligand vibrations. Apart from the spectrum of this complex, the νM—NCS frequencies resemble the νM—NH_2 frequencies in exhibiting a marked M-sensitivity in the Irving—Williams sequence.

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Since submission of this paper, the crystal structure of $[Zn(p\text{-toluidine})_2(NCS)_2]$ has been determined (M. R. Caira and L. R. Nassimbeni, Cryst. Struct. Comm., in press). The results confirm the tetrahedral structure proposed on the basis of our paper.

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