APPLICATION OF CRYSTAL FIELD THEORY TO THE INFRARED SPECTRA OF TRANSITION METAL COMPLEXES

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DOCTOR OF PHILOSOPHY

by
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CONTENTS

problem in the IR spectra of 8-quinolinol chelates of di- and trivalent metals of the first transition series. The metal-sensitivity of bands in the IR spectra of structurally differing substituted 8-quinolinol chelates receives an interpretation in terms of crystal field theory. The effect of halogen and methyl substituents in the IR spectra of the Cu(II) chelates is consistent with the band assignments based on crystal field effects and is related to both the resonance and inductive capacities of the substituents.

A total of 232 compounds have been synthesized and are discussed.

PUBLICATIONS

Parts of this work have been published as follows:

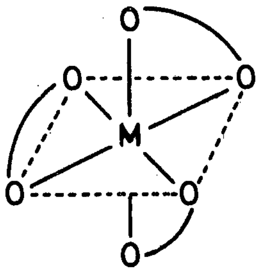
1. G.S. SHEPHARD and D.A. THORNTON, *Helv. Chim. Acta*, 54 (1971) 2212.
"Infrared Spectra of α-Thenoyltrifluoroacetonates of Metal Ions of the First Transition Series".

2. G.S. SHEPHARD and D.A. THORNTON, *J. Mol. Structure*, 16 (1973) 321.
"Infrared Spectra of Metal Anthranilates".

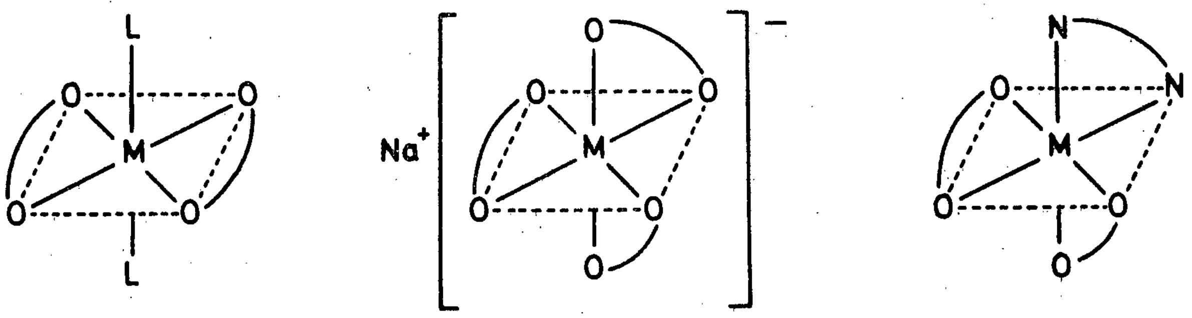
ABBREVIATIONS

ANA	anthranilate anion
bipy	2,2'-bipyridine
B.M.	Bohr magneton
BTA	benzoyltrifluoroacetonate anion
CFS	crystal field splitting
CFSE	crystal field stabilization energy
CFT	Crystal Field Theory
def.	deformation
δ	IR bending mode
i.p.	in-plane
IR	infrared
L	generalized ligand
M	central metal ion
MOT	Molecular Orbital Theory
ν	IR stretching mode
o.o.p.	out-of-plane
OX	8-quinolinolate (oxinate) anion
phen	1,10-phenanthroline
pic	picolinate anion
py	pyridine
quin	quinaldate anion
R	generalized substituent
TTA	2-thenoyltrifluoroacetonate anion

FORMULAE



Trivalent metal β-ketoenolates

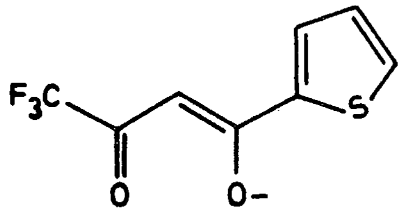


Divalent metal β-ketoenolates

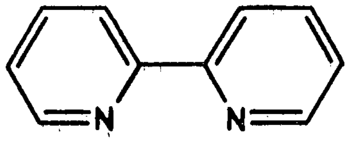
(L = H_2O, NH_3, py)

O–O

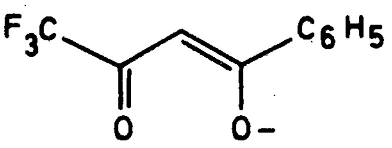
N–N



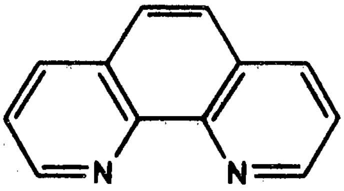
2-thenoyltrifluoroacetonate (TTA)



2,2'-bipyridine (bipy)

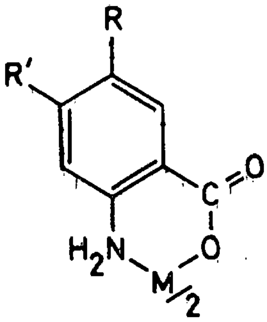


benzoyltrifluoroacetonate (BTA)



1,10-phenanthroline (phen)

Formulae and abbreviations of complexes appearing in text.



Divalent metal anthranilates

R = R' = H; M(ANA)$_2$

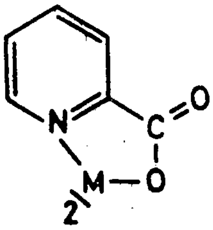
R = Cl, R' = H; M(5-Cl-ANA)$_2$

R = Br, R' = H; M(5-Br-ANA)$_2$

R = I, R' = H; M(5-I-ANA)$_2$

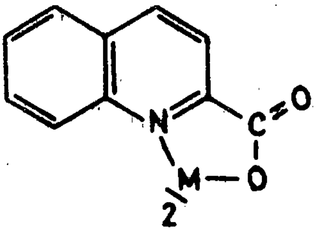
R = CH_3, R' = H; M(5-CH_3-ANA)$_2$

R = H, R' = NO_2; M(4-NO_2-ANA)$_2$



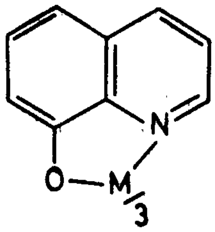
Divalent metal picolinates

$M(pic)_2$

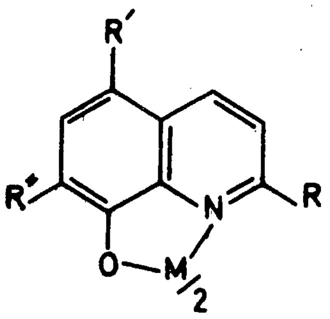


Divalent metal quinaldates

$M(quin)_2$



Trivalent metal oxinates



Divalent metal oxinates

R = R' = R" = H;	M(OX)$_2$
R = CH_3, R' = R" = H;	M(2-CH_3-OX)$_2$
R = CH_3, R' = R" = Br;	M(2-CH_3-5,7-Br_2-OX)$_2$
R = H, R' = Cl, R" = H;	M(5-Cl-OX)$_2$
R = H, R' = R" = Cl;	M(5,7-Cl_2-OX)$_2$
R = H, R' = R" = Br;	M(5,7-Br_2-OX)$_2$
R = H, R' = Cl, R" = I;	M(5-Cl-7-I-OX)$_2$

I. INTRODUCTION

1. CRYSTAL FIELD ASPECTS OF INFRARED SPECTRA

The theoretical treatment of bonding in transition metal compounds has led to the development of the Crystal Field Theory (CFT). This is based on an entirely electrostatic model in which the ligands produce a field approximately equivalent to a set of negative point charges. The effect of this electric field is to destroy the degeneracy of the d-orbitals of the transition metal, the resulting energy changes having an important bearing on the properties of the complex formed. The Molecular Orbital Theory, in which the degeneracy of the d-orbitals is removed by the overlap of metal and ligand orbitals, leads to similar results to those of CFT but can also account for additional effects such as π-bonding. The Ligand Field Theory (LFT) is a modified form of CFT which has been developed to take account of covalent bonding effects.

In an octahedral environment the influence of the crystal field is to remove the degeneracy of the d-orbitals of the metal such that they are split into two sets. This splitting results in three degenerate orbitals (t_{2g}) being stabilized by $4Dq$ and two degenerate orbitals (e_g) being destabilized by $6Dq$, the total crystal field splitting between the two sets being $10Dq$. The removal of the 5-fold degeneracy of the d-orbitals leads to an overall stabilization of the system except in those cases, namely d^0, d^{10} and high spin d^5 in which there is no net stabilization since the effect of the electrons in the t_{2g} orbitals is balanced by the destabilization resulting from the occupancy of the e_g orbitals. The decrease in energy of the system is termed the crystal field stabilization energy (CFSE). The CFSE of a metal ion in an octahedral environment is given by[1]

$$\mathrm{CFSE} = -(0.4\ N_{t_{2g}} - 0.6\ N_{e_g})10Dq$$

where $N_{t_{2g}}$ and N_{e_g} are the numbers of electrons in the t_{2g} and e_g orbitals respectively and $10Dq$ is the crystal field splitting parameter, being the energy difference between the t_{2g} and e_g orbitals. Jorgensen[2] has expressed $10Dq$ as

$$10Dq = fg$$

where f measures the crystal field splitting power of the ligand relative to water which is taken as unity and g is the spectroscopically determined magnitude of $10Dq$ for the octahedrally hydrated metal ion.

Of the various energy changes occurring on complex formation, the crystal field stabilization (CFS) effect represents only a small fraction of the total energy change. Although most of the bonding energy in transition metal complexes is accounted for by the electrostatic attraction between metal ion and ligands, the relatively small CFS effect is important when investigating differences between complexes in which other effects influencing the thermodynamic properties are constant or are expected to vary smoothly through the set of complexes being studied. Hence, to investigate the CFS effect on complex stability, a series of isostructural, isovalent transition metal complexes of constant ligand combination is used so that all energy changes are constant or smoothly varying. Examination of such series has shown[1,3] that a direct correlation exists between the CFSE and various thermodynamic properties such as lattice energies, heats of ligation and interionic separations.

The infrared (IR) stretching vibrations of metal-ligand

(M-L) bonds are principally dependent on two factors, namely the masses of the respective metal and ligand and the force constant of the M-L bond, this latter factor being determined by the M-L bond strength which is related to the stability of the metal complex. Hence, in the absence of a significant mass effect, the M-L stretching frequencies (νM-L) are expected to show a correlation with the complex stability and hence with the CFSE in an isostructural series of transition metal complexes. Such a relationship has been found in the β-ketoenolates of trivalent first transition series metals[4] in which the νM-O parallels the variation of CFSE with *d*-orbital population for an octahedral environment. Correlations of this sort have been extended by Thornton and coworkers[5-15] to include a large range of first transition series complexes such as the 2, 2'-bipyridyl (bipy) and 1,10-phenanthroline (phen) complexes of the divalent metals[5], divalent metal acetylacetonates and their nitrogen base adducts[6], di- and trivalent metal tropolonates[7]; the potassium salts of the divalent tris(acetylacetonates)[6], the di- and trivalent γ-substituted acetylacetonates[8], a large series of complexes with nitrogen donors[9] and trivalent oxalates and cyanides[10]. CFSE correlations have been used to assign νM-L in a large selection of divalent metal salicylaldimine complexes[11-13]. These correlations have been extended to the second transition series acetylacetonates[10] and to the tropolonato[14]- and tetrakis(tropolonato)lanthanide(III)[15] chelates. These latter complexes involve crystal field splitting of the degenerate 4*f*-orbitals and the CFS effects are small as compared with the effects noted for *d*-orbitals.

Since the CFS effect is a small perturbation on the total M-L bonding, it is necessary, in order to isolate the CFS effect, to find reference complexes in which these effects are absent.

Such compounds are those with a d^0, high spin d^5 and d^{10} configuration and in the lanthanides, those with a f^0, high spin f^7 and f^{14} configuration. These compounds exhibit zero CFSE and their νM-L frequencies are entirely dependent on the various other effects determining M-L bond strength and on the ionic mass effect. Following the method of George and McClure[3], an interpolation line is drawn between these points on the plot of νM-L against d-orbital population and the frequency values along this line may be considered to be those which would have been realized in the absence of a crystal field. The difference between the experimental frequencies (ν) and the value given by this interpolation line (ν_0) is the crystal field contribution to the total IR frequency and ($\nu - \nu_0$) has been shown to yield a good correlation with calculated CFSE's[4-7, 10, 14, 15].

2. SUBSTITUENT CONSTANTS

One of the earliest theories developed to derive a quantitative relationship between the structure of compounds and their chemical reactivity is the Hammett equation[16]. The fact that the effects of substituents in many reaction series involving benzene derivatives could be correlated with the acid strengths of the corresponding benzoic acids[17], led Hammett[16] to propose a general quantitative relation between the nature of a substituent (R) in such a system and the reactivity of a side chain *meta* or *para* to R. This relation has become known as the Hammett equation and is widely applied in the form

$$\log({}^{k}/_{k_o}) = \sigma\rho$$

Here k and k_o are rate or equilibrium constants for reactions of the substituted and the unsubstituted compounds respectively, σ is the substituent constant which depends solely on the nature and position of R and ρ is the reaction constant which depends on the reaction, the conditions under which it takes place and the nature of the side chain. The reaction constant is a measure of the sensitivity of the reaction series to ring substitution, while the substituent constant σ represents the ability of the substituent to withdraw or release electrons by a combination of its inductive (field) and resonance effects and is defined by the equation

$$\sigma = \log\ ({}^{K}/_{K_o})$$

where K and K_o are the ionization constants for the substituted and unsubstituted benzoic acids respectively. Hence the ionization of benzoic acid has been arbitrarily chosen as a standard reaction type for which ρ is fixed at unity and all

σ values are referred to hydrogen for which $\sigma=0$. A positive σ value for a substituent indicates that the substituent withdraws electrons relative to hydrogen; substituents with negative σ values repell electrons relative to hydrogen.

The Hammett relationship applies only to the *meta* and *para* substituents since *ortho* substituents give rise to steric interactions which make quantitative relationships unreliable. Hammett σ values which have been recalculated by Jaffe[18] using more recent values of ionization and rate or equilibrium constants, include both inductive and resonance effects. In attempting to separate these effects, Taft[19] proposed that regardless of the presence or absence of steric and resonance effects, the inductive effect (I) may be represented as

$$I = \rho^{*}\sigma^{*}$$

where the terms have similar meaning to those of Hammett except that σ^{*} is defined in terms of the specific rates for the acidic and basic hydrolysis of an ester having the substituent alpha to the carbonyl group.

$$\sigma^{*} = \frac{1}{2.48}\left[\log\left({}^{k}/_{k_0}\right)_B - \log\left({}^{k}/_{k_0}\right)_A\right]$$

Finding that σ^{*} calculated from the hydrolysis of acetate esters (substituent, $R = XCH_2$) correlates well with the acidity constants of the acids XCH_2COOH, Taft then defined[20,21] a new substituent parameter, σ' for the substituent X such that

$$\sigma' = 0.45\sigma^{*}$$

The choice of the coefficient 0.45 was intended to make σ' equal to $\log\left({}^{K}/_{K_0}\right)$ for the acidity constants of the 4 - X - bicyclo [2.2.2] octane-1-carboxylic acids. Since a large proportion of the available σ' values derive from data on the acidity constants of XCH_2COOH, this parameter is now defined[21] such that the inductive effect (I) is represented as

$$I = \rho'\sigma'$$

where ρ' depends only on the reaction and σ' is given by

$$\sigma' = 0.262 \log(^{K}/_{K_o})$$

where K_o is the acidity constant of acetic acid in aqueous solution at 25°C and K is the corresponding constant for the acid XCH_2COOH. Hence in both σ and σ' series the reference substituent is hydrogen. Subsequent to Taft's introduction of σ' as a pure inductive parameter, Swain and Lupton[22] separated the electronic effects of a substituent into its pure field ($\mathcal{F}$) and pure resonance ($\mathcal{R}$) components and showed that σ' is a function only of their field parameter.

Relationships between substituent constants and various IR bands in substituted aromatic, heterocyclic and aliphatic organic compounds have been found by various workers. Linear correlations of the symmetric and the asymmetric νN-H of anilines[23] and amines[24], νO-H of phenols[25] and νC=O of aliphatic ketones[26] with σ or σ* have been reported. In the field of metal co-ordination chemistry, correlations between σ or σ* have been reported amongst others for νC=O and νM-O of various alkylamine, aniline and pyridine adducts of Ni(II) and Zn(II) acetylacetonates[27-29] for νU=O of the alkylamine adducts of uranyl dibenzoylmethanate[30] and of the pyridine adducts of uranyl acetylacetonate[31] and for νM-L in metal salicylaldimine complexes[11-13].

3. METHODS OF ASSIGNING METAL-LIGAND VIBRATIONS IN IR SPECTRA

The importance of assignments of metal-ligand vibrations lies in the fact that they yield direct information concerning the structure of the complex and the nature of the metal-ligand bonds. Appearing below 700 cm^{-1} due to the high mass of the metal ion and the comparative weakness of the M-L bond, the assignment of these bands is complicated by intermolecular interactions, lattice modes, lowering of symmetry, vibrational coupling and the appearance of ligand vibrations activated by complex formation[32].

Assignment of M-L vibrations are usually made by the following methods:

1. Since M-L vibrations are absent in the free ligands, a comparison between the spectra of the free ligand and its metal complexes yield assignments for νM-L. The drawback of this method is that some ligand vibrations activated by complex formation may appear in the same region as the M-L vibrations[33].

2. Metal-ligand vibrations are expected to appear in the same region for complexes of identical metals and similar ligands. This method has yie~~lded~~ values of νCu-N in complexes[34] of Cu X_2 L_2 (X = Cl, Br; L = substituted pyridine) and of νM-O in substituted pyridine, alkylamine and aniline adducts of Ni(II), Co(II) and Zn(II) acetylacetonates[27-29].

3. Theoretical calculations such as normal co-ordinate analysis using empirical metal-ligand and other bond lengths yield theoretical values for the M-L and other vibrations of the complex.

4. As already noted, the M-L vibrations in a series of isostructural isovalent transition metal complexes of constant ligand combination are expected to follow the order of the CFSE's of the metal ions.

5. Metal-ligand vibrations show a shift if the complex is isotopically labelled. The νM-O bands in acetylacetonates[35,36] and the νM-N bands in metal salicylaldimine complexes[11,12] have been assigned by replacing the ordinary oxygen and nitrogen donor atoms by the isotopes ^{18}O and ^{15}N respectively.

The position of a band in the IR spectrum is dependent on the masses of the atoms involved in the particular vibration. Hence an IR spectrum of a labelled compound is usually distinctly different from that of the unlabelled complex. The spectral differences observed for the isotopic compounds depend on the ratio of the masses of the labelled and normal atoms. The greater the ratio, the larger is the isotopic shift of the relevant bands. The biggest shifts are found for tritiated and deuterated molecules which show shifts up to 1300 and 1000 cm^{-1} respectively[37]. Isotopic shifts for smaller ratios are considerably less, but can be as high as 40 cm^{-1} for ^{18}O-labelled molecules[37]. The observed isotopic shifts of an IR band depend on various factors such as hydrogen bonding in the molecule (which can reduce the expected shift), the number and nature of the atoms in the molecule which have been isotopically labelled and the extent of coupling of vibrational bands. The smaller the vibrational coupling, the purer is this absorption and the greater will be its isotopic shift.

The expected isotopic shifts can be calculated[37] by assuming the labelled atom to be part of a simple harmonic oscillator. The vibrational frequency of a diatomic molecule can be represented by the equation

$$\nu = \frac{1}{2\pi} \left({}^{k}/{}_{\mu}\right)^{\frac{1}{2}}$$

where ν = vibrational frequency

k = harmonic force constant and

μ = reduced mass of the molecule.

Hence the shifts may be calculated from

$$\nu^{i}/\nu = \left({}^{\mu}/{}_{\mu^{i}}\right)^{\frac{1}{2}}$$

where the superscript, i, refers to the labelled molecule. This yields a good approximation provided the vibration of the two atoms concerned is minimally affected by the remainder of the molecule. These expected shifts can be observed in vibrationally pure IR bands[37].

4. METAL CHELATES OF 2-THENOYLTRIFLUOROACETONATE AND BENZOYLTRIFLUOROACETONATE

The majority of reports on the metal complexes of 2-thenoyltrifluoroacetone (TTA) and benzoyltrifluoroacetone (BTA) relate to their role as synergists in the solvent extraction of metal ions using phosphorus esters[38-43]. Although many of the phosphate and phosphine oxide adducts of these complexes have been isolated, no systematic study of their IR spectra has been reported.

The molar heats of sublimation for some β-ketoenolates (including TTA and BTA) of various common metal ions were calculated by Berg and Truemper[44]. An attempt was made to relate these heats with the polarity of the molecule in that the greater the polarity the larger is the molar heat of sublimation. Berg and Reed[45] found that many chelates of TTA are sufficiently volatile and stable to be fractionally sublimed in a vacuum and recovered with high yields. The differences in the recrystallization zone temperatures observed among the chelates studied indicated that a number of mixtures could be resolved by the fractional sublimation of the TTA chelates. Similar studies[45] on the metal chelates of BTA showed that these were not suitable for sublimation studies since the chelates condensed not in well-defined zones as did the TTA chelates, but rather in most cases as liquids.

The stability constant data available for TTA and BTA divalent chelates[46-49] indicate that they follow the normal Irving-Williams[50] stability order. Shigematsu and coworkers[51] have studied the stability of a series of tri-n-octylphosphine oxide adducts of Sc(III) and Zn(II) β-ketoenolates and showed that the stability of the adducts depended on the nature of the substituents in the 1,3-positions. The formation of mono-alkylamine and -alkylamine hydrochloride adducts of [Cu(TTA)$_2$] in solution was studied by Ke and Li[52]. When bulky R_3N adducts are formed, the 2-thienyl group is forced out of plane and so acts as an electron withdrawing group by induction leading to stronger adduct formation.

Lintvedt and Holtzclaw[53] have studied the proton magnetic resonance spectra of various β-diketones including TTA and BTA and have shown that the CF_3 group strengthens the C = C and C = O bonds through its strong inductive effect. The aromatic groups are electron donating by a resonance effect, the thienyl moiety having a smaller effect than the phenyl. The upfield shift of the enolic proton of BTA and TTA relative to acetylacetone shows that the electron withdrawing effect of the CF_3 group predominates over the electron donating power of the aromatic group. Yamazachi and Takeuchi[54] found a relationship between the chemical shifts in the ^1H and ^{19}F nuclear magnetic resonance spectra of ten TTA chelates and the electronegativity and ionic radius of the corresponding metals.

The electronic spectra of Cr(III) and Fe(III) complexes of BTA and TTA have been reported [55-57] and Lintvedt and Kernitsky[56] have shown that the δ value for BTA occurs in the range of other substituted β-diketones, all of which lie within a narrow limit of the value for acetylacetone. Noskova and Kazanova[58] have shown from MO calculations based on electronic absorption spectra that in complexes of TTA with metals which do not participate in any significant π-bonding, the order of the π-bonds in these complexes shows no great difference to those calculated for the acetylacetonates. Rao and Li[42] showed from the electronic spectrum of [Ni(TTA)$_2$] that the

Ni(II) is octahedrally co-ordinated.

The IR spectra of metal TTA and BTA complexes have mainly been studied in the 4000 - 700 cm^{-1} region, the main bands of interest being the νC=O, νC=C and thienyl vibrations[40-43, 59-62]. The assignment of νC=O in these complexes was made by comparison with acetylacetonates and thus the assignments mirror the changes that have been made in the assignment of the corresponding band in the acetylacetonate spectra. The electron delocalization in the metal β-ketoenolate ring results in considerable coupling of the IR bands and hence few bands represent pure vibrations. The first two bands below 1700 cm^{-1} were originally empirically assigned by Lecompte to the νC=O and νC=C vibrations respectively[63,64]. Nakamoto and coworkers[65-68] reversed these assignments with normal co-ordinate analyses whereas a subsequent analysis[69] and ^{18}O-labelling studies[35,36] on Cr(III) and Cu(II) acetylacetonates showed that the original empirical assignments had been correct.

Noskova and coworkers[70] have investigated the spectra of TTA and some of its metal complexes in the region 3800 - 230 cm^{-1} and have assigned the vibrations of the chelate ring from theoretical considerations. They found that the vibrations of the terminal groups are superimposed on the chelate ring vibrations, suggesting[70] that no π-electron delocalization occurs throughout the entire molecule. Kassierer and Kertes[71] studied the spectra of various divalent TTA complexes and their phen adducts and have empirically assigned various bands including several M-O modes below 700 cm^{-1}.

5. METAL ANTHRANILATES

The bis(anthranilates) of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) have been reported in the literature[72-75]. These metal chelates precipitate from aqueous solutions as the anhydrous species $[M(ANA)_2]$ where ANA represents the anion of anthranilic acid. The high insolubility of these compounds for stability constant measurements has led most workers[76-79] to report only the first equilibrium constant, K_1, for the reaction.

Thermogravimetric determinations[80], magnetic moment measurements[75,81,82] and IR spectra[82-85] have been published and the use of 5-bromo-anthranilic acid (5-Br-ANA) as an analytical reagent has been discussed[72]. Structures for these compounds have been proposed from magnetic moment and IR measurements. Livingstone[75] suggested tetrahedral structures for the Ni(II) and Co(II) compounds based on their magnetic moments, while Lumme[81], from similar measurements, concluded that these two ions had a square planar high spin configuration. Hill and Curran[84] have studied the IR spectra of the chelates of Ni(II), Cu(II), Zn(II) and Cd(II) and noted the presence of a perturbed asymmetric carboxyl frequency and the lowering of the N-H stretching mode frequency. In view of this a *trans*-coplanar chelate structure around the metal ion has been suggested and the possibility of the metal acquiring an octahedral environment by co-ordinating with the carboxylate oxygen in planes directly above and below the metal ion in the crystal lattice has been postulated[84]. Sandhu and coworkers[82] suggested a similar structure from a study of the symmetric and asymmetric carboxylate bands of the sodium salt and the divalent metal complexes of anthranilic acid. From a comparison with metal acetates in which the carboxyl group is also bidentate, it was suggested[82] that there are two unequal M-O bond lengths and that the structures are tetragonal.

The polymeric nature of the chelates is supported by their negligible solubility[82,167]. Sandhu and coworkers[82] also report magnetic moment measurements which support the proposed distorted octahedral stereochemistry. On the basis of magnetic moment[168] and electron paramagnetic resonance studies[169], the Cu(II) chelate has been assigned a square planar structure.

6. METAL CHELATES OF PICOLINIC AND QUINALDIC ACIDS

Picolinic and quinaldic acids readily form metal complexes with divalent transition metal ions, although much of the relevant work in the literature appertains to the picolinates rather than to the quinaldates. The use of quinaldic acid as an analytical reagent has been investigated[86,87] and its chelates have been subject to stability constant[88], thermogravimetric[89,99] magnetic moment[81] and visible-ultraviolet spectroscopic[88] measurements.

The chelates of picolinic acid have been studied by visible-ultraviolet[90-93], infrared[91, 94-96] and electron spin resonance[92] spectroscopy. Lumme[97] has measured the stability constants of the common divalent metal chelates and has shown that they are more stable than the corresponding metal quinaldates. The dehydration and decomposition of the picolinates have been investigated by thermogravimetric analysis[91,98,100] and the effective magnetic moments[81,91,101] have been shown to be normal high spin values.

The Co(II), Ni(II) and Zn(II) picolinates are known to be isomorphous[102-105], having a *trans*-octahedral stereochemistry. The two picolinate anions occupy *trans*-planar positions with two water molecules co-ordinating in the apical positions to complete the six co-ordinate structure. In addition, another two water molecules are held in the crystal lattice. *Trans*-bis(picolinato)copper(II) dihydrate has been the subject of two x-ray investigations. From single crystal x-ray results Cox and coworkers[106] showed that the picolinate groups form a *trans*-planar structure with Cu(II) and that the two water molecules are unco-ordinated. This result was confirmed by Takenaka and coworkers[107] who reported that the structure shows extreme Jahn-Teller distortion from an octahedral stereochemistry, each Cu(II) atom being weakly co-ordinated in the apical positions by the carbonyl groups of the ligands above and below the chelate plane. Gillard and coworkers[108] have characterized two forms of bis(picolinato)copper(II) dihydrate by electronic and infrared spectroscopy, magnetic moment, thermal and x-ray measurements. The difference between the two forms lies in the position of the water molecules in the crystal lattice.

The infrared spectra of the picolinate (pic) and quinaldate (quin) chelates have received little attention in the literature. The IR spectra of picolinic and quinaldic acids have been reported between 4000 and 650 cm^{-1} by Lumme[94], while Isaac and coworkers[96] in a report on the IR spectra of monosubstituted pyridines have reported the IR bands of picolinic acid in the region 650 to 300 cm^{-1}. Lumme[95] has reported the spectra of various divalent ion pic and quin chelates in the range 4000 - 620 cm^{-1} and assigned various bands to the ligand groups. Kleinstein and Webb[91] have recorded the IR spectra of some pyridine carboxylic acid complexes in the 1000 - 250 cm^{-1} range and have empirically assigned νM-N and νM-O bands in the regions 450 -480 cm^{-1} and 410 - 420 cm^{-1} respectively.

7. METAL CHELATES OF 8-QUINOLINOL

One of the more widely used organic precipitants for inorganic metal ions is 8-quinolinol (oxine) with its mono- and disubstituted derivatives. The usefulness of these chelating agents for the gravimetric determination of a number of metal ions has been extensively investigated[109,110]. The oxine ligand plays an important role in some biological systems and its function is related at least in part to its chelating ability with metals[111].

Thus far, metal oxinate (OX) chelates have been the subject of various physicochemical investigations including X-ray diffration[112-120], infrared[121-131], ultraviolet-visible[93, 132-138], nuclear magnetic resonance[139], electron spin resonance[140,141] and mass[142,143] spectrometry. The magnetic susceptibility[144-148] of various chelates has been measured and the stability constants for 8-quinolinol and substituted 8-quinolinol chelates have been determined by various workers[149]. 8-Quinolinolates have been the subject of thermogravimetric and differential thermal analysis[150-153] and their heat stabilities[154,155] and heats of dehydration[156,157] have been reported. The use of 8-quinolinol in the extraction of metal ions into an organic solvent has been studied[158-160] and the heats and entropies of chelate formation have been calculated[161-163].

The IR spectra of a number of 8-quinolinol chelates have been previously published[121-131] but little attention has been given to substituted 8-quinolinols, except, to a limited extent, for methyl-substituted compounds. One of the earliest reports was by Stone[129] who reported the IR spectra of Mg(II) and Bi(III) oxinates so as to correlate the structure determined from the spectra with the large solubility difference between the two chelates. Charles and coworkers[122] have studied the IR spectra of about 17 chelates in the region 1200 to 650 cm^{-1}. The similarity between the spectra was noted and the characteristic band at 1100 cm^{-1} was found to be sensitive to metal ion substitution; this band is assigned to the C-O vibration. Magee and Gordon[125-127] report IR spectra in the range 5000 - 250 cm^{-1} for a variety of metal oxinates and assigned the bands in the region 1500 - 1600 cm^{-1} to νC=C, νC=N and ring vibrations and in the region 1200 - 1000 cm^{-1} to C-H deformation modes. They discussed the quantitative analytical applications of the IR spectra. Katritzky and Jones[164] have correlated the IR bands characteristic of the various monosubstituted quinoline nuclei with those of similarly substituted naphthalenes, and tentative assignments for specific molecular vibrational modes were suggested. Tackett and Sawyer[121] have reported the IR spectra of about 15 oxinates in the 800 - 400 cm^{-1} region, including the spectra of α- and β-$Cu(OX)_2$. Both forms have very similar spectra below 650 cm^{-1}, while the β-form shows unique peaks in the region 800 - 650 cm^{-1}, the difference being explained on the basis of *cis-trans*-isomerism[121]. Tentative assignments for some of the bands in this region are given by comparison with the spectra of pyridines, naphthalenes, phenols and benzene.

Assignments of M-L vibrations were first given by Larsson and Eskilsson[131] who assigned bands near 300 and 400 cm^{-1} as νM-O in the Fe(III) and Co(III) oxinate spectra respectively. Assignments were made by comparison with the ligand itself, the νM-N bands being expected in the very low frequency region due to the rigidity and mass of the 8-quinolinol ligand[131]. Kulkarni and Mukhedkar[123] have assigned νM-N and νM-O in the narrow range 540 - 480 cm^{-1} by comparison with ammine and pyridine N-oxide complexes, whereas Ohkaku and Nakamoto[130] quote these vibrations to be about or below 300 cm^{-1} from metal ion labelling studies.

X-ray diffraction studies have been made on a series of compounds of the type $[M(OX)_2(H_2O)_2]$ where M is Zn, Ni, Co, Cd and Pb. The results of these investigations[116,117,119] show that two chelating oxinate anions co-ordinate to the metal by forming a *trans*-planar structure, two water molecules bonding in the apical positions to complete the octahedral stereochemistry. Crystal structures of anhydrous metal oxinates other than Cu(II) and Pd(II) are not known, although Mande and Chetal[165] have reported that anhydrous Co(II) oxinate is tetrahedral from observations of the cobalt K X-ray absorption edge. Fanning and Jonassen[166] prepared two forms of anhydrous Cu(II) oxinate and studied their room temperature magnetic properties and IR spectra. Frazer and coworkers[148] measured the magnetic susceptibilities as a function of temperature for both forms down to 88°K. The crystal structure of the α-form was determined by Hoy and Morriss[112] and that of the β-form by Palenik[118]. The structure of the α-form consists of a chain of essentially planar $[Cu(OX)_2]$ molecules. Each Cu(II) atom is 6-co-ordinate and is weakly co-ordinated in the apical positions by oxygen atoms from neighbouring molecules; the Cu-O out-of-plane distance being 3.32 Å and the in-plane distance 1.94 Å. The β-form exists as a dimer-like unit in which the Cu(II) is 5-co-ordinate and the Cu-O out-of-plane distance is 2.83 Å. The Cu-O in-plane distance of 1.93 Å is almost identical with that observed for the α-form.

2. PREPARATION OF COMPOUNDS

(i) Complexes of 2-Thenoyltrifluoroacetone and Benzoyltrifluoroacetone

The di- and trivalent metal complexes were prepared by the general method previously reported[44] except that either the metal acetate, chloride or nitrate, buffered with sodium acetate was employed. Adjustment of the pH of the solution to 6 is necessary for precipitation of the Ca(II), Sc(III) and Ga(III) complexes. This method yields the dihydrates of the metal(II) complexes except for those of Ca(II) and Cu(II) obtained only in the anhydrous form. Dehydration of the Mn(II), Co(II) and Zn(II) TTA complexes is accomplished within 3 hours at 110° and 0.2 torr, that of the Ni(II) complex requires 5 hours at 180° at this pressure. Dehydration of the BTA chelates could not be achieved without decomposition. The Mn(III) complexes were prepared from Mn(III) acetate by an analogous procedure to that of the corresponding tropolonate[170]. The V(III) complex is very susceptible to oxidation and was prepared and handled throughout under nitrogen. The sodium salts of the divalent tris(β-ketoenolates) were prepared by an analogous procedure to that described in the literature for the ammonium salts[171]. The pyridine adducts were prepared by dissolving the divalent metal complex in pyridine from which the pyridine adduct crystallized after the addition of petroleum ether. The addition of concentrated ammonium hydroxide to an ethanolic solution of the dihydrate caused the bis(ammonia) adduct to precipitate. The bipy and phen adducts were prepared by heating equimolar proportions of the divalent chelate with the nitrogen base in benzene. The subsequent addition of petroleum prevent adduct formation. The phen adduct of Co(II) oxinate was obtained by the method of Lenzer[172], the other phen and bipy adducts being prepared by heating equimolar proportions of the nitrogen base and the dihydrated chelate in a benzene suspension. The substituted 8-quinolinol chelates were prepared in a similar procedure to that of the unsubstituted compounds, the anhydrous species being produced by heating at 120° - 140° and 0.2 torr. Addition of petroleum ether to a pyridine solution of the dihydrated metal chelate caused the bis(pyridine) adduct to precipitate. Quinaldine (2-methyl-8-quinolinol) formed a mono(pyridine) adduct without apparent solution. The sodium salts were prepared by mixing ethanolic solutions of sodium hydroxide and ligand.

III. RESULTS

1. ANALYSES OF COMPOUNDS

Table 1. Analytical data on the 2-thenoyltrifluoroacetonate complexes

Complex	Calculated		Found	
	%C	%H	%C	%H
$[Ca(TTA)_2]_n$	39.8	1.7	39.9	1.8
$[Mn(TTA)_2]_n$	38.6	1.6	38.3	1.5
$[Co(TTA)_2]_n$	38.3	1.6	38.0	1.5
$[Ni(TTA)_2]_n$	38.4	1.6	38.0	1.7
$[Cu(TTA)_2]$	38.0	1.6	38.0	1.8
$[Zn(TTA)_2]_n$	37.9	1.6	37.7	1.5
$[Sc(TTA)_3]$	40.7	1.7	41.0	2.1
$[V(TTA)_3]$	40.4	1.7	40.6	1.8
$[Cr(TTA)_3]$	40.3	1.7	41.1	2.1
$[Mn(TTA)_3]$	40.1	1.7	40.1	1.8
$[Fe(TTA)_3]$	40.1	1.7	39.2	1.9
$[Ga(TTA)_3]$	39.3	1.7	39.1	1.7
$Na[Mn(TTA)_3]$	39.0	1.6	38.4	1.6
$Na[Co(TTA)_3]$	38.7	1.6	38.7	1.6
$Na[Ni(TTA)_3]$	38.7	1.6	38.1	1.9
$Na[Zn(TTA)_3]$	38.3	1.6	37.9	1.9

ether caused the precipitation of the adducts which were collected on the filter, washed with petroleum ether and air dried.

(ii) Complexes of Anthranilic Acid

The metal complexes of anthranilic and substituted anthranilic acids were prepared either by the method of Hill and Curran[84] or by the addition of an ethanolic solution of the ligand (2 mole proportions) to an aqueous solution of the metal acetate, chloride or nitrate (1 gram) buffered with sodium acetate. The resulting precipitate was filtered, washed with water and ethanol and dried *in vacuo* over silica gel. The sodium salts were prepared by mixing ethanolic solutions of sodium hydroxide and ligand. The ^{15}N-labelled compounds were prepared from ^{15}N-anthranilic acid of 95 atom - % isotopic purity supplied by Prochem Ltd.

(iii) Chelates of Picolinic and Quinaldic Acids

The divalent metal picolinates were prepared by mixing an ethanolic solution of ligand (2 mole proportion) with a sodium acetate buffered aqueous solution of a metal salt (1 gram). The resulting solution was concentrated to about 15 ml. and the chelate allowed to crystallize out. All the divalent metals except Mn(II) yielded hydrates. Cu(II) forms a dihydrate which loses one mole of water on standing for 10 days and can be dehydrated *in vacuo* at room temperature. The corresponding quinaldates were prepared by adding an aqueous solution of metal salt to a methanolic solution of ligand whose pH had been adjusted to 5 by the addition of sodium carbonate. The resulting precipitates were filtered, washed with methanol and dried *in vacuo* over silica gel at room temperature. The Cu(II) chelate was dehydrated at 155° for 3 hours at 0.2 torr. Dehydration of the other chelates of picolinic and quinaldic acids was unsuccessful or else the resulting anhydrous compounds absorbed water while in the form of a Nujol mull. The potassium salts of the tris-(quinaldate) divalent chelates were prepared by dissolving the ligand (3 mole proportions) and potassium hydroxide (1 mole proportion) in methanol and adding the metal salt (1 gram). The solution was refluxed for a couple of hours and then the resulting precipitate was filtered from the hot solution, washed with methanol and dried at room temperature *in vacuo* over silica gel. Bipy and phen adducts were prepared by heating a suspension of the hydrated chelate with an equimolar proportion of the nitrogen base in benzene for 6 hours. The bis(pyridine) adducts were precipitated with petroleum ether from a pyridine solution of the hydrated chelate or were obtained by heating the chelate in a pyridine slurry.

(iv) Complexes of 8-Quinolinol

The metal oxinates were prepared by mixing an aqueous solution of each metal chloride with an ethanolic solution of oxine in a 1:1.05 molar ratio. The resulting complex was precipitated by buffering with sodium acetate, filtered and washed with ethanol to remove excess oxine. These products were dried or dehydrated according to standard procedure[110]. The α- and β-copper oxinates were prepared by the method of Fanning and Jonassen[166]. The Mn(III) chelate was prepared from the corresponding acetylacetonate following the procedure of Ray and coworkers[93], using 2-propanol as the solvent to

Table 2. Analytical data on the adducts of the 2-thenoyltrifluoroacetonate complexes

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Mn(TTA)_2(H_2O)_2]$	36.0	2.3		35.2	2.2	
$[Fe(TTA)_2(H_2O)_2]$	36.0	2.3		35.0	2.4	
$[Co(TTA)_2(H_2O)_2]$	35.8	2.3		35.9	2.4	
$[Ni(TTA)_2(H_2O)_2]$	35.8	2.3		36.1	2.6	
$[Zn(TTA)_2(H_2O)_2]$	35.3	2.2		35.4	2.1	
$[Mn(TTA)_2(py)_2]$	47.9	2.8	4.3	47.9	2.7	4.4
$[Co(TTA)_2(py)_2]$	47.3	2.7	4.3	47.0	2.6	4.6
$[Ni(TTA)_2(py)_2]$	47.4	2.7	4.2	47.5	2.6	4.2
$[Cu(TTA)_2(py)]$	43.1	2.2	2.4	42.8	2.2	2.3
$[Zn(TTA)_2(py)_2]$	46.9	2.7	4.2	46.6	2.6	4.2
$[Mn(TTA)_2(NH_3)(H_2O)]$	36.1	2.5	2.6	35.3	2.3	2.8
$[Mn(TTA)_2(NH_3)_2]$	36.4	2.7	5.3	36.4	2.7	5.4
$[Co(TTA)_2(NH_3)_2]$	35.9	2.6	5.2	36.1	2.6	5.1
$[Ni(TTA)_2(NH_3)_2]$	35.9	2.6	5.2	36.0	2.5	4.6
$[Zn(TTA)_2(NH_3)_2]$	35.5	2.6	5.2	35.1	2.5	4.6
$[Mn(TTA)_2(bipy)]$	48.0	2.5	4.3	48.1	2.5	4.4
$[Co(TTA)_2(bipy)]$	47.5	2.4	4.3	47.8	2.4	4.4
$[Ni(TTA)_2(bipy)]$	47.5	2.4	4.3	48.0	2.4	4.3
$[Cu(TTA)_2(bipy)]$	47.2	2.4	4.2	47.4	2.4	4.5
$[Zn(TTA)_2(bipy)]$	47.0	2.4	4.2	47.1	2.3	4.2
$[Mn(TTA)_2(phen)]$	49.9	2.4	4.1	49.9	2.3	4.1
$[Co(TTA)_2(phen)]$	49.3	2.4	4.1	49.3	2.3	4.1
$[Ni(TTA)_2(phen)]$	49.4	2.4	4.1	48.6	2.3	4.0
$[Cu(TTA)_2(phen)]$	49.0	2.4	4.1	48.7	2.4	4.2
$[Zn(TTA)_2(phen)]$	48.9	2.3	4.1	48.9	2.5	4.4

Table 3. Analytical data on the benzoyltrifluoroacetonate complexes

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Sc(BTA)_3]$	52.2	2.6		52.1	2.5	
$[Cr(BTA)_3]$	51.7	2.6		50.9	2.9	
$[Mn(BTA)_3]$	51.4	2.6		50.8	2.6	
$[Fe(BTA)_3]$	51.4	2.6		51.1	2.8	
$[Ga(BTA)_3].H_2O$	49.1	2.8		48.9	3.3	
$Na[Co(BTA)_3]$	49.5	2.5		49.7	2.4	
$Na[Ni(BTA)_3].H_2O$	48.4	2.7		48.1	2.6	
$Na[Zn(BTA)_3].H_2O$	47.9	2.7		47.7	2.6	
$[Mn(BTA)_2(H_2O)_2]$	46.1	3.1		46.0	3.2	
$[Co(BTA)_2(H_2O)_2]$	45.7	3.1		45.7	3.2	
$[Ni(BTA)_2(H_2O)_2]$	45.8	3.1		46.1	3.0	
$[Cu(BTA)_2]$	48.6	2.4		48.7	2.3	
$[Zn(BTA)_2(H_2O)_2]$	45.2	3.0		45.2	3.1	
$[Mn(BTA)_2(py)_2]$	56.3	3.5	4.4	56.0	3.3	4.3
$[Co(BTA)_2(py)_2]$	55.6	3.4	4.3	55.4	3.5	4.8
$[Ni(BTA)_2(py)_2]$	55.7	3.4	4.3	55.9	3.6	4.6
$[Cu(BTA)_2(py)]$	52.4	3.0	2.4	51.6	2.8	2.2
$[Zn(BTA)_2(py)_2]$	55.1	3.4	4.3	54.9	3.4	3.9
$[Mn(BTA)_2(bipy)]$	56.4	3.2	4.4	56.0	3.2	4.2
$[Co(BTA)_2(bipy)]$	55.8	3.1	4.3	56.0	3.3	4.3
$[Ni(BTA)_2(bipy)]$	55.8	3.1	4.3	55.8	3.1	4.4
$[Cu(BTA)_2(bipy)]$	55.4	3.1	4.3	55.2	3.1	4.4
$[Zn(BTA)_2(bipy)]$	55.3	3.1	4.3	54.9	3.1	4.3
$[Mn(BTA)_2(phen)]$	58.0	3.0	4.2	57.9	3.2	4.3
$[Co(BTA)_2(phen)]$	57.4	3.0	4.2	57.1	3.0	4.7
$[Ni(BTA)_2(phen)]$	57.4	3.0	4.2	57.4	3.0	4.7
$[Cu(BTA)_2(phen)]$	57.0	3.0	4.2	56.7	2.7	4.5
$[Zn(BTA)_2(phen)]$	56.9	3.0	4.2	57.0	2.9	4.3

Table 4. Analytical data on the complexes $[M(X\text{-}ANA)_2]$

M	X	Calculated			Found		
		%C	%H	%N	%C	%H	%N
Mn	H	51.4	3.7	8.6	51.0	3.7	8.5
Co	H	50.8	3.6	8.5	50.4	3.6	8.3
Ni	H	50.8	3.7	8.5	51.1	3.9	8.6
Cu	H	50.1	3.6	8.3	49.9	3.7	8.4
Zn	H	49.8	3.6	8.3	49.5	3.6	8.2
Mn	5-Cl	42.8	2.6	7.1	42.3	2.7	6.8
Co	5-Cl	42.0	2.5	7.0	42.1	2.5	7.1
Ni	5-Cl	42.0	2.5	7.0	41.5	2.5	6.8
Cu	5-Cl	41.5	2.5	6.9	41.0	2.4	6.8
Zn	5-Cl	41.4	2.5	6.9	41.3	2.7	6.8
Mn	5-Br	34.9	2.1	5.8	34.6	2.0	5.9
Co	5-Br	34.4	2.1	5.7	33.8	2.2	5.3
Ni	5-Br	34.4	2.1	5.7	33.7	2.2	5.7
Cu	5-Br	34.1	2.0	5.7	33.6	2.1	5.5
Zn	5-Br	33.9	2.0	5.6	34.2	2.3	5.6
Mn	5-I	29.2	1.8	4.9	29.3	1.9	5.0
Co	5-I	28.8	1.7	4.8	28.6	1.9	4.0
Ni	5-I	28.8	1.7	4.8	28.8	1.9	4.6
Cu	5-I	28.6	1.7	4.8	27.9	1.7	3.7
Zn	5-I	28.5	1.7	4.7	28.5	1.8	4.3
Mn	5-CH$_3$	54.6	4.6	7.9	54.2	4.5	7.9
Co	5-CH$_3$	53.5	4.5	7.8	53.1	4.6	7.8
Ni	5-CH$_3$	53.5	4.5	7.8	51.7	4.4	7.9
Cu	5-CH$_3$	52.8	4.4	7.7	52.1	4.5	7.7
Zn	5-CH$_3$	52.4	4.4	7.7	52.3	4.5	7.7
Mn	4-NO$_2$	40.6	2.4	13.5	40.8	2.4	13.3
Co	4-NO$_2$	39.9	2.4	13.3	38.8	2.4	12.8
Ni	4-NO$_2$	39.9	2.4	13.3	38.4	2.7	12.6
Cu	4-NO$_2$	39.5	2.4	13.2	39.2	2.4	12.9
Zn	4-NO$_2$	39.3	2.4	13.1	39.1	2.1	13.0
Mn[a]	5-NO$_2$	35.7	3.4	11.9	35.6	3.3	11.8
Co[b]	5-NO$_2$	36.8	3.1	12.3	36.7	3.0	12.4
Ni[c]	5-NO$_2$	31.8	4.2	10.6	31.8	4.2	10.8
Cu[a]	5-NO$_2$	35.0	3.4	11.7	34.5	3.2	11.5
Zn[b]	5-NO$_2$	33.6	3.6	11.2	33.0	3.5	11.8

[a] trihydrate [b] dihydrate [c] hexahydrate

Table 5. Analytical data on the salts Na(X-ANA)

X	Calculated			Found		
	%C	%H	%N	%C	%H	%N
H[a]	50.0	4.2	8.3	50.0	4.0	8.3
5-Cl[b]	39.7	3.3	6.6	39.5	3.3	6.6
5-Br[b]	32.8	2.8	5.5	32.9	2.7	5.6
5-I[b]	27.8	2.3	4.6	28.1	2.2	4.0
5-CH_3	55.5	4.7	8.1	54.3	4.7	8.1
4-NO_2[c]	35.0	3.8	11.9	35.3	3.7	11.6
5-NO_2	41.2	2.5	13.7	41.6	2.4	13.7

[a] hemihydrate [b] monohydrate [c] dihydrate

Table 6. Analytical data on the metal picolinate complexes

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Ca(pic)_2(H_2O)_2]$	45.0	3.8	8.8	44.9	3.1	9.1
$[Co(pic)_2(H_2O)_2].2H_2O$	38.4	4.3	7.5	37.9	4.3	7.5
$[Ni(pic)_2(H_2O)_2].2H_2O$	38.4	4.3	7.5	39.3	4.2	7.8
$[Zn(pic)_2(H_2O)_2].2H_2O$	37.8	4.2	7.3	37.7	4.2	7.5
$[Cu(pic)_2].2H_2O$	41.9	3.5	8.1	41.7	3.2	8.1
$[Cu(pic)_2].H_2O$	44.2	3.1	8.6	43.9	2.9	8.6
$[Cu(pic)_2]$	46.8	2.6	9.1	46.1	2.8	9.1
$[Mn(pic)_2]$	48.2	2.7	9.4	48.3	2.8	9.6
$[Co(pic)_2(bipy)].0{\cdot}5H_2O$	56.4	3.7	12.0	56.3	3.5	12.0
$[Ni(pic)_2(bipy)].0{\cdot}5H_2O$	56.4	3.7	12.0	56.4	3.6	11.9
$[Zn(pic)_2(bipy)]$	56.7	3.5	12.0	55.9	3.4	12.0
$[Co(pic)_2(phen)]$	59.6	3.3	11.6	59.0	3.3	11.8
$[Ni(pic)_2(phen)].0{\cdot}5H_2O$	58.6	3.5	11.4	58.7	3.4	11.7
$[Zn(pic)_2(phen)].2H_2O$	54.8	3.8	10.7	55.2	3.3	10.8
$[Co(pic)_2(py)_2].2H_2O$	53.1	4.5	11.3	52.8	4.2	11.3
$[Ni(pic)_2(py)_2].2{\cdot}5H_2O$	52.2	4.6	11.1	52.3	4.3	11.1
$[Zn(pic)_2(py)_2].2H_2O$	52.4	4.4	11.2	51.9	4.0	10.8
$Na(pic).0{\cdot}5H_2O$	46.8	3.3	9.1	45.8	3.3	9.1

Table 7. Analytical data on the metal quinaldate complexes

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Ca(quin)_2(H_2O)]$	59.7	3.5	6.7	59.7	3.5	7.2
$[Mn(quin)_2(H_2O)_2]$	55.2	3.7	6.4	55.3	3.7	6.5
$[Co(quin)_2(H_2O)_2]$	54.7	3.7	6.4	54.7	3.6	6.7
$[Ni(quin)_2(H_2O)_2]$	54.7	3.7	6.4	54.6	3.6	6.6
$[Cu(quin)_2(H_2O)]$	56.4	3.3	6.6	56.5	3.3	6.7
$[Cu(quin)_2]$	58.9	3.0	6.9	58.7	2.9	7.0
$[Zn(quin)_2(H_2O)]$	56.2	3.3	6.6	56.6	3.3	6.8
$[Co(quin)_2(bipy)]$	64.4	3.6	10.0	64.7	3.6	10.2
$[Ni(quin)_2(bipy)]$	64.4	3.6	10.0	63.9	3.5	9.9
$[Mn(quin)_2(phen)]$	66.3	3.5	9.7	66.0	3.4	9.9
$[Co(quin)_2(phen)]$	65.9	3.5	9.6	65.7	3.4	9.7
$[Ni(quin)_2(phen)]$	65.9	3.5	9.6	65.7	3.4	9.8
$[Cu(quin)_2(phen)]$	65.4	3.4	9.5	64.8	3.4	9.6
$[Zn(quin)_2(phen)]$	65.1	3.4	9.5	64.8	3.4	9.7
$[Mn(quin)_2(py)_2]$	64.6	4.0	10.0	63.7	3.9	9.9
$[Co(quin)_2(py)_2]$	64.2	3.9	10.0	64.2	3.9	10.2
$[Ni(quin)_2(py)_2]$	64.2	3.9	10.0	63.5	3.9	9.9
$[Zn(quin)_2(py)]$	61.4	3.5	8.6	61.3	3.7	8.9
$K[Mn(quin)_3].2H_2O$	55.7	3.4	6.5	55.4	3.8	6.5
$K[Co(quin)_3].2H_2O$	55.4	3.4	6.5	54.9	4.2	6.1
$K[Ni(quin)_3].2H_2O$	55.4	3.4	6.5	55.9	4.2	6.3
$Na(quin).1{\cdot}5H_2O$	54.1	4.1	6.3	53.6	3.7	6.7

Table 8. Analytical data on the metal 8-quinolinolate complexes

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$[Mn(OX)_2(H_2O)_2]$	57.0	4.2	7.4	56.9	4.2	7.2
$[Co(OX)_2(H_2O)_2]$	56.4	4.2	7.3	56.1	4.2	7.3
$[Ni(OX)_2(H_2O)_2]$	56.4	4.2	7.3	56.3	4.3	7.2
$[Zn(OX)_2(H_2O)_2]$	55.5	4.1	7.2	55.4	4.1	7.2
$[Mn(OX)_2]$	63.0	3.5	8.2	62.8	3.7	8.1
$[Co(OX)_2]$	62.3	3.5	8.1	61.6	3.6	7.9
$[Ni(OX)_2]$	62.3	3.5	8.1	61.6	3.5	8.0
α-$[Cu(OX)_2]$	61.4	3.4	8.0	60.9	3.4	7.8
β-$[Cu(OX)_2]$	61.4	3.4	8.0	61.2	3.4	8.0
$[Zn(OX)_2]$	61.1	3.4	7.9	60.9	3.9	7.9
$[Cr(OX)_3]$	66.9	3.8	8.7	66.5	3.9	8.2
$[Mn(OX)_3]$	66.5	3.7	8.6	66.7	3.7	8.8
$[Fe(OX)_3]$	66.4	3.7	8.6	65.6	3.6	8.6
$[Co(OX)_3]$	66.0	3.7	8.6	65.4	3.6	8.8
$[Ga(OX)_3]$	64.6	3.6	8.4	65.1	3.8	7.8
$[Co(OX)_2(bipy)]$	66.8	4.0	11.1	66.1	4.0	10.9
$[Ni(OX)_2(bipy)]$	66.8	4.0	11.1	66.4	4.1	10.7
$[Co(OX)_2(phen)]$	68.3	3.8	10.6	68.3	3.8	10.8
$[Ni(OX)_2(phen)]$	68.3	3.8	10.6	67.5	3.9	10.4
$[Zn(OX)_2(phen)]$	67.5	3.8	10.5	67.4	3.8	10.3
$[Ni(OX)_2(py)_2].H_2O$	64.3	4.6	10.7	63.6	4.7	10.3

Table 9. Analytical data on the substituted 8-quinolinolate complexes $[M(R\text{-}OX)_2(H_2O)_2]$

M	R	Calculated			Found		
		%C	%H	%N	%C	%H	%N
Co	5-Cl	47.8	3.1	6.2	48.1	3.1	6.4
Ni	5-Cl	47.8	3.1	6.2	47.9	3.1	6.5
Zn	5-Cl	47.1	3.1	6.1	46.9	3.0	6.5
Co	5, 7-di-Cl	41.5	2.3	5.4	41.5	2.3	5.6
Ni	5, 7-di-Cl	41.5	2.3	5.4	39.9	2.6	5.3
Zn	5, 7-di-Cl	41.0	2.3	5.3	40.9	2.2	5.6
Co	5, 7-di-Br	30.9	1.7	4.0	30.9	1.7	4.4
Ni	5, 7-di-Br	30.9	1.7	4.0	30.1	2.0	4.4
Zn	5, 7-di-Br	30.6	1.7	4.0	30.6	1.6	4.3
Mn	5-Cl-7-I	30.9	1.7	4.0	30.7	1.5	3.8
Co	5-Cl-7-I	30.7	1.7	4.0	30.8	1.7	3.7
Ni	5-Cl-7-I	30.7	1.7	4.0	30.8	1.7	3.9
Zn	5-Cl-7-I	30.4	1.7	3.9	30.1	1.6	4.0
Co[a]	$2\text{-}CH_3$	61.1	4.6	7.1	61.0	4.7	7.3
Ni[a]	$2\text{-}CH_3$	61.1	4.6	7.1	60.9	4.5	7.1
Cu[a]	$2\text{-}CH_3$	60.2	4.6	7.0	60.0	4.6	7.2
Zn[a]	$2\text{-}CH_3$	60.1	4.5	7.0	60.1	4.5	7.1
Ni	$2\text{-}CH_3\text{-}5$, 7-di-Br	33.1	2.2	3.9	33.2	2.2	4.2

[a] monohydrate

Table 10. Analytical data on the substituted 8-quinolinolate complexes $[M(R\text{-}OX)_2]$

M	R	Calculated			Found		
		%C	%H	%N	%C	%H	%N
Mn	5-Cl	52.4	2.4	6.8	52.3	2.4	7.1
Co	5-Cl	51.9	2.4	6.7	51.8	2.4	6.8
Ni	5-Cl	52.0	2.4	6.7	51.7	2.4	6.9
Cu	5-Cl	51.4	2.4	6.7	51.4	2.3	6.7
Zn	5-Cl	51.2	2.4	6.6	50.9	2.3	6.6
Co	5, 7-di-Cl	44.6	1.7	5.8	44.2	1.7	6.0
Ni	5, 7-di-Cl	44.6	1.7	5.8	44.4	1.7	5.8
Cu	5, 7-di-Cl	44.2	1.6	5.7	44.2	1.6	6.0
Zn	5, 7-di-Cl	44.0	1.6	5.7	44.0	1.7	5.6
Mn	5, 7-di-Br	32.8	1.2	4.3	33.0	1.3	4.5
Co	5, 7-di-Br	32.6	1.2	4.2	32.4	1.4	4.0
Ni	5, 7-di-Br	32.6	1.2	4.2	32.9	1.1	4.2
Cu	5, 7-di-Br	32.4	1.2	4.2	32.5	1.2	4.6
Zn	5, 7-di-Br	32.3	1.2	4.2	32.4	1.3	4.0
Mn	5-Cl-7-I	32.6	1.2	4.2	32.3	1.1	4.0
Co	5-Cl-7-I	32.4	1.2	4.2	32.4	1.2	4.0
Ni	5-Cl-7-I	32.4	1.2	4.2	32.2	1.2	4.3
Cu	5-Cl-7-I	32.1	1.2	4.2	31.8	1.2	3.4
Zn	5-Cl-7-I	32.1	1.2	4.1	31.8	1.1	4.0
Mn	$2\text{-}CH_3$	64.7	4.3	7.6	64.4	4.4	7.7
Co	$2\text{-}CH_3$	64.0	4.3	7.5	62.7	4.1	7.6
Ni	$2\text{-}CH_3$	64.0	4.3	7.5	62.7	4.3	7.4
Cu	$2\text{-}CH_3$	63.2	4.2	7.4	63.4	4.2	7.6
Zn	$2\text{-}CH_3$	62.9	4.2	7.3	63.1	4.2	7.6
Mn	$2\text{-}CH_3$-5, 7-di-Br	35.0	1.8	4.1	34.8	1.8	4.3
Co	$2\text{-}CH_3$-5, 7-di-Br	34.8	1.8	4.1	34.7	2.0	4.1
Ni	$2\text{-}CH_3$-5, 7-di-Br	34.8	1.8	4.1	34.8	2.0	4.0
Cu	$2\text{-}CH_3$-5, 7-di-Br	34.5	1.7	4.0	34.1	1.7	4.0
Zn	$2\text{-}CH_3$-5, 7-di-Br	34.4	1.7	4.0	34.2	1.7	4.2

Table 11. Analytical data on the complexes $[Ni(R\text{-}OX)_2(py)_2]$

R	Calculated			Found		
	%C	%H	%N	%C	%H	%N
5-Cl	58.6	3.5	9.8	58.1	3.6	9.6
5, 7-di-Cl	52.3	2.8	8.7	52.6	2.9	8.7
5, 7-di-Br	41.0	2.2	6.8	41.1	2.2	7.0
5-Cl-7-I	40.7	2.2	6.8	41.3	2.2	7.0
2-CH_3[a]	66.1	4.7	9.3	65.6	4.8	9.9
2-CH_3-5, 7-di-Br	42.4	2.6	6.6	42.3	2.6	6.8

[a] monopyridine adduct

Table 12. Analytical data on the salts Na(R-OX)

R	Calculated			Found		
	%C	%H	%N	%C	%H	%N
H[b]	53.2	5.0	6.9	51.8	4.6	6.7
5-Cl[b]	45.5	3.8	5.9	43.9	3.4	5.7
5, 7-di-Cl	45.8	1.7	5.9	44.9	1.7	6.0
5, 7-di-Br[a]	31.5	1.8	4.1	31.0	1.4	4.6
5-Cl-7-I[b]	29.7	2.2	3.8	30.4	1.1	3.6
2-CH_3[c]	51.1	6.0	6.0	50.6	5.9	6.0
2-CH_3-5, 7-di-Br	35.4	1.8	4.1	35.7	2.1	4.1

[a] monohydrate [b] dihydrate [c] trihydrate

2. INFRA RESULTS

All values are cm^{-1}.

Table 13. Vibrational frequencies of the complexes $[M(TTA)_3]$ (2000 - 200 cm^{-1})

Sc	V	Cr	Mn	Fe	Ga	Assignment
1603	1604	1600	1603	1602	1592	νC=O
1584	1575	1579	1585	1580	1583	νC=C
1550	1541	1549	1547	1550	1553	thienyl ring stretch
1517	1508	1515	1524	1517	1526	
1411	1409	1410	1406	1411	1410	
1363	1367	1363	1369	1362	1368	
1354	1355	1354	1354		1358	
1319	1319	1323	1319	1320	1320	
1297	1304	1300	1299	1298	1303	νC=C + νC-R
1258	1258	1260	1260	1258	1263	
1235	1235	1236	1235	1235	1236	νC-F
1197	1203	1203	1200	1202	1203	
1151	1160	1150	1165	1149	1146	δC-H i.p.
1135	1140		1140		1133	
1084	1088	1086	1087	1085	1086	δC-H i.p. thienyl
1068	1067	1070	1067	1068	1070	
1042	1042	1043	1035	1042	1043	δC-H i.p. thienyl
1022	1013	1021	1013[a]	1019	1019	
940	937	940	936[b]	938	939	δC-H o.o.p. thienyl
868	862	864	862	864	864	
850	850	850	850	850	852	$\nu C-CF_3$
800	801	797	799[c]	797	797[e]	δC-H o.o.p. thienyl
773	774	778	774	776	775	δC-H o.o.p. chelate
755	753	754	754	755	754	$\nu C-CF_3$
729	731	728	736[d]	725	729	
696	697	705	697	696	704	CF_3
690	690	694	687	691	690	
645	657	665	667	652	660	νM-O
			653			νMn-O
609	613	620		611	615	thienyl
595	597	602	601	593	595	νM-O
563	568	565	565	565	564	CF_3
533	540	552	539	530	540	νM-O
520	530	520	525	520	523	CF_3
			505			νMn-O
495	495	495	495	495	490	CF_3
465	464	465	464	465	464	thienyl
367	396	408	410	381	393	νM-O
			389			νMn-O
334	344	346	331	340	357	νM-O
317	296	337	312	288	261	νM-O
			290			νMn-O

Mean of doublet at: a) 1023 and 1003, b) 939 and 933, c) 803 and 795, d) 740 and 732, e) 802 and 794 cm^{-1}.

Table 14. Vibrational frequencies of the complexes $[M(TTA)_2]_n$ (2000 - 200 cm^{-1})

Ca	Mn	Co	Ni	Cu	Zn	Assignment
1603	1609	1607	1606	1600	1611	νC=O
1584	1594	1585	1579	1578	1585	νC=C
1544	1542	1548	1548	1548	1551	thienyl ring stretch
1516	1519	1509	1519	1514	1516	
1414	1412	1415	1414	1409	1413	
1369	1369	1368	1365	1364	1360	
1353	1357	1355	1352	1358	1352	
1302	1301	1310	1310	1328	1310	
				1299		νC=C + νC-R
1257	1259	1255	1259	1263	1261	
1235	1236	1236	1235	1236	1236	νC-F
1195	1194	1196	1195	1190	1196	
1150	1150	1151	1149	1155	1152	δC-H i.p.
1132	1130	1139	1139		1135	
1084	1082	1085	1084	1087	1085	δC-H i.p. thienyl
1063	1064	1065	1065	1069	1065	
1038	1036	1043	1044	1038	1041	δC-H i.p. thienyl
1010	1000	1011	1012	1020	1010	
935	938	933[a]	938	943	935	δC-H o.o.p. thienyl
865	871	862	864	866	863	
851	845	845	840	852	851	νC-CF_3
794	800	802[b]	802[c]	798	793	δC-H o.o.p. thienyl
770	773	774	775	779	775	δC-H o.o.p. chelate
752	755	750	753	756	752	νC-CF_3
727	723	728	724	726[d]	729	
696	696	703	707	708	704	CF_3
686	689	689	689	698	691	
646	650	657	664	675	659	νM-O
610	610	614	616	616	615	thienyl
585	591	591	592	604	596	νM-O
562	563	565	569	563	560	CF_3
				531		
521	525	525	523	522	523	CF_3
496	495	495	495	495	495	
470	462	465	465	463	463	thienyl
369	387	396	403	556	389	νM-O
319	328	335	342	356	330	νM-O

Mean of doublet at: [a]) 935 and 930, [b]) 811 and 792, [c]) 814 and 790, [d]) 731 and 720 cm^{-1}.

Table 15. Vibrational frequencies of the complexes $Na[M(TTA)_3]$ (2000 - 200 cm^{-1})

Mn	Co	Ni	Zn	Assignment
1619	1615	1622	1623	νC=O
1604	1604	1605	1605	
1583	1582	1582	1585	νC=C
1544	1542	1543	1544[a]	thienyl ring stretch
		1512	1515	
1510	1508	1508	1509	
1416	1415	1416	1415	
	1359	1359	1359	
1358	1353	1353	1353	
1305	1305	1304	1306	
1254	1255	1255	1255	νC=C + νC-R
1234	1234	1234	1234	νC-F
1196	1195	1195	1196	
1153	1153	1153	1153	δC-H i.p.
1133	1134	1134	1133	
1084	1084	1084	1084	δC-H i.p. thienyl
1062	1063	1063	1063	
1041	1041	1041	1041	δC-H i.p. thienyl
1013	1012	1013	1012	
938	939	940	938	δC-H o.o.p. thienyl
865	865	865	865	
850	850	850	850	$\nu C\text{-}CF_3$
790	792[b]	789	792[c]	δC-H o.o.p. thienyl
772	773	774	773	δC-H o.o.p. chelate
751	752	752	752	$\nu C\text{-}CF_3$
722	723	722	723	
699	702	704	701	CF_3
686	687	689	688	
649	655	659	652	νM-O
611	612	614	612	thienyl
587	591	592	591	νM-O
561	561	561	561	CF_3
522	521	521	521	
502	509	514	504	
471	477	487	472	δO-M-O
	459	460	459	thienyl
376	392	401	379	νM-O
325	332	336[d]	331	νM-O
302	307	311	303	νM-O
235	238	254	240	

Mean of doublet at: a) 1547 and 1542, b) 795 and 789, c) 794 and 789, d) 338 and 333 cm^{-1}.

Table 16. Vibrational frequencies of the complexes $[M(TTA)_2(H_2O)_2]$ (2000 - 200 cm^{-1})

Mn	Fe	Co	Ni	Zn	Assignment
1610	1603	1608	1608	1610	νC=O
1586	1583	1584	1584	1585	νC=C
1541	1540	1544	1548	1541	thienyl ring stretch
1515	1508	1512	1509	1516	
1413	1415	1414	1415	1414	
1358	1359	1360	1360	1359	
1351	1353	1351	1354	1353	
1306	1310	1313	1312	1312	
1260	1258	1261	1260	1263	νC=C + νC-R
1236	1236	1236	1237	1236	νC-F
1194	1195	1194	1196	1196	
1152	1149	1150	1152	1150	δC-H i.p.
1133	1140	1132	1133	1130	
1085	1085	1085	1085	1087	δC-H i.p. thienyl
1066	1064	1065	1065	1065	
1038	1044	1040	1045	1045	δC-H i.p. thienyl
1011	1010	1009	1011	1010	
935	936	935	937	934	δC-H o.o.p. thienyl
864	862	862	862	862	
852	850	851	850	851	νC-CF_3
794	794	793	791	793	δC-H o.o.p. thienyl
774	773	774	776	774	δC-H o.o.p. chelate
752	754	752	752	752	νC-CF_3
724	729	729	729	729	
701	701	703	706	702	CF_3
689	689	690	691	689	
653	654	658	663	655	νM-O
612	612	615	616	614	thienyl
590	591	591	591	591	νM-O
570	566	563	563	562	CF_3
523	525	522	523	521	
500	500	495		490	CF_3
465	465	464	465	462	thienyl
382	386	395	407	384	νM-O
300	305	311	314	300	νM-O

Table 17. Vibrational frequencies of the complexes [M(BTA)$_3$] (2000 - 200 cm^{-1})

Sc	Cr	Mn	Fe	Ga	Assignment
1610	1600	1609	1604	1604	νC=O
1600	1600	1598	1597	1613	νC=C
1578	1575	1575	1575	1583	νC=C phenyl
1544	1544	1540	1543	1547^a	νC=O + δC-H
1494	1495	1493	1495	1497	νC=C phenyl
1325	1327	1325	1326	1328	νC=C + νC-phenyl
1316				1316	
1293	1299	1291	1295	1300	νC=C + νC-R
1256	1257	1254	1256	1260	
1207		1202	1203	1196	νC-F
1189		1193	1190		
1144^b	1150	1145	1149	1144	δC-H i.p.
1100	1099	1098	1099	1100	δC-H i.p. phenyl
1078	1081	1077	1078	1081	
				1069	
1027	1030	1027	1028	1029	δC-H i.p. phenyl
1002	1003	1003	1003	1004	
948	950	945	945	948	νC-phenyl
845	845			846	νC-CF$_3$
820	816	819	819	818	δC-H o.o.p. chelate
804	809	807	807	810	
774	774	777	776	778	δC-H o.o.p. phenyl
755	753	763	752	754	νC-CF$_3$
721	726	724	722	727	
700	703	697	698	702	C-H phenyl + CF$_3$
680	682	682	681	683	CF$_3$
636	660	648	642	650	νM-O
594	604	605	595	597	νM-O
		596			νMn-O
543	558	571	538	553	νM-O
		542			νMn-O
520		525	525	532	CF$_3$
498	531	477	508	475	δO-M-O
445	458^c	450	445	448	phenyl
378	415	401	387	402	νM-O
		390			νMn-O
350	359	347	356	378	νM-O
322	339	321	288	271	νM-O
		296			νMn-O
300			310	289	

Mean of doublet at: ^{a}) 1553 and 1542, ^{b}) 1149 and 1139, ^{c}) 461 and 456 cm^{-1}.

Table 18. Vibrational frequencies of the complexes $[M(BTA)_2(H_2O)_2]$ (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu[a]	Zn	Assignment
1615	1615	1616	1608	1612	νC=O
1601	1602	1603	1601	1602	νC=C
1582	1582	1582	1578	1583	νC=C phenyl
1578	1578	1578	1571	1578	
1552	1552	1551	1552	1552	νC=O + δC-H
1540	1540	1540	1540	1540	
1522	1522	1522	1517	1523	
1518	1517	1518	1507	1518	
1492	1495	1495	1495	1495	νC=C phenyl
1457	1457	1457	1458	1457	
1438	1438			1438	
1324	1325	1325	1329	1325	νC=C + νC-phenyl
1312	1314	1316	1320	1315	
1289	1294	1296	1303	1296	νC=C + νC-R
1258	1258	1258	1257	1258	
			1194		νC-F
1192	1192	1192	1183	1193	
1166	1166	1167	1166	1166	δC-H i.p.
1151	1151	1151		1152	
1134	1135	1135	1150	1135	
1102	1102	1102	1098	1102	δC-H i.p. phenyl
1080	1080	1081	1081	1080	
1064				1067	
1028	1028	1029	1028	1028	δC-H i.p. phenyl
1004	1004	1004	1002	1004	
997	997	998	981	996	
943	945	946	948	943	νC-phenyl
934	933	934	935	933	
840	840	840	850	840	νC-CF_3
815	813	812	811	814	δC-H o.o.p. chelate
800	802	804		802	
776	775	774	771	777	δC-H o.o.p. phenyl
752	752	753	748	752	νC-CF_3
721	722	724	725	722	
701	700	700	699	700	C-H phenyl + CF_3
682	682	682	679	682	CF_3
639	645	652	668	643	νM-O
625					
589	590	591	606	590	νM-O
516	523	525	528[b]	521	CF_3
442	445	449	442[c]	443	phenyl
387	405	415	563	392	νM-O
347	334	345	362	304	
302		312	310		
241	244	253	277	228	νM-O

[a] Cu in the anhydrous form, $[Cu(BTA)_2]$

Mean of doublet at: [b]) 533 and 523, [c]) 448 and 435 cm^{-1}.

Table 19. Vibrational frequencies of the complexes $Na[M(BTA)_3]$ (2000 - 200 cm^{-1}

Co	Ni	Zn	Assignment
1615	1615	1617	νC=O
1602	1602	1602	νC=C
1582	1582	1582	νC=C phenyl
1545	1544	1542	νC=O + δC-H
1495	1496	1496	νC=C phenyl
1322	1323	1322	νC=C + νC-phenyl
1313	1314	1312	
1288	1288	1286	νC=C + νC-R
1256	1259	1255	
1186	1189	1186	νC-F
1156	1155	1156	δC-H i.p.
1130	1136	1129	
1101	1101	1101	δC-H i.p. phenyl
1078	1079	1077	
1065		1065	
1028	1029	1028	δC-H i.p. phenyl
1003	1003	1003	
946	946	944	νC-phenyl
846	846	845	νC-CF$_3$
816	814	816	δC-H o.o.p. chelate
805	805	804	
772	774	770	δC-H o.o.p. phenyl
752	754	752	νC-CF$_3$
723	724	723	
702	702	703	C-H phenyl + CF$_3$
685	684	684	CF$_3$
646	651	644	νM-O
588	589	588	νM-O
519	524	520	CF$_3$
		476	δO-M-O
443	446	440	phenyl
398	403	385	νM-O
345	346	346	
309	312		
255	257	251	νM-O
	241		

Table 20. Vibrational frequencies of the complexes $[M(TTA)_2(NH_3)_2]$ (4000 - 200 cm^{-1})

Mn	Co	Ni	Zn	$[Mn(TTA)_2(NH_3)(H_2O)]$	Assignment
3380	3380	3378	3380	3380	νN-H
3280	3288	3290	3288	3282	νN-H
3120	3100	3100	3103	3118	
1621					δN-H
1614	1606	1608	1612	1610	νC=O
1584	1583	1579	1580	1585	νC=C
1547	1542	1545	1545	1541	thienyl ring stretch
1513	1507	1510	1510	1512	
1417	1416	1417	1416	1415	
1353	1353	1353	1353	1352	
1303	1302	1303	1301	1303	
1258	1257	1256	1258	1259	νC=C + νC-R
1235	1236	1235	1236	1236	νC-F
	1218	1228	1221		
1192	1191	1190	1191	1193	νC-F
1154	1153	1153	1154	1152	δC-H i.p.
1136	1136	1137	1135	1137	
1085	1085	1086	1085	1085	δC-H i.p. thienyl
1063	1064	1063	1063	1064	
		1033			
1008	1007	1009	1005	1008	
934	934	936	933	934	δC-H o.o.p. thienyl
861	861	861	860	862	
851	850	850	851	850	$\nu C-CF_3$
789	788	785	789	792	δC-H o.o.p. thienyl
770	772	772	771	772	δC-H o.o.p. chelate
751	751	751	751	751	$\nu C-CF_3$
726	728	728	730	725	
699	702	703	700	700	CF_3
685	687	687	687	687	
650	654	658	652	652	νM-O
610	614	613	611	611	thienyl
584	587	587	586	586	νM-O
				565	CF_3
545	500	504	492	508	
522	522	523	522	522	
464	463	464	464	465	thienyl
372	384^a	391	373	378	νM-O
319	325^b	331	319	326^c	νM-O
303	308	309	305	306	νM-O
285	286	285	282	286	

Mean of doublet at: a) 387 and 381, b) 328 and 323, c) 331 and 322 cm^{-1}.

Table 21. Vibrational frequencies of the complexes [M(TTA)$_2$(py)$_2$] (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu[a]	Zn	Assignment
		1624			
1609	1602	1607	1602	1610	νC=O
1590	1572	1579	1582	1580	νC=C
1542	1544	1541	1551	1542	thienyl ring stretch
1514	1510	1523	1521	1515	
1508	1505	1505	1509	1507	py
	1450	1452			
1414	1418	1417	1419	1415	thienyl ring
1358	1359	1358	1363	1360	
1352	1355			1354	
1308	1310	1307	1320	1307	
1260	1253	1252	1260	1262	νC=C + νC-R
1236	1233	1234	1236	1237	νC-F
	1216	1223	1222	1224	py
1190[b]	1185	1183	1192	1195	νC-F
1151	1148	1146	1151	1151	δC-H i.p.
1132	1132	1137	1144	1133	
1086	1086	1085	1089	1085	δC-H i.p. thienyl
1073	1075	1075		1074	py
1064	1062	1063	1069	1063	
1039	1039	1042	1038	1041	δC-H i.p. thienyl
	1031	1037		1033	py
1008	1012	1014	1010	1012	
	947				
934	936	937	944	935	δC-H o.o.p. thienyl
	912				
865	859	861	864	861	
839	848	849	850	850	νC-CF$_3$
791					
782	785	783	788	784	δC-H o.o.p. thienyl
770	770	772	777	770	δC-H o.o.p. chelate
755	757	761	762	759	py
744	750	755		755	νC-CF$_3$
721	726	725		729	
708	700	703	713	700[c]	py
686	685	686	694	684	CF$_3$
649	652	658	668	650	νM-O
625	630	635	624	632	py
610	611	613	617	609	thienyl
584	586	586	596	584	νM-O
560	563	567	565	567	CF$_3$
521		524	525	522	
502	513	507		495	
476	491				δO-M-O
458	462	464	462	471	thienyl
418	428	434	419	425	py
365	380	387	540	368	νM-O
321	331	333	346	324	νM-O
303	309	310	310	302	νM-O
240	254	262	266	258	
		244			

[a] Cu forms the mono(pyridine) adduct

Mean of doublet at: [b]) 1195 and 1186, [c]) 703 and 698 cm^{-1}.

Table 22. Vibrational frequencies of the complexes [M(TTA)$_2$(phen)] (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu	Zn	Assignment
1619	1614	1619	1625	1624	νC=O
1601	1603	1603	1596	1605	νC=C
1542	1540	1543	1539	1544	thienyl ring
1520	1523	1524	1523	1523	
1508	1506	1504	1503	1508	phen
1433	1436	1430	1433		
1418	1418	1418	1418	1418	thienyl ring
1368	1360	1358	1354	1369	
1360	1354	1356		1360	
1311	1303	1307	1305	1304	
1295		1296	1297	1299	phen
1249	1250	1250	1249	1249	νC=C + νC-R
1231	1231	1232	1228	1232	νC-F
1184	1185	1191[a]	1184	1185	
1144	1144	1145	1145	1144	δC-H i.p.
1137	1135	1134	1135	1135	
1105	1107	1109	1110	1107	phen
1087	1088	1086	1086	1087	δC-H i.p. thienyl
1063	1065	1062	1064	1063	
1034	1035	1036	1034	1034	δC-H i.p. thienyl
1015	1018	1014	1016	1017	
936	936	938	933	936	δC-H o.o.p. thienyl
868	871	874	876	871	phen
862	862	862		862	δC-H o.o.p. thienyl
851	850	849	853	851	νC-CF$_3$
843					
810	805		808	809	δC-H o.o.p. thienyl
783	784	780	781	782	phen
768	770	771	768	769	δC-H o.o.p. chelate
751	749	747[b]	745[c]	749	νC-CF$_3$
728	728	728	725	729	
719	718		718	719	phen
712	713	711		711	
696	699	701	698	698	CF$_3$
683	685	686	684	684	
647	651	655	653	649	νM-O
	647	649	626		phen
608	610	611	609	609	thienyl
580	583	585	577	581	νM-O
565	566			565	CF$_3$
521	522	522	519	521	
510				509	phen
497	502	505	510	498	CF$_3$
476	480[d]	485	494	480	δO-M-O
464	465	463	464	465	thienyl
438	446	450	440	442	phen
422	427	427	430	425	
408	415		414	410	
364	379	386	367	368	νM-O
319	331	334	330	330	νM-O
298			307	300	νM-O
276	295	303	294	287	νM-N
231	237	261	268	250	
			260		
		240	243		

Mean of doublet at: [a] 1199 and 1184, [b] 752 and 742, [c] 750 and 740, [d] 484 and 475 cm^{-1}.

Table 23. Vibrational frequencies of the complexes [M(TTA)$_2$(bipy)] (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu	Zn	Assignment
1621	1616	1618	1623	1624	νC=O
1601	1601	1601	1603	1600	νC=C
1572	1581	1571	1572	1582	bipy
1541	1541	1541	1541	1541	thienyl ring
1524		1523	1522		
1507	1505	1504	1501	1507	bipy
1450	1447	1447	1450	1450	
1419	1419	1419	1420	1418	thienyl ring
1360	1359	1357[a]	1356	1359	
1314	1310	1310	1314	1313	
	1294	1294	1294	1293	νC=C + νC-R
1250	1250	1250	1250	1251	
1233	1231	1236	1229	1232	νC-F
	1200	1198	1199	1200	
1187	1185	1186	1182	1185	bipy
1160	1172	1172	1171	1173	
1140	1143	1146	1144	1144	δC-H i.p.
1133	1131	1130	1129	1131	
	1105	1105			bipy
1087	1086	1087	1085	1086	δC-H i.p. thienyl
1062	1063	1063	1062	1064	
1044	1042	1042	1046	1046	δC-H i.p. thienyl
1035	1025	1030	1035	1028	bipy
1018	1018	1020		1019	
972	976	976	982	978	bipy
937	936	937	933	936	δC-H o.o.p. thienyl
902					
861	864	864	863	863	δC-H o.o.p. thienyl
		859	856		
842	846	845			νC-CF$_3$
812	790	786		790	δC-H o.o.p. thienyl
782	780	778	778	779	δC-H o.o.p. chelate
767	767	768	772	769	bipy
748	744	752	751	745	νC-CF$_3$
738	737	737	741	737	bipy
728	730	730	728[b]	728	νC-CF$_3$
717	710	710	710	711	bipy
696	697	699	697	698	CF$_3$
685	685	686	684	684	
			661		
648	651	655	652	648	νM-O
628	635	638		633	bipy
608	610	612	609	608	thienyl
584	584	584	578	582	νM-O
521	523	523	519	522	CF$_3$
499	500	506	509	496	
	476	480			δO-M-O
464	462	462	463	464	thienyl
	443	447	444	442	bipy
414	416	418	415	413	
363	379	385	368	365	νM-O
323	331	334	330	330	νM-O
297	308	307		298	νM-O
237	277	288	289	243	νM-N
		261	270		
		243			

Mean of doublet at: [a]) 1359 and 1355, [b]) 733 and 724 cm^{-1}.

Table 24. Vibrational frequencies of the complexes [M(BTA)$_2$(py)$_2$] (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu[a]	Zn	Assignment
1634				1638	νC=O
1618	1615	1618	1610	1619	
1603	1606	1608		1605	νC=C
1583	1583	1582	1584	1583	νC=C phenyl
1543	1540	1539	1554	1543	νC=O + δC-H
1494	1497	1496	1495	1496	νC=C phenyl
1322	1323	1322	1331	1322	νC=C + νC-phenyl
1316	1316	1314		1312	
1292	1293	1293	1304	1292	νC=C + νC-R
1256	1253	1242	1258	1248	
1226	1220	1219	1220	1225	py
1191	1194	1193	1189	1199	νC-F
1182	1172	1172		1182	
	1156	1158			δC-H i.p.
1136	1135	1133	1152	1149	
1100	1097	1097	1100	1101	δC-H i.p. phenyl
1079	1077	1076	1081	1076	
		1071			py
1065	1063	1063		1068	
1040	1041	1042	1037	1041	py
1029	1030	1030	1031	1028	δC-H i.p. phenyl
1010	1013	1015		1015	py
1004	1003	1004	1006	1003	
943	942	943	950	943	νC-phenyl
810	805	807	811	810	δC-H o.o.p. chelate
796	798	800		798	
767	763	762	771	765	δC-H o.o.p. phenyl
755	755	757		757	νC-CF_3
	745	744			
718	720	722	726	719	
707		704	710	707	py
698	697	697	700	696	C-H phenyl + CF_3
693	686	687	683		CF_3
	678	677			py
636	646	652	664	639	νM-O
630	632	636	624		py
584	585	585	595	585	νM-O
522	522	524	524	523	CF_3
507				507	
476	486	491		475	δO-M-O
442	450	451	451	444	phenyl
422	427	434	421	428	py
			563		
370	391	407	551	373	νM-O
	343	345	362		
305	310	310	309	306	
255	255	261	267	255	

[a] Cu forms a mono(pyridine)adduct.

Table 25. Vibrational frequencies of the complexes [M(BTA)$_2$(phen)] (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu	Zn	Assignment
1627	1630	1630	1634	1635	νC=O
1617	1620	1617			νC=C
1602	1605	1605	1603	1603	phen
1584	1584	1584	1586	1584	νC=C phenyl
1544	1543	1538	1537	1544	νC=O + δC-H
1525	1524			1524	
1495		1493	1492		νC=C phenyl
1432	1433	1432	1436		
1320	1321	1321	1319	1320	νC=C + νC-phenyl
1314	1311	1312	1314	1312	
1291	1292	1294	1295	1292	νC=C + νC-R
1250	1251	1252	1250	1250	
1190[a]	1185	1185	1188	1187	νC-F
1140[b]	1137	1139	1137	1136	δC-H i.p.
1104	1105	1107	1108	1106	phen
1096	1100	1100	1100	1099	δC-H i.p. phenyl
1075	1078	1079	1077	1078	
1029	1028	1029	1029	1029	
1002	1008	1003	1003	1003	
943	944	946	943	945	νC-phenyl
867	871	873	876	871	phen
849	853	854	857	853	νC-CF$_3$
810	808	808	807	809	δC-H o.o.p. chelate
795	797	798	794	797	
	781	781	785	783	phen
765	763	763	765	763	δC-H o.o.p. phenyl
	749	747	745[c]	745	νC-CF$_3$
731	730	730	726	730	
718	719	720	719	719	phen
701	702	702	702	703	C-H phenyl + CF$_3$
684	690	690	691	685	CF$_3$
			651		
638	641	647	642	639	νM-O
583	583	584	578	581	νM-O
510	519	522	521	513	CF$_3$
	506	506	506	480	
476	480	485	489	471	δO-M-O
	441	444	461	444	phenyl
424	426	428	431	426	phen
404			404	403	
375	382	390	373	375	νM-O
339	344	346	333	339	
284	294	302	295	290	νM-N
249	256		242	254	
231	236	261	263	230	νM-L?

Mean of doublet at: [a]) 1198 and 1183, [b]) 1148 and 1131, [c]) 750 and 740 cm^{-1}.

Table 26. Vibrational frequencies of the complexes [M(BTA)$_2$(bipy)] (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu	Zn	Assignment
1630	1630	1630	1636	1635	νC=O
1616	1619	1618	1612	1617	νC=C
1601	1603	1604	1603	1602	bipy
1578	1582	1583	1585	1584	νC=C phenyl
1533	1540	1539	1535	1542	νC=O + δC-H
1523	1524	1523			
1491	1493	1492		1498	νC=C phenyl
1444	1447	1449	1431	1448	bipy
1319	1320	1320	1320	1320	νC=C + νC-phenyl
1288	1292	1294	1295	1292	νC=C + νC-R
1249	1249	1250	1249	1249	
1181	1189	1188	1190	1191	νC-F
1161	1175			1163	δC-H i.p.
1149	1135	1144	1145	1135	
1126		1136	1131		
1100[a]	1103	1104	1105	1102	δC-H i.p. phenyl
1077	1077	1078	1075	1077	
1061	1067	1056	1068		
1044	1043	1044	1044	1043	bipy
1027	1025	1029	1036	1027	
1020	1018	1021	1028	1018	δC-H i.p. phenyl
1011			1023		
1002	1003	1003	1004	1003	
976	975	975		976	bipy
943	944	946	943	944	νC-phenyl
933		931		931	
852	848	848		847	νC-CF$_3$
814	810	806	807	809	δC-H o.o.p. chelate
796	798	798	795	796	
772	766	768	772	770	δC-H o.o.p. phenyl
762		762	764	763	bipy
738	739	737	734	738	bipy
719	720	721	719	719	νC-CF$_3$
706[b]	700	703	702	701	C-H phenyl + CF$_3$
686	684	690	680	683	CF$_3$
651	653	655[c]	657[d]	654	bipy
637	641	645	644	638	νM-O
581	583	584	577	581	νM-O
507	516	521	520	511	CF$_3$
474	477	480	457	468	δO-M-O
441	443	445	442	441	phenyl
414	417	418	416	413	bipy
367	387	391	378	375	νM-O
333	344	342	335[e]	345	
300	302	307	319	300	
234	277	288	291	245	νM-N
	236	262	274		νM-L?

Mean of doublet at: [a])1106 and 1094, [b]) 711 and 702, [c]) 657 and 653, [d]) 661 and 653, [e]) 338 and 332 cm^{-1}.

Table 27. Vibrational frequencies of the ligands 2-thenoyltrifluoroacetone and benzoyltrifluoroacetone (2000 - 200 cm^{-1})

HTTA	Assignment	HBTA	Assignment
1650	νC=O	1658	νC=O
1600	νC=C	1610	νC=C
1525	thienyl ring	1582	νC=C phenyl
1412		1500	
1360		1284	
1278		1255	νC-F
1260		1206	
1240	νC-F	1164	
1200		1120	
1160		1100	δC-H i.p. phenyl
1112		1074	
1090	δC-H i.p. thienyl	1029	
1066		1003	
1033	δC-H i.p. thienyl	920	νC-phenyl
982		900	
938		814	
925	δC-H o.o.p. thienyl	773	δC-H o.o.p. phenyl
907		750	νC-CF_3
863	νC-CF_3	720	
804	δC-H o.o.p. thienyl	694	CF_3 + C-H phenyl
778		630	
747	νC-CF_3	582	
734		521	CF_3
721	CF_3	483	
683		442	phenyl
645		361	
610	thienyl	330	
589		293	
562	CF_3	250	
523			
473			
460	thienyl		
439			
356			
294			

Table 28. Vibrational frequencies and ^{15}N-induced shifts ($\Delta\nu$ >0.5 cm^{-1}) of the metal anthranilates (4000 - 250 cm^{-1})

Mn($\Delta\nu$)	Co($\Delta\nu$)	Ni($\Delta\nu$)	Cu($\Delta\nu$)	Zn($\Delta\nu$)	Na†($\Delta\nu$)	Assignment
3311(-6.0)	3314(-7.0)	3313(-6.0)	3282(-7.0)	3307(-7.0)	3443(-9.0)	νN-H
					3414(-10.0)	νN-H···O
3150(-3.0)	3145(-5.0)	3134(-6.0)	3130(-3.0)	3140(-7.0)	3336(-5.0)	νN-H
1620(-2.4)	1620(-2.4)	1620(-2.6)	1619^{a}(-1.9)	1622(-2.6)	1614(-1.2)	δNH_2 scissor
1594(-0.6)	1597	1598(-0.7)		1598(-1.4)	1584	νC=C
1553	1553(-0.6)	1553	1557(-0.9)	1554	1532	νCOO
1496	1497	1497(-1.0)	1496	1498	1489(-0.8)	νC=C
1412(+1.5)	1412(+1.4)	1413	1388^{b}(-9.4)	1412	1398(+0.9)	νCOO
1327(-2.2)	1329(-1.4)	1330(-1.6)	1388^{b}(-9.4)	1331(-1.9)	1326(-1.5)	νC-N
			1330			
1301(-0.9)	1303(-0.7)	1303(-0.8)	1306(-1.2)	1302(-1.0)	1317(-0.6)	
1244(-4.4)	1245(-4.2)	1245(-4.2)	1235(-3.6)	1244(-4.5)	1257(-3.1)]	δNH_2 wag
					1250(-4.7)]	
1169	1167	1156	1154	1167	1173	
1155	1156	1099(-0.6)		1155	1156(-0.8)	
1085	1091(-2.5)	1071(-2.0)	1115(-5.2)	1095(-4.8)	]	δNH_2 twist
			1087(-1.9)		]	
1004(-2.4)	1040(+1.0)	1043(+1.1)	1040	1065	1036	
				1055	1033	
953	954	954	954	954	954	
867(-1.2)	871(-1.2)	873(-1.9)	873(-2.0)	871(-0.6)	880(-1.0)	
					826	
	817^{c}	818^{c}	815(-4.5)		864(-0.8)]	δNH_2 rock
811^{d}	811^{c}	811^{c}	810(-4.0)	815(-3.6)	815(-0.8)]	
753	755(-1.0)	756(-0.8)	757(-0.6)	757(-2.0)	751	
					725(-1.0)	
718	719	718	717	718	706	
667	671	671(+1.4)	672(-0.8)	671	671	
638(-3.0)	649(-3.6)	662(-3.7)	695(-4.3)	655(-3.2)		νM-N
585(-0.6)	589(-0.9)	590(-0.7)	592(-1.4)	589(-1.6)		δCOO
561(-4.3)	566(-4.7)	570(-4.5)	570(-6.5)	567(-3.8)	569(-2.3)	

Table 28 continued ...

Mn(Δν)	Co(Δν)	Ni(Δν)	Cu(Δν)	Zn(Δν)	Na(Δν)	Assignment
				561[e]	539	
518(-0.8)	520(-1.5)	522(-1.4)	521(-2.2)	517(-1.1)	532	
					498	
461(-2.8)	467(-4.1)	475(-4.4)	485(-3.7)	466(-4.5)		νM-N+δCCC+δCCN
					470(-2.8)	δCCC+δCCN
					426	
414(-3.1)	424(-4.9)	427(-2.3)	427(-1.8)	419(-3.0)	413(-0.6)	
					378(-2.9)	δCCN
339(-2.5)	361(-0.6)	366(-1.3)	347[f](-2.5)	346(-1.0)		νM-O
295(-4.3)	305(-4.5)	318(-4.5)	333(-1.1)	296(-2.3)		νM-O+δCCN
			270			νCu-O
					286	

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† Na(I); others M(II)

[a] Mean of doublet at 1626(-2.1) and 1612(-1.7) cm^{-1}.

[b] The νCOO and νC-N bands coincide.

[c] Becomes singlet in ^{15}N-labelled complex.

[d] Becomes doublet in ^{15}N-labelled complex.

[e] Becomes weak shoulder in ^{15}N-labelled complex.

[f] Additional shoulder at 379 cm^{-1}.

Table 29. Vibrational frequencies of the 5-chloroanthranilates ($4000 - 250\ cm^{-1}$)

Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Na(I)	Assignment
3315	3317	3313	3275	3310	3421	νN-H
3150	3146	3136	3135	3142	3316	νN-H
1619	1620	1618	1626	1620	1615	δNH_2 scissor
1590	1593	1594	1601	1594	1586	νC=C
1562	1563	1563	1563	1563	1537	νCOO
1556	1557	1556		1557		
	1485	1486	1485		1508	νC=C
1435	1439	1433	1430	1438		
1395	1396	1393	1380	1396	1421	νCOO
1318	1318	1321	1321	1319	1322	νC-N
1281	1280	1278	1277	1280	1290	
1237	1239	1239	1234	1238	1244	δNH_2 wag
					1234	
1172	1176	1178	1175	1178	1157	
1106	1108	1108		1108		
1089	1090	1094	1101	1091	1097	δNH_2 twist
1010	1045	1069		1058		
951	951	951	952	952	946	
906	906	907	905	906		
895	897	899	898	896	890	
827	828	828	829	829	831	δNH_2 bend
812	818	820	815	815	817	
804	807	808	807	805		
760		768		763		
735	739	740	742	739	730	
					702	
689	693	695	707	693	689	
657	660	663	656	659	652	
631	641	653	681	646		νM-N
588	592	595	595	592		δCOO
521	521	521	516	520	533	
					469	δCCC + δCCN
470	479	490	501	476		νM-N + δCCC + δCCN
					428	
419	426	429	426	422	402	
					390	δCCN
406					374	
365	389	389	399	388		νM-O
332	338	339	375	332		νM-O + δCCN
			340			νCu-O
289	274	289	290	283	310	

Table 30. Vibrational frequencies of the 5-bromoanthranilates (4000 - 250 cm^{-1})

Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Na(I)	Assignment
3310	3313	3311	3274	3307	3413	νN-H
3148	3145	3137	3135	3141	3313	νN-H
1616	1616	1617	1622	1618	1609	δNH_2 scissor
1590	1590	1593	1600	1592	1585	νC=C
1557	1552	1552	1558	1553	1539	νCOO
1431	1431	1430	1426	1433		
1392	1391	1388	1378	1392	1418	νCOO
1318	1320	1322	1323	1320	1322	νC-N
1282	1281	1281	1276	1280	1289	
1236	1239	1239	1233	1237	1241	δNH_2 wag
1171	1175	1180	1173	1177	1160	
					1149	
1094	1085	1086		1085	1085	δNH_2 twist
1012	1048	1071	1094	1060		
951	951	951	951	951	945	
906	907	907	905	907	898	
882	886	887	885	883	880	
824	825	825	826	826	832	δNH_2 bend
810	816	818		815	815	
802	806	807	806	804	804	
726	729	730	732	729	725	
683	685	686	704	683	685	
642	650	660	680	651		νM-N
625	631	636	636	634	631	
583	588	591	589	587		δCOO
518	518	519	515	517	528	
					466	δCCC + δCCN
469	477	488	498	476		νM-N + δCCC + δCCN
					425	
419	426	430	424	424	403	
					379	δCCN
362	376[a]	382	368	370		νM-O
320	332	335	343	323		νM-O + δCCN
			325			νCu-O
					298	

[a] Mean of doublet at 379 and 373 cm^{-1}.

Table 31. Vibrational frequencies of the 5-iodoanthranilates (4000 - 250 cm^{-1})

Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Na(I)	Assignment
3310	3312	3313	3270	3305	3409	νN-H
3150	3144	3139	3135	3145	3313	νN-H
1615	1615	1615	1622	1616	1604	δNH_2 scissor
1585	1587	1590	1598	1588	1581	νC=C
1550	1546[a]	1547[b]	1556	1547[c]	1538	νCOO
1428	1430	1429	1421	1430		
1387	1388	1386	1377	1388	1419	νCOO
1318	1320	1321	1321	1321	1318	νC-N
1281	1281	1280	1276	1280	1290	
1242	1244	1242	1234	1243	1245	δNH_2 wag
1173	1176	1181	1174	1179	1167	
1164	1163	1163	1158	1162	1145	
1092	1096	1110		1095		
1078	1077	1079	1115	1065	1085	δNH_2 twist
1020	1055		1093		1073	
950	951	951	951	951	937	
909	910	910	908	909	920	
878	880	881	878	878	876	
822	822	823	823	823		δNH_2 bend
810	815			815	813	
801	805	806	805	804	803	
722	724	725	727	725	725	
					692	
681	685	684	702	682	685	
638	649	660	678	650		νM-N
617	621	624	624	622	619	
581	586	590	587	584	575	δCOO
518	518	520	517	516	523	
					465	δCCC + δCCN
466	476	486	494	475		νM-N + δCCC + δCCN
					427	
418	427	430	425	423	401	
					379	δCCN
357	370	380	364	366		νM-O
317	324	331	336	317		νM-O + δCCN
			310			νCu-O
269	289	301	282	272	293	
	275					

Mean of doublet [a]) 1550 and 1541, [b])1552 and 1541, [c]) 1552 and 1541 cm^{-1}.

Table 32. Vibrational frequencies of the 5-methylanthranilates ($4000 - 250\ cm^{-1}$)

Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Na(I)	Assignment
3312	3313	3313	3282	3308	3405[a]	νN-H
3152	3145	3138	3134	3143	3325[b]	νN-H
1629	1628	1628	1631	1630	1632	δNH_2 scissor
1607						νC=C
1593	1594	1596	1602	1597	1585	
1561	1553	1555	1571	1557	1553	νCOO
1506	1507		1509		1502	νC=C
1400	1400	1400		1400	1430	νCOO
1325	1326	1328	1328	1329	1316	νC-N
1294	1296	1293	1293	1293	1298	
1250	1251	1251	1245	1250	1251	δNH_2 wag
1226	1224	1224	1220	1225	1225	
1171	1174	1180	1174	1178	1168	
1148	1149	1149	1145	1149	1157	
1094	1099	1107	1111	1102	1081	δNH_2 twist
1017	1051	1075	1090	1066	1042	
950	950	951	951	951	946	
928	929	930	927	929	924	
908	909	908	907	907	861	
822	822	822	822	824	827	δNH_2 bend
809	814	815	816	812	813	
772	776	778	777	775	790	
725	725	725	724	724	752	
710	710	710	713	710	701	
681	683	685	682	683	681	
634	645	657	696	651		νM-N
591	595	599	598	595		δCOO
					558	
525	525	526	519	524	540	
					495	δCCC + δCCN
483	486	497	505	475		νM-N + δCCC + δCCN
472	477	480	481		474	
419	426	430	426	423	410	
					397	δCCN
368	384	392	382	383		
335	339	340	345	337	338	
309	321	323	345	299		νM-O
261	283	297	322	271		νM-O + δCCN
			308			νCu-O
					252	

Mean of doublet at: a) 3425 and 3385, b) 3340 and 3310 cm^{-1}.

Table 33. Vibrational frequencies of the 4-nitroanthranilates (4000 - 250 cm^{-1})

Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Na(I)	Assignment
3326^{a}	3315	3315	3225	3308	3378	νN-H
3275			3165			νN-H...O
3185	3144	3135	3140	3165	3280	νN-H
1628	1626	1626	1628	1632	1627	δNH_2 scissor
1613	1605		1605	1615		νC=C
1545	1564^{b}	1564^{c}	1568	1545	1563	νCOO
1525	1541	1541	1550	1530	1563	νNO_2
1493			1492	1493		νC=C
1443	1410	1411	1440	1435		
1347	1356	1358	1349	1343^{d}	1357	νNO_2
1284	1328	1329	1280	1289	1337	
1238	1245	1242	1232	1236	1260	δNH_2 wag
1175	1174	1179	1177	1172		
1145	1156	1155	1149^{e}	1142	1145	
1120			1122	1125	1109	
1078	1086	1090	1080	1068	1067	δNH_2 twist
1002	1044	1066		1050		
	976	976	982			
942	945	945	946	944	956	
899	893	894	899	898	880	
857	849	851		860	857	
841	843	846	845	840	836	
833				832		δNH_2 bend
814	813	814	816	813	807	
795	802^{f}	802^{g}	796	794		
742	740	741	739	742	739	
716	719	720		725		
707			709	710		
688	692	692		688	689	
	670	668		662^{h}		
625^{i}	657	672	692	647		νM-N
					617	
	601	604	612			
581	581	583	588	587^{j}	588	δCOO
				541		
532				528	537	
511	521	522	515	511	495	
452					476	δCCC + δCCN
440	445	452	489	450		νM-N + δCCC + δCCN
418	423	427	428	423	432	
358	362	370	369	361	393	
313	348	350	345	335		νM-O
					329	δCCN
289	307	315	310	286		νM-O + δCCN
			293			νCu-O
269	261	290			295	

Mean of doublet at: a) 3330 and 3322, b) 1567 and 1561, c) 1569 and 1560, d) 1352 and 1334, e) 1154 and 1143, f) 804 and 801 g) 804 and 800, h) 667 and 656, i) 628 and 621, j) 593 and 582 cm^{-1}.

Table 34. Vibrational frequencies of the 5-nitroanthranilates (4000 - 250 cm^{-1})

Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Na(I)	Assignment
3475	3437	3470	3452		3450	νN-H
3350		3415		3394	3425	νN-H...O
3310	3318	3310	3353	3284	3320	νN-H
1618	1626^a	1617	1633	1640	1642^b	νC=O
1589	1587	1587	1593	1588	1586	νC=C
1537	1537	1534	1563	1538	1554	νNO_2
			1504		1507	νC=C
		1439			1423	
		1407				
		1358				
1317	1318	1334	1318	1325	1340	νNO_2
1287	1290	1292			1305	
1266		1256	1263	1261	1254	δNH_2 wag
1152^c	1150	1147	1157	1149	1154	
1090	1081	1080	1087	1081	1085	δNH_2 twist
					955	
930	939	925	932	920	930	
839	832	832	834	834	837	
829		816		826	822	δNH_2 bend
802	807	805	804		811	
753	755	751	751	752	754	
713	722	724	725	725	716	
699	707	709	705		711	
647	651	650	647	652	647	
	558			571	557	δCOO
530^d	523^e	523	518	517^f	525	
449	460				484	δCCC + δCCN
404^g	413	402	403	431	425	
		361		389	384	δCCN
		346				

Mean of doublet at: a) 1634 and 1617, b) 1648 and 1637, c) 1156 and 1149, d) 539 and 520, e) 528 and 517, f) 521 and 512, g) 409 and 399 cm^{-1}.

Table 35. Vibrational frequencies of the complexes $M(pic)_2 \cdot nH_2O$ (2000 - 200 cm^{-1})

M→Ca n→2	Mn 0	Co 4	Ni 4	Cu 2	Cu 1	Cu 0	Zn 4	Na[a] 0.5	Assignment
1632	1667	1652						1656[b]	νCOO
1611	1632	1641	1635	1636	1653	1650	1658	1614	
1586	1600	1599	1600	1608	1608	1610	1601	1590	
1567	1575	1574	1573	1576	1575	1576	1575	1570	
	1435							1414	
	1412							1391	νCOO
1316	1352			1355	1354	1359		1341	
1300	1301[c]	1302	1302	1302	1302	1302	1303	1295	
	1273				1290	1290			
1260	1261	1267	1269	1272	1271	1272	1268	1264	
1240	1246	1248	1250	1250	1246	1250	1248	1241	
	1232								
1174	1168[d]	1174	1177	1177	1173	1174	1176	1175	
1152	1147	1155	1160	1155	1155	1156	1156	1159	
1094	1095	1097	1097	1097	1099	1100	1098	1098	
1049	1053	1052	1051[e]	1053	1051	1052	1052	1051	
1011	1017	1023	1027	1037	1035	1035	1025	1008	
				1023	1020	1021	1014		
	1000	983	984	978	984	985	984	999	
922	942	932	933	929	929	930	933		
	900	926	920				927		
819	846	864	862	859	856[f]	853	863	854	
	838			827	828	828	845	842	
767	782	767	770	773	778	778	767		
759	751				773			755	
750	711								
710	702			718	715	715		710	
693	697	704	706	700	697	698	704	704	
								683	
633	639	646	652	661	662	663	647	629[g]	py ring
	562	584	568				587		
529	553	547	546	553	550	549	543	521	
428	445	447	450	453	452	451	449	412[h]	py ring
417	433	426	442	462	461	461	425		νM-O
	409			423	423	423			νM-O
286	330	336[i]	349[j]	387[k]	388[l]	388[m]	330		νM-N
265	302	300	310	338	338	340	294		νM-N
	255	250	258	268	259	261	261		δO-M-N
231	245		234	231	232	234		230	

[a] Na(I), others M(II)

Mean of doublet at: [b]) 1664 and 1648, [c]) 1303 and 1299, [d]) 1170 and 1166, [e]) 1053 and 1048, [f]) 859 and 853, [g]) 632 and 626, [h]) 416 and 407, [i]) 340 and 331, [j]) 350 and 347, [k]) 390 and 383, [l]) 393 and 383, [m]) 390 and 386 cm^{-1}.

Table 36. Vibrational frequencies of the pyridine adducts of the metal picolinates (2000 - 200 cm^{-1})

Co	Ni	Zn	Assignment
1641	1642	1639	νCOO
1601	1602	1600	
1575	1575	1571	
1490		1489	
1451	1452	1449	
1295	1295	1294	
1261	1263	1262	
1244	1246	1243	
1222	1221	1216	
1172	1173	1172	
1155	1156	1157	
1095	1096	1095	
1073	1073	1071	
1042	1044	1042	
1020	1024	1017	
1011	1013	1012	
977	978	977	
926	928	920	
895	895	894	
851	852	849	
776	778	772	
762	763	760	
	715		
705	704	705	
641	645	640	py ring
632	636	633	
535	540		
435	440	430	py ring
		422	νM-O
303	316	293	νM-N
271	296	288	νM-N
234	251	246	δO-M-N

Table 37. Vibrational frequencies of the bipy adducts of the metal picolinates (2000 - 200 cm^{-1})

Co	Ni	Zn	Assignment
1656	1655	1658	νCOO
1648	1647		
1599	1598	1600	
1572	1572	1573	
1450	1445	1446	
1357	1360	1362	
1317	1318	1318	
1287	1287	1288	
1266		1264	
1250	1248	1251	
		1246	
1221	1220	1220	
1169	1171	1171	
1158	1158	1157	
1120		1121	
1090	1091	1091	
1064	1065	1064	
1046	1046	1045	
1020	1023	1020	
914		914	
904	902	904	
846	844	844	
783	784	784	
762	762	769	
		763	
736	735	736	
704	705	703	
655	656	656	heterocyclic ring
642	646	643	
632	634	629	
554	552	550	
527	534	528	
450	452	446	heterocyclic ring
430	434	431	
412	414	412	
284	298	288	νM-N (quin)
264	271	250	νM-N (bipy)
241	230	239	δO-M-N

Table 38. Vibrational frequencies of the phen adducts of the metal picolinates (2000 - 200 cm^{-1})

Co	Ni	Zn	Assignment
1658	1659	1659	νCOO
1600	1601	1600	
1573	1573	1573	
1525	1526	1525	
1432	1434	1433	
1355	1360	1359	
1289	1290	1291	
1263	1263	1264	
1246	1247	1246	
1226	1227	1227	
1212	1214	1213	
1195	1198	1195	
1171	1172	1171	
1150	1150	1151	
1104	1106	1104	
1096	1095	1096	
1046	1046	1046	
1023	1025	1025	
1018		1019	
1001	1003	1001	
974	975	976	
956	955	956	
920	920	922	
868	870	867	
855	855	855	
845	844	841	
804	806	803	
778	778	779	
760	762	760	
730	731	731	
726	728	726	
704	705	704	
644	647	644	heterocyclic ring
608	610	608	
558	560	558	
547	549	549	
527	533	528	
514	512	514	
444	450	444	heterocyclic ring
429	433	430	
289	304	289	νM-N (phen)
268		250	νM-N (pic)
238	255	242	δO-M-N

Table 39. Vibrational frequencies of the complexes $K[M(quin)_3].2H_2O$ (2000 - 200 cm^{-1})

Mn	Co	Ni	Assignment
1641	1642	1645	νCOO
1600	1602	1605	
1569	1570	1573	
1514	1514		
1393		1400	νCOO
1350	1352	1350	
1300	1300	1300	
1260	1262	1265	
1222	1225	1215	
1180	1183	1185	
1160	1161	1162	
1146	1145	1145	
1124	1124	1124	
1027	1027	1027	
974	977	979	
	972	976	
960	962	964	
901	903	904	
882	885	886	
861	863	864	
810	812	811	
780	781	780	
760	760		
745	750		
638	640	641	py ring
634	634	634	
602	606	607	
551	561	568	δCOO
523	525	525	
502	504	505	
485	490	478	
406	409	413	py ring
394		358	
372	380	384	νM-O
296	312	320	νM-N
	271	271	δO-M-N
228		229	

Table 40. Vibrational frequencies of the complexes $M(quin)_2.nH_2O$ (2000 - 200 cm^{-1})

M→Ca n→1	Mn 2	Co 2	Ni 2	Cu 1	Cu 0	Zn 1	Na[a] 1.5	Assignment
1635	1642	1620	1632	1641	1651	1639	1638	νCOO
				1603	1601			
1586	1572	1571	1572	1573	1572	1578	1567	
1560	1558	1557	1560					
1513	1514	1517	1516	1519	1517	1518	1510	
1399	1395	1408	1413		1391	1395	1410	νCOO
1349	1351	1355	1352	1355	1366	1354		
1300	1303	1304		1311	1310	1315	1305	
1279	1274	1269	1273	1274	1281	1277		
1268	1264					1272		
1220	1222	1226	1216	1223	1216	1223	1217	
1208	1212	1216	1206	1214	1208	1210	1209	
1181	1183	1186	1188	1191	1190	1188	1177	
1161				1186		1183		
1152	1158	1166	1160	1158	1153	1158	1154	
			1145	1142		1142	1143	
1116	1117	1123	1122	1128		1124	1111	
1026	1025	1030	1026	1029	1029	1028	1050	
	999	1008	998	1005	1002	1005	1020	
	988	995	974	980	976	974	988	
	973		966	966	969	964	976	
957	964	970	957	958		957	956	
925	904	901	906	905	908	905	896	
886		892	878	886	884	887		
874	861	857	853	859	855	858	852	
856				849		849		
817	811	812	805	810	816	811	805	
808		805		802	809	802		
785	791	788		792	782		783	
778	781	780	770	775	772	777	772	
764	755	760						
750					743			
738	730	725	743	742	737	742	743	
725				725	727	727	732	
634	638	641	641	648	645	642	656	py ring
			631	631	637	632	630	
600	606	604	607	609	614	608	594	
554			568	573	580	567	557	δCOO
524	524	523	526	527	524	524	525	
				510	482	510	503	
499	504	501	499	496	496	497	491	
486	486	488				486	470	
396	402	404	408	408	407	403	398	py ring
380	378	375	381	385	440	374		νM-O
	332		358			363	362	
272	280	300	314	371	397	301		νM-N
	264	271	272	288	328	270		δO-M-N
		252	254	263	276		266	
					253			
222		222	223	230	223	231	232	

[a] Na(I), others M(II)

Table 41. Vibrational frequencies of the complexes $[M(quin)_2(py)_2]$ (2000 - 200 cm^{-1})

Mn	Co	Ni	Zn^a	Assignment
1656	1657	1658	1655	νCOO
1598	1600	1601	1598	
1571	1571	1572	1571	
1514	1515	1516	1514	
	1487	1487		
	1444	1447	1445	
1370	1363		1369	
1355	1355	1357	1355	
	1347	1347	1347	
	1295	1293	1297	
1272	1278	1280	1277	
	1262	1265	1260	
1219	1240	1242	1241	
			1223	
1207	1213	1213	1213	
1180	1179	1181	1179	
1164			1153	
1153	1152	1151	1143	
1115	1113	1113	1114	
1073	1070	1070	1070	
1038	1043	1044	1040	
1026	1027	1029	1027	
1007	1009	1011	1008	
	989	991	988	
			975	
965	962	963	962	
891	896	896	897	
858	864	864	864	
811	813	813	813	
801	807	806	805	
775	777	776	776	
759	768	769	764	
745	748	748	748	
704	710	709	710	
679	677	677		
639	639	640	639	py ring
623	630	632	627	
603	603	603	602	
552	559	564	567	δCOO
			556	
524	524	525	524	
			511	
500	501	502	498	
481		490	487	
414	433	438	427	py ring
402	411	413	408	
391	402	404	402	
366	378	381	369	νM-O
296	310	315	294	νM-N
	270	270	270	δO-M-N
231	243	247		
		239		
	219	223	224	

[a] mono(pyridine) adduct

Table 42. Vibrational frequencies of the complexes $[M(quin)_2(bipy)]$ (2000 - 200 cm^{-1})

Co	Ni	Assignment
1661	1656	νCOO
1607	1608	
1600	1600	
1569	1570	
1512	1513	
1493		
1446	1447	
1358	1361	
1346	1346	
1312	1313	
1298	1297	
1281	1283	
1275		
1262	1264	
1252	1251	
1211	1211	
1177	1179	
1165	1167	
1153	1153	
1108	1109	
1060	1060	
1042	1046	
1022	1025	
	1018	
994	995	
961	962	
895	895	
864	866	
858	859	
817	819	
810	810	
800	800	
781	781	
771	771	
748	749	
737	737	
	691	
654	654	
637	638	heterocyclic ring
632		
604	604	
553	558	δCOO
525	526	
498	499	
489	492	
468	467	
441	446	
417	417	heterocyclic ring
399	401	
365	373	νM-O
296	310	νM-N (quin)
262	271	νM-N (bipy)
250	243	
219	219	

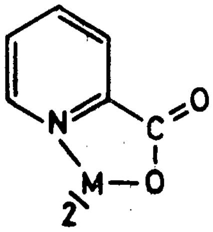
Table 43. Vibrational frequencies of the complexes
$[M(quin)_2(phen)]$ (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu	Zn	Assignment
			1669		νCOO
1656	1663	1661	1649	1662	
	1621		1618		
1597	1602	1598	1603	1599	
			1594	1584	
1569	1571	1571	1574	1570	
1521	1522	1522	1519	1523	
1509		1513	1508	1512	
1498	1498	1498	1498	1499	
1431	1431	1432	1431	1432	
1422	1406				
1362	1361	1364	1359	1367	
1347	1344	1346	1342	1348	
1319				1322	
1298	1297	1296	1299	1299	
1273	1268	1264	1271	1272	
1261	1258		1252	1260	
1230	1229	1232	1229	1233	
1213	1211	1212	1209	1213	
1179	1177	1179	1181	1180	
1160			1170		
1155	1154	1154	1153[a]	1154	
1116			1115	1114	
1109	1108	1108	1105	1108	
1103					
1090			1092	1092	
1027	1025	1027	1025	1027	
1001					
990	995	998	994		
981	988			980	
963	966	967	966	966	
	955	954	954	958	
895	896	896	899	897	
867	870	871	889	869	
			867		
		861	860	860	
856	854	854	853	855	
819	822	823	820	820	
810	813	813	814	812	
801	802	802	804	803	
	781		782		
778	776	776	775	777	
749	756	757	754	751	
731	745	745	744	731	
725	730	730	731		
			724		
		686	686		
	645	647	644	643	heterocyclic ring
639	638	639	633	638	
602	604	604	608	604	
			567	567	
549	552	556	554[b]	551	δCOO

Table 43 continued ...

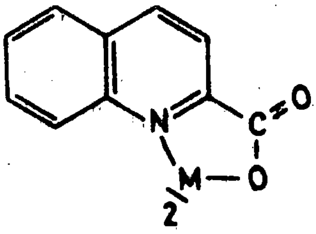
Mn	Co	Ni	Cu	Zn	Assignment
525	525	527	525	525	
513			513	513	
501	502	501	501	501	
490			486	488	
440	448	451	448	445	heterocyclic ring
423	426	429	423	423	
398[c]	401	401	401	401	
369	368	375	411	368	νM-O
			380		νCu-O
300	296	310	314	287	νM-N (quin)
272	288	295	285		νM-N (phen)
	271	270	270	275	δO-M-N
239	235	238	246[d]	238	

Mean of doublet at: a) 1156 and 1149, b) 557 and 550, c) 402 and 393, d) 250 and 242 cm^{-1}.



Divalent metal picolinates

$M(pic)_2$



Divalent metal quinaldates

$M(quin)_2$

Table 45. Vibrational frequencies of the complexes $[M(OX)_2(B)_2]$ (2000 - 200 cm^{-1})

M →	Mn	Co	Ni	Zn	Ni[a]	Assignment
B →	H_2O	H_2O	H_2O	H_2O	py	
	1608	1609	1609	1609	1607	
	1579	1581	1582	1582	1579	
	1511	1511			1511	
	1506	1504	1505	1505	1502	
	1428	1428	1427	1428	1431	
	1392		1395	1395		
	1328	1328	1330	1331	1332	
	1284	1285	1287	1286	1288	
	1242	1243	1237[b]	1244	1227	
	1206	1208	1210	1209	1222	
	1179		1179	1180	1178	
	1140	1140	1139	1139	1154	
	1110	1110	1112	1112	1113	νC-O
	1071	1072	1072	1071	1074	
					1063	
	1036	1037	1036	1038	1043	
					1017	
					1010	
	980	980	979	979	981[c]	
					963	
	958	957	956	956	952	
	907	913	916	913	912	
					882	
	860	860	856	857	855[d]	
	822	822	821	822	824[e]	
	804	806	806	805	805	
	793	792	790	793	792	
	786	785		786	771	
	746	749	747	748	753	
	744	746	738	744	743	
					736	
					714	
					700	
	647	646	645	645	658	ring torsion
					634	
	604	609	627	608	611	νM-O
	588	590	595	590		
	564	571	574	570	567	νM-O
		532				
	501	506	508	505	501	νM-O+νM-N+δC-O
					444	ring torsion
					428	
	379	388	392	392	383	νM-N
	286	293	304	262	292	νM-N
					255	
					247	

[a] monohydrate

Mean of doublet at: [b]) 1242 and 1232, [c]) 982 and 979 [d]) 858 and 852, [e]) 826 and 822 cm^{-1}.

Table 44. Vibrational frequencies of the complexes $[M(OX)_2]$ (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu		Zn	Assignment
			α	β		
1607	1604	1603	1603	1601	1605	
1578	1578	1581	1576	1578	1580	
1499	1501	1501	1505	1502	1500	
			1415	1427		
1324	1324	1327	1329	1328	1325	
1281	1276^{a}	1276^{b}	1283	1282	1280	
1236	1231	1229	1236	1234	1235	
			1224	1225		
1208	1211	1211		1217	1215	
1178	1176	1174	1180	1177	1181	
1136	1138	1137	1149	1135	1175	
1108	1111	1112	1119	1114	1111	νC-O
1059	1062^{c}	1058	1058	1054	1060	
1035	1035	1035	1035	1035	1036	
984	980	979	981	971		
961			966	950		
			949^{i}			
905	910	914	927	855^{d}	910	
870				835		
				829		
824^{e}	823	822	821	817	823	
806	804	804	805	806	805	
789	788	787	787	795	789	
746			753	779		
731	732	737	746	742	734	
	676	672	724	733		
652	650	651	645	645	652	ring torsion
600	614	617	632	632	605	νM-O
578^{f}	598^{g}	598				
	570	574	585	583	568	νM-O
		545				
504	493					
491	504	507	522	522	500	νM-O+νM-N+δC-O
393	408	412			409	ring torsion
388	387	391	408	407	391	νM-N
287	286	287	302	293	284	
250	267^{h}	294	332	328	251	νM-N
232	235	236			231	

Mean of doublet at: [a] 1281 and 1271, [b] 1285 and 1267, [c] 1065 and 1058, [d] 856 and 853, [e] 825 and 822, [f] 581 and 574, [g] 602 and 594, [h] 270 and 263, [i] 951 and 946 cm^{-1}.

Table 46. Vibrational frequencies of the complexes [M(OX)$_2$B] (2000 - 200 cm^{-1})

M →	Co	Ni	Zn	Co	Ni	Assignment
B →	phen	phen	phen	bipy	bipy	
	1602	1604	1604	1604	1606	
	1571	1583	1572	1579	1575	
	1497	1502	1498	1500	1499	
	1437	1432	1431	1444		
	1418	1394	1419	1433		
	1370	1371	1368	1371	1371	
	1342	1343	1345	1331	1339	
	1327	1332	1329	1318	1335	
	1286	1289	1286	1290	1292	
				1252	1254	
	1225	1224	1225	1227	1226	
	1171	1171	1171	1175	1176	
	1156	1160	1156	1157	1158	
	1134	1136	1135	1140	1140	
	1112	1115	1112	1112	1114	νC-O
		1107	1105			
	1055	1056	1056	1059	1060	
				1045	1045	
	1035	1035	1035	1033		
				1020	1023	
	997	996	998	1005	1003	
	970	969	971	965	965	
	958	957	957	950	954	
	934	937	939			
	908	912	907	907	911	
	867	869	866	861	861	
	854	854	853			
	819	820	819	824	825	
	801	801	800	805	805	
	786	785	786	795	795	
	736	740	734	753[a]	753[b]	
	728	734	726	734[c]	734[d]	
		687	689[e]	685	682	
	657	658	656			
	653	654	654	654	654	ring torsion
	641	643	640	632	634	
	608	611	608	608	611	νM-O
	591	592	591			
	565	570	565	566	571	νM-O
	550	551	549			
	532					
	507	507	505	494	498	
	498	501	497	504	505	νM-O+νM-N+δC-O
	444	450	441	439	443	ring torsion
	424	427	423	412	414	
	379	385	379	379	383	νM-N
	291	300	288			νM-N(phen)
	259	289	236			νM-N
	245	257	249			
	228	229				
				283	289	νM-N
				263	276	νM-N(bipy)
				245	258	

Mean of coublet at: a) 758 and 748, b) 758 and 747, c) 737 and 730, d) 736 and 732, e) 692 and 686 cm^{-1}.

Table 47. Vibrational frequencies of the complexes $[M(OX)_3]$ (2000 - 200 cm^{-1})

Cr	Mn	Fe	Co	Ga	Assignment
1601	1603	1595	1591	1603	
1579	1576	1578	1577	1582	
1502	1500	1498	1502	1501	
1428	1428	1426	1425	1429	
1328	1322	1327	1327	1330	
1285	1276	1280	1290	1285	
1238	1234	1239	1238	1241	
1224	1222	1210	1222	1226	
1213				1216	
1175	1174	1173	1175	1178	
1135	1140	1132	1139	1140	
1115	1107^a	1107	1114	1115	νC-O
1060	1062	1064	1064		
	1053				
1035	1034	1036	1034	1040	
962	976				
920	908^b		929	917	
	890				
859	856	869	854	870	
	830			835	
823	820	823	820	826	
803	805	804	803	806	
786	785	789	779	788	
	758			773	
	752	754		760	
	744	747		752	
750	734	740	752	744	
	644	647	648	646	ring torsion
644	631	629	657	632	νM-O
	618	620			
594	587	595	597	601	
575	579	569	586	579	νM-O
531	535	524	532	528	νM-O+νM-N+δC-O
	518			518	
	504	497	509	501	
	499				
470	468	471	479	470	
450	445	442	464	447	ring torsion
408	410	401	424	407	νM-N
	404				νMn-N
	388	393	391		
			361		
362	341	314	414	296	νM-N
	327				νMn-N
333	288	260	380	280	νM-N
	270	289			
	237			242	

Mean of doublet at: [a]) 1114 and 1100 [b]) 911 and 905 cm^{-1}.

Table 48. Vibrational frequencies of the complexes $[M(2\text{-}CH_3\text{-}OX)_2]$ (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu	Zn	Assignment
1614			1611	1610	
1597	1602	1601	1600	1598	
1570	1576	1575	1571	1572	
1514	1515	1513	1508	1512	
	1508			1509	
1435			1440	1434	
1426					
1337	1333	1330	1340[a]	1336	
1307	1306	1306	1308	1310	
1283	1281	1275	1285	1285	
				1270	
1245	1243	1243	1244	1250	
1215	1214	1213	1212	1215	
1176	1178	1178	1177	1181	
1142	1143	1146	1146	1143	
1105	1109	1108	1108	1110	νC-O
1071	1065	1064	1056	1065	
1039	1036	1035	1033	1034	
1019			1023		
978	975	980	978	980	
953	957	955	965	957	
			949		
925	925	925	928	927	
874[b]	875	874	877	871	
			854	848	
832[c]	832	831	834[d]	834	
803			802	799	
796	797	796	798	795	
758			759	758	
751	753	748	745	748	
739	742			740	
703	705	703	703	705	
		677			
587	604	615	634	609	νM-O
578	591	593	617	602	
			589		
570	574[e]	574	576	569	
		551			
507	511	516	523	511	νM-O+νM-N+δC-O
452	467	475	481	471	νM-N
		452	444		ring torsion
434	435	437	428	431	
			345		
330	330	320	331		
302	320	348	359	312	νM-N
237	288	302	307	258	chelate ring def.
	271	256	252	269	
		236			

Mean of doublet at: [a]) 1347 and 1332, [b]) 876 and 872, [c]) 834 and 829, [d]) 837 and 831, [e]) 575 and 572 cm^{-1}.

Table 49. Vibrational frequencies of the complexes $[M(2\text{-}CH_3\text{-}OX)_2B]$ (2000 - 200 cm^{-1})

M →	Co	Ni	Cu	Zn	Ni	Assignment
B →	H_2O	H_2O	H_2O	H_2O	py	
	1608	1610	1608	1608	1600	
	1597	1600	1596	1595	1588	
					1576	
	1571	1571	1573	1571	1561	
	1513	1514	1514	1513		
	1509	1508	1509	1508	1507	
					1447	
	1429	1435	1435	1430	1437	
					1373	
	1337	1328	1339	1341	1358	
			1320			
	1311	1308	1309	1311	1296[a]	
	1279	1271	1290	1285	1267	
	1249	1243	1248	1250	1238	
	1213	1213	1214	1218	1217	
	1181	1178	1181	1181	1174	
	1143	1144	1146	1147	1153	
					1143	
				1120	1121	
	1110	1108	1115	1110	1111	νC-O
		1063			1071	
	1064	1054	1064	1065	1062	
	1036	1030	1038	1038	1037	
	1017	1010	1021	1020	1010	
	978	980	981	980	970	
	957	965	956	957	959	
		940				
	925	924	933	926	946	
	878		882	878		
	871	874	867	868	875	
	833	835	832	834	828	
	803[b]	798	800	804	796	
	759		756	757	757	
	753	750	751	752	744	
	704	704	704	705	706	
		673[c]			682	
					629	ring torsion
	604	612	605	601	605	νM-O
		593	592			
	566	569	576	569	568	
		551				
	512	515	513	511	515[d]	νM-O+νM-N+δC-O
	466	475	472	471	461	νM-N
	446	453	446	442	445	ring torsion
	429	433	433	433	434	
	319	347	334	310	339	νM-N
		320				
	294	298	281	260	298	chelate ring def.
					264	
		236			234	

Mean of doublet at: [a]) 1300 and 1291, [b]) 805 and 800, [c]) 678 and 668, [d]) 517 and 513 cm^{-1}.

Table 50. Vibrational frequencies of the complexes $[M(5\text{-}Cl\text{-}OX)_2]$ (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu	Zn	Assignment
1603	1603	1603	1604	1602	
1583	1578	1577	1576	1577	
1502	1501	1507	1504	1499	
1400		1407	1402	1399	
1370	1370	1376	1376	1369	
1329	1326	1325	1328	1328	
1321	1310			1319	
1284			1276		
1261	1264	1270	1259	1259	
1244	1244	1245	1244	1244	
1207	1213	1213	1214		
1164	1163	1160	1160	1162	
1133	1133		1140	1132	
1089	1085	1092	1091	1087	νC-O
1045	1045	1046	1045	1045	
954	962	984	977	965	
933		954	957		
833	833	837	839	832	
		818	823		
810	809	811	812	814	
789	785	777	781	785	
740	741	764	751	742	
704		741	725		
671		725			
664	672	693	683	674	νM-O
646	645	642	644	645	ring torsion
601	622	674	632	614	νM-O
	600	603	598	600	
538	541	562	555	543	νM-O+νM-N+δC-O
				514	
503	505	512	505	503	
445	456	451	457	456	
427	424			431	ring torsion
381	396	482	412	390	νM-N (+νM-O?)
				364	
	347	348	347	348	
238	264	263	303	242	νM-N
	239				

Table 52. Vibrational frequencies of the complexes $[M(5\text{-}Cl\text{-}7\text{-}I\text{-}OX)_2]$ (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu	Zn	Assignment
	1599	1590	1583		
1564	1560	1562	1556	1560	
1497		1493	1487		
	1390	1395	1396		
		1320	1323		
	1283	1288		1286	
1253	1251	1248	1251	1254	
1237	1235		1240	1236	
1222		1223	1224	1222	
1202	1199	1208	1203^{a}	1200	
1143	1142	1140^{b}	1145	1141	
1110	1106	1121	1117	1113	νC-O
1052	1052	1049	1046	1053	
967	963	985	978	970	
935	931	960	948	937	
888	886	897	893	886	
880	878	871	883		
852	850	859	856	850	
			825		
809	808	809	808	810	
786	786	776	781	787	
748	746	769	755	749	
		752		741	
709	707	719	715	710	
667	666	694	666	667	
	645	659			
642	637	654	659	640	ring torsion
603	603	617	608	601	νM-O
596	592				
579	575	602	592	581	
566	561	588	579	569	νM-O
	540	558	551		
511	508	529	510	510	νM-O+νM-N+δC-O
455	433	513	488	445	νM-N
486	485	482		483	
396	397^{c}	451	411	396	νM-N
		428			
317	311	378^{d}	355^{e}	312	chelate ring def.
265	259	333	301	254	
283		270			
245	238	250	246	245	

Mean of doublet at: [a] 1207 and 1198, [b] 1142 and 1137, [c] 404 and 390, [d] 387 and 368, [e] 364 and 345 cm^{-1}.

Table 53. Vibrational frequencies of the complexes $[M(5\text{-}Cl\text{-}7\text{-}I\text{-}OX)_2(B)_2]$ (2000 - 200 cm^{-1})

M →	Mn	Co	Ni	Zn	Ni	Assignment
B →	H_2O	H_2O	H_2O	H_2O	py	
	1597		1600	1601	1601	
	1559	1561	1560	1561	1551	
	1489	1490	1493	1492	1486	
	1393	1393	1394	1394		
			1370	1369	1362	
	1285	1285			1287	
					1276	
	1247	1250	1250	1251	1254	
	1224	1224	1223	1224	1219	
	1195	1197	1198	1198	1199	
	1142	1144	1144	1145	1153	
	1108	1111	1112	1112	1111	νC-O
					1071	
	1053	1050	1057	1052	1040	
					1012	
	958	963	963	963	964	
	930	933	936	934	938	
	885	887	886	879	883	
	869	874[a]	878		871	
	851	854	854	851	850	
	805	804	804	804	810	
	784	783	781	783	790	
					761	
	745	747	749	748	750	
	704	705	708[b]	708	706	
	664	662	661	662	678	
	644	646	646	646	653	ring torsion
					629	
	601	604	607	603	602	νM-O
	592	595	597	594		
	575	577	579	579	577	
	561	564	568	567	565	νM-O
	503	505	508[c]	508	505	νM-O+νM-N+δC-O
	480	477	477	476	481	
	428	435	441	434	437	νM-N
					425	ring torsion
	391	398	403	398[d]	399	νM-N
	348	351	351		353	
	302	315	318	308	324	chelate ring def.
					295	
	247	263	273		277	chelate ring def.
					252	
	237	246		237	240	

Mean of doublet at : a) 877 and 870, b) 710 and 706, c) 511 and 504, d) 403 and 393 cm^{-1}.

Table 54. Vibrational frequencies of the complexes $[M(2\text{-}CH_3\text{-}5,7\text{-}Br_2\text{-}OX)_2]$ (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu	Zn	Assignment
1602	1604	1608		1603	
1569	1572	1572	1570	1570	
1556	1560	1561	1561	1560	
1493	1494	1496	1496	1497	
1426	1429	1432		1449	
1388					
1364	1369	1364	1373	1370	
1332	1333	1323	1331	1331	
1324	1326		1318	1320	
1270	1271	1274	1277	1279	
1245	1249	1250	1263	1252[a]	
1228	1229		1255	1230	
1220	1221	1223		1213	
1202	1203	1204	1204	1206	
1194	1195	1196	1190	1196	
1141	1142	1147	1147	1148	
			1122	1125	
1110	1112	1113	1115	1116	νC-O
1030	1030	1035	1031	1035	
1020	1021				
972	970	975	970	972	
941	943	945	949	952	
930	931	933	935	931	
864	864	863	865	870	
821	819	821	820	833[b]	
789	789[c]	788	784	785	
			755	758	
739	740	744	744	742	
723	724		725	724	
689	693	687	681	682	
668	670	671	675	673	
647	643	648			ring torsion
641	650	654	663	659	νM-O
614	614				
598	596	601		600	
579	585	587	596	589	νM-O
538	537	534	532	533	δC-O
467	470		475	467	
440	455	475	503	497	νM-N
428					
389	400	389		389	ring torsion
364	379	398	404	374	νM-N
		368	372		
313	331	332	349	328	chelate ring def.
		318			
268	273	278	288	300	
238	236	241	237	237	

Mean of doublet at: [a]) 1256 and 1248, [b]) 834 and 831, [c]) 792 and 786 cm^{-1}.

Table 55. Vibrational frequencies of the complexes $[Ni(2\text{-}CH_3\text{-}5,7\text{-}Br_2\text{-}OX)_2(B)_2]$ (2000 - 200 cm^{-1})

py	H_2O	Assignment
1603	1606	
1565	1557	
1555		
1490	1498	
1446	1431	
1358	1362	
	1330	
	1322	
1281	1275	
1253	1254	
1215	1219	
1202	1195	
1151	1147	
1116	1113	νC-O
1070	1082	
1063	1056	
1038	1033	
1012		
982	980	
941	941	
927	932	
	880	
874	871	
864	863	
829	835	
823	824	
790	787	
757		
742	744	
740		
705		
700		
691	686	
668	671	
655	654	νM-O
629		ring torsion
598	603	
585	586	νM-O
530	536	δC-O
468	469	νM-N
432		ring torsion
383	394	νM-N
363	367	
328	316	
	280	
233	237	

Table 56. Vibrational frequencies of the complexes $[M(5,7-Cl_2-OX)_2]$ (2000 - 200 cm^{-1})

Co	Ni	Cu	Zn	Assignment
1598	1594		1598	
1571	1572	1568	1582	
1495	1497	1499	1495	
	1402	1404	1394	
1294	1296	1297	1294	
1284	1256			
1241	1228	1244	1239	
	1206			
1199	1198	1207	1200	
1172				
1143	1145	1150	1144	
1109	1124	1121	1111	νC-O
1054	1051	1053	1055	
969	987	986	970	
889	900	900	889	
875	871	882^a	873	
809	806	819^b	810	
786	776	784	787	
751	769	755	750	
740	760		739	
674	697	671	674	
659				
649	661	665	649	νM-O
	621			
595	602	608	595	νM-O
	540			
513	516	490	514	
	501	515	500	νM-O+νM-N+δC-O
460	453			
427			427	ring torsion
394	397	417	389	νM-N
357	366	371^c	354	νM-N
	338			
271	273	304	259	chelate ring def.
237	257	263		

Mean of doublet at: a) 886 and 877, b) 823 and 814, c) 375 and 366 cm^{-1}.

Table 57. Vibrational frequencies of the complexes $[M(5,7\text{-}Cl_2\text{-}OX)_2(B)_2]$

M →	Co	Ni	Zn	Ni	Assignment
B →	H_2O	H_2O	H_2O	py	
	1600	1606	1605	1606	
	1571	1578	1574	1557	
	1497	1501	1499	1491	
			1420		
	1400	1405	1401	1397	
	1369	1375	1373	1359	
	1295	1295	1297		
	1254	1251	1253	1254	
	1246		1243		
	1230	1236	1236	1221	
	1195	1200	1207	1196	
	1143	1146	1145	1143	
	1117	1119	1120	1112	νC-O
	1057	1064	1063	1075	
	1050			1069	
				1042[a]	
	963	970	972	965	
	889	891	891	884	
	863	865	870	874	
	809	807	815	816	
	806		807	810	
	790		790	793	
	783	782	783	765	
				756	
	753	750	745	749	
	724	728		715	
				702	
	669	668	669[b]	678	
	654	656	657	655	νM-O
				633	ring torsion
	604				
	593	600	602	593	νM-O
		538			
	509	510	511	508	νM-O+νM-N+δC-O
	489	488			
	449	452	455	437	ring torsion
	402	404	399	402	νM-N
	358	362	361	357	νM-N
		339		349	
	263	285	261	293	chelate ring def.
				255	
		240		243	

Mean of doublet at: a) 1043 and 1040, b) 671 and 667 cm^{-1}.

Table 58. Vibrational frequencies of the complexes $[M(5,7\text{-}Br_2\text{-}OX)_2]$ (2000 - 200 cm^{-1})

Mn	Co	Ni	Cu	Zn	Assignment
1595	1597	1587	1579	1596	
1567	1567	1569	1560	1567	
1488	1490	1491	1490	1486	
1390	1390	1397	1395	1392	
1365	1370			1368	
1286	1289	1289		1285	
1279			1262	1277	
1248		1255	1251	1255	
1238	1238		1236	1237	
1225	1224	1225	1220	1224	
		1204	1205	1215	
		1189	1198	1204	
1140	1139	1143	1142	1141	
1106	1107	1123	1116	1111	νC-O
1051	1054	1050	1048	1052	
944	949	969	964	954	
		883	886	886	
864	866	875	882	876	
			874	865	
807	809	804	814[a]	808	
785	785	774	782[b]	786	
		768	754	747	
740	739	725	725	741	
692	695	692	695	696	
666	667	654		669	
637	640	703	660	647[c]	νM-O
595	597	597	599	597	
573	577	606	593	580	νM-O
			564		
506	515	529	511	505	νM-O+νM-N+δC-O
490	490	489	484	488	
430	439			428	ring torsion
400	417[d]	511	475	443	νM-N
363	370	358	353	389	
339	351	433	375	343	νM-N
265	282	374	322	293	
	252	269	256	243	
		249			
	230	229	236		

Mean of doublet at: [a]) 820 and 807, [b]) 784 and 780, [c]) 649 and 644, [d]) 419 and 415 cm^{-1}.

Table 59. Vibrational frequencies of the complexes $[M(5,7\text{-}Br_2\text{-}OX)_2(B)_2]$ (2000 - 200 cm^{-1})

M →	Co	Ni	Zn	Ni	Assignment
B →	H_2O	H_2O	H_2O	py	
		1605		1605	
	1566	1561	1568	1554	
	1489	1492	1491	1486	
	1392	1394	1394	1396	
	1363	1367	1362	1356	
	1288	1287	1288	1288	
	1251	1250	1250	1253	
	1244		1243	1242	
	1221	1225	1222	1216	
	1189	1206	1195^a	1152	
	1141	1140	1141	1140	
	1112	1111	1113	1110	νC-O
	1047	1058	1050	1072^b	
	1037		1034	1044	
				1017	
	941	950	942	948	
		880		877	
	866	874	865	864	
	803	806	805^c	813	
	782	783	782	791	
				765	
				755	
	747	744	746	746	
		726		713	
				701	
	689	691	689	691	
	664	665	664	675	
	645	650	645	647	νM-O
				634	ring torsion
	598	598	598	597	
	574	582	575	578	νM-O
		567			
	506	511	504	502	νM-O+νM-N+δC-O
	481	488	480	487	
	441	450	439	440	νM-N
		432		430	ring torsion
	385	335	354		
	342	352	334	341	νM-N
				328	
				270	
				250	
	240	233		243	

Mean of doublet at: [a]) 1200 and 1189, [b]) 1075 and 1068, [c]) 807 and 803 cm^{-1}.

Table 60. Vibrational frequencies of the compounds Na(R-OX) (2000 - 200 cm^{-1})

$2-CH_3$	$2-CH_3-$ $5,7-Br_2$	H	$5,7-Cl_2$	$5,7-Br_2$	5-Cl	5-Cl-7-I
1612	1603	1590	1600	1598	1599	1598
1592	1563	1572	1562	1562	1579	1553
1560	1550			1554		
1512						
1495	1495	1499	1498	1488	1499	1494
1434	1439	1426	1412	1450	1416	1455
	1401	1389	1401	1407	1390	1410
				1394		1397
1368	1350	1365	1351	1342	1354	1345
1334		1317			1317	
1298	1276	1282		1285	1265	1286
1287	1264		1250	1249	1246	1249
1241	1248	1234	1233	1221	1232	1211
	1216					
1184	1192	1205	1191	1194	1197	1188
1174				1183		1160
1140	1145		1147	1140	1133	1139
1099	1104	1106	1102	1102	1083	1104
						1098
1070	1088	1068	1051	1059	1045	1049
1033	1043	1036		1020		
1005						
973	977	980				
950	931	948	955	932	945	950
912	919					918
	888	897	874	877	885	873
867	874	870	862			
	856			854		
832	829	823			832	841
804	825		805	807		805
	793	796	791	792	793	789
748	742	755	749			740
738	736	718	729	734	734	
	694		681	693		693
				681		
	664	660	641	674		675
	635			633	655	650
		602			603	632
585	599	590	595	592	597	596
577	572		582			565
557	536	558		566		551
518	530	544	503		532	
501	463	496	496	494	491	498
		484		486		483
446			428	429		426
410	414		400			
	368		374	375	391	393
331	325	353	344	351	359	363
286	293	282	283	314	283	290
271						
250	255	254	242	265	255	252
230		231				

IV. DISCUSSION

1. THE IR SPECTRA OF TRANSITION METAL 2-THENOYLTRIFLUOROACETONATES AND BENZOYLTRIFLUOROACETONATES

(i) Di- and Trivalent Metal 2-Thenoyltrifluoroacetonates

Despite the amount of work done on various aspects of 2-thenoyltrifluoroacetonate (TTA) chelates, no crystallographic studies have been made on these complexes. Like their acetylacetonate analogues, the metal(II) derivatives are isolated as the dihydrates except for the Ca(II) and Cu(II) compounds which are precipitated as the anhydrous complexes. *Trans*-octahedral conformation has been established[173] for the acetylacetonate dihydrates and is presumed for the TTA dihydrates. Certainly, none of the complexes $M(TTA)_2(H_2O)_2$ exhibits any spectral differences which could be ascribed to isomerism and their spectral band patterns are practically identical with those of the octahedral $M(TTA)_3$ compounds. The structure of the sodium salts of the *tris* compounds is assumed octahedral as has been shown for the acetylacetonate analogues[174].

Dehydration of the dihydrates is readily effected by moderate heating under reduced pressure, except for the thermolabile Fe(II) dihydrate complex. The anhydrous complexes other than that of copper yield spectra which are practically identical (with respect to the band frequencies and intensities) with those of the dihydrates. This suggests that they are analogous with the anhydrous metal(II) acetylacetonates[173] in being correctly formulated as polynuclear octahedral species, $[M(TTA)_2]_n$, n>1. That $Ni(TTA)_2$ is octahedral has been shown by Rao and Li[42] from a discussion of its electronic spectrum. Even $Ca(TTA)_2$ yields an IR spectrum consistent with this structure and there is evidence that other Ca(II) β-ketoenolates are probably not tetrahedral monomers[6]. The structures of Cu(II) chelates are usually square planar as has been shown to be the case for Cu(II) acetylacetonate[173]. The spectrum of $Cu(TTA)_2$ shows several unique features, namely a unique strong band at 556 cm^{-1}, splitting of the ligand band near 530 cm^{-1} and reversal of the relative intensities of the two bands near 1600 cm^{-1}, which are consistent with a square planar structure in contrast to the octahedral structures of the other anhydrous TTA complexes.

The IR spectra of 2-thenoyltrifluoroacetone (HTTA) and its complexes are depicted in Figures 1 and 2, and the frequencies are listed in Tables 13 - 16 and 27. The far IR spectra of these chelates are densely populated. Kassierer and Kertes[71] have made empirical assignments for three bands below 700 cm^{-1}, namely the band near 650 cm^{-1} as coupled νM-O, the band near 580 cm^{-1} as an out-of-plane bend and that near 400 cm^{-1} as νM-O from its metal sensitivity. Noskova and coworkers[70], from theoretical analysis of the vibrational spectra, derived assignments for most of the bands below 600 cm^{-1}, those of importance being the bands at 590, 520, 397, 330 and 250 cm^{-1} which were assigned as νM-O coupled with a ring deformation.

In seeking assignments for metal-ligand vibrations, the possibility of coupling between these and ligand vibrations must be acknowledged. Previous work[4,5,9,10,12,14] has established that practically without exception, the band assigned to νM-L by an independent technique (such as isotopic labelling) in a series of transition metal complexes of a common ligand is strongly metal-sensitive in the order of the CFSE's. Since the CFSE is a function of both the electronic configuration of the metal and of $10Dq$, a knowledge of the spin states of those metal ions with a $d^4 - d^7$ configuration which can exist in either high or low spin states is required for a calculation of CFSE. Table 61 shows the room temperature magnetic moments of the relevant complexes, all of which have a high spin configuration in common with the corresponding acetylacetonates[175]. Using the tabulated values of g (the metal ion parameter) the CFSE is calculated from the formula

$$\mathrm{CFSE} = -(0{\cdot}4\ N_{t_{2g}} - 0{\cdot}6\ N_{e_g})\ \delta g$$

The CFSE's in Table 61 are given in terms of δ which is constant for a series of complexes as used here which have constant ligand combination. For the divalent metals, assuming Cu(II) to be octahedral, the order of CFSE's is Ca = Mn<Co<Ni>Cu>Zn and for the trivalent series Sc<V<Cr>Mn>Fe = Ga. Due to Jahn-Teller distortion, the Cu(II) chelate is expected to yield a square planar compound. The resulting additional stabilization is expected to reverse the Ni>Cu order and hence to yield the order of the Irving-Williams[50] stability sequence, namely Mn<Co<Ni<Cu>Zn.

The spectra of the divalent anhydrous chelates and their dihydrates exhibit a band-for-band similarity. The νM-O bands will be assigned as those bands which are metal-sensitive strictly in the Irving-Williams sequence. The absorption maximum exhibiting maximum metal sensitivity is the pronounced band near 400 cm^{-1} and this is therefore assigned as the principal (or least-coupled) νM-O. This assignment is in agreement with those of Kassierer and Kertes[71] and of Noskova and coworkers[70]. This region in the spectrum of HTTA is free from ligand vibrations whereas all the other bands which are assigned as νM-O coincide with strong absorptions in the ligand and will hence be assigned as coupled νM-O. Strong coupling of the metal-oxygen modes leads to a lowering of the metal ion sensitivity of the νM-O bands as is observed in these spectra. Of the unique features in the spectrum of the Cu(II) complex, the most striking is the strong band at 556 cm^{-1}, which clearly (Fig. 1) corresponds with those near 400 cm^{-1} in the spectra of the complexes of other ions. The abnormally high νCu-O value is not unexpected if the Cu(II) complex is the only 4-co-ordinate complex of the series since the bonding capacity of the metal ion is distributed over four bonds rather than six. A similar situation[176] exists for the complexes: tetrahedral monomeric [Co Cl_2 py_2] (νCo-N = 252 cm^{-1}) and octahedral polymeric [Co Cl_2 $py_2]_n$ (νCo-N = 224 cm^{-1}). The high νCu-O value is also expected on theoretical grounds since the Jahn-Teller distortion which gives rise to square planar Cu(II) complexes results in additional stabilization of this compound. The highest metal-sensitive band is that near 650 cm^{-1} referred to by Kassierer and Kertes[71] and since its metal sensitivity lies in the order of the CFSE's, it is assigned as a coupled νM-O. The remaining bands, assigned on the basis of their shifts induced by changing the metal ion to coupled νM-O bands are those near 590 cm^{-1} (assigned by Kassierer and Kertes[71] as an out-of-plane bend) and the bands in the region 300 - 350 cm^{-1}. In this part of the spectra of the sodium salts of the tris chelates, two metal-sensitive bands are observed and previous workers[71] report for the dihydrates a very weak absorption, not detected in this study, near 330 cm^{-1} corresponding closely to the absorption in the anhydrous chelates.

Thus it seems likely that two weak νM-O bands are generally found in this region of the spectra of TTA chelates, only one being observed in this study in the hydrated and anhydrous chelate spectra. The above assignments agree with those of Noskova and coworkers[70] except that the band at 520 cm^{-1} assigned by them as νM-O + ring deformation shows no metal ion sensitivity. Since it corresponds in position to a band in other fluorinated β-ketoenolates[177], it is assigned to a vibration involving the CF_3 group, as are the absorptions at 500 and 560 cm^{-1}. The remaining two bands in the far IR spectra near 460 and 610 cm^{-1} are assigned empirically to thienyl deformation vibrations. The latter band, when compared with the spectra of benzoyltrifluoroacetone and its chelates, is unique to HTTA and its compounds.

The bands assigned to νM-O in the Ca(II), Mn(II) and Zn(II) chelates provide reference frequencies which are only dependent on those factors determining the metal-ligand stretching frequency other than crystal field effects. An interpolation line drawn between these points (which represent zero CFSE) is used to estimate the frequencies (ν_0) which would be realized in the absence of crystal field stabilization (Fig. 3). The difference between ν_0 and the observed frequencies (ν) therefore represents that part of νM-O which is attributable to the CFSE. The values of $(\nu-\nu_0)$ for the bands near 650 and 400 cm^{-1} (designated as $(\nu M\text{-}O)_1$ and $(\nu M\text{-}O)_2$) are shown in Table 61 and correlate qualitatively with the CFSE values. Similar conclusions generally pertain to the less sensitive metal-ligand bands.

In the complex ions with zero CFSE, the νM-O values usually exhibit an increase in the order Ca<Mn<Zn. Since

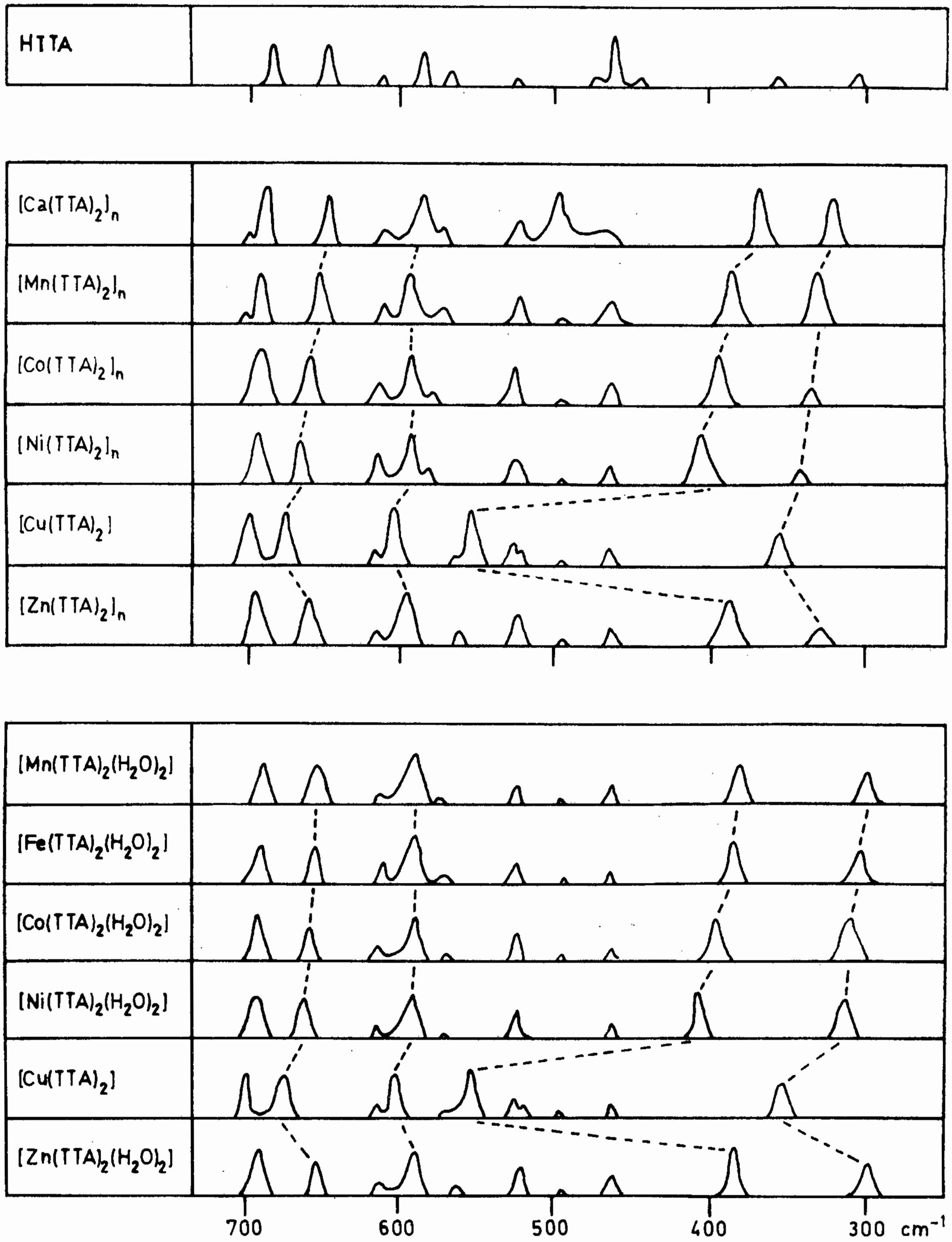
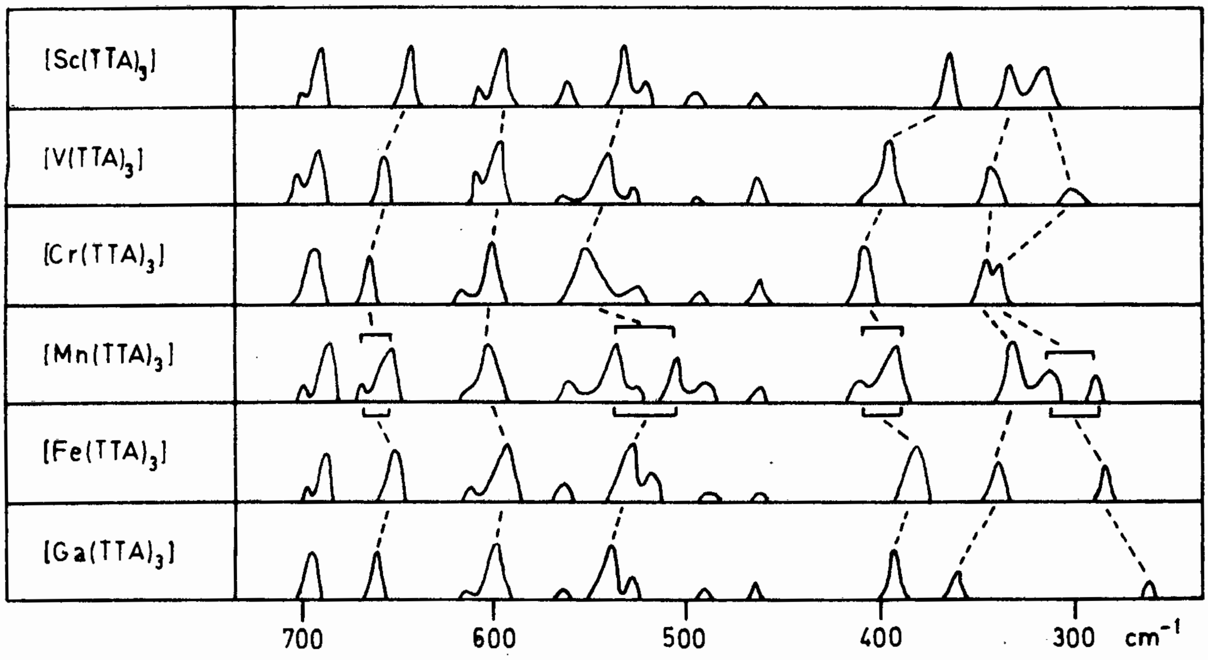


Fig. 1. The IR spectra of the anhydrous and hydrated divalent metal 2-thenoyltrifluoroacetonate complexes, 700 - 200 cm^{-1}. **Linked peaks** : νM-O.



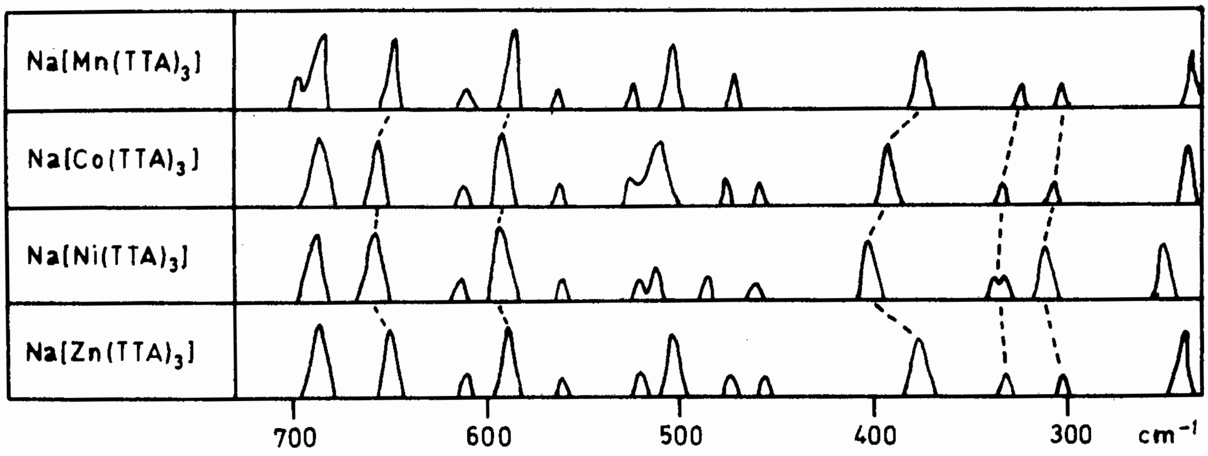


Fig. 2. The IR spectra of the complexes [M(TTA)$_3$] and Na[M(TTA)$_3$], 700 - 200 cm^{-1}. Linked peaks : νM-O.

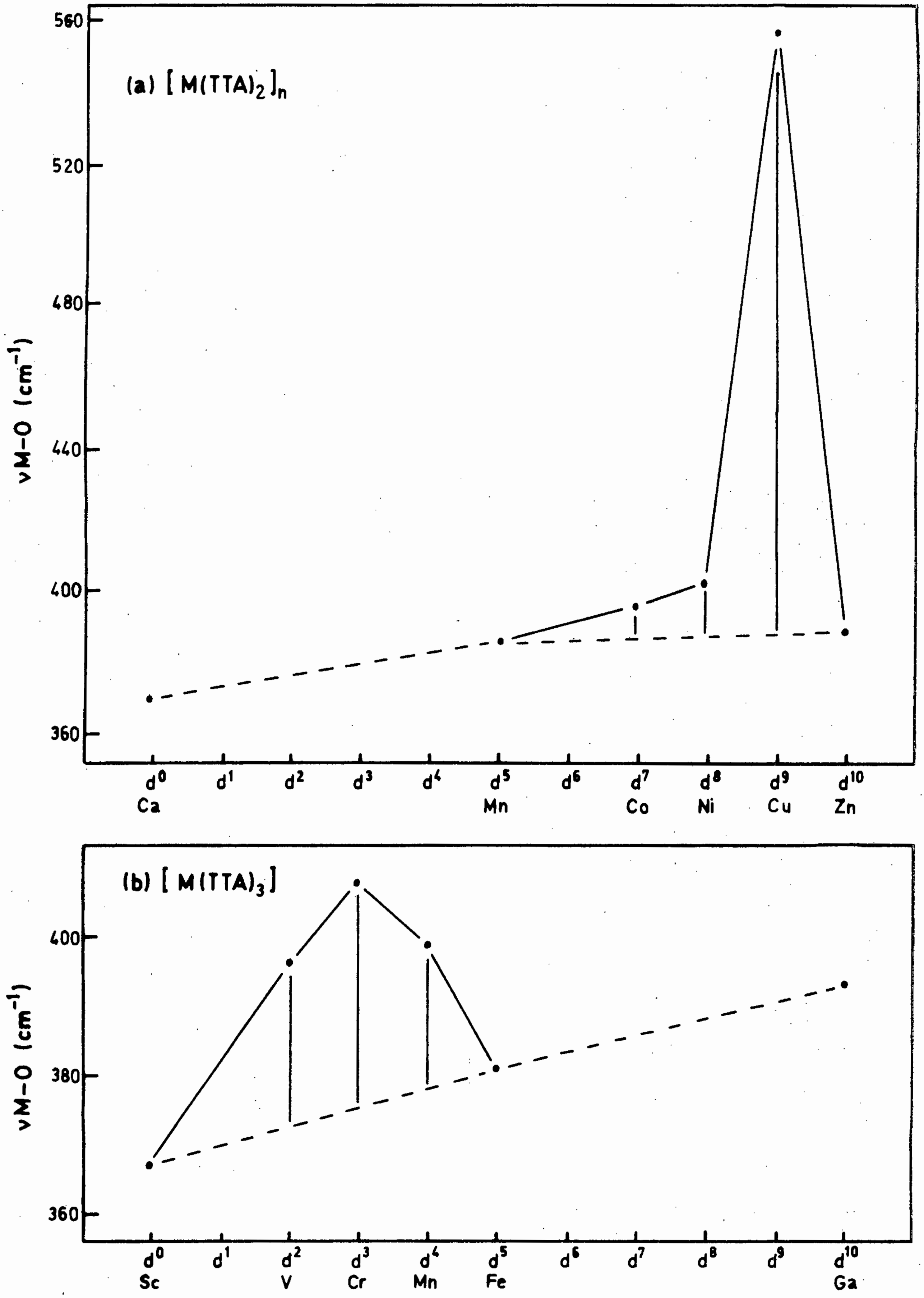


Fig. 3. Relationship between frequency and *d*-orbital population for the most sensitive νM-O band. The dashed line is the interpolation line and the vertical lines represent ($\nu-\nu_0$). The point for Mn(III) is taken as the mean of the bands at 410 and 389 cm^{-1}.

this is the inverse of what would be expected from the relative ionic masses, it would appear that the mass effect is small and overshadowed by the effect of the ionic radius contraction; this contraction is expected to lead to a decrease in M-O bond length and hence an increase in νM-O. Since the variation in ionic mass for the ions of the first transition series is relatively small, the insignificant contribution of the mass effect to the IR frequencies is not surprising. In addition, independent evidence for small mass effects has recently been cited[178].

The spectra of the complexes [M(TTA)$_3$] bear a close similarity to the spectra of the divalent ion complexes, the most metal-sensitive band being found near 400 cm^{-1}. The order of the frequencies of this band is also the order yielded by the calculated CFSE's of the trivalent ions, namely Sc<V<Cr>Mn>Fe (Table 61). The unique character of the spectrum of the spin-free d^4 Mn(III) complex is apparent from Figure 2: it is distinguished by a splitting of the metal-sensitive bands. Of the trivalent ions studied, Mn(III) is the only one for which strong Jahn-Teller distortion is expected. Crystallographic studies of Mn(III) acetylacetonate reveal tetragonal structure, although the static distortion is very small[170,179]. Assuming similar distortion in Mn(TTA)$_3$, splitting of the νMn-O bands is a logical result of the existence of short and long Mn-O bond lengths. The mean value of νMn-O for each metal-sensitive band is usually in the order expected from the calculated CFSE's, namely Cr>Mn>Fe.

The metal-sensitive bands found in the divalent metal chelate spectra near 650, 590, 350 and 300 cm^{-1} also appear in the spectra of the trivalent compounds. However, unlike the metal(II) compounds, two νM-O bands are found below the 400 cm^{-1} band. A unique feature of the group of trivalent metal complexes is the appearance near 540 cm^{-1} of an extra metal-sensitive band assigned here as an additional coupled νM-O. Values of $(\nu-\nu_0)$ are calculated (Figure 3) by the same procedures as were described for the dihydrates and exhibit a good qualitative correlation with the calculated CFSE's (Table 61).

Like their trivalent analogues, the metal(II) complexes $Na[M(TTA)_3]$ have a spectral band pattern that is very closely related to the other divalent metal TTA chelates. The band which shifts most on changing the metal ion is that in the range 380 - 400 cm^{-1} while smaller shifts are observed for the bands near 650, 590, 330 and 300 cm^{-1}. Like the trivalent series, the sodium salts of the tris TTA chelates exhibit two sets of metal-sensitive bands between 350 and 300 cm^{-1}. The fact that νM-O for the $Na[M(TTA)_3]$ compounds has a lower value than νM-O for the polymeric anhydrous $[M(TTA)_2]_n$ compounds must indicate some additional stabilization associated with the polymeric state since (on the basis that some oxygen donor atoms are bidentate in the polymers) the inverse relationship would normally be expected. A similar situation has been observed for the corresponding acetylacetonates[6]. The frequencies associated with ligand vibrations are very similar to those of the other divalent and trivalent metal TTA chelates. A feature of these tris compounds lies in the appearance of a band near 480 cm^{-1} which is fairly strongly metal-sensitive in the CFSE order. This band is not assigned as an additional νM-O since it occurs in the spectra of the phen adducts and there the order Ni<Cu is maintained despite the reversal of this order for all the bands assigned as νM-O. Hence this

Table 61. CFSE data on metal 2-thenoyltrifluoroacetonates

M	Configuration	μeff (289K) B.M.	g kK	C F S E		$(\nu-\nu_0)$	
				Dq	δ	$(\nu M\text{-}O)_1$ cm^{-1}	$(\nu M\text{-}O)_2$ cm^{-1}
$[M(TTA)_2]_n$							
Ca	d^0	-	-	0	0	0	0
Mn	d^5	5.51	8.5	0	0	0	0
Co	d^7	4.99	9.3	8	7.44	4	8
Ni	d^8	-	8.9	12	10.68	9	15
Cu	d^9	-	12.0	6[a]	7.20[a]	18	167
Zn	d^{10}	-	-	0	0	0	0
$[M(TTA)_2(H_2O)_2]$							
Mn	d^5	5.94	8.5	0	0	0	0
Fe	d^6	5.30	10.0	4	4.00	1	4
Co	d^7	4.86	9.3	8	7.44	4	12
Ni	d^8	-	8.9	12	10.68	9	24
Zn	d^{10}	-	-	0	0	0	0
$[M(TTA)_3]Na$							
Mn	d^5	5.3	8.5	0	0	0	0
Co	d^7	3.7	9.3	8	7.44	5	15
Ni	d^8	-	8.9	12	10.68	8	23
Zn	d^{10}	-	-	0	0	0	0
$[M(TTA)_3]$							
Sc	d^0	-	-	0	0	0	0
V	d^2	-	18.6	8	14.88	9	24
Cr	d^3	-	17.0	12	20.40	16	33
Mn	d^4	6.16	21.0	6[a]	12.60[a]	9[b]	21[c]
Fe	d^5	5.89	14.0	0	0	0	0
Ga	d^{10}	-	-	0	0	0	0

[a] Omitting extra stabilization due to Jahn-Teller distortion

[b] Mean of doublet: 667 and 653 cm^{-1}

[c] Mean of doublet: 410 and 389 cm^{-1}

band is tentatively assigned as an O-M-O bend. The calculated values of $(\nu-\nu_0)$ for the tris compounds are also shown in Table 61.

Tables 13 - 16 show tentative vibrational assignments for bands in the region 2000 - 700 cm^{-1}. These assignments are based on the published theoretical and empirical studies on the IR spectra of metal β-ketoenolates. Due to the extensive delocalization occurring in the chelate ring of metal β-ketoenolates, few bands represent pure (uncoupled) vibrations. The assignments of νC=O and νC=C to the first two bands below 1700 cm^{-1} are obtained by comparison with the spectra of metal acetylacetonates in which these assignments have been established by normal co-ordinate analysis[69] and by ^{18}O-labelling studies on Cr(III) and Cu(II) acetylacetonates[35,36]. The first heterocyclic ring stretching frequency for a 2-substituted thiophene occurs well below the carbonyl region[180,181] (1523 ±9 cm^{-1}). Bands are observed in this region in the spectra of the chelates of TTA. Previous assignments[43,53,59,62,70,71] of bands in this region have been made by comparison with the metal acetylacetonates. Lintvedt and Holtzclaw[53] assigned the first two bands below 1700 cm^{-1} to νC=C and νC=O respectively from the work by Nakamoto and coworkers[67]. Similar assignments were made by Noskova and coworkers[70] from an independent theoretical study, except that the band given by them as νC=O is assigned in this study to the thienyl vibration. The assignment of the higher frequency band to νC=O was made by several workers[43,59,62,71] following the empirical assignment of Lecompte[64]. Kassierer and Kertes[71] assigned the three bands in this region to various νC=O modes, while Ohwada[59] suggested that the upper two are νC=O and that the band near 1540 cm^{-1} is νC=C of the chelate ring. Holtzclaw and Collman[62] followed the assignment of Lecompte for νC=O but (while recognizing the fact that the thienyl absorptions are likely to intrude into this region) they made no definite assignments for the thienyl vibrations or for νC=C of the chelate ring. With the frequency of the 2-thienyl vibration given by Katritzky and Boulton[180], there are no complications from the overlap of these bands with νC=O and νC=C and the assignment is comparatively straightforward, the bands near 1600, 1580 and 1540 cm^{-1} being νC=O, νC=C and a thienyl ring stretch respectively. Further thienyl ring vibrations[180] occur at 1442 ±12 and 1354 ±7 cm^{-1} and thienyl C-H deformation frequencies are at 1081 ±3, 1043 ±7, 925 ±8, 853 ±7 and 800 cm^{-1}. Bands near all of these frequencies are observed in the spectra of HTTA and its chelates. Vibrational bands originating in the CF_3 group are assigned (Tables 13 - 16) by comparison with the spectrum of CF_4[182] and normal co-ordinate studies of tri- and hexafluoroacetylacetonates[67].

(ii) Di- and Trivalent Metal Benzoyltrifluoroacetonates

The properties and spectra of benzoyltrifluoroacetone (HBTA) and its chelates closely resemble those of the TTA compounds studied in the previous Section. Like their TTA analogues the metal(II) complexes precipitate from aqueous solution in the form of the bis(hydrate) species except for the Cu(II) chelate which is anhydrous. Attempts to dehydrate the other divalent metal complexes by heating *in vacuo* were unsuccessful: the compounds decomposed before losing their water of hydration. Similar unsatisfactory high temperature properties were noted by Berg and Reed[45] who, in studying the fractional sublimation of metal chelates, found that many of the chelates of BTA condensed as liquids and were not suitable for sublimation studies. Although no X-ray crystallographic studies have been carried out on these complexes, the structures are reasonably assumed to be the same as those proposed for the TTA complexes, namely *trans*-octahedral co-ordination in the dihydrates and a square planar co-ordination in the Cu(II) compound. Manganese(II) did not form the complex $Na[Mn(BTA)_3]$ but the Co(II), Ni(II) and Zn(II) compounds were synthesized and the structures assumed to have the octahedral co-ordination proposed for the trivalent compounds, $[M(BTA)_3]$.

Previous studies[43,53,61,183] on the IR spectra of BTA compounds have been concerned mainly with the νC=O and νC=C bands and no systematic study of the far IR spectra has previously been undertaken. Room temperature magnetic moments (Table 62) show that all the complexes for which alternative spin states are possible, have the high spin configuration. Hence the order of CFSE's (Table 62) is Sc<Cr>Mn>Fe = Ga and Mn<Co<Ni>Cu>Zn if we ignore the extreme Jahn-Teller distortion of Cu(II) which leads to the formation of a square planar complex. If this extra stabilization is taken into account, the expected order is Mn<Co<Ni<Cu>Zn. For the assignment of metal-oxygen modes in the far IR, use is made of the fact that the νM-O bands are expected to be metal-sensitive in the order of the CFSE's.

The IR spectra of HBTA and its compounds are shown in Figure 4 and the frequencies are listed in Tables 17 - 19 and 27. The spectra of the divalent metal hydrates show a strongly metal-sensitive band in the 390 - 420 cm^{-1} range which corresponds with the position of the principal νM-O in the TTA chelates. As found in the previous Section, the Cu(II) complex shows several unique features such as the doubling of the bands near 440 and 520 cm^{-1} and the presence of a unique band at 563 cm^{-1}. This latter band corresponds with the bands near 400 cm^{-1} as shown in Figure 4 and this set of absorptions is assigned to the principal or least-coupled νM-O. The rather high value of νCu-O is expected from the similar band patterns of the BTA and TTA chelate spectra in which νCu-O for the TTA compound was assigned to the band at 556 cm^{-1}. The metal-sensitive bands above this region appear within the same range as those of TTA compounds, namely near 650 and 590 cm^{-1}; they are assigned to coupled νM-O. In all these cases, the bands follow the Irving-Williams stability order. Although the BTA chelates show bands near 340 and 310 cm^{-1}, these bands are not strictly metal-sensitive in the order of the CFSE's and they are therefore not assigned (as similar bands were in the spectra of the TTA complexes) to coupled νM-O vibrations. However, near 250 cm^{-1}, a strong metal-sensitive band appears and this is assigned to a coupled νM-O. The spectrum of HBTA is free from strong absorptions near 400 cm^{-1} where the principal νM-O band appears, but strong absorptions occur near all the other bands assigned to νM-O. For this reason only the 400 cm^{-1} band is assumed to have any significant degree of vibrational purity. Of the remaining bands in the far IR, that near 520 cm^{-1} is assigned to a ligand vibration associated with the CF_3 group (by analogy with the TTA complex spectra) and the band at 440 cm^{-1} is assigned to a ligand vibration involving the phenyl group. In both these

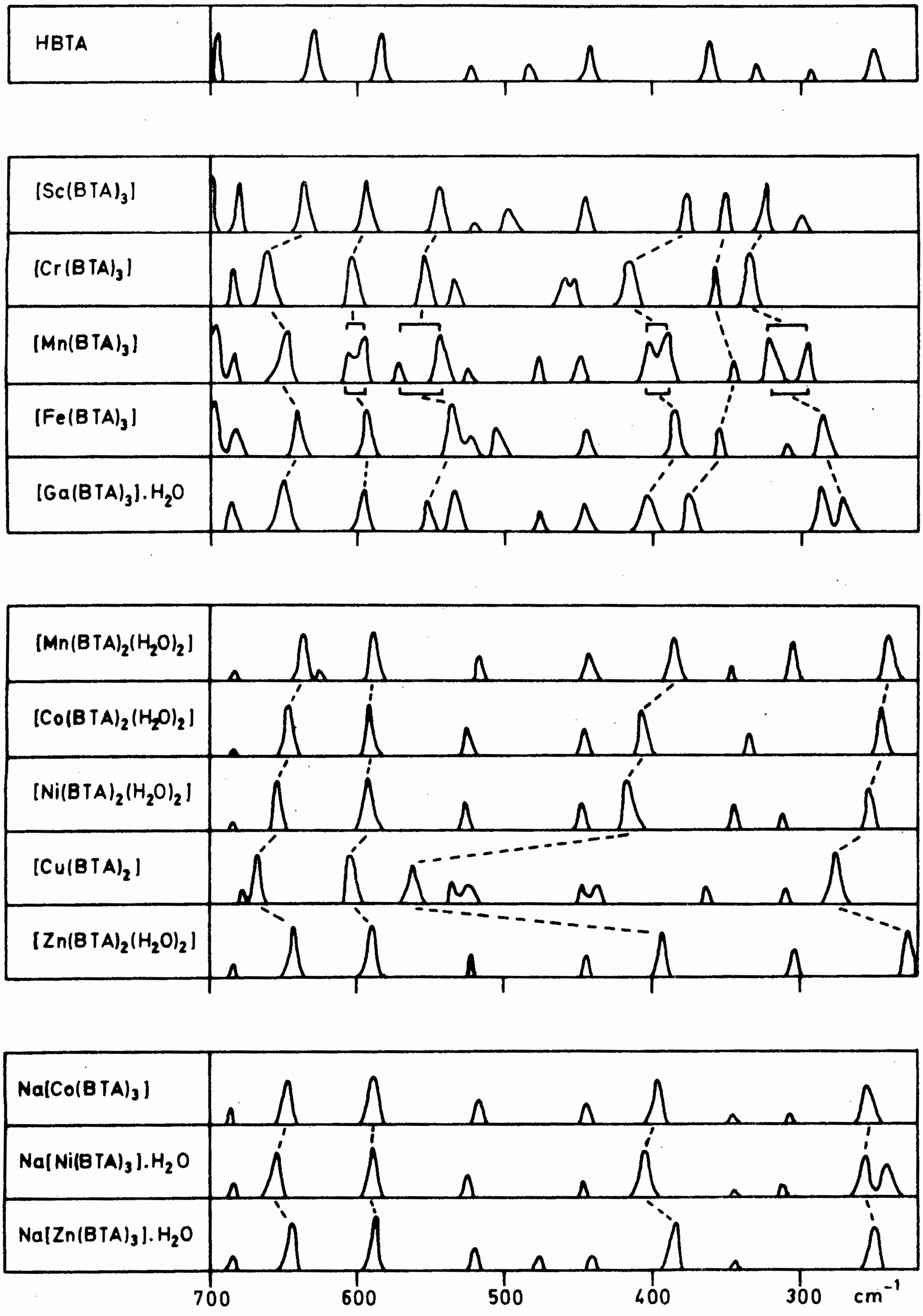


Fig. 4. The IR spectra of the divalent and trivalent metal benzoyltrifluoroacetonates, 700 - 200 cm^{-1}. Linked peaks: νM-O.

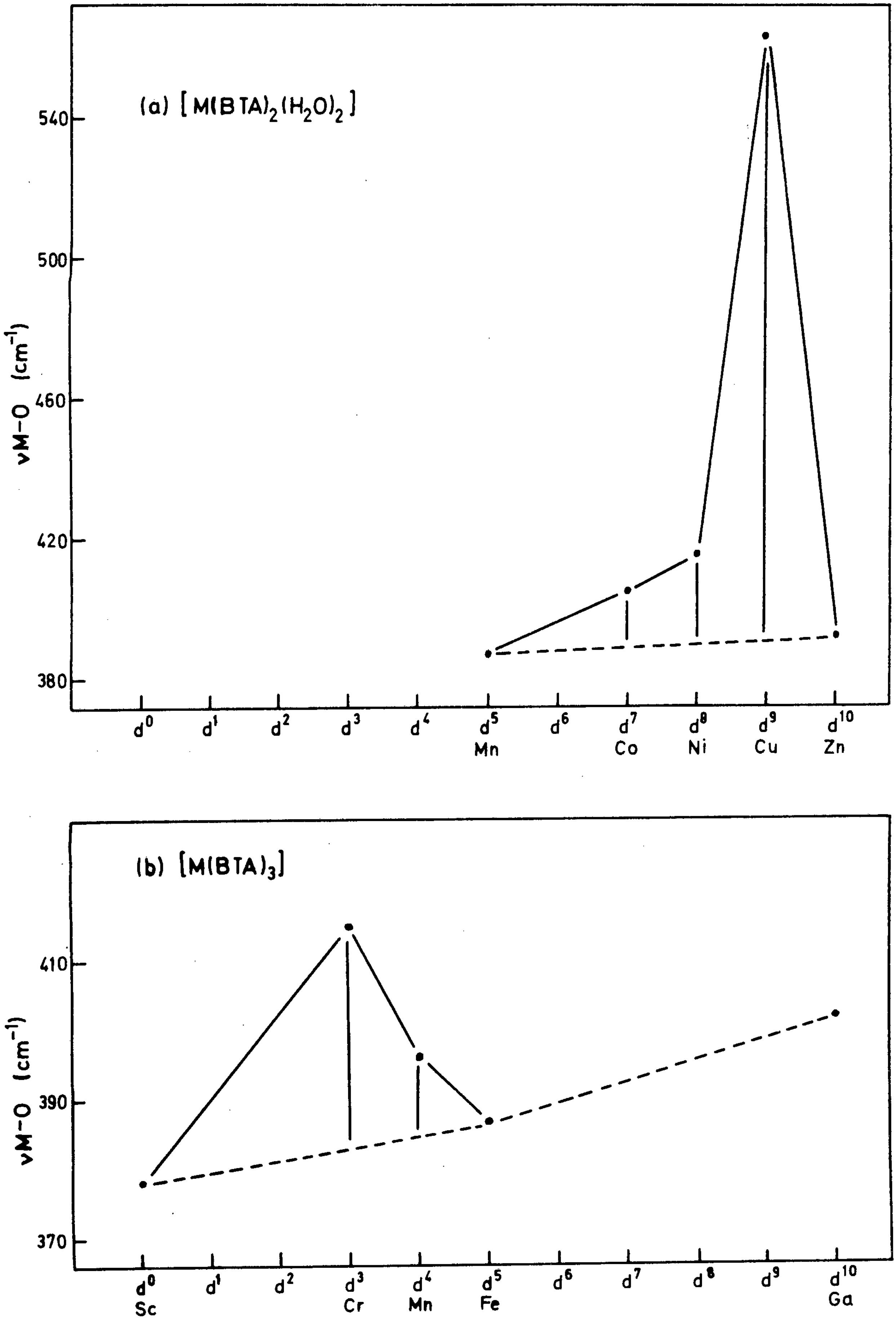


Fig. 5. Relationship between frequency and *d*-orbital population for the most sensitive νM-O band. The point for Cu(II) is from the anhydrous complex and that for Mn(III) is taken as the mean of the bands at 401 and 390 cm^{-1}.

ligand vibrations, the Cu(II) complex exhibits some unique features indicative of its differing structure, *i.e.* both bands are split into doublets whereas single peaks occur in the spectra of the complexes of all other metal ions. The bands associated with the CF_3 group in the TTA complexes at 560 and 500 cm^{-1} are either absent in the BTA complex spectra or are too weak to be observed.

Table 62 shows the values of $(\nu-\nu_0)$ derived from the 650 and 400 cm^{-1} bands (designated $(\nu M-O)_1$ and $(\nu M-O)_2$ in the Table) by drawing the interpolation line between the reference frequencies of the Mn(II) and Zn(II) complexes which have zero CFSE. Measuring the frequency increment for the other metal complexes above this line gives values of $(\nu-\nu_0)$ which represent the contribution of the crystal field to the frequencies of the Co(II), Ni(II) and Cu(II) complexes. These values show a qualitative correlation with the CFSE's calculated in Table 62 in terms of δ. Similar results are obtainable for the less-sensitive metal-oxygen bands.

In those bands assigned to $\nu M-O$ the order of the reference frequencies is Zn(II)>Mn(II) (as was observed in the TTA complexes) again showing the predominance of the effect of ionic radius contraction over the mass effect.

The spectra of the trivalent chelates $M(BTA)_3$ shown in Figure 4 have several features in common with those of the divalent hydrated analogues, the most outstanding being the appearance of metal-sensitive bands near 650, 590 and 400 cm^{-1}. This last vibration, as in the case of the metal(II) complexes, is assigned to the principal $\nu M-O$, the other two bands representing coupled $\nu M-O$ vibrations. Of the trivalent metal complexes studied, that of the high spin Mn(III) ion is the only one expected on theoretical grounds to exhibit any appreciable Jahn-Teller distortion. As observed for Mn(TTA)$_3$, this unique feature of Mn(III) is evidenced by a splitting of several of the metal-oxygen bands and is indicative of the type of distortion which has been experimentally verified in Mn(III) acetylacetonate[170,179]. Despite the extra Jahn-Teller stabilization which may be expected to arise from this distortion, the mean value of νMn-O for each metal-sensitive doublet lies in the order predicted by CFT, namely Cr>Mn>Fe. Thus the amount of distortion is relatively small compared, for instance, with that generally observed in tetragonal Cu(II) complexes. In the region near 550 cm^{-1} a metal-sensitive band appears which is not observed in the dihydrates and corresponds to an additional coupled νM-O vibration by analogy with the TTA complexes. Below the 400 cm^{-1} band, two series of bands showing metal ion sensitivity are observed and these (also by comparison with the TTA complexes) are assigned to coupled νM-O vibrations. As in the dihydrates, two ligand bands, one associated with the CF$_3$ group near 520 cm^{-1} and the other with the phenyl group near 450 cm^{-1}, are observed in these spectra. An additional band appearing between these two ligand modes is assigned empirically to an O-M-O bend by analogy with the assignment proposed for the corresponding band in the sodium salts of the tris TTA complexes. Table 62 gives the values of (ν-ν_0). Figure 5 indicates the variation of frequency with *d*-orbital population for the trivalent and divalent chelates.

Of the series of complexes Na[M(BTA)$_3$], only those with M = Co(II), Ni(II) and Zn(II) proved synthesizable.

Table 62. CFSE data on metal benzoyltrifluoroacetonates

M	Configuration	μeff (289K) B.M.	g kK	CFSE Dq	CFSE δ	$(\nu-\nu_0)$ $(\nu M\text{-}O)_1$ cm^{-1}	$(\nu-\nu_0)$ $(\nu M\text{-}O)_2$ cm^{-1}
$[M(BTA)_2(H_2O)_2]$							
Mn	d^5	4.2	8.5	0	0	0	0
Co	d^7	3.8	9.3	8	7.44	4	16
Ni	d^8	-	8.9	12	10.68	11	25
Cu[a]	d^9	-	12.0	6[b]	7.20[b]	26	172
Zn	d^{10}	-	-	0	0	0	0
$[M(BTA)_3]$							
Sc	d^0	-	-	0	0	0	0
Cr	d^3	-	17.0	12	20.40	20	32
Mn	d^4	5.2	21.0	6[b]	12.60[b]	7	11[c]
Fe	d^5	5.7	14.0	0	0	0	0
Ga	d^{10}	-	-	0	0	0	0

a Cu(II) is anhydrous

b omitting extra stabilization due to Jahn-Teller distortion

c νMn-O taken as mean of bands at 401 and 390 cm^{-1}

Calculation of $(\nu-\nu_0)$ values for this series is not possible since the Mn(II) reference point is not available. Nevertheless, assignments of the M-O modes are made by finding the metal-sensitive bands which follow the order Co<Ni>Zn. These are observed in similar regions to those of the other divalent BTA chelates. The band of maximum sensitivity occurs near 400 cm^{-1} and is therefore assigned to the least-coupled νM-O. The other assignments mirror those of the divalent hydrates, the bands near 650, 590 and 250 cm^{-1} being ascribed to coupled νM-O and the bands near 520 and 440 cm^{-1} to CF_3 and phenyl vibrations, respectively. The bands between 400 and 300 cm^{-1} are ligand vibrations while the Zn(II) complex shows a band at 476 cm^{-1}. By analogy with the corresponding TTA and the trivalent BTA chelates, this band is assumed to be the O-M-O bend.

Tentative assignments for the bands between 2000 and 700 cm^{-1} are shown in Tables 17 - 19 for the three groups of compounds studied in this work. Previous workers[43,53,61,183] have proposed assignments for the νC=O and νC=C vibrations. The first two bands below 1700 cm^{-1} are now assigned as νC=O and νC=C, respectively. From the relative constancy of the 1580 cm^{-1} band throughout all the spectra of HBTA and its chelates, this absorption is assigned to the first (highest frequency) ring stretching mode of the phenyl group; no previous workers have assigned this vibration. The vibrational bands associated with the CF_3 group and the chelate ring are tentatively assigned by comparison with the spectra of the TTA chelates. The phenyl group skeletal vibrations are assigned[184] near 1580, 1495 and 1460 cm^{-1}, this latter vibration being masked in most cases by the Nujol band at 1470 cm^{-1}.

The C-H deformation modes of monosubstituted benzenes[184] occur in the regions 1175 - 1125, 1110 - 1070, 1070 - 1000 (one band), 770 - 730 and 710 - 690 cm^{-1}. Bands in these regions are assigned to C-H modes. The bands occurring between 1550 and 1520 cm^{-1} are assigned by comparison with the spectra of other fluorinated β-ketoenolates[177] to the combination band : νC=O + δC-H.

It is of interest to compare the spectra of the TTA and BTA chelates with respect to the electronic effects of the CF_3 and aromatic substituents on the β-ketoenolate ring.

Table 63. IR data on substituted β-ketoenolates

[ML_3]		νM-O†				νC=O†			
L	M→	Sc	Cr	Mn	Fe	Sc	Cr	Mn	Fe
BA		683	691	686	685	1553	1555	1557	1551
AA		665	682	672	667	1580	1574	1593	1575
BTA		636	660	648	642	1610	1600	1609	1604
TTA		645	665	660[a]	652	1603	1600	1603	1602
TFA		610	626	620	609	1624	1615	1616	1616

† Values for BA, AA and TFA are taken from ref. 177

[a] Mean of doublet at 667 and 653 cm^{-1}

Since the only band expected to have any degree of metal-oxygen vibrational purity is the principal νM-O band near 400 cm^{-1}, only this band will be considered in comparing the substituent effects in BTA and TTA compounds. Both β-ketoenolates contain a CF_3 and an aromatic group and thus any differences are expected to arise from the differing natures of the aromatic moieties. The coplanarity[52,67] of both aromatic groups with the plane of the β-ketoenolate implies that both will act as electron releasing substituents through a resonance mechanism[52,53,185]. The effect of an electron releasing moiety in a β-ketoenolate is to strengthen the metal-oxygen bond and hence increase νM-O[185]. In view of the fact that the 2-thienyl group is a weaker electron releasing group by a resonance mechanism than the phenyl group[53], the order of νM-O is expected to be BTA>TTA as is observed for the principal νM-O band in all the corresponding divalent and trivalent complexes. The difficulty of finding corresponding νM-O bands to compare BTA and TTA with the other β-ketoenolates necessitates the use of the metal-sensitive band of highest frequency found in most metal β-ketoenolates[177] within the range 690 - 610 cm^{-1}. A comparison of this band in the spectra of the benzoylacetonates (BA) and trifluoroacetylacetonates (TFA) of the trivalent metals[177] with the corresponding band near 650 cm^{-1} in the BTA and TTA chelates shows that the latter two lie between the former two, with TFA at the lower and BA at the upper limit. The CF_3 group has an electron withdrawing inductive effect[52,53,185]. This leads to a decrease in the M-O bond strength and hence produces the lowest νM-O value. The phenyl group, being electron releasing, yields the highest νM-O value. It is therefore consistent that the BTA and TTA chelates give νM-O values intermediate between the two extremes. The νM-O bands lie below those of the acetylacetonates showing that, relative to acetylacetone (AA), the TTA and BTA ligands have a net electron withdrawing effect. A similar result was shown by Lintvedt and Holtzclaw[53] on the basis of the proton magnetic resonance spectra of the free ligands. In addition, the νC=O bands of BTA and TTA lie above those of AA and are intermediate between those of the BA and TFA chelates, the TFA compounds giving the highest carbonyl frequencies and those of BA the lowest. Hence a weakening of the M-O bond results in a strengthening of the C=O bond (Table 63) and implies some constancy of bond order summation around the carbonyl oxygen atom.

(iii) The IR Spectra of the Nitrogen Base Adducts of 2-Thenoyltrifluoroacetonates and Benzoyltrifluoroacetonates of the Divalent Metals

Divalent metal β-ketoenolates form adducts with bases containing nitrogen donors (N-bases) in which the compound assumes octahedral co-ordination by bonding to four oxygen atoms of the two β-ketoenolate rings and two nitrogen atoms of the adducted base. Among the compounds reported here, pyridine (py) and ammonia (NH_3), like water, form bis adducts which are assumed to have the *trans*-octahedral structure of the bis(hydrates). This structure has been experimentally verified for the py adducts of Ni(II) and Co(II) acetylacetonate[186,187]. Exceptionally, the py adduct of $Cu(O-O)_2$, where O-O represents the TTA or BTA anion, is a 5-co-ordinate species. The structure is most probably square pyramidal as experimentally verified for the mono(quinoline) adduct of copper acetylacetonate[188]. The formation of a 5-co-ordinate Cu(II) compound is indicative of the electron withdrawing effect of the ligand as a whole, yielding further evidence for the fact that the electron withdrawal of the CF_3 group predominates over the donor effect of the aromatic groups. The bidentate ligands, bipy and phen, form mono adducts with all the divalent metals from Mn(II) to Zn(II) including Cu(II). Since neither the β-ketoenolate ion nor bipy nor phen can span *trans* positions, the mixed ligand complexes have a *cis* configuration.

The spectra of the N-base adducts resemble those of the hydrated β-ketoenolates, *i.e.* the IR bands of the adducted base are superimposed on the bands arising from the TTA and BTA ligands. The spectra of the adducts are shown in Figures 6 - 8 and the frequencies listed in Tables 20 - 26.

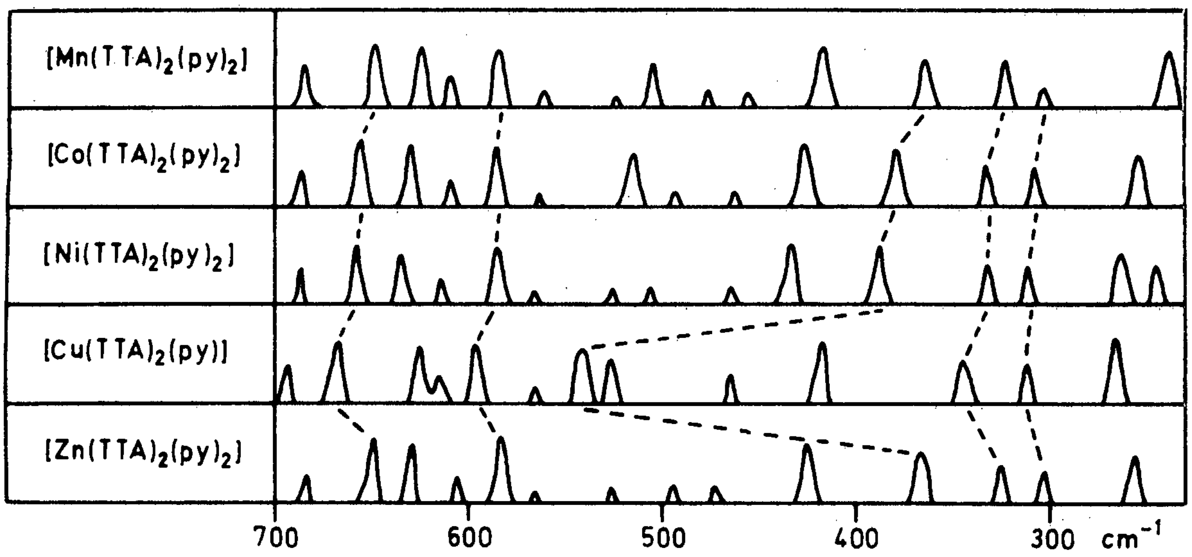
The far IR spectra of the complexes $M(TTA)_2(NH_3)_2$ (Figure 6) have precisely the band pattern of the dihydrates except for the appearance below 350 cm^{-1} of two metal-sensitive bands rather than one. This second band near 320 cm^{-1} corresponds with the band observed in this region for the tris complexes of the divalent metals and is hence assigned to a coupled νM-O. Consistent with previous assignments is the fact that only bands previously assigned to νM-O show a metal-sensitivity in the CFSE order. The most important feature of these spectra relative to the dihydrates lies in the lowering of all νM-O frequencies. Assuming this frequency decrease to reflect a reduction of force constant, the effect of replacing H_2O by NH_3 is to reduce the M-O bond strength relative to the dihydrate. Since the ligand field strength of ammonia (f = 1.25) is greater than that of water (f = 1.00) NH_3 is assumed to bond more strongly with the metal ion than H_2O. This increase in metal-adduct interaction leads to a decrease in the M-O bonding which is reflected in the decrease in νM-O. This inverse relationship which exists between the ligand field strength of the adducted base and νM-O for the chelate has been well authenticated in studies of various other ligand systems[27,28,189,190]. The band which shifts most on adduct formation is, as expected, that near 400 cm^{-1}

assigned to the principal νM-O; the observed shift is between 10 and 16 cm^{-1}.

During the course of this study one example of a mixed adduct species comprising one NH_3 and one H_2O molecule was isolated. That this complex, $[Mn(TTA)_2(H_2O)(NH_3)]$ yielded νMn-O values intermediate between those of the bis(aquo) and the bis(ammine) adducts is consistent with the above discussion.

The pyridine adducts, like their bis(ammine) analogues, exhibit a decrease in the values of νM-O relative to the bis(aquo) adducts. The Cu(II) adducts show a similar reduction in νM-O due to the change in co-ordination number from 4 to 5 on adduct formation. Marov and coworkers[191] have shown, from electron paramagnetic resonance measurements, that the σ-bonds are not greatly affected by formation of the pyridine adduct $Cu(TTA)_2(py)$ but that the degree of covalency of the π-bonds decreases slightly. Hence it may be suggested that the Cu-py bond is very weak leading to a relatively small reduction in νCu-O on change of co-ordination number. Besides the pyridine deformation vibrations near 630 and 430 cm^{-1}, an additional band appears near 480 cm^{-1} in both the BTA and TTA compounds. This band is assigned by analogy with previous spectra to an O-M-O bend. The two series of bands in the region 350 - 300 cm^{-1} are as insensitive to metal change in the BTA chelates as they were observed to be in the dihydrates.

The bipy and phen adducts form a series of octahedral complexes of the metals from Mn(II) to Zn(II). Their spectra exhibit metal-sensitive bands in similar regions to those assigned in the previous two Sections to the νM-O



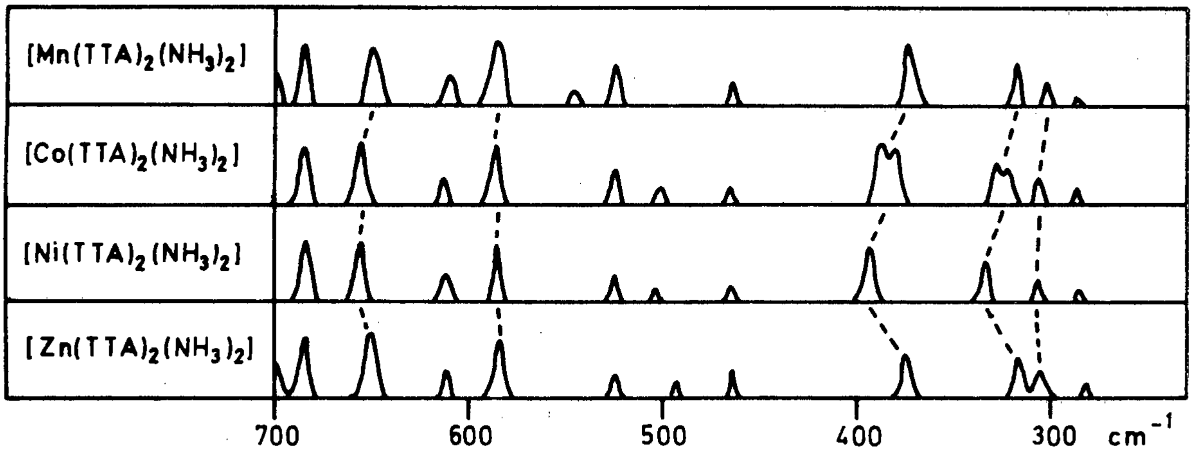


Fig. 6. The IR spectra of the pyridine and ammine adducts of the divalent metal TTA chelates, 700 - 200 cm^{-1}.

Linked peaks: νM-O.

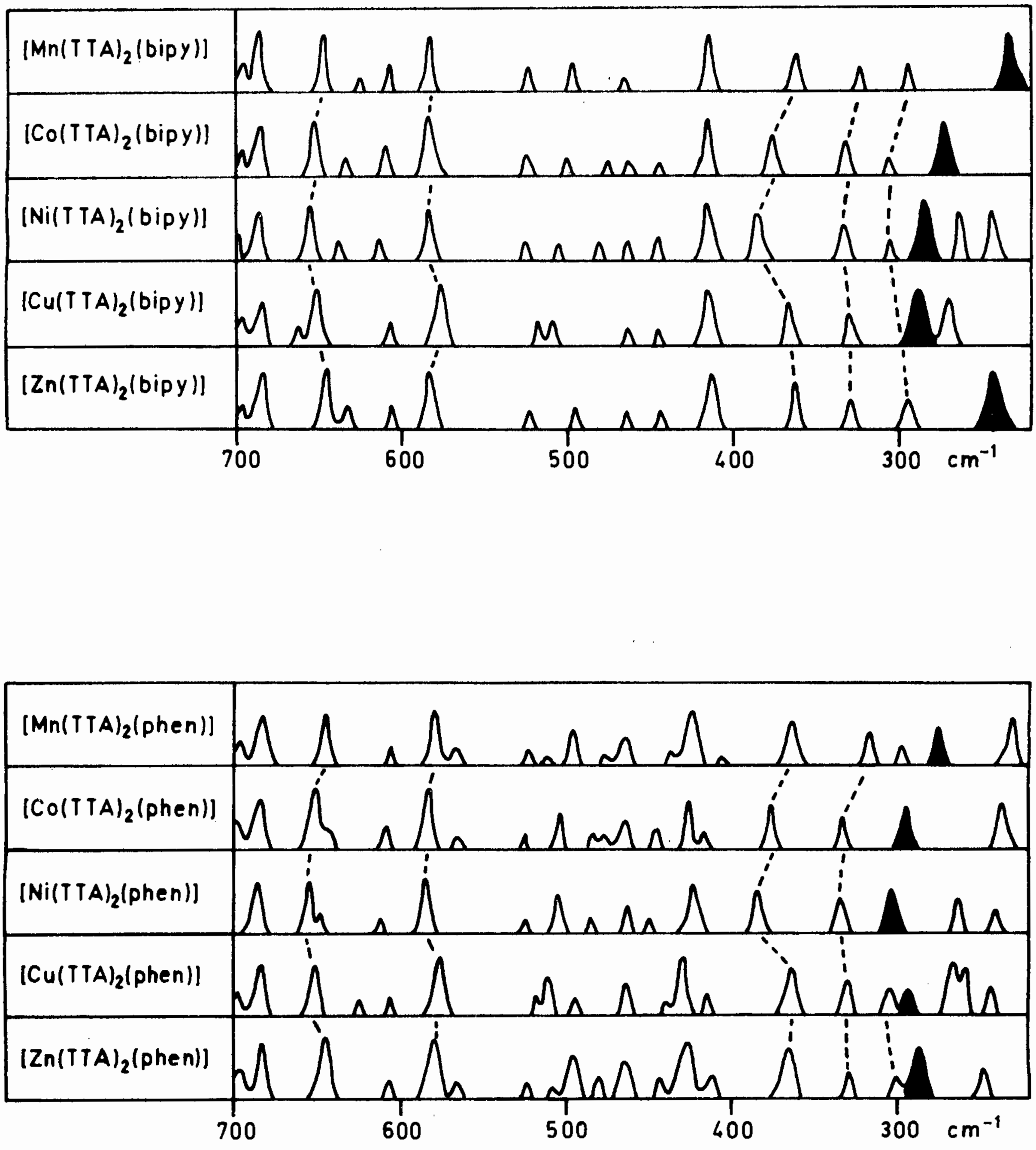


Fig. 7. The IR spectra of the bipy and phen adducts of the divalent metal TTA chelates, 700 - 200 cm^{-1}. Linked peaks: νM-O; solid peaks: νM-N.

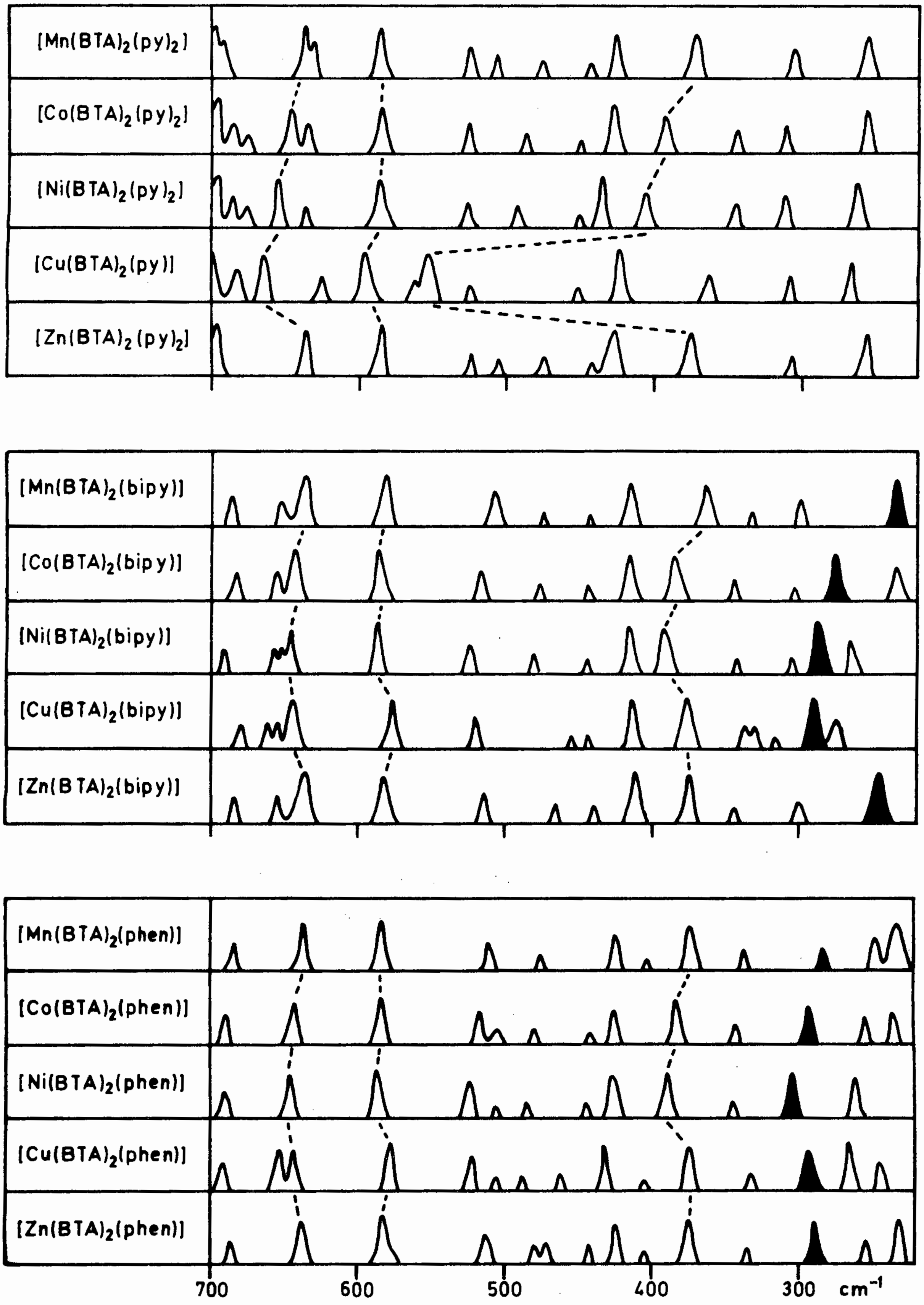


Fig. 8. The IR spectra of the py, bipy and phen adducts of the divalent metal BTA chelates, 700 - 200 cm^{-1}. Linked peaks: νM-O; solid peaks: νM-N.

vibrations. The bands are at lower frequencies than those of the H_2O or py adducts due to the relatively high ligand field strength of phen and bipy ($\delta = 1.43$) compared with H_2O, NH_3 and py. All the νM-O bands follow the frequency order predicted by the CFSE's for an isostructural octahedral series, namely Mn<Co<Ni>Cu>Zn. The well-defined frequency order Ni>Cu and the absence of any form of band splitting suggests that the adducts do not undergo any appreciable Jahn-Teller distortion. Previous examples[192] of bipy and phen adducts of Cu(II) β-ketoenolates have been found to exhibit two M-O bond lengths which has resulted in a doubling of the νM-O bands.

The bipy and phen adducts all show characteristic bands in the 630 and 450 - 400 cm^{-1} regions. Again, a band appearing near 480 cm^{-1} (which shows some metal-sensitivity but not in the order shown by the M-O bands) is assigned to the O-M-O bend. The region below 300 cm^{-1} is complicated by the appearance here of M-N modes. In designating these as M-N modes it is acknowledged that there is possibly coupling between the M-O and M-N vibrations. The first band below 300 cm^{-1} in both bipy and phen adducts of the TTA and BTA chelates (Figures 7 and 8) is assigned empirically to νM-N. It shows considerable metal-sensitivity in the order given by the νM-O bands, except for the bipy compounds which yield the order Ni<Cu. It should be noted that IR frequencies depend on the strength of specific bonds and that certain bonds can give a slightly different stability order to that given by the complex as a whole[193]. Like the analogous acetylacetonates[5], the phen adducts yield νM-N bands of higher frequency than the bipy compounds.

Table 64. νM-O and νC=O values for the adducts $[M(O\text{-}O)_2(B)]$

B →		$(H_2O)_2$	$(O\text{-}O)^-$	$(NH_3)_2$	$(py)_2$	bipy	phen
δ →		1	1.2[a]	1.25	1.25	1.43	1.43
M							
$[M(TTA)_2(B)]$							
Mn	νM-O	382	376	372	365	363	364
	νC=O	1610	1612[b]	1614	1609	1621	1619
Co	νM-O	395	392	384[f]	380	379	379
	νC=O	1608	1609[c]	1606	1602	1616	1614
Ni	νM-O	407	401	391	387	385	386
	νC=O	1608	1613[d]	1608	1607	1618	1619
Cu	νM-O				540[i]	368	367
	νC=O				1602[i]	1623	1625
Zn	νM-O	384	379	373	368	365	368
	νC=O	1610	1614[e]	1612	1610	1624	1624
$[M(BTA)_2(B)]$							
Mn	νM-O	387			370	367	375
	νC=O	1615			1626[g]	1630	1627
Co	νM-O	405	398		391	387	382
	νC=O	1615	1615		1615	1630	1630
Ni	νM-O	415	403		407	391	390
	νC=O	1616	1615		1618	1630	1630
Cu	νM-O				551[i]	378	373
	νC=O				1610[i]	1636	1634
Zn	νM-O	392	385		373	375	375
	νC=O	1612	1617		1628[h]	1635	1635

[a] Assuming $\delta(TTA)_3 = \delta(BTA)_3 = \delta(AA)_3 = 1.2$

Mean of doublets at: [b]) 1619 and 1604, [c]) 1615 and 1604, [d]) 1622 and 1605, [e]) 1623 and 1605, [f]) 387 and 381, [g]) 1634 and 1618, [h]) 1638 and 1619 cm^{-1}.

[i] Copper forms a mono(pyridine) adduct.

the CFSE's for these adducts, a value of f for the ligand combination can be estimated from the average environment relationship

$$f = {}^{1}/_{3} f(\mathrm{N{-}N})_3 + {}^{2}/_{3}\, f(\mathrm{O{-}O})_3$$

where (N-N) represents the adducted base and (O-O) the β-ketoenolate. Hence the CFSE values for a given metal ion and common β-ketoenolate ligand will show the same order as the f values of the adducted bases, increasing from the dihydrate to the phen adduct. An inverse relationship is found between the complex stability as a whole expressed by the CFSE and the strength of the M-O bond in a series of these adducts with common metal but varying N-base.

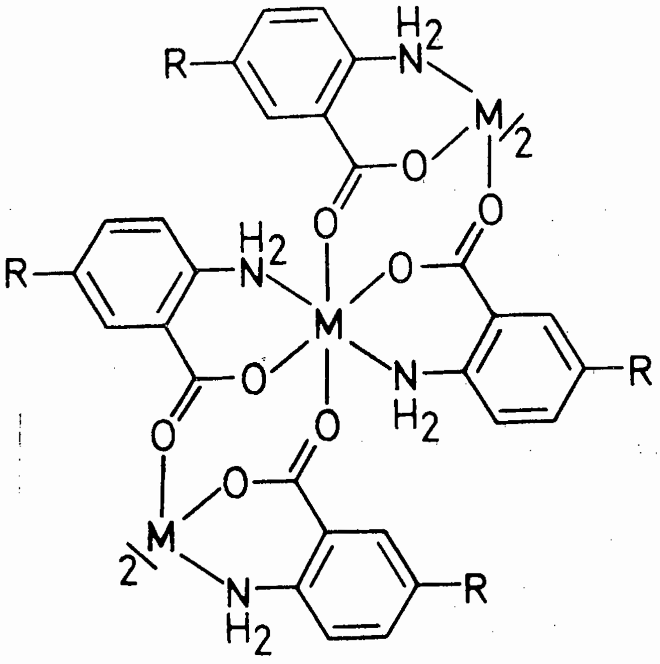
A comparison of the νC=O frequencies with νM-O shows that νC=O generally follows an inverse order to that shown by νM-O indicating some measure of constancy of bond order summation about the carbonyl oxygen atom. This effect has previously been demonstrated in substituted β-ketoenolates[185].

2. IR SPECTRA OF METAL ANTHRANILATES

Studies on the IR spectra of metal anthranilates have been confined previously to investigations of the amino and carboxyl vibrational regions[82-85,196]. Empirical assignments have been made for these vibrations and the shift of 150 - 200 cm^{-1} to lower frequencies of νN-H has been cited as evidence for covalent M-N bonds[84,85]. Doskey and Curran[196] reported assignments for the stretching and bending modes of the amino group in Zn(II), Cd(II), Sn(II) and Pb(II) chelates by labelling of the amino group with deuterium.

The magnetic moments[75,81,82,167] insolubility[82,167] and electronic spectra[167] of metal anthranilates indicate that these compounds have a polymeric octahedral structure. Sandhu and coworkers[82] have found IR evidence from the νC=O stretching region which indicates that the carboxyl group acts as a bidentate donor, there being two unequal M-O bonds. Thus the available evidence indicates that the complexes have tetragonal structure consisting of a *trans*-planar arrangement of two anthranilate ligands about the metal ion with the *trans*-axial positions occupied by those carboxyl oxygen atoms of the neighbouring molecules which are not involved in chelation. Formula I shows the partial structure. Crystallographic studies on glycine complexes of Zn(II) and Cd(II) have shown that an amino acid can act as a tridentate ligand in this fashion[197].

This Section describes the application of ^{15}N-labelling, metal ion substitution and the effect of varying the ligand substituent (R) to the assignment of ligand and metal-ligand vibrations in the IR spectra of the sodium salts and first transition series metal complexes of anthranilic acid and its 5-substituted analogues.



(I)

(i) Ligand Vibrations

The spectra of the sodium salt and metal(II) complexes and their ^{15}N-induced shifts are listed in Table 28 and shown in Figure 9. All shifts are to lower wavenumber except where otherwise indicated.

The two strong bands near 3300 and 3150 cm^{-1} have previously[82,84,85,196] been empirically assigned to the asymmetric and symmetric N-H stretching frequencies of the chelates, being 100 to 200 cm^{-1} lower than the corresponding bands in the sodium salt. These assignments are confirmed by isotopic labelling which shows a shift on ^{15}N-substitution of 3 to 7 cm^{-1} for these bands. The theoretically expected shift[37] for a pure νN-H band has been stated to be 7 cm^{-1}. A third, weak band which is too broad in the complexes for the detection of any shift induced by labelling occurs in the region between the two νN-H bands. Its sensitivity to ^{15}N-

labelling in the sodium salt, its breadth and the considerable shift on chelation suggest its assignment to hydrogen-bonded νN-H···O. For each series of complexes with common substituent (R) νN-H shows a shift upon changing the metal ion in the order Mn>Co>Ni>Cu<Zn. This order, it will be shown, is the inverse of that followed by the M-L vibrations which parallel the Irving-Williams[50] stability sequence. Thus the increase in M-L bonding occurs at the expense of the N-H bonds. Similar inverse relationships between the strengths of N-H and M-L bonds have been found in various complexes with nitrogen donor ligands[198].

In the region 1650 to 1500 cm^{-1}, the strong band at about 1550 cm^{-1} has been empirically assigned[82-85,196] as νCOO asymmetric, while it was suggested that the remaining bands in this region are skeletal vibrations of the aryl ring[82,84]. Doskey and Curran[196] assigned a band at 1590 cm^{-1} in the Zn(II) chelate to a NH_2 bending mode. However, the ^{15}N-sensitivity of the band near 1620 cm^{-1} in this study leads to the assignment of this band to the amino scissoring frequency. This frequency is near the value reported for the scissoring mode in metal hydrazine complexes[199]. Three other ^{15}N-sensitive bands in the spectra can reasonably be assigned to the amino bending modes, namely the wagging mode near 1250 cm^{-1}, the twisting mode near 1100 cm^{-1} and the rocking mode near 825 cm^{-1}. Decker and Frye[85] used the strong band in the region 1100 - 1000 cm^{-1}, without suggesting an assignment, to find an order of metal chelate stabilities. This band shows a very variable ^{15}N-shift, giving both positive and negative shifts and corresponds in the Mn(II), Ni(II) and Cu(II) spectra to the band assigned here as the twisting mode of the amino group. Hence the validity of its use as a criterion for complex stability is

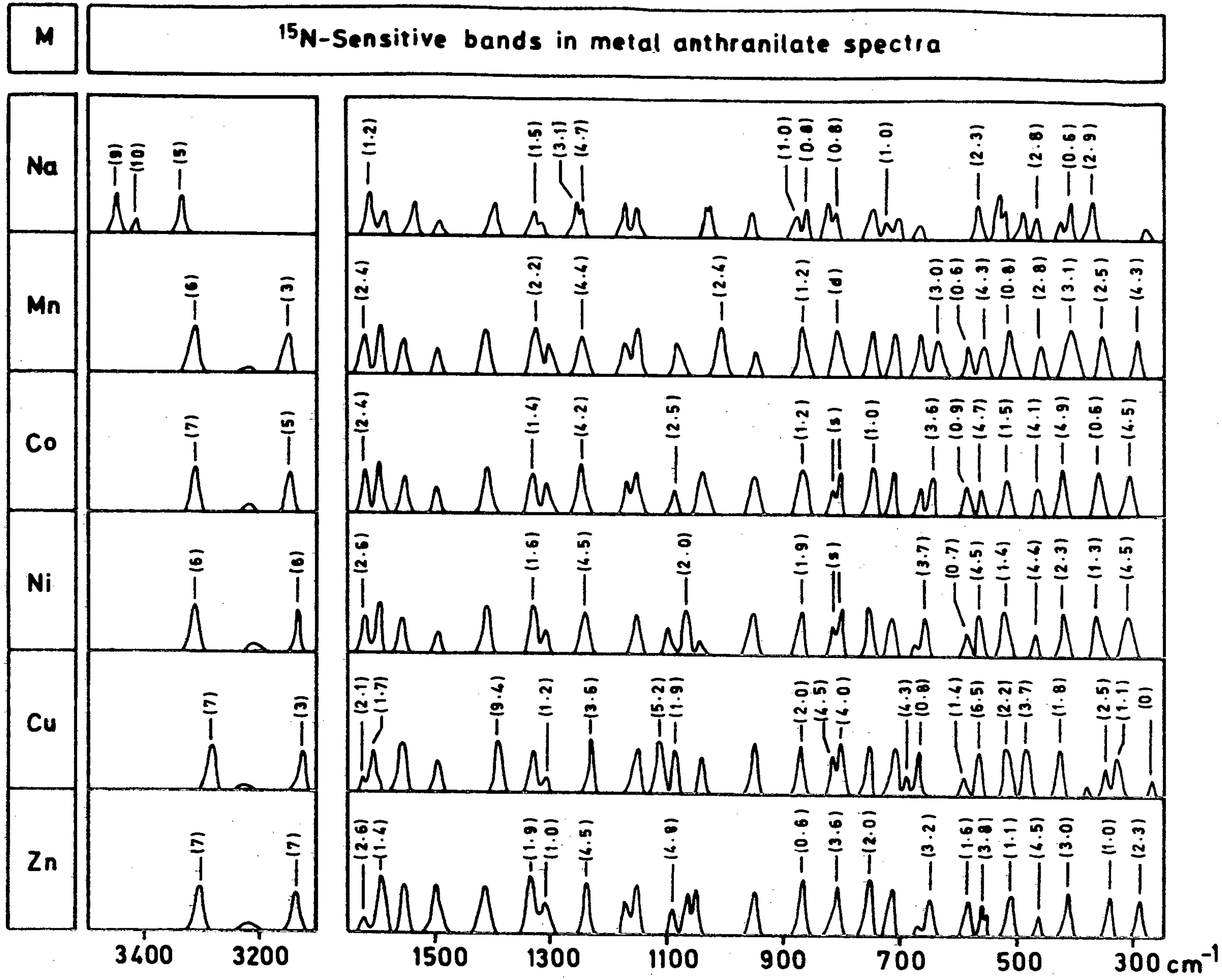


Fig. 9. The IR spectra of metal anthranilates (R = H) with ^{15}N-induced shifts in parentheses. (d=doublet, s=singlet in ^{15}N-labelled spectrum) Absence of data implies a shift <1.0 cm-1

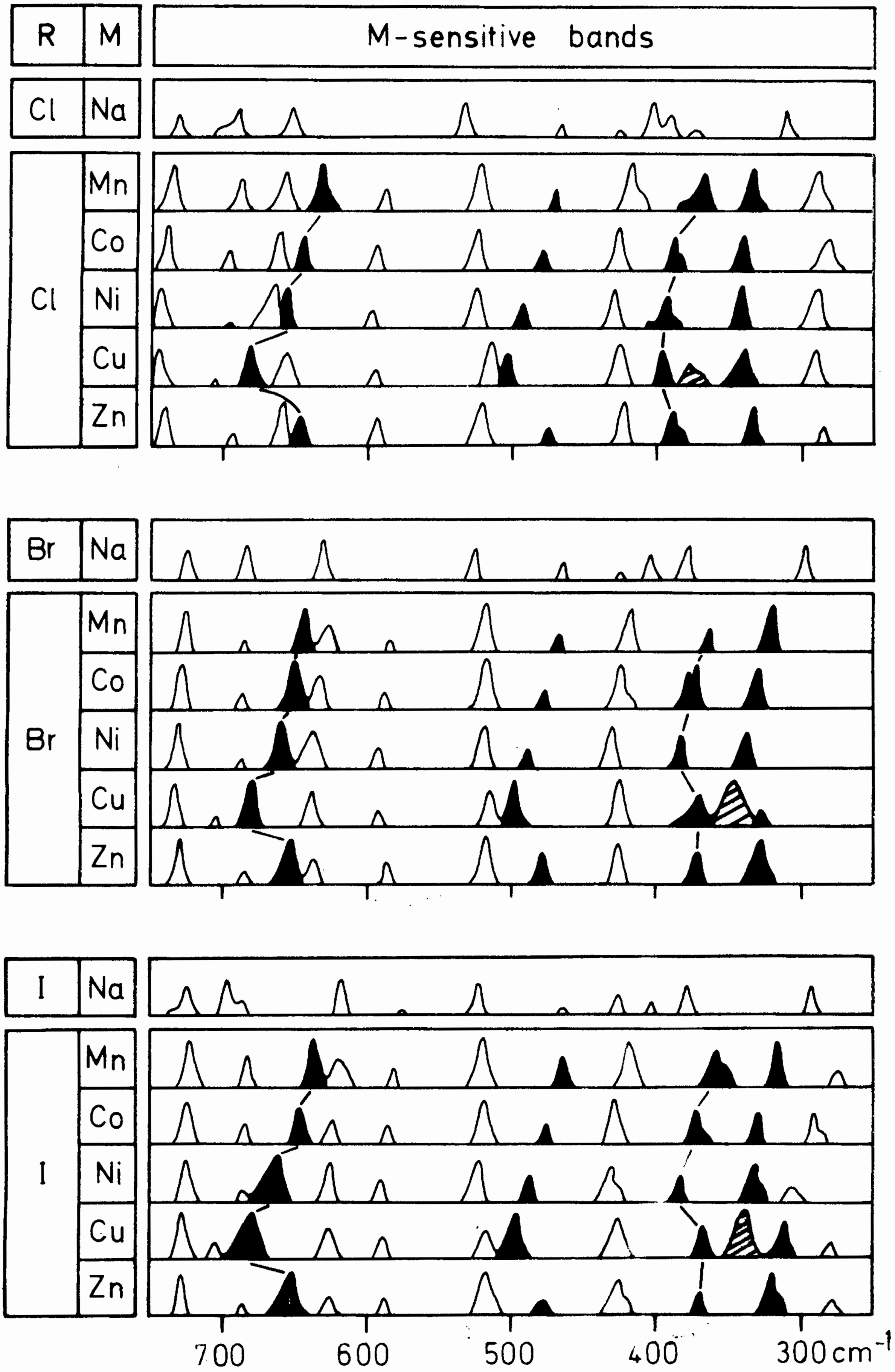


Fig. 10. The IR spectra of metal anthranilates (R=5-Cl, 5-Br and 5-I). Solid peaks (linked): principal νM-N and νM-O; solid peaks (unlinked): coupled νM-N and νM-O; shaded peaks: additional νCu-O.

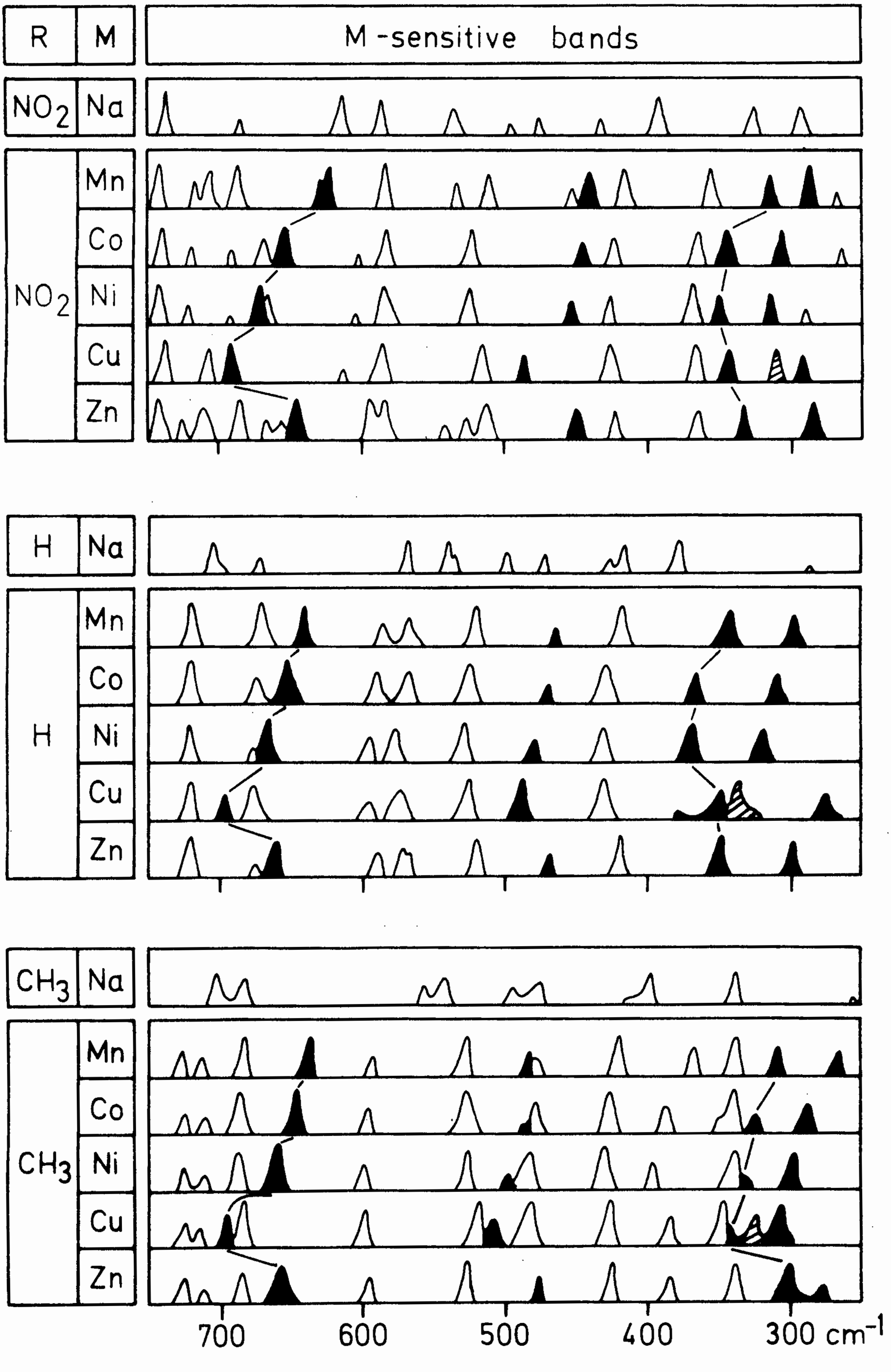


Fig. 11. The IR spectra of metal anthranilates (R = 4 - NO_2, H and 5-CH_3). Solid peaks (linked): principal νM-N and νM-O; solid peaks (unlinked): coupled νM-N and νM-O; shaded peaks: additional νCu-O.

extremely doubtful. Doskey and Curran[196] assigned the amino deformation vibrations at 1590, 1049 and 650 cm^{-1} for the Zn(II) chelate.

The previous empirical assignments[82-85] of the bands near 1550 and 1400 cm^{-1} to the asymmetric and symmetric carboxyl stretching vibrations are confirmed by their lack of sensitivity to ^{15}N-labelling. It has been suggested by Spinner[200] that these bands are in fact νC=O and νC-O$^-$, respectively in the classical structure O=C-O$^-$. The fact that these modes occur about 150 cm^{-1} below the carboxyl frequencies in aromatic acids supports the proposal that the carboxyl group is bidentate in metal anthranilates. McAuliffe and Perry[201] have suggested that the separation between the two carboxyl frequencies depends on the symmetry of the carboxyl moiety. The symmetry of this group in the ionically bonded sodium salts is at a maximum and these show the smallest separation, ranging between about 115 and 140 cm^{-1} according to the nature of R. In the chelates of Mn(II), Co(II), Ni(II) and Zn(II) the separation increases to between 140 and 170 cm^{-1} for the various substituents, the separation remaining approximately constant for the chelates of one particular ligand. However, the Cu(II) chelates show the Jahn-Teller effect by having elongation of the axial bonds (as will be discussed in connection with the νM-O frequencies) and such a situation leads to a decrease in the strength of the axial M-O bonds. McAuliffe and Perry[201] suggest that such a situation should lead to an increase in the carboxyl frequency separation. Such an increase is here observed in the Cu(II) chelates in which the separation is 20 cm^{-1} greater in each Cu(II) spectrum than in the other four complexes with common substituent, R.

The ^{15}N-sensitive band near 1330 cm^{-1} is assigned to νC-N, its frequency being similar to that proposed for the corresponding vibration in N-aryl Schiff base complexes[12].

The sodium salt of anthranilic acid itself shows three ^{15}N-sensitive bands (at 569, 470 and 378 cm^{-1}) in the far IR. By analogy with metal glycine chelates[202], the lowest band is reasonably assigned to δCCN, while the 470 cm^{-1} band is assigned to δCCC coupled with δCCN. The band at 569 cm^{-1} is uniquely observed in the sodium salt and complexes of anthranilic acid itself. This band shows similar ^{15}N-sensitivity to the bands which will be assigned to νM-N. However, since it is unique in R = H complexes and corresponds to a ligand vibration in the salt, it is not assigned to a M-N mode. The fact that this band is sensitive neither to metal nor to substituent change suggests that this band must originate in a ligand vibrational mode which looses its intensity when the 5-position of the aryl ring is substituted.

The bands in the spectra of the complexes which occur near 520 and 420 cm^{-1} are in regions of ligand absorption as is shown by the appearance of bands in similar positions in the sodium salt spectra. The band which appears in the narrow range 575 to 600 cm^{-1} in the metal complexes shows no corresponding band in the sodium salts. Although this is one of the criteria on which νM-L bands will be assigned, the fact that this band is insensitive to metal ion substitution, ^{15}N-labelling and substituent change suggests its assignment to a bending mode of the carboxyl group (δCOO) by analogy with corresponding bands in metal glycine complexes[202].

(ii) Metal-Ligand Vibrations

In seeking assignments for νM-O and νM-N it must be borne in mind that coupling between these two vibrations and between each of these and ligand vibrations can occur. Figures 10 and 11 depict the spectra below 750 cm^{-1} arranged so as to illustrate the effect of metal ion substitution.

Previous workers[4,5,7,9,10,12] have shown that, practically without exception, the band assigned to νM-L by an independent technique (such as isotopic labelling) in a series of transition metal complexes of a common ligand is strongly metal-sensitive in the order of the CFSE's. The assignment of M-L vibrations is made here with the aid of these two methods, namely isotopic ^{15}N-labelling and sensitivity to metal ion substitution.

Assuming octahedral co-ordination for the metal anthranilates and allowing for Jahn-Teller distortion (which is likely to give extra stability by forming a tetragonal Cu(II) complex) the order of CFSE's is Mn<Co<Ni<Cu>Zn, *i.e.* the Irving-Williams stability sequence observed generally for first transition series octahedral metal complexes in which Cu(II) undergoes Jahn-Teller stabilization. Hence νM-L is expected to follow this order. In addition, the νM-N bands are expected to be found only in the chelates and not in the sodium salt where no Na-N bond is formed as is shown by the absence of a shift in its νN-H band relative to the free ligand. In the region 600 - 700 cm^{-1} there is a band which is strongly ^{15}N-sensitive ($\Delta\nu$ = 3 to 4.5 cm^{-1}) and follows the Irving-Williams sequence. The only ligand band or bands found in this region are observed to be present in the salts as well as in the chelates and are neither metal- nor ^{15}N-sensitive. Hence the metal-sensitive band has no corresponding band in the sodium salt and is assigned as the principal (least-coupled) νM-N band.

It is interesting to note that the order of νM-N and the ligand band in this region interchange for Cu(II) anthranilate as is shown by the ^{15}N-labelling technique. A similar change for the Cu(II) chelates with R = Cl, CH_3 is suggested by the constancy of the ligand band. The shift on labelling (of between 3 and 4.5 cm^{-1}) is similar to that for νM-N observed on ^{15}N-labelling of metal salicylaldimine complexes[11,12] indicating that a shift of this magnitude is probably fairly general for νM-N vibrations.

Each series of complexes exhibits a band within the range 450 - 510 cm^{-1} which is metal-sensitive in the Irving-Williams order and is also ^{15}N-sensitive (in the complexes with R = H). This band is distinguished from the principal νM-N band by a somewhat smaller metal-sensitivity and by the presence of a corresponding ^{15}N-sensitive ligand band (assigned as δCCC + δCCN) in the sodium salt spectra. On this evidence it is assigned to νM-N coupled with δCCC and δCCN.

For the assignment of νM-O, use is made of the distortions expected on theoretical grounds in the Cu(II) chelates. McAuliffe and Perry[201] have suggested that anhydrous amino acid complexes have octahedral structures with a bidentate carboxyl group. It was suggested at the beginning of this Section that the structures of the anthranilates might show slight tetragonal distortions from regular octahedral stereochemistry. On theoretical grounds, Cu(II) is expected to be stabilized by tetragonal distortion and hence Cu(II) anthranilates are expected to show a significant difference between the coplanar and *trans*-axial Cu-O bond lengths. In the Section dealing with ligand vibrations evidence of this was found in the carboxyl stretching region. Hence the Cu(II) complexes will

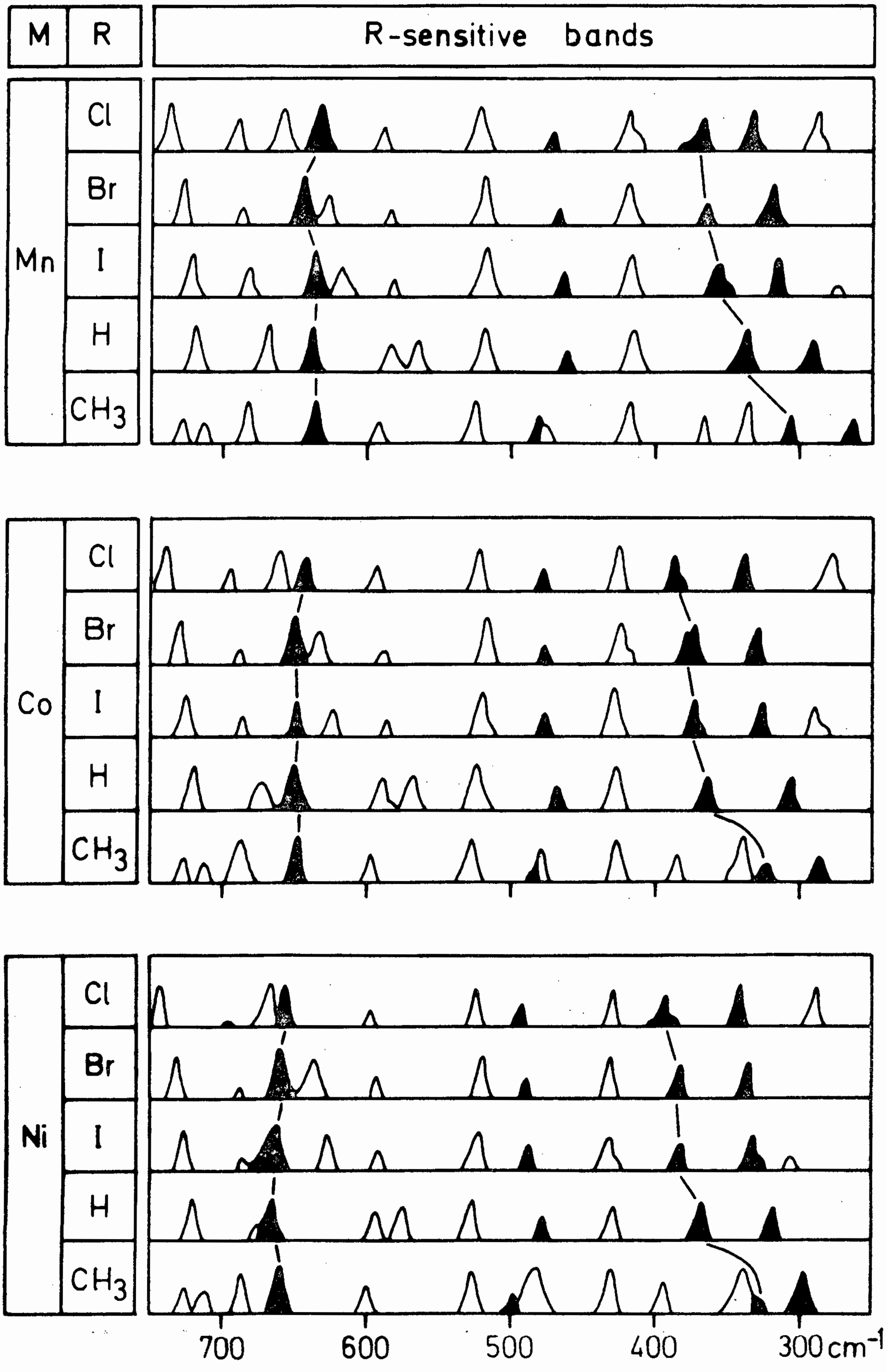


Fig. 12. Effect of ligand substitution in the IR spectra of the Mn(II), Co(II) and Ni(II) anthranilates. Solid peaks (linked): principal νM-L; solid peaks (unlinked): coupled νM-L.

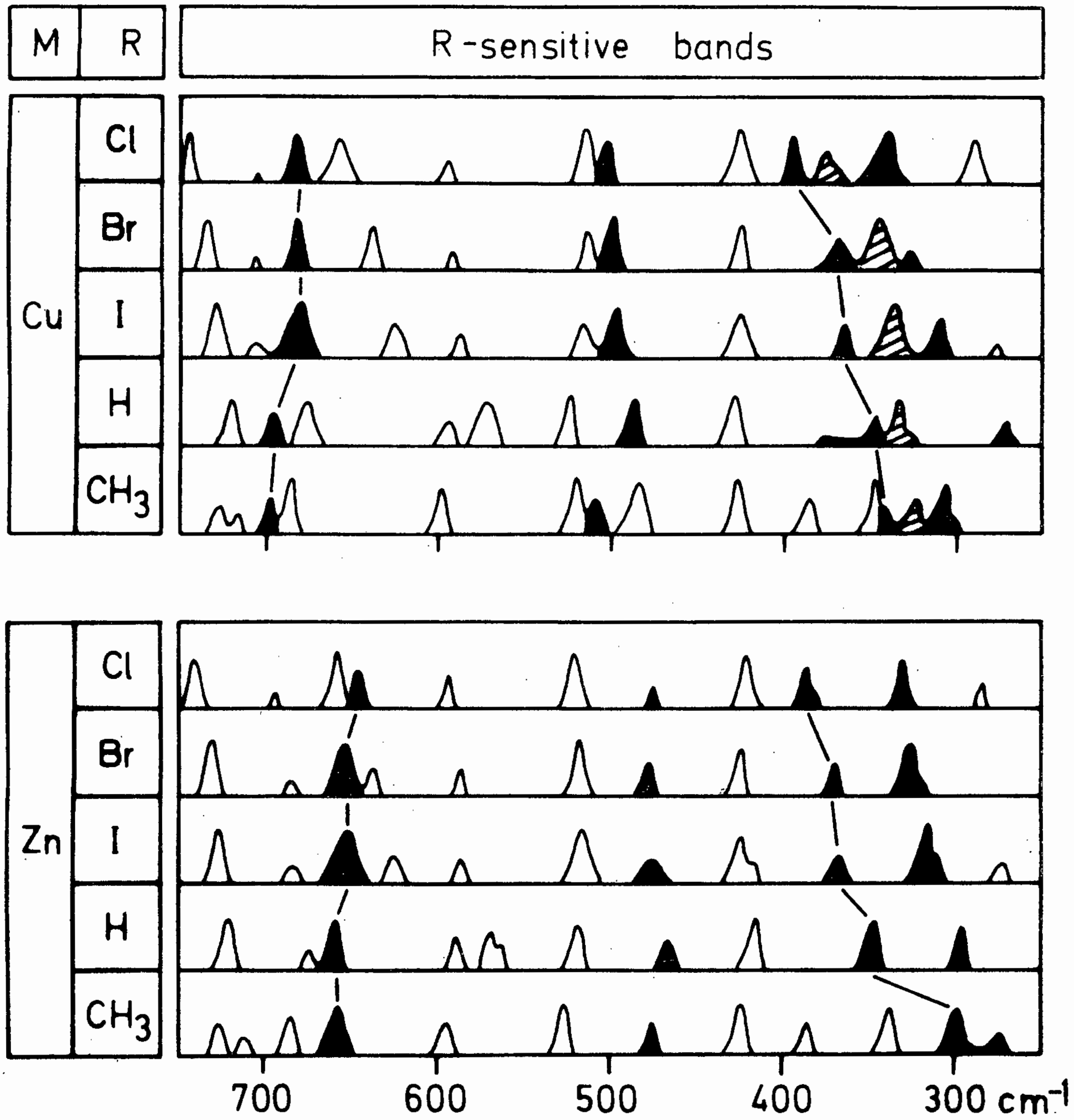


Fig. 13. Effect of ligand substitution in the IR spectra of the Cu(II) and Zn(II) anthranilates. Solid peaks (linked): principal νM-L; solid peaks (unlinked): coupled νM-L; shaded peaks: additional νCu-O.

show only one species of Cu-N bond, but two species of Cu-O bond. An analogous situation has been crystallographically confirmed[203] in [Cu(HFA)$_2$(bipy)] where HFA = hexafluoroacetylacetonate anion. It has previously been shown[4,5,7,179] that significant tetragonal distortion can result in a splitting of νM-L bands and thus for the Cu(II) complexes we expect splitting of νCu-O but not νCu-N. It can be seen in Figures 10 and 11 that a pair of adjacent bands in the 250 - 400 cm^{-1} range becomes a set of three or four bands in the spectrum of the Cu(II) complex. Both these bands show metal-sensitivity in the Irving-Williams order and occur in a region of the spectrum which is fairly free from ligand vibrations. The higher-frequency band shows little shift on ^{15}N-labelling and is generally the more metal-sensitive of the two and so is assigned as the principal νM-O. The lower-frequency band shows considerable shift on labelling and, being in the general region of the ligand band assigned to δCCN, it is assigned to νM-O + δCCN.

(iii) <u>Substituent Effects</u>

Figures 12 and 13 show the spectra of the 5-substituted metal anthranilates placed in order of substituent effects. Only those bands which have been assigned as νM-L show any appreciable sensitivity to ligand substitution which further supports the assignments made above. Bands assigned as νM-L are listed in Table 65.

A substituent on an aryl ring can exert both mesomeric and inductive effects. However, conjugation is not possible between the 5-position of anthranilic acid and the M-L bonds, nor is the NH$_2$ group theoretically capable of π-bonding in

Table 65. Metal-ligand vibrations of the substituted anthranilates (cm^{-1})

Assignment	M	R →	NO_2[a]	Cl	Br	I	H(^{15}N Shift)	CH_3
		σ' →	0.63[b]	0.47	0.45	0.38	0	-0.05
νM-N	Mn		625[c]	631	642	638	638(3.0)	634
	Co		657	641	650	649	649(3.6)	645
	Ni		672	653	660	660	662(3.7)	657
	Cu		692	681	680	678	695(4.3)	696
	Zn		647	646	651	650	655(3.2)	651
νM-N+δCCC+δCCN	Mn		440	470	469	466	461(2.8)	483
	Co		445	479	477	476	467(4.1)	486
	Ni		452	490	488	486	475(4.4)	497
	Cu		489	501	498	494	485(3.7)	505
	Zn		450	476	476	475	466(4.5)	475
νM-O	Mn		313	365	362	357	339(2.5)	309
	Co		348	389	376[d]	370	361(0.6)	321
	Ni		350	389	382	380	366(1.3)	323
	Cu[e]		345	399	368	364	347(2.5)[f]	345
	Cu[g]		310	375	343	336	333(1.1)	322
	Zn		335	388	370	366	346(1.0)	299
νM-O+δCCN	Mn		289	332	320	317	295(4.3)	261
	Co		307	338	332	324	305(4.5)	283
	Ni		315	339	335	331	318(4.5)	297
	Cu		293	340	325	310	270(0)	308
	Zn		286	332	323	317	296(2.3)	271

[a] R = 4-NO_2, other substituents are in the 5-position

[b] 4-NO_2 group can also show mesomeric effect

[c] Mean of doublet at 628 and 621 cm^{-1}

[d] Mean of doublet at 379 and 373 cm^{-1}

[e] Cu(II) compounds show three νM-O bands

[f] Additional shoulder at 379 cm^{-1}

[g] May be νCu-O+δCCN

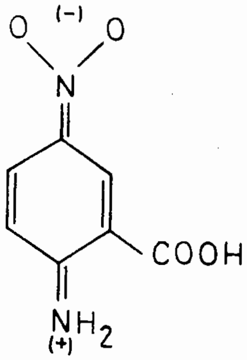
complexes in which the N acts as a donor atom. Hence of the two mechanisms for the transmission of electronic effects only the inductive mechanism can influence the M-L bonds in metal anthranilates. The substituents in Figures 12 and 13 have been ordered according to the substituent parameter σ' derived by Taft[20] as a measure of the pure inductive effect. The order of electron withdrawing inductive effects for these substituents is Cl>Br>I>H>CH_3. It is observed that νM-O decreases in the same order. This implies that as the electron withdrawing power of the substituent increases from R = CH_3 to R = Cl, so does the M-O bond strength, whereas a decrease might have been expected for a pure inductive effect. However, the oxygen can both σ- and π-bond with the metal and if the substituent has a σ-electron withdrawing effect then this enhances M-L π-bonding. This leads to a back donation of electron density into the M-O bond and yields a stronger M-O bond and hence a higher νM-O.

Although the monotonic ordering of the substituent effects on νM-N is not so precisely observed as it is for νM-O, νM-N shows a general tendency to shift in the opposite direction to νM-O. Hence substituents with an increasing electron withdrawing capacity decrease νM-N by the inductive effect of electron withdrawal weakening the M-N bond. In this case no M-N π-bonding is possible and so the M-O bond is stabilized at the expense of the M-N bonding.

(iv) IR Spectra of Nitro-Substituted Anthranilates

Previous workers[84,85,167] have used the low frequency shift of νN-H on complexation as a criterion for chelate formation. On examination of the spectra of the 4- and 5-NO_2

substituted anthranilic acids (Tables 33 and 34) only the former gives a large shift of νN-H on going from the sodium salt to the divalent metal complexes. This indicates the formation of a M-N bond and hence a chelate structure. The absence of any meaningful shift in νN-H in the R = 5-NO_2 compounds suggests the absence of M-N interaction. Thus these compounds contain the substituted acid as a monodentate ligand.



(II)

Further evidence on the difference between these two compounds can be seen in the 1700 - 1500 cm^{-1} region and in the far IR where the R = 4-NO_2 complexes show a band pattern similar to that of the anthranilates themselves. The bands in the former region are assigned by analogy with those in the previous Sections. In the R = 4-NO_2 chelates the bands near 1630, 1610 and 1490 cm^{-1} are assigned as the NH_2 scissoring vibration and the two characteristic aromatic skeletal vibrations respectively. The asymmetric carboxylate frequency is near 1560 cm^{-1} while the bands near 1540 and 1350 cm^{-1} correspond to regions of absorption for asymmetric and symmetric νNO_2 vibrations characteristic of an aromatic nitro group[184]. The R = 5-NO_2 compounds show similar bands except for the νCOO which has shifted up to near 1630 cm^{-1}, *i.e.* in the same region as that of its sodium salt. By analogy with the complexes of anthranilic acid itself, corresponding ligand bands have been assigned (Tables 33 and 34) in the spectra of the nitro compounds below 1300 cm^{-1}.

The nitro group has a strong electron withdrawing inductive effect ($\sigma' = 0.63$). On the basis of this effect alone, which was seen to operate exclusively in the 5-substituted anthranilates, we would expect no great difference between the effects of the 4- and 5-NO_2 substituents on the amino group and thus on M-N bonding. Hence some other effect must be predominating to prevent M-N bonding in the R = 5-NO_2 compounds but is not strongly operative in the 4-substituted analogue. Such an effect is that of resonance in which the nitro moiety, acting as a strong electron withdrawing group, can give rise to the quinoid structure shown in Formula II. The electrons of the lone pair are shifted into the ligand and the nitrogen of the amino group is left with a positive charge. This strips the amino group of its ability to form a M-N co-ordinate bond. Hence 5-nitroanthranilic acid is incapable of chelating while in the 4-nitro species case the amino group is *meta* to the nitro group and so resonance interaction between the two groups is minimized. In the chelates of anthranilic acid no resonance effects involving the NH_2 moiety are possible from theoretical considerations, but they can (and do) operate in the ligands themselves. The halogen substituents also have a strong resonance effect but they are π-electron donors as is the NH_2 group and so it loses none of its ability to donate its lone pair to the formation of the M-N bond.

The assignment of νM-L bands is made by comparison with the metal anthranilates. The 4-NO_2 group can affect the M-O bond by both inductive and mesomeric mechanisms since the nitro group can enter into conjugation with the carboxylate group. The NO_2 moiety is electron withdrawing by both mechanisms. In the 5-substituted anthranilates, it was shown that inductively electron withdrawing groups increase νM-O by M → L π-bonding, strengthening the M-O bond. In this case however the substituent has led to a decrease in the M-O bond strength relative to the unsubstituted species. Hence the back donation of π-electrons has not been able to overcome the large mesomeric and inductive electron withdrawing effect of the nitro group. The position of νM-O between the values for R = H and R = $5\text{-}CH_3$ suggests that this π-bonding effect is still operative although insufficient in extent to prevent the weakening of the M-O bond relative to the unsubstituted (R = H) compound.

Examining the regions of the spectra where νM-N was assigned for the 5-substituted compounds, corresponding metal-sensitive bands are seen in the $4\text{-}NO_2$ spectra. However, whereas in the 5-substituted complexes no corresponding ligand band occurs near the principal νM-N, a strong ligand band appears at 617 cm^{-1} in the spectrum of the sodium salt of the 4-nitro compounds (Figure 11). The νM-N mode would be expected to be coupled with this ligand mode. The result is that when compared with the pure νM-N of the complexes with R = H, this band, assigned as coupled νM-N, shows erratic behaviour. A comparison of the coupled νM-N vibrations observed in the 440 - 510 cm^{-1} range may then be expected to yield a better criterion of M-N bond strength. This band in the R = $4\text{-}NO_2$ compounds occurs up to 20 cm^{-1} lower than the corresponding vibration in the anthranilates themselves.

The 4-nitro substituent cannot affect the position *meta* to it by the mesomeric effect but only by its strong inductive effect ($\sigma' = 0.63$)[20]. Since no M-N π-bonding is possible, the electron pull of the substituent cannot be compensated by a back donation of π-electrons and hence the M-N bond order is expected to decrease. Consistent with this is the reduced νM-N value.

3. IR SPECTRA OF METAL PICOLINATES AND QUINALDATES

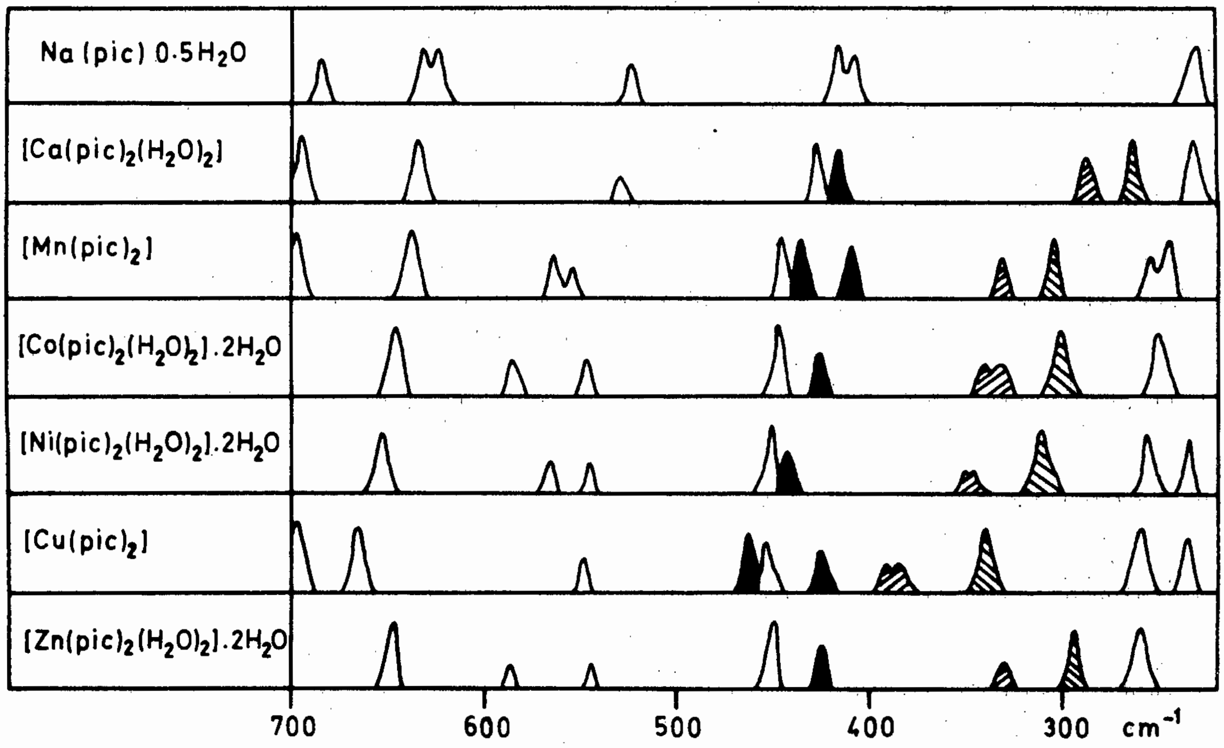
The structures of the complexes of picolinic acid have elicited considerable interest[92,102-108,204,205]. Unlike metal anthranilates, they commonly crystallize as hydrates[91,98]. Crystallographic studies show that the tetrahydrates of Co(II), Ni(II) and Zn(II) picolinates have a *trans*-octahedral structure[102-105,205] with two water molecules bound in the axial positions, and two held in the lattice as water of crystallization. There is some support for this structure from thermogravimetric[98,100] magnetic[81,91] and spectroscopic studies[91,95]. In the present work, three forms of Cu(II) picolinate (anhydrous, monohydrate and dihydrate) were isolated. Thermogravimetric[98,106] electronic spectroscopic[108] and crystallographic[106,107] work show that the water in the hydrates is not co-ordinated. The basic structure is *trans*-planar but there is some degree of polymeric association involving axial tetragonal co-ordination of the unco-ordinated carbonyl groups of neighbouring chelate molecules. In this sense, the structure resembles that proposed for metal(II) anthranilates. The anhydrous Mn(II) complex is considered from ultraviolet spectroscopy[91] to have polymeric octahedral structure but whether this arises from bridging ligands (as in many acetylacetonate complexes[173]) or resembles the polymerisation established for the Cu(II) picolinates, is not known. The structure of the dihydrated Ca(II) complex is possibly tetrahedral, although octahedral structures for Ca(II) have been proposed for the β-ketoenolate complexes[6].

The IR spectra of the picolinates are depicted in Figure 14 and the frequencies are listed in Table 35. The spectra of the anhydrous Mn(II) and Cu(II) complexes differ from those of the remaining ions in displaying an additional band in the 400 - 460 cm^{-1} region. Since the Cu(II) complex certainly, and the Mn(II) complex probably, involve axial co-ordination from the neighbouring carbonyl groups, there will be present in the complexes two types of M-O bond (long and short). Hence splitting of νM-O but not νM-N is to be expected and for this reason the band within this range is assigned to νM-O. The second band in this region, that near 450 cm^{-1}, is assigned to the out-of-plane vibration characteristic of 2-substituted pyridines[96]. Its relative constancy of position in the chelate spectra supports this assignment. If the mean of the νM-O frequencies is taken, it is seen that they follow the normal Irving-Williams[50] stability sequence. The splitting in the Cu(II) spectrum is larger than that shown for Mn(II) since a d^9 system is expected to show tetragonal distortion of this kind on theoretical grounds. The increase of νM-O on going from Ca(II) to Mn(II) to Zn(II) is due to the decreasing ionic radii in proceeding across the periodic table.

If tetragonal distortion involves axial elongation of Cu-O bonds, then splitting of νCu-N will not be anticipated. Moreover, νM-N is expected to follow the order of CFSE's in the presence of Jahn-Teller stabilization, namely Mn<Co<Ni<Cu>Zn. This order is observed for two bands in the 200 - 400 cm^{-1} region and these bands are accordingly assigned to νM-N. The remaining two lower frequency bands within this range (near 260 and 230 cm^{-1}) are not markedly metal-sensitive. That near 260 cm^{-1}, since it is not present in the spectrum of sodium picolinate, is possibly δO-M-N. The only other band showing any degree of metal ion sensitivity is that near 650 cm^{-1}, assigned to the pyridine ring in-plane vibration. It appears as a doublet in the spectrum of the sodium salt, the corresponding out-of-plane vibration being the doublet at 416 and 407 cm^{-1}. The large difference of about 40 cm^{-1} in the position of νM-N for the compounds of Ca(II) and Mn(II) which both exhibit zero CFSE as compared with the small differences in νM-O is almost certainly a result of the preference of Ca(II) for oxygen rather than nitrogen donors.

Consistent with the assignment of these bands as νM-L is the fact that no corresponding bands are observed in the spectrum of the sodium salt. The assignment of the band of highest frequency to νM-O on the basis of its doublet character in the Cu(II) and Mn(II) spectra is confirmed by the work of Wood and Jones[206] who suggested from calculations on co-ordinate bond energies in $Ni(pic)_2$ that the Ni-O bond is slightly stronger than the Ni-N bond. Crystallographic evidence[103,105,107] of a shorter M-O than M-N bond is also consistent with these results.

The spectra of the three Cu(II) chelates are shown in Figure 14. The lack of any meaningful differences in any of the bands, and especially in the νM-L bands, is consistent with the known crystal structures[107]. It provides further evidence for the existence of the water molecules in the hydrates as lattice water. Known structures of the metal(II) picolinates indicate that the carboxyl group is bound via the carboxylic oxygen and hence the COO moiety is monodentate except in the Cu(II) and Mn(II) complexes where some form of polymerisation is suggested. The presence in the spectra of the asymmetric carboxyl bands in the 1660 to 1600 cm^{-1} range *i.e.* well below that expected for a free νC=O is evidence that some of the resonance of the carboxylate group is preserved[95]. The higher values of νCOO and νM-O in the picolinates (compared



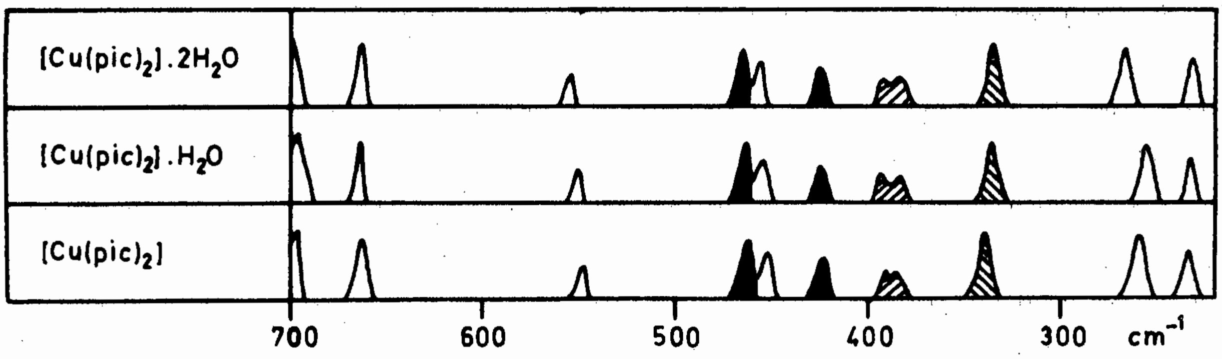


Fig. 14. The IR spectra of metal picolinates, 700 - 200 cm^{-1}.

Solid peaks: νM-O; shaded peaks = νM-N.

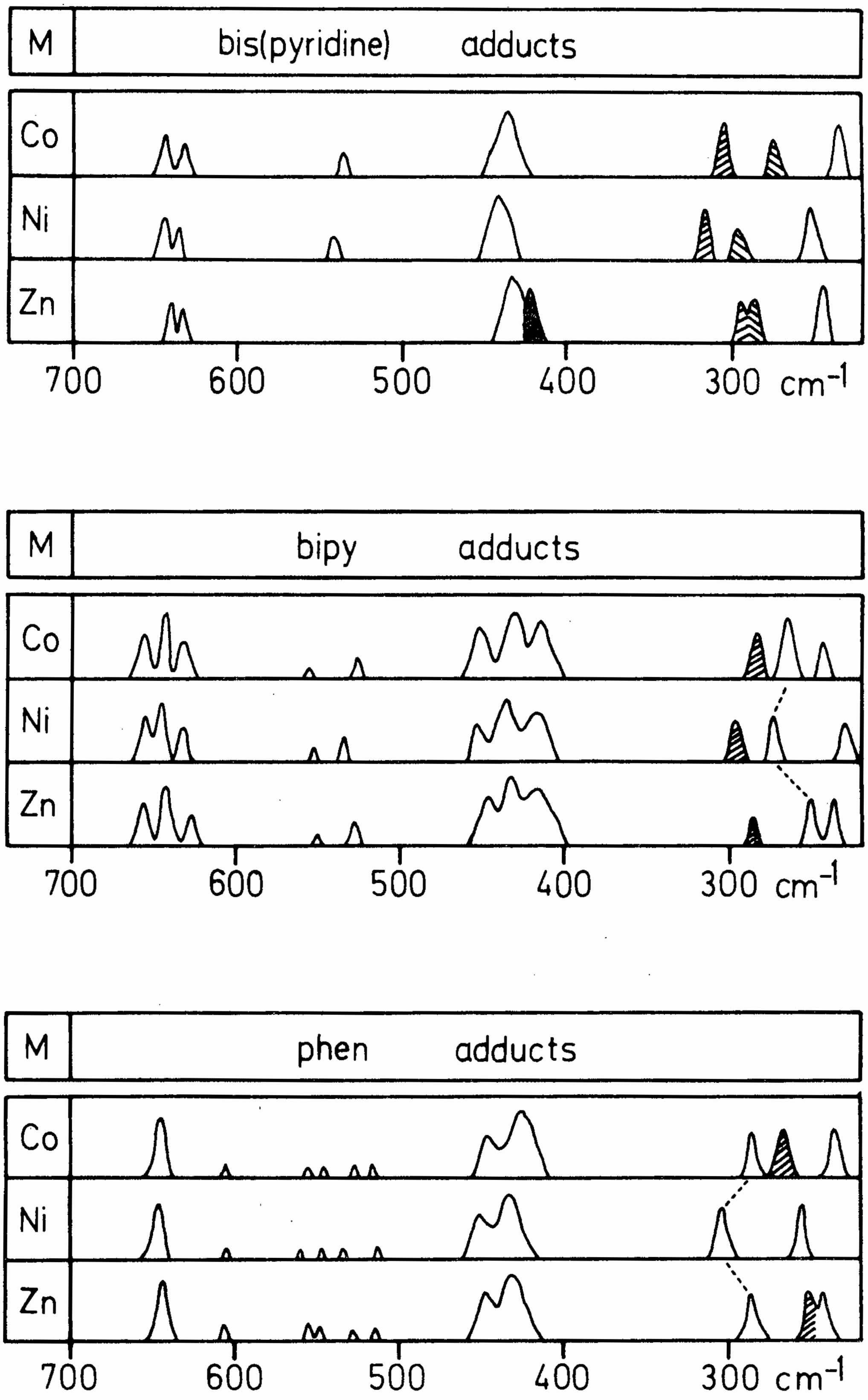


Fig. 15. The IR spectra of the py, bipy and phen adducts of metal picolinates, 700 - 200 cm^{-1}. Solid peaks: νM-O; shaded peaks: νM-N (pic); linked peaks: νM-N (adduct).

with the anthranilates) is further confirmation of the monodentate character of the acid moiety.

In order to observe the effect of replacing the co-ordinated water with ligands of greater ligand field strength, py, phen and bipy adducts of Co(II), Ni(II) and Zn(II) were prepared. In all cases however, this led to an increase in the absorption in the 450 - 400 cm^{-1} range due to the presence of the heterocyclic ring out-of-plane vibrations which obscured the νM-O bands. In the complexes of pyridine, the νM-N bands appear in the regions 290 - 320 and 270 - 300 cm^{-1}. This low-frequency shift is expected since the py leads to stronger metal-adduct bonds and hence weaker metal-chelate interaction. This confirms the assignment of these bands as νM-L. The replacement of water by bipy and phen causes the νM-N bands to fall below 300 cm^{-1} and thus appear in the region of the corresponding νM-N bands of the adduct. The spectra of these compounds (Figure 15) each show two metal-sensitive bands between 200 and 300 cm^{-1}. By analogy with the metal acetylacetonate adducts[5] where νM-N (phen) is found near 300 cm^{-1} and νM-N (bipy) near 250 cm^{-1}, the bands below 300 cm^{-1} in the picolinates are tentatively assigned as νM-N (phen) >νM-N (pic) and νM-N (bipy) < νM-N (pic). However the possibility of coupling between these M-N modes must also be acknowledged. The tentative assignments given above suggest νM-N decreases in the order H_2O>py>bipy>phen which is the order of increase of the ligand field strength of the adducted bases.

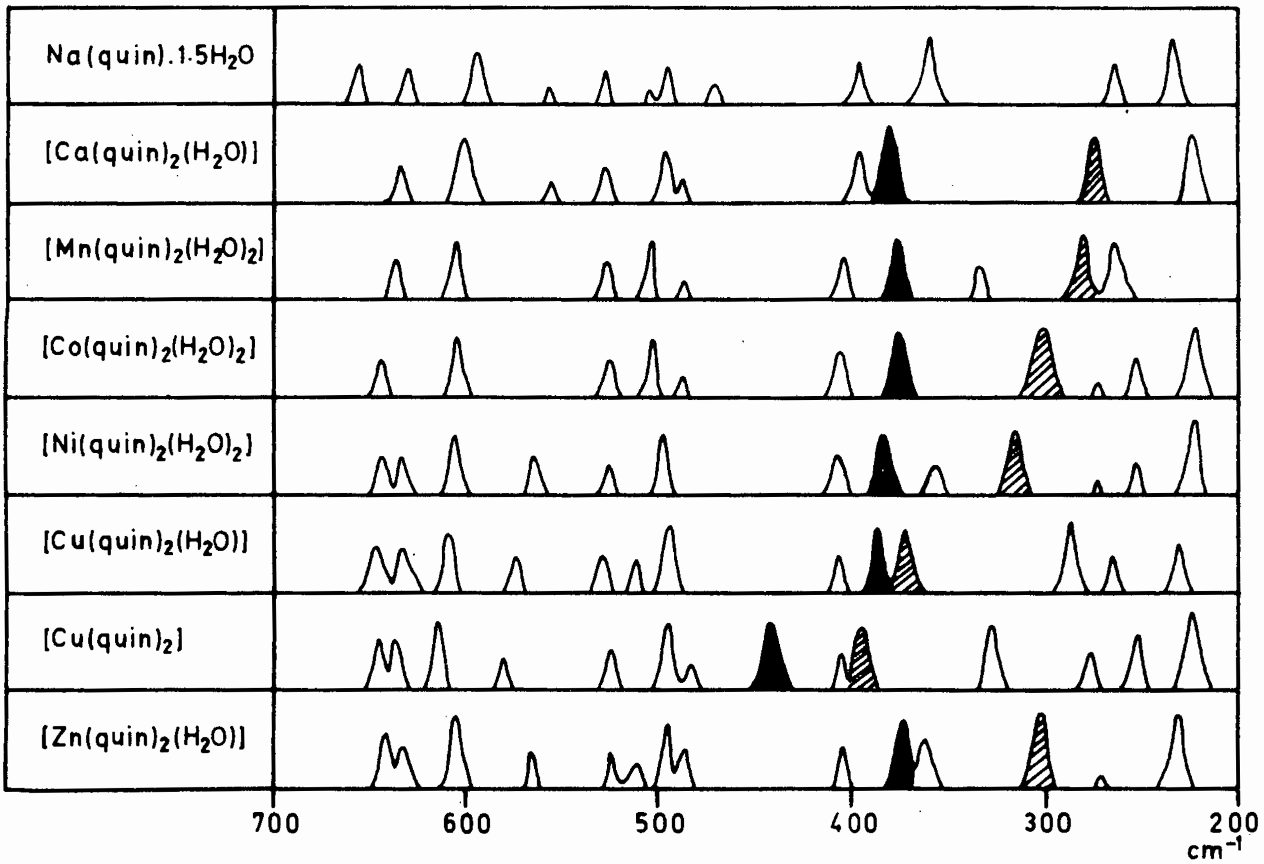
The structures of the metal(II) chelates of quinaldic acid have not been the subject of any crystallographic determinations. The Mn(II), Co(II) and Ni(II) ions precipitate as the dihydrates which may be assumed to have *trans*-octahedral structures analogous to the picolinates. Such structures have been suggested on the basis of thermogravimetric[89] and magnetic moment[81] studies. The Cu(II) amd Zn(II) monohydrate compounds may have monomeric 5-co-ordinate or dimeric 6- co-ordinate structures. Unlike the picolinates, the water in the copper chelate will be shown to be co-ordinated. The structures of the potassium salts of the tris chelates are expected to be regular octahedral.

The IR spectra of the hydrates and the potassium salts are depicted in Figure 16. The M-L modes for an octahedral set of compounds and 5- co-ordinate Cu(II) are expected to follow the Irving-Williams sequence as did the py adducts of the TTA and BTA compounds in Section 1(iii). The difference in co-ordination number gives an order Cu>Ni. Any dimerisation for Cu(II) is expected to be very weak and unlikely to produce the order Ni>Cu expected for an isostructural octahedral series. The νM-O and νM-N bands will be assigned by analogy with the corresponding picolinates. Hence the metal-sensitive bands in regions near 380 and 300 cm^{-1} which are absent in the corresponding sodium salt spectrum are assigned to νM-O and νM-N respectively. The only other band not observed in the spectrum of the salt is that near 270 cm^{-1} and since it shows only a small sensitivity in the hydrates and none in the potassium tris compounds, it is assigned to δO-M-N. The remaining bands below 700 cm^{-1} all appear in both chelate and salt. Those near 640 and 400 cm^{-1} are assigned to the characteristic heterocyclic ring vibrations. The second νM-N band observed in the picolinates is absent in the spectra of these compounds, possibly having moved below 200 cm^{-1}. The band near 560 cm^{-1} which shows some metal sensitivity but is absent in the Mn(II) and Co(II) spectra may be tentatively assigned as δCOO.

Comparison of the spectra of the hydrated and anhydrous

Cu(II) chelates (Figure 16) shows considerable differences. Both νM-L bands move significantly to higher wavenumbers thus indicating that the co-ordination number of copper has decreased. These spectral differences imply that, unlike its picolinate analogue, the hydrated Cu(II) compound contains co-ordinated water. Its structure, like most 1:1 adducts of a square planar species[207], is most probably square-based pyramidal. Of the three bands at 408, 385 and 371 cm^{-1} in the hydrate spectrum, that assigned as the pyridine vibration remains constant at 407 cm^{-1} in the anhydrous chelate, whereas the other two which are assigned to νM-L increase. Other bands showing a significant high-frequency shift are the COO and O-M-N bending vibrations and the ligand band near 230 cm^{-1}. The structure of the anhydrous chelate is probably square planar, the absence of any doublet character for νM-O being indicative of an absence of any significant interaction with neighbouring carboxyl groups.

Comparison of νM-L bands in the picolinate and quinaldate chelates shows that they are at a higher frequency in the picolinates, indicating stronger M-L bonds. This result is expected as stability constant measurements[97] have shown that picolinic acid is a stronger ligand than quinaldic acid. The effect of the fused phenyl ring is to act as an electron sink, resulting in a withdrawal of electron density from the co-ordination sites. In strong π-bonding ligands this can lead to increased metal-ligand π-bonding resulting in a strong ligand with a high ligand field strength. However, Kleinstein and Webb[91] have shown from ultraviolet spectra that picolinic acid is a non-π-bonding ligand. Hence the fused phenyl ring results



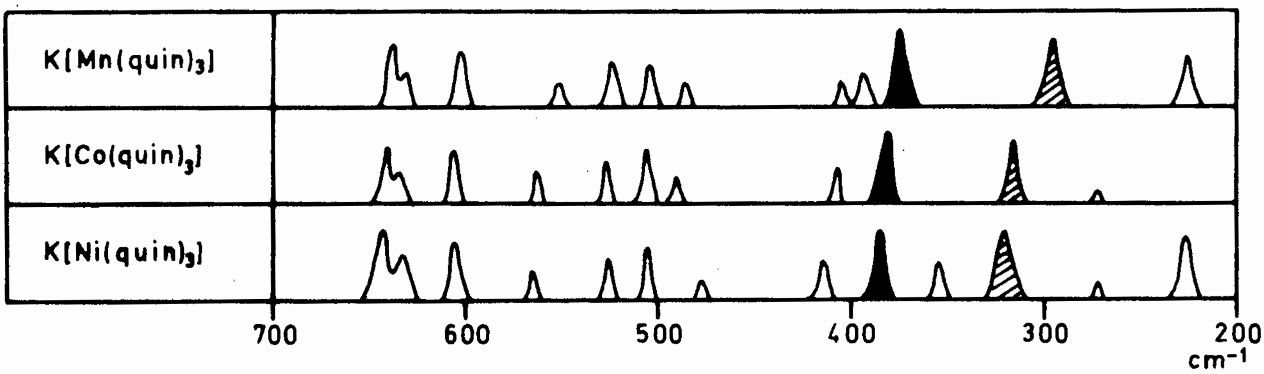


Fig. 16. The IR spectra of metal quinaldates, 700 - 200 cm^{-1}. Solid peaks: νM-O; shaded peaks: νM-N.

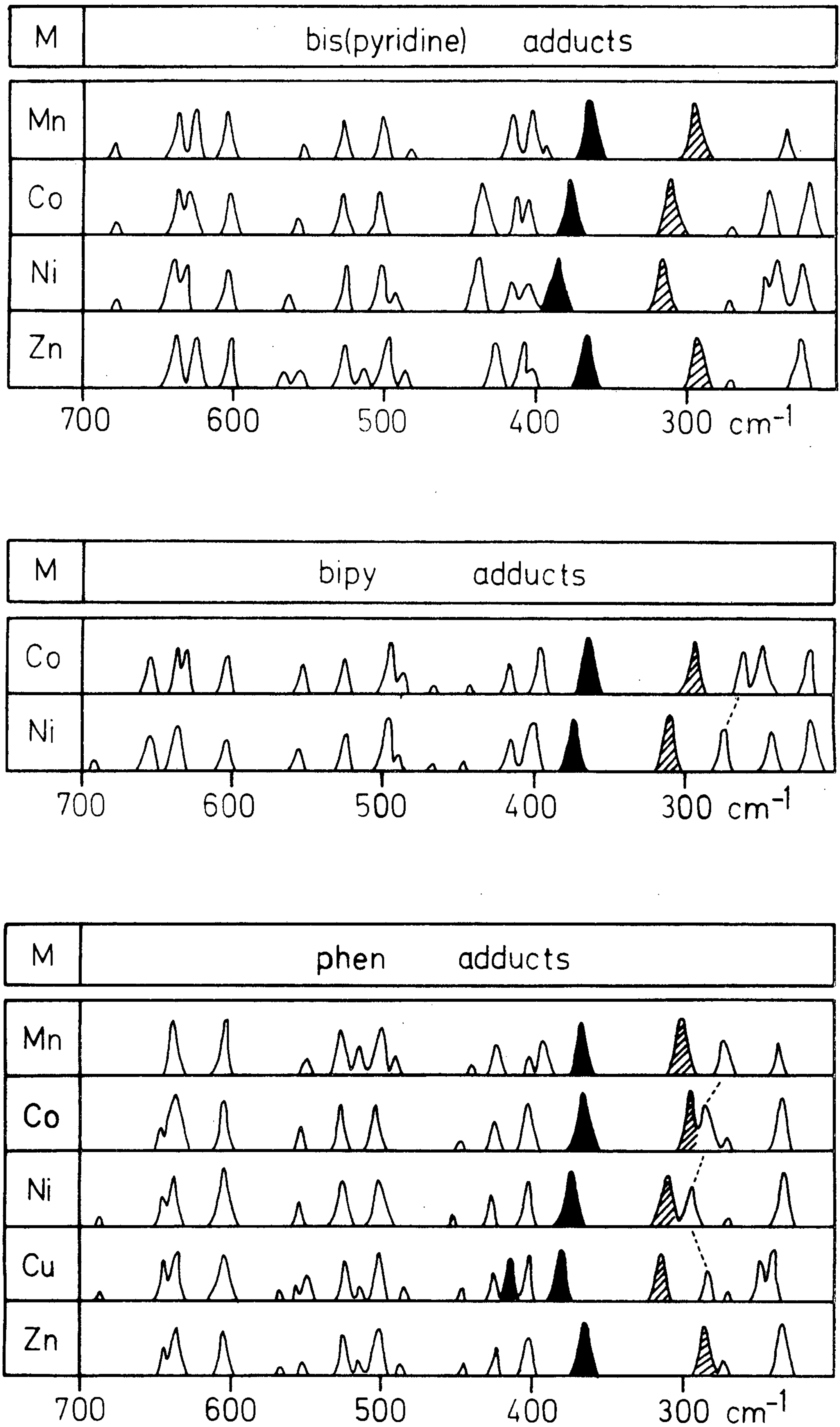


Fig. 17. The IR spectra of py, bipy and phen adducts of metal quinaldates. Solid peaks: νM-O; shaded peaks: νM-N (quin); linked peaks: νM-N (adduct).

in a decrease of the bonding power of the ligand, resulting in a weaker complex. The fact that the Cu(II) chelate forms H_2O and phen adducts is a further indication of the weak nature of the quinaldate chelate.

The pyridine adducts of Mn(II), Co(II), Ni(II) and Zn(II) quinaldates show metal-sensitive bands in the regions near 370 and 300 cm^{-1} where νM-O and νM-N were assigned. However, instead of the expected decrease in frequency, these bands tend to show either no change or, in certain cases, an increase in νM-L. These results may be rationalized by considering the very weak nature of the quinaldate ligand. This can give rise to relatively strong metal-water bonding as is seen by the formation of a 5- co-ordinate copper compound. Hence the replacement of water by pyridine might very well make no difference in metal-adduct bonding and therefore result in the absence of any significant decrease in νM-L. The remaining bands in the far IR spectra are assigned by analogy with the hydrates, those near 560 and 270 cm^{-1} being the COO and O-M-N bending modes respectively. The bands observed in the ranges 640 - 620 and 440 - 400 cm^{-1} are assigned to the heterocyclic ring vibrations.

The spectra of the bipy compounds (Figure 17) are of little interest since only the Co(II) and Ni(II) compounds were preparatively accessible. Nevertheless they show bands in the order Co<Ni near 360 and 300 cm^{-1} which are assigned as νM-O and νM-N respectively. Unlike the py adducts, the much larger ligand field strength of bipy has resulted in a lowering of these bands relative to the hydrates. The strong band near 270 cm^{-1}, lying in the order Co<Ni, is tentatively assigned (unlike the very weak δO-M-N which it obscures) to νM-N (bipy).

Table 66. νM-L values for the picolinates and quinaldates

	Picolinates			Quinaldates		
	μeff B.M.	νM-O cm^{-1}	νM-N* cm^{-1}	μeff B.M.	νM-O cm^{-1}	νM-N cm^{-1}
Mn	6.0	433(409)	330	4.4	378	280
Co	4.9^a	426	336	5.1^a	375	300
Ni	-	442	349	-	381	314
Cu^b	-	461(423)	388	-	440	397
Zn	-	425	330	-	374	301

*highest-frequency band [a]ref. 81 [b]anhydrous

The phen adducts of the quinaldates are of some interest as a complete series including the Cu(II) compound is formed. The formation of $Cu(quin)_2(phen)$ is indicative of the low M-L bond strength resulting in the formation of complexes of a higher co-ordination number than is usual in Cu(II) complexes (where 4-co-ordination is most common). The νM-O band lies in the same region as that of the bipy adducts in the order Mn~Co<Ni<Cu>Zn. There appears an extra band in the Cu(II) complex which is suggestive of Jahn-Teller distortion resulting in two M-O bond lengths. This distortion results in extra stabilization of the complex as is shown by the order Cu>Ni. The νM-N bands *i.e.* both νM-N (quinaldate) and νM-N (phen) are expected near 300 cm^{-1} where two metal-sensitive bands are observed. While acknowledging the probability of coupling between the various νM-L modes, the higher band, showing the same order as that of νM-O is tentatively assigned to primarily νM-N (quin). This band shows the order Cu>Ni expected for a significantly distorted Cu(II) compound. The lower band is hence tentatively assigned to νM-N (phen) and shows the inverse order, namely Ni>Cu. This order may be rationalized by considering the possible structure of the compound as revealed by its IR spectrum. The presence of a doublet in the νM-O band and its absence in the νM-N band suggests that both the quinaldate nitrogen donor atoms lie in the equatorial plane with one oxygen in the plane and one oxygen axially oriented giving rise to two M-O distances but only one M-N distance. Thus the phen ligand must span positions between the plane and the apex. Since it has been shown to be a completely rigid ligand[5] and unable to undergo any distortion it will almost certainly yield equal Cu-N bond distances. The fact that Cu(II) prefers to be distorted could be the reason for the order Cu<Ni in νM-N (phen). The Cu-N distances, although equal, may be longer than would have been the case if the ligand spanned positions in the plane. Hence, instead of yielding the usual distortion of two different M-N bonds, the phen ligand as a whole may be displaced to a slightly greater distance from the metal than in the undistorted case. This then gives rise to the observed νM-N order.

The remaining bands in the spectrum are assigned by comparison with the hydrates. It is interesting to note that the band near 550 cm^{-1}, assigned as δCOO, shows a splitting in the Cu(II) compound as does the asymmetric νCOO, both features being indicative of the differing M-O bonds.

The asymmetric νCOO bands of the hydrated chelates lie in the same region as that of the sodium salt indicating that the resonance of the carboxyl group is retained in the chelates. This has been used to indicate that quinaldic acid gives weak, essentially ionic M-O bonds[95]. In both the picolinate and quinaldate compounds νCOO is at a maximum for the bipy and phen adducts (when the M-O bond is expected to be weakest) thus suggesting an inverse relationship between the M-O and COO bond orders.

4. THE IR SPECTRA OF 8-QUINOLINOLATES

(i) The IR Spectra of the Metal Chelates of 8-Quinolinol and 2-Methyl-8-Quinolinol

The divalent metal chelates of oxine (8-quinolinol, 8-hydroxyquinoline) are reported to precipitate from aqueous solution as the dihydrates which readily undergo thermal dehydration at moderate temperatures[110]. The structures of the Co(II), Ni(II) and Zn(II) dihydrates have been shown by X-ray crystallography to have a *trans*-planar arrangement of the oxine molecules forming a 5-membered chelate ring, the water co-ordinating in the axial positions to produce a 6-co-ordinate octahedral stereochemistry[116,117,119]. The Mn(II) chelate is expected to be isomorphous, while the anhydrous Cu(II) compound has been isolated[166] in two forms. The α-form consists of a chain of planar chelates[112] weakly bound in the perpendicular direction by Cu-O bonds of length 3.32 Å, while the β-form[118] exists as dimers with the out-of-plane distance of 2.83 Å. The structures of the anhydrous chelates have not been determined, but tetrahedral stereochemistry has been proposed[130,139,165].

The far IR spectra of the oxine chelates have been studied by various workers[121,123,130,131]. Assignments of M-L modes in the region 540 - 480 cm^{-1} were made empirically by Kulkarni and Mukhedkar[123] while other workers[130,131] have assigned these vibrations to bands below 400 cm^{-1}. Such low frequencies for these modes seems surprising when the relatively large stability constant data[149] and calculated bond energies[206] are considered.

The IR spectra of the anhydrous and hydrated oxine chelates are shown in Figure 18 and the frequencies listed in Tables 44 and 45. Those bands exhibiting a metal ion dependence which parallels the order of the CFSE's will be assigned to νM-L or coupled νM-L. Table 67 shows that all these chelates have high spin configurations and hence, for octahedral stereochemistry, we expect the order of νM-L to be metal ion dependent in the Irving-Williams[50] stability sequence. The hydrated chelates show five bands below 650 cm^{-1} which exhibit this order, namely those in the regions 630 - 600, 590 - 560, 520 - 500, 410 - 380 and 330 - 260 cm^{-1}. These bands are therefore assigned to M-L vibrations. Examination of the spectrum of sodium oxinate indicates ligand bands near all of these frequencies. Thus, the possibility of coupling between these ligand bands and the νM-L bands as well as coupling between the M-O and M-N modes must be considered. The sodium compound has been assumed (from its solubility characteristics) to be a salt rather than a chelate[135]. Previous workers[130,131] have suggested from general considerations that νM-N frequencies are lower than νM-O frequencies in these compounds. Wood and Jones[206] have calculated co-ordinate bond energies for a variety of Ni(II) complexes and found that Ni-N bond energies of various nitrogen donor ligands are of the order 57.0 kcal./mole. They subsequently determined the Ni-O bond energy in the oxine chelate to be 64.4 kcal./mole. Thus the Ni-O is the stronger bond and it would be expected that its IR absorption frequency would be at a higher frequency than νNi-N. The two higher-frequency bands are thus assigned to νM-O and the two lower-frequency bands to νM-N. The band near 500 cm^{-1} previously assigned by Tackett and Sawyer[121] to the C-O deformation, shows the least metal-sensitivity of all the coupled νM-L bands and is assigned to νM-O + νM-N extensively coupled with δC-O. Table 44 shows that the two Cu(II) chelates have nearly identical spectra below 700 cm^{-1}, slight differences occurring above 700 cm^{-1}.

The spectra of the anhydrous oxinates are very similar to their hydrated analogues and also show metal-sensitive bands in the same regions. Since these bands follow the order Mn<Co<Ni<Cu>Zn which is characteristic of octahedral systems with tetragonally distorted Cu(II) and since no great spectral differences occur on dehydration, these chelates undoubtedly have a polymeric octahedral structure (except for the basically square planar Cu(II)). The Co(II) chelate has been assigned a 6- co-ordinate structure by Lenzer[172] on the basis of its magnetic moment. A tetrahedral set of compounds is expected to yield the order Co>Ni in CFSE (and hence in νM-L) as has been observed for the tetrachlorometal(II) compounds[208].

The water in the metal dihydrate compounds was replaced by various nitrogen bases. In this way the Ni(II) py, Co(II), Ni(II) and Zn(II) phen and Co(II) and Ni(II) bipy adducts were prepared. As these heterocyclic ligands have a higher ligand field strength than the H_2O which they replace, they are expected to bond with greater strength and the consequent reduction in M-L (L = Oxine) bond strength should lead to a decrease in the νM-L values. It can be seen from Tables 45 and 46 that all νM-L bands undergo a small shift towards lower frequency on the displacement of H_2O, the bipy and phen adducts retaining the order Co<Ni>Zn (Figure 20). The spectra of these compounds below 300 cm^{-1} is rather complex due to the intrusion in this region of the νM-N bands of the adducted heterocyclic base. In the bipy complex these νM-N bands are expected at comparatively low frequencies[5] and hence the higher band is tentatively assigned as νM-N (oxine) and the lower-frequency bands as νM-N (bipy). In the phen compounds the νM-N (phen) is expected[5] near 300 cm^{-1} and hence the higher-frequency band is tentatively assigned to this mode and the lower-frequency band to νM-N (oxine). The overlap of oxine, bipy and phen bands in this region supports the view that the oxine band is correctly assigned to νM-N rather than νM-O. The spectra of these adducts exhibit the bands in the regions 450 - 400 and 650 - 600 cm^{-1} which are characteristic of the heterocyclic pyridine ring. The oxine complexes are expected to show similar bands assigned, respectively, as out-of-plane and in-plane ring vibrations of the pyridine nucleus[96]. Hence the band near 650 cm^{-1} in the oxine chelate spectra is assigned to an in-plane ring deformation in agreement with the work of Tackett and Sawyer[121]. In the anhydrous species, the higher band near 400 cm^{-1} is assigned to the corresponding out-of-plane vibration.

The spectra of the oxine chelates between 1700 and 700 cm^{-1} comprise, principally, those bands which are characteristic of the aromatic system. Ring stretching modes representing νC=C and νC=N are found in the 8-quinolinol ligand[164] in the ranges 1620 - 1560 and 1500 - 1350 cm^{-1}. Peaks occurring within the broad range 1300 - 700 cm^{-1} are generally assigned to the in-plane and out-of-plane deformation modes of the C-H groups[126,164]. Charles and coworkers[122] have assigned the band at 1100 cm^{-1} to νC-O from its atomic mass dependence. This band tends to exhibit a metal ion dependence which parallels the variation in νM-O. This stabilization by the crystal field of bonds adjacent to the M-L bond may be interpreted as a thermodynamic effect in which the increased stability of the molecule is transmitted beyond the M-L bond.

Some trivalent metal chelates were prepared in order to investigate whether similar metal-sensitive bands occur in their spectra. Figure 19 shows the spectra of the Cr, Mn, Fe, Co and Ga chelates. Table 67 indicates that the first three are high spin whereas the Co(III) oxinate, in common with the large majority of Co(III) compounds, is spin paired. Hence the CFSE's of these metals can be calculated, the pairing energy in the Co(III) compound being ignored as it is unable to change the CFSE order of Cr>Mn>Fe<Co>Ga. Examination of the spectra of these compounds shows four bands between 400 and 650 cm^{-1} which exhibit the corresponding metal-sensitivity. These bands occur in similar regions to the νM-L bands in the divalent chelates. The reversal of the Cr > Mn order and the appearance of unique bands in the Mn(III) spectrum is symptomatic of Jahn-Teller distortion expected on theoretical grounds for a high spin d^4 system. The presence of tetragonal distortion in $Mn(OX)_3$ was demonstrated by Burns and coworkers[132] from measurements of its ultraviolet spectrum. In the IR spectrum below 400 cm^{-1}, two bands show considerable metal-sensitivity in the order of the CFSE's. The bands are assigned by comparison with the analogous divalent series, the higher-frequency bands being νM-O and the lower-frequency bands νM-N. The 1100 cm^{-1} band, assigned[122] to νC-O, shows a rough correlation with νM-O, the Mn(III) peak being split into a doublet.

The reaction of 2-methyl-8-quinolinol ($2\text{-}CH_3\text{-}OX$) with metal ions in aqueous solution results in the precipitation of chelates[152] which are formulated as $[M(2\text{-}CH_3\text{-}OX)_2(H_2O)]$

Table 67. IR data on the oxine complexes.

M	μeff(290K) B.M.	νM-O cm^{-1}		νM-N cm^{-1}		
$[M(OX)_2(H_2O)_2]$						
Mn	4.5	604	564	379	286	
Co	4.6[a]	609	571	388	293	
Ni	-	627	574	392	303	
Zn	-	608	570	392	262	
$[M(OX)_2]$						
Mn	4.5	600		388	250	
Co	4.6[a]	614	570	387	267[d]	
Ni	3.3[b]	617	574	391	294	
Cu(α)	-	632	585	408	332	
Cu(β)	-	632	583	407	328	
Zn	-	605	568	391	251	
$[M(OX)_3]$						
Cr	-	644	575	408	362	333
Mn	5.0[c]	631	579	410(404)[e]	341(327)[e]	288
Fe	4.4	629	569	401	314	260
Co	diamagnetic	657	586	424	414	380
Ga	-	632	579	407	296	280

[a] ref. 172 [b] ref. 146 [c] ref. 132

[d] Mean of doublet at 270 and 263 cm^{-1} [e] Extra νMn-N band

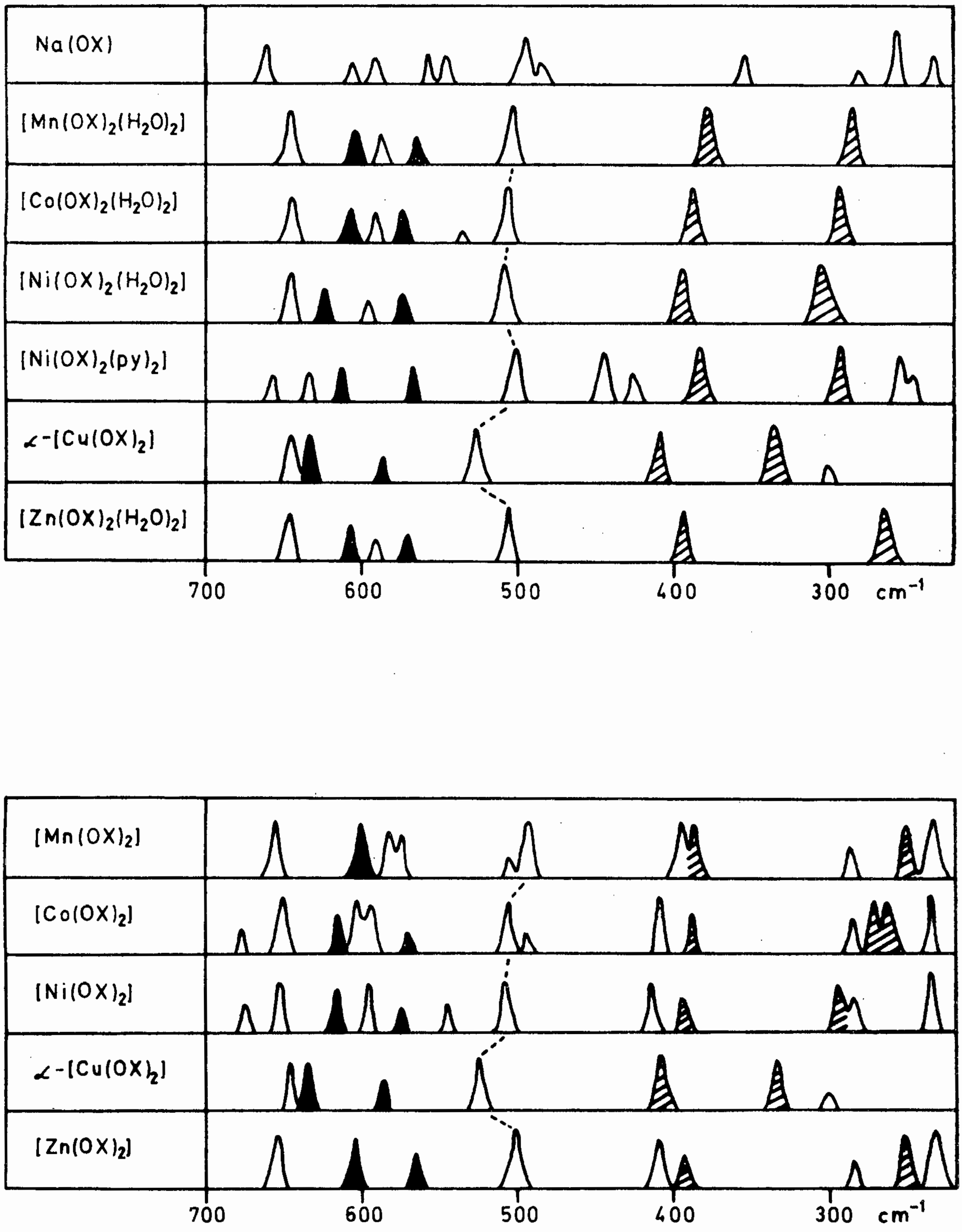


Fig. 18. The IR spectra of divalent metal oxinates, 700 - 200 cm^{-1}. Solid peaks: νM-O; shaded peaks: νM-N; linked peaks: coupled νM-L.

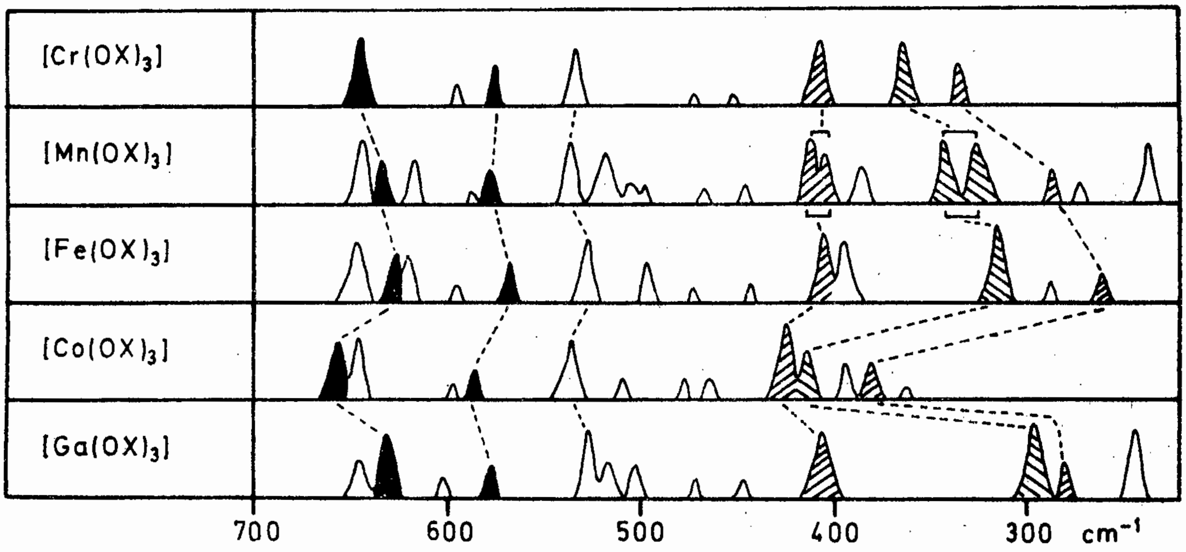


Fig. 19. The IR spectra of trivalent metal oxinates. Solid peaks: νM-O; shaded peaks: νM-N; linked peaks (unshaded): coupled νM-L.

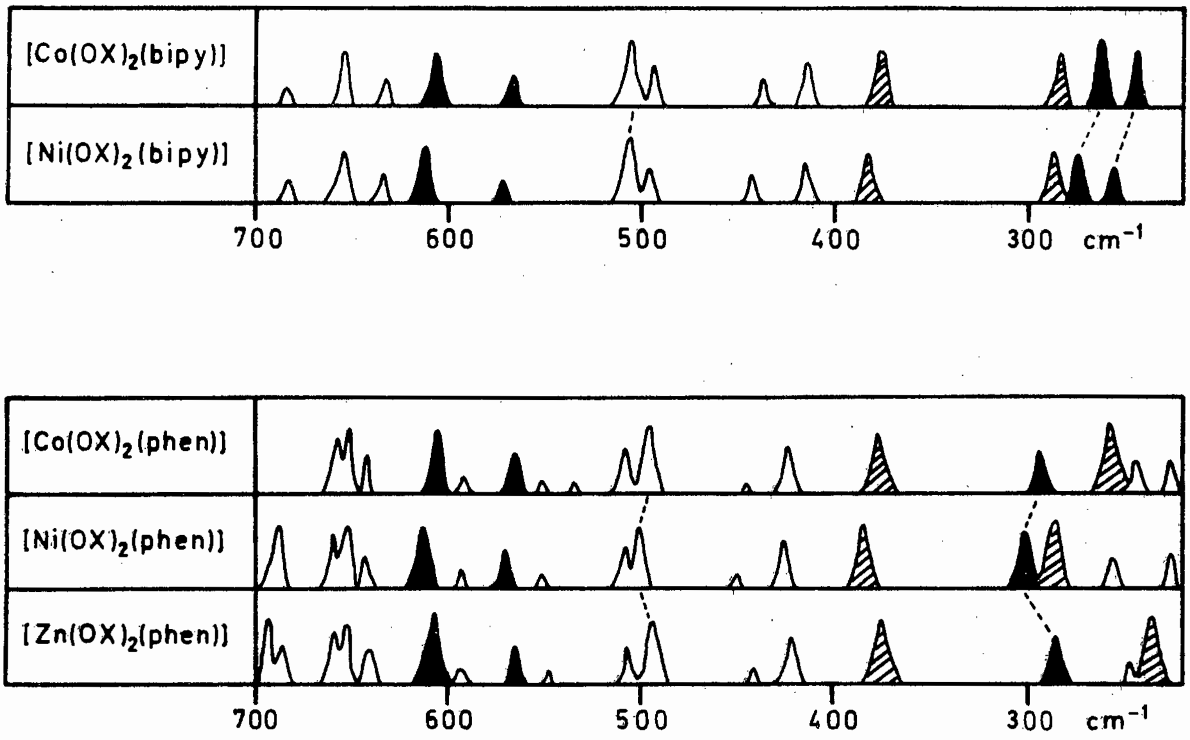


Fig. 20. The IR spectra of the bipy and phen adducts of divalent metal oxinates. Solid peaks (unlinked): νM-O; shaded peaks: νM-N (OX); solid peaks (linked): νM-N (adduct); linked peaks (unshaded): coupled νM-L.

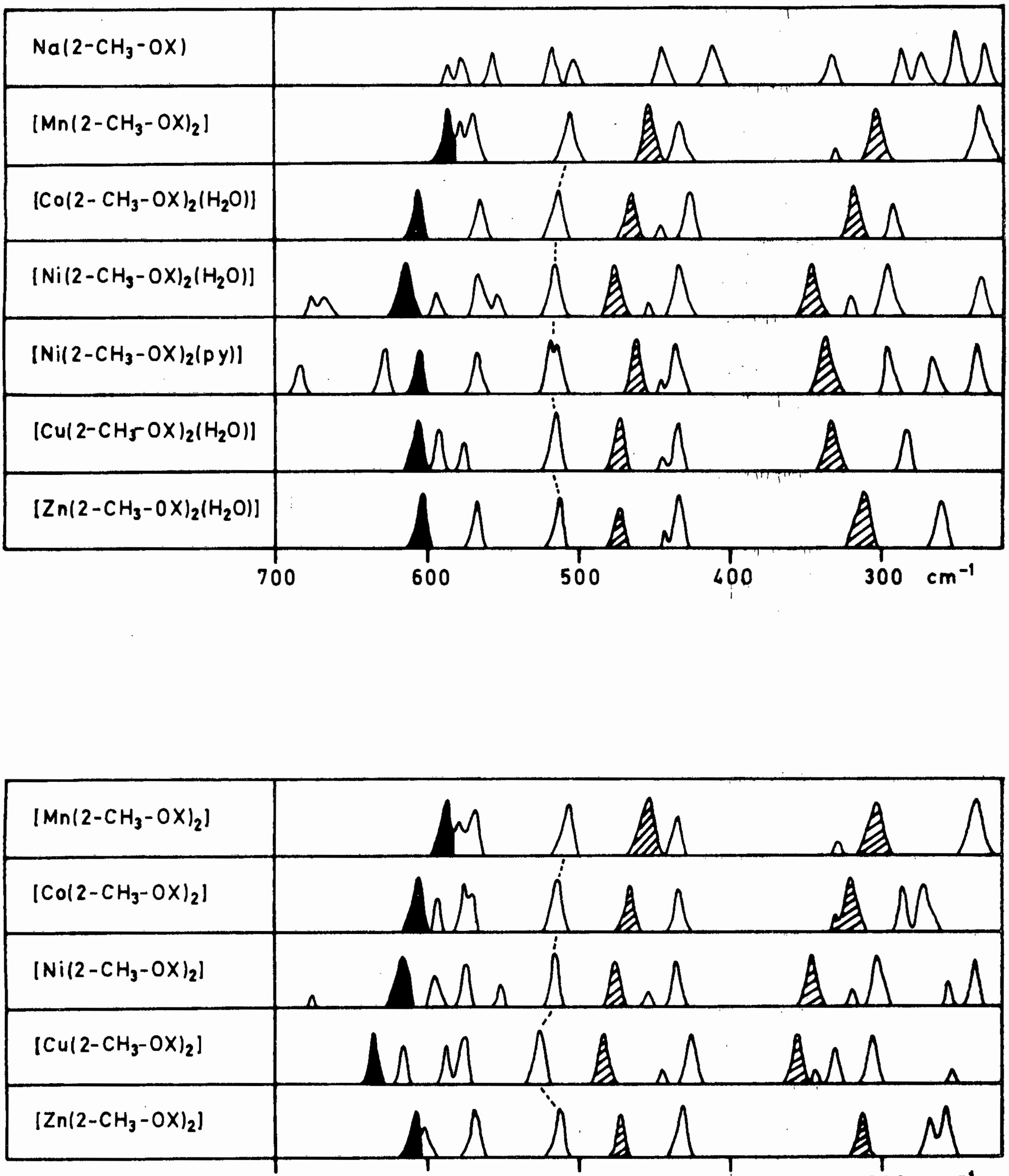


Fig. 21. The IR spectra of the 2-methyloxinates, 700 - 200 cm^{-1}. Solid peaks: νM-O; shaded peaks: νM-N; linked peaks: νM-L.

where M = Co(II), Ni(II), Cu(II) and Zn(II). The Mn(II) chelate precipitates in the anhydrous form. The formation of the monohydrates which suggests 5- co-ordination may be the result of the steric effect of the 2-CH_3 group[138,209,210] adjacent to the donor atom. Pentaco-ordination results when only five donor atoms are allowed to approach the central metal ion closely. It has been shown that the stereochemical arrangement of these donor atoms may be based upon a trigonal bipyramid or a square pyramid[211]. These two idealized geometries are rarely found in practice and compounds with so-called "trigonal bipyramidal" or "square pyramidal" geometries may often be severely distorted from the idealised forms[211]. Aiding the assignment of a 5- co-ordinate structure for the 2-CH_3-OX chelates is the fact that the water molecule is expected to yield a much weaker M-L bond than the 2-CH_3-OX ligand. Furlani[207] has stated that compounds containing one bond weaker than the other four, as in 1:1 addition to a square planar moiety, favour a square pyramidal structure. Hence these chelates may be assigned this basic stereochemistry, although the possibility of distortion, especially an increase in the apical angle (angle between apical bond and equatorial bonds) above the regular value of 90° must be acknowledged. Table 68 shows that the Co(II) and Ni(II) chelates are high spin. Sacconi[212] has reported CFSE's for square pyramidal systems with apical angles of 90° and 105°. In both cases the order for high spin compounds is Co<Ni>Cu>Zn. Hence the νM-L bands in the IR spectra are expected to show this order.

There are altogether six bands in the far IR (Figure 21) which exhibit some metal ion dependence in the CFSE order.

The bands near 600 and 500 cm^{-1}, lying in similar regions to bands in the oxine spectra, are assigned, by comparison, to νM-O and νM-L+δC-O. The metal-sensitive bands near 470 and 330 cm^{-1} are assigned to νM-N. The band near 450 cm^{-1} shows some metal dependence but as it appears in the anhydrous compounds only in the Ni(II) and Cu(II) chelates and, in these cases, in the inverse order to the other νM-L bands, it is assigned as the heterocyclic ring vibration. As in the case of oxine, the pyridine adduct of $Ni(2-CH_3-OX)_2$ was prepared. It forms only the mono(adduct) and hence its structure is assumed to be identical to the aquo compound. The νM-L bands show significant shifts towards lower wavenumbers due to the increased ligand field strength of pyridine compared with that of water. This confirms the assignment of these bands to νM-L vibrations. The band at 500 cm^{-1} shows no shift, which, together with its very small metal-sensitivity, indicates that it is extensively coupled with the ligand vibration found in this region in the spectrum of the sodium salt. The band below 300 cm^{-1} shows considerable shift on changing metal ion but is insensitive to change in the adducted base. Hence it is assigned to a chelate ring deformation.

Table 68 shows that upon dehydration these chelates retain their high spin configurations. The structure of the Cu(II) chelate is reasonably expected to be square planar. If attention is given to the steric hindrance of the $2-CH_3$ group, the other chelates will probably tend towards tetrahedral stereochemistry. Such a structure has been suggested for Zn(II) on the basis of its ultraviolet spectrum[138]. Although Co(II) and Zn(II) ions are frequently encountered in tetrahedral environments, Ni(II) is more often found in a 6- co-ordinate structure and is hence assigned a polymeric octahedral stereochemistry. The IR spectra shown in Figure 21 indicate metal-sensitive bands following the Irving-Williams sequence in similar regions to the νM-L bands in the spectra of the hydrated chelates.

Table 68. IR data on the 2-methyl-8-quinolinol complexes

M	μeff(290K) B.M.	νM-O cm^{-1}	νM-N cm^{-1}	
$M(2\text{-}CH_3\text{-}OX)_2(H_2O)$				
Co	3.7	604	466	319
Ni	2.8	612	475	347
Cu	-	605	472	334
Zn	-	601	471	310
$M(2\text{-}CH_3\text{-}OX)_2$				
Mn	4.9	587	452	302
Co	4.3	604	467	320
Ni	3.1	615	475	348
Cu	-	634	481	359
Zn	-	609	471	312

The order Ni<Cu>Zn is the sequence expected for octahedral Ni(II) and square planar Cu(II); the decrease to the Zn(II) value being due to the absence of CF effects in a d^{10} system. A square planar Ni(II) system is expected to yield the order Cu<Ni since the Cu(II) ion always contains an extra electron occupying an antibonding orbital relative to the Ni(II) con-

figuration. Irrespective of its structure, Mn(II) is expected below a tetrahedral Co(II) value since in its high spin state it has zero CFSE. Tetrahedral Ni(II) is expected to yield the order Co>Ni and hence the Ni(II) compound is neither square planar nor tetrahedral. Octahedral Ni(II) and tetrahedral Co(II) have equal CFSE's in terms of the crystal field splitting parameter (10*Dq*) but, since 10*Dq* in tetrahedral systems is theoretically $\frac{4}{9}$ of its value in octahedral compounds[1], the CFSE order for these ions is Ni>Co. Since this is the order of νM-L observed, it appears that the difference in co-ordination number is insufficient to reverse this order. Hence it follows that the νM-L of a series containing tetrahedral Co(II) and Zn(II), octahedral Ni(II) and square planar Cu(II) follow the Irving-Williams sequence. Similar results were found for the divalent chelates of *N-p*-tolylsalicylaldimine[12,190].

The νM-L bands of Cu(II) and Zn(II) generally show a high frequency shift on dehydration due to the decrease in co-ordination number. The larger shifts in the case of the Cu(II) chelate are possibly due to a simultaneous increase in the CFSE on the attainment of a square planar system. The bands of the Co(II) and Ni(II) compounds show little change indicating that the effect of their changes in co-ordination number are counterbalanced by changes in the CFSE on going from a 5-co-ordinate to a tetrahedral or octahedral system.

The formulation of these compounds as monohydrates does not necessarily imply 5- co-ordination since an octahedral environment can be attained by a bridging bidentate oxygen donor leading to a dimeric structure. If a 6- co-ordinate structure of this type is postulated, then the Cu(II) chelate would be expected to show Jahn-Teller distortion resulting in the retention of an essentially 5- co-ordinate structure. If the Co(II) and Ni(II) hydrates are octahedral and Cu(II) square pyramidal a similar order in νM-L to that observed in the hydrated quinaldates and the py adducts of TTA and BTA may be expected, namely Co<Ni<Cu. The absence of a Ni<Cu order or of a splitting in νM-L as observed in the anthranilates and picolinates indicates a monomeric 5- co-ordinate structure for these compounds, although long-distance interactions could result in quasi-octahedral stereochemistry. It seems unlikely that a system in which steric interference has been experimentally demonstrated[138,209] should give rise preferentially to an octahedral stereochemistry by a bridging ligand when precipitated from aqueous solution. Of the two basic 5- co-ordinate structures, square pyramidal co-ordination predicts the order of νM-L exhibited, whereas trigonal bipyramidal structure yields a CFSE order that parallels the Irving-Williams order[212].

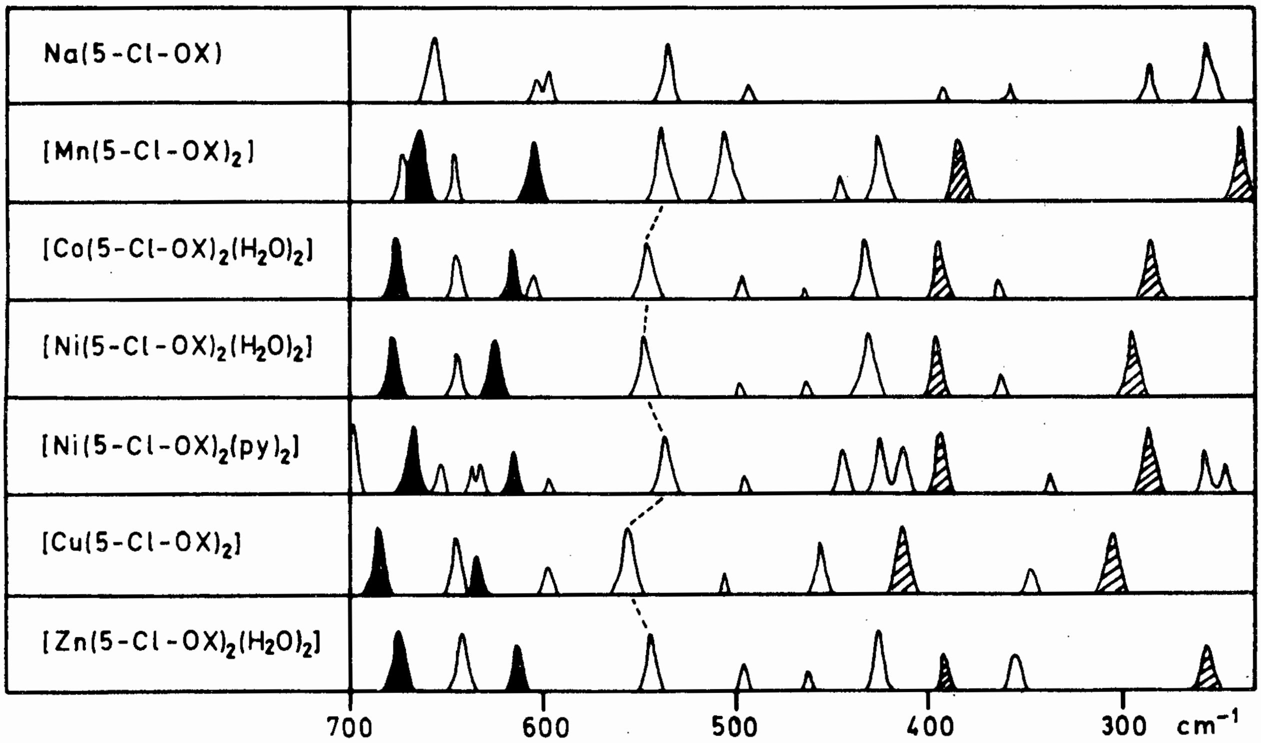
Comparison of the spectra of the Cu(II) chelates of oxine and 2-methyloxine, which are assumed to have basically the same square planar structure, shows that the νM-L bands at 632, 522, 408 and 332 cm^{-1} in the oxinate spectrum correspond with the bands at 634, 523, 481 and 359 cm^{-1} in the 2-methyloxinate spectrum. The lower two bands have been assigned to νM-N and show considerably larger values in the substituted compound. This increase is rationalized by considering the electron donating effect of the 2-CH$_3$ group which increases electron density at the ring nitrogen. The increased charge density there should permit formation of a stronger co-ordinate bond with the metal ion and result in an increased value of νM-N. π-Electron density calculations[213] show that the 2-CH$_3$ group influences the π-electron density mainly at the 1- and 3-positions of the quinoline nucleus. The highest-frequency metal-sensitive band has been assigned to νM-O and shows little shift on 2-substitution indicating that the inductive effect of the methyl group is not transmitted across the fused ring system to any appreciable extent. The absence of shift in the 500 cm^{-1} band could be ascribed to the very low νM-N character of this band as it is extensively coupled with νM-O and δC-O. The fact that it is the lower-frequency metal-sensitive bands that shift on 2-substitution is indicative that these bands have been correctly assigned to νM-N rather than to νM-O.

(ii) The IR Spectra of Halogen-Substituted 8-Quinolinols

The IR spectra of the 5-Cl-, 5-Cl-7-I-, 2-CH_3-5,7-di-Br-, 5,7-di-Cl- and 5,7-di-Br-8-quinolinol chelates are shown in Figures 22-26 and the frequencies listed in Tables 50-59. No previous IR studies on the chelates of these ligands appear to have been made. Assignments of M-L vibrations in these compounds will be made by procedures similar to those adopted for the 8-quinolinolates. The higher-frequency metal-sensitive bands will be assigned to coupled νM-O and the lower-frequency bands to coupled νM-N.

The structures of the hydrated Co(II), Ni(II) and Zn(II) and the anhydrous Cu(II) chelates of 5-Cl-OX are assumed to be similar to the corresponding oxinates. Attempts to prepare a second, β-form of the copper chelates of substituted 8-quinolinols were unsuccessful. The anhydrous Mn(II) chelate is presumed to be polymeric octahedral. The far IR spectra of these chelates (Figure 22) show five metal-sensitive bands corresponding in position to those of the oxinates. The bis(pyridine) adduct of the Ni(II) compound shows a similar band pattern (with all the bands assigned as νM-L moved to lower frequencies by up to 10 cm^{-1}). The assignment of these bands follows that of the oxinates, namely the higher-frequency bands to νM-O, the lower-frequency bands to νM-N and the band near 550 cm^{-1} to νM-L coupled with δC-O. Substituent effects suggest the 400 cm^{-1} νM-L band has considerable νM-O character. Dehydration of these hydrates results in the Co(II) compound retaining its high spin state whereas the anhydrous Ni(II) compound is diamagnetic. Hence it has square planar structure resembling that of the Cu(II) chelate. The result of this structural similarity can be seen in the νM-L vibrations where the order is generally Ni>Cu. This stability order is predicted on the basis of CFT since the orbital of highest energy is occupied in the Cu(II) chelate, but is unoccupied in the low spin Ni(II) compound. The Co(II) and Zn(II) chelates have either a polymeric octahedral or tetrahedral stereochemistry, although the lack of an increase in νM-L on dehydration of the Zn(II) chelate suggests that the co-ordination number remains the same. The far IR shows bands in the sodium salt near all the νM-L vibrations and hence coupling of the ligand and metal-ligand vibrations is considered highly probable. The bands at 430 and 640 cm^{-1} are assigned to the ring torsions of the heterocyclic system.

The spectra of the hydrated chelates of 5-Cl-7-I-OX show metal-sensitive bands in the normal Irving-Williams order near 600, 570, 500, 450, 400, 320 and below 300 cm^{-1} as compared with the 5 bands observed in the 5-Cl-OX compounds. Again the py adduct of the Ni(II) chelate shows all these bands are



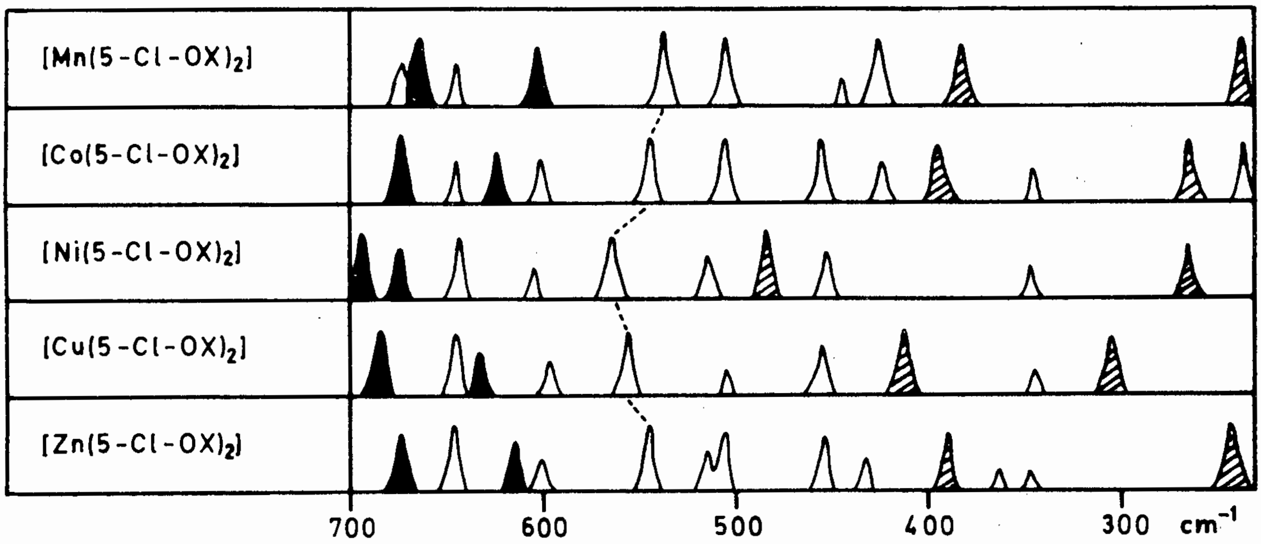


Fig. 22. The IR spectra of the 5-chloro-oxinates, 700 - 200 cm^{-1}. Solid peaks: νM-O; shaded peaks: νM-N; linked peaks: coupled νM-L.

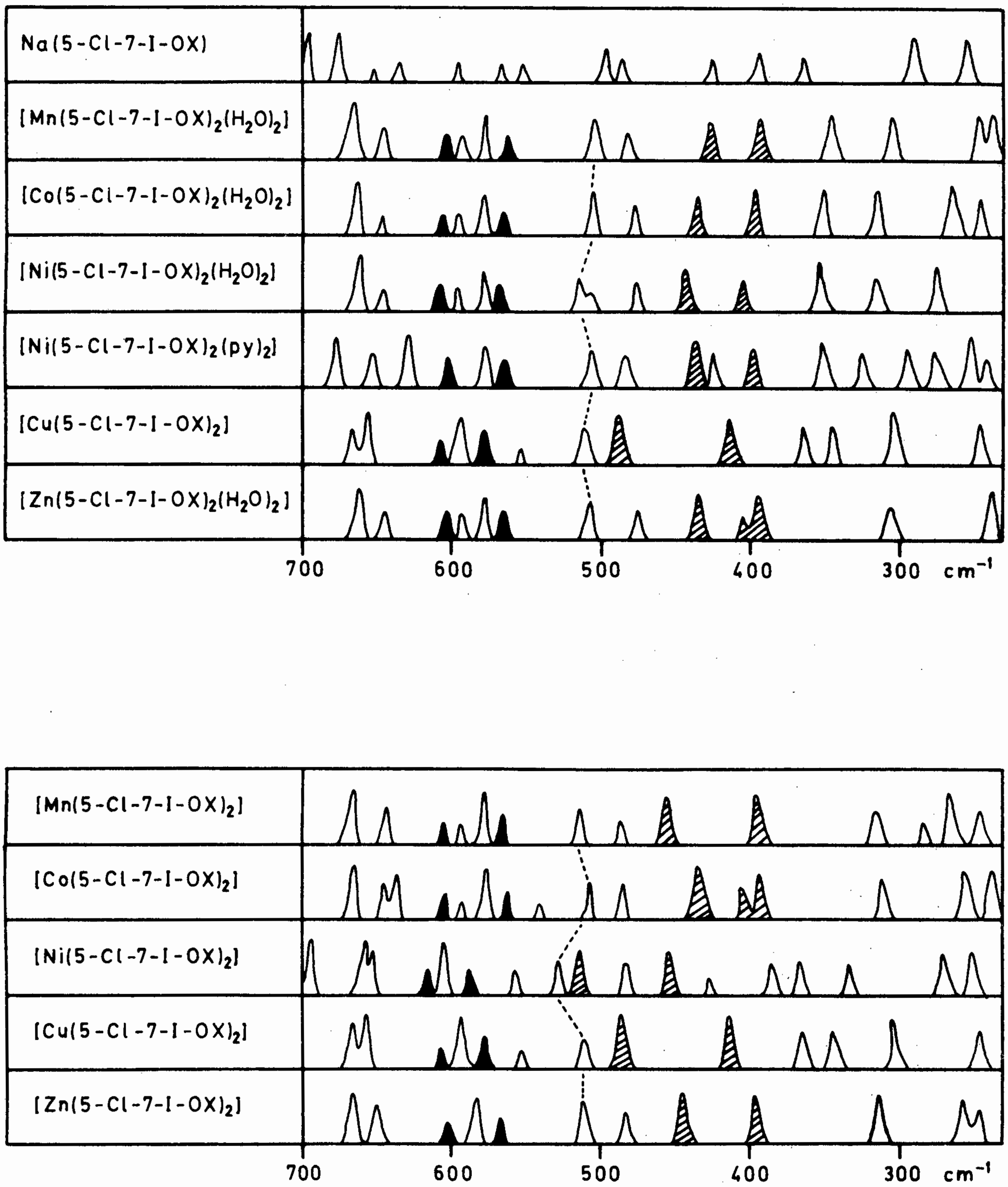


Fig. 23. The IR spectra of the 5-chloro-7-iodo-oxinates, 700 - 200 cm^{-1}. Solid peaks: νM-O; shaded peaks: νM-N; linked peaks: coupled νM-L.

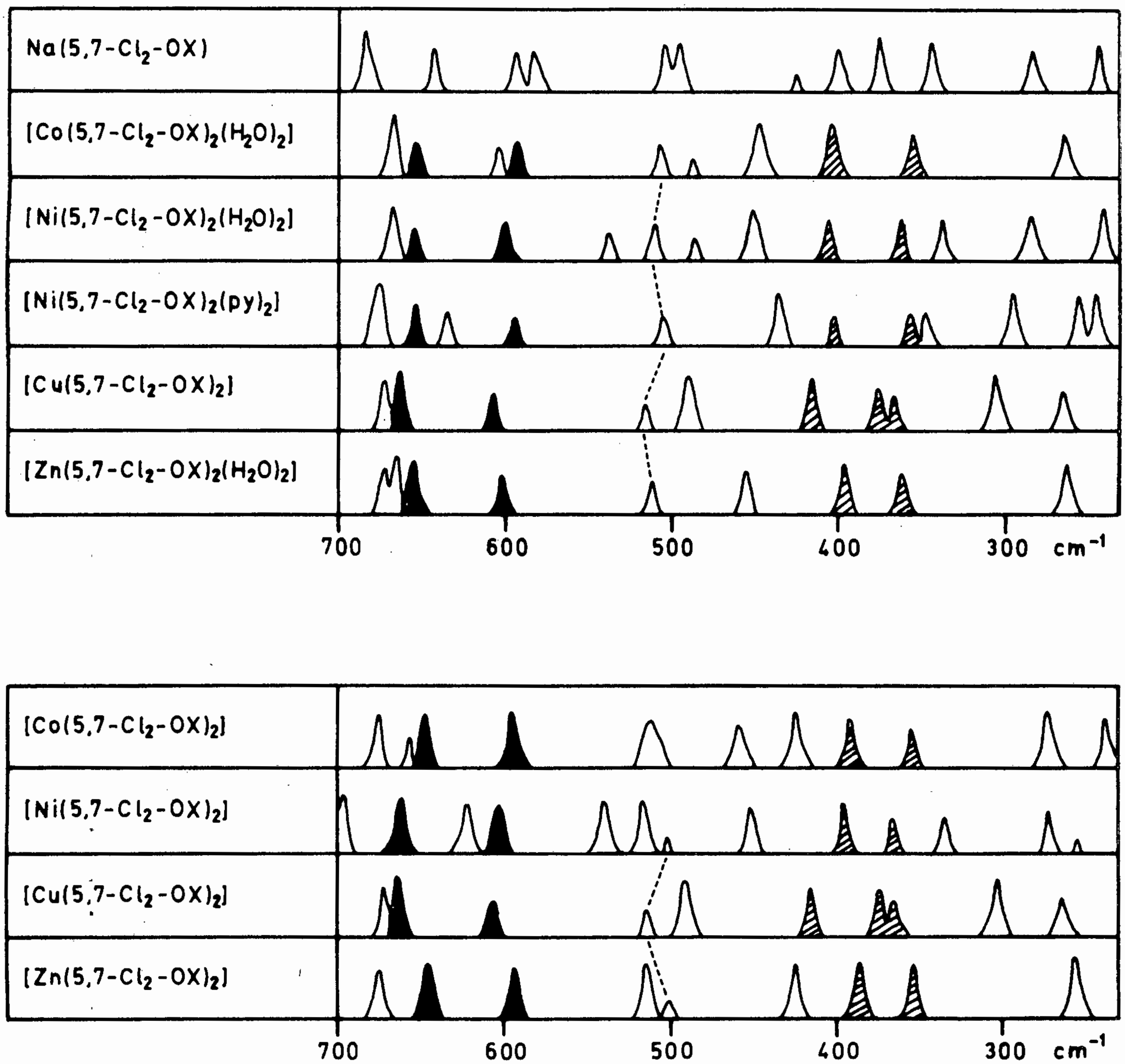


Fig. 24. The IR spectra of the 5,7-dichloro-oxinates, 700 - 200 cm^{-1}. Solid peaks: νM-O; shaded peaks: νM-N; linked peaks: coupled νM-L.

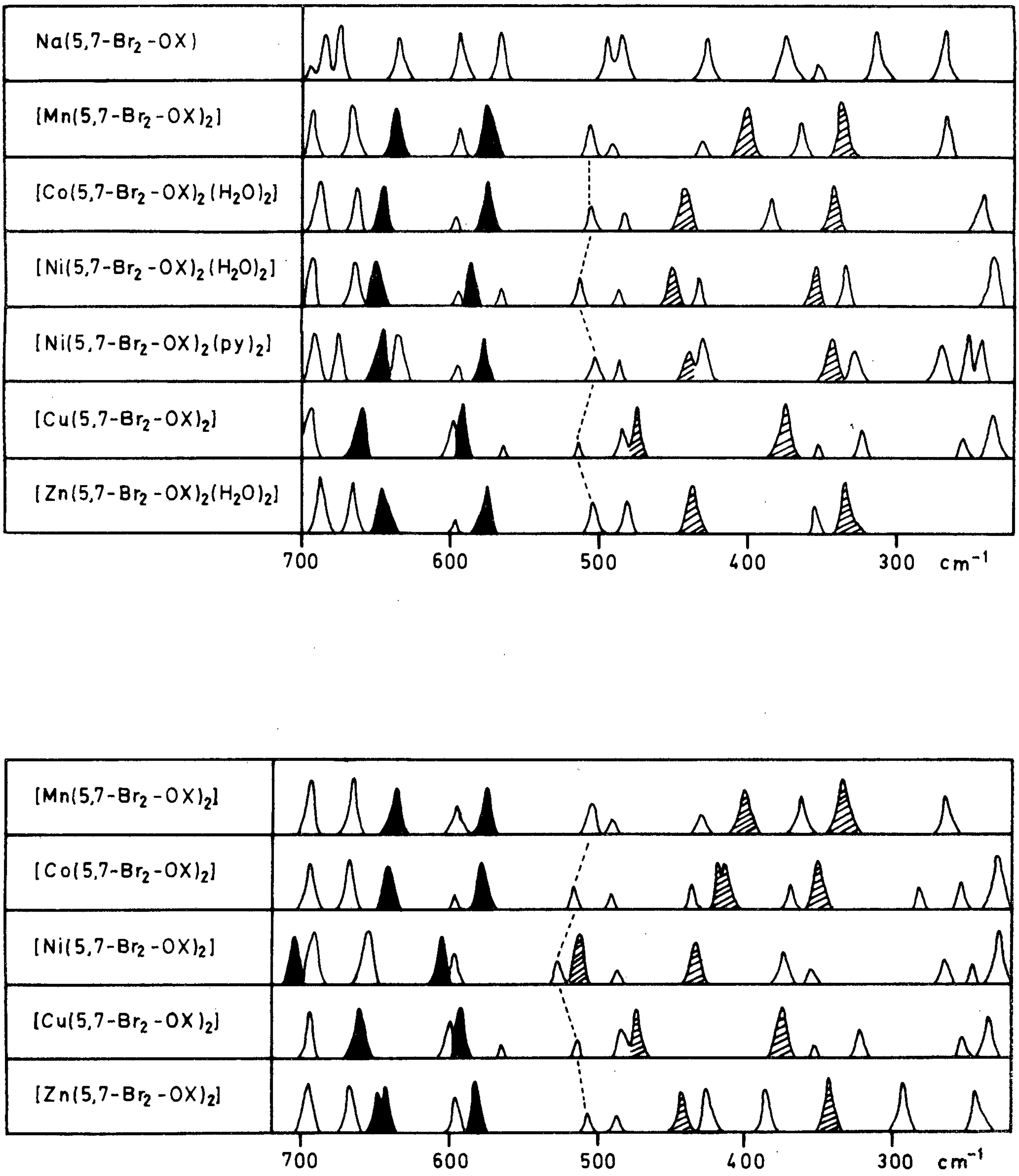


Fig. 25. The IR spectra of the 5,7-dibromo-oxinates, 700 - 200 cm^{-1}. Solid peaks: νM-O; shaded peaks: νM-N; linked peaks: coupled νM-L.

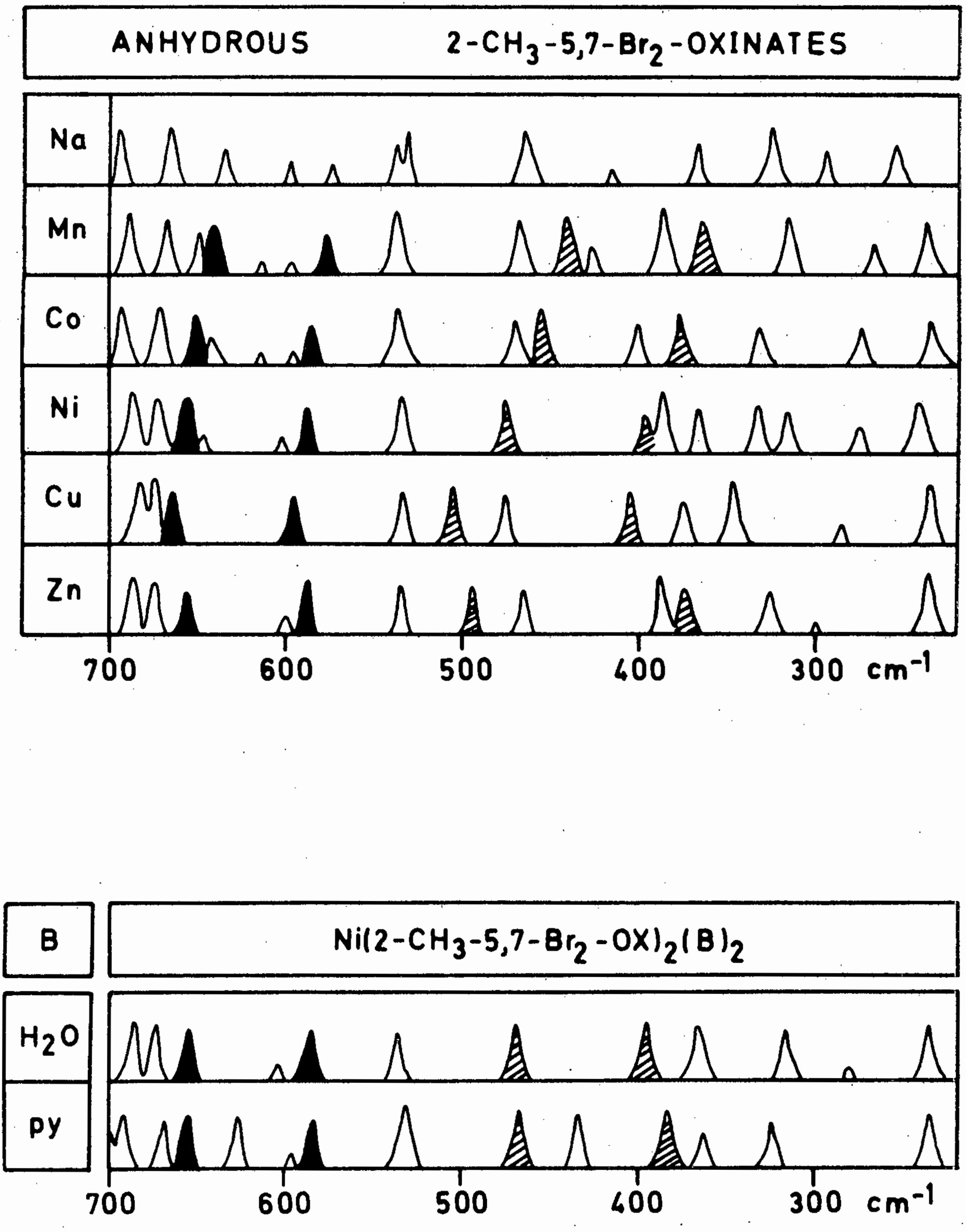


Fig. 26. The IR spectra of the 2-methyl-5, 7-dibromo-oxinates, 700 - 200 cm^{-1}. Solid peaks : νM-O; shaded peaks: νM-N.

lowered in frequency except for the two lower-frequency bands near 300 cm^{-1}. Hence, despite their large metal-sensitivity, these bands are assigned rather to a chelate ring deformation. The two higher-frequency bands are assigned to νM-O and that at 500 cm^{-1} (again showing a very small shift) to the coupled νM-L. The lower bands belong to coupled metal-nitrogen vibrations. Dehydration of these compounds yields a diamagnetic square planar Ni(II) species, the νM-L values of which are raised to yield the expected stability order of Ni>Cu. The order of Mn(II) and Co(II) is the inverse of that normally found and may suggest that the Mn(II) compound is only 4- co-ordinate as opposed to a 6- co-ordinate polymeric octahedral Co(II) complex.

The spectra of the hydrated metal chelates of 5,7-di-Cl-OX show νM-O bands near 650 and 600 cm^{-1} and νM-N bands near 400 and 360 cm^{-1}. All four bands are moved towards lower wavenumbers in the Ni(II) compound upon the replacement of H_2O by py. The band near 500 cm^{-1} which shows some shift on changing metal ion may be assigned to the extensively coupled νM-L. The band below 300 cm^{-1} (again strongly metal-sensitive in the order Co<Ni<Cu>Zn) shows an increase in frequency in the Ni(II) pyridine adduct and is thus, by analogy with the 5-Cl-7-I-OX compounds, assigned to the chelate ring deformation. All the anhydrous chelates are high spin (Table 69). The Cu(II) compound is most likely square planar, whereas the other chelates are presumed to have polymeric octahedral structure. All the previously assigned νM-L bands show the same order as that observed for the hydrated series.

Table 69. IR data on halogen-substituted 8-quinolinols

M	μeff. (290K) B.M.	νM-O cm^{-1}		νM-N cm^{-1}	
$M(5\text{-}Cl\text{-}OX)_2(H_2O)_2$					
Co	4.3	673	613	394	286
Ni	-	678	622	395	294
Zn	-	676	613	391	257
$M(5\text{-}Cl\text{-}OX)_2$					
Mn	4.8	664	601	381	238
Co	3.8	672	622	396	264
Ni	diamagnetic	693	674	482	263
Cu	-	683	632	412	303
Zn	-	674	614	390	242
$M(5\text{-}Cl\text{-}7\text{-}I\text{-}OX)_2(H_2O)_2$					
Mn	4.4	601	561	428	391
Co	3.5	604	564	435	398
Ni	-	607	568	441	403
Zn	-	603	567	434	398[a]
$M(5\text{-}Cl\text{-}7\text{-}I\text{-}OX)_2$					
Mn	5.1	603	566	455	396
Co	4.9	603	561	433	397[b]
Ni	diamagnetic	617	588	513	451
Cu	-	608	579	488	411
Zn	-	601	569	445	396
$M(5,7\text{-}Cl_2\text{-}OX)_2(H_2O)_2$					
Co	3.6	654	593	402	358
Ni	-	656	600	404	362
Zn	-	657	602	399	361
$M(5,7\text{-}Cl_2\text{-}OX)_2$					
Co	3.6	649	595	394	357
Ni	2.4	661	602	397	366
Cu	-	665	608	417	371[c]
Zn	-	649	595	389	354
$M(5,7\text{-}Br_2\text{-}OX)_2(H_2O)_2$					
Co	3.9	645	574	441	342
Ni	-	650	582	450	352
Zn	-	645	575	439	334
$M(5,7\text{-}Br_2\text{-}OX)_2$					
Mn	4.4	637	573	400	339
Co	4.4	640	577	417[d]	351
Ni	diamagnetic	703	606	511	433
Cu	-	660	593	475	375
Zn	-	647[e]	580	443	343

In the spectra of the hydrated and anhydrous chelates of 5,7-di-Br-OX the lower two metal-sensitive bands occur near 350 and above 400 cm^{-1} and are assigned to νM-N. The two νM-O bands are found near 650 and 590 cm^{-1}. All these bands show the usual sensitivity in the Ni(II) spectrum towards replacement of H_2O by pyridine. In the series of anhydrous chelates, Ni(II) is diamagnetic and thus has a square planar structure. All bands assigned in the hydrates to νM-L follow the expected order of Mn<Co<Ni>Cu>Zn. The general increase in νZn-L on dehydration strongly suggests tetrahedral co-ordination.

The chelates of 2-CH_3-5,7-di-Br-OX (except that of Ni(II)) precipitate from aqueous solution as the high spin anhydrous species. Similar steric effects to those observed for the chelates of 2-CH_3-OX probably account for the inability of these compounds to form hydrates. Exceptionally, the Ni(II) compound forms a dihydrate octahedral compound and thus the high spin anhydrous chelate is assumed polymeric 6- co-ordinate. This indicates that the 2-CH_3-OX ligand is unable to enforce a square planar stereochemistry. Thus the Ni(II) ion prefers an octahedral structure with some steric interference to the weakly CFSE - stabilized tetrahedral system. The Co(II) and Zn(II) compounds are, like their 2-CH_3-OX analogues, expected to be tetrahedral while the structure of the high spin Mn(II) chelate is uncertain. The expected order of νM-L for such a series is identical to the Irving-Williams order as was discussed for the 2-CH_3-OX compounds. Five bands following this order are found near 650, 580, 440-500, 380 and 330 cm^{-1}. By comparison with the 5,7-di-Br-OX chelates the two higher bands are νM-O and those in the range 440-500 and near 380 cm^{-1} are assigned to νM-N. The spectra of the bis(aquo) and bis(pyridine) adducts show similar νM-L bands to those above. The band near 330 cm^{-1} in the anhydrous chelates is assigned to a chelate ring deformation since there is no corresponding band in the Ni(II) adducts. The strong band near 535 cm^{-1} is assigned to the C-O deformation mode, the absence of any shift indicating the absence of νM-L coupling.

(iii) Substituent Effects in 8-Quinolinols

The effect of the 2-CH_3 group has already been discussed in Section 4(i). This group is electron donating and yields a stronger M-N bond and hence a higher νM-N compared with the unsubstituted chelate. Its effect on νM-O is small. These results were used as corroboration for the assignment of the higher-frequency metal-sensitive bands to νM-O and the lower-frequency bands to νM-N. Further confirmation of these assignments is provided by comparison of the spectra of the Cu(II) chelates of 5,7-di-Br-OX and its 2-CH_3 analogue (Figure 27 and Table 70). The higher-frequency metal-sensitive bands show little effect from 2-substitution whereas the lower-frequency bands are shifted towards higher frequency by nearly 30 cm^{-1}. This is indicative of the electron releasing nature of the methyl group which increases the donor capacity of the heterocyclic nitrogen atom.

Table 70. Effect of 2-CH_3-substitution on νM-L

Compound	νM-O (cm^{-1})		νM-N (cm^{-1})	
α-Cu(OX)$_2$	632	585	408	332
Cu(2-CH_3-OX)$_2$	634	-	481	359
Cu(5,7-di-Br-OX)$_2$	660	593	475	375
Cu(2-CH_3-5,7-di-Br-OX)$_2$	663	596	503	404

The Cu(II) chelates will be chosen for examining the effects of the halogen substituents since their structures are all expected to be square planar. The spectra, showing the νM-L bands, are depicted in Figure 28. The frequencies of the νM-O bands exhibit an order 5-Cl>5,7-Cl_2>5,7-Br_2>H>5-Cl-7-I. The band near 500 cm^{-1} which has been assigned to νM-L + δC-O shows a roughly similar trend which is indicative of greater νM-O than νM-N character. Since this band is extensively coupled, an exactly similar or as sensitive a trend would not be expected. Since the halogens are substituted in the fused phenyl ring, their primary effect is on the νM-O values. The νM-N bands follow, approximately, an inverse relationship to the trend of the νM-O bands which is interpreted as indicating that the increase in M-O bond strength results in a decrease in M-N bond strength.

The νM-N values for the 7-substituted compounds are considerably higher than those in the unsubstituted chelate. If the above inverse relationship were to be strictly observed, they would be expected below or near the oxinate value. Hence some additional effect would appear to be strengthening the M-N bond. Halogens in the 7-position can enter into direct conjugation with the M-N bond. Since they are π-electron donors, this will lead to an increase in the bond order and thus of νM-N.

In $Cu(5\text{-}Cl\text{-}OX)_2$, the νM-O bands lie well above those in the unsubstituted compound. The lowest-frequency νM-N band follows the inverse relationship by lying below that in the oxinate itself. However, the band at 412 cm^{-1} does not follow this trend and may hence be considered to contain a large amount of νM-O character. The halogen atom withdraws

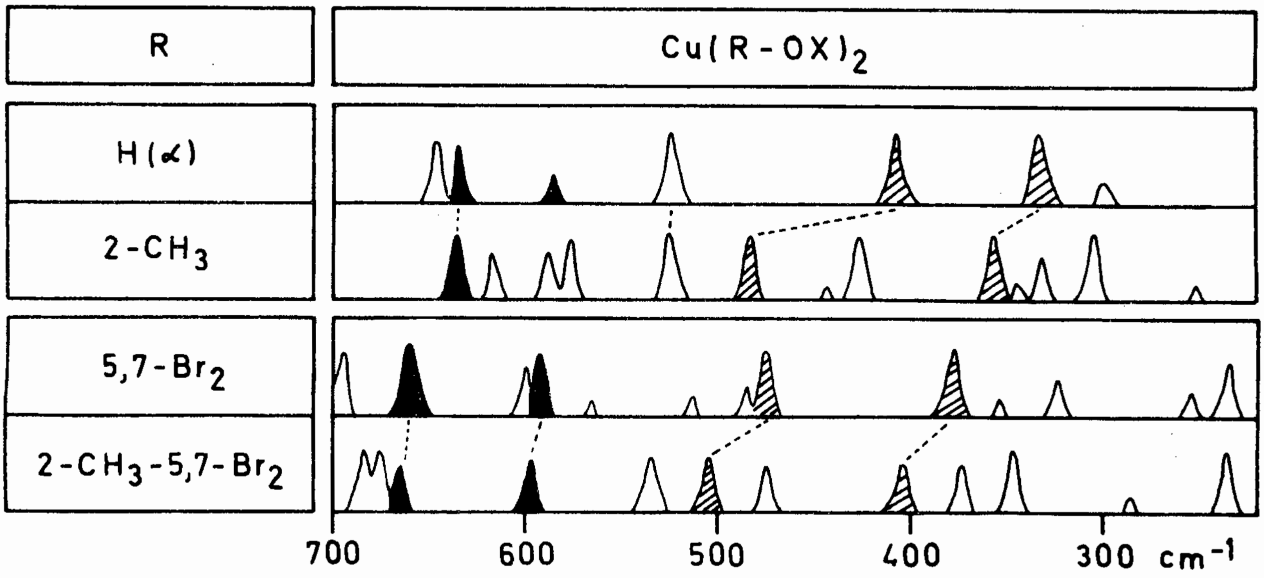


Fig. 27. The effect of 2-methyl-substitution on the IR spectra of the Cu(II) oxinate and 5,7-dibromo-oxinate chelates.

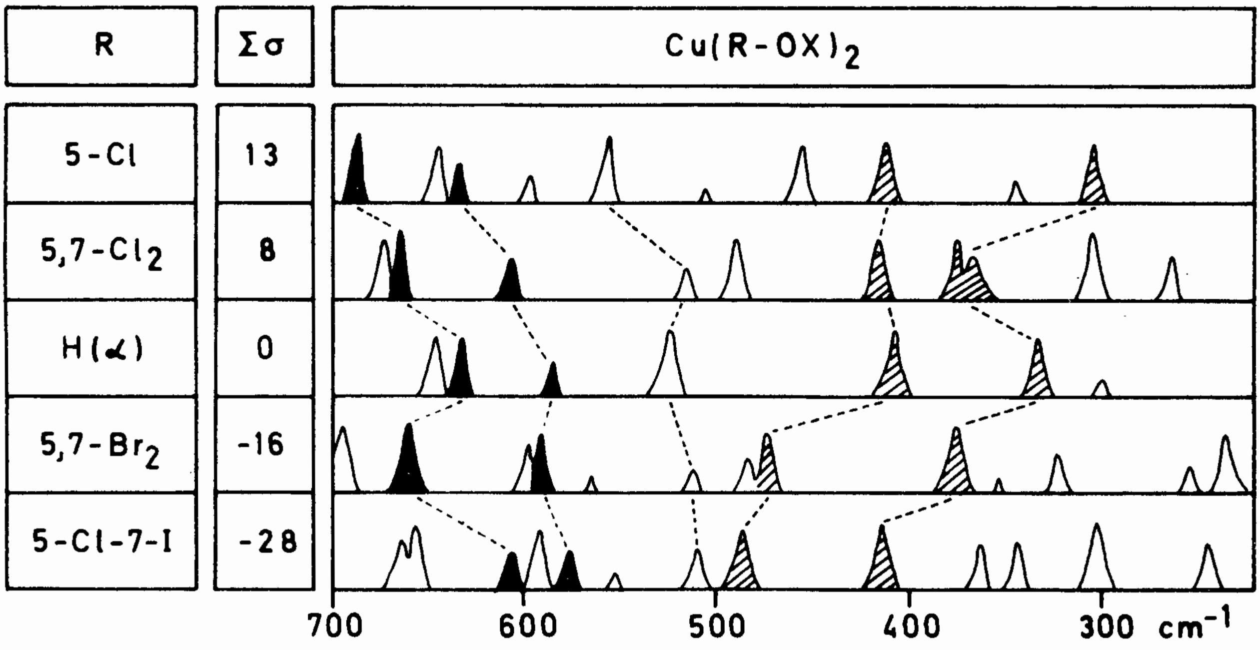


Fig. 28. The effect of halogen-substitution on the IR spectra of Cu(II) oxinates. Solid peaks: νM-O; shaded peaks: νM-N; linked peaks (unshaded): coupled νM-L.

electron density inductively and donates it by resonance *i.e.* it is a σ-acceptor and a π-donor. Generally, the inductive effect is the larger of the two, but since the effect of the halogen is to strengthen νM-O, it would appear that the π-donor effect is outweighing the σ-acceptor effect in this system. The decrease in νM-O values relative to Cu(5-Cl-OX)$_2$ shown on 7- substitution indicate that opposite effects operate in the 7- and 5-positions. Since it has been found that halogens in the *ortho*-position of phenols have little steric effect[214], the halogen in the 7-position must now be acting as an electron withdrawing substituent via its σ-acceptor effect.

The introduction of the halogen substituents into the 8-quinolinol molecule results in a redistribution of electron density. Such changes also influence the M-O and M-N bonds and lead to the variation in νM-L shown above. This electron redistribution results in the shielding or deshielding of the protons in the quinoline ring system. These effects have been observed in the proton magnetic resonance (pmr) spectra of substituted 8-quinolinols and have been shown[215] to correlate with Diehl's additive substituent constants ($\Sigma\sigma$)[216]. These constants were derived by Diehl to account for shifts of bands in the pmr spectra of substituted benzenes[216], each substituent having a separate value for its effect on *ortho*, *meta* and *para* positions. He showed that these effects in disubstituted benzenes are additive and found a correlation between his constants and Hammett's σ_m and σ_p. Using these constants, the electronic effects at the 8-position of the quinoline nucleus can be calculated (Table 71) to give the values +13, +8, -16 and -28 for the substituents 5-Cl, 5,7-di-Cl, 5,7-di-Br and

5-Cl-7-I respectively. The positive signs indicate increased electron density. Hence these constants correctly predict the order of the halogen νM-O values, the highest electron density at position 8 yielding the highest νM-O. The νM-L values of the unsubstituted chelate appear at lower wavenumbers than these constants would predict. This suggests some additional stability associated with the halogeno-compounds. Since these constants have been correlated with Hammett σ values, it indicates that both resonance and inductive effects are operative in substituted 8-quinolinols.

Table 71. Substituent effects in halogen-substituted Cu(II) 8-quinolinolates

Substituent	Diehl's constant (Σσ)	νM-O(cm^{-1})		νM-N(cm^{-1})	
5-Cl	+ 13	683	632	412	303
5,7-Cl_2	+ 8	665	608	417	371[a]
H(α)	0	632	585	408	332
5,7-Br_2	- 16	660	593	475	375
5-Cl-7-I	- 28	608	579	488	411

[a] Mean of bands at 375 and 366 cm^{-1}.

V. REFERENCES

1. B.N. FIGGIS, *Introduction to Ligand Fields*, Interscience, New York, (1966) p.244.

2. C.K. JORGENSEN, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon, London, (1962) P.110.

3. P. GEORGE and D.S. McCLURE, *Progr. Inorg. Chem.*, *1* (1959) 381.

4. R.D. HANCOCK and D.A. THORNTON, *J. Mol. Structure*, *4* (1969) 361.

5. G.C. PERCY and D.A. THORNTON, *J. Mol. Structure*, *10* (1971) 39.

6. R.D. HANCOCK and D.A. THORNTON, *J.S. Af. Chem. Inst.*, *23* (1970) 71.

7. L.G. HULETT and D.A. THORNTON, *Spectrochim. Acta*, *27A* (1971) 2089.

8. C.A. FLEMING and D.A. THORNTON, *J. Mol. Structure*, in press.

9. J.M. HAIGH, R.D. HANCOCK, L.G. HULETT and D.A. THORNTON, *J. Mol. Structure*, *4* (1969) 369.

10. R.D. HANCOCK and D.A. THORNTON, *J. Mol. Structure*, *6* (1970) 441.

11. G.C. PERCY and D.A. THORNTON, *Inorg. Nucl. Chem. Letters*, *7* (1971) 599.

12. G.C. PERCY and D.A. THORNTON, *J. Inorg. Nucl. Chem.*, *34* (1972) 3357.

13. G.C. PERCY and D.A. THORNTON, *J. Inorg. Nucl. Chem.*, *34* (1972) 3369.

14. L.G. HULETT and D.A. THORNTON, *J. Mol. Structure*, *13* (1972) 115.

15. L.G. HULETT and D.A. THORNTON, *Chimia*, *26* (1972) 72.

16. L.P. HAMMETT, *Physical Organic Chemistry*, McGraw-Hill, New York, (1940) p. 184.

17. L.P. HAMMETT, *Chem. Rev.*, *17* (1935) 125.

18. H.H. JAFFE, *Chem. Rev.*, *53* (1953) 191.

19. R.W. TAFT, *J. Amer. Chem. Soc.*, *75* (1953) 4231.

20. R.W. TAFT, in M.S. NEWMAN (editor), *Steric Effects in Organic Chemistry*, Wiley, New York, (1956) p. 591.

21. R.W. TAFT and I.C. LEWIS, *J. Amer. Chem. Soc.*, *80* (1958) 2436.

22. C.G. SWAIN and E.C. LUPTON, *J. Amer. Chem. Soc.*, *90* (1968) 4328.

23. P.J. KRUEGER and H.W. THOMPSON, *Proc. Roy. Soc.*, *234A* (1957) 143.

24. P.J. KRUEGER and D.W. SMITH, *Canad. J. Chem.*, *45* (1967) 1605.

25. P.J. STONE and H.W. THOMPSON, *Spectrochim. Acta*, *10* (1957) 17.

26. H.W. THOMPSON and D.A. JAMESON, *Spectrochim. Acta*, *13* (1958) 236.

27. J.M. HAIGH, N.P. SLABBERT and D.A. THORNTON, *J. Mol. Structure*, *7* (1971) 199.

28. J.M. HAIGH, N.P. SLABBERT and D.A. THORNTON, *J. Inorg. Nucl. Chem.*, *32* (1970) 3635.

29. N.P. SLABBERT and D.A. THORNTON, *Inorg. Nucl. Chem. Letters*, *5* (1969) 921.

30. J.M. HAIGH and D.A. THORNTON, *J. Inorg. Nucl. Chem.*, *33* (1971) 1787.

31. J.M. HAIGH and D.A. THORNTON, *J. Mol. Structure*, *8* (1971) 351.

32. K. NAKAMOTO, *Instrument News*, *20* (1970) 1.

33. K. NAKAMOTO, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Edn., Wiley-Interscience, New York, (1970).

34. M. GOLDSTEIN, E.F. MOONEY, A. ANDERSON and H.A. GEBBIE, *Spectrochim. Acta*, *21* (1965) 105.

35. S. PINCAS, B.L. SILVER and I. LAULICHT, *J. Chem. Phys.*, *46* (1967) 1506.

36. H. JUNGE and H. MUSSO, *Spectrochim. Acta*, *24A* (1968) 1219.

37. S. PINCAS with I. LAULICHT, *Infrared Spectra of Labelled Compounds*, Academic Press, London, (1971).

38. H. IRVING and D.N. EDGINGTON, *J. Inorg. Nucl. Chem.*, *15* (1960) 158.

39. T.V. HEALY, *J. Inorg. Nucl. Chem.*, *19* (1961) 314.

40. J.R. FERRARO and T.V. HEALY, *J. Inorg. Nucl. Chem.*, *24* (1962) 1463.

41. W.R. WALKER and N.C. LI, *J. Inorg. Nucl. Chem.*, *27* (1965) 411.

42. G.N. RAO and N.C. LI, *J. Inorg. Nucl. Chem.*, *28* (1966) 2931.

43. G.N. RAO and N.C. LI, *Canad. J. Chem.*, *44* (1966) 2775.

44. E.W. BERG and J.T. TRUEMPER, *J. Phys. Chem.*, *64* (1960) 487.

45. E.W. BERG and K.P. REED, *Anal. Chim. Acta*, *42* (1968) 207.

46. G. NG and D.E. GOLDBERG, *J. Inorg. Nucl. Chem.*, *29* (1967) 707.

47. L.G. VAN UITERT, W.C. FERNELIUS and B.E. DOUGLAS, *J. Amer. Chem. Soc.*, *75* (1953) 457.

48. L.G. VAN UITERT, W.C. FERNELIUS and B.E. DOUGLAS, A E C Report, *NYO - 626*, March 1, 1951.

49. L.G. VAN UITERT, W.C. FERNELIUS and B.E. DOUGLAS, A E C Report, *NYO - 727*, May 2, 1951.

50. H. IRVING and R.J.P. WILLIAMS, *J. Chem. Soc.*, (1953) 3192.

51. T. SHIGEMATSU, R. WAKE, T. HONJYO and M. MATSUI, *Bull. Inst. Chem. Res. Kyoto Univ.*, *46* (1968) 269.

52. C.H. KE and N.C. LI, *J. Inorg. Nucl. Chem.*, *31* (1969) 1383.

53. R.L. LINTVEDT and H.F. HOLTZCLAW, *J. Amer. Chem. Soc.*, *88* (1966) 2713.

54. M. YAMAZAKI and T. TAKEUCHI, *Kogyo Kagaku Zasshi*, *73* (1970) 2634.

55. A.M. FATTA and R.L. LINTVEDT, *Inorg. Chem.*, *10* (1971) 478.

56. R.L. LINTVEDT and L.K. KERNITSKY, *Inorg. Chem.*, *9* (1970) 491.

57. C.K. MATHEWS, *J. Inorg. Nucl. Chem.*, *31* (1969) 2853.

58. M.P. NOSKOVA and N.N. KAZANOVA, *Zh. Strukt. Khim.*, *10* (1969) 718.

59. K. OHWADA, *J. Inorg. Nucl. Chem.*, *29* (1967) 833.

60. L.J. BELLAMY and R.F. BRANCH, *J. Chem. Soc.*, (1954) 4491.

61. M. YAQUB, R.D. KOOB and M.L. MORRIS, *J. Inorg. Nucl. Chem.*, *33* (1971) 1944.

62. H.F. HOLTZCLAW and J.P. Collman, *J. Amer. Chem. Soc.*, *79* (1957) 3318.

63. R. DUVAL, C. DUVAL and J. LECOMPTE, *Compt. rend.*, *224* (1947) 1632.

64. J. LECOMPTE, *Discuss. Faraday Soc.*, *9* (1950) 125.

65. K. NAKAMOTO and A.E. MARTELL, *J. Chem. Phys.*, *32* (1960) 588.

66. K. NAKAMOTO, P.J. McCARTHY, A. RUBY and A.E. MARTELL, *J. Amer. Chem. Soc.*, *83* (1961) 1066.

67. K. NAKAMOTO, Y. MORIMOTO and A.E. MARTELL, *J. Phys. Chem.*, *66* (1962) 346.

68. M. MIKAMI, I. NAKAGAWA and T. SHIMANOUCHI, *Spectrochim. Acta*, *23* (1967) 1037.

69. G.T. BEHNKE and K. NAKAMOTO, *Inorg. Chem.*, *6* (1967) 433.

70. M.P. NOSKOVA, L.A. GRIBOV and Yu. A. ZOLOTOV, *Zh. Strukt. Khim.*, *10* (1969) 474.

71. F. KASSIERER and A.S. KERTES, *Proc. Int. Conf. Solvent Extraction Chem.* (*5th*), Jerusalem, 1968, publ. 1969, p.305.

72. R.J. SHENNAN, *J. Soc. Chem. Industry*, *61* (1942) 164.

73. S. PRASAD, J.M. RAO and A.R. CHOUDHURG, *Proc. Inst. Chemists* (*India*), *34* (1962) 17.

74. J.V. DUBSKY and J. TRTILEK, *Chem. Listy*, *20* (1935) 76.

75. S.E. LIVINGSTONE, *J. Chem. Soc.*, (1956) 1042.

76. P.O. LUMME, *Suomen Kemi.*, *B31* (1958) 232.

77. P.O. LUMME, *Suomen Kemi.*, *B33* (1960) 85.

78. A. YOUNG and T.R. SWEET, *J. Amer. Chem. Soc.*, *80* (1958) 800.

79. P.O. LUMME, *Suomen Kemi.*, *B33* (1960) 69.

80. P.O. LUMME, *Suomen Kemi.*, *B32* (1959) 253.

81. P.O. LUMME, *Suomen Kemi.*, *B32* (1959) 203.

82. S.S. SANDU, B.S. MANHAS, M.R. MITTAL and S.S. PARMAR, *Indian J. Chem.*, *7* (1969) 286.

83. M.M. STIMSON, *J. Chem. Phys.*, *22* (1954) 1942.

84. A.G. HILL and C. CURRAN, *J. Phys. Chem.*, *64* (1960) 1519.

85. J. SMITH DECKER and H. FRYE, *Z. Naturforschg.*, *B21* (1966) 522.

86. Y. MARIN and C. DUVAL, *Anal. Chim. Acta*, *6* (1952) 47.

87. P. RAY and M.K. BOSE, *Z. Anal. Chem.*, *95* (1933) 400.

88. P. LUMME, *Ann. Acad. Sci. Fenn.*, *AII* (1955) 68.

89. G. THOMAS and R.A. PARIS, *Anal. Chim. Acta*, *25* (1961) 159.

90. G.W.A. FOWLES, R.W. MATTHEWS and R.A. WALTON, *J. Chem. Soc.* (A), (1968) 1108.

91. A. KLEINSTEIN and G.A. WEBB, *J. Inorg. Nucl. Chem.*, *33* (1971) 405.

92. J. AMMETER, *Chimia*, *22* (1968) 469.

93. M.M. RAY, J.N. ADHYA, D. BISWAS and S.N. PODDAR *Austral. J. Chem.*, *19* (1966) 1737.

94. P.O. LUMME, *Suomen Kemi.*, *B30* (1957) 204.

95. P.O. LUMME, *Suomen Kemi.*, *B31* (1958) 294.

96. R. ISAAC, F.F. BENTLEY, H. STERNGLANZ, W.C. COBURN, C.V. STEPHENSON and W.S. WILCOX, *Applied Spectroscopy*, *17* (1963) 90.

97. P.O. LUMME, *Suomen Kemi.*, *B30* (1957) 182.

98. G. D'ASCENZO and W.W. WENDLANDT, *Anal. Chim. Acta*, *50* (1970) 79.

99. P.O. LUMME, *Suomen Kemi.*, *B32* (1959) 198.

100. P.O. LUMME, *Suomen Kemi.*, *B32* (1959) 241.

101. L. SACCONI and R. CINI, *Ann. Chim.*, *42* (1952) 723.

102. P. LUMME, R. VIERTOLA and G. LUNDGREN, *Suomen Kemi.*, *B42* (1969) 270.

103. P. LUMME, G. LUNDGREN and W. MARK, *Acta Chem. Scand.*, *23* (1969) 3011.

104. H. LOISELEUR, G. THOMAS, B. CHEVRIER and D. GRANDJEAN, *Chem. Comm.*, (1967) 182.

105. A. TAKENAKA, H. UTSUMI, N. ISHIHARA, A. FURUSAKI and I. NITTA, *Nippon Kagaku Zasshi*, *91* (1970) 921.

106. E.G. COX, W. WARDLAW, and K.C. WEBSTER, *J. Chem. Soc.*, (1936) 775.

107. A. TAKENAKA, H. UTSUMI, T. YAMAMOTO, A. FURUSAKI, and I. NITTA, *Nippon Kagaku Zasshi*, *91* (1970) 928.

108. R.D. GILLARD, S.H. LAURIE and F.S. STEPHENS, *J. Chem. Soc.* (A), (1968) 2588.

109. R. BERG, *Die Analytische Verwendung von O-Oxychinolin(Oxin) und seiner Derivate*, 2nd ed., F. Enke, Stuttgart, 1938.

110. R.G.W. HOLLINGSHEAD, *Oxine and Its Derivatives*, Vols. I to IV, Butterworths, London, 1954.

111. S. CHABERECK and A.E. MARTELL, *Organic Sequestering Agents*, Wiley, New York, 1959.

112. R.C. HOY and R.H. MORRISS, *Acta Cryst.*, *22* (1967) 476.

113. J.A. BEVAN, D.P. GRADDON and J.F. McCONNELL, *Nature*, *199* (1963) 373.

114. K. FOLTING, M.M. COX, J.W. MOORE and L.L. MERRITT, *Chem. Comm.*, (1968) 1170.

115. C.K. PROUT and A.G. WHEELER, *J. Chem. Soc. (A)*, (1966) 1286.

116. L.L. MERRITT, *Anal. Chem.*, *25* (1953) 718.

117. G.J. PALENIK, *Acta Cryst.*, *17* (1964) 696.

118. G.J. PALENIK, *Acta Cryst.*, *17* (1964) 687.

119. L.L. MERRITT, R.T. CADY and B.W. MUNDY, *Acta Cryst.*, *7* (1954) 473.

120. F. KANAMARU, K. OGAWA and I. NITTA, *Bull. Chem. Soc. Jap.*, *36* (1963) 422.

121. J.E. TACKETT and D.T. SAWYER, *Inorg. Chem.*, *3* (1964) 692.

122. R.G. CHARLES, H. FREISER, R. FRIEDEL, L.E. HILLIARD and W.D. JOHNSTON, *Spectrochim. Acta*, *8* (1956) 1.

123. B.A. KULKARNI and A.J. MUKHEDKAR, *Poona University J. of Sci. and Tech.*, *36* (1969) 21.

124. H.F. ALY, F.M. ABDEL KERIM and A.T. KANDIL, *J. Inorg. Nucl. Chem.*, *33* (1971) 4340.

125. R.J. MAGEE and L. GORDON, *Talanta*, *10* (1963) 967.

126. R.J. MAGEE and L. GORDON, *Talanta*, *10* (1963) 851.

127. R.J. MAGEE and L. GORDON, *Talanta*, *10* (1963) 961.

128. J.P. PHILIPS and J.F. DEYE, *Anal. Chim. Acta*, *17* (1957) 231.

129. K.G. STONE, *J. Amer. Chem. Soc.*, *76* (1954) 4997.

130. N. OHKAKU and K. NAKAMOTO, *Inorg. Chem.*, *10* (1971) 798.

131. R. LARSSON and O. ESKILSSON, *Acta Chem. Scand.*, *22* (1968) 1067.

132. A.R. BURNS, T.J. CARDWELL and R.W. CATTRALL, *Austral. J. Chem.*, *24* (1971) 661.

133. H.H. PERKAMPUS and K. KORTUM, *Z. Anal. Chem.*, *190* (1962) 111.

134. J. MOELLER and A.J. COHEN, *J. Amer. Chem. Soc.*, *72* (1950) 3546.

135. J. MOELLER and F.L. PUNDSACK, *J. Amer. Chem. Soc.*, *76* (1954) 617.

136. L. MORPURGO and R.J.P. WILLIAMS, *J. Chem. Soc. (A)*, (1966) 73.

137. J.C. TOMKINSON and R.J.P. WILLIAMS, *J. Chem. Soc.*, (1958) 1153.

138. O. POPOVYCH and L.B. ROGERS, *Spectrochim. Acta*, *21* (1965) 1229.

139. B.C. BAKER and D.T. SAWYER, *Anal. Chem.*, *40* (1968) 1945.

140. H.R. GERSMANN and J.D. SWALEN, *J. Chem. Phys.*, *36* (1962) 3221.

141. G.F. KOKOSZKA and H.C. ALLEN, *J. Chem. Phys.*, *42* (1965) 3730.

142. A.E. JENKINS, J.R. MAJER and M.J.A. READE, *Talanta*, *14* (1967) 1213.

143. J.R. MAJER, M.J.A. READE and W.I. STEPHEN, *Talanta*, *15* (1968) 373.

144. D.C. PATEL, R.C. SHARMA and P.K. BHATTACHARYA, *J. Indian Chem. Soc.*, *48* (1971) 233.

145. M. SEGUIN, *Compt. Rend.*, *222* (1946) 952.

146. F. BASOLO and W.R. MATOUSH, *J. Amer. Chem. Soc.*, *75* (1953) 5663.

147. G.W. INMAN, W.E. HATFIELD and R.F. DRAKE, *Inorg. Chem.*, *11* (1972) 2425.

148. M.J. FRAZER, G.V. ROBINS and F.B. TAYLOR, *J. Chem. Soc. (A)*, (1969) 2451.

149. A.E. MARTELL, ed., *Special Publication of the Chemical Society No. 25*, The Chemical Society, London, 1971.

150. R.G. CHARLES, *Anal. Chim. Acta*, *27* (1962) 474.

151. W.W. WENDLANDT and G.R. HORTON, *Anal. Chem.*, *34* (1962) 1099.

152. M. BORREL and R. PARIS, *Anal. Chim. Acta*, *5* (1951) 573.

153. M. BORREL and R. PARIS, *Anal. Chim. Acta*, *4* (1950) 267.

154. R.G. CHARLES and A. LANGER, *J. Phys. Chem.*, *63* (1959) 603.

155. R.G. CHARLES, A. PERROTTO and M.A. DOLAN, *J. Inorg. Nucl. Chem.*, *25* (1963) 45.

156. R.H. GORE and W.W. WENDLANDT, *Thermochim. Acta*, *2* (1971) 93.

157. R.H. GORE and W.W. WENDLANDT, *Anal. Chim. Acta*, *52* (1970) 83.

158. C. WOODWARD and H. FREISER, *Anal. Chem.*, *40* (1968) 345.

159. O. NAVRATIL and J. KOTAS, *Collection Czechoslov. Chem. Commun.*, *30* (1965) 1824.

160. D. DYRSSEN, *Svensk. Kem. Tidskr.*, *66* (1954) 234.

161. D. FLEISCHER and H. FREISER, *J. Phys. Chem.*, *63* (1959) 260.

162. R.G. CHARLES, *J. Phys. Chem.*, *61* (1957) 1640.

163. G. GUTNIKOV and H. FREISER, *Anal. Chem.*, *40* (1968) 39.

164. A.R. KATRITZKY and R.A. JONES, *J. Chem. Soc.*, (1960) 2942.

165. C. MANDE and A.R. CHETAL, *Current Science*, *23* (1964) 707.

166. J.C. FANNING and H.B. JONASSEN, *J. Inorg. Nucl. Chem.* *25* (1963) 29.

167. J.R. HUTCHISON, Ph.D.Thesis, Princeton, (1968); Diss. Abstr., *B29* (1969) 2799.

168. P. RAY and D.N. SEN, *J. Indian Chem. Soc.*, *25* (1948) 473.

169. P. SPACU, V. VOICU and I. PASCARU, *J. Chim. Phys.*, *60* (1963) 368.

170. T.S. DAVIS, J.P. FACKLER and M.J. WEEKS, *Inorg. Chem.*, *7* (1968) 1994.

171. W.O. McSHARY and M. CEFOLA, *J. Inorg. Nucl. Chem.*, *31* (1969) 2777.

172. S. LENZER, *J. Chem. Soc.*, *Suppl. 1* (1964) 5768.

173. J.P. FACKLER, *Progr. Inorg. Chem.*, *7* (1966) 361.

174. B. GRANOFF, Ph.D. Thesis, Princeton, (1966); Diss. Abstr., *B 27* (1967) 4341.

175. B.N. FIGGIS and J. LEWIS, *Progr. Inorg. Chem.*, *6* (1964) 37.

176. R.J.H. CLARK and C.S. WILLIAMS, *Inorg. Chem.*, *4* (1965) 350.

177. R.D. HANCOCK, Ph.D. Thesis, University of Cape Town, (1969).

178. L.G. HULETT and D.A. THORNTON, *J. Inorg. Nucl. Chem.*, *35* (1973) 2661.

179. A. FORMAN and L.E. ORGEL, *Mol. Physics*, *2* (1959) 362.

180. A.R. KATRITZKY and A.J. BOULTON, *J. Chem. Soc.*, (1959) 3500.

181. A. HIDALGO, *J. Physique Radium*, *16* (1955) 366.

182. P.J.H. WOLTZ and A.H. NIELSON, *J. Chem. Phys.*, *20* (1952) 307.

183. T. SHIGEMATSU, M. TABUSHI, M. MATSUI and M. MUNAKATA, *J. Bull. Chem. Soc. Jap.*, *41* (1968) 2656.

184. L.J. BELLAMY, *The Infrared Spectra of Complex Molecules*, Methuen, London, (1959).

185. R.D. HANCOCK and D.A. THORNTON, *J. Mol. Structure*, *4* (1969) 377.

186. R.C. ELDER, *Inorg. Chem.*, *7* (1968) 1117.

187. J.T. HASHAGEN and J.P. FACKLER, *J. Amer. Chem. Soc.*, *87* (1965) 2821.

188. S. OOI and Q. FERNANDO, *Chem. Comm.*, (1967) 532.

189. L.G. HULETT and D.A. THORNTON, *Spectroscopy Letters*, *5* (1972) 323.

190. G.C. PERCY, Ph.D.Thesis, University of Cape Town, (1972).

191. I.N. MAROV, O.M. PETRUKHIN, V.V. ZHUKOV, V.N. RUDIN, Yu.N. DUBROV, Yu. A. ZOLOTOV and A.N. ERMAKOV, *Zh. Neorg. Khim.*, *15* (1970) 2716.

192. L.G. HULETT and D.A. THORNTON, *Spectrochim. Acta*, *29A* (1973) 757.

193. K. NAKAMOTO, Y. MORIMOTO and A.E. MARTELL, *J. Amer. Chem. Soc.*, *83* (1961) 4528.

194. R.G. INSKEEP, *J. Inorg. Nucl. Chem.*, *24* (1962) 763.

195. J.S. STRUKL and J.L. WALKER, *Spectrochim. Acta*, *27A* (1971) 209.

196. M.A. DOSKEY and C. CURRAN, *Inorg. Chem. Acta*, *3* (1969) 169.

197. B.W. LOW, F.L. HIRSHFELD and F.M. RICHARDS, *J. Amer. Chem. Soc.*, *81* (1959) 4412.

198. J. FUJITA, K. NAKAMOTO and M. KOBAYASHI, *J. Amer. Chem. Soc.*, *78* (1956) 3295.

199. L. SACCONI and A. SABATINI, *J. Inorg. Nucl. Chem.*, *25* (1963) 1389.

200. E. SPINNER, *J. Chem. Soc. (B)*, (1967) 874.

201. C.A. McAULIFFE and W.D. PERRY, *J. Chem. Soc. (A)*, (1969) 634.

202. T.J. LANE, J.A. DURKIN and R.J. HOOPER, *Spectrochim. Acta*, *20* (1964) 1013.

203. M.V. VEIDIS, G.H. SCHREIBER, T.E. GOUGH and G.J. PALENIK, *J. Amer. Chem. Soc.*, *91* (1969) 1859.

204. F.S. STEPHENS, *J. Chem. Soc. (A)*, (1970) 2377.

205. S.C. CHANG, J.K. MA, J.T. WANG and N.C. LI, *J. Coord. Chem.* *2* (1972) 31.

206. J.L. WOOD and M.M. JONES, *J. Phys. Chem.*, *67* (1963) 1049.

207. C. FURLANI, *Co-ord. Chem. Rev.*, *3* (1968) 141.

208. A. SABATINI and L. SACCONI, *J. Amer. Chem. Soc.*, *86* (1964) 17.

209. O. POPOVYCH and L.B. ROGERS, *Spectrochim. Acta*, *16* (1960) 49.

210. H. IRVING and L.D. PETTIT, *Proc. Intern. Symp. Anal. Chem.*, Birmingham University, Birmingham, England, (1962) 122, Publ. 1963.

211. B.F. HOSKINS and F.D. WILLANS, *Co-ord. Chem. Rev.*, *9* (1972) 365.

212. L. SACCONI, *Pure Appl. Chem.*, *17* (1968) 96.

213. M.R. CHAKRABARTY, E.S. HANRAHAN and A.R. LEPLEY, *Tetrahedron*, *23* (1967) 2879.

214. D.H. McDANIEL and H.C. BROWN, *J. Amer. Chem. Soc.*, *77* (1955) 3756.

215. E.S. HANRAHAN and M.R. CHAKRABARTY, *J. Magn. Resonance*, *2* (1970) 19.

216. P. DIEHL, *Helv. Chim. Acta*, *44* (1961) 829.