Abstract

Certain α-diketones condense with o-aminophenol to form 2,2'-(substituted)-bibenzoxazolines. Of these only the unsubstituted compound undergoes rearrangement (under ordinary conditions) in the presence of metal ion to form Schiff base chelate. Successful methods have been developed in the present investigation to form metal chelates with the 2,2'-substituted bibenzoxazolines. Additionally, metal chelates of 2,2'-(substituted)-binaphthoxazinines and certain α -dianils of N-methyl or N-phenyl-o-phenylenediamine were also synthesized.

These studies indicate that the inability of 2,2'-(substituted)-bibenzoxazolines to undergo rearrangement and hence to form Schiff base chelates is not due to steric hindrance between the substituted groups as was previously thought, but rather due to electronic factors.

Physicochemical investigations (electronic, vibrational, n.m.r. spectroscopy; mass spectrometry; vapour pressure osmometry and magnetic measurements) on a large number of metal chelates with tridentate Schiff bases such as salicylaldehyde-2-mercaptoanil, acetylacetone-mono-(2-hydroxyanil), etc., have indicated oxygen or sulfur bridged binuclear structure for all the chelates studied. Previously, X-ray structure analysis had established the binuclear structure for a few of these chelates.

Substituted pyridine N-oxides form a variety of

complexes with copper (II) which have varied composition and structural pattern. Low frequency i.r. spectra make it possible to distinguish the different structures.

The metal-oxygen stretching frequencies in 1:4 complexes were found to correlate with substitution parameters and acid dissociation constants of the substituted pyridine N-oxides.

The lowering of magnetic moment in the 1:1 complexes was found to be a function of the bridge metal-oxygen stretching frequencies. A higher stretching frequency seemed to facilitate the antiferromagnetic exchange interaction between the two copper ions in these binuclear complexes. This phenomenon can be explained in terms of Anderson's theory of superexchange.

Metal Complexes of Schiff Bases and Pyridine N-oxides

by Abdul Malek

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List of Symbols and Abbreviations

AAP	acetylacetone-mono-(2-hydroxyanil)
AASP	acetylacetone-mono-(2-mercaptoanil)
Anal.	analysis
A	angstrom
Calcd.	calculated
cm	centimeter
DMSO	dimethyl sulfoxide
i.r.	infrared
M	molarity or metal
ml	milliliter
mol	mole
m.p.	melting point
μ_{eff}	magnetic moment
n.m.r.	nuclear magnetic resonance
ν	frequency in wave numbers or stretching vibrations
obs.	observed
ϕ phi	phenyl group
$pK_{BH^+_z}$	Conjugate acid dissociation constant for substituted pyridine N-oxide
Py	Pyridil group or pyridine
PyO	Pyridine N-oxide
ppm	parts per million
SAP	salicylaldehyde-2-hydroxyanil
SASP	salicylaldehyde-2-mercaptoanil
σ sigma	substitution parameter
u.v.	ultraviolet

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Statement of Claims to Original Research

1) Synthesis of new metal chelates:

a) In spite of previous claims to the contrary, the reaction of 2,2'-(substituted)-bibenzoxazolines (I) with metal ions leading to tetradentate Schiff base chelates was successfully carried out in the present study.

b) 2,2'-(substituted)-binaphthoxazinine (II) and α-dianils of N-methyl or N-phenyl-o-phenylenediamine and some of their nickel chelates were also synthesized for the first time.

c) The successful preparation of all the above-mentioned chelates invalidates the previous hypothesis that (I) do not rearrange and do not form metal chelates because of steric hindrance between the substituted groups in the 2 and 2' positions.

2) Structure of Tridentate Schiff base metal chelates

a) A large number of metal chelates of salicylaldehyde-2-hydroxyanil (SAP), salicylaldehyde-2-mercaptoanil (SASP), acetylacetone-mono-(2-hydroxyanil) (AAP), and acetylacetone-mono-(2-mercaptoanil) (AASP) have been prepared. Physicochemical investigations (electronic, vibrational, n.m.r. spectroscopy; mass spectrometry, vapor pressure osmometry and magnetic measurements) have indicated oxygen or sulfur-bridged binuclear structure for all of the chelates studied. Previously, X-ray crystal structure analysis and magnetic measurements had established the binuclear structure for a very few of these chelates.

b) Low frequency i.r. and Raman spectra of these metal chelates have been recorded and tentative assignments for some metal-ligand vibrations made.

3) Properties of Copper (II) Complexes with Pyridine N-oxides:

a) The low frequency i.r. spectra of a number of 1:1, 1:2 and 1:4 complexes of copper (II) with 4-substituted pyridine N-oxides have been recorded and their metal-halogen and metal-oxygen stretching frequencies assigned.

b) The metal-oxygen stretching frequencies in 1:4 complexes were found to correlate with substitution parameters and acid dissociation constants of the pyridine N-oxides.

c) The lowering of magnetic moment in the 1:1 complexes was found to be a function of bridge metal-oxygen stretching frequencies. A higher stretching frequency seemed to facilitate the antiferromagnetic exchange interaction between the two copper ions in these binuclear complexes. This phenomenon can be explained in terms of Anderson's theory of superexchange.

CHAPTER I

GENERAL INTRODUCTION

The condensation of primary amines with active carbonyl compounds forms a class of compounds known as Schiff bases, which contains the characteristic azomethine or imino group ($> C=N-$). The Schiff bases are known to be potential donor ligands; the most effective one usually bears a functional group sufficiently close to the imino group so that upon reaction with a metal ion a five or six membered chelate ring can be formed.

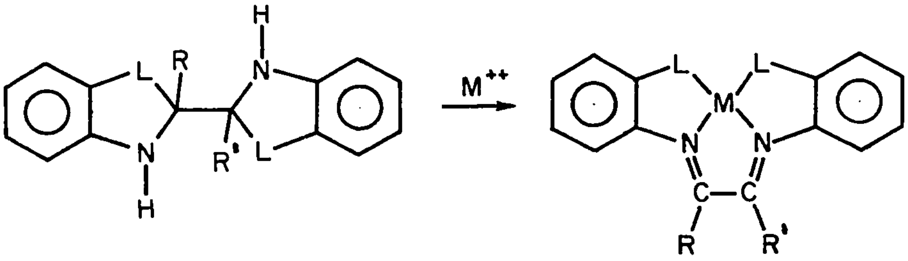
The easy mode of the reaction and great synthetic flexibility make possible the formation of many ligands of diverse chemical nature. Consequently metal complexes of Schiff bases have occupied a central role in the development of co-ordination chemistry. The huge number of publications ranging from purely synthetic to modern physico-chemical to biochemically relevant studies of these complexes bear testimony to their importance. This subject has been treated in some recent books(1) and reviews.(2,3,4,5,6,7)

A) Role of metal ion in Schiff condensation reactions and quadridentate Schiff base chelates:

In recent years much attention has been given to the role a metal ion often plays in the condensation reactions.(2,6,7) These reactions are of intrinsic interest but their investigation has been stimulated by the implications for chemical synthesis, catalysis, and analytical or biological applications.

Using the so-called "co-ordination template reaction" involving a metal ion, various polycyclic ligands have been synthesized,(8,9) some of which bear close resemblance to compounds of biological interest, e.g. porphyrins.

It has been shown(2,7) that the metal ions mediate the condensation of α-diketone with o-hydroxy, o-amino, o-mercaptoamines and β-mercaptoethylamines. The most significant feature of this reaction is that it results in stabilization of the Schiff bases by the agency of complexation with the metal ions, in the absence of which heterocyclic compounds would have formed. In certain cases a metal ion induces rearrangement of the heterocyclic compound to the corresponding Schiff base and forms a chelate,(10,11,12,13) scheme I.



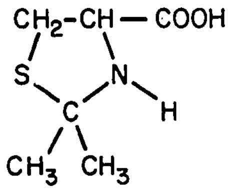
Scheme I

L = sulfur or oxygen atoms

A study of these systems is of importance both from the point of view of theoretical interest and practical application.

The inherent specificity of this rearrangement reaction towards certain metal ions and its dependence on pH provide a versatile set of conditions for effecting the selective separation of metal ion mixtures from solutions.(13)

The treatment of Wilson's disease(14) with 2,2-dimethylthiazolidine-4-carboxylic acid (I) is thought(15) to involve such a metal ion induced rearrangement and subsequent chelate formation.



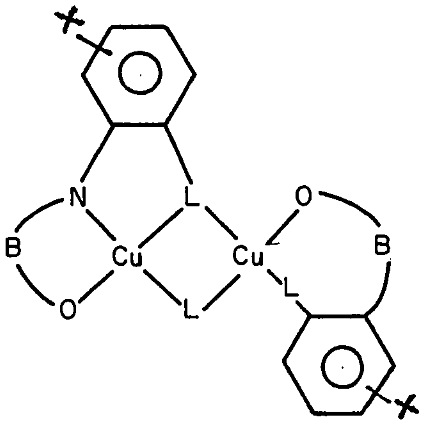
I

B) Tridentate Schiff Base Chelates

Unlike the reaction of o-aminophenol with α-diketones, its condensation with aldehydes such as salicylaldehyde and other diketones such as acetylacetone results in the formation of non-heterocyclic compounds which act as tridentates and easily react with metal ions to form chelates. O-aminothiophenol also reacts with these aldehydes and ketones, but with the formation of heterocyclic thiazolines(16) which, however, undergo rearrangement in the presence of metal ions and also act as tridentates.(17)

Recently there has been considerable interest in the metal chelates of these tridentate Schiff bases for the following two reasons:

i) The binuclear nature of their structures(18,19) (II) in which the two monomeric units are linked through oxygen or sulfur bridging atoms, II



where X and B are generalized ring and bridging group substituents respectively and L = oxygen or sulfur atoms.

ii) The subnormal magnetic properties of the oxygen bridged copper (II) chelates.

Although no elaborate structural studies have been carried out on the individual chelates, it has been assumed that all these chelates have binuclear structure and discrete tricoordinate metal chelates derived from these Schiff bases do not exist.(2)

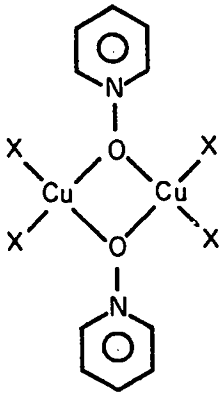
The electronic spectra and the temperature dependence of the magnetic susceptibilities of the binuclear copper (II) complexes have been interpreted in terms of an antiferromagnetic spin-spin coupling occurring via a super-exchange through the orbitals of the bridging oxygen atoms.(18,20,23,142)

Although a clear understanding of the mechanism of this super-exchange is at present lacking,(21) it would certainly involve the bridging M-O bonds through which such an exchange must function. The extent of magnetic exchange should therefore somehow be associated with the $M{<}^{O}_{O}{>}M$ bridge metal-ligand vibrational frequencies and their correlation with the magnetic properties should, therefore, be very interesting and be helpful in understanding the process of super-exchange. So far no attempt has been made in this direction.

C) Copper (II) Complexes of Aromatic N-oxides

Aromatic N-oxides such as pyridine or quinoline N-oxides also form oxygen-bridged binuclear complexes with copper (II) halides (III) and have subnormal magnetic moments involving spin-spin interaction via a super-exchange mechanism.(22,23)

III



For a study of vibrational spectra and its correlation with magnetic properties, the pyridine N-oxides - copper halide system is a logical first choice in preference to the tridentate Schiff base chelates because of the non-rigidity and simplicity of the structures of the former system.

Moreover, the copper-copper internuclear distance of 3.30 Å in the binuclear pyridine N-oxide complexes(24,25) is more than that observed (2.99 Å) in the tridentate Schiff base chelates.(18) Therefore the super-exchange process should be less complicated by direct copper-copper interaction in the case of pyridine N-oxide complexes.

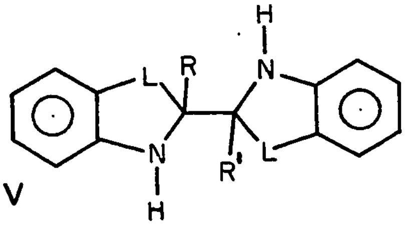
CHAPTER II

THE ROLE OF METAL ION IN MOLECULAR REARRANGEMENT AND QUADRIDENTATE SCHIFF BASE CHELATES

A) Introduction:

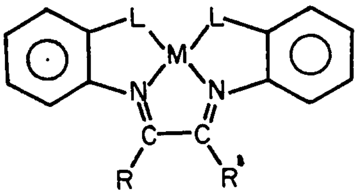
The fact that a metal ion often plays an important role in affecting the course and nature of a chemical reaction is well known. There is little doubt that σ, π, or delocalized bonding of some sort between molecules (both organic and inorganic), atoms, and transition metals at surfaces or in complex species in solution is an essential of all catalytic reactions.

It has been shown(10-18) during recent years that metal ions change the nature of the condensation product of α-diketones with o-hydroxy, o-mercaptoamines and β-mercaptoethylamine. In the absence of metal ions, the condensation product is exclusively heterocyclic (IV). But the presence of metal ions results in stabilization of the Schiff base (V) through complex formation.



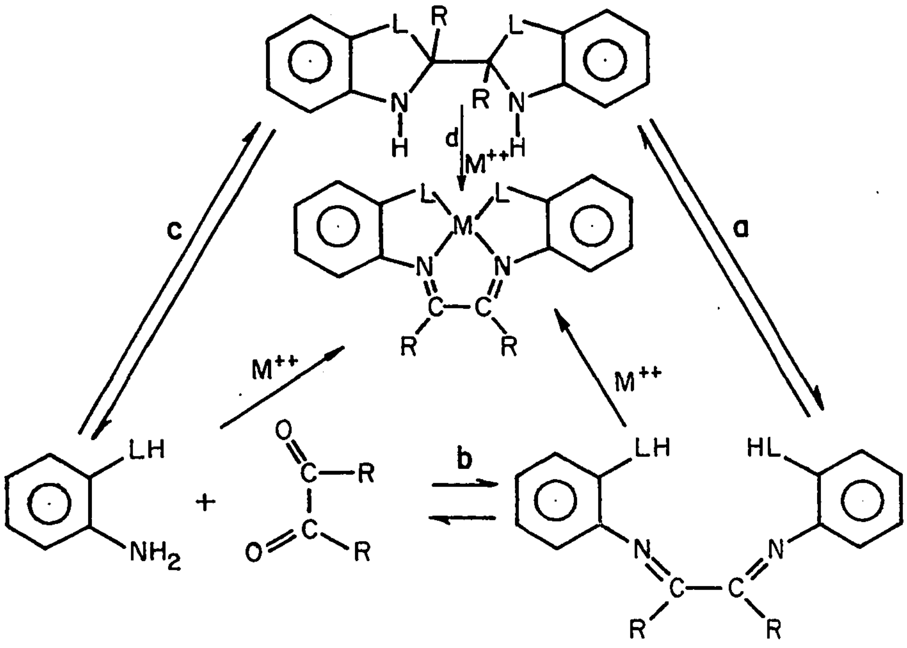
IV

V



The exact manner in which such an effect occurs is of considerable significance. In this regard a number of possibilities can be considered. i) If an equilibrium, a, exists between the heterocycles and the Schiff base, the formation of a stable metal complex could occur with the latter.

ii) These systems can involve sequestration of the product of an equilibrium, b, which would in the absence of the metal ion go on to the formation of a different final product; this essentially involves stabilization of an intermediate in a thermodynamically directed process. iii) If an equilibrium, c, exists between the heterocycle and the two starting materials, these could react with the metal ion in a stepwise manner to give the Schiff base chelate. iv) The metal ion can react directly with the heterocycle along path d, inducing a rearrangement which can result in the final product. These processes are shown in scheme II.



Scheme II

where L = oxygen or sulfur

R = H, CH_3, Φ or Py

Jadamus et al.(26) have shown recently from kinetics studies that these heterocyclic compounds (with L = sulfur atoms) react with various metal ions which involve paths (i), (ii), and (iv). No case of path (iii) was observed.

It has been shown(26,27) that the sulfur analogs of structural type (IV) undergo metal ion induced rearrangement more readily than the oxygen analogs. Metal chelates of the thio analog of (IV) in which R and R' are different substituted groups were isolated. But the oxygen analog reacts with metal ions only when R = R' = H. This is surprising, because one would expect the C-S bond rupture to be more difficult than that of the C-O bond. For example, the condensation product of o-aminothiophenol with salicylaldehyde is the heterocyclic benzthiazoline whereas that of o-aminophenol is a Schiff base (chapter III of this thesis). No chelates of the oxygen analog of structural type (V) with R and R' groups other than hydrogen atoms have been reported and no satisfactory explanation exists why those compounds do not form chelates. Bayer et al.(12,13) explained this lack of chelate formation by assuming that there is steric hindrance between the substituted groups which destabilizes the chelate.

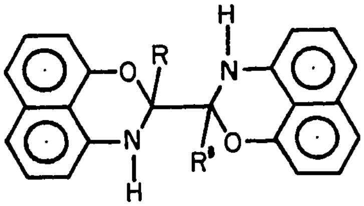
But from an examination of models it seems highly unlikely that steric hindrance between the substituted groups is a major factor which can account for such a striking difference in reactivity of these compounds.

The metal chelates of structural type (V) in which

L = N - R" (R" = H, CH_3, C_6H_5, etc.) have not yet been reported. It was felt that a comparison of the physico-chemical properties of the chelates of structural type (V) where L = S, O, or N - R" would provide an understanding of the differences in the reactivities of the parent ligand molecules.

Naphthaoxazinines (VI) provide a case analogous to that of structural type (IV)

VI



but with the difference that in the former case a six membered heterocyclic ring is involved. It would be of further interest to study the reactivity of these compounds with metal ions and compare them with those of structural type (V).

B) Experimental

1) Materials: -

O-aminophenol obtained from Eastman Organic Chemicals was recrystallized from ethanol before use. N-methyl-o-phenylenediamine monohydrochloride (Eastman), N-phenyl-o-phenylenediamine (Eastman), Glyoxal, 40% aqueous solution (Fisher Scientific Company), Pyruvaldehyde, 40% aqueous solution (J. T. Baker Chemical Co.), Diacetyl (Fisher), Benzil (Eastman), and 2,2'-Pyridil (Aldrich Chemical Co. Inc.) were used without further purification. 8-amino-1-naphthalenesulfonic acid obtained from Eastman was used for the preparation of 8-amino-1-naphthol hydrochloride without prior purification. Nickel chloride hexahydrate and nickel acetate tetrahydrate were obtained from Fisher. Deuterated water, chloroform and dimethyl sulfoxide were obtained from Stohler Isotope chemicals.

2) General methods of preparation: -

i) Benzoxazolines and their chelates: Benzoxazoline and its 2,2'-mono or disubstituted analogs were prepared by the method described by Murase.(28) They were recrystallized from ethanol.

The nickel chelates of these compounds were obtained by the following procedure:

After 0.01 mole of the ligand was dissolved in 50 ml of dry acetone, the solution was shaken in a stoppered flask in the presence of solid sodium hydroxide pellets for 24 hours, Immediately after the addition of the pellets, a red/yellow color began to appear slowly. Fine particles of the di-sodium salt of the Schiff base were easily separated from the sodium hydroxide pellets by decantation and subsequent filtration. The yellow disodium salt was very unstable in water and alcohols. The nickel chelate was obtained by direct addition of the crude sodium salt to ethanolic solution of nickel chloride (0.01 moles) with vigorous stirring. On addition of water to the ethanol solution the blood-red chelate was precipitated. This was filtered, washed with water and then acetone. Recrystallization from ethanol yielded the pure compound which was dried under vacuum over P_2O_5.

The nickel chelate of 2,2'-bibenzoxazoline was also prepared by direct reaction of nickel acetate with the ligand in ethanol solution as described by Bayer.(12) Both the methods of preparation yielded identical compounds.

ii) Naphthoxazinines and their chelates:

2,2'-naphthoxazinines were prepared by the condensation of 8-amino-1-naphthol with α-diketones in 1:2 molar ratio. 8-amino-1-naphthol hydrochloride was obtained from 8-amino-1-naphthalene sulfonic acid by an alkali fusion reaction.(29) The following procedure was used for the preparation of naphthoxazinines:

0.02 moles of 8-amino-1-naphthol hydrochloride was dissolved in 100 ml water which was previously boiled and cooled to 70° C. To this solution a slight excess of the calculated amount of sodium acetate was added to neutralize the acid. 0.01 moles of the α-diketone dissolved in a little water was then added to the 8-amino-1-naphthol solution and the mixture held at this temperature with occasional shaking for about an hour. Precipitates were either immediately or gradually formed. After cooling they were filtered and washed with water. Recrystallization from ethanol yielded pure compounds.

The nickel chelates of 2,2'-binaphthoxazinine were obtained by the reaction of the ligand with nickel acetate. 0.01 moles of the ligand was dissolved in 30 ml ethanol. After 0.01 moles of nickel acetate dissolved in 50 ml of ethanol was added, the mixture was refluxed for one hour. A dark green product formed. This was filtered and recrystallized from dichloromethane by using a Soxhlet extraction system.

iii) Condensation products of α-diketones with N-methyl or N-phenyl-o-phenylenediamine and their chelates.

A solution of 0.02 moles of N-methyl or N-phenyl-o-phenylenediamine in water or ethanol was cooled in an ice bath. 0.01 moles of the diketone dissolved in water or ethanol was then added slowly with stirring to the amine solution over a period of one hour. The precipitate of Schiff base appeared gradually. The reaction mixture was left stirring overnight. The resulting Schiff base was collected by filtration and was recrystallized from ethanol.

The nickel chelates of these Schiff bases were prepared by using either one of the following two methods: -

Method A: A mixture of 0.02 moles of N-methyl or N-phenyl-o-phenylenediamine and 0.01 moles of the α-diketone dissolved in 50 ml of acetone was placed in a stoppered flask. 0.01 moles of nickel chloride dissolved in 20 ml of 1:1 ammoniacal solution was added and the contents were allowed to stand at room temperature with occasional stirring for about a week. Red or green colored chelates were formed slowly. At the end of the reaction the volume of the solution was reduced by evaporation to increase the yield. After collection by vacuum filtration, the chelate was purified by repeated recrystallization from ethanol-water mixture.

Method B: This method is essentially the same as the previous one, except that the reaction of the metal ion was carried out directly with the Schiff base. The Schiff base was obtained by a separate preparation. Both the methods provided the same chelate.

3) Analyses: -

Microanalyses for carbon, hydrogen and nitrogen were performed by Scandinavian Microanalytical Laboratory, Box 25, 2730 Herlev- DK, Denmark.

Nickel was determined by EDTA titrimetric method (30,31) after the sample had been "dry ashed" at 600° C. for one hour and dissolved in dilute hydrochloric acid. Results of analyses are shown in Table (I).

Table I

Analytical Data for Tetradentate Chelates and the Ligands

Compound	% Carbon		% Hydrogen		% Nitrogen		% Nickel	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$C_{14}H_{12}N_2O_2$	69.9	70.0	5.1	5.0	11.6	11.6		
$C_{14}H_{10}N_2O_2Ni\cdot 2H_2O$	49.8	50.5	4.0	4.2	8.3	8.4	18.0	17.6
$C_{15}H_{14}N_2O_2$	70.3	70.9	5.5	5.6	11.0	11.0		
$C_{16}H_{16}N_2O_2$	70.9	71.6	6.1	6.0	9.9	10.4		
$C_{16}H_{14}N_2O_2Ni\cdot 2H_2O$	54.1	53.2	4.9	5.0	7.6	7.8	15.8	16.3
$C_{16}H_{14}N_2O_2Cd\cdot 2H_2O$	45.5	46.3	4.4	3.9	6.4	6.7		
$C_{16}H_{16}N_4Ni\cdot 2H_2O$	67.0	66.0	6.0	5.5	-	10.6		
$C_{21}H_{18}N_2O_2$	76.2	76.3	5.6	5.5	8.5	8.5		
$C_{22}H_{14}N_2O_2Ni\cdot 2H_2O$	60.7	61.0	4.0	4.2	5.8	6.5		
$C_{26}H_{20}N_4Ni\cdot 2H_2O$	64.2	64.9	6.0	5.0	17.1	11.2		
$C_{26}H_{22}N_6Ni\cdot 2H_2O$	60.9	60.8	4.5	5.1	14.3	16.4	11.4	11.5
$C_{28}H_{26}N_4$	79.3	80.7	6.1	6.3	13.3	13.0		

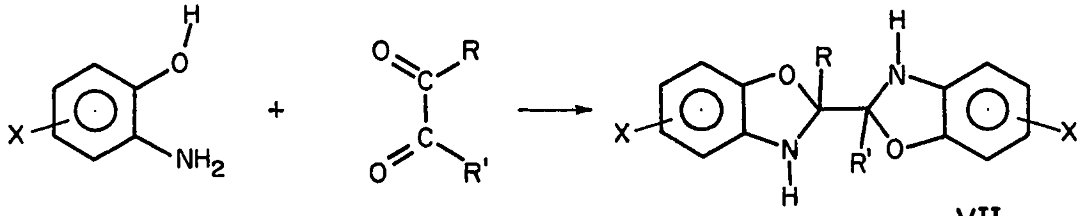
4) Spectroscopic measurements: -

Same as described in Chapter III, section B (d).

C) Results and Discussion

1) Structures of the free ligands:

It has been reported(28) previously that the di-condensations of o-aminophenols with α-diketones result in the formation of heterocyclic compounds, scheme (III), (VII).

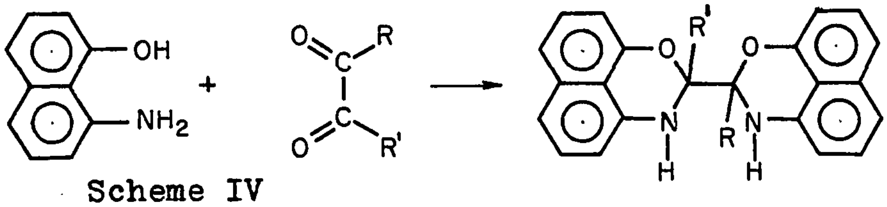


Scheme III

VII

Although in some restricted cases(10) it is possible to isolate the intermediate Schiff bases, in most cases the heterocyclic compound (VII) is the only product.

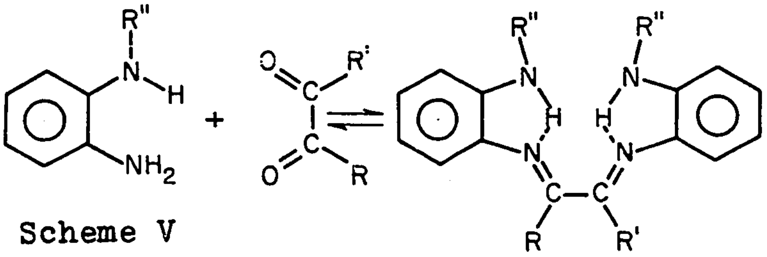
8-amino-1-naphthol was found in the present study to condense with α-diketones forming exclusively the heterocycle naphthoxazinine, scheme IV, structure (VI).



Scheme IV

VI

Unlike the previous two cases, two moles of N-methyl- and N-phenyl-o-phenylenediamines were found to condense with α-diketones giving yellow colored Schiff bases, scheme V, structure VIII.



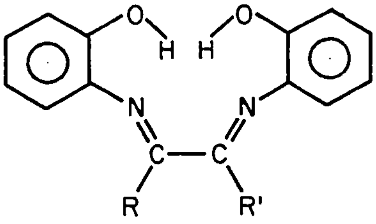
Scheme V

VIII

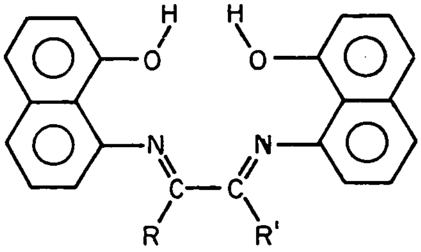
Physicochemical evidence in favour of structures VI and VIII and additional evidence supporting structure VII are discussed under the heading of the following physical methods. The results are summarized in Table (II) and Table (III).

i) i.-r. spectra:

All the above three types of compounds have a characteristic sharp band around 3300 cm^{-1} - see Table (II). This band is absent in the corresponding metal chelates - Fig. (1). In his investigations with 2,2'-bibenzoxazoline compounds, structure VII, Murase(28) assigned this band to N-H stretching frequency. The presence of this sharp band in the condensation products of 8-amino-1-naphthol with α-diketones indicates that the resultant compounds have the heterocyclic structure VI. No broad O-H stretching band in the high frequency region was observed in the spectra of these compounds. This indicates the absence of possible Schiff base forms (IX) and (X).



IX



X

Figure 1

Comparison of High Frequency (4000-1500 cm^{-1}) i.r. Spectra of Nickel Tetradentate Chelates and the Corresponding Free Ligands

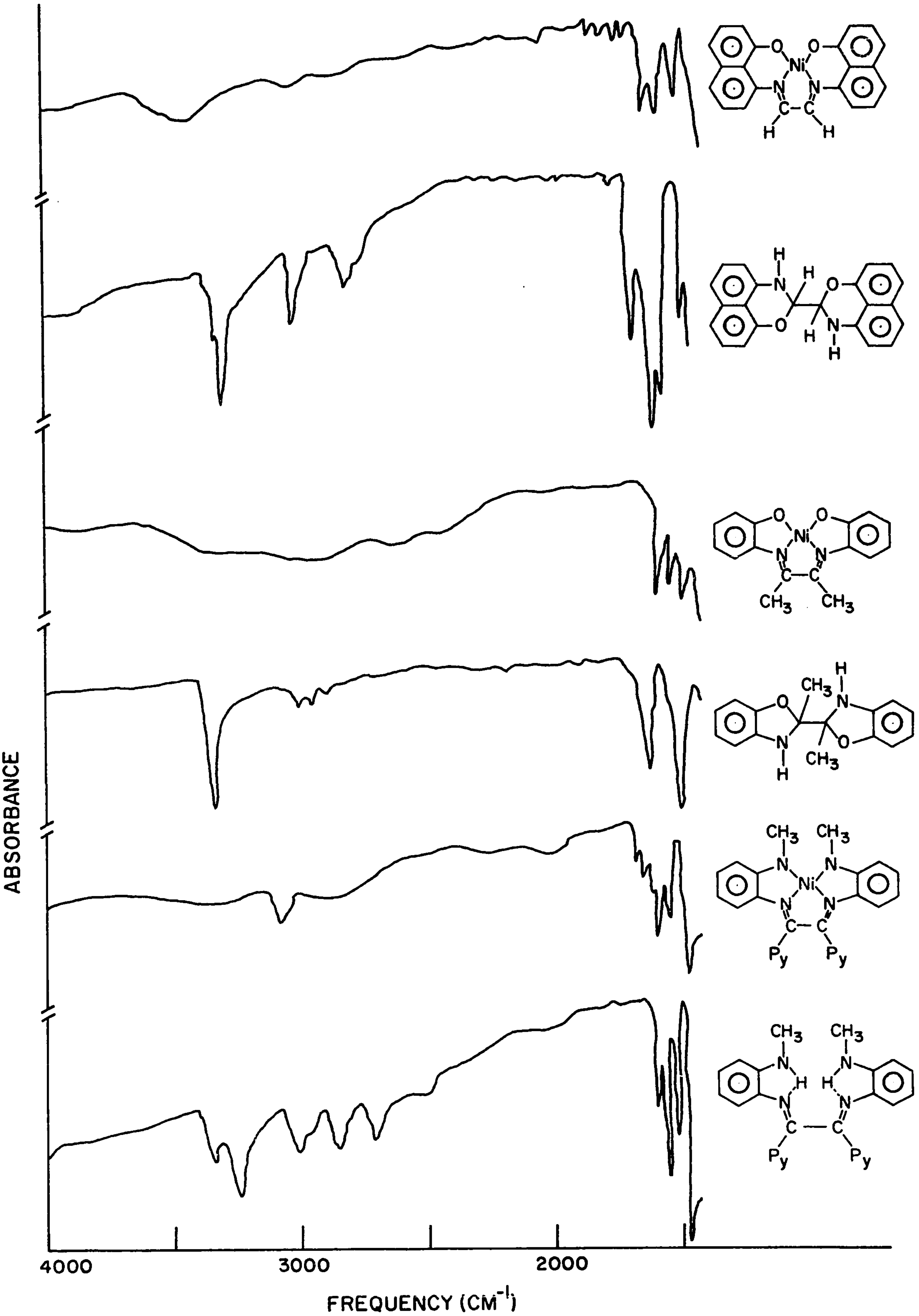

ABSORBANCE
FREQUENCY (CM^{-1})
4000
3000
2000
Ni
O
N
C
H
CH$_3$
Py

Table II

Certain Significant i.r., u.v., and n.m.r. Spectral Bands in the Compounds of Structural Type VI_x, VII_x and $VIII_x$.

Compound	R	R'	R"	n.m.r. Peaks (δ p.p.m.) N-H or N-CH_3	n.m.r. Peaks (δ p.p.m.) C-H or CH_3	i.r. bands N-H Str. (cm^{-1})	u.v. bands ($m\mu$)
VI A	H	H		7.18^{b}	5.24^{b}	3340^{s}	323^{s}, 336^{s}
VI B	CH_3	CH_3			1.48^{b}	3375^{s}	325^{s}, 336^{s}
VII A	H	H		7.20"	5.25"	3380^{s}	237^{s}, 293^{s}
VII B	H	CH_3		7.09' 7.18"	1.25' 5.00"	3340^{s} 3425^{m}	235^{s}, 294^{s}, 378^{w}
VII C	CH_3	CH_3		7.17'	1.29'	3335^{s}	236^{s}, 293^{s}
VIII C	ϕ	ϕ	CH_3	2.34' 3.95'		3350^{m}, 3325^{s}	315^{s}, 253^{s}
VIII D	Py	Py	CH_3	2.64' 4.35'		3350^{m}, 3270^{s}	314^{s}, 252^{s}

' = singlet, " = doublet, b = broad, s = strong, m = medium
w = weak, ϕ = phenyl group, Py = Pyridyl group

Table III

Principal Peaks in the Mass Spectra of Compounds of Structural Type VI_x, VII_x, and $VIII_x$.

Compound	R	R'	R"	m.p.	m/e (%)
VI A	H	H		215° C	340(30),208(5),171(90),170(100)
VI B	CH_3	CH_3		259-261° C	368(5),367(8),185(21),184(100),183(100)
VII A	H	H		210-212° C	240(5),239(22),238(100),133(70),120(97)
VII B	H	CH_3		191° C	254(100),147(88),146(88),134(90),120(73)
VII C	CH_3	CH_3		241° C	268(40),161(100),146(31),134(63)
VII D	CH_3	Φ		220-221° C	330(6),223(23),195(100),167(18),145(19), 133(100)
VIII C	Φ	Φ	CH_3	175-178° C	418(54),312(8),298(100),282(100),221(44), 209(100)
VIII D	Py	Py	CH_3	143°(Decomp)	420(28),299(100),285(28),256(8),220(18), 210(18)

The N-H band in the condensation products of N-(substituted)-o-phenylenediamine with α-diketones is relatively broader and split; this indicates intramolecular hydrogen bonding of the N-H hydrogen with the azomethine nitrogen (VIII).

ii) u.v. spectra: -

The u.v. spectra of the di-condensation products of o-aminophenol and 8-amino-1-naphthol with α-diketones are closely related to those of the primary amines themselves, Table (IV). All of these compounds are colorless. The presence of the chromophore such as conjugated azomethine ($>$C=N-) linkage in these compounds should therefore be discounted. This implies that these compounds are heterocyclic.

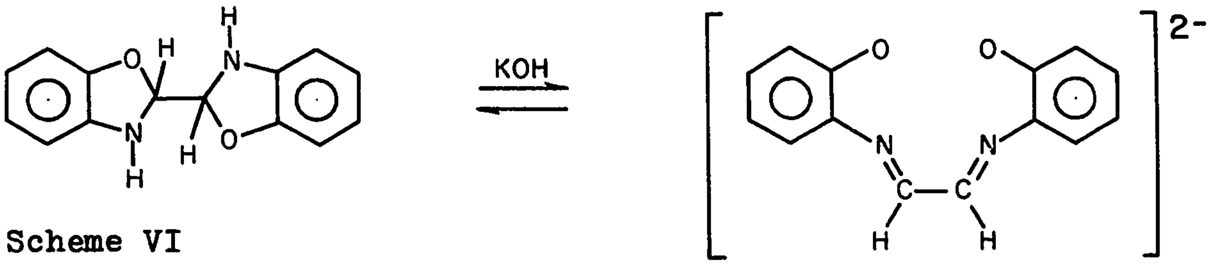
The spectra of the dicondensation products of N-(methyl or phenyl)-o-phenylenediamine with α-diketones on the other hand are different than those of the primary amines, Table (IV). These compounds are yellow in color. This indicates the presence of chromophoric ($>$C=N-) linkage, structure (VIII).

Base induced rearrangement: - Murase(32) reported earlier that although compound (VII) (R = R' = H) was insoluble in aqueous alkali, a reddish yellow color was produced when an excess of potassium hydroxide was added to its ethanol solution and another absorption maximum was observed at 467 $m\mu$ (ϵ_m 2445). This was explained by assuming that 2,2'-bibenzoxazoline tautomerizes to Schiff base under the influence of base, scheme VI.

Table IV

Near u.v. and Visible Absorption Bands in the Cyclic Forms, Sodium Salts and the Nickel Chelates of Compounds VI_x, VII_x and $VIII_x$

Compound	R	R'	R"	Free Ligand in Ethanol (mμ)	Sodium Salt in DMSO (mμ)	Ni-Chelate in Ethanol (mμ)
8-Amino-1-naphthol:HCl				320^{s}, 331^{s}		
VI A	H	H		323^{s}, 336^{s}	370^{s}, 510^{w}	322^{s}, 372^{m}, 648^{m}
VI B	CH_3	CH_3		325^{s}, 336^{s}	368^{s}, 454^{w}	
O-Aminophenol				232^{s}, 286^{s}		
VII A	H	H		237^{s}, 293^{s}	293^{s}, 325^{m}, 480^{m}, 506^{m}	293^{s}, 325^{m}, 530^{m}
VII B	H	CH_3		235^{s}, 294^{s}, 378^{w}	285^{s}, 333^{s}, 436^{s}	284^{s}, 334^{m}, 500^{m}
VII C	CH_3	CH_3		236^{s}, 293^{s}	296^{s}, 322^{s}, 422^{m}	281^{s}, 335^{m}, 490^{m}
N-Methyl-o-phenylenediamine:HCl				242^{s}, 292^{m}		
N-Phenyl-o-phenylenediamine				238^{s}, 278^{m}, 297^{m}		
VIII A	H	H	CH_3			230^{s}, 314^{s}, 346^{m}
VIII B	H	H	ϕ			222^{vs}, 286^{s}, 436^{m}, 462^{m}
VIII C	ϕ	ϕ	CH_3	253^{s}, 315^{s}	No change	
VIII D	Py	Py	CH_3	252^{s}, 314^{s}	No change	252^{s}, 268^{s}, 307^{s}, 420^{s}



Scheme VI

This author also showed that 2,2'- di or mono substituted bibenzoxazolines did not undergo such a rearrangement under identical conditions.

In the present study it was found that substituted bi-benzoxazolines and substituted naphthoxazinines developed a reddish yellow color when a small piece of solid NaOH was added to their dimethylsulfoxide or acetone solutions. The observation was supported by the appearance of new absorption bands in their spectra, Table (IV). In all cases the absorption band of the ligands near 300 mμ shifted to a higher wavelength after the addition of NaOH. Typical examples are shown in Fig. (2) and Fig. (3) and the results are shown in Table (IV). This change in the u.v. spectra may be related to the tautomerization of the heterocyclic compound to the corresponding Schiff base. The reason why only unsubstituted 2,2'- bibenzoxazoline and 2,2'-binaphthoxazinine and not their substituted analogs undergo such a change in ethanol and methanol has not been established. It is possible that the Schiff base anion of the substituted analog is such a strong base that it will immediately rearrange to the heterocyclic form in a protic solvent such as alcohol or water.

Figure 2

U.V. Spectra of 2,2'-dimethyl-bibenzoxazoline in DMSO

a) Normal Spectrum

b) Spectrum after Addition of NaOH

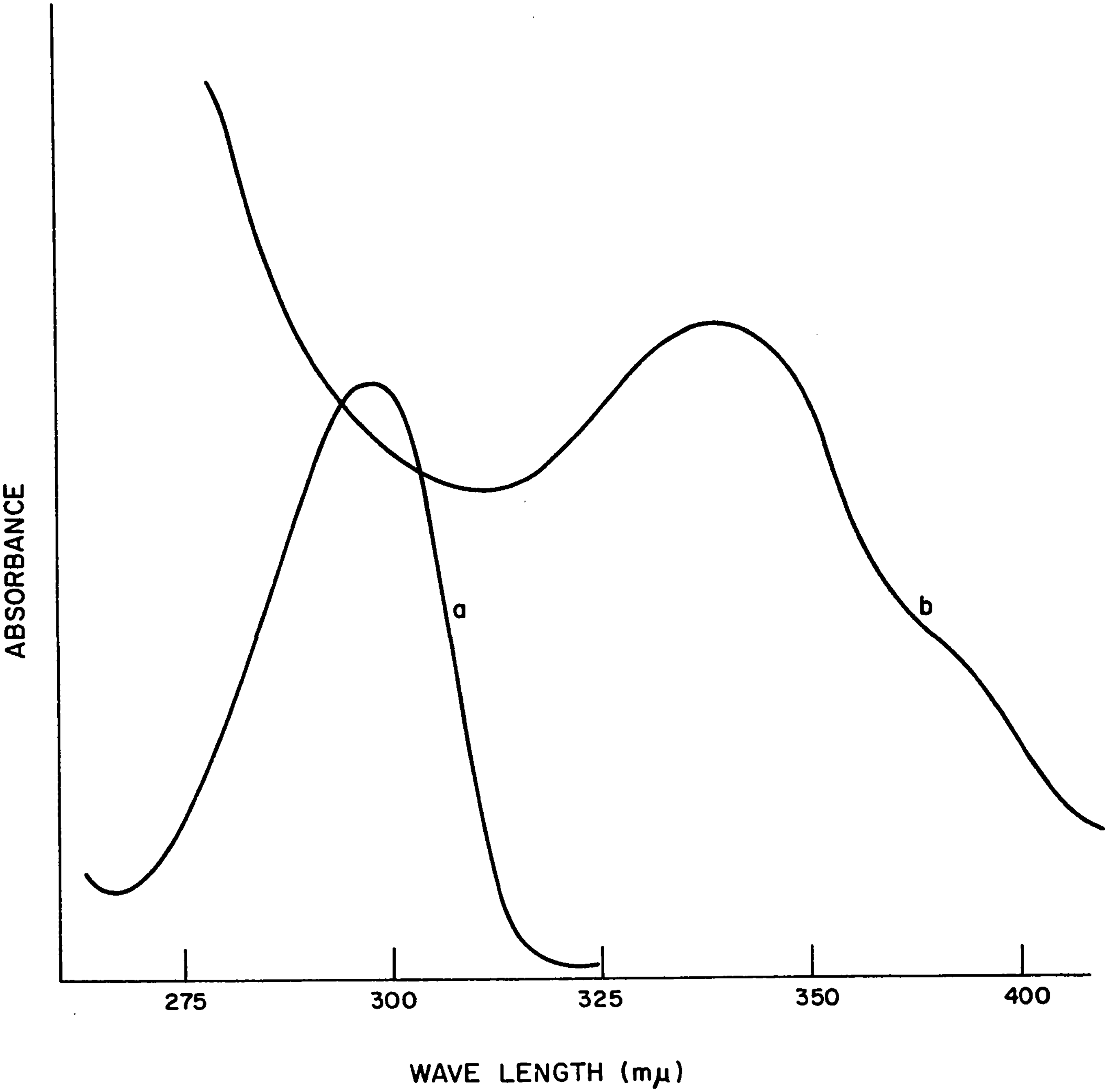
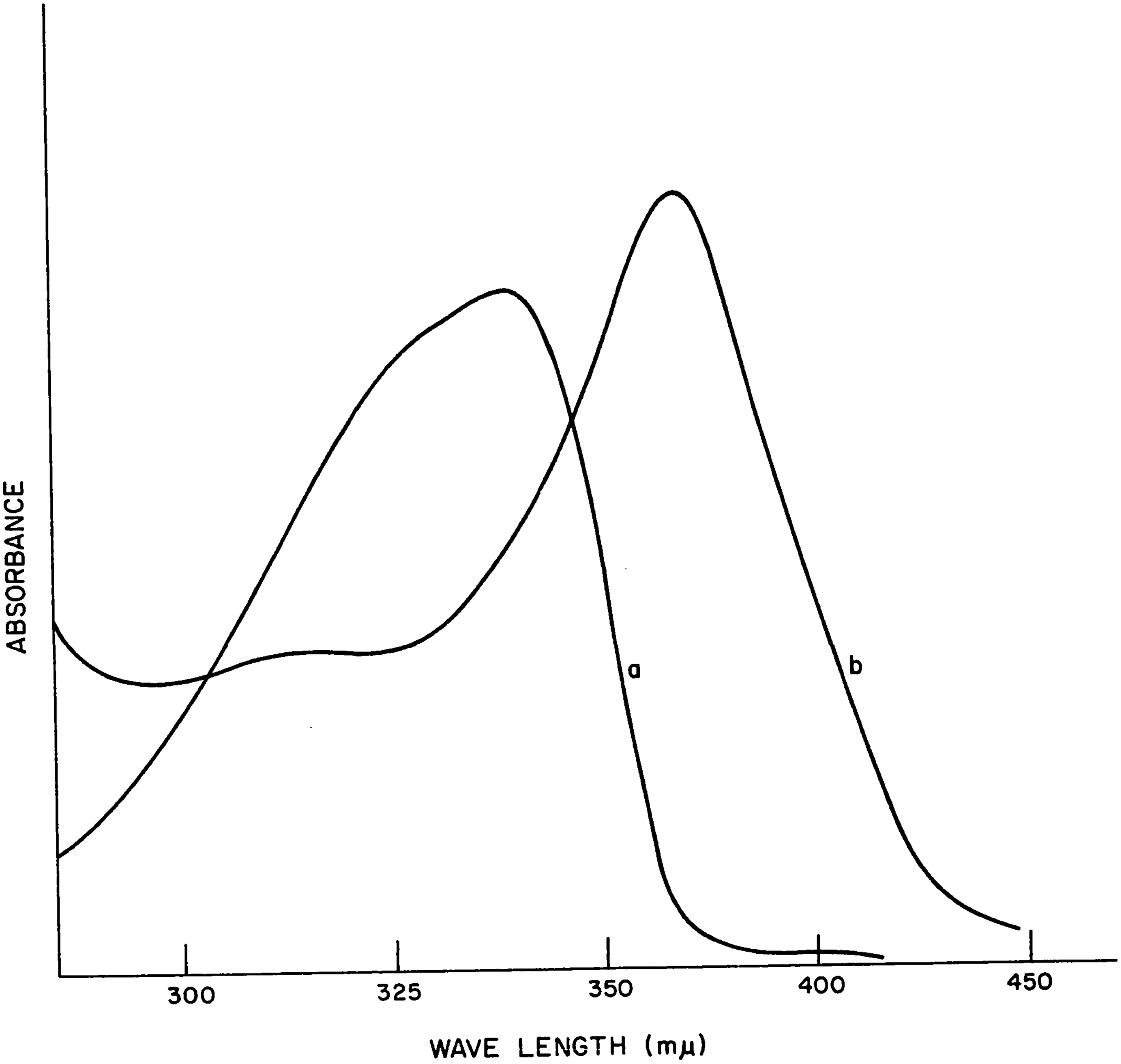

ABSORBANCE
a
b
275
300
325
350
400
WAVE LENGTH (mμ)

Figure 3

U.V. Spectra of 2,2'-dimethyl-binaphthoxazinine in DMSO

a) Normal spectrum

b) Spectrum after Addition of NaOH


ABSORBANCE
a
b
300
325
350
400
450
WAVE LENGTH (mμ)

The u.v. spectra of the compounds of structural type (VIII) do not undergo any change on the addition of alkali. This indicates that these compounds have the open Schiff base structure.

iii) Mass spectra

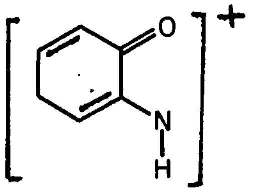
The fragmentation pattern in the mass spectra of the compounds of structural types (VI), (VII), and (VIII) are readily reconcilable with their molecular structures.

In Table (III) the melting points of the compounds and m/e values are listed. The relative peak intensities are indicated within brackets. Each peak indicated by its m/e value in Table (III) is usually accompanied by a few other peaks of relatively lower intensities; those are not listed.

The mass spectra of compounds of structural type (VI) and (VII) are uncluttered in the mass region between the molecular peak M and M/2 and have very few peaks of low intensity. This indicates the presence of stable closed structures. The central carbon-carbon bond between the heterocyclic rings is easily cleaved, breaking the molecule into two halves.

The spectra of the compounds of structural type (VIII) have complicated patterns between M and M/2. This high mass region has various intense peaks which are assignable to different fragments of the parent molecule. An open-type structure of these compounds is therefore indicated.

It is interesting to note that the mass spectra of (VII_x) have a characteristic peak at m/e = M - 107. The mass number 107 can be assigned to the fragment



This indicates that the heterocycle is broken at the aliphatic end (breaking the C-O and C-N bonds) before the whole molecule is broken into two halves. The spectra of (VI) do not have such characteristic intense bands at M - 156. This difference in the mass spectra of these compounds may be due to the relatively greater stability of 6-membered heterocyclic rings of (VI) compared to 5-membered rings of (VII).

iv) n.m.r. spectra

The results of the n.m.r. spectra are shown in Table (II). These results are compatible with the heterocyclic structures of compounds (VI_x) and (VII_x) and open Schiff base structures of ($VIII_x$). The N-H signal in the ($VIII_x$) compounds appears ~~at~~ up field compared to those of (VI_x) and (VII_x). The N-H signal was identified by the fact that it exchanges readily with water; the N-H signal vanishes when D_2O is added to the solution of these compounds.

In the bibenzoxazoline compounds (VII A) and (VII B), the C-H and N-H protons mutually split each other. This is exemplified by the spectra of (VII A), Fig. (4). On deuteration the N-H signal vanishes and the C-H doublet collapses into a singlet.

Figure 4

N.M.R. Spectra of 2,2'-bibenzoxazoline in Deuterated DMSO

a) Normal spectrum

b) Spectrum after Addition of D_2O.


b
a
8.0
7.0
6.0
5.0
4.0
3.0
δ (P.P.M.)

2) Quadridentate Schiff base metal chelates.

In spite of previous claims(12,13,32) that the compounds of structural type (VII) (R = R' = substituted groups) do not form metal chelates, successful methods have been developed in the present study for the preparation of these metal chelates. Additionally the preparation of the metal chelates of (VI) and (VIII) are reported for the first time. The U.V. spectra of the nickel chelates of these compounds are shown in Table (IV) and compared with the spectra of the corresponding sodium salts.

i) Factors affecting the rearrangement of the heterocycles to the Schiff base form.

Bayer and his co-workers(12,13) were the first to show that (VII) and its thio analog rearrange in the presence of metal ions to form the metal chelates (V). They showed in the case of (VII) that such a rearrangement and subsequent chelate formation took place only when R and R' are hydrogen atoms. No chelates were formed when one or both of the hydrogen atoms were replaced by substituted groups.

Bayer explained this lack of chelate formation in terms of steric hindrance from larger R groups. But the fact that the thio analogs of these compounds,(10,11,12) and (VIII) readily form metal chelates dispels the validity of such an explanation.

Murase(32) showed that 2,2'-bibenzoxazoline (VII) (R = R' = H) developed a color when an excess of KOH was added to its solution in ethanol and another absorption maximum was observed at 467 mμ. He ascribed this color and the new band to the Schiff base structure (IX). He also showed that no such phenomenon was observed in the case of 2-substituted or 2,2'-disubstituted compounds. He concluded that the substituted bibenzoxazolines (VII) did not form metal chelates because of their inability to rearrange to the corresponding Schiff base chelates. In the case of 2,2'-binaphthoxazinine (VI) also a similar trend was observed. Through direct reaction with metal acetates, chelate formation took place only when R and R' were H atoms.

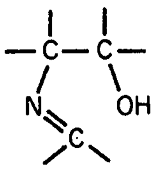
It was found in the present study that all the compounds of structural type (VI) and (VII) developed a red or yellow color in molten NaOH-KOH mixture. These colored compounds could be extracted into DMSO. It was later found that the same color also developed when these compounds were shaken in acetone or DMSO in the presence of solid NaOH pellets for several hours. This change in color was associated with shifting of the u.v. bands to higher wave length, Table (IV), indicating the tautomerization of the heterocyclic compounds to the open Schiff base form. In acetone the Na-salt of the Schiff base precipitated out and could easily be separated. The metal chelates were then easily prepared by simply adding the Na-salt to the metal salt in ethanol solution.

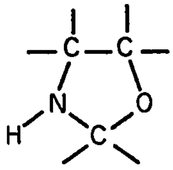
The sodium salts of these compounds are very unstable in water, methanol and ethanol. In ethanol the sodium salts were shown to be converted back to the original cyclic compounds. The rate of this rearrangement to the cyclic form, scheme (VI), is very fast in the case of the 2,2'-(substituted) compounds and is much slower in the case of the unsubstituted one.

It is now evident from the present study that the reason why VI and VII (where R or R' are substituted groups) do not form metal chelates under mild conditions is not because of steric hindrance between the substituted groups, as was assumed before,(12,13) but rather due to other factors such as electronic, kinetic, or other steric effects.

It was confirmed in some cases that the condensation of β -aminoalcohols results in an equilibrium mixture of Schiff base (XI) and oxazolidine (XII).

XI





XII

Bergmann(33) discussed this in a review and showed that replacement of the hydrogen atoms in ethanolamine by methyl groups favoured the formation of the cyclic form (XII). He speculated that the position of the equilibrium was dependent less on steric factors than on effects of electronic nature and on hyper conjugation.

The dramatic effects of substituent groups on equilibria involving ring-chain tautomerism of a large number of systems, such as hemiacetal $\rightleftharpoons$ hydroxy ketone or aldehyde, pseudo acid $\rightleftharpoons$ keto or aldehydo acid, cyclic aldol or ketol $\rightleftharpoons$ dicarbonyl compound, lactone $\rightleftharpoons$ eneoic acid, etc., have been observed.(34)

It was found that the accumulation of substituents along the chain of a bifunctional system appears to selectively stabilize the corresponding cyclic forms; this is known as gem-dimethyl effect. This effect had been explained in terms of (i) the relationship of the size of the substituent groups with the bond angle of the methylene carbon atom on which the substituent is linked and (ii) possible restriction of free rotation in substituted acyclic molecules, thereby decreasing the entropy.(34)

It is probable that the striking differences observed in the reactivity of substituted bibenzoxazoline and substituted bi-naphthoxazinine in the present study are also due to gem-dimethyl effect and hyperconjugation.

CHAPTER III

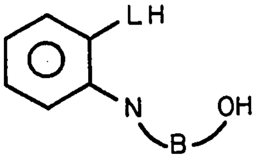
METAL CHELATES OF TRIDENTATE SCHIFF BASES

A) Introduction

The existence of discrete tri-coordinated transition metal complexes has never been authenticated except for a single case.(35) Tris (trimethylphosphine sulfide) copper (I) cation is the first structure reported of a trigonal monomeric copper complex and this is the only such compound known so far. The authors did not suggest why this is a unique compound.

The dibasic tridentate Schiff bases of structural type (XIII), where L is oxygen or sulfur and B is an aliphatic or aromatic linking group

XIII



offer good possibilities for the formation of discrete tri-coordinated complexes with divalent metal ions. Aside from possible analytical applications, these compounds should be of considerable theoretical interest as to their stability and d orbital splitting in the trigonal crystal field.

1) Historical background

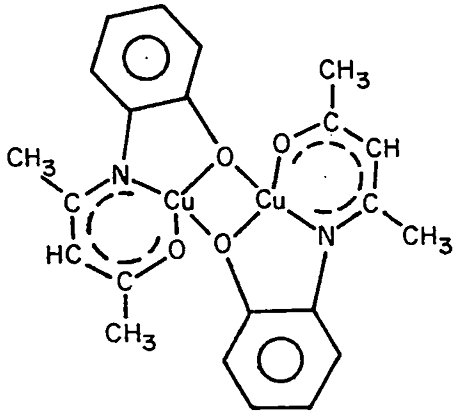
In 1937 Pfeiffer(36) prepared salicylal-o-hydroxyanil copper (II) and claimed the preparation of a tri-coordinate complex. Calvin(37), in 1946, recorded a subnormal magnetic moment of 1.58 B.M. for this compound. However, this anomalous moment was attributed to possible impurities. Subsequently Muto(17,38,39), Kishita and co-workers(40-44) prepared a large number of copper (II) complexes with Schiff bases of structural type XIII. Most of these so-called tricoordinated complexes have been found to possess subnormal magnetic moments.

Kato et al.(45) in a recent review have listed the magnetic moments of a large number of these compounds and other copper (II) complexes with subnormal moments.

2) Geometry and structure

In view of the observed subnormal magnetic moments, Kishita et al.(40) first suggested that these tridentate Schiff base copper (II) chelates have binuclear structures with copper-copper distance small enough to permit magnetic exchange interaction between them. Previously it had been shown(46) that copper (II) acetate which also had subnormal magnetic moment possessed a binuclear structure. The prediction of Kishita et al.(40) has been confirmed recently by X-ray crystal structural analysis.(18,19,47-49) Barclay et al.(18,19) were the first to show that acetylacetone-mono-(o-hydroxyanil)-copper (II) has a binuclear structure (XIV).

XIV



The most interesting feature of this compound is that the copper atom attains four co-ordination through dimer formation. The magnetic interaction in this compound is supposed to take place by a superexchange mechanism involving the p-orbitals of the bridging atoms.(18,19) All the tridentate Schiff base complexes of copper (II),(45) iron,(50) and oxovanadium (IV) (51) ions showing subnormal magnetic moments are supposed to have this basic binuclear oxygen bridged structure.

The magnetic criterion of the binuclear structure fails in the case of diamagnetic chelates of nickel, zinc, cadmium, etc. Moreover, tridentate copper (II) Schiff base chelates containing carboxylic groups(52) and sulfur donor atoms(17) show normal magnetic moments. In the absence of any X-ray structural data there is no easy way to predict whether these diamagnetic compounds have monomeric or dimeric structures.

Recently, salicylidene-o-aminophenol, a dibasic tridentate Schiff base, has been used for the spectrofluorimetric determination of aluminium(53-54) and gallium.(55) It was also found to be useful for spectrophotometric determination of copper(56) and nickel.(57) The composition of some of these complexes has been reported to be 1 to 1 (metal to ligand) from analytical results of the isolated complexes and from solvent extraction experiments.(57)

While the present work was in its conclusive phase

Brubaker et al.(58) reported the synthesis of some nickel (II) complexes with sulfur containing β-ketoamine ligands; these include one described in this work. From a molecular weight determination Brubaker et al. showed that these compounds are at least dimeric; they proposed binuclear sulfur bridged structure for these compounds.

Except for the crystal structure determination of acetylacetone-mono-(o-hydroxyanil) copper (II)(18,19) and β-hydroxy-α-naphthaldehyde-[β-hydroxy-α-naphthylmethylimid] copper (II)(47), no systematic efforts have so far been made to determine the structural characteristics of tridentate Schiff base chelates. Attempts have been made in this work to elucidate the structures of a number of tridentate Schiff base chelates of nickel (II), copper (II), zinc (II), cadmium (II), and palladium (II) by using mass spectrometry, vibrational and electronic spectroscopy, n.m.r., magnetic measurements and vapour pressure osmometry.

From these studies it can be concluded that discrete chelates of dibasic tridentate Schiff bases do not exist. They all have the basic binuclear structure (III).

The structures of other three co-ordinate copper complexes involving thiourea,(59) phosphine,(60) halide,(60) cyanide,(61) olefines,(62) and acetylenic(63) ligands, have been reported. In each case the structure is polynuclear with bridging ligand groups.

3) Magnetic moments and low-frequency vibrational spectra

As mentioned earlier, oxygen-bridged copper (II) complexes formed with tridentate Schiff bases, heterocyclic N-oxides and other ligands have been the object of studies during recent years, because of their subnormal magnetic moments. The antiferromagnetic exchange interactions in these complexes are supposed to take place through the bridging oxygen atoms and thought to involve the successful overlapping of oxygen p orbitals with the metal d orbitals.

It was thought that metal-oxygen vibrational force constant for the bridge vibrations would be an important factor in determining the extent of superexchange in these compounds. With this point in mind the low-frequency infrared and Raman spectra of these compounds have been obtained and some tentative assignments for the metal-ligand stretching frequencies have been made.

B) Experimental

a) Materials

O-aminophenol obtained from Eastman Organic Chemicals was recrystallized from ethanol. O-aminothiophenol (Eastman), salicylaldehyde (Aldrich Chemical Co. Inc.), acetylacetone (Eastman) were used without further purification. Analytical grade metal salts were obtained from Fisher Scientific Company. Pure metal isotopes were obtained from Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830. Zinc-68, zinc-64, copper-65, and copper-63 were obtained as the oxides, whereas nickel-62 and nickel-58 were in pure metallic form. The minimum isotope purity claimed by the suppliers was 98.50%. Deuterated solvents (water, chloroform, acetone, dimethylsulfoxide and pyridine) for n.m.r. measurements were obtained from Stohler Isotope Chemicals.

b) General methods of preparation

The Schiff bases were obtained by condensation of primary amines with the respective aldehydes or ketones in ethanol or water at room temperature or below.

The copper chelates were obtained by the reaction of copper acetate with the Schiff bases in ethanol-water mixtures. The nickel chelates were usually prepared by the addition of an aquo-ammoniacal solution of nickel chloride to the boiling solution of the Schiff base in acetone. The copper and nickel chelates did not have any sharp melting point but generally charred above 215-220° C. These and all other chelates of tridentate Schiff bases were dried at 100° C. over P_2O_5.

1) Salicylaldehyde-2-hydroxyanil (SAP)

Equimolar ratio (0.01 moles) of salicylaldehyde and o-aminophenol were reacted at room temperature in ethanol. After stirring for four hours, the product was filtered and recrystallized from ethanol. m.p., 195° C.

Analysis:

Calculated for $C_{13}H_{11}NO_2$: Parent mass, 213; C, 73.2; H, 5.2; N, 6.6%.

Found: Parent mass, 213; C, 73.2; H, 5.4; N, 6.6%.

2) Salicylaldehyde-2-hydroxyanil copper (II): (Cu-SAP)

The green copper (II) chelate was prepared by treating the Schiff base with copper (II) acetate, both dissolved in water/ethanol mixtures.(40) The chelate precipitated out immediately. The mixture was heated in a water bath at 80° C. for half an hour after which it was allowed to cool to room temperature and then filtered. The crude product was dissolved in pyridine. After water was added to the pyridine solution, the pyridinate of the chelate crystallized out. The crystals were collected on a filter paper and the pyridine was removed by heating at 90-100° C. for three hours. A relatively pure chelate was obtained in this process. The chelate was then recrystallized from nitrobenzene as dark green rod-like crystals.

Analysis:

Calculated for $(C_{13}H_9NO_2Cu)_2$: Parent mass, 504;

C, 56.8; H, 3.3; N, 5.1%

Found: Parent mass, 504; C, 56.9; H, 3.4; N, 5.1%.

3) Salicylaldehyde-2-hydroxyanil nickel (II): (Ni-SAP)

This was prepared by adding an ammoniacal solution of nickel (II) chloride to the hot acetone solution of the Schiff base in equimolar (0.01 moles) ratio. The mixture was heated in a water bath for one hour and allowed to cool. The shiny red crystals were filtered and recrystallized from dichloromethane.

Analysis:

Calculated for $(C_{13}H_9NO_2Ni)_2 \cdot H_2O$: Parent mass, 542; C, 54.2; H, 3.9; N, 4.9%.

Found: Parent mass, 542; C, 54.0; H, 4.3; N, 9.7%.

4) Salicylaldehyde-2-hydroxyanil zinc (II): (Zn-SAP)

This chelate was prepared by adding aqueous solution of zinc chloride to an equimolar (0.01 mole) amount of the ligand in acetone solution. The pH was then raised by slow addition of sodium acetate. The yellow chelate formed was purified by treating with pyridine in a manner similar for that of salicylaldehyde-2-hydroxyanil copper (II), (3).

Analysis:

Calculated for $C_{13}H_9NO_2Zn$: C, 56.4; H, 3.3, N, 5.1%.

Found: C, 55.4; H, 3.4; N, 5.1%.

5) Salicylaldehyde-2-hydroxyanil cadmium (II): (Cd-SAP)

The yellow chelate was prepared as described in (3) and purified by treating with pyridine as described in (2).

Analysis:

Calculated for $C_{13}H_9NO_2Cd$: C, 48.3; H, 2.8; N, 4.3%.

Found: C, 48.1; H, 2.9; N, 4.2%.

6) Salicylaldehyde-2-mercaptoanil: (SASP)

Equimolar amounts (0.01 moles) of 2-aminothiophenol and salicylaldehyde were dissolved in ethanol (30 ml). The resulting solution was kept at ice temperature for about two hours; meanwhile the crude product precipitated. Recrystallization from ether gave colorless prismatic crystals.(17) m.p. 130-132° C.

Analysis:

Calculated for $C_{13}H_{11}NOS$: Parent mass, 229; C, 68.1;
H, 4.8; N, 6.1%.

Found: Parent mass, 229; C, 68.1; H, 4.1; N, 6.2%.

7) Salicylaldehyde-2-mercaptoanil copper (II): (Cu-SASP)

The deep green chelate was prepared(17) and recrystallized in the manner described in (2).

Analysis:

Calculated for $(C_{13}H_9NOSCu)_2$: Parent mass, 580;
C, 53.7; H, 3.1; N, 4.8%.

Found: Parent mass, 580; C, 53.5; H, 3.2; N, 4.8%.

8) Salicylaldehyde-2-mercaptoanil nickel (II): (Ni-SASP)

The dark red chelate was prepared and recrystallized by the method described in (3).

Analysis:

Calculated for $(C_{13}H_9NOSNi)_2$: Parent mass, 544;
C, 54.6; H, 3.2; N, 4.9%.

Found: Parent mass, 544; C, 51.0; H, 3.2; N, 4.6%.

9) Salicylaldehyde-2-mercaptoanil zinc (II): (Zn-SASP)

The yellow chelate was prepared and purified by the methods described in (4).

Analysis:

Calculated for $C_{13}H_9NOSZn$: C, 53.4; H, 3.1; N, 4.8%.

Found: C, 54.9; H, 3.4; N, 5.4%.

10) Salicylaldehyde-2-mercaptoanil cadmium (II): (Cd-SASP)

Prepared by the method described in (5).

Analysis:

Calculated for $C_{13}H_9NOSCd$: C, 46.0; H, 2.7; N, 4.1%.

Found: C, 46.0; H, 2.8; N, 4.0%.

11) Acetylacetone-mono-(2-hydroxyanil): (AAP)

0.02 moles of o-aminophenol was dissolved in oxygen free water. 0.02 moles of acetylacetone dissolved in a small volume of water was then added to the o-aminophenol solution and the reaction mixture was stirred for four hours at room temperature. The crystalline product which precipitated out was collected by filtration and recrystallized from ethanol. m.p. 195-196° C.

Analysis:

Calculated for $C_{11}H_{13}NO_2$: Parent mass, 191; C, 69.1;
H, 6,9; N, 7.3%.

Found: C, 69.1; H, 6.8; N, 7.3%, Parent Mass, 191.

12) Acetylacetone-mono-(2-hydroxyanil) copper (II): (Cu-AAP)

This was obtained by the reaction of copper acetate with acetylacetone-mono-(2-hydroxyanil) by the method described in (2). On recrystallization from nitrobenzene, green prismatic crystals were obtained.

Analysis:

Calculated for $(C_{11}H_{11}NO_2Cu)_2$: Parent mass, 504;
C, 52.3; H, 4.4; N, 5.5%.

Found: Parent mass, 504; C, 52.6; H, 4.4; N, 5.5%.

13) Acetylacetone-mono-(2-hydroxyanil) nickel (II): (Ni-AAP)

The red chelate was prepared and purified following the procedure described in (3)

Analysis: Calculated for $((C_{11}H_{11}NO_2Ni)_2 \cdot 2H_2O)$:
Parent mass, 494; C, 46.5; H, 5.3; N, 4.9.

Found: Parent mass, 494; C, 46.2; H, 5.1; N, 5.1.

14) Acetylacetone-mono-(o-mercaptoanil): (AASP)

1:1 molar ratio (0.02 moles) of o-aminothiophenol and acetylacetone were mixed in water (200 ml) at 0° C. and left stirring overnight. The colorless precipitate was filtered and recrystallized from ether. m.p. 85-87° C.

Analysis:

Calculated for $C_{11}H_{13}NOS$: Parent mass, 207; C,
63.7; H, 6.3; N, 6.8%.

Found: C, 63.7; H, 6.3; N, 6.9%, Parent mass, 207.

15) Acetylacetone-mono-(o-mercaptoanil) nickel (II): (Ni-AASP)

This chelate was prepared from acetylacetone-mono-(o-mercaptoanil) and nickel chloride hexahydrate by following the procedure described in (3). The dark red compound was recrystallized from chloroform.

Analysis:

Calculated for $(C_{11}H_{11}NOSNi)_2$: Parent mass, 526;

C, 50.1; H, 4.2; N, 5.3%.

Found: Parent mass, 526; C, 50.2; H, 4.2; N, 5.2%.

Molecular weight by vapor pressure osmometry (in S-tetrachloroethane), 521.

16) Acetylacetone-mono-(o-mercaptoanil) palladium (II): (Pd-AASP)

This was prepared from palladium (II) chloride and acetylacetone-mono-(o-mercaptoanil) by following the method described in (3). The final product was recrystallized from chloroform.

Analysis:

Calculated for $C_{11}H_{11}NOSPd$: C, 42.4; H, 3.6; N, 4.5%.

Found: C, 44.4; H, 3.9; N, 4.5%.

c) Analyses

Microanalyses for carbon, hydrogen and nitrogen were performed by Scandinavian Microanalytical Laboratory, Box 25, 2730 Herlev- DK, Denmark.

d) Spectroscopic Measurements

Low resolution mass spectra were obtained with an A.E.I.-MS-902 double focusing mass spectrometer using 70 ev electrons and 8 kv accelerating voltage. The samples were introduced by direct evaporation. The temperature required to obtain an adequate signal for the metal chelates was in the range 200-220° C. A lower temperature range (120-130° C.) was sufficient to obtain the spectra of the free ligands.

Visible and ultraviolet spectra were recorded with an UNICAM SP 800 ultraviolet spectrophotometer and with a Beckman DB spectrophotometer connected to a Sargent-Welch SRLG recorder. Absorbance measurements were made in ethanol using 1 cm quartz cells.

Infrared spectra in the range 4000-250 cm^{-1} were recorded with a Perkin-Elmer Model 521 Grating Spectrophotometer. The samples were measured either as KBr pellets, CsBr pellets or as Nujol mulls supported between CsBr plates.

Calibration of frequency readings was performed with polystyrene films. The spectra in the range 300-170 cm^{-1} were obtained by using a Perkin-Elmer Model 301 Far infrared Double Beam Spectrophotometer. The samples were introduced as thick Nujol mulls on polyethylene window. The average error in frequency reading was 0.5 cm^{-1}.

Raman spectra were recorded with Jarrell Ash 25-300 spectrometer equipped with a Kr^{+} Coherent Radiation model 52K laser source. The line 647.1 nm (15,453.56 cm^{-1}) was used for most of the measurements. The spectra of green copper chelates were obtained by using green 520.8 nm (19,201.23 cm^{-1}) line. Calibration of the frequency readings was obtained from the spectrum of water. The samples were introduced as fine powder in glass capillary tubes.

N.M.R. spectra were obtained by using Varian model T-60 instrument. The specifications given by the manufacturers are as follows: H_o field strength 14,092 G ; H Rotating

Field frequency 60 MHz (for proton resonance at 14,092 G); Resolution: the full line width at half amplitude is $\ngtr$ 0.5 Hz; Sensitivity: average signal to noise ratio 12:1.

Tetramethylsilane was used as internal or external standard. Measurements were made in d-chloroform, d-dimethylsulfoxide and d-pyridine.

Magnetic moments were measured for solid samples by the Gouy method using iron (II)-ammonium sulfate 6-hydrate as the standard. A model SM 12/5 balance (Stanton Instruments Ltd.) was used for all measurements. The values given by Selwood(64) were used for the diamagnetic correction of the ligands. The effective magnetic moment μ_{eff} per metal atom was calculated from the expression $\mu_{eff} = 2.83 \;\; x_M \; T$ B.M., where x_M is the molar susceptibility. The samples were measured as fine powder in narrow glass tubes after careful packing. Packing and magnetic measurements were done in duplicate.

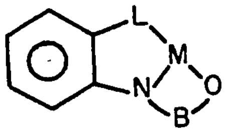
e) <u>Vapor pressure osmometry</u>

Molecular weight determination in solution was performed by using Mechrolab (high temperature) Model 301 A vapor pressure osmometer. The operating temperature of the instrument was set at 37° C. Pyridine and 5-tetrachloroethane were used as solvents. Benzil (Eastman Organic Chemicals) was used for calibration. Duplicate measurement was performed for each sample, and the results agreed within 3-4%.

C) Results and Discussion

1) Structures of the free ligands

The tridentate Schiff bases studied in the present work form chelates with bivalent metal ions, which in a general monomeric formulation can be shown as (XV).



XV

L = oxygen or sulfur

B = aliphatic or aromatic linking groups.

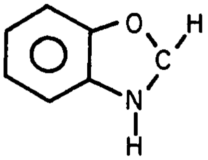
The free ligands can have structures which differ from that in the above formulation but on chelation rearrange to the Schiff base form. In the following sections the structures of the free ligands will be discussed.

i) Salicylaldehyde-2-hydroxyanil (SAP)

This compound was prepared by the condensation of salicylaldehyde with o-aminophenol. The color and spectral (i.r., u.v., and mass spectra) data were in accord with the Schiff base structure shown by the general structure (XIII). The compound is orange in color and has an absorption band at 448 mμ which indicates the presence of chromophoric group -CH=N-.

The i.r. spectrum of the ligand has a band near 1648 cm^{-1} which shifts to lower frequencies in the metal chelates. This band has previously been assigned(65) to the >C=N- stretching frequency. The shifting of the band to lower frequency probably arises from weakening of the >C=N- bond through delocalization of the π electrons in the chelate ring. In addition the free ligand has a broad band around 2600 cm^{-1}, which disappears on chelate formation. This band can be readily assigned to the OH groups in the free ligand. A comparison of the ligand and the chelate spectra in the region 4000-1500 cm^{-1} is shown in Fig. (5).

The mass spectrum of this compound shows very strong peaks (100%) at m/e 213 corresponding to the parent mass. Another strong peak (95%) appears at m/e 120 which corresponds to the fragment:



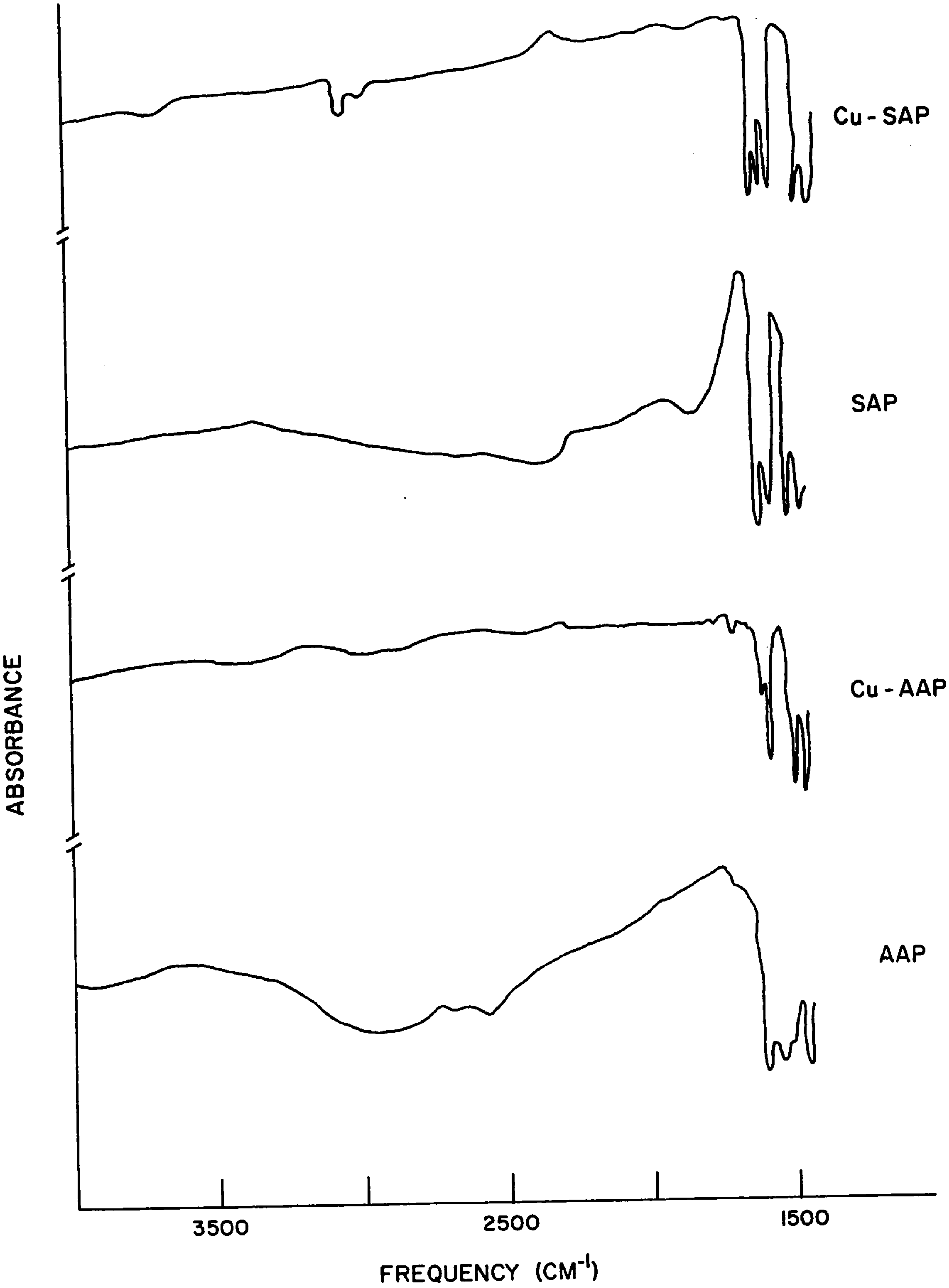
Elias et al.$^{(66)}$ have shown recently that the formation of stable heterocyclic species similar to the above fragment is characteristic of the mass spectra of ortho-substituted aromatic Schiff bases. Studies of other Schiff bases obtained from salicylaldehyde are also in agreement with the predominance of the phenol-imine tautomer.$^{(67,68)}$

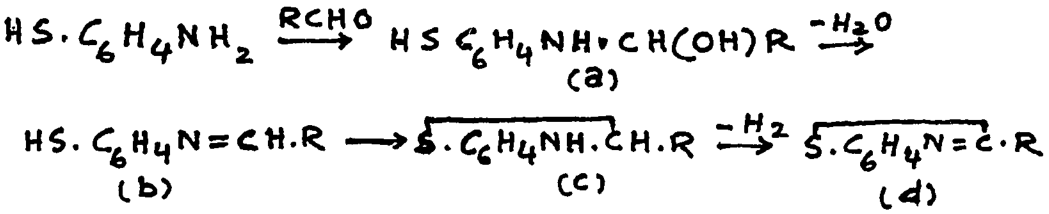
ii) Salicylaldehyde-2-mercaptoanil (SASP)

Unlike the case with 2-aminophenol, 2-aminothiophenol condenses with aldehydes and ketones to form heterocyclic benzothiazoles. It seems probable from the results of several investigators$^{(69-72)}$ that the mechanism of the reaction is as follows:

Figure 5

High Frequency (4000-1500 cm^{-1}) i.r. Spectra of Cu-SAP, SAP, Cu-AAP, AAP.


Cu - SAP
SAP
Cu - AAP
AAP
ABSORBANCE
3500
2500
1500
FREQUENCY (CM⁻¹)



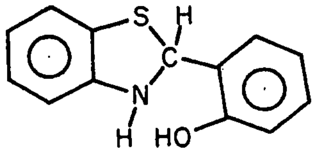
$$HS.C_6H_4NH_2 \xrightarrow{RCHO} \underset{(a)}{HS\,C_6H_4NH.CH(OH)R} \xrightarrow{-H_2O}$$

$$\underset{(b)}{HS.C_6H_4N{=}CH.R} \longrightarrow \underset{(c)}{\overline{S.C_6H_4NH.C}H.R} \xrightarrow{-H_2} \underset{(d)}{\overline{S.C_6H_4N{=}C}.R}$$

Although the thiazolines (c) were isolated as intermediates in the formation of the thiazoles (d), neither the aldols (a) nor the anils (b) have been isolated.

Charles et al.(16) concluded from chemical and u.v. spectral evidence that the condensation product of 2-aminothiophenol with salicylaldehyde is the thiazoline, (XVI).

XVI



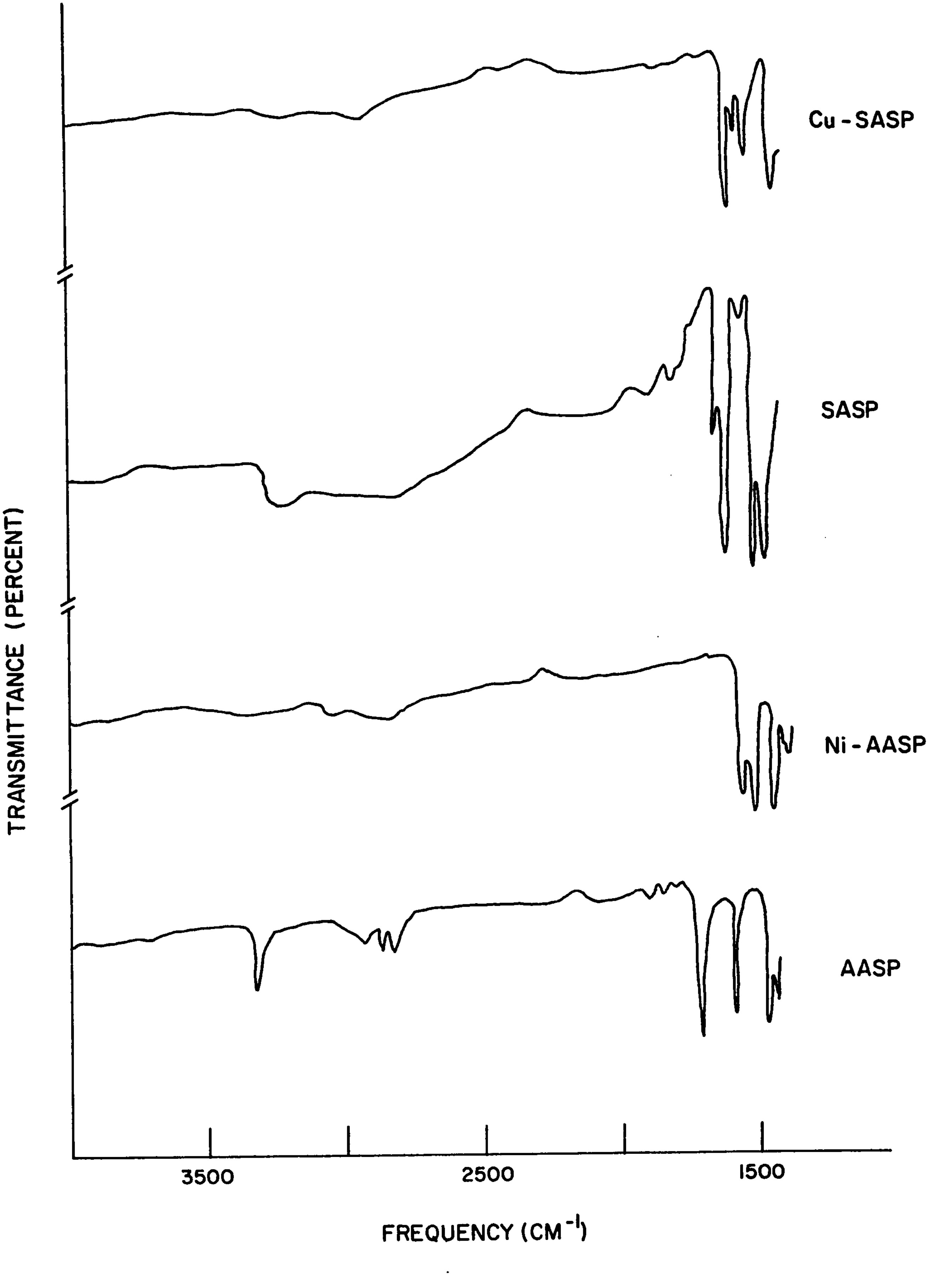
The i.r. spectrum shows a sharp band near 3200 cm^{-1} characteristic of N-H stretching frequency (Chapter II of this thesis) in addition to a very broad band in the region 2700 cm^{-1} to 3100 cm^{-1} which is due to O-H group. Both of these bands are absent in the spectra of the chelates, Fig. (6).

The n.m.r. spectra has a peak at 5.45 δ p.p.m. due to N-H and a peak at 8.43 δ p.p.m. due to the O-H proton, both of which disappear when D_2O is added to the solution of the compound. The rapid hydrogen exchange observed is consistent with the properties of those groups.

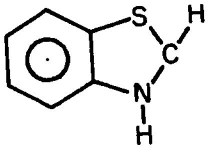
The mass spectrum of this compound has a strong peak (100%) at m/e 136 (in addition to the parent peak) cor-

Figure 6

High Frequency (4000-1500 cm^{-1}) i.r. Spectra of Cu-SASP, SASP, Ni-AASP, AASP.


Cu - SASP
SASP
Ni - AASP
AASP
TRANSMITTANCE (PERCENT)
3500
2500
1500
FREQUENCY (CM^{-1})

responding to the fragment:



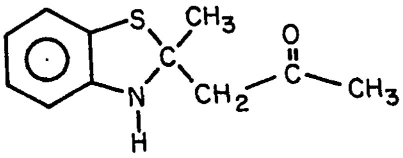
indicating a probable cyclic structure of this compound.

Thus, i.r,, n.m.r. and mass spectral data obtained in the present study substantiate the heterocyclic (or closed) structure for the compound proposed by Charles et al.

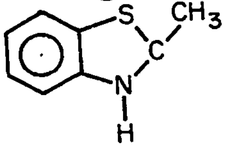
iii) Acetylacetone-mono-(2-mercaptoanil):(AASP)

The condensation product of o-aminothiophenol with acetylacetone is colorless. This suggests that this compound does not possess the imino group $\rangle C{=}N-$. All evidence obtained in the present study indicates that this compound is heterocyclic with a structure that can be formulated as (XVIIIa).

XVIIIa



The mass spectrum supports this possibility since in addition to the parent peak at m/e 207, there is a very strong peak at m/e 150 corresponding to the fragment



The i.r. spectra show the characteristic sharp N-H stretching band at 3340 cm^{-1} and the $\rangle C{=}O$ stretching frequency at 1730 cm^{-1}. Both of these bands disappear on chelate formation, Fig. (6).

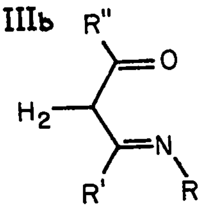
The n.m.r. spectrum shows two methyl signals at 1.80 and 2.00 δ p.p.m., a doublet for the $-CH_2-$ group around 3.14 δ p.p.m. and the N-H resonance at 5.03 δ p.p.m. The N-H signal was identified by hydrogen exchange with D_2O. There was no signal at low field region indicating the absence of -OH group.

Metal chelate formation which is accompanied by rearrangement of the ligand to the Schiff base form drastically changed the n.m.r. spectra of the ligand, Fig. (7). In the spectra of the nickel chelate the signals due to N-H and $-CH_2-$ protons disappeared and only $-\overset{|}{\underset{|}{C}}-H$ signal was obtained at 5.21 δ p.p.m.

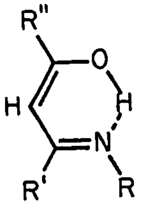
iv) Acetylacetone-mono-(2-hydroxyanil): (AAP)

Condensation of acetylacetone and related β-diketones with mono or diamines have been the subject of a variety of physico-chemical studies(73-80) in recent years. The interest in the condensation product of such reactions rests in the possibility of three distinct tautomeric forms:

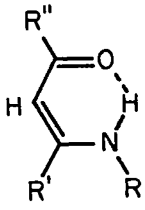
XVIIIb



XIX



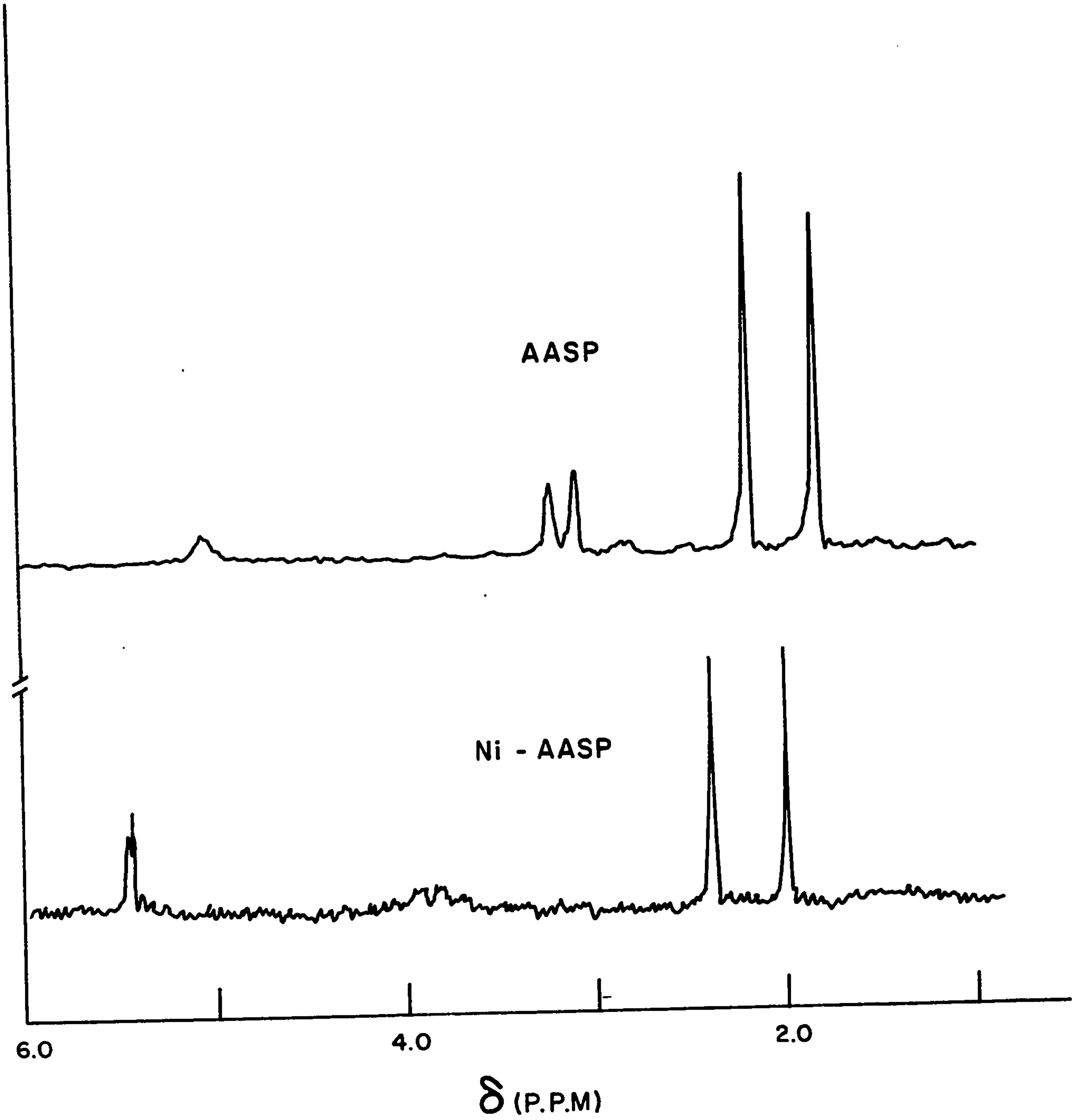
XX



No evidence for the keto-imine form XVIIIb was obtained in any of these studies. A clear distinction between XIX and XX has been accomplished recently through p.m.r. studies. It

Figure 7

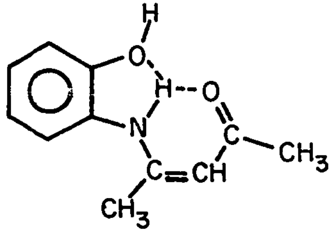
N.M.R. Spectra of AASP and Ni-AASP in Deuterated Chloroform


AASP
Ni - AASP
6.0
4.0
2.0
δ (P.P.M)

has been shown(81-85) that the chelated keto-amine XX predominates to the extent of >95 mole % in nonpolar solvents.

In the light of the preceding it seems very likely that the condensation product of o-aminophenol with acetylacetone will predominantly be a ketoamine (XXI).

XXI



The i.r. spectra of the ligand show a very broad band in the region 3200 cm^{-1} to 2500 cm^{-1} assignable to the OH and hydrogen bonded N-H groups. The $>C=O$ stretching frequency (shifted because of H-bonding with N-H proton) appears at 1610 cm^{-1}. On chelation the OH and N-H broad bands disappear and the $>C=O$ band is shifted to lower frequencies, Fig. (5).

In addition to the i.r. spectra, the n.m.r. spectrum is in accord with the ketoamine form of the ligand, (XXI). A single CH_3 signal is obtained at 1.95 δ p.p.m. The N-H signal appears at 3.62 δ p.p.m.; the methylene ring proton signal and the ring proton signals appear at 5.10 δ p.p.m. and 6.60-7.20 δ p.p.m. respectively. On deuteration the N-H signal vanishes due to exchange with D_2O.

The results of the crystal structure analysis strongly suggest(19) that the complex formation takes place through the ketoamine form. It is very likely that the free ligand also exists in this form.

2) Tridentate Schiff base chelates

As pointed out earlier the subnormal magnetic moment was used as a qualitative criterion to determine the structures of a large number of tridentate copper (II) compounds once the basic bi-oxygen-bridged binuclear structure was established for one of them by X-ray structural studies.(18,19) But such criteria break down in the case of tridentate complexes which are either diamagnetic or have normal magnetic moments. In the face of formidable difficulties in X-ray structural investigations of a large number of similar compounds it is often desirable to find some easier and indirect means of obtaining structural information regarding them. In this work stereochemical information about a large number of tridentate Schiff base chelates with copper, nickel, palladium, zinc, and cadmium metal atoms have been obtained by the use of mass spectrometry, electronic and vibrational spectroscopy, vapour pressure osmometry, n.m.r. and magnetic moment determinations.

i) Mass spectrometry

The value of mass spectrometry in the studies of organic compounds is now well established. The technique is of increasing importance for metal co-ordination compounds, e.g. phthalocyanins,(86) porphyrins,(87) π-cyclopentadienyl complexes,(88) metal carbonyls,(89) metal halides,(90) and Schiff base complexes, dithiocarbamates, acetylacetonates,(91) etc.

Mass spectrometry has been found to be a powerful tool in the present study of tridentate Schiff base chelates. Although many of these compounds have very high melting points, enough volatilization was effected in the temperature range 180-240° C. to obtain good mass spectra for the copper and nickel chelates.

Figure (8) shows the mass spectra of the copper and nickel chelates of acetylacetone-mono-(o-hydroxyanil) and also the spectrum of the complex prepared with pure ^{58}Ni isotope. These spectra, which are typical of all the tridentate Schiff base complexes, very clearly show the dimeric nature of these compounds.

The mass spectra of the copper and nickel chelates of acetylacetone-mono-(o-hydroxyanil) have the same pattern, thereby indicating similar structures of these compounds. A typical spectrum has three characteristic regions, A, B, and C. Region A occurs at high m/e values and corresponds to dimeric (2M) mass number. The region B corresponds to the monomeric (M) mass; there are usually few remarkable peaks in between these two regions. Region C which contains the smaller fragments and low m/e peaks is less characteristic and will not be discussed here.

The tridentate Schiff base complexes of all the different ligands studied with the same metal ion also have similar patterns of mass spectra and the relative ratio of the peak heights are about the same.

The spectrum shown in Fig. (8a) of acetylacetone-mono-(o-hydroxyanil) copper (II) is representative of the

Figure 8

Mass Spectra of the Copper (II) and Nickel (II) Chelates of AAP.

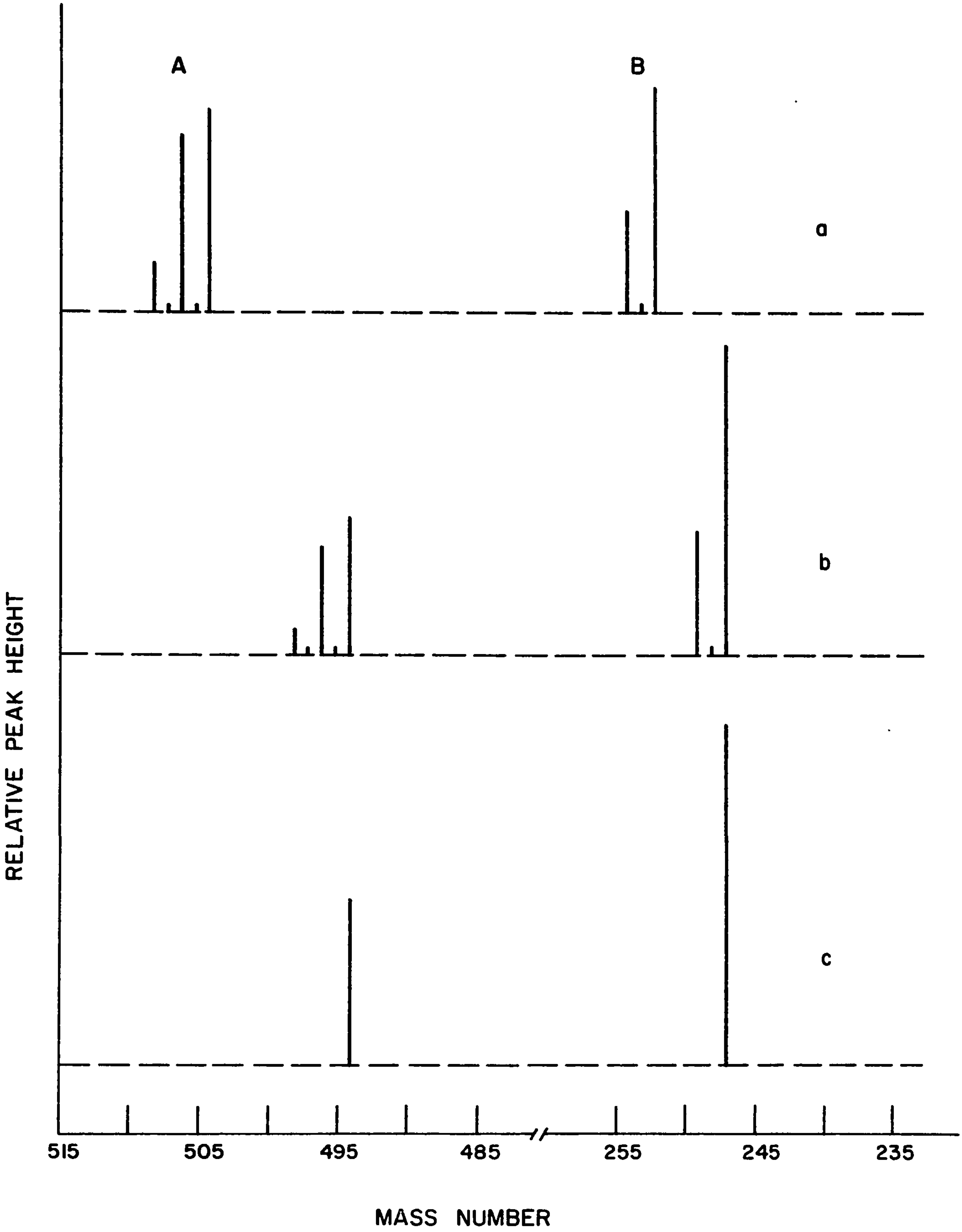
A) Dimeric Mass

B) Monomeric Mass

a) Cu-AAP

b) Ni-AAP

c) Ni-AAP with Nickel-58 Single Isotope.


A
B
a
b
c
RELATIVE PEAK HEIGHT
515
505
495
485
255
245
235
MASS NUMBER

other copper (II) chelates studied in the present work. The spectrum in the region A has three peaks of different heights separated by two m/e units. In the region B there are two intense peaks also separated by two m/e units. This pattern can be explained on the basis of isotopic distribution of naturally occurring copper. There are two predominant isotopes of copper, ^{63}Cu and ^{65}Cu, with natural abundance of 69.9% and 30.91% respectively. The peaks at 252 and 254 m/e values correspond to the monomer of the complex containing copper-63 and copper-65 respectively. Similarly for the dimeric species, the m/e values at 504, 506, and 508 correspond to combinations of the two metal isotopes ^{63}Cu-^{63}Cu, ^{63}Cu-^{65}Cu, and ^{65}Cu-^{65}Cu respectively.

Neglecting the contributions from the less common isotopes of carbon, hydrogen, nitrogen, and oxygen, the relative intensities of the different peaks for the dimer and the monomer species can be calculated from the statistical distribution of ^{63}Cu and ^{65}Cu in nature. The observed and calculated relative intensities are shown in Table (V). The results are found to agree well.

Nickel also has two predominantly occurring isotopes, ^{58}Ni and ^{60}Ni, with natural abundance of 67.88% and 26.23% respectively. This explains why the mass spectra of copper and nickel tridentate chelates have similar patterns. The intensity distribution of the different isotope containing species of acetylacetone-mono-(o-hydroxyanil) nickel (II) are shown in Table (V). The nickel chelates of the

Table V

Mass Spectra of Tridentate Schiff Base Chelates. Intensity Distributions for Certain Metal Isotope Containing Species.

Mass	Isotopes Contained	Peak height (cm)	Relative Intensity	
			Cal.	Obs.
a) Acetylacetone-mono-(o-hydroxyanil) copper (II)				
508	65-65	0.7	0.2	0.3
506	65-63	2.6	1.0	1.0
504	63-63	3.0	1.1	1.2
254	65	1.5	1.0	1.0
252	63	3.3	2.2	2.2
b) Acetylacetone-mono(o-hydroxyanil) nickel (II)				
498	60-60	0.4	0.3	0.2
496	60-58	1.6	1.0	1.0
494	58-58	2.0	1.3	1.3
249	60	1.8	1.0	1.0
247	58	4.5	2.5	2.6

other tridentate chelates also have similar pattern and intensity distribution in their mass spectra.

Fig. (8c) shows the mass spectra when a metal ion containing a single isotope (Nickel-58) is used for the preparation of the chelate. The multi-peak patterns in the region A and B collapse to give single peaks corresponding to this isotope.

ii) Magnetic moments and nuclear magnetic resonance spectra

The copper (II) complexes with tridentate Schiff bases containing oxygen donor atoms have subnormal magnetic moments, Table (VI). These results compare well with the previously reported values. The complexes of copper (II) containing sulfur donor atoms and the pyridinates of all the copper (II) complexes studied possess normal magnetic moments.

All the complexes of nickel (II) except Ni-SAP and Ni-AAP are diamagnetic; this suggests a planar arrangement of the donor atoms around the nickel atom and a similarity of their structures with that of acetylacetone-mono-(o-hydroxyanil) copper (II), (XIV). Elemental analyses of Ni-SAP and Ni-AAP show that two water molecules are co-ordinated to each dimeric molecule of the chelate; the observed paramagnetism in these two chelates is therefore not surprising.

N.M.R. measurements are of limited usefulness in the structural studies of these complexes. The chelates of copper (II) and the pyridine solutions of nickel (II) chelates are paramagnetic. A comparison of the n.m.r. spectra of the dimer with the monomer would have been of interest.

Table VI

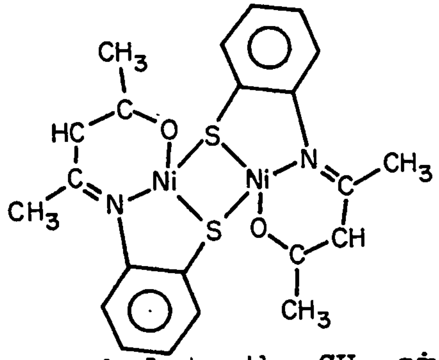
Magnetic Moment Data for the Tridentate Schiff Base Chelates of Copper (II), Nickel (II) and their Pyridine Adducts.

Compound	T^{o}K	μ(B.M.)
Cu-SAP	296	1.30
Cu-SAP.Py	296	1.86
Ni-SAP.H_2O	297	1.50
Cu-AAP	296	1.38
Cu-AAP.Py	296	1.85
Ni-AAP.H_2O	296	1.53
Cu-SASP	297	1.90
Cu-SASP.Py	296	1.90
Ni-SASP	297	diamagnetic
Ni-AASP	297	diamagnetic

Py = Pyridine

But n.m.r. spectra nevertheless indicate very clearly the drastic rearrangement that some of the ligands undergo on complex formation. A typical case is the condensation product of o-aminothiophenol with acetylacetone and its reaction with nickel (II). The above condensation product is a heterocyclic compound, (XVIII). The n.m.r. spectrum, Fig. (7), shows two $-CH_3$ signals at 1.80 and 2.20 δ p.p.m.; a doublet for the $-CH_2-$ group around 3.14 δ p.p.m. and the N-H resonance at 5.03 δ p.p.m. On reaction with nickel (II) ion, the heterocyclic compound rearranges to the Schiff base and presumably forms the binuclear chelate, XXII.

XXII



In the spectrum of the chelate the CH_3 signals are shifted downfield by 0.20 δ p.p.m. The signals for $-CH_2-$ and N-H protons vanish. A new peak for the γ proton appears at 5.23 δ p.p.m. Fig. (7).

iii) Vapour Pressure Osmometry

In order to ascertain whether the complexes of tridentate Schiff bases are monomeric in pyridine and dimeric in weak coordinating solvents, molecular weights were determined in these solvents using vapour pressure osmometry method. The instrument was calibrated for each solvent by using Pyridil and Benzil as standards. The results are shown in Table (VII).

Table VII

Molecular Weights Determined by Vapor Pressure Osmometry.

Compound	Conc. (M)	Solvent	Molecular weight	
			Obs.	Cal. for (monomer)
Cu-SAP	0.05	Pyridine	274	274.8
Ni-SAP	0.025	"	279	269.9
Cu-SSP	0.025	"	289	290.7
Cu-AAP	0.025	"	250	252.7
Ni-AAP	0.025	"	251	247.9
Ni-AASP	0.025	"	259	264.0
Ni-SSP	0.01	S-tetrachloroethane	567	286.0
Ni-AASP	0.02	"	521	264.0

It is seen that in pyridine solution all the chelates are monomeric. Unfortunately most of the chelates are insoluble in non-coordinating solvents; only the nickel chelates were sufficiently soluble in 1,1,2,2-tetrachloroethane. Molecular weight determination in this solvent indicated that the nickel chelates are dimeric.

Cryoscopic determination of the molecular weights for tri-coordinated copper (II) complexes made by Ohta(90) has shown that N-salicylidene-N'-n-caprinylhydrazine copper (II) and N-salicylidene-N'-n-palmitylhydrazine copper (II) are dimeric.

iv) Vibrational spectra

The high frequency infrared spectra of some of the tridentate Schiff base chelates have been discussed in the previous section in connection with the structures of the free ligands. It has been demonstrated how infrared spectra give clear indication of chelate formation.

In this section the low frequency infrared and Raman spectra of the chelates will be discussed in terms of their binuclear structures. Tentative assignment for the metal-ligand vibrations will be made, and the possibility of correlation of the metal-oxygen stretching frequencies with the magnetic moments of the copper chelates will be discussed.

The structure of acetylacetone-mono-(o-hydroxyanil) copper (II) as determined by X-ray diffraction(18,19) shows the molecule to be a dimer with two copper atoms of the asymmetric unit bridged together by the phenolic oxygen atoms of the ligand molecules. The skeleton structural unit has very nearly a square planar arrangement.

In the case of chelates from other ligands, three isomers are possible depending on which one of the two oxygen atoms or a mixture of these are in the bridge. Attempts in this study and others(92) to separate the isomers were unsuccessful. In the light of the structural evidence for crystalline acetylacetone-mono-(2-hydroxyanil) copper (II), it would seem reasonable that these compounds also have one isomer in which the oxygen atom from the aminophenolic (more acidic) moiety acts as a bridge between the copper atoms.

In the case of chelates having sulfur donor atoms it is believed that the sulfur atom bridged binuclear single isomer exists. This belief is based on two factors (aside from vibrational spectral evidence):

i) A large number of complexes exist in which sulfur atom acts as a bridge between two metal atoms. The bridge-forming ability of sulfur appears much stronger than that of oxygen or chlorine.(93)

ii) A bridging sulfur atom is known to inhibit the process of spin-exchange between bridged copper (II) atoms. All tridentate Schiff bases of copper (II) having oxygen donor atoms possess subnormal magnetic moments, whereas their sulfur analogs show normal magnetic properties.(17)

The symmetrical fragmentation of these chelates along the bridge (forming monomers) does not permit useful mass spectral technique in isomer identification.

The vibrational spectra of the chelates having the same ligand but different metal atoms show striking similarity, Fig. (9), except for the shifting of a few bands in the low frequency region. This indicates that the chelates have more or less similar structure.

From a comparison of the vibrational spectra of a ligand with the spectra of its chelates of different metal ions, it is possible to select the bands which are metal sensitive. Some of these appear as strong bands in the spectra of the chelates only and are absent in the spectra of the ligands. These bands are assignable to metal-ligand stretching vibrations.

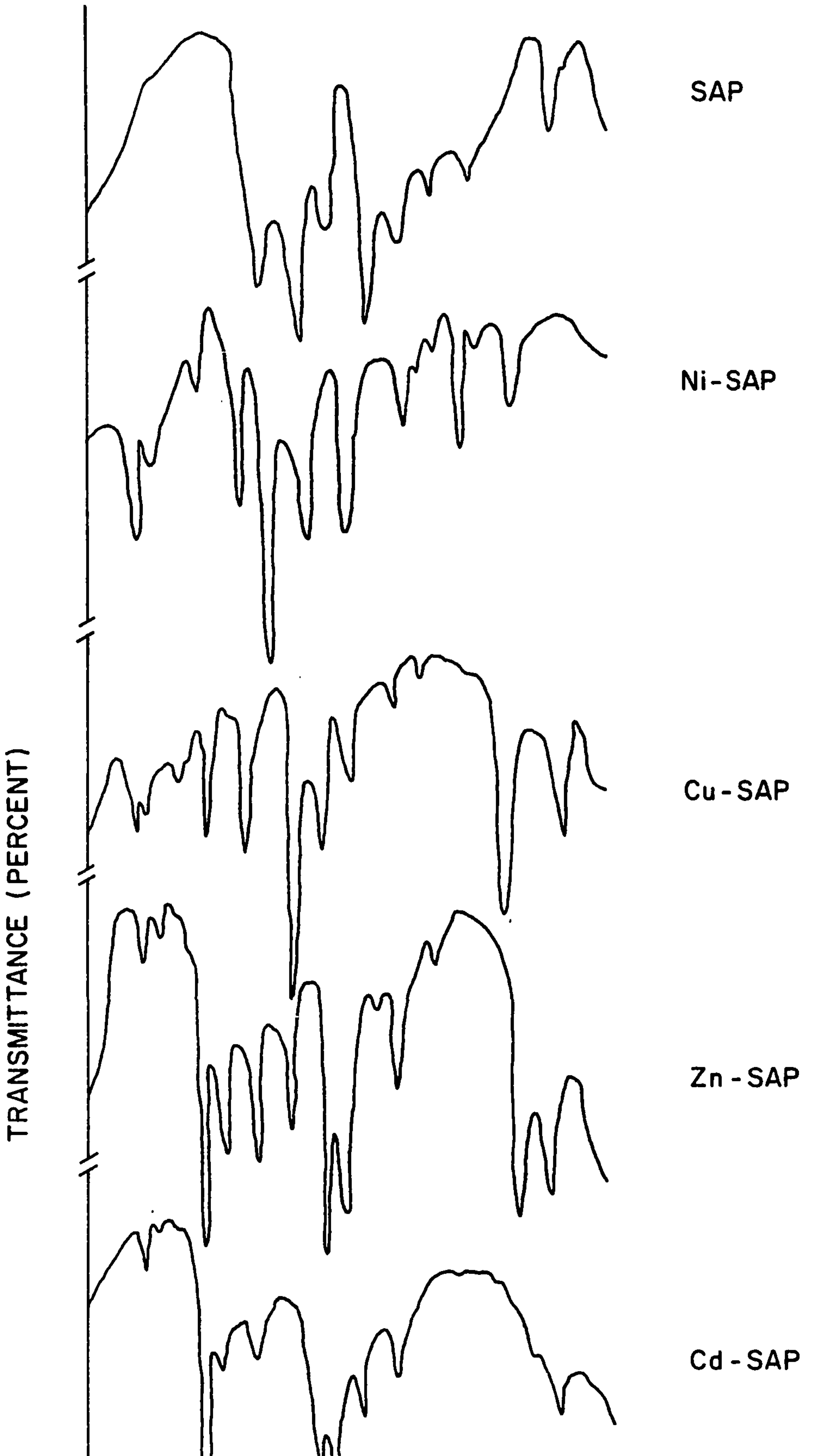
Moreover, when a sulfur atom is substituted for an oxygen atom in the ligand, one may expect a shift in the metal-ligand vibration due to difference in mass between oxygen and sulfur atoms. By comparing the spectra of the chelates of the same metal atom with the two ligands, useful information regarding metal-ligand vibrational bands can be obtained.

Because of large atomic polarizabilities, the intensity of the metal-ligand vibrational bands in the Raman(153) spectra is expected to be enhanced. Indeed, in the Raman spectra of these chelates metal-sensitive intense bands were observed, some of which appeared as new bands which were absent in the ligand spectrum.

In the spectra of the tridentate Schiff base chelates studied, there are three regions in the low frequency spectra where metal-sensitive bands appear:

Figure 9

Comparison of the Low Frequency (700–300 cm^{-1}) i.r. Spectra of SAP with its Metal Chelates.



TRANSMITTANCE (PERCENT)
SAP
Ni-SAP
Cu-SAP
Zn-SAP
Cd-SAP
700
500
300
FREQUENCY (CM^{-1})

i) There is a strong band in the region 585-650 cm^{-1} both in the i.r. and Raman spectra (but not at identical frequency) of all the chelates. This band is absent in the spectra of the ligands.

ii) Another band appears in the region 450-550 cm^{-1}. However, there are considerable uncertainties in identifying this band, since this region is crowded with ligand absorption bands. In the Raman spectra this band is more easily identifiable since this is much more intense compared to nearby bands.

iii) Two intense bands occur in the region 230-400 cm^{-1}. These appear as new bands in the chelates only and are absent in the ligand spectra. The difference in frequency between these bands varies in different chelates from a minimum value of 23 cm^{-1} to a maximum of 100 cm^{-1}. Both of these bands are shifted to lower frequencies when a sulfur atom is substituted for an oxygen atom in the ligand.

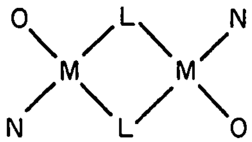
All of the above bands are assignable to metal-ligand vibrational frequencies and their pattern reflects the dimeric structure of the chelates.

Ueno and Martell(94) reported the infrared spectra of the metal chelates of bisacetylacetone-ethylenediimine and bissalicylaldehydeethylenediimine and related chelates. They observed metal sensitive bands in the same region as (i) and (ii) discussed above which they assigned to metal-donor linkages. This agreement in the results seems significant in the light of the fact that the ligands used in the present study have similarities with those used by Ueno and Martell.

For most cyclic systems, e.g. metal chelates, the concept of group vibration is inapplicable and normal coordinate analyses are necessary to determine which bonds and angles vary during each normal vibration. However, it has been shown(95) that there are some vibrations which have predominant metal-ligand character and these can be associated with specific metal-ligand bonds in the chelate. To some extent the spectra of these complexes can be separated into a part arising from the ligand and a part due to the skeletal vibrations. The feasibility and usefulness of the assignment of metal-ligand vibrations in metal complexes and chelates has been demonstrated in a large number of publications. Adams(96) recently summarized the data on metal-ligand vibrations.

In the light of the above discussion, attempts were made to assign the metal-sensitive bands observed in the present study to vibrations of specific metal-ligand bonds. The skeletal structure, (XXIII)

XXIII



L = oxygen or sulfur atom

is common to all the chelates of tridentate Schiff bases investigated. Assuming planarity this structure has C_{2h} symmetry; consequently there will be four in-plane i.r. active metal-ligand stretching vibrations of B_u type and four Raman active vibrations of A_g type. Because of the presence of centre of symmetry the i.r. active and Raman active bands will be mutually exclusive. Of these four stretching vibrations one will be metal-nitrogen, one metal-oxygen (for the terminal bonds) and two due to the "bridge" which may either be metal-oxygen or metal-sulfur depending on whether an oxygen or a sulfur atom is in the bridge. This simplified view of the metal-ligand stretching vibrations is very approximate and was used here as a guide in sorting out the metal-ligand vibrational band. It is realized that these bands, though assignable to particular metal-ligand bonds, will by no means be "pure", but could be mixed with ligand and ring vibrations.

The band in the region 585-650 cm^{-1} can be assigned to the terminal metal-oxygen stretching frequency, since the absorption band due to metal-oxygen single bonds, e.g. in alkoxides, was found to appear in the region 500-680 cm^{-1}.(96)

Metal-nitrogen frequencies associated with bonds of order ~ 1 are found in the wide range 600 to < 200 cm^{-1} (96). The lowest frequencies are associated with complexes of heterocyclic bases such as pyridine and the highest values are associated with amines, ethylendiamine, etc. In the present study, the assignment of the band in the region 450-550 cm^{-1} to the metal-nitrogen stretching frequency would be in agreement with previous assignments. Moreover, the greater intensity of this band compared to nearby ligand bands in the Raman spectra seems to be consistent with the better atomic polarizability of the metal-nitrogen bond.(153)

The two bands in the region 230 to 400 cm^{-1} are assigned to bridge metal-ligand vibrations. Because of lower bond order the bridge stretching bands would be shifted to lower frequencies; this has been observed in the case of metal-halogen vibrations.(96)

Fig. (10) compares the spectra of the zinc chelates with salicylaldehyde-2-hydroxyanil and its thio analog. It is seen that in the case of the chelate containing sulfur in the bridge, the metal-ligand vibrations are shifted to lower frequencies. This may be due to differences in the mass between oxygen and sulfur atoms.

Tentative assignments of the metal-ligand vibrations are shown in Tables (VIII), (IX), (X), and (XI).

Nakamoto and co-workers(95,97-99) have shown in recent years that use of metal isotopes offers a convenient method of detecting metal-ligand stretching frequencies in simple metal chelates and complexes. Use of nickel, copper, and zinc isotopes was made in the present study to ascertain the validity of the metal-ligand vibrations in tridentate Schiff bases. However, no measurable change was found in the far infrared and Raman spectra of the complexes containing pure metal isotopes.

Considering the rigidity and complexity of the structures of tridentate Schiff base chelates, it seems unlikely that localized pure metal-ligand vibrational bands

Figure 10

Comparison of the Low Frequency (700-300 cm^{-1}) Spectra of Zn-SAP and Zn-SASP.

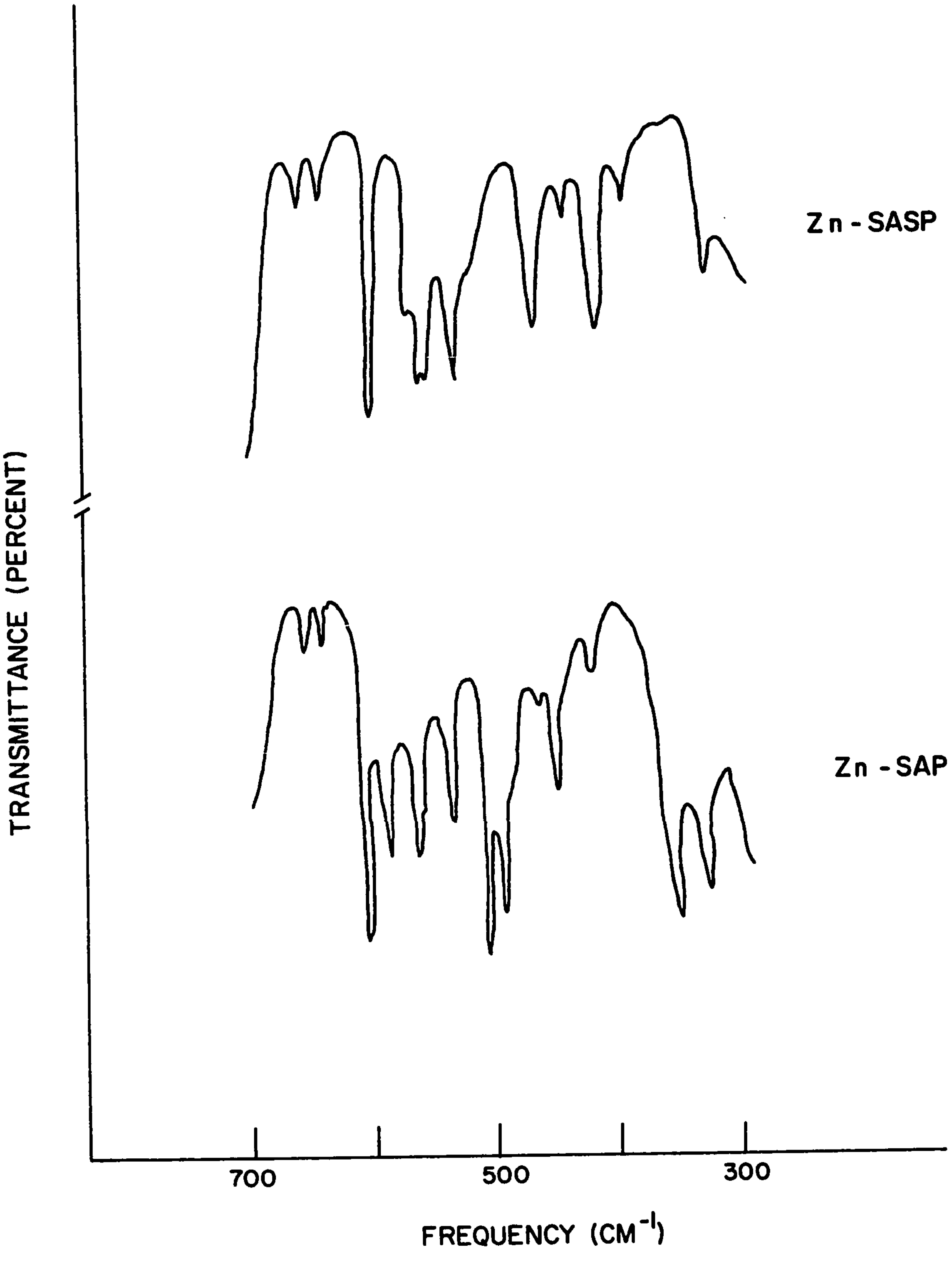

Zn - SASP
Zn - SAP
TRANSMITTANCE (PERCENT)
700
500
300
FREQUENCY (CM^{-1})

Table VIII

Metal-Ligand Vibrational Bands of the Chelates of Salicylaldehyde-2-hydroxyanil.

Metal	i.r. (cm^{-1})	Raman (cm^{-1})	Assignments
Ni	662	618	$(M-O)^t$
Cu	603	592	$(M-O)^t$
Zn	611	598	$(M-O)^t$
Cd	608	592	$(M-O)^t$
Ni	550	571	M-N
Cu	538	555	M-N
Zn	513	492	M-N
Cd	498	505	M-N
Ni	398, 345	380, 315	$(M-O)^b$
Cu	355, 322	322, 290	$(M-O)^b$
Zn	358, 335		$(M-O)^b$
Cd	323	315, 293	$(M-O)^b$

t = terminal, b = bridge

Table IX

Metal-Ligand Vibrational Bands of the Chelates of Salicylaldehyde-2-mercaptoanil.

Metal	i.r. (cm^{-1})	Raman (cm^{-1})	Assignments
Ni	615		$(M-O)^t$
Cu	604	598	$(M-O)^t$
Zn	599	602	$(M-O)^t$
Cd	598	595	$(M-O)^t$
Ni	450		M-N
Cu	432	418	M-N
Zn	425	434	M-N
Cd	418	418	M-N
Ni	388, 290		$(M-S)^b$
Cu	350, 268	365, 262	$(M-S)^b$
Zn	334, 234	328, 243	$(M-S)^b$
Cd	318, 230	318, 238	$(M-S)^b$

Table X

Metal-Ligand Vibrational Bands in the Spectra of the Chelates of Acetylacetone-mono-(o-hydroxyanil).

Metal	i.r. (cm^{-1})	Assignments
Ni	602	$(M-O)^t$
Cu	585	$(M-O)^t$
Pd	522	$(M-O)^t$
Ni	498	M-N
Cu	485	M-N
Pd	488	M-N
Ni	396, 332	$(M-O)^b$
Cu	388, 336	$(M-O)^b$
Pd	373, 310	$(M-O)^b$

Table XI

Metal-Ligand Vibrational Bands of the Chelates of Acetylacetone-mono-(o-mercaptoanil).

Metal	i.r. (cm^{-1})	Assignments
Ni	646	$(M-O)^t$
Pd	640	$(M-O)^t$
Ni	450	M-N
Pd	446	M-N
Ni	380, 322	$(M-S)^b$
Pd	376, 309	$(M-S)^b$

will be observed in their spectra. A particular metal-ligand vibration is probably mixed extensively with other metal-ligand or ligand vibrations.

Lack of observable isotope effect in the vibrational spectra of these chelates is, therefore, not surprising.

The assigned metal-ligand stretching frequencies in Tables (VIII), (IX), (X), and (XI) are probably extensively mixed with other vibrations. But they have considerable metal-ligand vibrational character in view of the fact that they appear as new bands in the chelates and are metal sensitive.

Vibrational spectra and magnetic moments in copper (II) chelates

It has been shown in the case of pyridine N-oxide copper (II) binuclear complexes that the electronic absorption maxima(23) and the metal-oxygen stretching frequencies (Chapter IV, Section 5 of this thesis) correlate with the room temperature magnetic moments. Ginsberg et al.(142) measured the magnetic susceptibility of a series of 5-substituted N-(2-hydroxyphenyl) salicylideneimine complexes of copper (II). They showed that the magnetic exchange interaction in these complexes was dependent on the electronic nature of the substituted groups. It would be interesting to see whether the bridge metal-oxygen stretching frequencies in these complexes have any correlation with exchange interaction or the electronic parameters of the substituent groups. But in the light of the above study with metal isotopes, the prospects of such correlation do not seem to be promising.

v) Electronic spectra

The electronic spectral maxima(23) of 1:1 copper (II)-pyridine N-oxide complexes were reported to have a linear relationship with the lowering of the magnetic moments in these complexes, thus indicating both exchange interaction and dimeric structures of these complexes. No such correlation of the electronic spectra with the magnetic moments of tridentate copper (II) complexes have been reported. Moreover, no systematic study of the absorption spectra in the visible and ultraviolet regions of tridentate Schiff base complexes with other metal ions have appeared in the literature. Some isolated descriptions of the absorption bands are, however, found in a few papers.(57,58,93)

Electronic spectral evidence of molecular association in nickel (II) acetylacetonate have been obtained recently.(100) These workers have shown that in benzene solution nickel (II) acetylacetonate is trimeric with an absorption band at ~ 645 mμ. With the addition of excess pyridine the absorption band maximum shifts to 590 mμ and the bis-pyridine derivative of the monomer is formed.

It has been shown(17,42) earlier that the complexes of copper (II) with tridentate Schiff bases are readily soluble in pyridine and form monopyridinates when recrystallized from this solvent. These monopyridinates have normal magnetic moments, while the corresponding pyridine free complexes have subnormal magnetic moments.(17,42,45) This may imply that pyridine ruptures the binuclear structure of these complexes and forms the pyridinates of the monomer. Molecular weight determination by vapor pressure osmometry carried out in this investigation shows that the complexes of copper and nickel with tridentate Schiff bases are monomeric in pyridine solution.

Fig. (11a) shows the electronic spectra of salicylaldehyde-2-hydroxyanil-nickel (II) in dichloromethane. With the addition of pyridine the absorption maximum shifts from 414 mμ to 420 mμ. The maximum at 420 mμ increases in intensity with the addition of successive drops of pyridine. An isosbestic point is formed at 416 mμ. This shift in absorption maxima may be ascribed to the change from dimeric to monomeric-pyridinate species of this complex. Similar changes are observed in the spectra of copper (II) complexes of salicylaldehyde-2-hydroxyanil, Fig. (11b).

The absorption maxima of the different tridentate Schiff base chelates and their changed position after the addition of pyridine are shown in Table (XII). Although the change in absorption maxima for these complexes is small for any rigorous quantitative evaluation, these results indicate a change from dimer to monomer on a qualitative basis.

Figure 11

Effects of Pyridine on the u.v. Bands of the Binuclear Chelates of Tridentate Schiff Bases

a) Cu-SAP
  1) Normal spectrum
  2) Spectrum after Addition of Pyridine

b) Ni-SAP
  1) Normal spectrum
  2) Spectrum after Addition of Pyridine

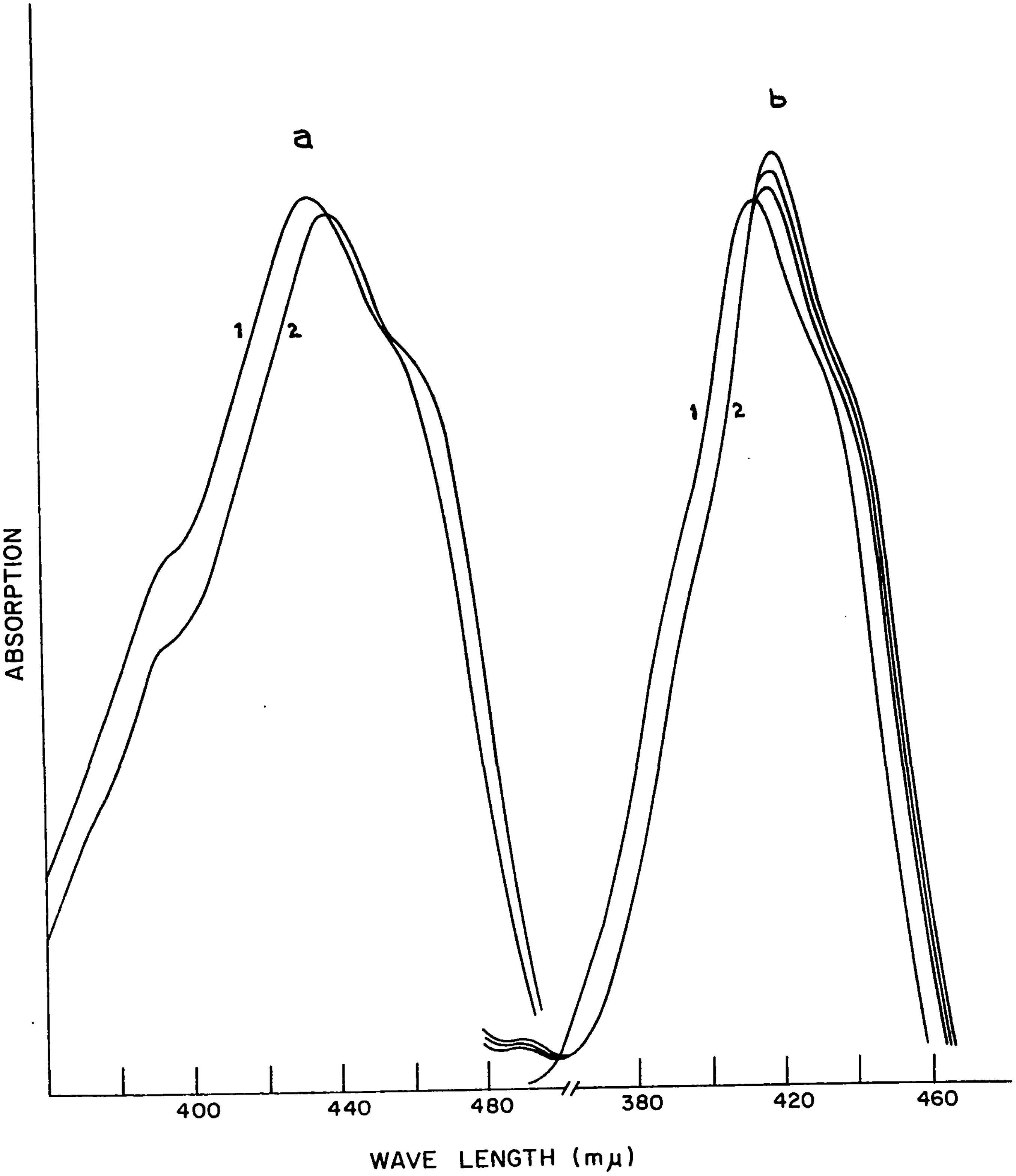

a
b
1
2
1
2
ABSORPTION
400
440
480
380
420
460
WAVE LENGTH (mμ)

Table XII

Change in the u.v. Bands of the Tridentate Schiff Base Chelates after the Addition of Pyridine.

Compound	Solvent	u.v. Band (mμ)	Shifted Position after Addition of Pyridine (mμ)
Cu-SAP	DMSO	434	439
Ni-SAP	Methylenechloride	414	420
Cu-AAP	Ethanol	363	367
Ni-AAP	Ethanol	366	370
Cu-SASP	DMSO	414	418
Ni-SASP	Ethanol	422	425
Ni-AASP	Ethanol	374	382

CHAPTER IV

PYRIDINE N-OXIDE COMPLEXES

A) Introduction

During recent years a large number of metal complexes of pyridine N-oxides have been prepared and characterized.(101) The reasons for the tremendous interest in these complexes mainly are:

a) Complexes of various composition are formed which depend on the relative ratio of the reactants, solvent and temperature.

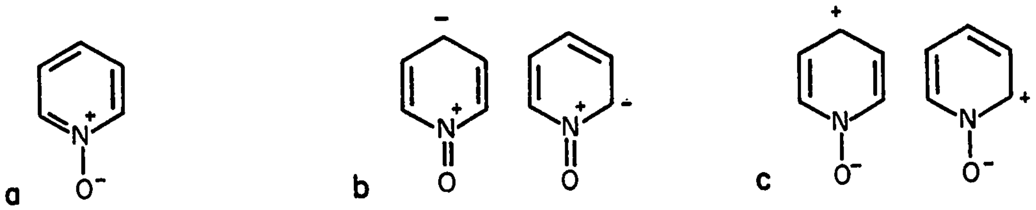
b) The copper (II) halide complexes of pyridine N-oxides show interesting structural varieties. Some of these complexes are polymeric, dimeric or are of intermediate association. Polymerization can take place either through the oxygen atom of the pyridine N-oxides or through the halogen atoms or both. The oxygen-bridged dimers or polymers have interactions between the metal ions, which result in reduced magnetic moments.

c) The basicity of the pyridine N-oxides may be systematically varied by appropriate substitution on the aromatic ring; thereby the substitution parameters of different groups and some electronic properties of the metal ions (which are dependent on those substitution parameters in the complex) can be determined easily.

1) Ligand properties of pyridine N-oxide

The formation of the N-oxide greatly alters the reactivity of the pyridine molecule. The reactivity of the former, as well as certain other characteristic physical properties such as pK, basicity, etc., have been attributed to a different electronic configuration of the molecule. Nearly equal contributions from canonical structures XXIVa, XXIVb, and XXIVc have been suggested for unsubstituted parent molecule.(102,103)

XXIV



Electron withdrawing substituents at the 2- or 4- position enhance contributions from structural type (XXIVb); electron donating groups on the other hand enhance contribution of structural type (XXIVc).

The basicity of the pyridine N-oxides may therefore be systematically varied by appropriate substitution on the aromatic ring with a concomitant minimal change in steric interaction at the reaction site. For a correlation of electronic change with physicochemical and structural properties of metal complexes, pyridine N-oxides have offered an excellent system (where such a complex formation is possible). These properties, plus the ready availability of an extended series of substituted pyridine N-oxides,(104) have greatly contributed to the abundance of co-ordination chemical studies utilizing these ligands.

2) Substituent parameters and oxygen-vibrations of pyridine N-oxides and their complexes

Long before the preparation of the corresponding metal complexes, Shindo(105) found that the N-O stretching frequencies of pyridine N-oxides occur between 1200-1300 cm^{-1}. He also showed that these frequencies correlate well with the Hammett's σ constants. Recently Kubota and Miyazaki$^{(105)}$ reported that a plot of the half-wave reduction potentials of substituted pyridine N-oxides against Hammett's σ constants likewise gave a good linear relationship.

Following the first report of Quagliano et al.$^{(106)}$ on the complex formation of pyridine N-oxides with metal ions, a large number of metal complexes have been prepared and attempts have been made to correlate substituent constants for the various groups with observable properties of the complexes. Although many reasonable correlations have been reported, no single set of substituent parameters have been employed. Most of the reports used a hybrid set of Hammett's σ , σ^{+}, σ^{-} or σ_{e} substituent parameters, which make the comparison of various properties of analogous systems difficult.

Recently Nelson$^{(107)}$ et al. have suggested a substitution parameter which is defined in terms of an internally self-consistent set of values based upon the measured conjugate acid dissociation constants, $K_{BH_O}{}^{+}$ for pyridine N-oxide. The substituent constant σ_{PyNO} is then defined as

$$\sigma_{PyNO} = \frac{\Delta pK_{BH^+}}{\rho}$$

where $\Delta pK_{BH}{}^{+} = pK_{BH_O}{}^{+} - pK_{BH_Z}{}^{+}$

and ρ is the reaction constant.

$pK_{BH_O}{}^{+}$ and $pK_{BH_Z}{}^{+}$ are the negative logarithms of the conjugate acid dissociation constant $K_{BH}{}^{+}$ for the unsubstituted and substituted pyridine N-oxides respectively. Garvey et al.(101) in a recent review have summarized the previous results on pyridine N-oxide complexes and showed that all the presently available data could be satisfactorily correlated with σ_{PyNO}.

Correlations of N-O stretching frequencies with substituent parameters for 4-substituted pyridine N-oxides coordinated with nickel (II),(108,109) titanium,(110) chromium,(111) iron (II),(111) cobalt (II),(111) copper (II),(111) and dioxouranium(111) have appeared. The N-O stretching frequencies in both the free ligands and the complexes of pyridine N-oxides shift to higher energy when electron withdrawing groups are placed at the 4-position. This has been explained(108) in terms of an increased π bond order in the nitrogen-oxygen bond brought about by an increase in the formal positive charge on the nitrogen atom, thereby improving the energy match between the p orbitals of nitrogen and oxygen atoms.

Upon coordination with metal ions, however, the $\nu_{N\text{-}O}$ for pyridine N-oxides decreased from values for the free ligands by 12 to 60 cm^{-1}, thus clearly demonstrating metal-oxygen bond formation.(112,113) The effects of substituent constants on the metal-ligand stretching frequencies in pyridine N-oxide complexes should be of interest and importance. But the difficulty of assigning unambiguous metal-ligand vibrational frequencies and the uncertainty of the degree of vibrational coupling have impeded progress in this field and have led to contradictory assignments(108,109) in some cases. One might expect that the effect of substituents on ν_{M-O} in these complexes should be similar but opposite to the effect of ν_{N-O} and one such example has been reported.(110)

Previous workers have shown that the ν_{M-O} values of the substituted pyridine N-oxide complexes with TiF_4 (110) shifted to higher frequencies with increasing electron donor properties of the substituents and correlated well with σ_{PyNO}. They suggested that this correlation was proof of the validity of their assignment of the metal-ligand stretching frequencies.

The electronic spectrum is another physical property which has been investigated.(108,109,114) A linear correlation of optical absorption band maxima (charge transfer and d-d transition) for substituted pyridine N-oxide complexes of oxovanadium (IV) with appropriate sigma substituents has been found.(114)

3) Copper (II) - Pyridine N-oxide complexes

The copper (II) complexes with pyridine N-oxides have attracted special interest(106,115-131) during recent years mainly because of two reasons:

a) the variety of complexes which are formed with different metal to ligand compositions and the multivarious structural patterns they assume.

b) the magnetic interaction that takes place between the metal ions which results in reduced magnetic moments for the condensed complexes.

a) Structures

While most of the metal ions studied form tetrakis and hexakis complexes with pyridine N-oxides, the chemistry of copper (II) with these donors is quite complex. The aromatic N-oxides - copper (II) complexes may be divided into general categories which reflect their chemical composition and physical properties. Most complexes which have been isolated and characterized are: i) low magnetic moment dimeric 1:1 complexes, ii) low and normal magnetic moment 1:2 dimeric complexes, iii) trans or distorted Cis 1:2 monomeric complexes with normal magnetic moments, iv) polymeric complexes, v) adduct of most of the above complexes with small polar molecules, like DMSO, DMF, CH_3OH or H_2O; and vi) tetrakis and hexakis complexes with normal magnetic moments.

The crystal structures(123,126,130,132-138) of a number of representative complexes from the above types have been determined. Watson(131) in a recent review paper discussed the geometry and physical properties of these complexes in terms of their crystal structure.

b) Magnetic interactions

The 1:1 complexes of copper (II) halides with pyridine N-oxides and some of the condensed 1:2 complexes have abnormally low magnetic moments(116-120) at room temperature. Certain copper containing tridentate Schiff base chelates (as discussed in the previous chapters of this thesis) and other bi- or polynuclear copper (II) complexes(45,119) also show similar properties.

These complexes are usually characterized as oxygen bridged dimer or polymeric species. The temperature dependent magnetic susceptibility of the copper (II) ions in these complexes has been fitted to Bleany-Bower's equation,(139) which is derived from the assumption of a simple scalar interaction of the form $-2J_{ij}S_iS_j$.

$$\chi' = \frac{g^2N\beta^2}{3kT}\left[1+\frac{1}{3}\exp(J/kT)^{-1}+N\alpha\right]$$

where χ' is the susceptibility per gram atom of copper, J is the exchange integral (antiferromagnetic for all known copper dimers) equal to the singlet-triplet splitting, g is the magnetic field splitting factor, and $N\alpha$ is the temperature independent paramagnetism.

The magnetic exchange energies in pyridine N-oxide 1:1 complexes are larger than in many other complexes with smaller Cu(II)-Cu(II) separations. For example, the magnetic moments of cupric acetate monohydrate, acetylacetone-mono-(o-hydroxyanil) copper (II) and (pyridine N-oxide) copper (II) chloride are 1.43 B.M., 1.37 B.M., and 0.77 B.M. at room temperature, respectively,(45) whereas the corresponding metal-metal distances in these structures are 2.64 Å,(46) 2.99 Å,(18) and 3.25 Å(126) respectively. The interaction in these complexes has been classified as superexchange occurring through the p orbitals of the bridging oxygen atoms.(45)

4) Aim of the present study

A correlation was reported between the substituent parameter σ_R and the exchange energy $2J$, for a limited number of 1:1 4-substituted complexes of type $[CuCl_2L]_2$;(121) however, subsequent reports on a more extended series of complexes did not confirm this correlation.(23,142)

Recently, Kidd and Watson(141) reported the exchange energies for a series of 4-substituted complexes and showed that although there was no correlation between all members of this series when σ_R was plotted against the exchange energy, the data indicated two classes of complexes which correlated independently.

Muto et al.(23) showed recently that a correlation exists between the room temperature magnetic moment of the pyridine N-oxide complexes with copper (II) halides and of an electronic transition in the region of 700-1000 nm. This was substantiated by later workers.(141) This correlation means that the factors which affect the electronic energy levels also affect the superexchange mechanism.

Although considerable differences(23,119,142) exist as to the mechanism of the superexchange process, there seems to be little doubt that this exchange interaction depends on a successful overlapping of metal d orbitals containing the unpaired electrons with the p orbitals of the intervening oxygen atoms.

On the basis of the preceding it seems very likely that the extent of interaction in these complexes would be correlated with the metal-oxygen stretching force constant and hence the position of the bridge $\mathrm{M}\begin{array}{c}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{array}\mathrm{M}$ vibrational frequencies. Moreover it is anticipated that substituted groups on the pyridine ring which affect the electron density on the oxygen and the extent of magnetic interaction should also affect the metal-oxygen stretching frequencies. Such correlation if found to exist will throw more light on the mechanism of the superexchange process. No attempts have so far been made in this direction.

The low frequency infrared spectra of a number of pyridine N-oxide-copper (II) complexes have been reported recently.(109,124,131) In these cases the workers were mainly concerned with the assignment of metal-halogen stretching frequencies, Although tentative assignment of the metal-oxygen stretching frequencies for a number of 1:2 and 1:4 copper (II) - pyridine N-oxide complexes have been attempted,(109,127) no systematic effort has been made to compare these assignments with those of the corresponding 1:1 complexes and to correlate these with the substituent parameters or the magnetic properties.

The low frequency infrared spectra of a number of 1:1, 1:2, and 1:4 complexes of copper (II) with an extended series of pyridine N-oxides have been recorded in this study and assignments for the metal-oxygen and metal-halogen stretching frequencies have been made. These results will be discussed in terms of the reported structures, magnetic moments, and substituent parameters for these complexes.

B) Experimental

1) Materials

Pyridine N-oxide (Eastman Organic Chemicals), 4-methyl and 4-nitropyridine N-oxides (Pfaltz and Bauer Inc.), 4-methoxy and 4-cyanopyridine N-oxides (Aldrich Chemical Co. Inc.) were used without further purification.

Anhydrous cupric chloride (Fisher Scientific Company), anhydrous cupric bromide (Allied Chemical; B & A) and cupric perchlorate, hydrated (The G. Frederick Smith Chemical Co.) were also used without any further treatment.

2) Preparation of the complexes

Most of the complexes prepared for this study were reported previously.(23,109,127,143) Some of these complexes could be recrystallized from absolute ethanol or 1-butanol. Others changed composition and/or structure when heated to dissolution in these solvents and were used without further recrystallization. The preparation was repeated at least twice for each of these complexes. All the complexes were dried under vacuum over P_2O_5 for at least 24 hours. Different experimental procedures were used for the preparations of 1:1, 1:2 and 1:4 complexes, as discussed below.

i) 1:1 complexes

An ethanol solution of the ligand was slowly added with stirring to an ethanolic solution containing anhydrous cupric chloride or bromide in slight excess of 1:1 molar ratio. The products either crystallized immediately or upon standing for a short time, and were filtered under vacuum, washed several times with small portions of ethanol and dried under vacuum over P_2O_5. Recrystallization was possible for some of the complexes.

ii) 1:2 complexes

The 1:2 complexes were generally prepared by the slow addition of a warm solution of the cupric halide in ethanol to an excess (more than two times the molar amount of the metal halide) of hot solution of the ligand in the same solvent. The reaction mixture was heated at 70-80° C. for half an hour and then allowed to cool. On standing overnight crystals of the 1:2 complexes precipitated. In most cases the complexes could be recrystallized from ethanol.

iii) 1:4 complexes

These complexes were precipitated immediately from the ethanol solution of stoichiometric mixtures of copper (II) perchlorate hexahydrate and the ligands. They were purified by repeated washing with ethanol and dried under vacuum over P_2O_5.

3) Analytical Data

Microanalyses for carbon, hydrogen and nitrogen were performed by Scandinavian Microanalytical Laboratory, Box 25, 2730 Herlev - DK, Denmark. Copper was determined by electrode-position(145) on platinum plates. The results of the analyses are compared with theoretical values in Table (XIII).

4) Spectral Measurements

Infrared spectra in the range 1400-250 cm^{-1} were recorded with a Perkin-Elmer Model 521 Grating Spectrophotometer. The samples were measured as Nujol mulls supported

Table XIII

Analytical Data for Pyridine N-Oxide Complexes

Ligand	Complex	% Carbon		% Hydrogen		% Nitrogen		% Copper	
		Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
Pyridine N-oxide	$CuLCl_2$	26.2	26.2	2.4	2.2	5.9	6.1	27.3	27.7
	$CuLBr_2$	19.0	18.9	1.8	1.6	4.3	4.4	19.9	19.9
	CuL_2Cl_2	40.8	37.0	4.1	3.1	7.9	8.6	20.8	19.5
	CuL_2Br_2	32.4	29.0	3.2	2.4	6.1	6.8	17.5	15.3
	$CuL_2(NO_3)_2$	35.6	31.8	3.5	2.7	13.8	14.8	16.8	15.9
	$CuL_4(ClO_4)_2$	31.8	29.2	3.5	2.0	12.7	13.6	9.2	9.9
4-Methylpyridine N-oxide	$CuLCl_2$	29.8	29.6	2.9	2.9	5.6	5.8	25.3	26.1
	$CuLBr_2$	21.6	21.7	2.2	2.1	3.9	4.2	19.3	19.1
	$CuL_4(ClO_4)_2$	40.7	41.2	4.3	4.1	7.8	8.0	9.1	9.1
4-Cyanopyridine N-oxide	$CuLBr_2$	21.2	21.0	1.4	1.2		8.2	18.1	18.5
	CuL_2Cl_2	37.6	38.4	2.4	2.2	14.8	14.9	17.1	17.0
	CuL_2Br_2	31.0	31.1	1.8	1.7	11.8	12.1	13.7	13.7
	$CuL_4(ClO_4)_2$	37.9	38.8	2.3	2.2	15.5	15.1		
4-Nitropyridine N-oxide	$CuLCl_2$	21.8	21.9	1.5	1.5	10.3	10.2	23.0	23.1
	$CuLBr_2$	16.4	16.5	1.2	1.1	7.5	7.7	17.5	17.5
	CuL_2Cl_2	28.9	28.9	2.0	1.9		13.5	15.6	15.3
	$CuL_4(ClO_4)_2$	29.0	29.2	2.0	2.0	13.7	13.6	7.9	7.7
4-Methoxypyridine N-oxide	$CuLCl_2$	27.7	27.8	2.8	2.7		5.4	24.3	24.5
	$CuLBr_2$	20.8	20.7	2.1	2.0		4.0	18.2	18.2
	$CuL_4(ClO_4)_2$	37.3	37.9	4.0	3.7	7.1	7.4	7.9	8.3

between cesium bromide plates. Calibration of frequency readings was performed with polystyrene film. The reproducibility of the spectra was checked by running the spectra 2 to 3 times. The average error in frequency reading was 0.5 cm^{-1}.

The spectra in the range 300-170 cm^{-1} were obtained by using a Perkin-Elmer Model 301 Far Infrared Double Beam Spectrophotometer. A Perkin-Elmer Model FIS-3 Far Infrared Spectrophotometer was also used to record the spectra of some of the complexes in the region 400-30 cm^{-1}. The results were in good agreement with those obtained with the other two instruments.

In order to record the spectra in the far infrared region the samples were introduced as thick Nujol mulls on a polyethylene window.

C) Results and Discussion

1) Infrared spectra and structures of copper (II) pyridine N-oxide complexes

In view of variable chemical composition and different possible structures for pyridine N-oxide-Cu (II) complexes, study of the chemical and spectral properties of these compounds may be greatly assisted if X-ray crystal structural data are available. Fortunately a number of such crystal structures(131) of representative compounds have been determined during recent years. Fig. (12) illustrates some of the structures of these complexes.

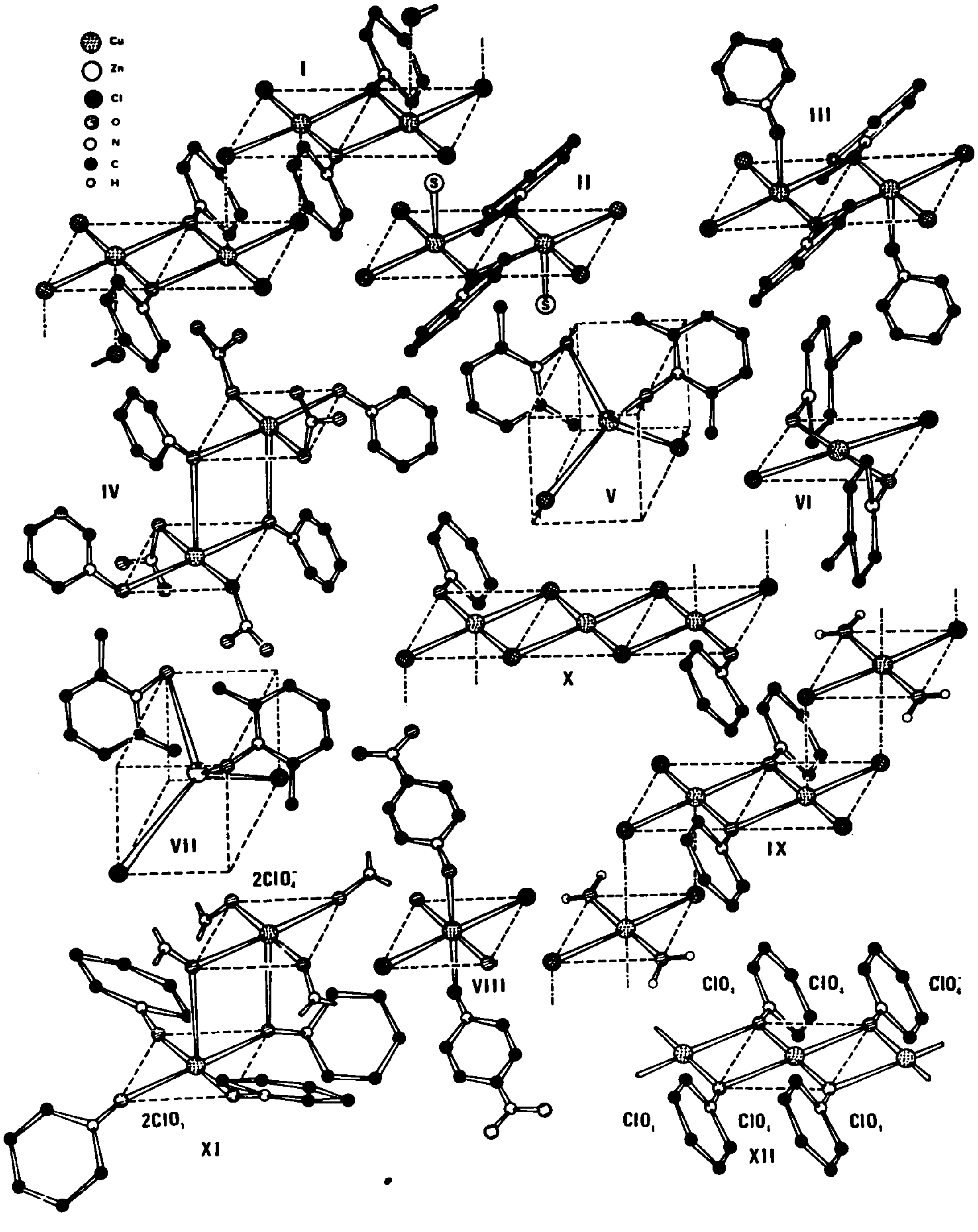
The physical properties of the 1:1 complexes have been explained on the basis of the structure of Di-μ-(pyridine N-oxide)-bis [dichloro-copper (II)] ,Fig. (12,I), which is an infinite chain of oxygen-bridged dimers joined by weak chlorine bridges.(132)

The 1:2 complexes have two different structural varieties. One type represented by the structure of dichlorobis(pyridine N-oxide) copper (II) (133) is dimeric and may be considered as a pyridine N-oxide adduct of the 1:1 complex, Fig. (12,III). The other type is monomeric. The structures of the monomeric 1:2 complexes are essentially square planar and may exist as cis or trans isomers, Fig. (12,VI). The 1:4 complexes have square structures.(138)

The low frequency infrared spectra of a number of 1:1, 1:2 and 1:4 pyridine N-oxide-copper (II) complexes have been recorded. The spectra of some of these complexes were reported previously,(109,127) and the results are in good

Figure 12

Idealized Crystal Structures of the Metal Complexes of Pyridine N-oxides. Reproduced from Reference (131).


Cu
Zn
Cl
O
N
C
H
I
II
S
S
III
IV
V
VI
X
VII
IX
2ClO$_4^-$
VIII
ClO$_4$
ClO$_4$
ClO$_4^-$
2ClO$_4$
XI
ClO$_4$
ClO$_4$
ClO$_4$
XII

agreement with the present study. These spectra can best be understood in terms of the crystal structures as discussed above.

2) Metal-halogen stretching frequencies

The metal-halogen stretching frequencies in the pyridine N-oxide copper (II) halide complexes can be assigned with relative ease. Previous far-infrared spectral studies on complexes containing metal-halogen bonds indicate that metal-chlorine stretching frequencies occur in the range 250-350 cm^{-1} and metal-bromine frequencies from 200-250 cm^{-1}. (143-145)

Comparison of the spectra of the copper chloride complexes with those of the bromides and the free ligands facilitated the assignment of the infrared-active copper-halogen stretching frequencies. The copper-bromine stretching band appeared as much lower frequencies in all cases(Fig.13 Although maxima were observed with some ligands in the 200-350 region, the bands which have been assigned to metal-halogen vibrational modes are generally considerably more intense. For some of the complexes the metal-chlorine stretching frequencies have been assigned previously and the present results are essentially consistent with the earlier work. Results are shown in Table (XIV). It may be noted that the metal-halogen stretching frequencies for these complexes appear within a narrow range (300-332 cm^{-1} for metal-chlorine vibrations, 250-280 for metal-bromine vibrations), Table (XIV).

Table XIV

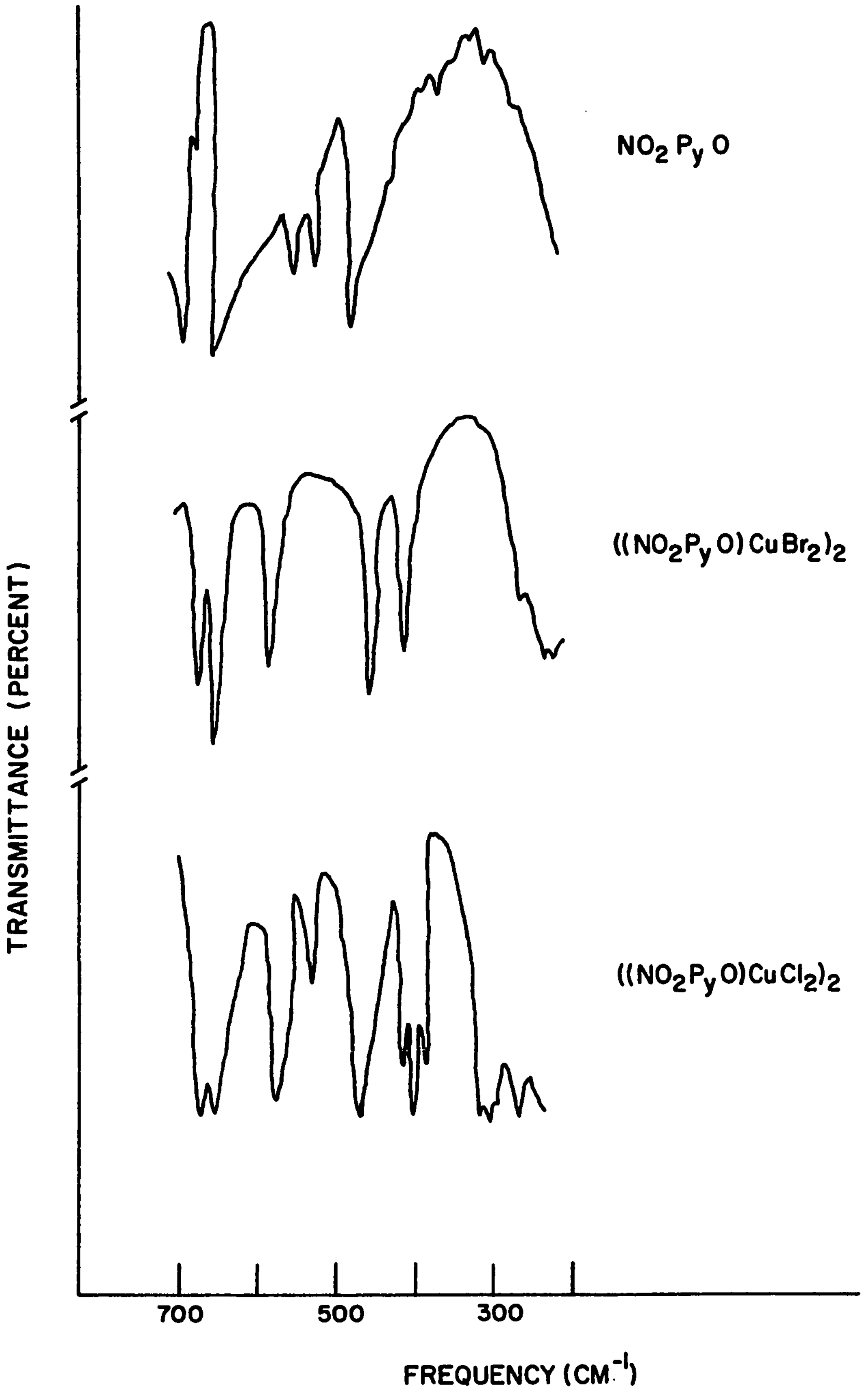
Metal-Halogen Stretching Frequencies in Substituted Pyridine N-oxide Copper (II) Halide Complexes.

Ligand	M-Cl		M-Br	
	1:1	1:2	1:1	1:2
Pyridine N-oxide	316^{vs}	335^{vs}	268^{vs}	
4-Picoline N-oxide	331^{vs}, 320^{vs}	332^{vs}, 314^{m}	268^{s}, 230^{s}	
4-methoxy Pyridine N-oxide	330^{vs},	330^{vs}	255^{s}	
4-chloropyridine N-oxide*	317^{s}, 314^{m}	341^{vs}		
4-Nitropyridine N-oxide	308^{vs}	350^{vs}	279^{vs}, 265^{m}	
4-cyanopyridine N-oxide	332^{vs}, 318^{vs}	312^{vs}, 290^{vs}	250^{s}	253^{s}

* data from reference 127

<u>Figure 13</u>

<u>Low Frequency i.r. Spectra of 4-nitropyridine N-oxide and its 1:1 Complex with Cupric Halides.</u>



TRANSMITTANCE (PERCENT)
NO_2PyO
$((NO_2PyO)CuBr_2)_2$
$((NO_2PyO)CuCl_2)_2$
700
500
300
FREQUENCY (CM^{-1})

The nature of substituent groups on the pyridine ring does not seem to have much effect on the metal-halogen vibrational frequencies.

3) Metal-oxygen vibrational bands

The metal-oxygen vibrational frequencies in the pyridine N-oxide-copper (II) halide complexes were assigned to these bands which appeared in addition to ligand and metal-halogen absorptions. These were found as strong bands in a clear region of the spectra. In contrast to the metal-halogen stretching frequencies, the metal-oxygen bands were found to be very much dependent on the nature of substituents on the pyridine ring and encompass a much broader (510-350 cm^{-1}) region. This is not surprising in view of the fact that the different substituted pyridine N-oxides used for the present study have widely varying pK_a values. The metal-oxygen stretching frequencies should be dependent on the availability of electron density on the oxygen atom.

The assignment of the metal-oxygen stretching frequencies of 1:4, 1:2 and 1:1 complexes are shown in Tables (XV) and the results are discussed in the following section.

i) 1:4 and 1:2 complexes

Whyman et al.(109,127) had previously assigned the metal-oxygen stretching frequencies to some of the 1:4 and 1:2 monomeric complexes. The present assignments are consistent with those reported earlier, except for the 4-methoxy pyridine N-oxide complex. A very strong band close to 475 cm^{-1}

Table XV

Summary of Metal-Oxygen Stretching Frequencies (cm^{-1}) for 1:1, 1:2, and 1:4 Complexes of Pyridine N-oxide with Copper (II).

Ligand	1:1 Complexes		1:2 Complexes		1:4 Complexes
	Chloride	Bromide	Chloride	Bromide	Perchlorates
Pyridine N-oxide	400^{s}	405^{s}	385^{s}	420^{vs}	420^{s}
4-Picoline N-oxide	440^{s}	450^{s}	426^{s}	*417^{m}	440^{s}
4-Methoxy Pyridine N-oxide	504^{vs}	501^{vs}	478^{vs}		475^{s}
4-chloropyridine N-oxide	*437^{s}	*439^{s}	*420^{s}		**447^{s}
4-cyanopyridine N-oxide	468^{s}	388^{m}	392^{s}	365^{s}, 332^{s}	380^{s}
4-nitropyridine N-oxide	400^{m}	412^{m}	375^{s}		375^{s}

* Data obtained from reference 127
** Reference 109

is assigned to ν_{M-O} in this complex, whereas the earlier workers reported a value near 340 cm^{-1}. The latter band may be associated with internal vibrations of the ligand, which became activated after complex formation. A band of medium intensity in this region is present in all the complexes formed with 4-methoxy pyridine N-oxide. For the different chloride and bromide complexes with 1:4, 1:2 and 1:1 metal to ligand compositions this band remains unaltered in position. In contrast to the 475 cm^{-1} band, the band at 340 cm^{-1} does not appear to be sensitive to the stoichiometry and the nature of the complexes, Fig. (14).

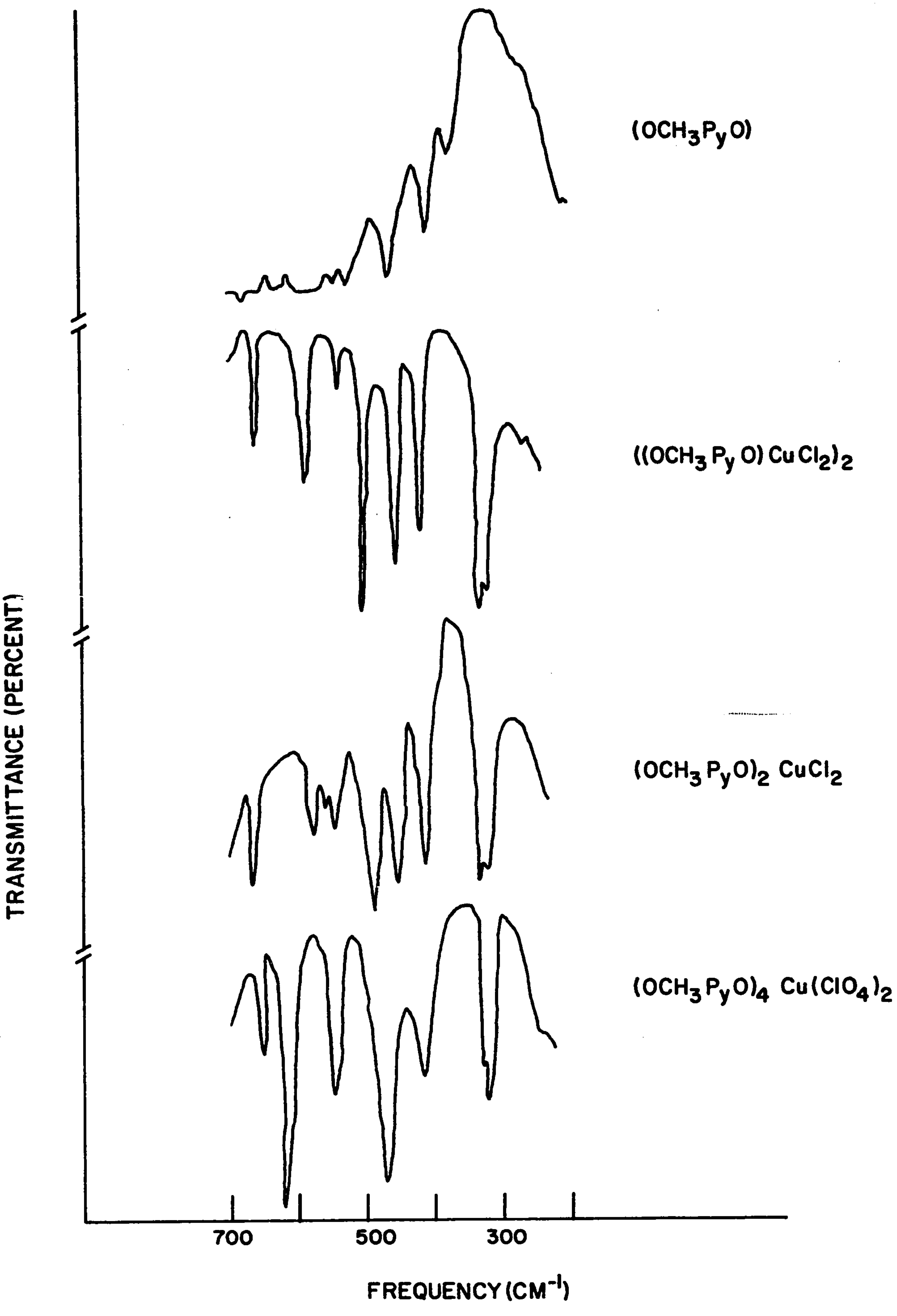
ii) <u>1:1 complexes</u>

The 1:1 complexes also have absorption bands in the same region as the 1:2 and 1:4 complexes which are assignable to metal-oxygen stretching frequencies. Earlier reports (127) dismissed the idea that these might also be metal-oxygen vibrational bands, on the ground that the ν_{M-O} arising from "terminal" and "bridged" pyridine N-oxide ligands should not occur at very similar energies. However, these authors did not give any satisfactory explanation for the occurrence of these bands. These bands are now assigned to the bridged metal-oxygen stretching frequencies in these complexes, Table (XV).

The possibility of appearance of terminal and bridged metal-oxygen vibrational frequencies in a very similar region should not be surprising in the light of X-ray struc-

Figure 14

Comparison of the Low Frequency i.r. Spectra of 4-methoxypyridine N-oxide and its 1:1, 1:2 (monomeric) 1:4 Complexes with Copper (II).


(OCH$_3$PyO)
((OCH$_3$PyO)CuCl$_2$)$_2$
(OCH$_3$PyO)$_2$ CuCl$_2$
(OCH$_3$PyO)$_4$ Cu(ClO$_4$)$_2$
TRANSMITTANCE (PERCENT)
700
500
300
FREQUENCY (CM^{-1})

tural data. In Table (XVI) the metal-oxygen bond lengths of a number of 1:1, 1:2 and 1:4 complexes are listed together with their assigned M-O stretching frequencies. It is seen that despite wide structural and chemical difference among them, the average metal-oxygen bond lengths in the complexes fall between 1.91 and 2.20 A units. The metal-oxygen bond length in $[PyOCuCl_2]_2$(an oxygen bridged 1:1 dimeric compound) and $[2,6\text{-}(CH_3)_2PyO]_2CuCl_2$ (a trans monomeric compound) are only slightly different. It therefore seems reasonable to assume that these compounds will have comparable metal-oxygen stretching frequencies. The tentative assignment of ν(M-O) for the 1:1 complexes, Table (XV), was made on this basis.

Further evidence in support of the above assignments of metal-oxygen stretching frequencies in 1:4 and 1:1 complexes came from the correlation of ν(M-O) with the substituent parameters of pyridine N-oxides and the magnetic moments, as will be discussed in sections C(4) and C(5) of this chapter.

It is interesting to note that the metal-oxygen stretching band in 1:1 complexes appears at a relatively higher frequency than the corresponding 1:2 or 1:4 complexes. A typical case is shown in Fig. (14), which compares the spectra of 1:1, 1:2 and 1:4 complexes of 4-methoxy pyridine N-oxide. The occurrence of super-exchange in the 1:1 complexes probably strengthens the bridge metal-oxygen bond. The increase of the M-O stretching frequency in the 1:1 complex-

Table XVI

M-O Bond Distances and Stretching Frequencies (ν_{M-O}) in Pyridine N-oxide Complexes.

Compound	Structural Type	M-O Bond Length(Å)	ν(M-O)
$[PyOCuCl_2]_2$	1:1 (Dimer)	1.98(a) 2.04	400^{s}
$(2,6\text{-}(CH_3)_2PyO)_2CuCl_2$	1:2 (Monomer)	1.93(b) 1.97	408^{m} 370^{s}
$(PyO)_2Cu(NO_3)_2$	1:2 (Dimer)	1.96(c) 2.44	415^{vs} 354^{vs}
$(PyO)_4Cu(ClO_4)_2$	1:4 (Monomer)	1.93(d) 1.92	420^{vs}

a, reference 130; b, reference 134; c, reference 137; d, reference 138.

es may be due to this superexchange.

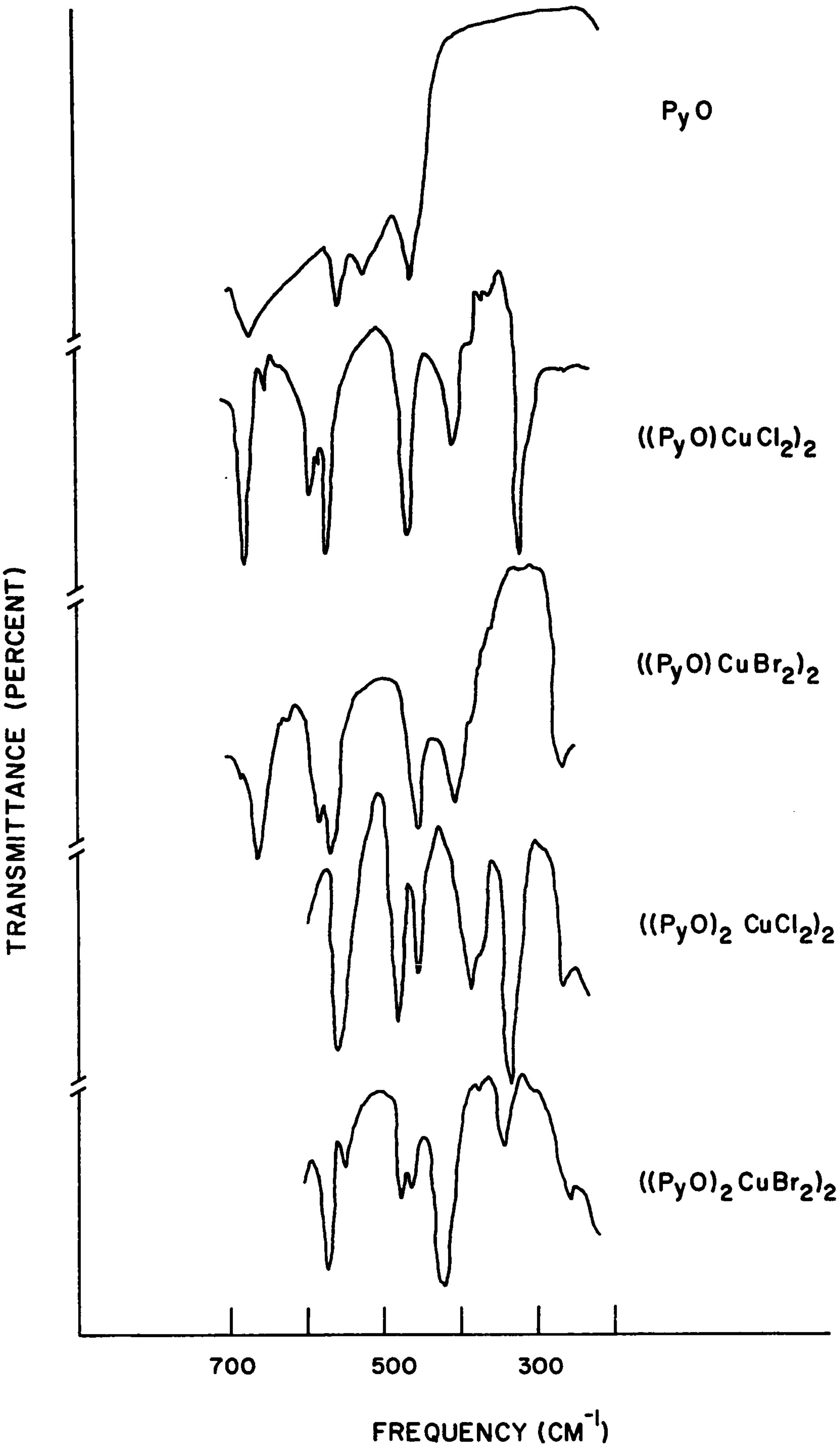
iii) 1:2 dimeric complexes

The infrared spectra of 1:2 dimeric complexes appear to be in accord with their molecular structures. As discussed before, the structures of these complexes may be considered as the pyridine N-oxide adducts of the 1:1 binuclear complexes. While the spectra of 1:1, monomeric 1:2 and 1:4 complexes show one band assignable to the metal-oxygen vibration, the 1:2 dimeric compounds show more than one such band, corresponding to the non-equivalent metal-oxygen bonds of the bridging and apical types. A comparison of the spectra of 1:1 and dimeric 1:2 complexes of cupric chloride and bromide with pyridine N-oxide is shown in Fig. (15). The 1:2 complex of cupric bromide with 4-cyanopyridine N-oxide has two M-O bands at 365 and 332 cm^{-1} and may likewise have dimeric structure. The X-ray structure for the latter compound has not been reported.

Pyridine N-oxide forms 1:2 complex with copper (II) nitrate. The crystal structure reveals the complex to be an oxygen-bridged dimer(137), Fig. (12,IV). It is composed of two centrosymmetrically related complex monomers. The copper atom has a distorted tetragonal pyramidal environment of five oxygen atoms, but unlike the 1:2 complex of copper (II) halides, the bridging N-oxide ligands occupy one basal site and one apical site. Four metal-oxygen bonds of nearly equal lengths (mean value 1.96 Å) are coplanar; the fifth bond (2.44

Figure 15

Low Frequency i.r. Spectra of Pyridine N-oxide and its 1:1 and 1:2 (dimeric) Complexes with Copper (II) Halides.



TRANSMITTANCE (PERCENT)
PyO
((PyO)CuCl$_2$)$_2$
((PyO)CuBr$_2$)$_2$
((PyO)$_2$ CuCl$_2$)$_2$
((PyO)$_2$CuBr$_2$)$_2$
700
500
300
FREQUENCY (CM^{-1})

Å) is perpendicular to this plane. The infrared spectrum has two strong M-O bands at 415 and 354 cm^{-1} corresponding to the two unequal metal-oxygen bonds.

4) Correlation of metal-oxygen stretching frequencies with substituent parameters in the complexes of copper (II) with pyridine N-oxides

The crystal field or ligand field strength of pyridine N-oxide ligands may be systematically changed by addition of substituents to the pyridine ring. It should, therefore, be possible to correlate this change in ligand field with the corresponding change in the electronic, magnetic, and bonding parameters of their complexes having similar structures.

With the assignment of the metal-oxygen stretching frequencies, attempts can now be made to correlate the change in these frequencies with the substituent parameters. A successful correlation will in turn prove the validity of these assignments. However, it should be remembered that although these stretching vibrations may have predominantly metal-oxygen character they may be mixed or coupled with other vibrations and any correlation with other parameters of the ligand or the complex can at best be taken as qualitative.

i) 1:4 complexes

Recent reports on the metal complexes with pyridine N-oxide confirm the correlation of physico-chemical properties of the complexes with the electronic nature of the substituents.(108-110,112,121-122,146-151) Hatfield and his co-workers(109) prepared the complexes of type $\left[R\text{-}(PyO)_4Cu\right](ClO_4)_2$, with R at 4 position in the pyridine ring. They found that the d-d bands correlated with σ^+ value of R. All previous work used various sets of Hammett's substituent functions such as σ , $\sigma^{\pm}$, σ_R etc. or a hybrid set of them all. However, as discussed earlier, the usefulness of σ_{PyNO} has recently been demonstrated.(101) This parameter has been used for the present discussion.

The metal-oxygen stretching frequencies, $pK_{BH_z}{}^{+}$ and σ_{PyNO} of the pyridine N-oxides are shown in Table (XVIII). Plotting of ν_{M-O} against σ_{PyNO} and $pK_{BH_z}{}^{+}$ are shown in Fig. (16) and Fig. (17) respectively. It is seen that ν_{M-O} progressively falls off with the increase in electron withdrawing power of the 4-substituted group. The non-linearity of this correlation may indicate that the strongly electron withdrawing effect of Cl, CN, or NO_2 groups is counterbalanced by increasing metal to ligand back bonding in these complexes. Recently Muto et al.(23) has shown that such metal to ligand back-bonding affects the d-d band position in a number of 4-substituted 1:4 complexes of pyridine N-oxides with copper (II) perchlorates.

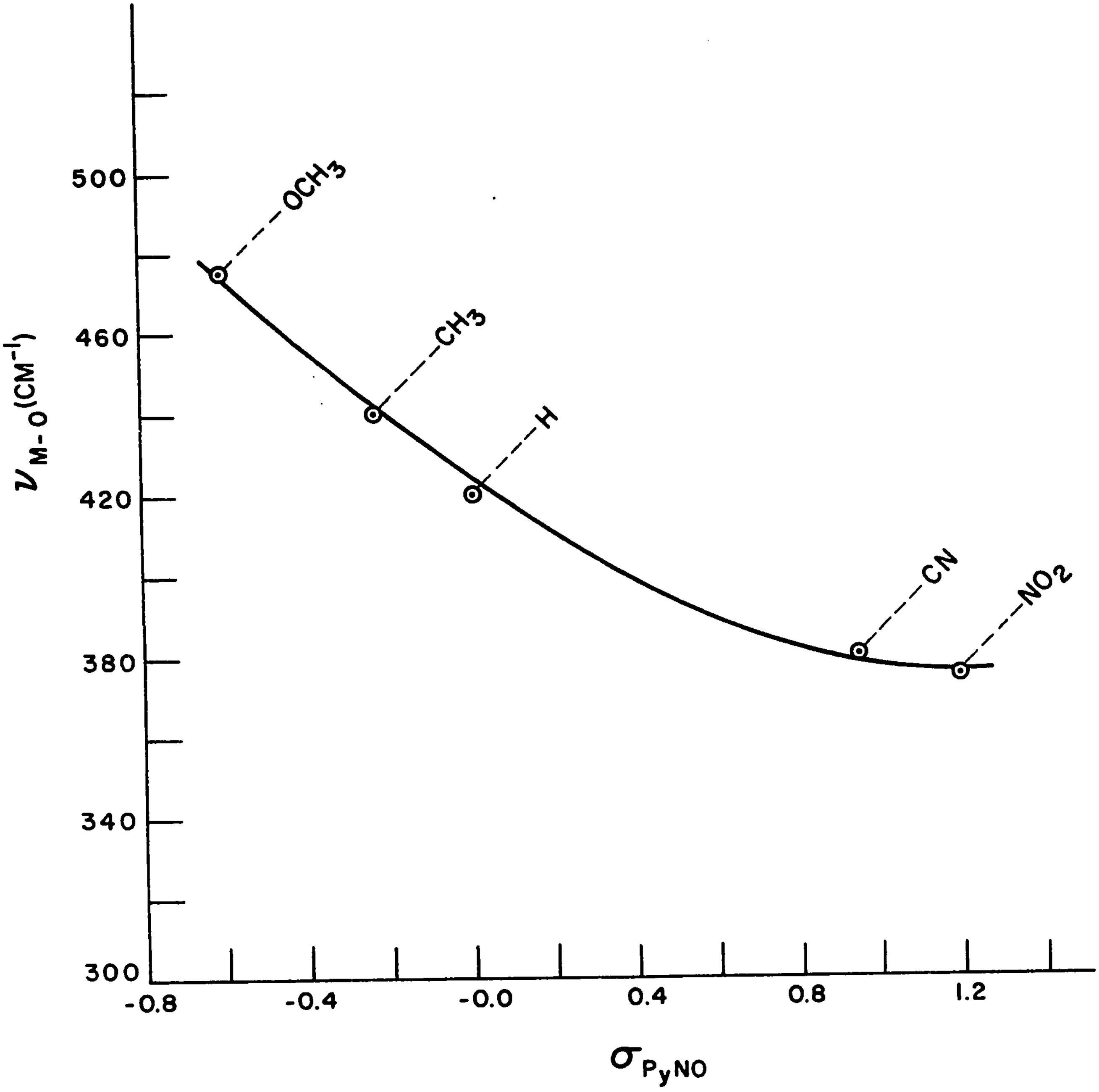
ii) <u>1:1 complexes</u>

The metal-oxygen stretching frequencies of a number of 1:1 complexes along with the σ_{PyNO} and $pK_{BH_z}{}^{+}$ of the ligands are shown in Table (VIII) and plots of ν_{M-O} vs. σ_{PyNO} and ν_{M-O} vs. $pK_{BH_z}{}^{+}$ are shown in Fig. (18) and Fig. (19)

Table XVII

Dissociation Constants ($pK_{BH_z^+}$), Substitution Parameters ($\sigma_{Py\,NO}$) and Metal-Oxygen Stretching Frequencies (ν_{M-O}) in the 1:4 Complexes of Substituted Pyridine N-oxide with Copper (II) Perchlorates.

Ligand 4-Substituted Group	$pK_{BH_z^+}$	$\sigma_{Py\,NO}$	ν (M-O) (cm^{-1})
H	0.79	0.0	420^s
CH_3	1.29	-0.240	440^s
OCH_3	2.05	-0.603	475^s
CN	-1.17	0.94	380^s
NO_2	-1.7	1.19	375^s


OCH3
CH3
H
CN
NO2
500
460
420
380
340
300
ν M-O (CM⁻¹)
-0.8
-0.4
-0.0
0.4
0.8
1.2
σ PyNO

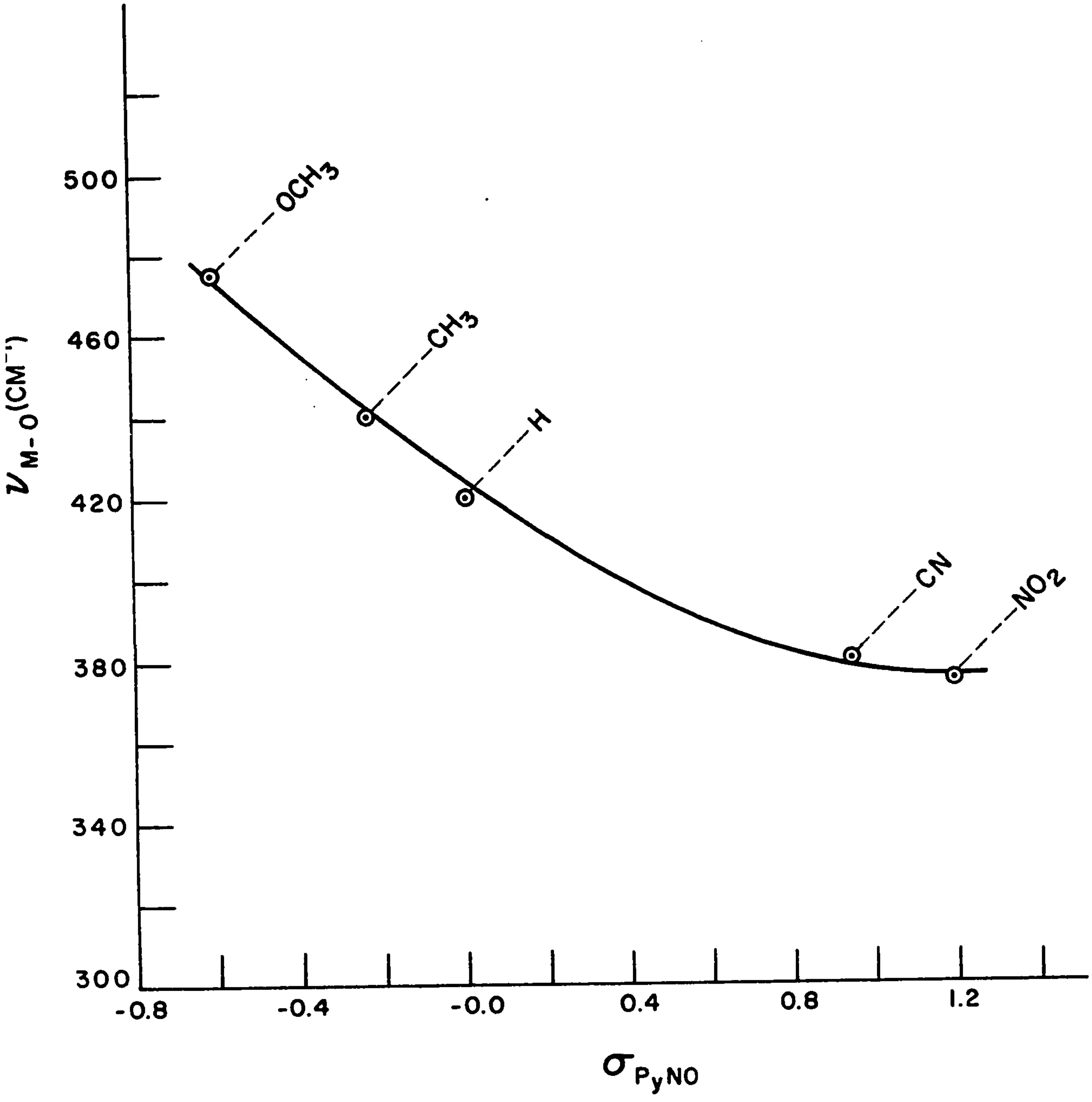

ν_{M-O}(CM^{-1})
500
460
420
380
340
300
-0.8
-0.4
-0.0
0.4
0.8
1.2
σ_{PyNO}
OCH$_3$
CH$_3$
H
CN
NO$_2$

Figure 17

Plot of $pK_{BH_Z}{}^{+}$ vs. ν_{M-O} for the 1:4 Complexes of Pyridine N-oxides with Copper (II).

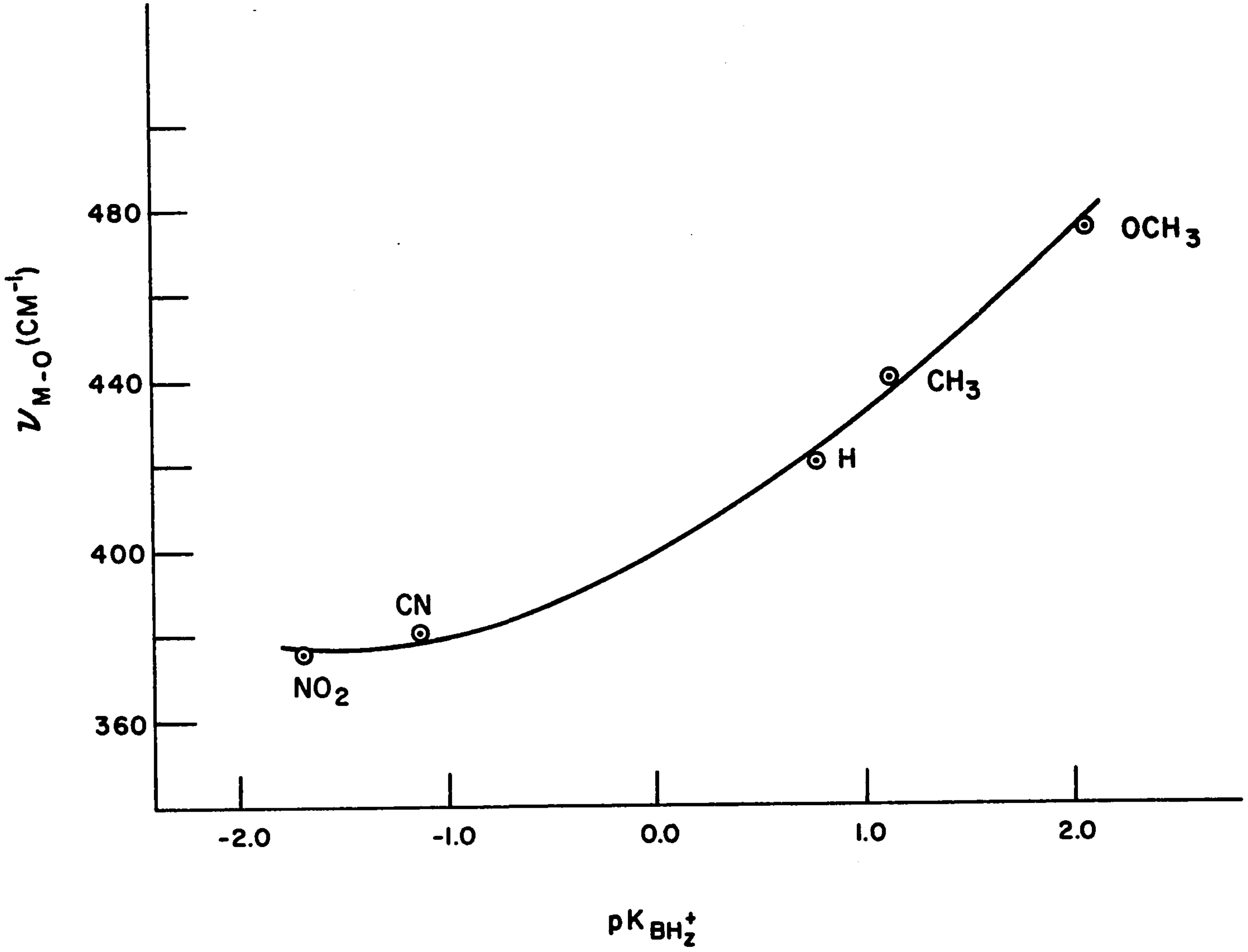

OCH$_3$
CH$_3$
H
CN
NO$_2$
480
440
400
360
-2.0
-1.0
0.0
1.0
2.0
ν_{M-O}(CM^{-1})
pK$_{BH_z^+}$

Table XVIII

Dissociation Constants ($pK_{BH_z}^{+}$), Magnetic Moments (μ), Substitution Parameters (σ_{PyNO}) and Metal-Oxygen Stretching Frequencies (ν_{M-O}) in the 1:1 Complexes of Substituted Pyridine N-oxide with Copper (II) Halides.

Ligand 4-Substituted Group	Halogen	$pK_{BH_z}^{+}$	σ_{PyNO}	μ(B.M.) Watson	μ(B.M.) Muto	ν_{M-O} (cm^{-1})
H	Cl	0.79	0.0	0.63	0.73	400
H	Br	0.79	0.0		0.54	405
CH_3	Cl	1.29	-0.240	0.49	0.49	440
CH_3	Br	1.29	-0.240		0.48	450
OCH_3	Cl	2.05	-0.603	0.33		504
OCH_3	Br	2.05	-0.603			501
NO_2	Cl	-1.7	1.19	0.95	1.18	400
NO_2	Br	-1.7	1.19		0.45	412
Cl	Cl	0.36	0.206		0.51	437(a)
Cl	Br	0.36	0.206		0.46	439(a)
CN	Cl	-1.17	0.94	0.36		468
CN	Br	-1.17	0.94	0.79	0.79	388
$3CH_3$	Cl	1.08	-0.139		0.55	413(a)
$3CH_3$	Br	1.08	-0.139		0.52	415(a)
OC_2H_5	Cl				0.53	420(b)

a, reference 127; b, reference 152.

Figure 18

Plot of σ_{PyNO} vs. ν_{M-O} for the 1:1 Complexes of Pyridine N-oxides with Copper (II) Halides.

⊙ Chloride

△ Bromide

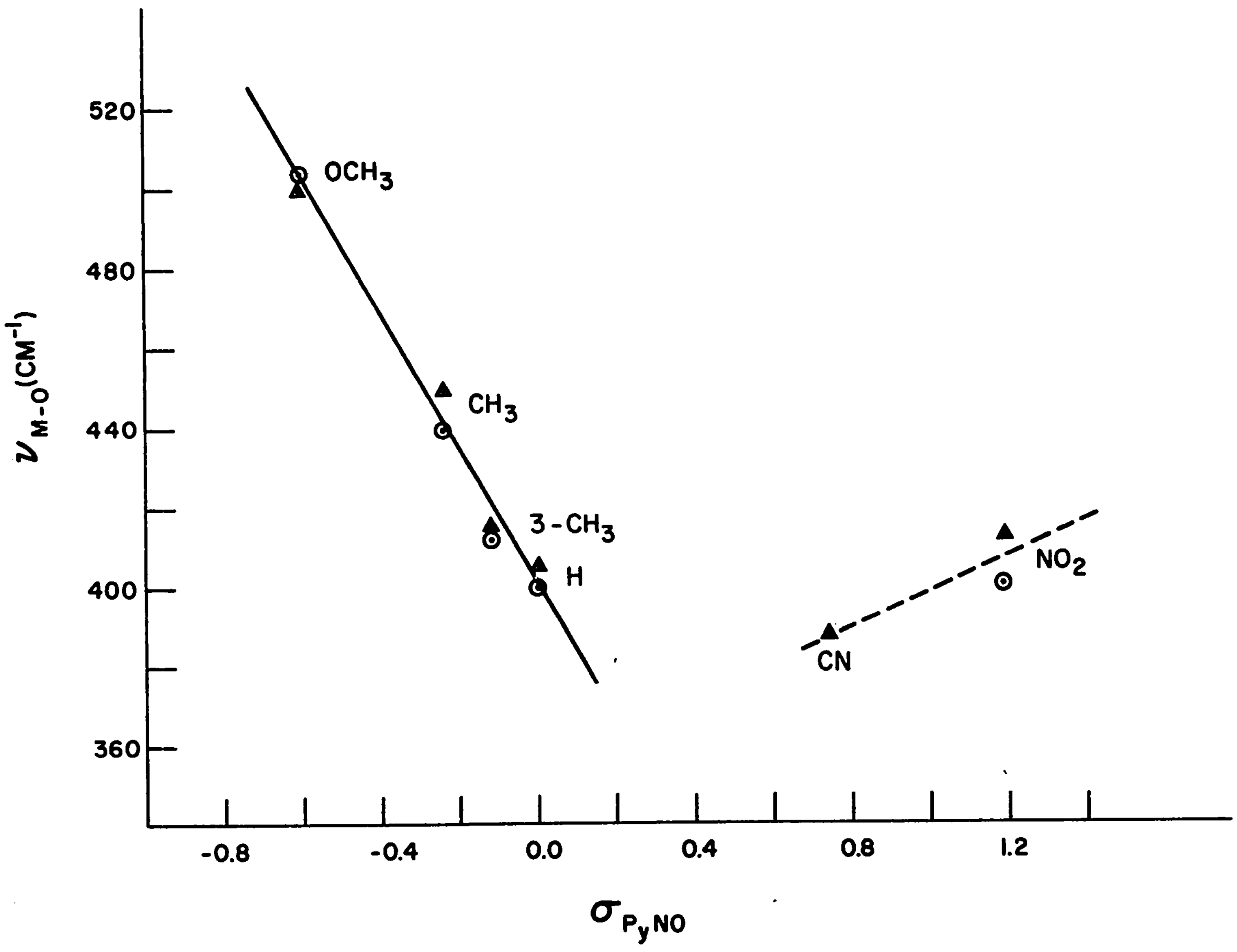
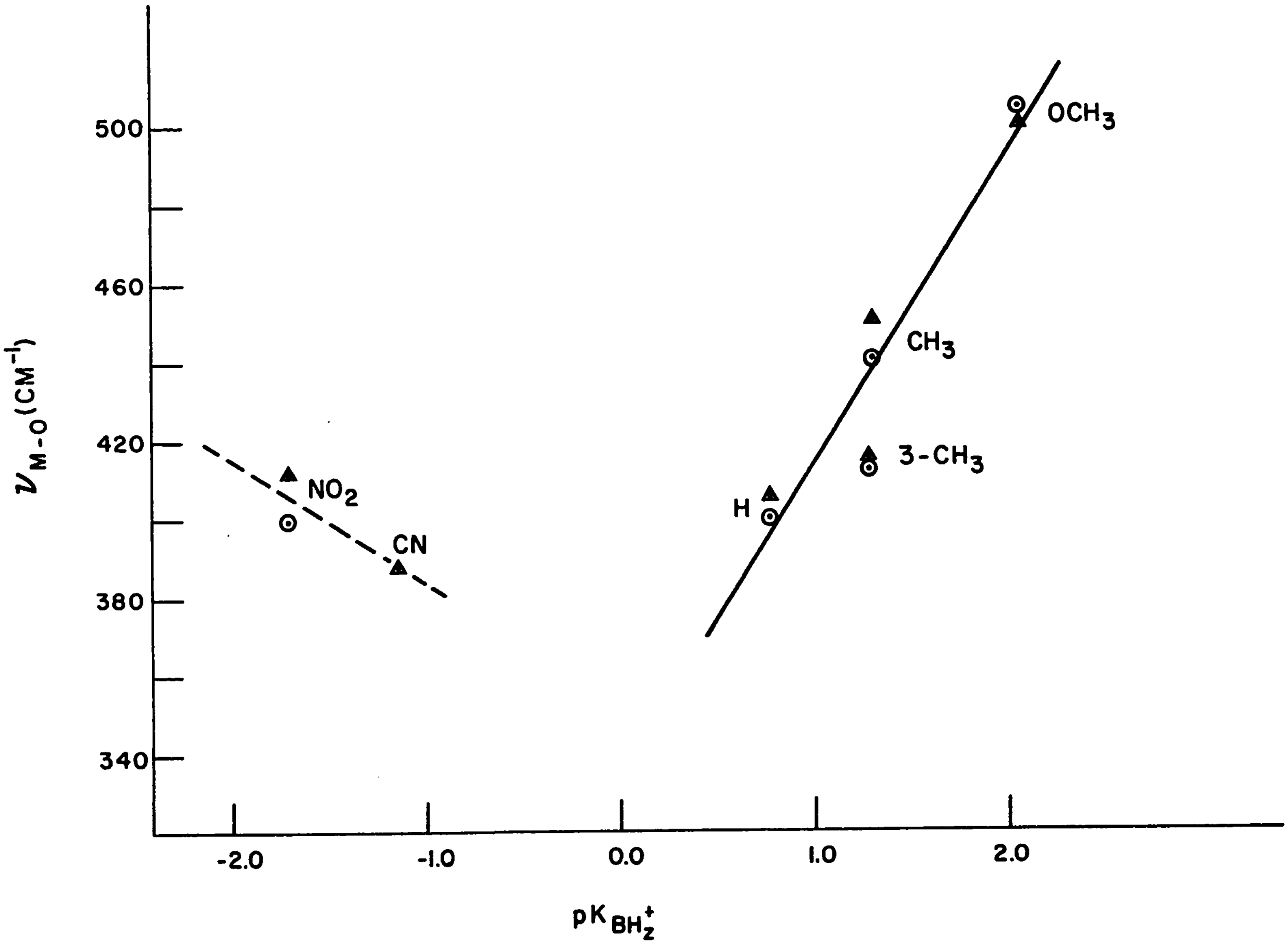

OCH3
CH3
3-CH3
H
NO2
CN
520
480
440
400
360
-0.8
-0.4
0.0
0.4
0.8
1.2
ν M-O (CM-1)
σ PyNO

Figure 19

Plot of $pK_{BH_z}{}^{+}$ vs. ν_{M-O} for the 1:1 Complexes of Pyridine N-oxides with Copper (II) Halides.

⊙ Chloride

△ Bromide



$\nu_{M-O}(CM^{-1})$
500
460
420
380
340
-2.0
-1.0
0.0
1.0
2.0
$pK_{BH_z^+}$
NO_2
CN
H
CH_3
$3-CH_3$
OCH_3

respectively.

It is seen that a linear correlation of ν_{M-O} with σ_{R_yNO} and $pK_{BH_z^+}$ exists for the complexes with electron donating substituents on the pyridine ring. A different correlation may exist for the electron withdrawing groups [illegible]. CN, and NO_2, but the limited number and wider scattering of the points do not make it too obvious.

In this correlation of ν_{M-O} with the substituent parameters the structures of all these complexes were assumed to be strictly identical. But it has been amply demonstrated (131) that inter and intramolecular interactions and steric factors modify the structures which in turn is very likely to affect the M-O stretching frequencies, d-d band positions and other physico-chemical properties of these complexes. It is therefore not too surprising that no single correlation exists between the substituent parameters of the ligands with the physico-chemical parameters of these complexes.

5) Infrared spectra and magnetic moments in 1:1 complexes of copper (II) halide with substituted pyridine N-oxides

The magnetic moments of a large number of 1:1 complexes of copper (II) halide with pyridine N-oxide have been measured by different workers since the initial report by Quagliano et al.(106) Watson(131) has recently collected all the previously reported values of the room temperature magnetic moments of these complexes. Although there are considerable differences in the values of the magnetic moments (for the same compounds) reported by different workers, the most recent measurements by two groups of workers(131) seem to be in reasonable agreement. The most recent values have been used in the present study.

The magnetic moments (μ_{eff}) and ν_{M-O} for a number of 1:1 copper (II) halide complexes with substituted pyridine N-oxides are shown in table (XVIII) and a plot of ν_{M-O} vs. (μ_{eff}) is shown in Fig. (20). It is seen from the plot that the magnetic moment progressively increases as the metal-oxygen stretching frequency decreases. A qualitative interpretation of this correlation of magnetic moment with ν_{M-O} can be offered on the basis of Anderson's theory of superexchange.

The lowering of magnetic moment in dimeric copper (II) complexes is due to spin-spin interaction between paramagnetic ions and may arise because the distance between paramagnetic ions is small (direct exchange) or because the intervening atoms, which are diamagnetic in their ground state, are capable of transmitting the magnetic exchange interaction (superexchange).

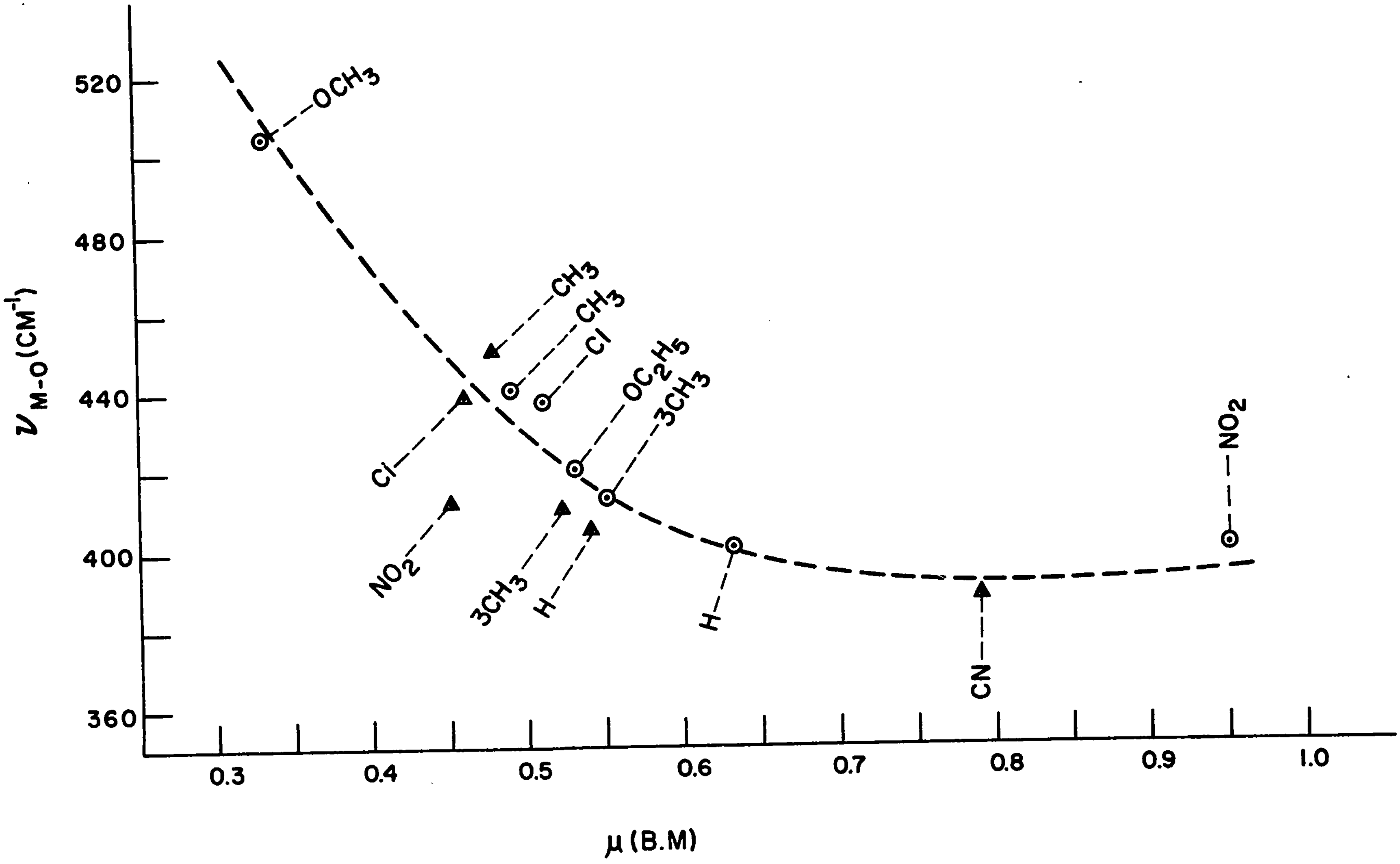
The room temperature magnetic moments of cupric acetate monohydrate; acetylacetone-mono-(o-hydroxyanil) Cu (II), and pyridine N-oxide-Cu(II) chloride, are 1.43 B.M., 1.37 B.M., and 0.77 B.M. respectively,(23) whereas the metal-metal distances in the established structures are 2.64 Å, 2.99 Å, and 3.25 Å respectively. This would indicate that the observ-

Figure 20

Plot of μ_{eff} vs. ν_{M-O} for the 1:1 Complexes of Pyridine N-oxides with Copper (II) Halides.

⊙ Chloride

△ Bromide


520
480
440
400
360
ν_{M-O} (CM^{-1})
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
μ (B.M)
OCH$_3$
CH$_3$
CH$_3$
Cl
OC$_2$H$_5$
3CH$_3$
Cl
NO$_2$
3CH$_3$
H
H
CN
NO$_2$

ed demagnetization for copper (II) halide complexes with pyridine N-oxides is mainly produced by a superexchange mechanism involving bridging oxygen atoms.

Now, from the point of view of Anderson's theory, (20,23) superexchange takes place because of overlap of the ligand atom orbitals with the magnetic orbitals on the metal. The actual wave functions are antibonding mixtures of metal atom d orbitals with ligand atom s and p orbitals. Exchange is a consequence of contact between magnetic wave functions that have a common ligand atom orbital component but a different metal atom orbital component. The reason why superexchange can take place over large distances is simply that the actual magnetic wave functions themselves spread over large distances because of covalent binding effects in the "core" electrons. Qualitatively speaking, the theory predicts that for superexchange, the greater the overlap between the metal atom magnetic orbital and the orbitals of the bridging ligand atom, the greater will be the magnitude of the exchange integral. Since the metal-oxygen stretching frequency will be dependent on the extent of overlapping of oxygen and metal orbitals, it is easy to see why a correlation between ν_{M-O} and the extent of magnetic exchange interaction in these complexes should exist.

Additionally, the extent of overlap between the bridging oxygen and metal orbitals will be dependent on the electron density on the oxygen atom. It is obvious from

Fig. (20) that the exchange interaction is higher (lower magnetic moment) for the complexes with strong electron donors at 4 position on the pyridine ring and lower for strongly electron withdrawing groups. This supports the theory of superexchange mechanism in these complexes.

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