TRANSITION METAL CHELATES OF SOME QUINQUEDENTATE AND TRIDENTATE LIGANDS

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by

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DECLARATION

This Thesis is my original work and has not been presented for a degree in any other University.

CHANDRESH. HEMSHANKER. VYAS

This Thesis has been submitted for examination with our approval as University Supervisors.

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ABSTRACT

Transition metal chelates containing tridentate and quinquedentate ligands have been prepared and studied.

Three bis-Schiff bases, N,N'-disalicylidene-4-R-2, 6-di(aminomethyl) anisole (R = Cl, Br, CH_3) were synthesized by the condensation of corresponding diamines and salicylaldehyde. The bis-hydroxymethyl derivatives of p-substituted phenolic ethers, were treated with acetonitrile in presence of sulphuric acid, to give the corresponding bis-amides, which on hydrolysis gave the diamines. By the loss of two protons the Schiff bases act as doubly negatively charged ONONO-quinquedentate ligands, forming neutral complexes of the type M(ONONO) (M = Ni, Cu, Fe, Co). FAB mass spectra in all cases show the parent protonated molecular ion $(MONONOH)^+$ for each metal complex, except for copper, where no such ion was observed. Although this could indicate the presence of five-coordinate monomeric species a detailed study of the electronic spectra suggests otherwise. It is therefore concluded that nickel(II), copper(II), iron(II) and cobalt(II) form high-spin, polymeric six-coordinate complexes, presumably with oxygen-bridging. However the uranyl complexes, UO_2(ONONO)

have a pentagonal bipyramidal structure with the ligand acting as a dinegatively charged quinquedentate.

The Schiff base, N-salicylidene-6-aminomethyl-2, 4-dichlorophenol was synthesized by the same procedure as above. Due to the loss of two protons, the Schiff base acts as doubly negatively charged ONO-tridentate ligand and neutral copper complex of the type Cu_2L_2 was formed. A binuclear dimeric structure has been suggested for the complex.

Structural elucidation entailed the use of reflectance spectra, Fast Atomic Bombardment mass spectra, X-ray diffraction patterns and magnetic susceptibility. The C, H and N -micro analysis and metal determination were carried out on all compounds which were synthesized. Gravimetric methods were used to determine all metals (Ni, Cu, Co, Fe), except for uranium which was determined by calorimetric method.

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CHAPTER ONE

INTRODUCTION

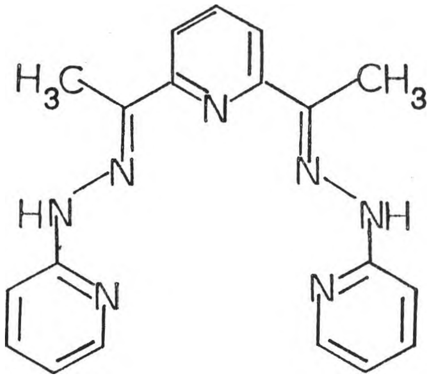
TRANSITION METAL COMPLEXES OF SOME QUINQUEDENTATE AND TRIDENTATE LIGANDS

1: INTRODUCTION

1.1 Metal complexes of Quinquedentate ligands

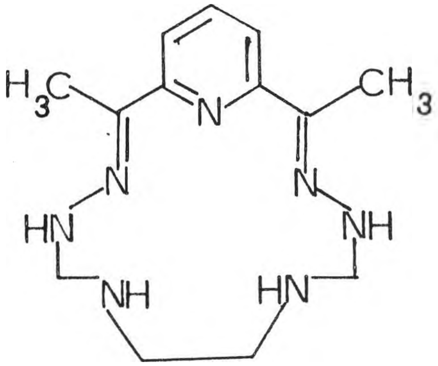
While numerous complexes of transition metal ions with monodentate, bidentate, tridentate and quadridentate ligands have been prepared and studied with respect to the magnetic, electronic and structural properties, similar studies with quinquedentate and hexadentate ligands are more recent and scarce.

Curry and *et.al*. have reported the synthesis and characterization of various complexes of iron, cobalt and copper with 2,6-diacetylpyridine-bishydrazones[1]. The ligand of interest of their work was 2,6-diacetylbis (2'-pyridyl hydrazone) pyridine (I; phH), which formed a complex with cobalt (II). Magnetic and electronic studies were carried out on the iodide complex and a six coordinate structure was suggested for the complex (Co(phH)I)I



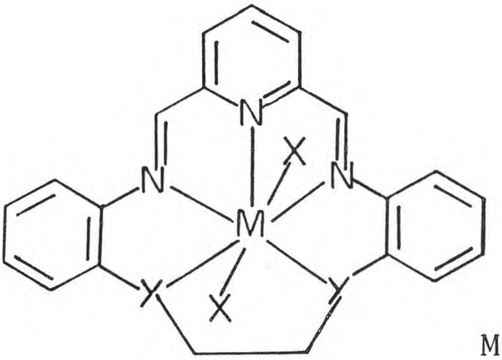
(I)

X-ray crystal analysis[2] of the complex $[FeB(NCS)_2]ClO_4$ (where B is a quinquedentate macrocyclic ligand, II) showed that the configuration about the iron atom, was that of pentagonal bipyramid. In this seven coordinate complex, the five nitrogen atoms of the ligand and the metal ion lie in the equatorial plane whereas the thiocyanate groups are in axial position.



(II)

Pentagonal bipyramidal complexes of the first-row transition elements are relatively rare. In fact for transition metals with non-spherical distribution of electrons, a planar pentagonal arrangement was considered unlikely, because of crystal field effects. The preparation of complexes of a novel series of planar pentadentate macrocyclic ligands, and an X-ray structure analysis, of one of the complexes of Mn^{II} or Zn^{II} ions has been reported.[3] X-ray crystal analyses show, that the donor atoms in the macrocycle, defined the five equatorial co-ordination positions of a distorted pentagonal bipyramid (III).



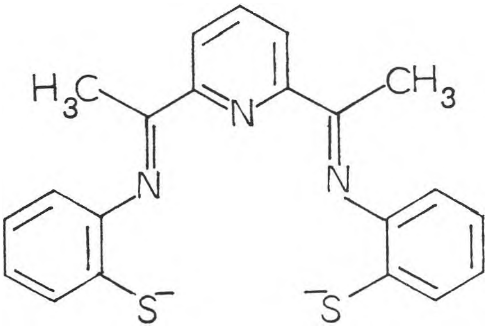
M = Mn or Zn

X = ClO_4^-

Y = NH,O,S

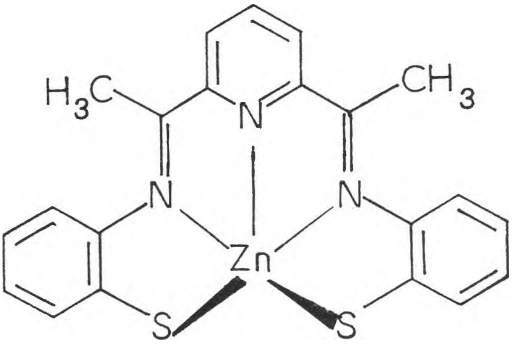
(III)

In 1972, Lindoy and Busch[4] worked with quinquedentate ligands which included metal-ion induced rearrangement of 2,6-bis(2-methyl-2-benzothiazolinyl) pyridine (IV), yielding five coordination zinc and cadmium complexes of the corresponding Schiff base.



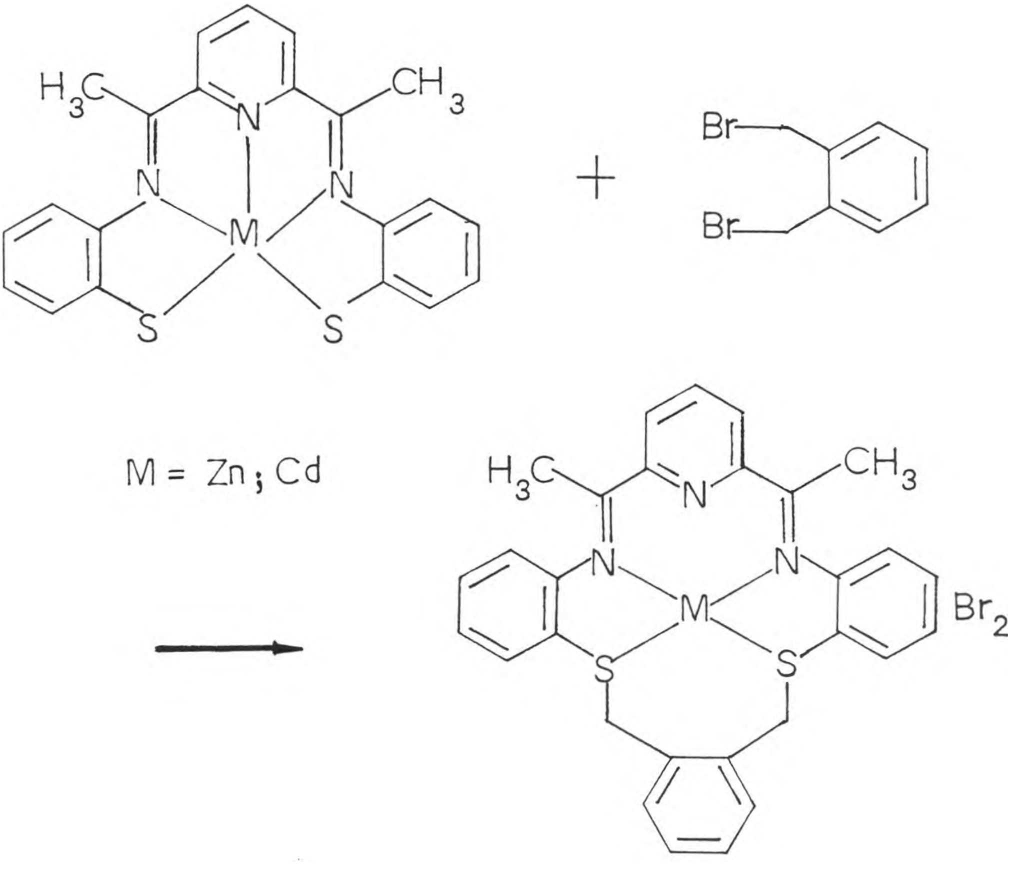
(IV)

A detailed X-ray crystal structure determination by Goedken and Christoph[5] showed that the zinc complex had a helical five-coordinate structure (V).



(V)

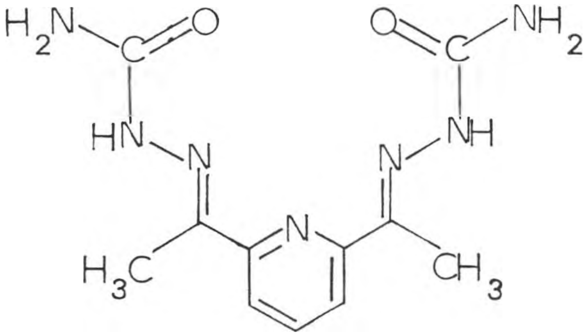
It has been reported[6] that the helical five-coordinate zinc and cadmium complexes of ligand (IV), readily react with methyl iodide to yield complexes of the corresponding S, S' - dimethylated ligand, which contain two coordinated iodide ions and appear to be seven-coordinate. The corresponding reactions with a bifunctional alkyl halide α,α'-dibromo-o-xylene or 1,4-diiodobutane, result in a number of ring-closing S-alkylation reactions according to the scheme (1.1) below:-



SCHEME (1.1)

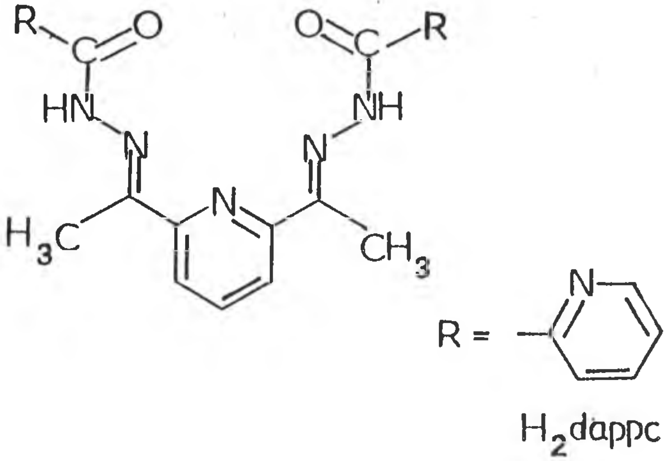
On S-alkylation, the helical configuration of the ligand may partially collapse towards a planar configuration.

Wester and Palenik have reported transition metal chelates of 2,6-diacetylpyridinebissemicarbazone (VI; dapsc). X-ray crystal studies showed that complexes of the type $M(dapsc)(NO_3)_2.3H_2O$ (M = Ni,Cu)[7]; $M(dapsc)Cl_2.3H_2O$ (M = Fe, Co, Ni, Zn)[8] and $[M(dapsc)(Cl)(H_2O)]^+Cl^-.2H_2O$ (M = Mn, Fe Co, Zn)[9] have a pentagonal bipyramidal structure. Magnetic and spectral properties of cobalt complexes of the same ligand were also studied[10].



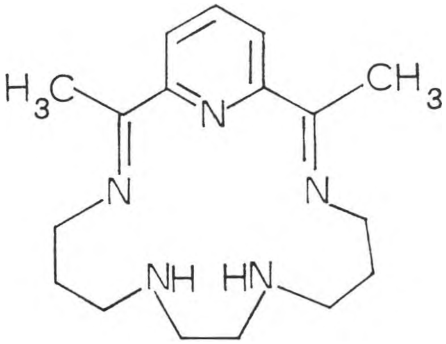
(VI)

The coordinating properties of 2,6-diacetylpyridine bis(picolinoylhydrazone)(VII; H_2dappc) have been investigated[11]. X-ray analysis was carried out on Mn(dappc).$9H_2O$. The manganese ion was in a pentagonal-bipyramidal environment with the dappc ligand, occupying the pentagonal girdle and two water molecules in the axial sites.



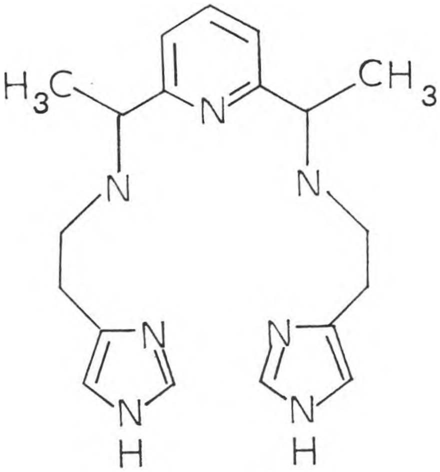
(VII)

X-ray crystal determination of the complex [PbL(SCN)](SCN) (where L is a quinquedentate macrocyclic ligand, VIII) showed that the lead atom is six-coordinated, bonded to five N atoms of the ligand and a S atom of a thiocyanate ion, leaving the remaining thiocyanate ligand uncoordinated[12].



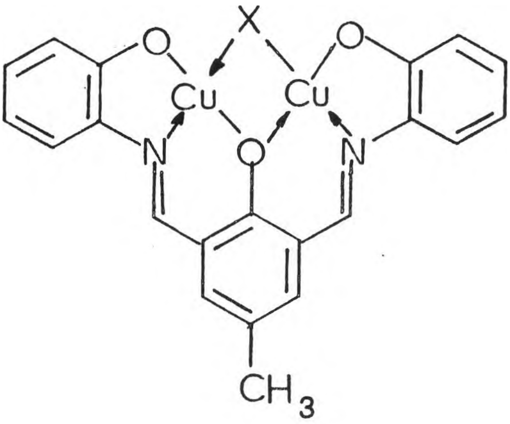
(VIII)

Crystal and molecular structures[13] of two complexes $[Cu^{II}(imep)](ClO_4)_2$ and $[Zn^{II}(imep)](ClO_4)_2$ (IX; imep) showed that the coordination about the metal ion is intermediate between an idealized trigonal bipyramid and a square pyramid.



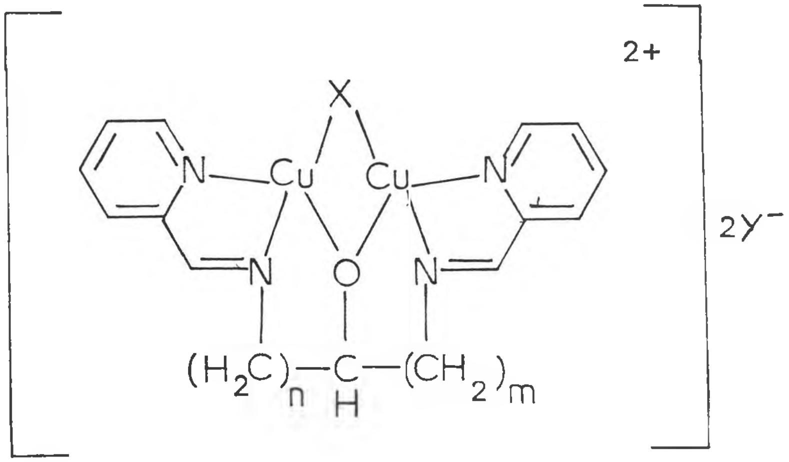
(IX)

The possible relevance of the results, concerned synthesis of potential nitrogen-fixing systems.



(XI)

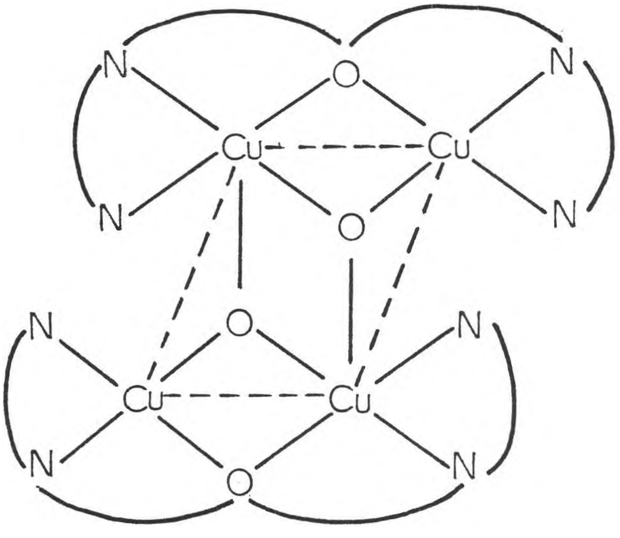
The original ligand has been modified extensively[15-20]. Recently pentadentate binucleating ligands were studied[21]. The study dealt with binuclear Cu(II) complexes based on 1,3-diaminopropan-2-ol and 1,5-diaminopentan-3-ol as backbones (XII). The compounds featured a bridging ligand X.



X = OH, OR, Cl, Br; Y = ClO_4^-, Br

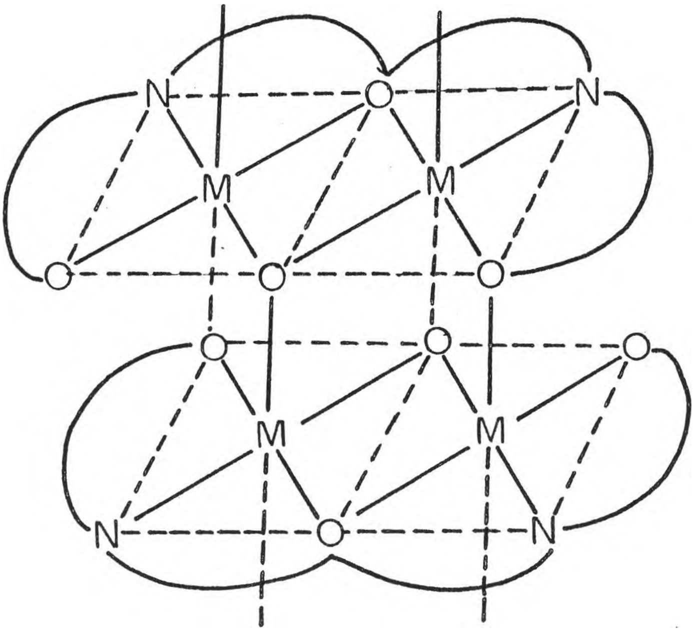
(XII)

Through detailed X-ray and magnetic property analyses, a tetranuclear crystal structure (XIII) was proposed.



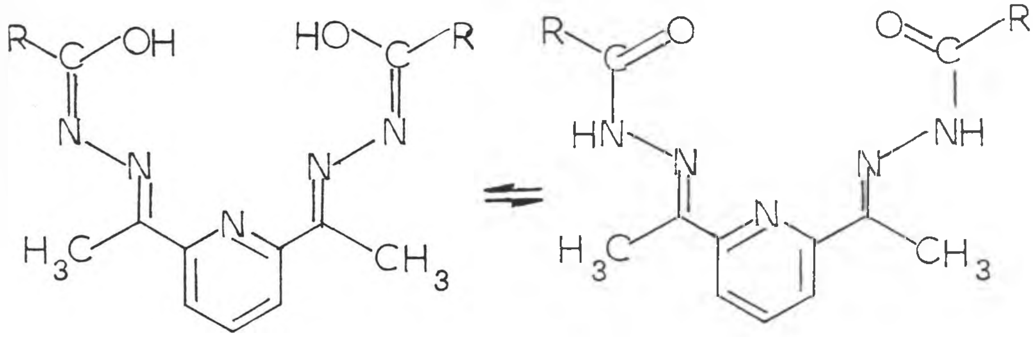
(XIII)

A number of nickel(II) and cobalt(II) derivatives of a trianionic binucleating ligand (XI) have structures based on a tetranuclear $[LM_2(X)]_2$ core where $X^- = OH^-$ or OR^-; (XIV)[22]. Additional ligands occupy four "axial" co-ordination sites on each metal centre.



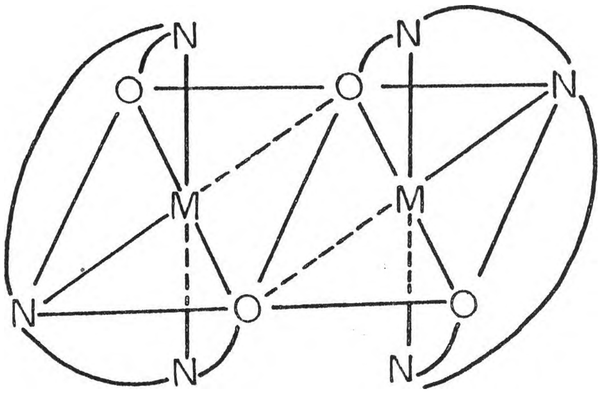
(XIV)

Two Schiff bases (HONNNOH) (XV); (R = ph and 2-thienyl) were prepared[23] by condensation of 2,6-diacetylpyridine with substituted hydrazines, $RCONHNH_2$. These behaved as ONNNO quinquedentate ligands, forming neutral complexes of the type M(ONNNO) (M = Co, Ni, Zn, Cd, Cu).



(XV) (XVI)

The cobalt, nickel and copper complexes are six-coordinate, presumably with oxygen-bridging (XVII) while the zinc and cadmium complexes have helical five coordinate structure, similar to (V)[4,5]. X-ray crystal studies reveal that the UO_2(ONNNO) complex (R = Ph) has a pentagonal bipyramidal structure with the ligand acting as a dinegatively charged quinquedentate.

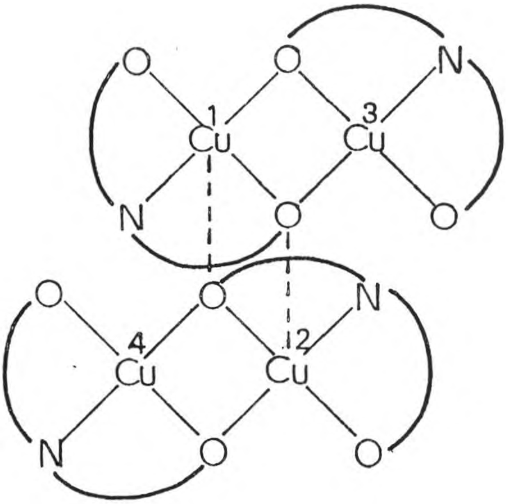


(XVII)

1.2 Metal Complexes of Tridentate ONO-donor ligands

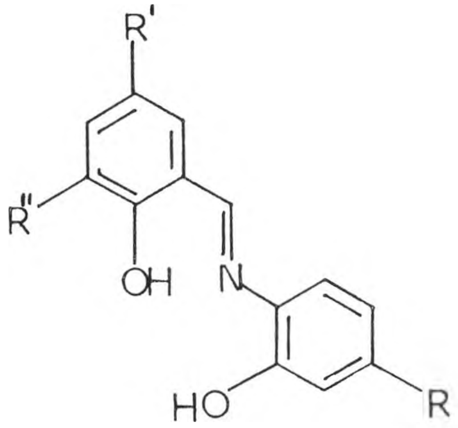
Most of the binuclear complexes have been prepared from tridentate Schiff bases containing ONO or ONS donor atoms; they are derived from the condensation of salicylaldehyde or acetylacetone with O-aminophenols and aminothiols[20].

X-ray and magnetic studies[24,25] have been carried out on the complex, acetylacetonemono-(O-hydroxy-5-nitroanil)-copper(II). It has been suggested that it has a binuclear dimeric complex[26]. The dimeric molecules are arranged in layers, actually forming a tetrameric crystal structure as shown schematically in figure (XVIII).



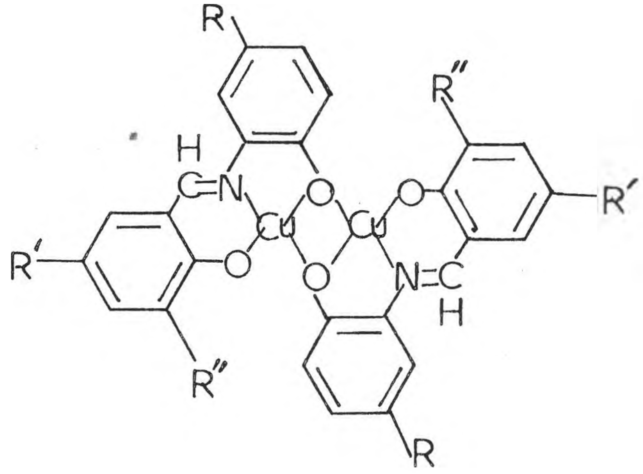
(XVIII)

The interaction of the Schiff bases, derived from 5-substituted salicylaldehyde and substituted and unsubstituted O-aminophenol, of the type (XIX) with transition metal ions has been investigated[25,27-29].

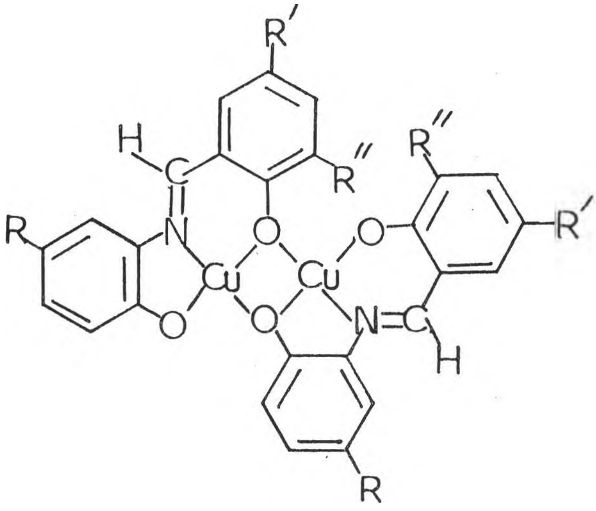


(XIX)

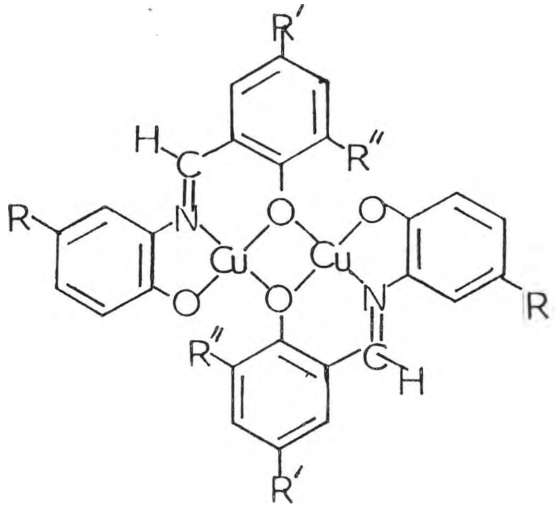
Three isomers were depicted for these complexes, (XX, XXI and XXII). It has not been possible to separate these isomers.



(XX)

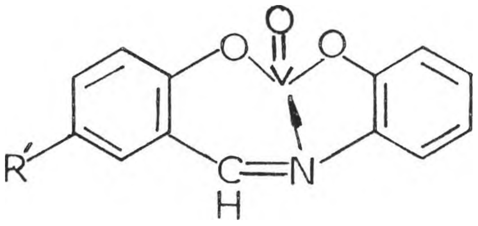


(XXI)



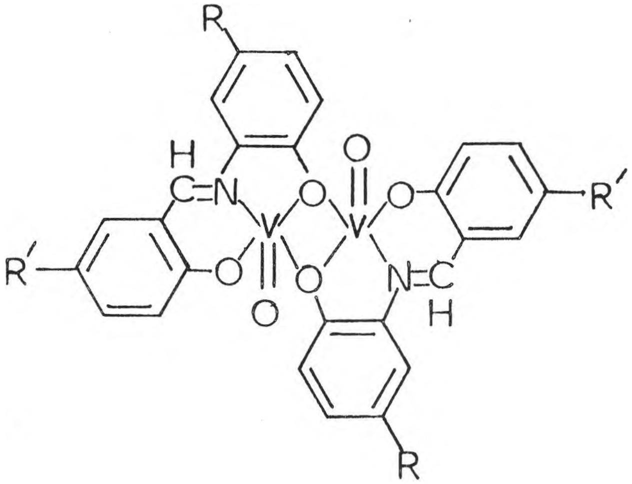
(XXII)

Ginsberg <u>et al</u>[30] have proposed that the series of 5-substituted N-(2-hydroxyphenyl)salicylideneimine complexes of VO^{2+} (XXIII), forms tetranuclear or highly polymeric units due to interaction of the vanadyl oxygen in each dimer molecule (XXIV) with a vanadium atom in a second molecule.



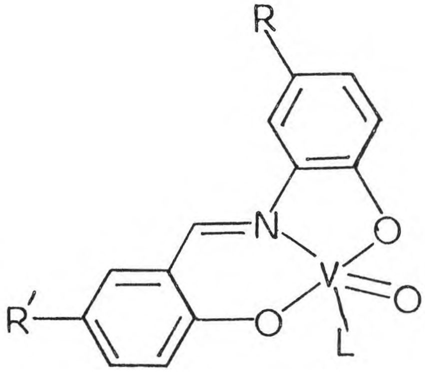
(XXIII)

The coordination around the vanadium atom is assumed to be distorted square pyramidal.



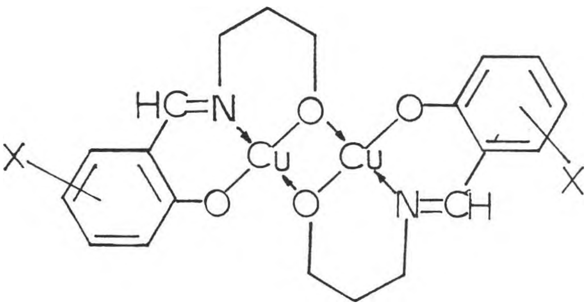
(XXIV)

It has been suggested that two of these vanadyl complexes, where R = NO_2, R' = NO_2 and R = H, R' = Cl; (XXV), have five-coordinated monomers, in which a molecule of water, ethanol or pyridine occupies one of the coordination positions L.

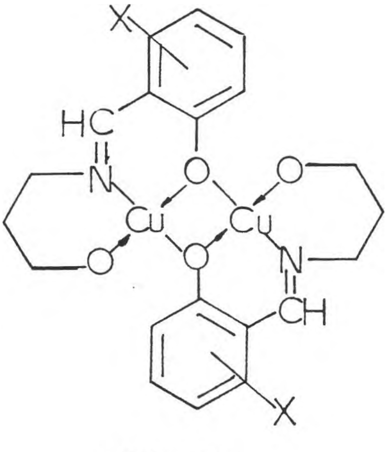


(XXV)

The synthesis and properties of binuclear copper(II) complexes with N-hydroxyalkyl-salicylideneimines have been described[31,32]. The empirical formulae are, (A) Cu(sal.N.ROH)X and (B) Cu(sal.N.RO) where sal.N = $O.C_6H_4.CH = N$. ROH = CH_2CH_2OH, $CH_2CH(CH_3)OH$, $C(CH_3)_2CH_2OH$ and $(CH_2)_3OH$ and X = Cl^-, NO_3^- and ClO_4^-. It has been suggested that one of the compounds, $[Cu(sal.N.CH_2CH_2CH_2O]_2$ has a binuclear structure. Two dimeric configurations are possible, one with bridging alcoholic oxygen atoms (XXVI) and the other with bridging phenolic oxygen atoms (XXVII). Through experimental data[31] configuration (XXVI) is preferred for the complex. The copper(II) environment is very close to square planar.

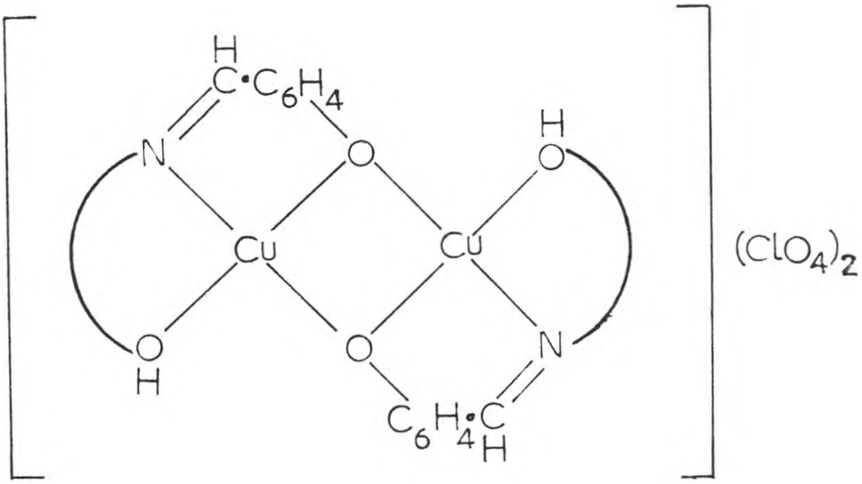


(XXVI)



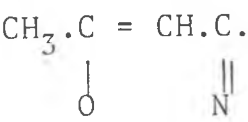
(XXVII)

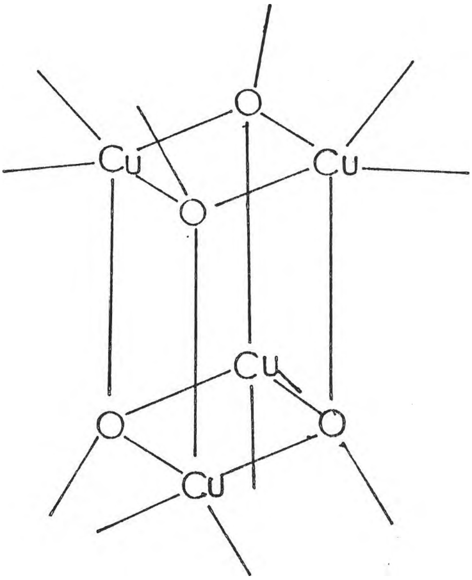
Perchlorate complexes, (X=ClO_4^-) were prepared and spectral data indicated that complexes $[Cu(sal.N.CH_2CH_2OH)ClO_4.H_2O]$ and $[Cu(sal.N.CH_2CH(CH_3)OH)ClO_4.C_2H_5OH]$ have binuclear structure and square pyramidal configuration (XXVIII) about the metal atom[31].



L = H_2O or C_2H_5OH

(XXVIII)

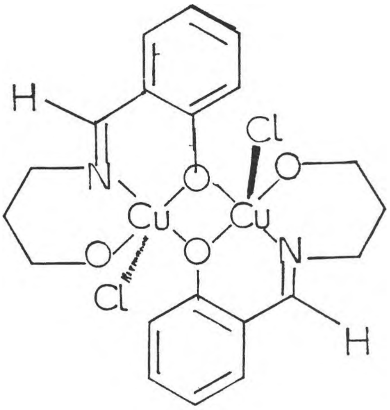
Bertrand *et al* carried out X-ray analysis on the complex $[Cu(Acac.N.CH_2CH_2O)]_4$ where (Acac.N. =  $\mathrm{CH_3.\underset{O}{\underset{|}{C}} = CH.\underset{N}{\underset{\|}{C}}.CH_3}$). The structure consisted of a tetrameric molecule (XXIX)^{33}.



(XXIX)

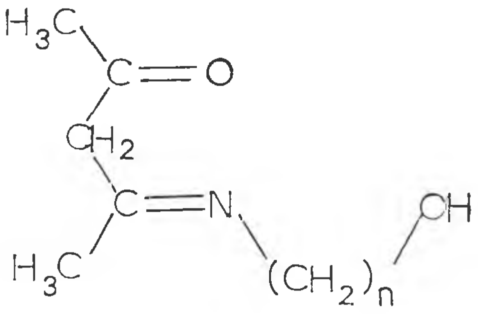
The crystal and molecular structures of two complexes, $[Cu(5NO_2\text{-sal.N.}(CH_2)_3.O]_2$ and $[Cu(2Me\text{-sal.N}(CH_2)_3O]_2$ have been studied[34]. The structures and magnetic properties of both complexes support a general correlation, between decreasing strength of antiferromagnetic interaction and increasing distortion towards tetrahedral metal environment in binuclear copper(II) complexes.

Spectral and magnetic studies have been reported[31,35] on two copper(II) chloro-complexes namely $Cu(\text{sal.N.}(CH_2)_2OH)Cl$ and $Cu(\text{sal.N.}(CH_2)_3OH)Cl$. Both are antiferromagnetic and the first complex has a binuclear structure with phenolic oxygen bridges. The environment about the metal atom is closer to planarity. It has been reported that the second complex, Cu(sal.N.$(CH_2)_3$OH)Cl is penta-coordinated with trigonal bipyramidal configuration (XXX).



(XXX)

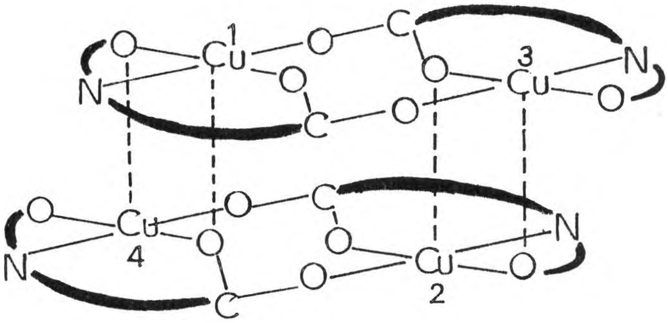
The synthesis of copper(II) complexes of the schiff bases derived from acetylacetone and aminoalcohol has been reported[33]. Complexes of ligand, HL_A when n = 2 and HL_B when n = 3, (XXXI) were studied.



(XXXI)

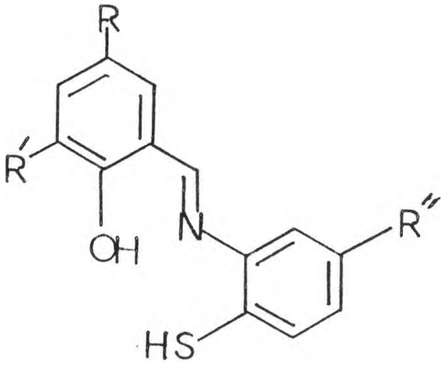
It was suggested that the CuL_A complex has a tetrameric molecular structure and the CuL_B complex has a dimeric molecular structure, with exact planar Cu_2O_2 ring.

Ison and Kokot[36] studied the copper(II) complex of 2-hydroxynaphth-1-ylmethylene-anthranilic acid. The X-ray analysis showed that it has a dimeric molecular structure and is arranged in the form of layers as shown in figure (XXXII). The two copper atoms in the binuclear molecule are linked by carboxylic acid groups through an "anti-syn" arrangement of the Cu-O bonds .



(XXXII)

One interesting crystal structure of ONS-tridentated ligand complex, was reported[36]. A copper(II) complex of N-(2-thiophenyl)-salicylideneimine, (ONS; XXXIII) was prepared. Polymeric structures (XXXIV and XXXV) involving an infinite chain of square pyramidal copper atoms, linked by sulphur and oxygen atoms were postulated.

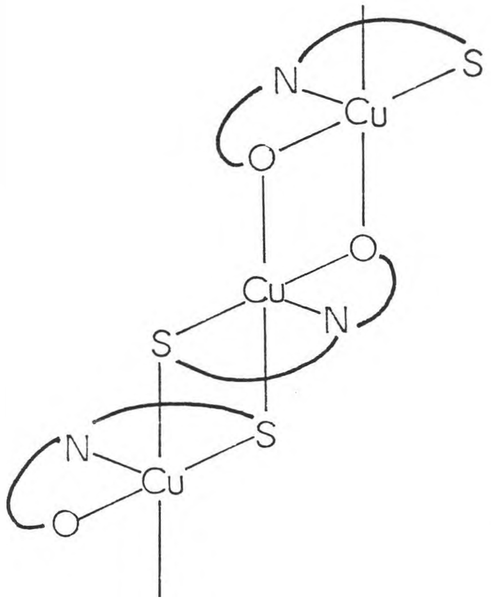


R = H, Cl, Br, NO_2

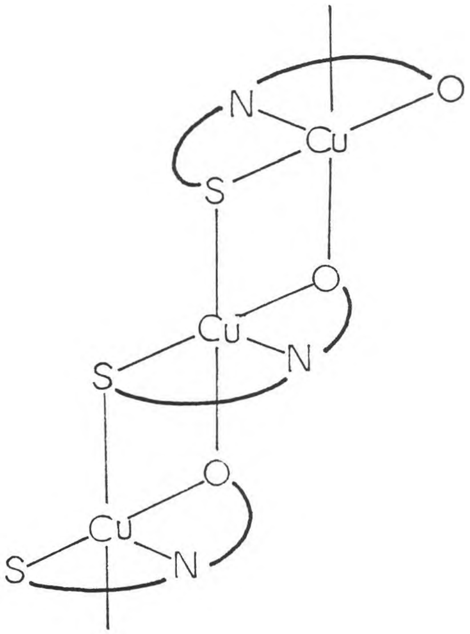
R' = H, Cl

R'' = H, Cl

(XXXIII)

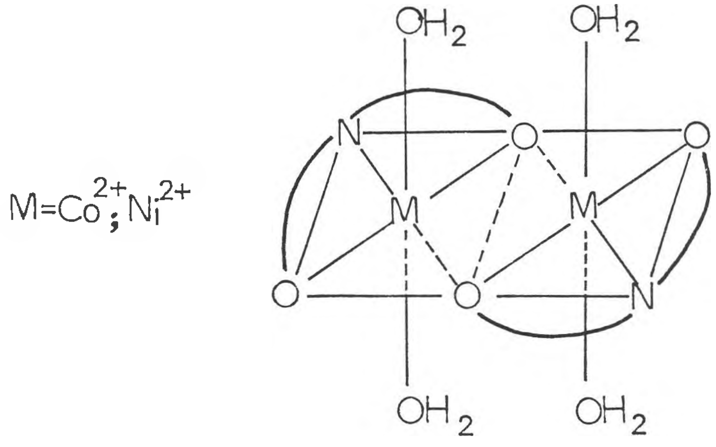


(XXXIV)



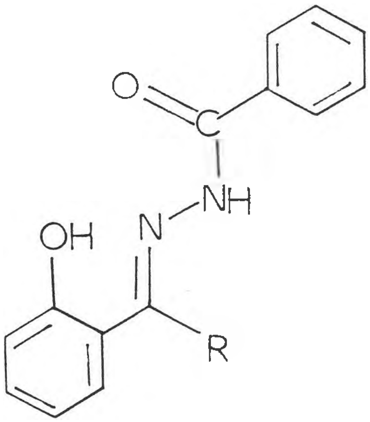
(XXXV)

Binuclear nickel(II), cobalt(II) and copper(II) complexes, with N-salicylideneamino acids have been synthesized and characterized[37-39]. A dimeric configuration has been proposed for the $[Ni(sal:Glycine)(H_2O)_2]_2$ complex (XXXVI).



(XXXVI)

The hydrazones are versatile ligands and can coordinate to metal atoms in different manners. The synthesis and characterisation of Zn(II), Cd(II) and Hg(II) complexes of benzonyl hydrazones whose structures depicted below (XXXVII) have been reported[40].



R = H, Me, Et, n-Pr

(XXXVII)

The Zn(II) and Cd(II) complexes are dimeric, having two tetrahedral units stacked together through phenoxide bridges, and Hg(II) complexes are six-coordinated.

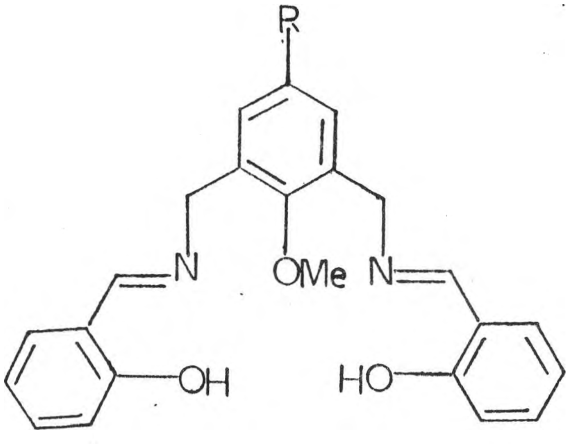
CHAPTER TWO

METAL COMPLEXES OF SOME ONONO QUINQUEDENTATE LIGANDS

2. METAL COMPLEXES OF QUINQUEDENTATE LIGANDS

2.1 Objectives

The metal complexes of potentially quinquedentate ligands have been discussed in section 1.1. These complexes show a variety of structural arrangements. Recently some potentially quinquedentate bis-Schiff bases (XXXVIII; R = Cl, Br, CH_3) having ONONO as a donor set have been synthesized[41].



(XXXVIII)

In order to understand the chelating nature of these Schiff bases we proposed to do the following:-

2.1.1 Synthesize the ligands and to report the experimental details with view to ascertaining the accuracy of the patent literature which has previously been reported[42-45].

2.1.2 Obtain and interpret the electronic spectra of any transition metal complexes we obtain. We were in particular interested in any five - coordinate complexes since their electronic spectra are inadequately understood theoretically and experimentally.

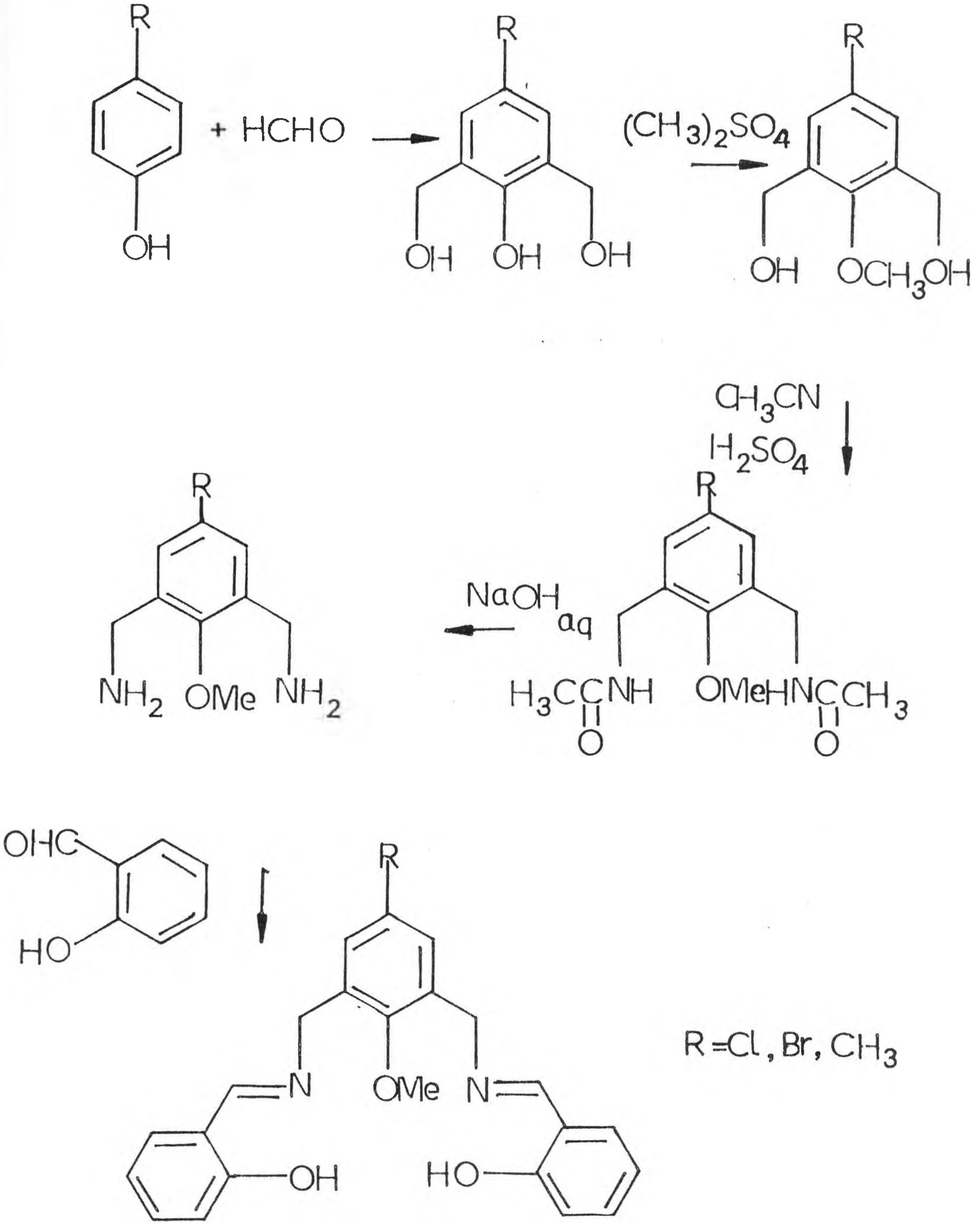
2.1.3 Determine the magnetic susceptibilities of the complexes obtained. Apart from helping in the understanding of the possible structures, this may also show any spin-exchange interactions e.g. antiferromagnetism in the complexes.

2.1.4 Obtain mass spectra and X-ray diffraction patterns and to use these as aids for structural elucidation.

2.2 General synthetic procedure to Bis-Schiff Base

Phenols with a substituent (R = Cl, Br or CH_3) in the para position react readily with formaldehyde to give di-hydroxymethyl derivatives, which are then converted to 2,6-di(hydroxymethyl)-4-R-anisole derivatives respectively by reaction with dimethylsulphate. Further by Ritter reactions, these derivatives are treated with acetonitrile and

SCHEME 2.2



sulphuric acid, and thus transformed successively to corresponding bis amides and the latter to diamines by base hydrolysis[46,47]. The diamines react exothermally with salicylaldehyde in ethanolic solution, giving the corresponding Schiff bases. A general synthetic route for preparation of the bis-Schiff base is shown in scheme (2.2).

2.3 Results and Discussion

The Schiff bases N,N'-disalicyldene-4-R-2,6-di(aminomethyl) anisole (XXXVIII; R = chloro-, bromo-, methyl-) were prepared by the condensation of 2,6-bis(aminomethyl)-4-R-anisole and O-salicylaldehyde. The Schiff bases are doubly deprotonated in the presence of metal ions with the concomitant formation of the metal chelate of the type [M(ONONO)] (HONONOH = XXXVIII; M =(Ni(II), Cu(II), Fe(II), Co(II), UO_2^{2+}). These compounds are listed in table 2.1 and are stable on standing. The nickel(II), copper(II), cobalt(II) and iron(II) complexes are insoluble in common organic solvents, suggesting that they may have a polymeric structure. Their molecular weights were determined by FAB mass spectrometry and results are shown in Table 2.1 and Figures A.1 - A.14 in the appendix.

The nickel complexes are high spin (μ_{eff}, 2.8 B.M.) . Most likely structures for the complexes are either a monomeric five coordinate structure similar to structure (V)[4,5] for a zinc

TABLE 2.1 Metal Complexes of Schiff Bases (XXXVIII; HONONOH)

Compound	R	Colour	Analysis, Found (calcd)%				M.W.$^{(a)}$	μ_{eff} (B.M.) at 298°K
m			C	H	N	Met		
Ni(ONONO)	Cl	light green	58.97	4.33	5.83	12.43	465	2.81
			(59.33)	(4.11)	(6.02)	(12.61)		
Cu(ONONO)	Cl	dark green	58.48	4.02	6.00	13.28	472	1.82
			(58.73)	(4.07)	(5.97)	(13.51)		
Co(ONONO)	Cl	light brown	59.39	4.41	6.29	12.42	466	4.29
			(59.31)	(4.11)	(6.01)	(12.65)		
Fe(ONONO)	Cl	dark brown	59.89	4.15	5.89	11.86	463	5.11
			(59.70)	(4.14)	(6.05)	(12.07)		
UO_2(ONONO)	Cl	orange	40.53	2.72	4.26	34.84	677	diam.
			(40.81)	(2.83)	(4.14)	(35.16)		

TABLE 2.1 (Continued)

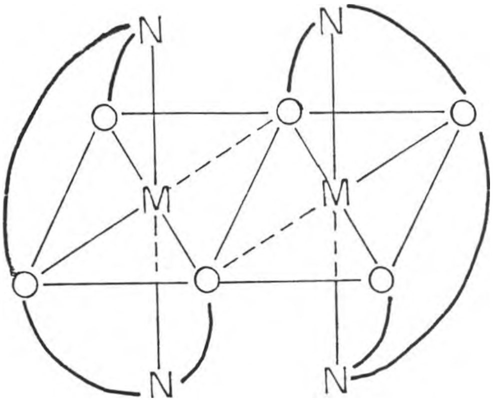
Compound m	R	Colour	Analysis, Found(Calcd)% C	H	N	Met	M.W.[(a)]	μ_{eff} (B.M) at 298°K
Ni(ONONO)	Br	light green	53.82	4.03	5.37	11.26	510	2.80
			(54.16)	(3.75)	(5.49)	(11.51)		
Cu(ONONO)	Br	dark green	53.47	3.59	5.54	12.47	516	1.84
			(53.65)	(3.72)	(5.44)	(12.34)		
Co(ONONO)	Br	light brown	53.92	3.85	5.21	11.30	510	4.29
			(54.14)	(3.75)	(5.49)	(11.55)		
Fe(ONONO)	Br	dark brown	54.53	3.58	5.43	10.78	507	5.16
			(54.47)	(3.78)	(5.52)	(11.01)		
UO_2(ONONO)	Br	orange	38.11	2.94	3.74	33.56	723	diam.
			(38.30)	(2.65)	(3.88)	(32.99)		

TABLE 2.1 (Continued)

Compound m	R	Colour	Analysis, Found(Calcd)% C	 H	 N	 Met	M.W$^{(a)}$	μ_{eff}(B.M) at 298^{o}K
Ni(ONONO)	Me	light green	64.53 (64.75)	4.95 (4.98)	6.38 (6.29)	13.35 (13.18)	445	2.81
Co(ONONO)	Me	light brown	64.57 (64.72)	5.11 (4.98)	6.23 (6.29)	13.00 (13.23)	446	4.30
Fe(ONONO)	Me	dark brown	64.93 (65.17)	4.66 (5.01)	6.08 (6.33)	12.47 (12.63)	443	5.12
UO_2(ONONO)	Me	orange	44.14 (43.91)	3.25 (3.38)	4.37 (4.26)	35.89 (36.25)	657	diam.

a) Molecular weight $(M+H)^+$ obtained from F.A.B. mass spectra.

complex, or a polymeric oxygen-bridged six-coordinate structure (XXXIX).



(XXXIX)

The FAB mass spectra have $(M+H)^+$ parent ion peaks at $M/Z = 465$ (R = Cl), $M/Z = 510$ (R = Br) and $M/Z = 445$ (R = CH_3). The presence of these peaks confirm the existence of the Ni(ONONO) moiety, although it does not distinguish between structures (V) and (XXXIX). A short review of the FAB technique is contained in appendix A.2.5. The reflectance spectra of the complexes (Figure 2.1) have bands at 9090, 15150 and 25640 cm^{-1}. These are assigned as the $3T_{2g} \leftarrow 3A_{2g}$ (γ_1) $3T_{1g}(F) \leftarrow 3A_{2g}$ (γ_2) and $3T_{1g}(P) \leftarrow 3A_{2g}$ (γ_3)

transitions, respectively. The calculated value of Racah parameter B and 10Dq (Refer Appendix A.2.4) agree very well with the observed γ_1, γ_2 and γ_3 transitions. The complexes have the following values, 10Dq = 9090 cm^{-1} and B = 955 cm^{-1}. Some five-coordinate nickel complexes[48-51] have an asymmetrical band in the region 12000 - 15000 cm^{-1}. The spectra of a five-coordinate nickel complex of approximately square pyramidal or trigonal bipyramidal stereochemistry, exhibit multiple absorption in visible region and are quite dissimilar from the spectra of six-coordinate nickel complexes[52,53]. The band at 9090 cm^{-1}, reported for these complexes, would appear to be too low for five-coordinate complexes but is quite acceptable for a $\gamma_1(3T_{2g} \leftarrow 3A_{2g})$ transition in octahedral complexes[54]; thus a polymeric oxygen-bridged six coordinate structure (XXXIX) is suggested.

The copper complexes have magnetic moments of ca. 1.83 B.M. and are insoluble in common organic solvents. The FAB mass spectra do not show $(M+H)^+$ parent ion peaks at M/Z = 470 (R = Cl) and M/Z = 514 (R = Br). Disintergration of the parent peak may be occuring before detection. The spectra (Figure A.2 and A.7) exhibit peaks at M/Z values higher than those expected for monomeric species and this may be indicative of the presence of polymeric species which

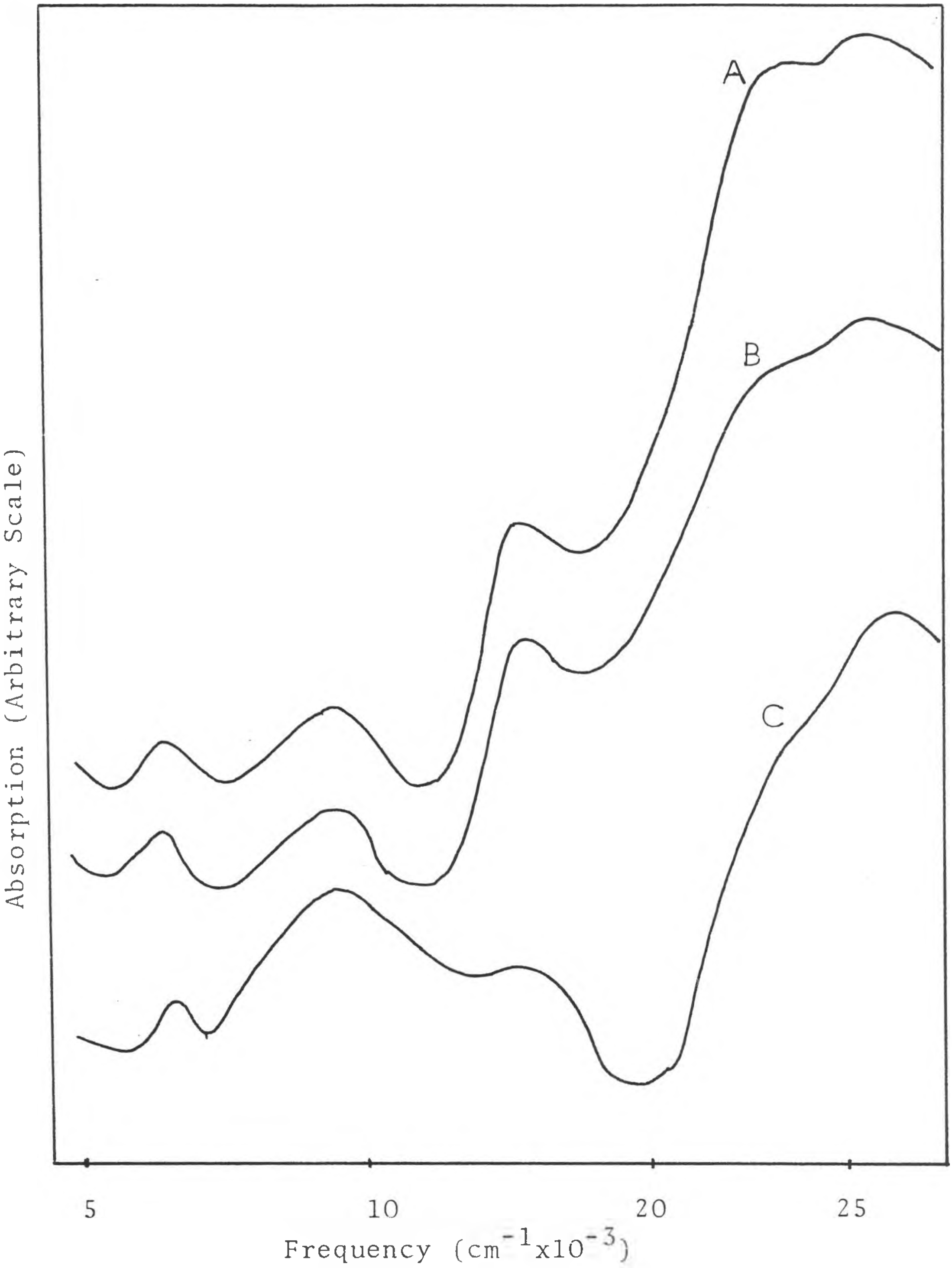


Fig. 2.1 Reflectance spectra of Ni(ONONO)Complexes

A. R = Chloro
B. R = Bromo
C. R = Methyl

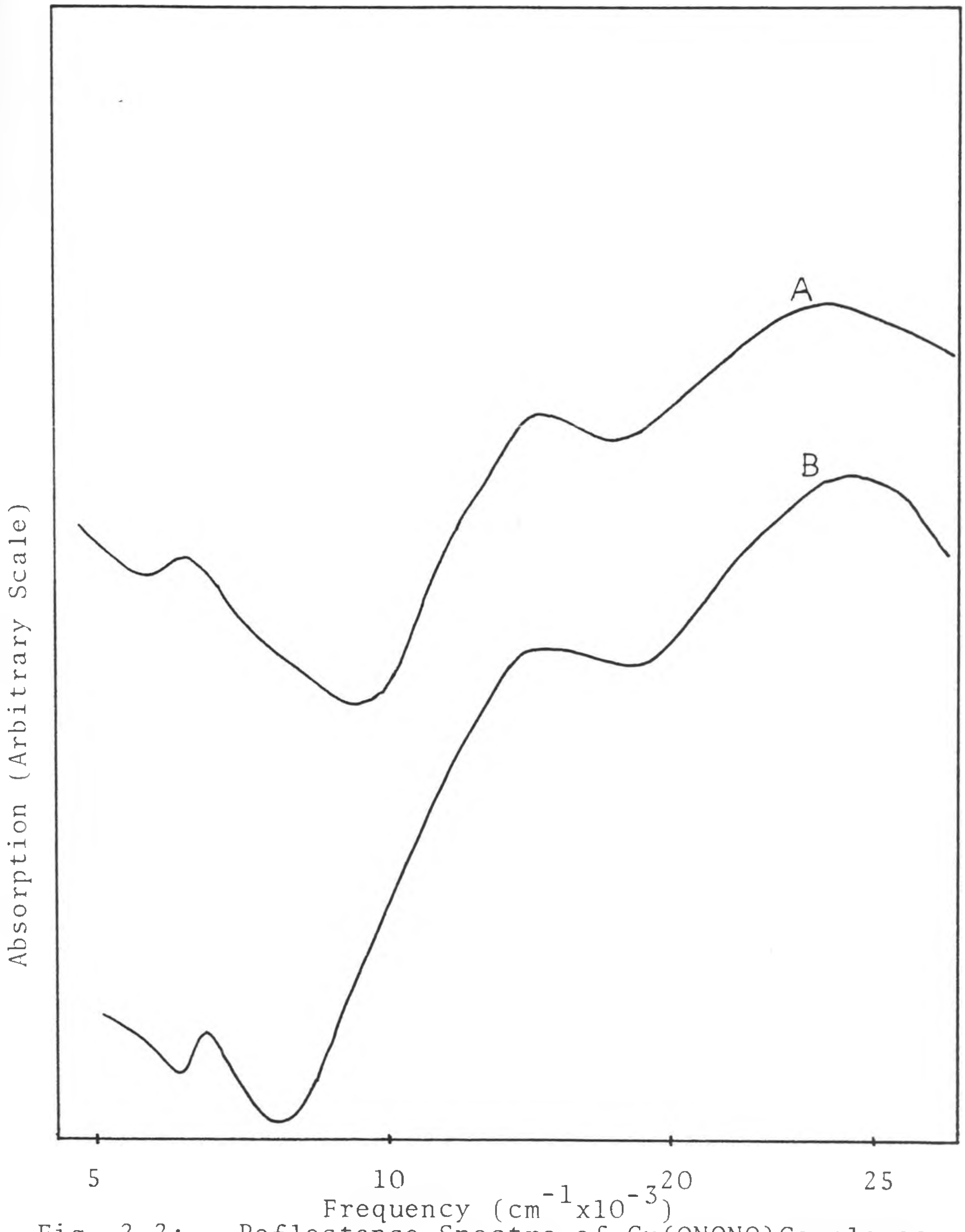


Fig. 2.2: Reflectance Spectra of Cu(ONONO)Complexes

A. R = Chloro

B. R = Bromo

are undergoing fragmentation somewhat haphazardly. It is unlikely that the complexes are five-coordinate. The electronic spectrum for five-coordinate trigonal bipyramidal $CuCl_5^{3-}$ ion in $Co(NH_3)_6$. $CuCl_5$ has two intense absorption bands, lying at 8200 and 10200 cm^{-1}. The spectrum of $CuCl_5^{3-}$ is very similar to that of five coordinate trigonal bipyramidal $[Co(Me_6tren)Cl]^+$ ion (figure 2.3.1), except it is shifted to lower energies[54]. Hathaway *et al* have reviewed the electronic spectra of copper(II) complexes[55,56]. The reflectance spectra of the copper complexes (figure 2.2) show only one broad ligand-band at 15690 cm^{-1} typical of tetragonally distorted octahedral copper(II) complexes[54]. The complexes have similar powder X-ray diffraction patterns to that of nickel complexes, indicating that they are isostructural. A polymeric oxygen-bridged six-coordinate structure (XXXIX) is therefore suggested for the copper complexes.

The cobalt complexes are high spin (μ_{eff}, ca. 4.3 B.M) and are insoluble in common organic solvents. Although the μ_{eff} is somewhat less than the usual 4.7-5.00 B.M expected for six-coordinate Co(II) complexes, it is still considerably higher than the "spin only" value of 3.83 B.M. The

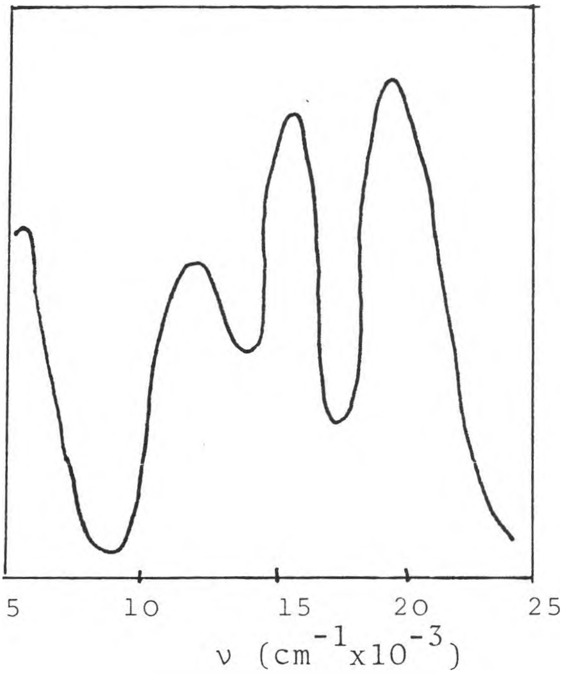


Fig. 2.3.1. The reflectance spectra of the Five coordinate trigonal bipyramidal Co(Me$_6$tren)cl$^+$ion

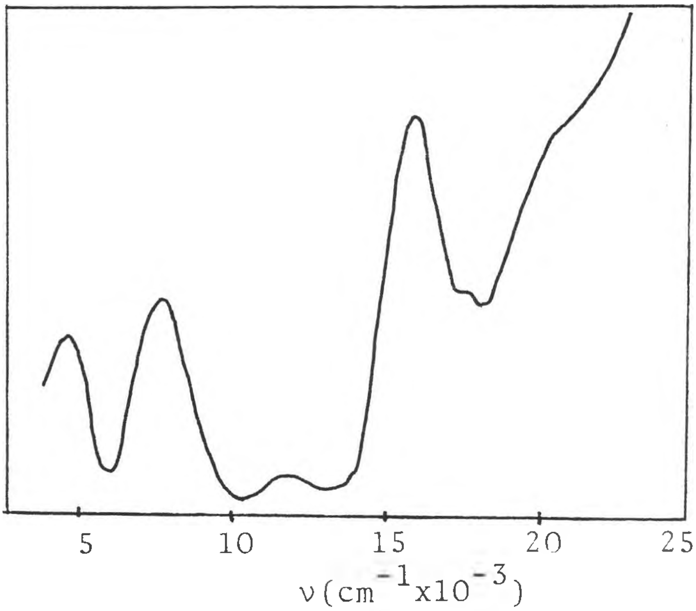


Fig. 2.3.2. The refectance spectra of the Five coordinate square pyramidal β-Co(paphy)cl$_2$

The electronic spectra (figure 2.3) display four bands at 8330, 10870, 15870 and 21500 cm^{-1}. In the absence of X-ray structural analysis, it is instructive to investigate the origin of the observed bands. The energy states for high spin five-coordinate cobalt(II) complexes have been calculated by several workers[51,52,57]. The transitions for [CoCl(tren Me)] Cl [trenMe = tris(2-dimethylaminoethyl)amine] have been calculated for a trigonal bipyramidal ligand field; these and the observed bands are as follows[54,57]:

	Calc.	Obs.
$^4A_2'(F) \rightarrow {}^4E''(F)$	4000 cm^{-1}	5500 cm^{-1}
$^4A_2'(F) \rightarrow {}^4E'(F)$	12000 cm^{-1}	12500 cm^{-1}
$^4A_2'(F) \rightarrow {}^4A_2'(P)$	15800 cm^{-1}	15600-16100 cm^{-1}
$^4A_2'(F) \rightarrow {}^4E''(P)$	20000 cm^{-1}	20000 cm^{-1}

The observed bands for Co(ONONO) complexes are significantly different especially in the occurrence of bands at 8330 and 10870 cm^{-1}.

Moreover, Lever[54] cites a number of five coordinate complexes whose structures (Figure 2.3.1 and 2.3.2) are clearly different. A five coordinate structure is therefore most unlikely.

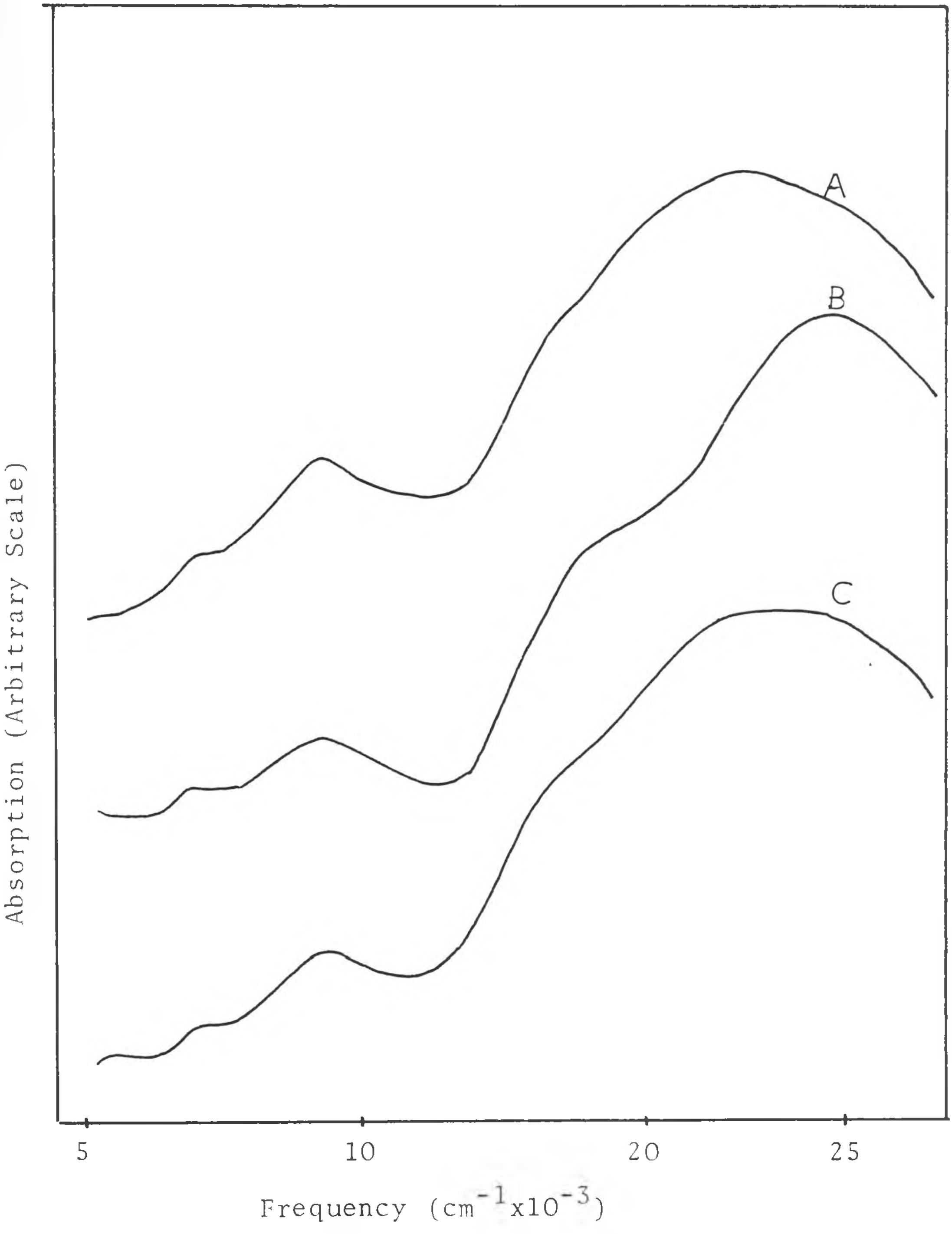


Fig. 2.3 Reflectance spectra of Co(ONONO)Complexes

A. R = Chloro
B. R = Bromo
C. R = Methyl

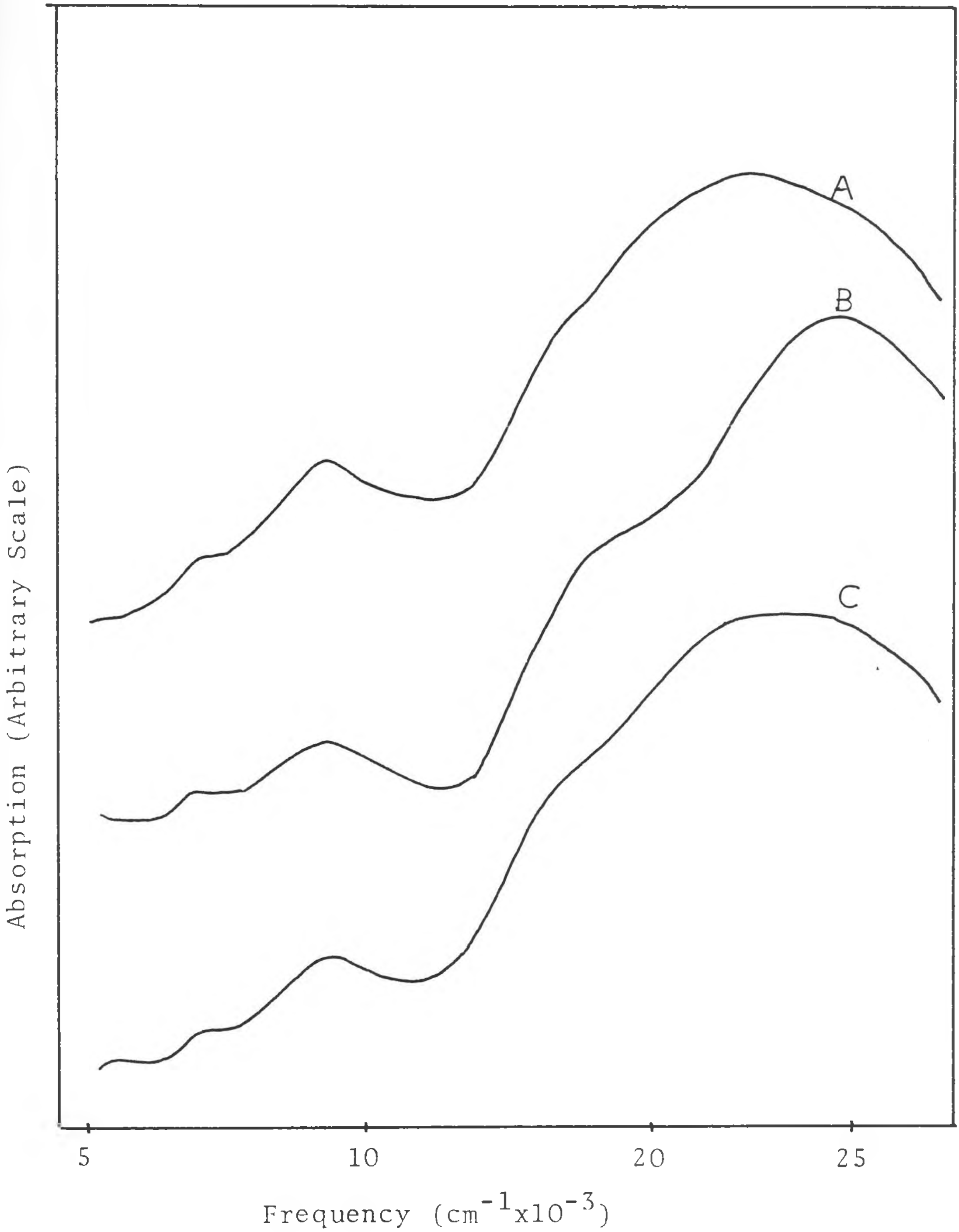


Fig. 2.3 Reflectance spectra of Co(ONONO)Complexes

A. R = Chloro
B. R = Bromo
C. R = Methyl

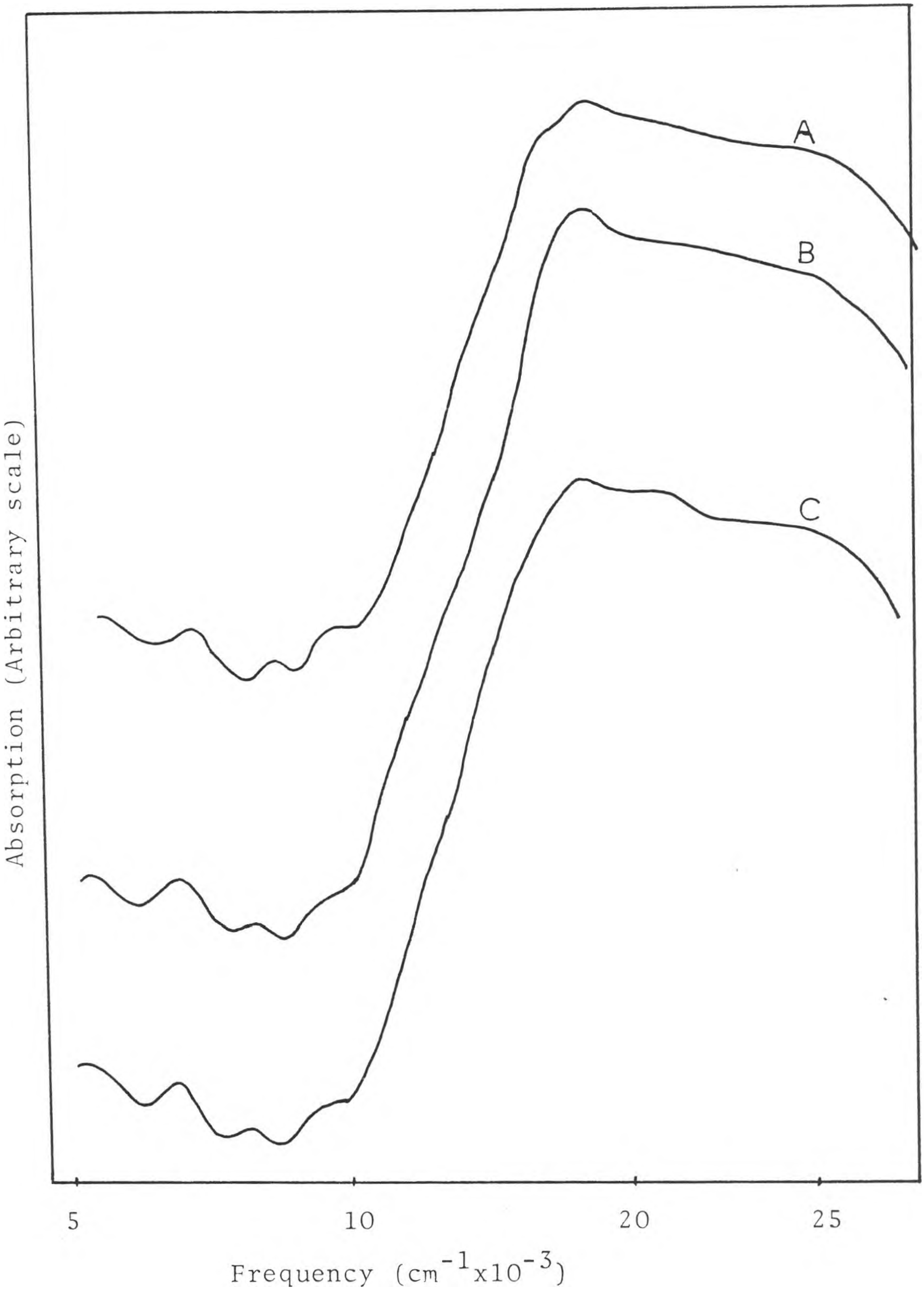


Fig. 2.4: Reflectance spectra of Fe(ONONO)Complexes

A. R = Chloro

B. R = Bromo

C. R = Methyl

In six-coordinate cobalt(II) complexes two bands are usually observed viz: $4T_{2g} \leftarrow 4T_{1g}$ at 8000-10000 cm^{-1} and $4T_{1g}(P) \leftarrow 4T_{1g}$ near 20000 cm^{-1}. The $4A_{2g} \leftarrow 4T_{1g}$ transition is not normally observed being formally a two electron transition. Theoretically the transition energy ratio γ_2/γ_1 is almost invariant at 2.1-2.2, within the range of D_q/B values found for octahedral cobalt(II) complexes. If therefore, we made a tentative assignment of the observed bands as:

ν_1	8330 cm^{-1}
ν_2	15870 cm^{-1}
ν_3	21500 cm^{-1}

the ratio $\nu_2/\nu_1 = 1.905$ will be outside the usual 2.1-2.2 range. Using transition energy ratio diagrams[54] the Racah parameter is easily computed to $B = 960$ cm^{-1} as compared to the free ion value, $B_o = 970$ cm^{-1}. This essentially means absence of the nephelauxetic effect and the band assignments must therefore be rejected as false.

Using the Tindimubona[58] computer program and assuming that cobalt(II) is in a tetrahedral environment where only ν_1 = 8330 and ν_2 = 15870 cm^{-1}, the following values are obtained;

$$10\ Dq = 5230\ cm^{-1}$$

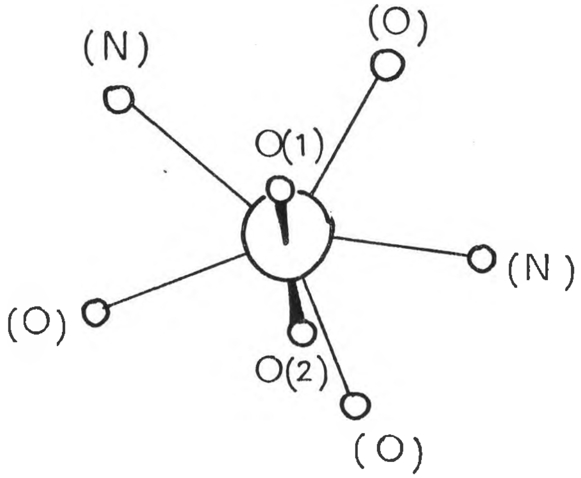
$$B = 604\ cm^{-1}$$

Although these values cannot be dismissed on any logical grounds, it is difficult to envisage how a quinquedentate ligand can generate a tetrahedral field. The FAB mass spectra have $(M + H)^+$ parent ion peaks at M/Z = 466 (R = Cl), M/Z = 510 (R = Br) and M/Z = 446 (R = CH_3). The presence of these peaks confirm the existence of the Co(ONONO) moiety. The structure of these complexes is still uncertain but a polymeric six-coordinate structure similar to (XXXIX) is suggested.

The iron complexes are dark brown in colour and have magnetic moments within the range 5.10-5.20 B.M. These values are normal for high-spin iron(II) complexes. The FAB mass spectra have $(M+H)^+$ parent ion peaks at M/Z = 463 (R = Cl), M/Z = 507 (R = Br) and M/Z = 443 (R = CH_3). The presence of these peaks confirms the existence of the Fe(ONONO) moiety. The electronic spectra (figure 2.4) show a peak at 7150 cm^{-1}, a rather broad absorption centred at ca. 8900 cm^{-1} and a strong peak at ca. 18200 cm^{-1}.

The later is considered to be a charge-transfer band, which is quite common for iron(II) complexes in the region above 16000 cm^{-1}. The peak at 7150 cm^{-1} and the associated broad band at 8900 cm^{-1} are assigned as the $^5E_g \leftarrow {}^5T_{2g}$ transition of spin-free octahedral iron(II), since this transition usually gives rise to a broad absorption, it splits into two components due to the Jahn-Teller effect[54]. It is unlikely that the complexes are five - coordinate since iron(II) complexes which are trigonal bipyramidal e.g. Fe(dien Me)Cl_2 and $[Fe(Me_6tren)Cl]^+Cl^-$, exhibit peaks at 8600 cm^{-1} and 10000 cm^{-1} respectively. In addition both complexes show a weak band at ca. 4000 cm^{-1}.

In a 1:1 absolute ethanol - 2,2-dimethoxy propane mixture, uranyl acetate reacts with the ligands (XXXVIII; R = Cl, Br or CH_3) to give bright orange monoligand complexes $[UO_2(ONONO)]$. The FAB mass spectra show $(M + H)^+$ parent ion peaks at M/Z = 677 (R = Cl), M/Z = 723 (R = Br) and M/Z = 657 (R = CH_3). The presence of this strong protonated molecular ion peak confirms the existence of the UO_2(ONONO) moiety. It is suggested that the complexes, N,N'-disalicylidene-4-R-2,6-di(aminomethyl) anisole-dioxouranium(VI); (R = chloro-, bromo-, methyl-) have a pentagonal bipyramidal structure(XL). The pentagonal base is defined by two oxygen atoms of the deprotonated chelate, two azomethinic nitrogens and the ether linkage oxygen. The uranylic oxygens O(1) and O(2) are apical. The suggested structure is in agreement with the confirmed structures, for several other similar uranyl complexes of quinquedentate N_2O_3 chromophores[23,59-67].



(XL)

2.4 Experimental

4-chloro-2,6-di(hydroxymethyl)phenol

Para-chlorophenol (32g, 0.25 mol) was dissolved in aqueous sodium hydroxide (10g, 0.25 mol in 40 ml). The mixture was cooled to room temperature. Formaldehyde (38.7 ml, 0.5 mol of 37-40%) was added dropwise with continuous stirring and the mixture was kept at 30-40°C. After 20 hours separation of sodium salt commenced; after 48 hours it was collected, washed with little water and dried. The colour of the compound was creamish-white[42]. The mother liquor, after being kept for 24 hours, yielded a further quantity of sodium salt (total: 44.25g). A sample of sodium salt was dissolved in minimum amount of hot water and treated with 3M-acetic acid, when the free chlorodi(hydroxymethyl)phenol was precipitated. After recrystallization the melting point was 156-158°C (lit. 159-161°C). It gave intense blue colouration with alcoholic ferric chloride.

4-Chloro-2,6-di(hydroxymethyl)anisole (1)

The crude sodium salt of chlorodi(hydroxymethyl)phenol (128g) was dissolved in boiling aqueous sodium hydroxide (12g, 0.3 mol in 475 ml) and dimethylsuphate (65 ml, 0.65 mol) was added, at such a rate, that the mixture which was vigorously stirred, maintained itself at the boiling point. After addition was completed, boiling continued for an hour and then the mixture was allowed to cool overnight. The product was collected, washed with water and redissolved in boiling water (260 ml). After removal of the insoluble oil, the clear solution was cooled. 4-chloro-2,6-di(hydroxymethyl)anisole (50g, 53%) crystallized as white needles[42], m.p. 124-126°C. After recrystallization from water the compound had a m.p of 128°C. By the same method 4-Bromo-2,6-di(hydroxymethyl)anisole (2) was synthesized[43].

4-Methyl-2,6-di(hydroxymethyl)anisole (3)

The crude sodium salt of methyldi(hydroxymethyl) phenol (47g) was dissolved in boiling aqueous sodium hydroxide (6g). Dimethylsulphate (35 ml, 0.35 mol) and acetone (50 ml) were added dropwise at such a rate that the vigorously stirred mixture, maintained itself at the boiling point. After refluxing for an hour with stirring, the mixture was allowed to stand overnight. The brown mixture was later transferred to a large beaker. The sides of the beaker were scratched with a glass rod and was left in the ice compartment for 36 hours. A solid crystalline mass appeared. The liquid was filtered and the crystals were collected, crystallized from water and the brown insoluble oil was removed. 4-Methyl-2,6-di(hydroxymethyl)anisole (17g, 49%) crystallized as white needles[44,45], m.p. 99-102°C. After recrystallization from water, the compound had a m.p of 103-104°C.

N,N'-diacetyl-4-Chloro-2,6-di(aminomethyl)anisole (4)

To an ice-cooled solution of acetonitrile (58 ml), concentrated sulphuric acid (29ml) was added dropwise over a period of half an hour while stirring. The temperature was maintained between 0°-5°C. 4-Chloro-2,6-di(hydroxymethyl)anisole (23g, 0.12 mol) was added with stirring. After stirring at 60°C for 8 hours,the reaction mixture was poured onto crushed ice and left overnight. The precipitate formed after neutralization with concentrated ammonia was collected by filtration, washed with water and dried to give 24.8g (ca.80%) of bis-amide, m.p. 196-202°C. This was recrystallized twice from absolute ethanol to give crystals with m.p. 213°-214°C.

By the same method the amides shown in Table 2.2 were prepared.

TABLE 2.2: The Ritter reaction of 2,6-di(hydroxymethyl)-R-anisole

2,6-di(hydroxymethyl)-4-R-anisole		CH_3CN	H_2SO_4	Rxn temp	time	Products		m.p[a]	Solvent for recryst
R	g(moles)	ml	ml	°C	(hr)	No	g(% yield)	°C	
Cl	23.0(0.12)	58	29	60	15	4	24.8(80)	213-214 (196-202)	abs.ethanol
Br[b]	24.7(0.1)	80	25	60	16	5	32.6(100)	229-230 (224-226)	abs.ethanol
CH_3[c]	40.0(0.22)	150	50	60	24	6	31.0(70)	207-208 (199-203)	abs.ethanol

a: The melting points of the crude products are shown in parentheses.

b: Prepared according to ref.[43]; m.p 130°C

c: Prepared according to ref. 44 and 45; m.p 103-104°C

N,N'-disalicylidene-4-Chloro-2,6-di(aminomethyl)anisole(10)

To a 10% aqueous solution of sodium hydroxide made up by dissolving sodium hydroxide (42g, 1.05 mol), in ethanol (100ml) and water (320ml), N,N'-diacetyl-4-chloro-2,6-di(aminomethyl)anisole (10.0g, 0.35 mol) was added. The mixture was heated under reflux for 48 hours, cooled overnight and then extracted with three 20ml portions of ether. After combined ether extracts were dried over potassium hydroxide, the solvent was distilled off, the residue solidified on standing, giving 7.0g of diamine(7). No precise melting point could be obtained. To a solution of crude diamine(7) (6g, 0.03 mol) in absolute ethanol (30ml), salicylaldehyde (7.2g, 0.06 mol) and three drops of 10 M-hydrochloric acid in ethanol (20ml) was added. The mixture was heated on the water - bath for 10 minutes then allowed to cool overnight in the refrigerator. Yellow crystals of bis-Schiff base were formed. The crystals were filtered off, washed with absolute ethanol and dried, m.p. 80-82^{o}C; after recrystallization from absolute ethanol, they were dried in vacuo ; yield, 8.7g [60% based on the diamide(4)], m.p. 85-86^{o}C. By the same method other Schiff bases described below were prepared.

N,N'-disalicylidene-4-Bromo-2,6-di(aminomethyl) anisole(11)

A mixture of diamide(5) (8.2g, 25mmol), sodium hydroxide (40g,1 mole), ethanol (50ml) and water(350ml) was heated under reflux for 65 hours to give 6.0g of diamine(8). A solution of diamine(8) (6.0g, 24 mmol) in absolute ethanol (50ml) was treated with salicylaldehyde (7.5g, 0.06 mol) and three drops of 10M-hydrochloric acid in ethanol (30ml), giving yellow crystals of bis-Schiff base (11) (10g, 89%), m.p. 127-128°C. Recrystallization from absolute ethanol caused no change in the melting point. The crystals were then dried *in vacuo*.

N,N'-disalicylidene-2,6-di(aminomethyl)-4-Methyl-anisole(12)

A mixture of amide(6) (10g, 37 mmol), 20% aqueous solution made up of sodium hydroxide (120g, 3 mol), ethanol (100ml) and water (500 ml), was heated under reflux for 69 hours to give 6.5 g of diamine(9). A solution of diamine(9) (6.5g, 35 mmol) in absolute ethanol (50 ml) was treated with salicylaldehyde (8.8g, 73 mmol) and four drops of 10M-hydrochloric acid in ethanol (30ml), giving yellow crystals of bis-Schiff base(12) (6.1g, 42%), m.p. 65-68°C. Recrystallization from ethanol brought the m.p to 67-68°C, the crystals were then dried *in vacuo*.

Uranium and Nickel complexes

Uranium and Nickel complexes of N,N'-disalicylidene-4-R-2,6-di(aminomethyl)anisole, where R = chloro bromo or methyl

Type I - M(ONONO); R = Chloro

The metal acetate hydrate (4.9 mmol) in hot absolute ethanol (20ml) was added dropwise to a solution of the Schiff base (4.9 mmol) in hot 2:1 mixture (30 ml) of absolute ethanol and 2,2-dimethoxypropane. The mixture was heated on the waterbath for 10 minutes, whereupon the complexes separated out. The coloured complexes were filtered off, washed with little absolute ethanol and then dried *in vacuo* over phosphorus pentoxide; yield, 70-80%.

Type II - M(ONONO); R = Bromo

A solution of metal acetate hydrate (4.42 mmol) in hot absolute ethanol (20 ml) was added dropwise to a solution of the Schiff base (4.42 mmol) in hot 1:1 mixture (20 ml) of absolute ethanol and 2,2-dimethoxypropane. The same procedure as described above was followed, yield, 80-85%.

Type III-M(ONONO); R = Methyl

A solution of metal acetate hydrate (2.57 mmol) in hot absolute ethanol (10 ml) was added dropwise to a solution of the Schiff base (2.57 mmol) in hot 1:1 mixture of absolute ethanol and 2,2-dimethoxypropane. The same procedure as described above was followed yield, 85%.

Copper and Cobalt complexes

Copper and Cobalt complexes of N'N-disalicylidene-4-R-2,6-di(aminomethyl)anisole

Type I-M(ONONO); R = Chloro

These complexes were prepared from the metal nitrate hydrate (4.9 mmol) by the same method as that described for Type I-Chloro complexes. The mixture was heated on the water bath for 10 minutes then allowed to stand for an hour, whereupon the metal complexes started depositing on the side of the beaker; yield 55-65%.

Type II - M(ONONO); R = Bromo

These complexes were prepared from the metal nitrate hydrate (4.42 mmol) by the same method described for Type I - Chloro complexes. The mixture was heated on the waterbath for 10 minutes then allowed to stand for an hour, whereupon the metal complexes started depositing on the side of the beaker; yield 40-50%.

Type III - Co(ONONO); R = Methyl

A hot solution of cobalt nitrate trihydrate (0.63g, 2.57 mmol) in absolute ethanol (8ml) was added to a hot solution of the Schiff base (2.57 mmol) in 2:1 mixture (12ml) of absolute ethanol and 2,2-dimethoxypropane. Rest of the procedure is same as that of above;yield 85%.

Iron Complexes

Iron complexes of N,N'-disalicylidene-4-R-2,6-di(aminomethyl)anisole

Type I - M(ONONO); R = Chloro

A hot solution of ferrous chloride tetrahydrate (0.97g, 4.9 mmol) in absolute ethanol (10 ml) was added dropwise to the solution of the Schiff-base (4.9 mmol) in a hot 1:1 mixture (20ml) of absolute ethanol and 2,2-dimethoxypropane. The mixture was heated on the water-bath for 5 minutes, whereupon a fine dark brown complex was deposited. The complex was filtered, washed with little absolute ethanol and dried *in vacuo* over phosphoric oxide; yield 2.2g (90%).

Type II - M(ONONO); R = Bromo

Ferrous chloride tetrahydrate (0.88g, 4.42 mmol) in hot absolute ethanol (10 ml) was added to a solution of the Schiff base (4.42 mmol) in hot 1:2 mixture (30 ml) of absolute ethanol and 2,2-dimethoxypropane. The same procedure was followed as above; yield, 2.2g (95%).

Type III - M(ONONO); R = Methyl

A solution of ferrous chloride tetrahydrate (0.35g, 1.76 mmol) in hot absolute ethanol (15 ml) was added dropwise to a solution of the Schiff base (1.76 mmol) in hot 1:3 mixture (20 ml) of absolute ethanol and 2,2-dimethoxypropane. The same procedure as described above was followed, yield 0.75g (90%).

2.5 Conclusion

Our study has led us to the following conclusions:-

2.5.1 Some of the patent literature[42-45], relating to the preparation of N,N'-disalicylidene-4-R-2,6-di(aminomethyl)anisole; where R = Cl, Br, CH_3, is inaccurate. The procedures we have reported give good yields.

2.5.2. Quinquedentate ligands did not yield five - coordinate complexes as we had hoped. The ligands are perhaps not sufficiently sterically hindered to exclude coordination in the sixth site. The cobalt(II), iron(II), copper(II) and nickel(II) complexes have been assigned octahedral structures on the basis of their electronic and FAB mass spectra.

2.5.3. The uranyl complex has a pentagonal bipyramidal structure in which the ONONO donor atoms occupy the equatorial plane. An equatorial crystal field perturbation per see would not be expected to yield significant stabilization energy. This may be the reason for the absence of five coordinate transition metal complexes of these ligands.

2.5.4. The magnetic moments of the complexes are normal and magnetic spin-exchange interactions are therefore absent.

CHAPTER THREE

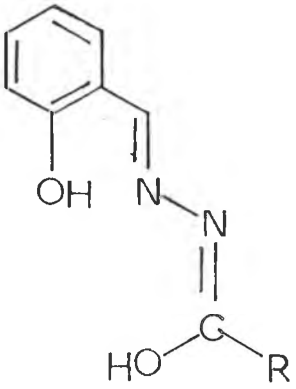
METAL COMPLEX OF ONO TRIDENTATE LIGAND

3. METAL CHELATE OF ONO-TRIDENTATE SCHIFF BASE

3.1 Objectives

The metal complexes of potentially tridentate Schiff bases have been discussed in section 1.2. This chapter describes complexes of a potentially tridentate ligand derived by the condensation of 6-aminomethyl-2,4-dichlorophenol and salicylaldehyde. This ligand has the ONO donor set.

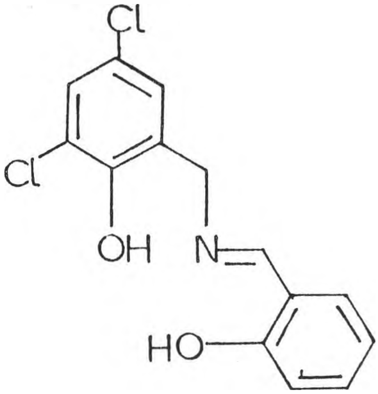
Oxygen-bridged copper(II) complexes with sub normal magnetic moments have been known[68] for some time and there has been considerable discussion on the mechanism of spin-exchange in such complexes. A survey of the oxygen-bridged copper(II) complexes reveals that there is a general relationship between magnetic moments and the stereochemistry of the bridging oxygen[33,69-78]. Complexes with tetrahedral coordination about oxygen exhibit normal magnetic moments at room temperature, while complexes with planar three-coordination about oxygen exhibit low magnetic moments. Ohta[79] has prepared copper(II) complexes of the type $[Cu(Sah-2H)]_2$ and $[Cu(Sal-2H)NH_3]_n$; (Sah; XLI). We propose to establish whether our ligand can give similar complexes and whether such complexes exhibit magnetic spin-exchange interactions.



(XLI)

3.2 Results and Discussion

The Schiff base N-salicylidene-6-aminomethyl-2,4-dichlorophenol (XLII) was prepared by the condensation of 6-aminomethyl-2,4-dichlorophenol and salicylaldehyde. The Schiff base is doubly deprotonated during the formation of metal complexes. The reaction of copper acetate and the Schiff base gives a complex of the type Cu(ONO) (HONOH = XLII).



(XLII)

The dark green copper complex obtained is quite stable on standing and is not soluble in common organic solvents like alcohols, chloroform and acetone. Several attempts were made to synthesize metal complexes of the ligand (XLII) using various metal salts e.g. nickel acetate, uranyl acetate, copper nitrate, cobalt nitrate, ferrous chloride and zinc chloride. The only complex successfully isolated was that of copper(II) while the other salts formed coloured solutions only.

The molecular weight of copper(II) complex was determined by FAB mass spectrometer and results are shown in the experimental section 3.3 and figure A.15 in the appendix. The copper(II) complex is paramagnetic (μ_{eff}=1.78 B.M) and has slightly lower value for magnetic moment, than the normal range of 1.8-2.1 B.M. Bivalent copper(II) complexes are known[31,36,69-78], to have sub-normal μ_{eff} values, much lower than "spin-only" value (1.73 B.M). This is due to the appreciable magnetic interaction between two copper atoms.

It is unlikely that the complex is six coordinate, tetrahedral, square planar or five coordinate. The electronic spectra for six coordinate copper(II) complexes[54] usually have one intense absorption band near 16000cm^{-1}. The spectra of complexes, $K_2PbCu(NO_2)_6$ and $K_2BaCu(NO_2)_6$ are shown in figure (3.2.1). The electronic spectrum for tetrahedral copper(II) derivatives[54], generally give a single broad band in the near infra red region and is blank between 10000-20000cm^{-1}. The spectra of Cs_2CuCl_4 and Cs_2CuBr_4 exhibit a band at 8000cm^{-1} and 9000cm^{-1} respectively, due to a transition to the components of the ^2E level in D_{2d} symmetry[80]. The electronic spectrum for square

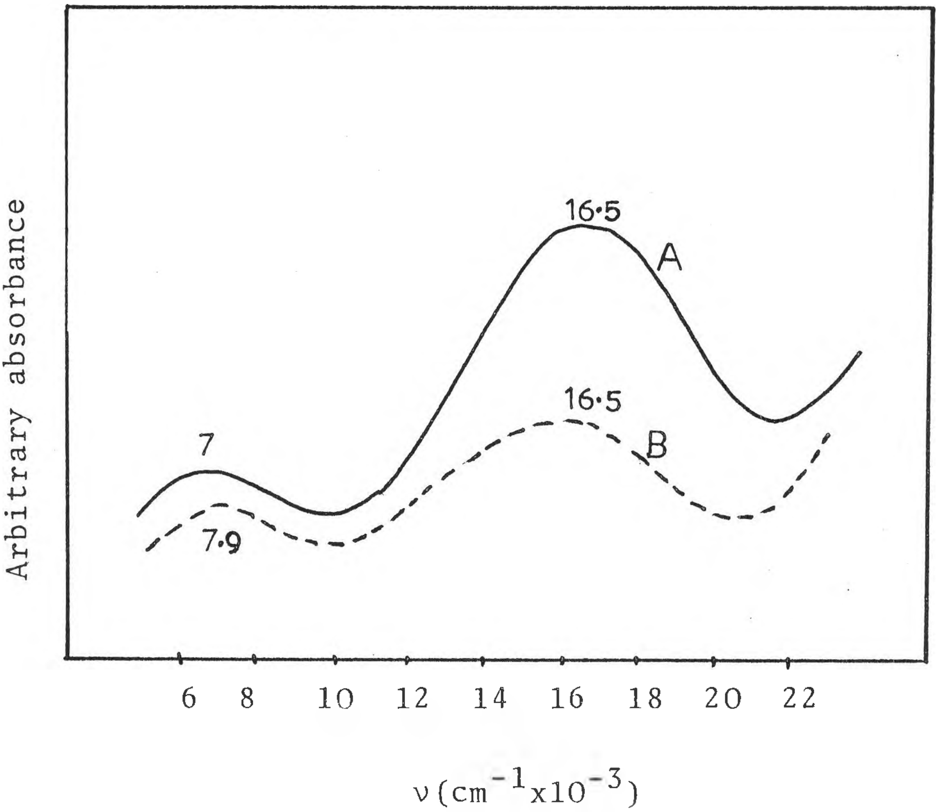


Fig. 3.2.1: The electronic spectrum of

A: = $K_2Cu(NO_2)_6$

B: = $K_2BaCu(NO_2)_6$

coplanar copper(II) derivatives, usually have intense multiple bands between 10000-20000cm^{-1} region[80]. A square planar ion $CuCl_4^{2-}$ in $Pt(NH_3)_4.CuCl_4$ has bands in the visible region between 10900 and 14300cm^{-1}. The five-coordinate copper(II) complexes having trigonal bipyramidal and square pyramidal stereochemistry have been described in Chapter 2, section 2.3.

The electronic spectrum of the complex Cu(ONO) (figure 3.1) shows two distinct d-d transition bands at ca.7400cm^{-1} and 15700cm^{-1}. These values are quite agreable for dimeric complexes[36,69-78]. The FAB mass spectrum has a $(M+H)^+$ parent ion peak at M/Z=296. This peak is ideally for that of the ligand (XLII). The mass spectrum shows no metal containing peak, which is possibly due to thermal instability of the metal chelate in the mass spectrometer. The X-ray diffraction pattern obtained on the slide is different from the patterns obtained for copper complexes in chapter 2. Ruling out all the above possibilities through electronic spectra, it is suggested that the most likely structure for the complex Cu(ONO) should be that of dimeric oxygen-bridged structure (XLIII). Detailed study is yet required to ascertain the structure of the complex.

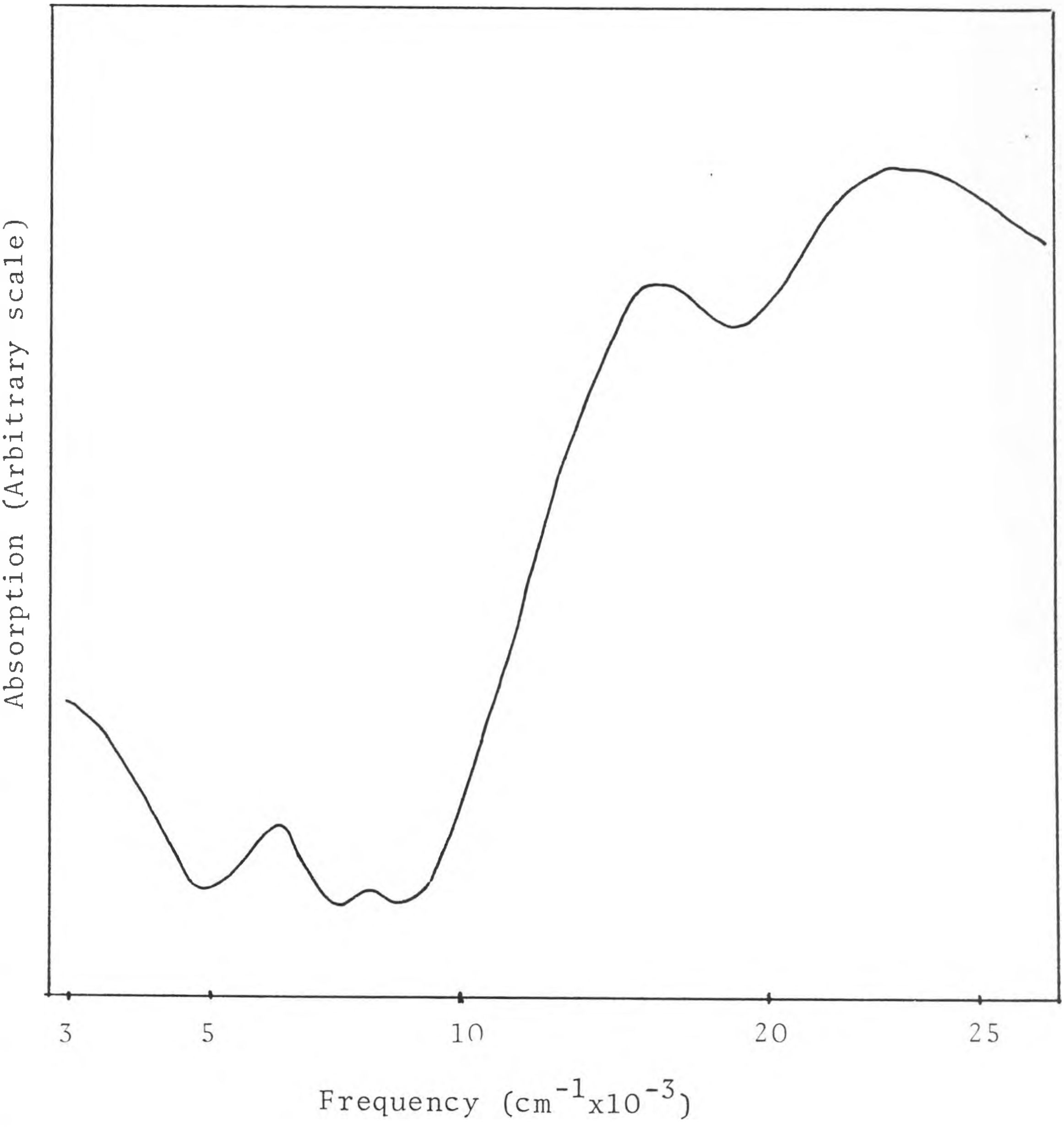
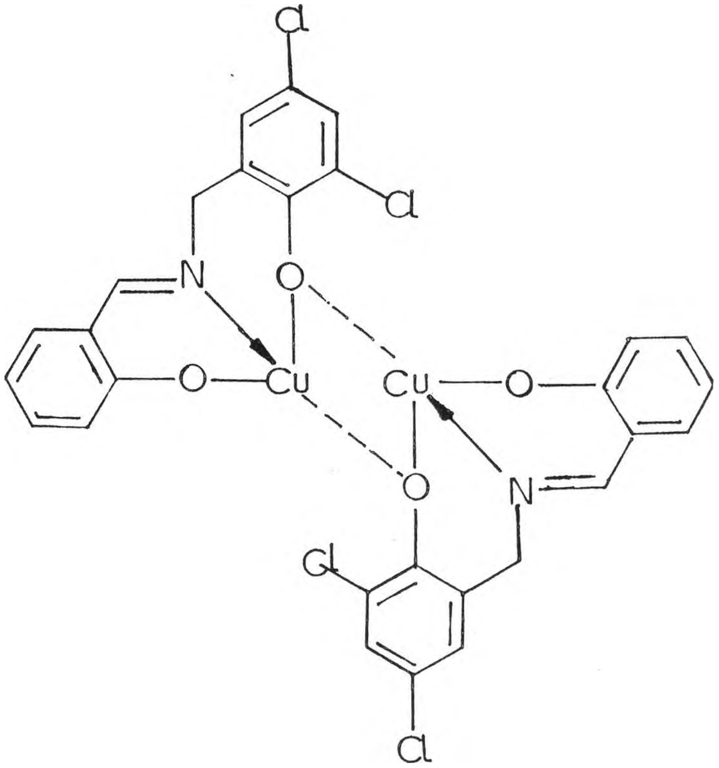


Figure 3.1 Reflectance spectra of Cu(ONO) complex



(XLIII)

3.3 Experimental

The procedure for the synthesis of the ligand is similar to that described in chapter 2, sec. 2.2.

2,4-dichloro-6-(hydroxymethyl)phenol[81]

2,4-dichlorophenol (326g,2mol) was melted and then added slowly into a solution of sodium hydroxide (88g, 2.2mol) in 130ml water. After cooling the mixture, 216g of formaldehyde (37-40%) was added while stirring, the solution was covered with high boiling petroleum ether and left to react for 2 days at 40°C. It was left standing for 2 days at room temperature then left in an ice compartment to cool for 6 hours, and filtered. The sodium salt was dissolved by mechanical stirring in 1 litre water and added dropwise into an ice cooled solution of 70ml glacial acetic acid in 600ml of water. It was filtered and after drying, recrystallized from benzene. The melting point of the product; $2,4,6\text{-}Cl_2(HOCH_2)C_6H_2OH$ was 82-83°C; yield 56%.

N-acetyl-6-aminomethyl-2,4-dichlorophenol

2,4-dichloro-6-(hydroxymethyl)phenol (30g, 0.16mol) was added to an ice-cooled solution of acetonitrile (120ml) and concentrated sulphuric acid (40ml) with stirring. The mixture was stirred at 45°C for 12 hours. The upper layer was discarded and the viscous residue was poured onto the crushed ice and allowed to stand overnight at room temperature. The precipitates formed were collected by filtration, washed with water and dried to give 36g (98%) of the amide. After recrystallization from absolute ethanol the melting point was 160-162°C.

6-aminomethyl-2,4-dichlorophenol

N-acetyl-6-aminomethyl-2,4-dichlorophenol (25g, 0.11mol) was dissolved in 5% sodium hydroxide solution (640ml). The mixture was heated under reflux for 48 hours. The solvent was removed by distillation and the residue washed with water. There was 15g (70%) of amine; after recrystallization from absolute ethanol, m.p. 195-196°C.

N-salicylidene-6-aminomethyl-2,4-dichlorophenol

To a solution of amine (10g, 0.05mol) in absolute ethanol (350ml), 6g of salicylaldehyde was added. The mixture was heated under reflux for one hour and then filtered. To the hot filtrate, hot water was added dropwise until the solution became turbid. The mixture was cooled and then filtered to give 9.5g (62%) of the Schiff base in crystalline form, m.p. 160-163°C; after recrystallization from absolute ethanol, m.p. 165-166°C.

N-salicylidene-6-aminomethyl-2,4-dichlorophenol copper(II)

A hot solution of copper acetate monohydrate (0.68g, 3.39mmol) in absolute ethanol (15ml) was added dropwise to a solution of the Schiff base (3.39mmol) in hot 2:1 mixture (20ml) of absolute ethanol and 2,2-dimethoxypropane. The mixture was heated on the water-bath for 10 minutes, and left to cool. After an hour fine crystalline complex was deposited on the sides of the beaker. The dark green crystals of the complex were filtered off, washed with little absolute ethanol and then dried *in vacuo* over phosphorous pentoxide, yield, 0.98g(80%) (Found: C, 46.96; H, 2.53; N, 3.88; Cu, 17.48. calcd: C, 47.08; H, 2.54; N, 3.91; Cu, 17.76). FAB mass spectrum showed peak at M/Z=296.

3.4 Conclusion

Our results show that the copper complex we isolated has the $[CuL-2H]_2$ moiety (L=N-salicylidene-6-aminomethyl-2, 4-dichlorophenol) similar to complexes previously prepared by Ohta[79]. The dimeric structure we have tentatively assigned to the complex should have been confirmed by sub-normal magnetic moments indicating antiferromagnetism. The observed value, μ_{eff} = 1.78B.M. is rather high to be considered subnormal. This, together with the reluctance of the other transition metals to form complexes with this ligand are areas for further ivestigation.

APPENDIX

APPENDIX

A.1 Analytical Methods

Carbon, hydrogen and nitrogen were determined by Mr. Ken. Jones and Mrs. Olive Collins of the Microanalytical Laboratory, Imperial College of Science and Technology; London, U.K.

Metal determinations were carried out after the compounds had been decomposed with a mixture of concentrated sulphuric and nitric acids.

Nickel was determined gravimetrically as the dimethylglyoxime complex.

Cobalt was determined gravimetrically as $Co(Py)_4(NCS)_2$.

Iron was determined gravimetrically as Fe_2O_3.

Copper was determined gravimetrically as $[Cu(en)_2]HgI_4$.

Uranium was determined[82] by using calorimetric method. Uranium was extracted by 8-Hydroxyquinoline and the resulting bright orange colored metal complex solution was measured spectrophotometrically at 420 mμ.

A.2 Physical Measurements

A.2.1 Reflectance spectra: All reflectance spectra were obtained on a Cary-14 spectrophotometer using reflectance attachment calibrated against zinc oxide.

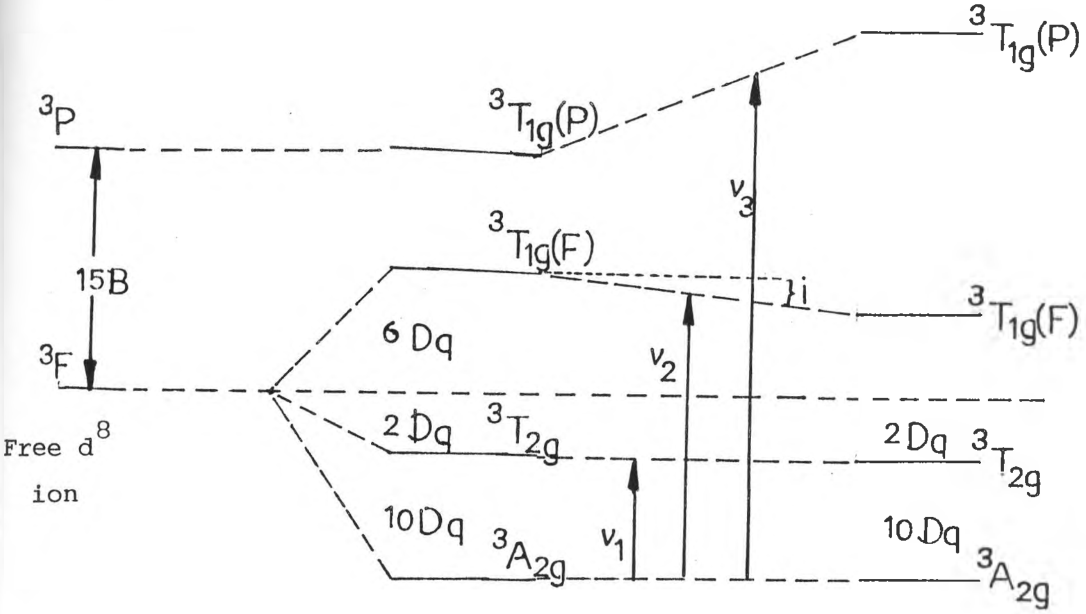
A.2.2 X-ray Measurements: The X-ray diffraction patterns were obtained on a Nicolet R3m X-ray Diffractometer using CoK_{α} radiation ($\lambda=1.7928^{o}A$).

A.2.3 Magnetic Susceptibility Measurements:

The room temperature magnetic moments were determined by the Evans balance having direct digital read-out. The basic principle is same as Guoy Balance. The Evans tubes were calibrated against known standards, i.e. $CuSO_4.5H_2O$ and $CoHg(NCS)_4$. Diamagnetic corrections were calculated from Pascal's constants[83,84].

A.2.4 Electronic Spectra

Case I: Weak and Intermediate crystal field situations for d^2, d^7 (tetrahedral); d^3, d^8 (octahedral).



weak octahedral crystal field (10 Dq small)
No interaction between T_{1g} levels
$10Dq = \nu 1$
$15B = \nu_3 - 12Dq$

Intermediate crystal field (large Dq)
Interaction between T_{1g} levels
$10Dq = \nu_1$
$15B = ?$

Intermediate Field

In the intermediate field case the T_{1g} levels interact. This interaction is described by the secular determinant:

$$\begin{bmatrix} 15B + 12Dq-\nu_{2,3} & 4Dq \\ 4Dq & 18Dq-\nu_{2,3} \end{bmatrix} =0$$

$\nu_{2,3}$ could be regarded as the 'unknown' in the quadratic equation, and it may take the values ν_2 and ν_3.

solving:-

$10Dq=\nu_1$

$$15B=\nu_3 + \nu_2 - 3\nu_1 = \frac{(\nu_2-20Dq)(\nu_2 - 10Dq)}{(\nu_2 - 18Dq)}$$

$$= \frac{(\nu_3-20Dq)(\nu_3-10Dq)}{(\nu_3 - 18Dq)}$$

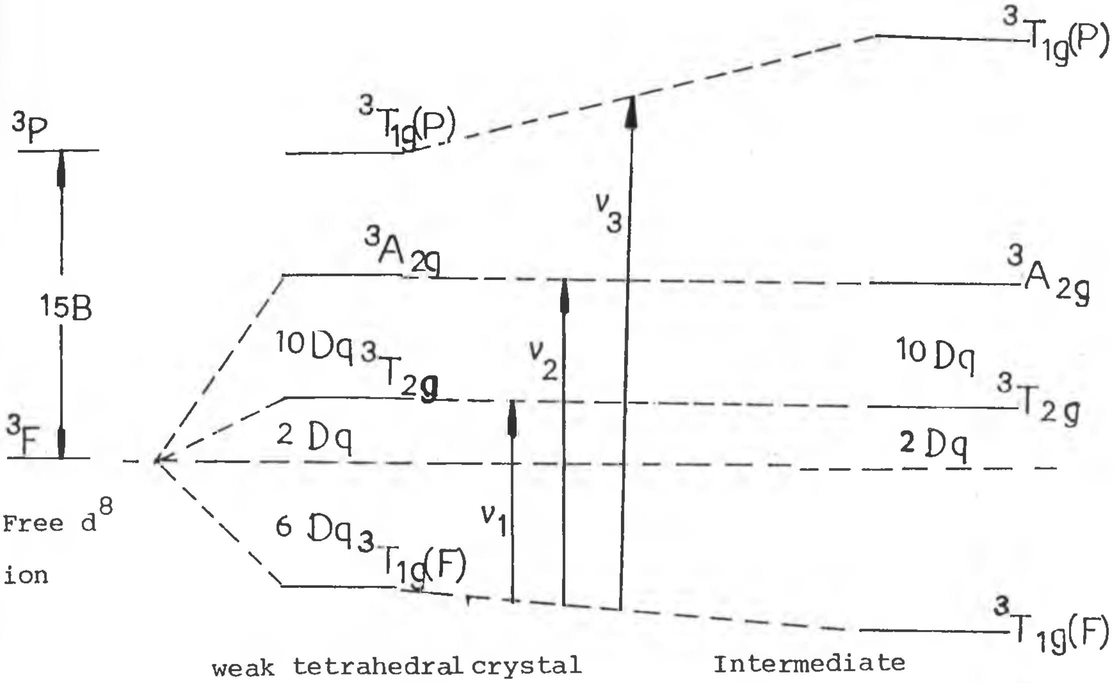
$$\nu_2 = 7.5B+15Dq-\tfrac{1}{2} \left[225B^2-180Dq.B+100Dq^2\right]^{\frac{1}{2}}$$

$$\nu_3 = 7.5B+15Dq+\tfrac{1}{2} \left[225B^2-180Dq.B+100Dq^2\right]^{\frac{1}{2}}$$

$$340Dq^2-18(\nu_2+\nu_3)\ Dq +\nu_2\nu_3 = 0$$

The above expressions are applicable in all cases, and they reduce to the weak field expressions as $Dq \rightarrow 0$.

Case II: Weak and Intermediate crystal field situations for d^2, d^7 (octahedral); d^3, d^8 (tetrahedral).



weak tetrahedral crystal field ($Dq \ll B$)
No interaction between T_{1g} levels
$8\,Dq = \nu_1$
$15B = \nu_3 - 6\,Dq$

Intermediate crystal field ($Dq \simeq B$)
Interaction between T_{1g} levels
$Dq = ?$
$15B = \nu_3 + \nu_2 - 3\nu_1$

Intermediate Field

In the intermediate field case, the T_{1g} levels interact. *This interaction is described by the* secular determinant:

$$\begin{bmatrix} 15B-E & 4Dq \\ 4Dq & (-6Dq-E) \end{bmatrix} = 0$$

E may be regarded as the 'unknown' in the quadratic equation, and it represents the energies of $3T_{1g}$ (P) and $3T_{1g}$(F) relative to the 3_F energy level.

solving:-

$$\nu_1 = -7.5B+5Dq+\tfrac{1}{2}\ [225B^2+180Dq.B+100Dq^2]^{\frac{1}{2}}$$

$$\nu_2 = -7.5B+15Dq+\tfrac{1}{2}\ [225B^2+180Dq.B+100Dq^2]^{\frac{1}{2}}$$

$$\nu_3 = (225B^2+180Dq.B+100Dq^2)^{\frac{1}{2}}$$

$$10Dq = \tfrac{1}{2}\ [(2\nu_1-\nu_3) + (\nu_3^2+\nu_1\nu_3-\nu_1^2)]^{\frac{1}{2}}$$

$$15B = (\nu_3-2\nu_1+10Dq) = (\nu_3+\nu_2-3\nu_1)$$

$$340Dq^2 + 18(\nu_3-2\nu_2)Dq+\nu_2^2-\nu_2\nu_3 = 0$$

Attempts have been made by Beech[85] to write a computer programme in Fortran IV to calculate 10Dq and B of metal complexes with the above electronic configurations. A similar program was obtained from Tindimubona[58] (BBC BASIC). The program seems to compute the two parameters rapidly and accurately for all configurations except for d^7 octahedral.

A.2.5 Mass Spectra:

The spectra were obtained by Fast Atomic Bombardment technique using VG-7070E mass spectrometer with additional attachments.

Mass Spectrometry

The last decade has been a number of attempts to overcome one of the problems associated with structural mass spectrometry, namely the requirement that the sample must be presented to the instrument in the gas phase before it is ionised. This has proved especially troublesome in the case of compounds of biological and biomedical importance, where their thermal instability and general polar nature precludes volatisation except for a few low molecular weight examples. Perhaps the major development in mass spectrometry has been Fast Atom Bombardment (FAB) mass spectrometry. There are four areas in which mass spectrometry can provide answers to question: isotope analysis, quantitation, fingerprinting and structure elucidation.

The Fast Atomic Bombardment Technique:-

In the FAB technique[86,87,88], the sample is presented in a liquid matrix of low volatility (e.g. glycerol) and desorbed by "bombardment" with a high flux of neutral particles such as Argon or Xenon atoms. The technique has provided successful analysis for many organometallics. This technique is effectively used with samples which are ionic, involatile, thermally unstable and/or relatively heavy. This set of sample characteristics makes it highly complementary to electron impact.

The fast atom gun:

The FAB gun consists of a saddle field cold cathode ion source, the anode of which is enclosed by the cathode. Extraction electrodes are therefore not required. The beam emerging from the source is concentrated about the axes within a diameter of 2mm. Gas is admitted via swagelock coupling in the vacuum housing and a length of silicone rubber.

A deflection plate mounted near the beam exit aperture removes any ions emerging with the neutral beam. This plate is connected to the anode.

The Source:

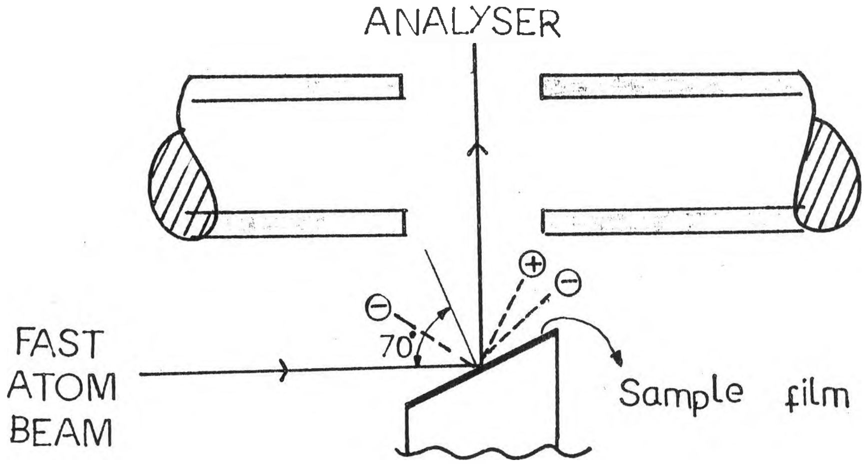
The source of fast atoms in prototype apparatus consists of a cold cathode discharge ion source and a collision chamber. The discharge ion source produces a beam of Ar^+ of controlled energy which is focused into the collision chamber which contains a high pressure of argon gas. Resonant charge exchange occurs and a particle beam emanates from the collision chamber which consists of a mixture of Ar atoms and Ar^+, the later having escaped without being charge exchanged. The ionic component is cleansed from the beam by a set of electrostatic deflector plates.

Ion Chamber:

The ion chamber is not heated and there is no filament. The materials (1 μg) can be introduced into the system by first depositing them from solution onto a metal stage which is fixed to the shaft of a solid sample insertion probe. This can then be introduced to the ion source through an axially mounted vacuum lock, in order to intercept the fast atom beam.

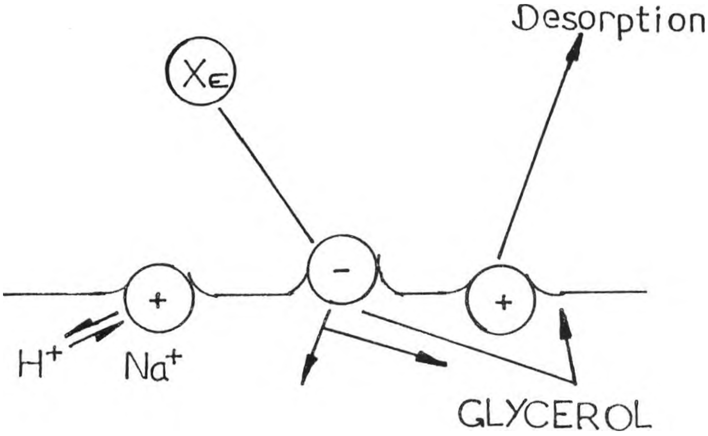
The fast atoms produced by the gun enter the ion chamber, where they strike the target on which the sample has been deposited. The sample is ionised and the ions produced by the sputtering mechanism are then accelerated to the normal spectrometer potential and passed into the analyser region of the instrument.

The source schematic in figure (A.2.5.1) indicates that positive ions, negative ions and also neutral species are desorbed by the bombardment.



(A. 2.5.1)

Figure (A.2.5.2) illustrates schematically the several roles of the non volatile fluid matrix. Sample molecules can be ionized by chemical reactions in solution. Solvation provides charge seperation, lowering the energy required for desorption. Solution equilibria lead to replacement of active protons with ubiquitous alkali metal cations.

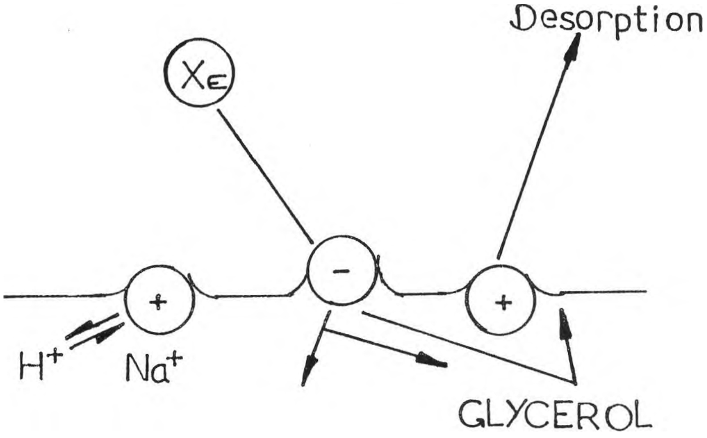


(A.2.5.2)

Sufficient energy is transferred by the impact through the matrix to desorb preformed ions, molecules and clusters from the surface.

A final contribution of the fluid matrix, is constantly in bringing the new sample ions to the surface so that ion desorption can be even and prolonged.

The introduction of the fluid matrix, which is the distinguishing and novel feature of the FAB technique, permits the use of a high flux primary beam and generation of a strong, steady and prolonged secondary (sample) ion current. These currents are comparable to those generated by electron impact.



(A.2.5.2)

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The introduction of the fluid matrix, which is the distinguishing and novel feature of the FAB technique, permits the use of a high flux primary beam and generation of a strong, steady and prolonged secondary (sample) ion current. These currents are comparable to those generated by electron impact.

The experimental variables available in FAB experiment include selection of the particles and energy of the primary (bombarding) beam and selection of the fluid matrix and its supporting stage.

The mass spectra obtained by this method are characterised by high pseudo-molecular ion sensitivity, giving $(M+H^+)$, $(M+Na^+)$ in positive ion spectra and $(M-H^-)$ in the negative ion case.

The spectra of either polarity contain structurally sensitive fragment ions and both first and second fields-free 'Metastables' are observable.

The ion source has the facility of producing both positive and negative ion mass spectra with equal ease and similar efficiency and also has a very large potential mass range.

In general FAB has superiority in producing non-thermally induced structurally-related fragmentation and a ready access to metastable information.

Advantages of FAB method of ionisation

(i) Ionisation occurs from the solid which may be at room temperature i.e. sample volatilisation, is not necessary and thermal effects are avoided.

(ii) Sample preparation is easy in comparison with derivatisation or field desorption techniques.

(iii) The method works in either polarity and gives good pseudo-molecular ion sensitivity, together with structurally significant fragmentation.

(iv) Mass spectra may be obtained from molecules of relatively high molecular weight e.g. vitamins, peptides antibiotics and Schiff base complexes mass upto 10000 amu can be analysed.

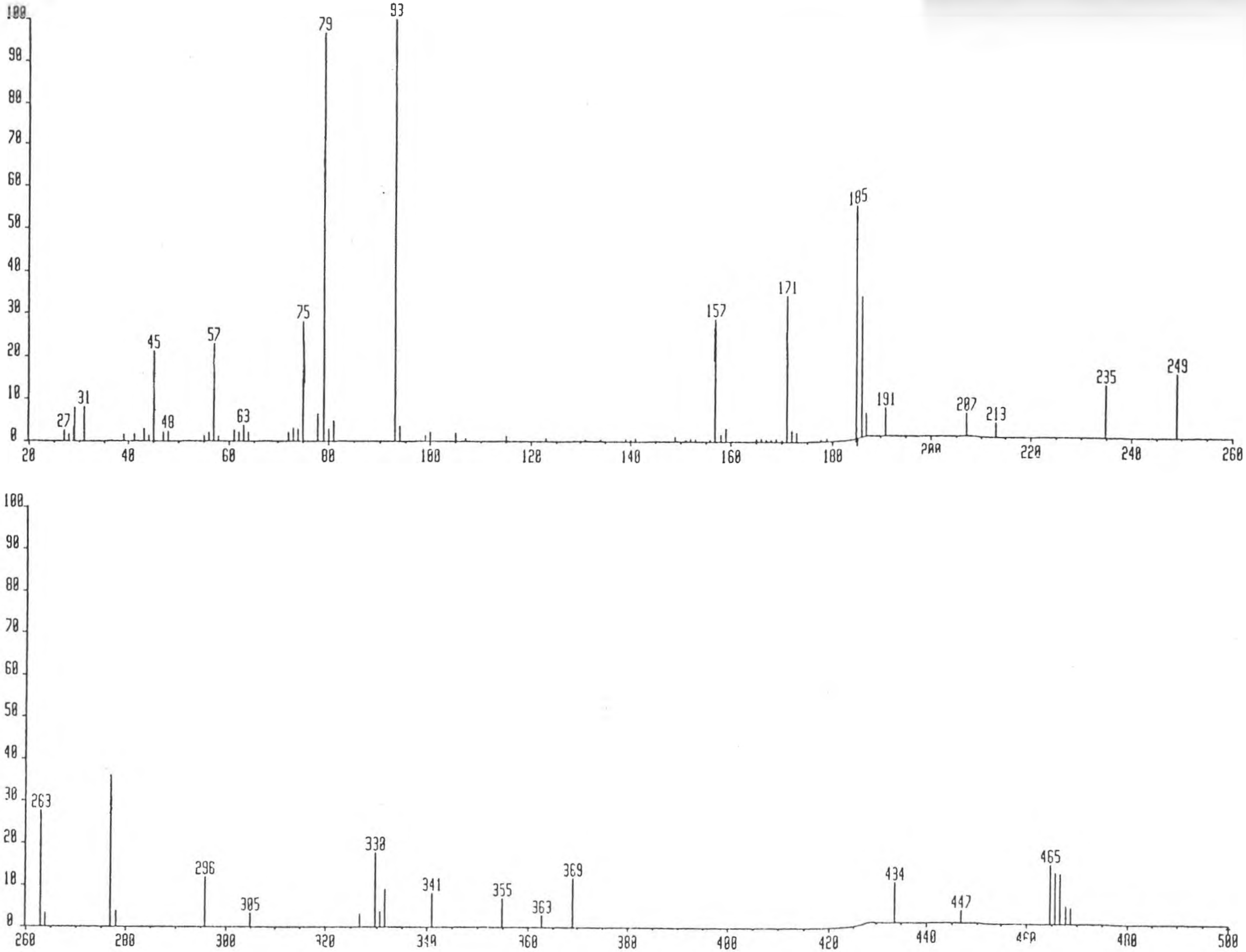


Fig. A.1. Mass spectrum for Ni(ONONO) complex when R = Cl

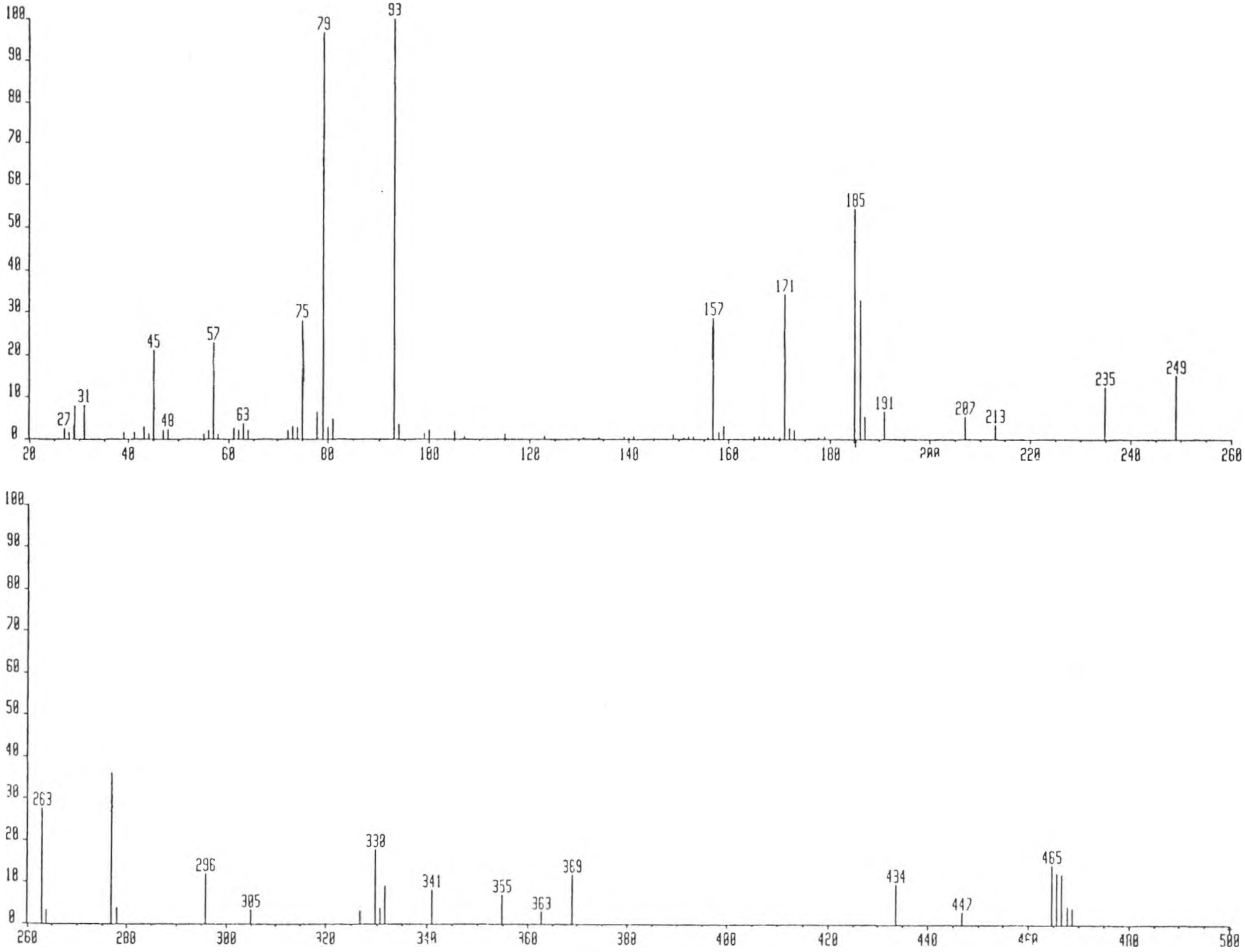


Fig. A.1. Mass spectrum for Ni(ONONO) complex when R = Cl

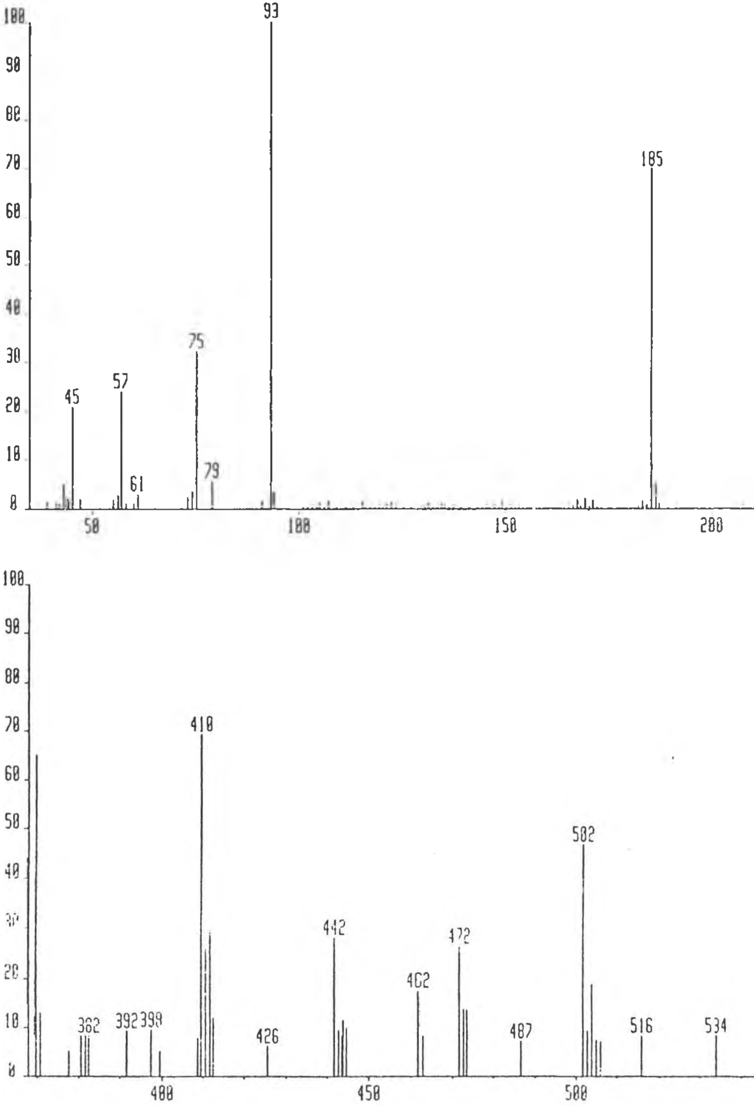
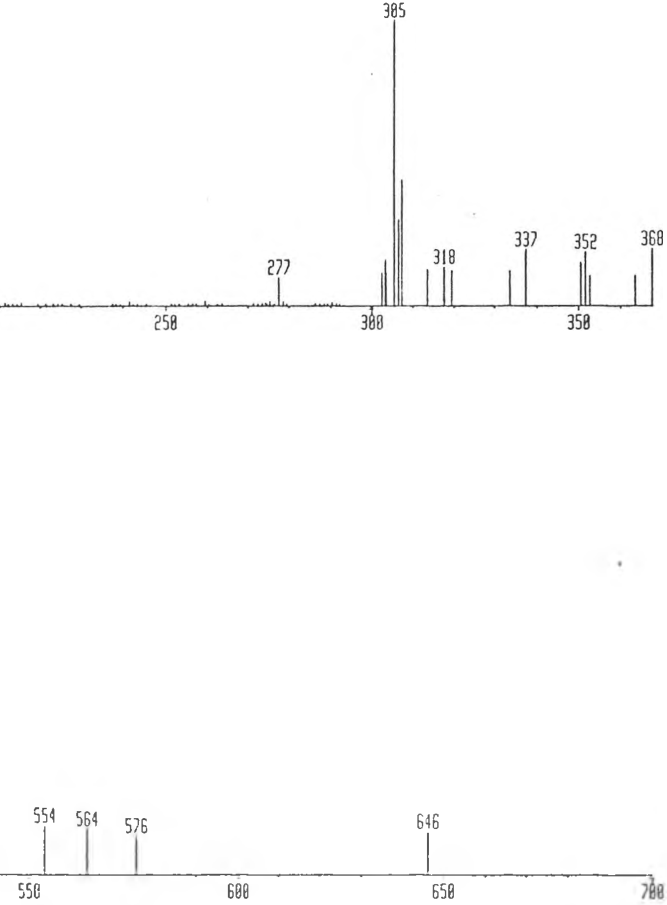


Fig. A.2. Mass spectrum for Cu(ONONO)



complex when R = Cl

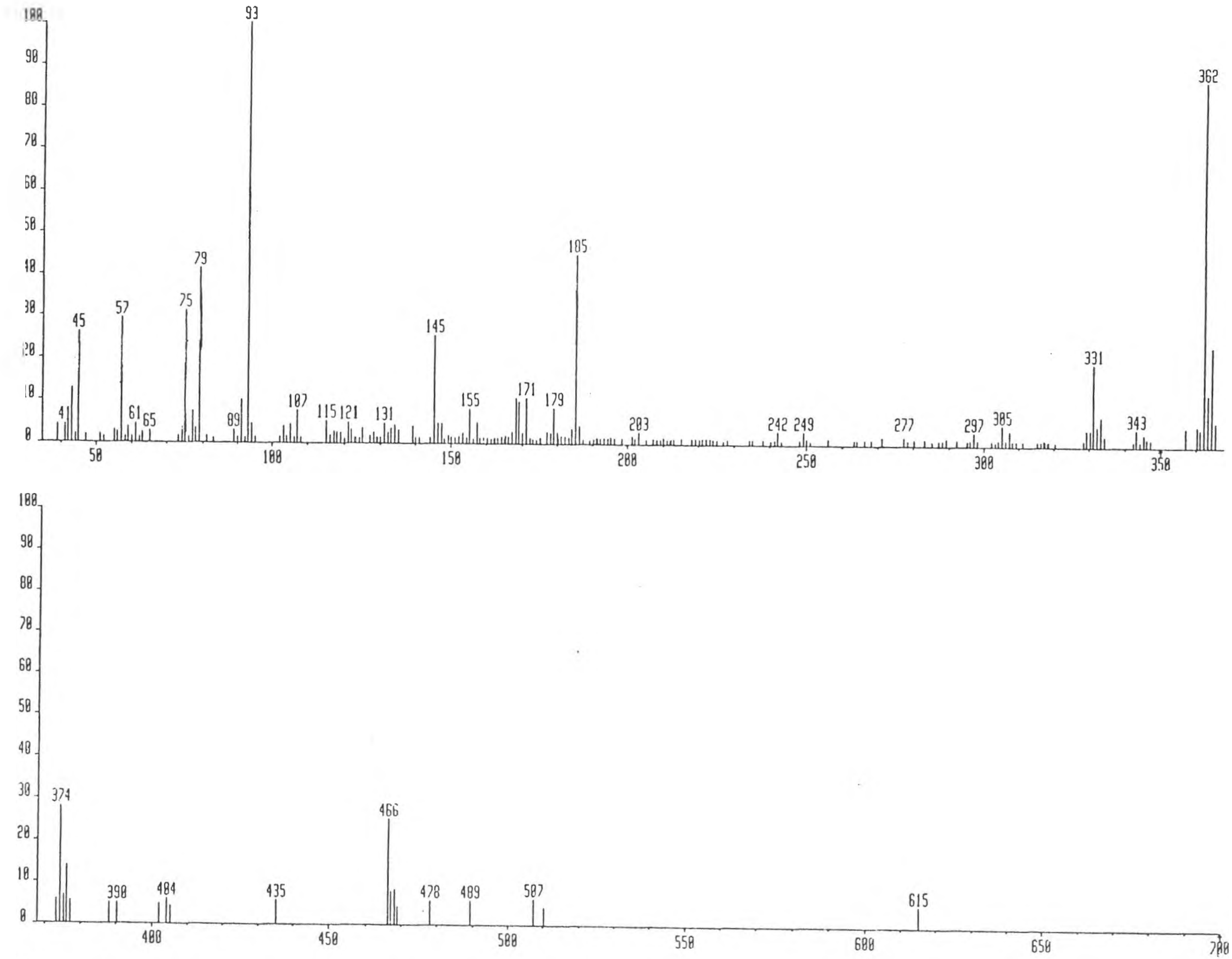


Fig. A.3. Mass spectrum for Co(ONONO) complex when R = Cl.

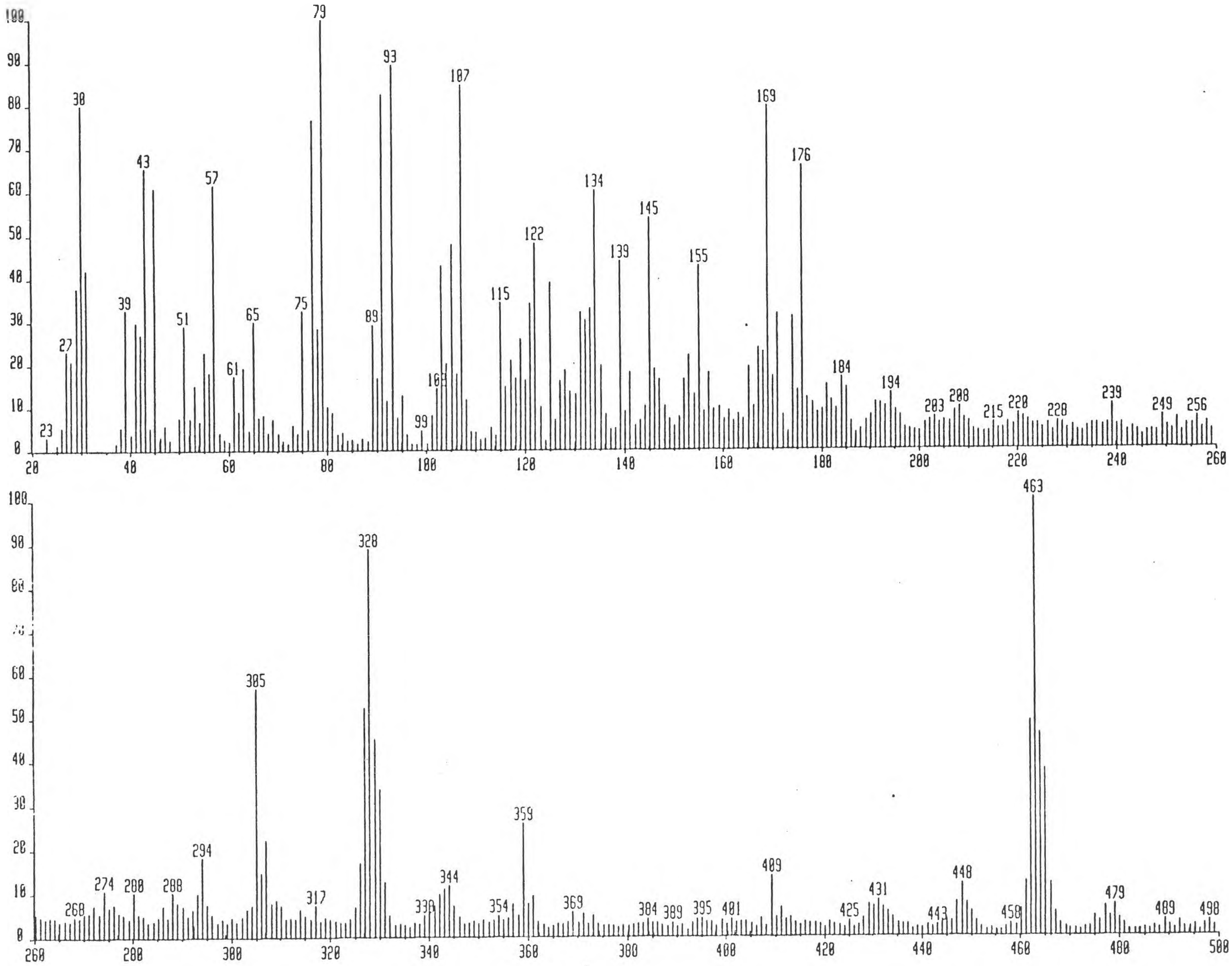


Fig. A.4. Mass spectrum for Fe(ONONO) complex when R = Cl

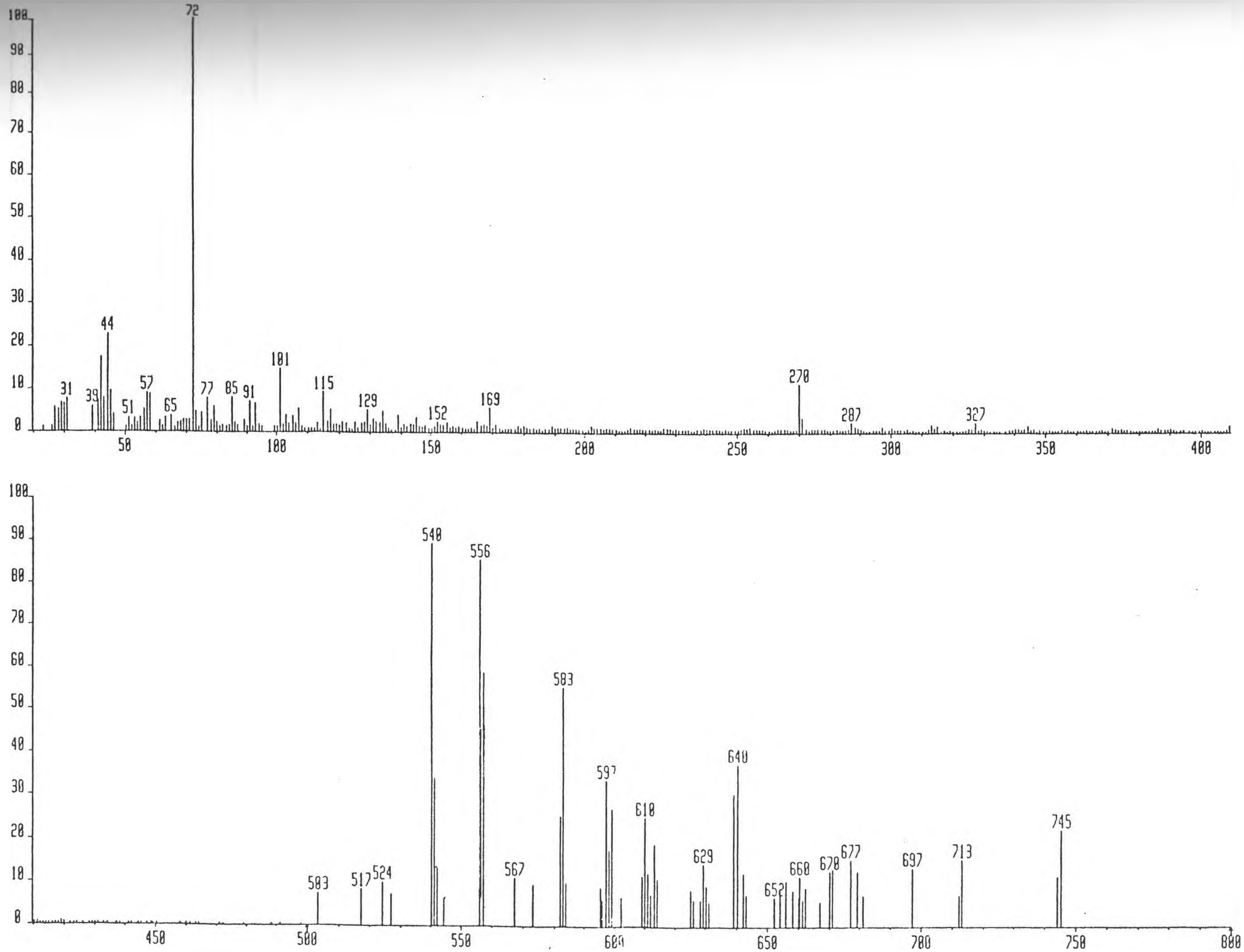


Fig. A.5. Mass spectrum for UO_2(ONONO) complex when R = Cl

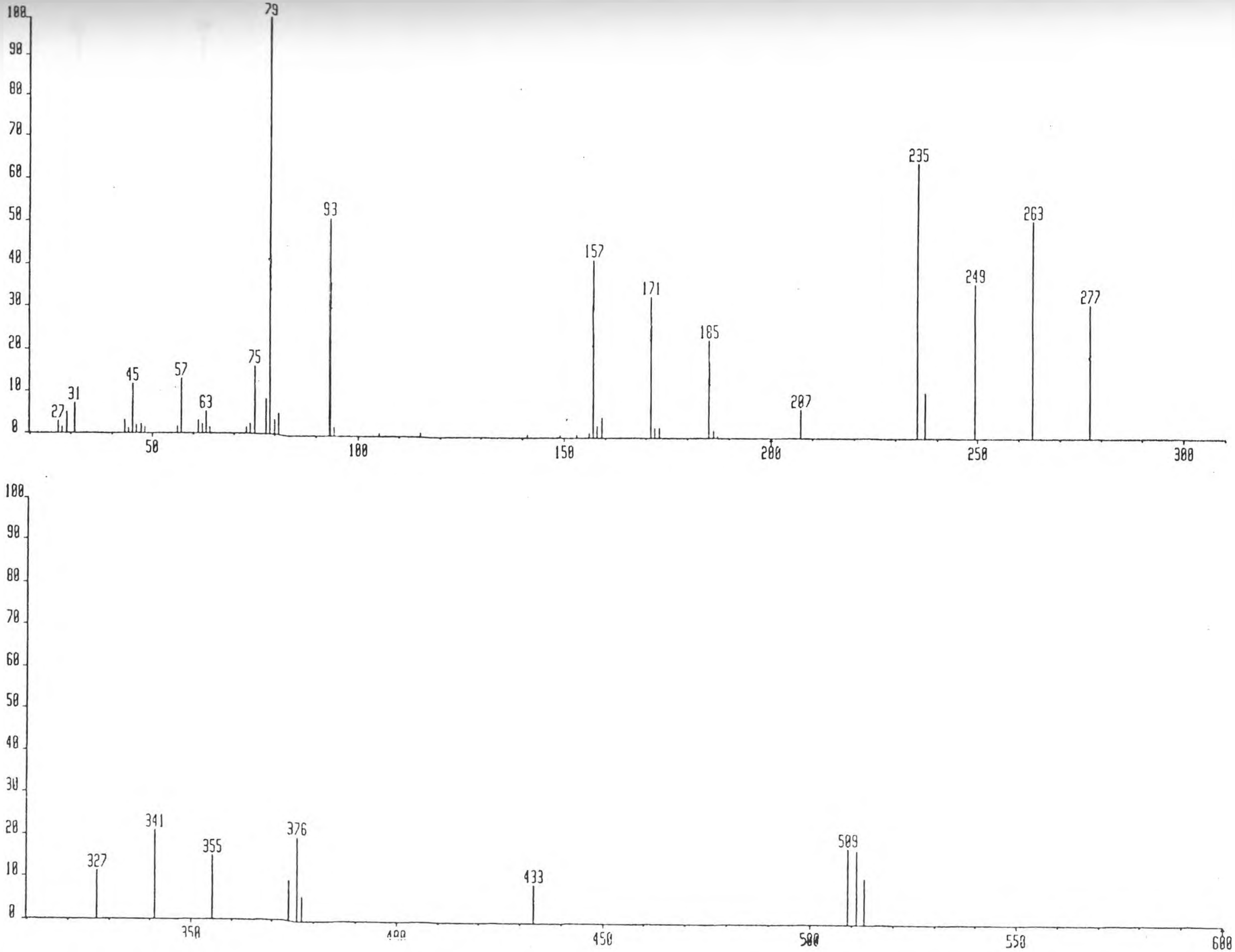


Fig. A.6. Mass spectrum for Ni(ONONO) complex when R = Br

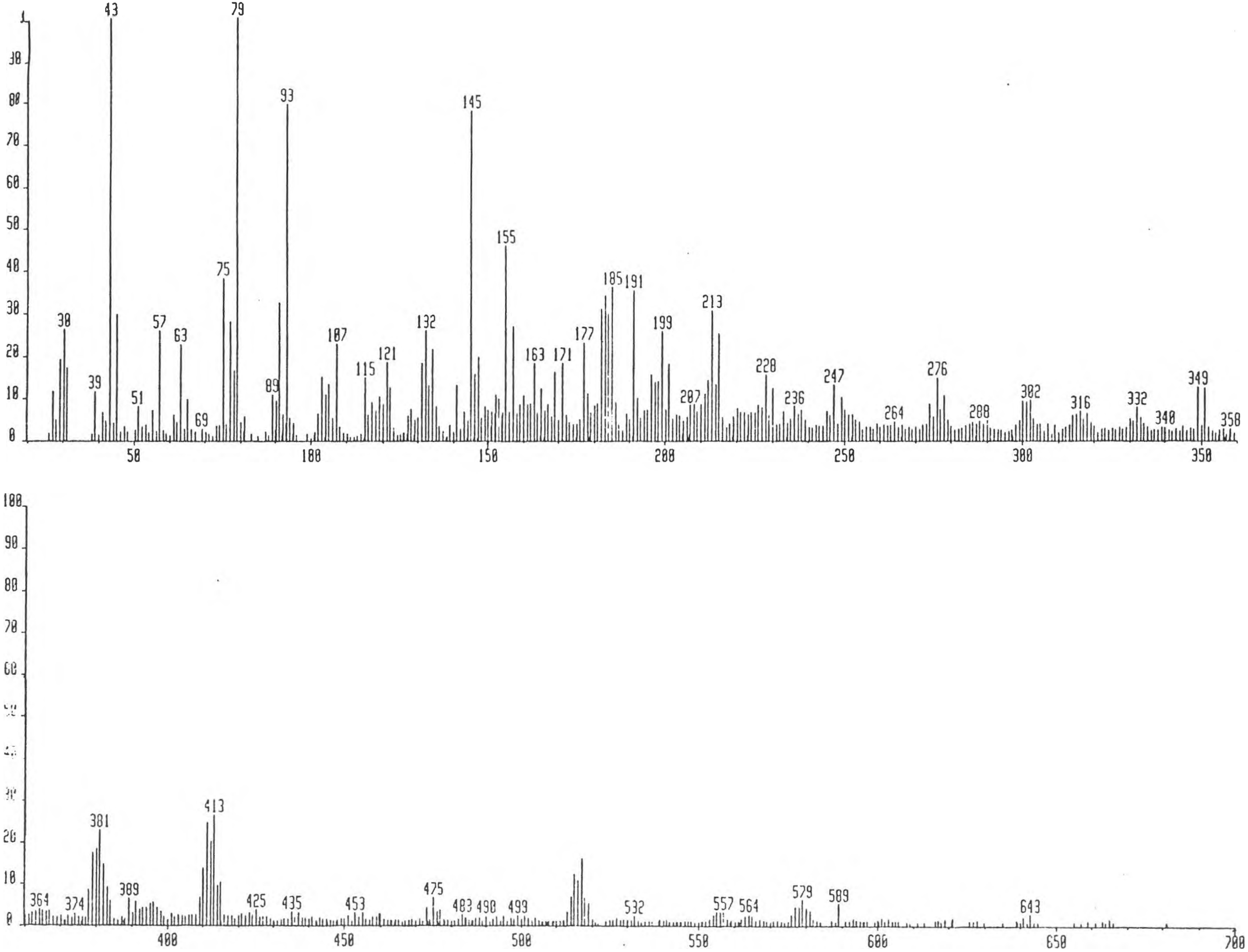


Fig. A.7. Mass spectrum for Cu(ONONO) complex when R = Br

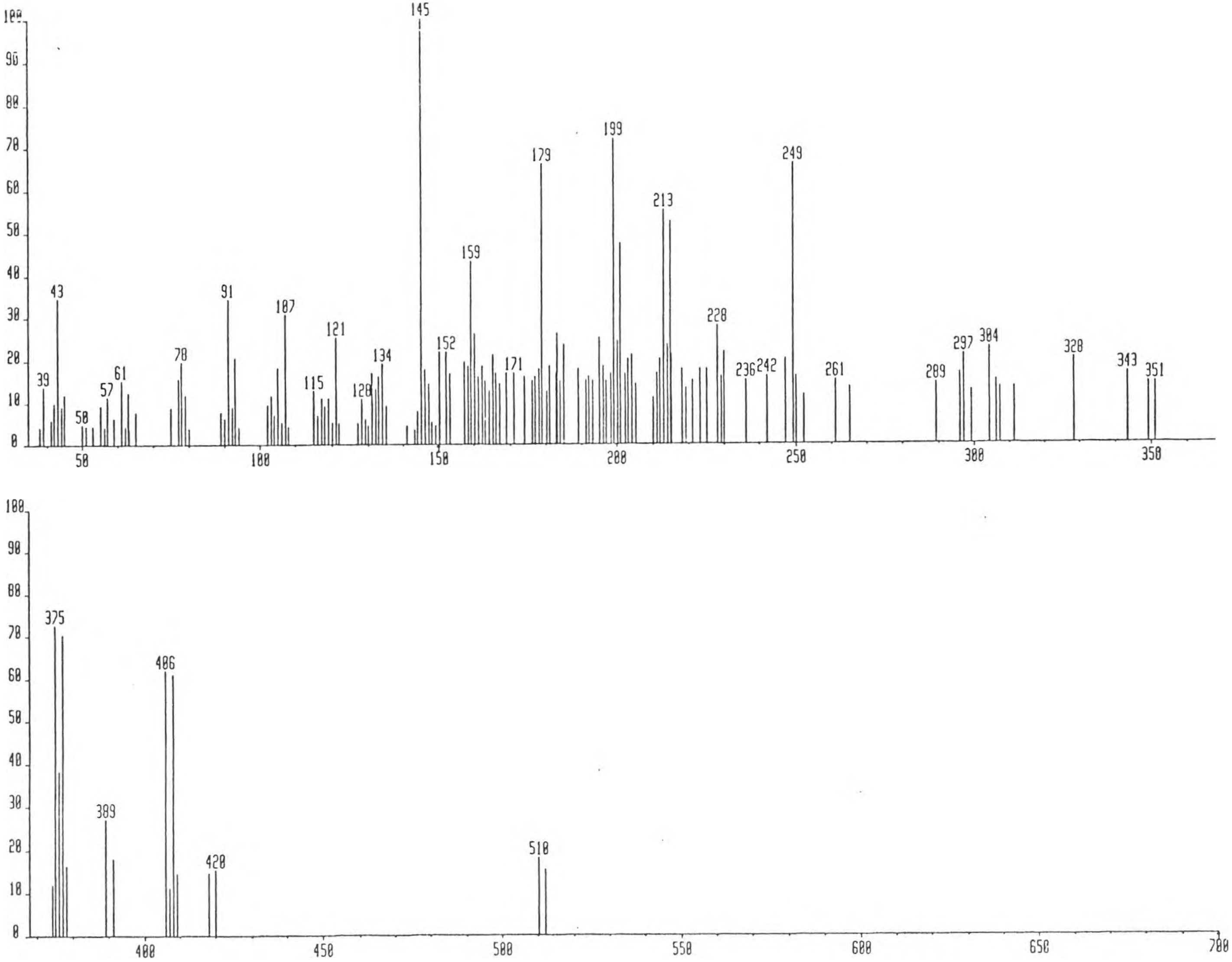


Fig. A.8. Mass spectrum for Co(ONONO) complex when R = Br

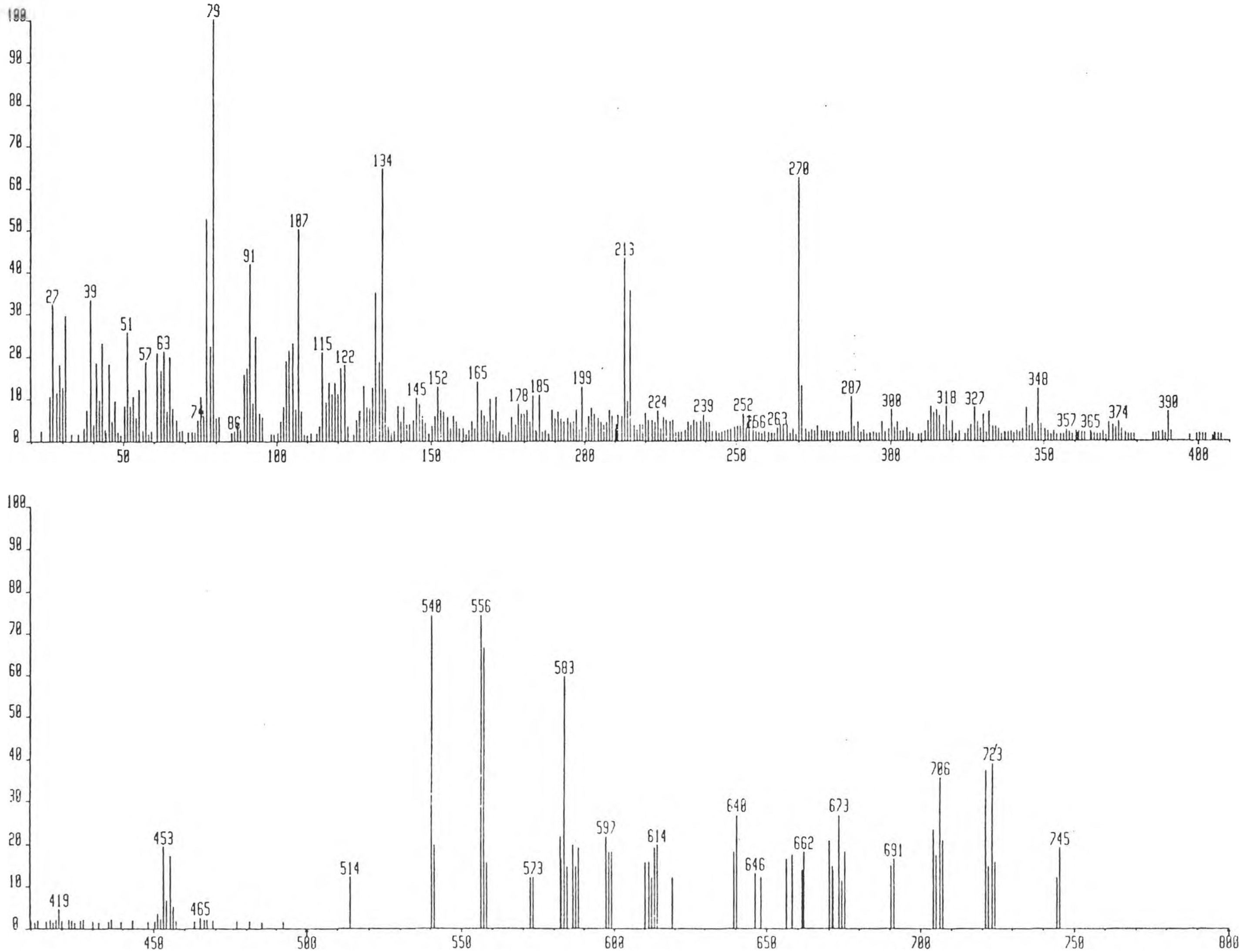


Fig. A.10. Mass spectrum for UO_2 (ONONO) complex when R = Br

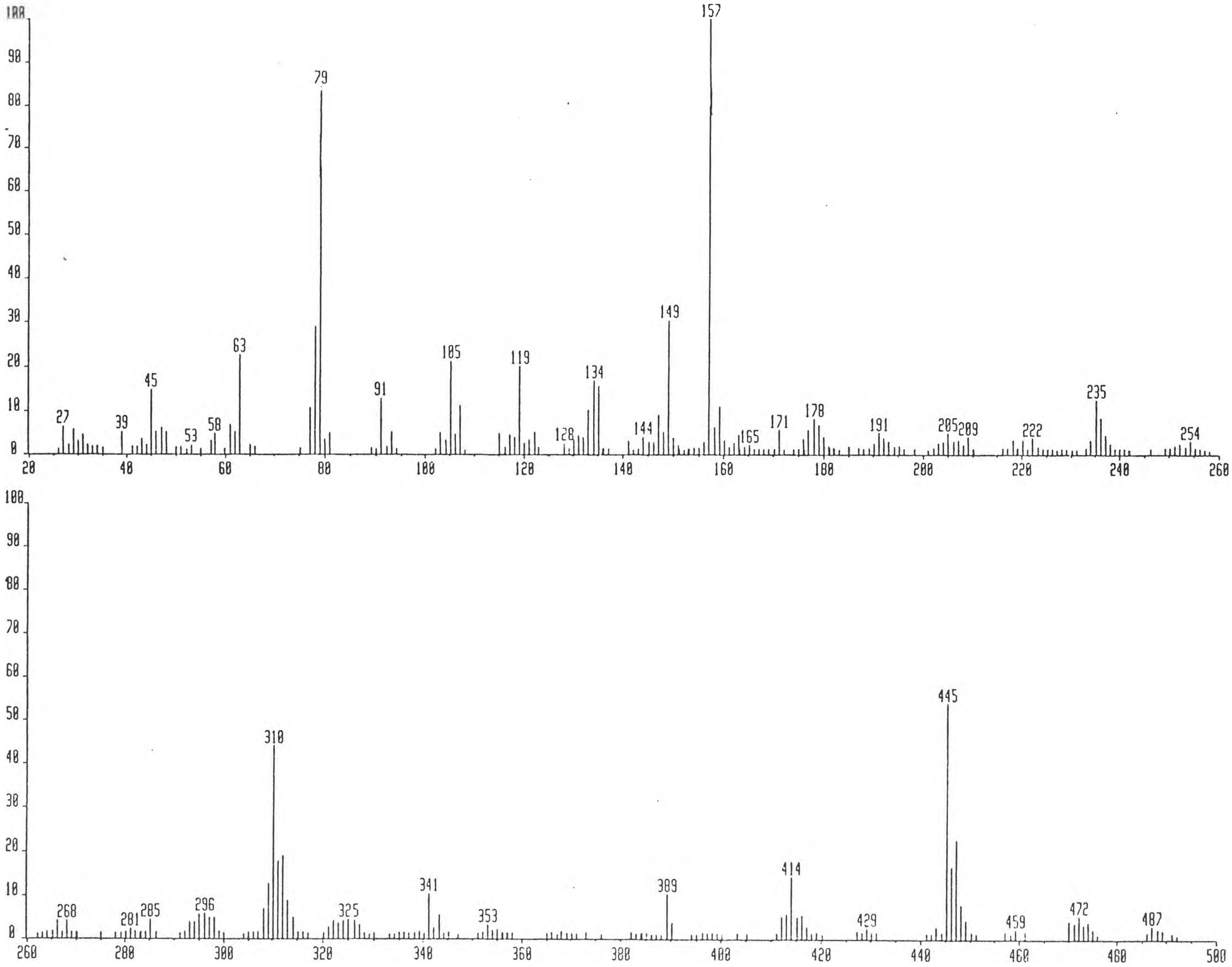


Fig. A.11. Mass spectrum for Ni(ONONO) complex when R = CH_3

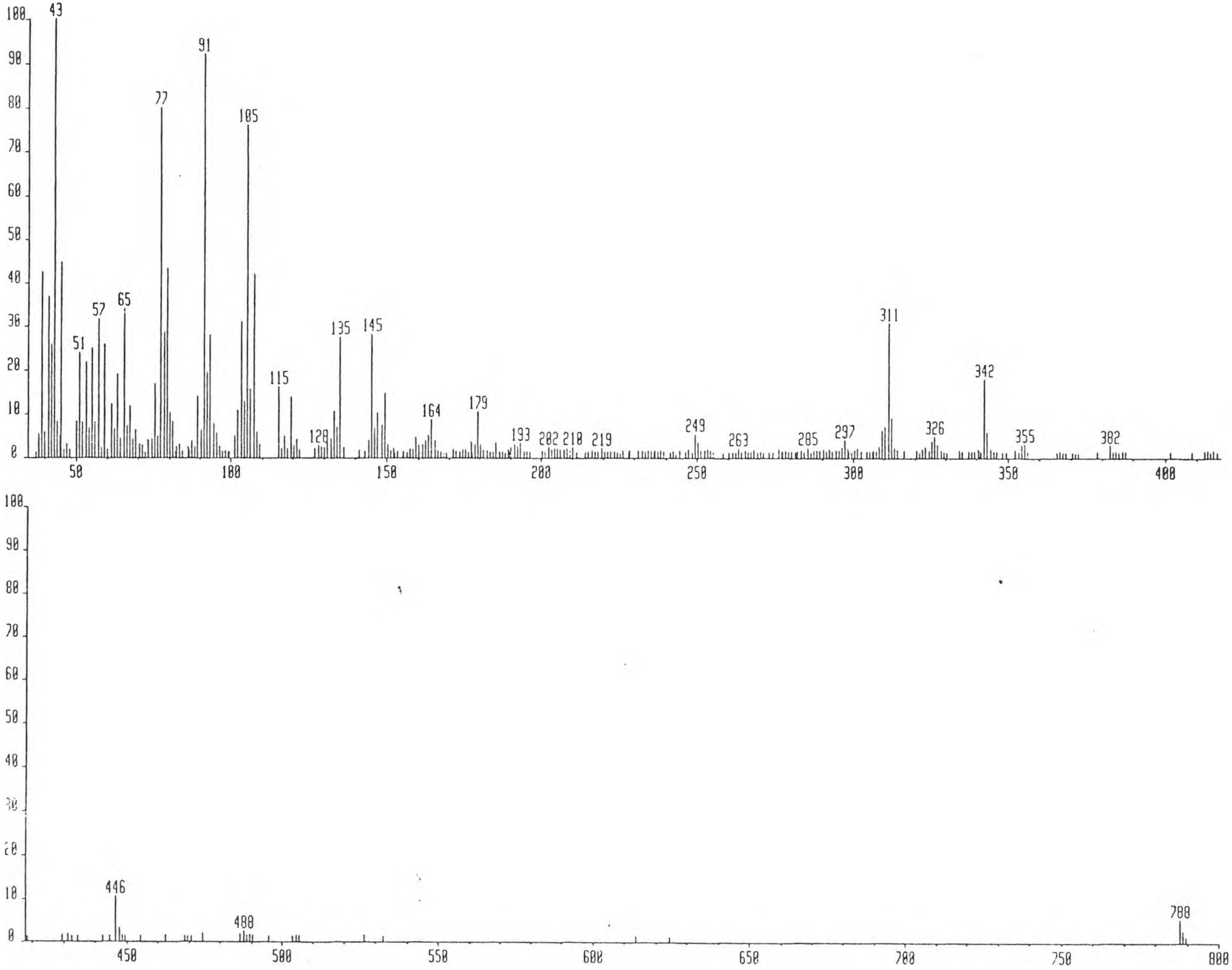


Fig. A.12. Mass spectrum for Co(ONONO) complex when R = CH_3

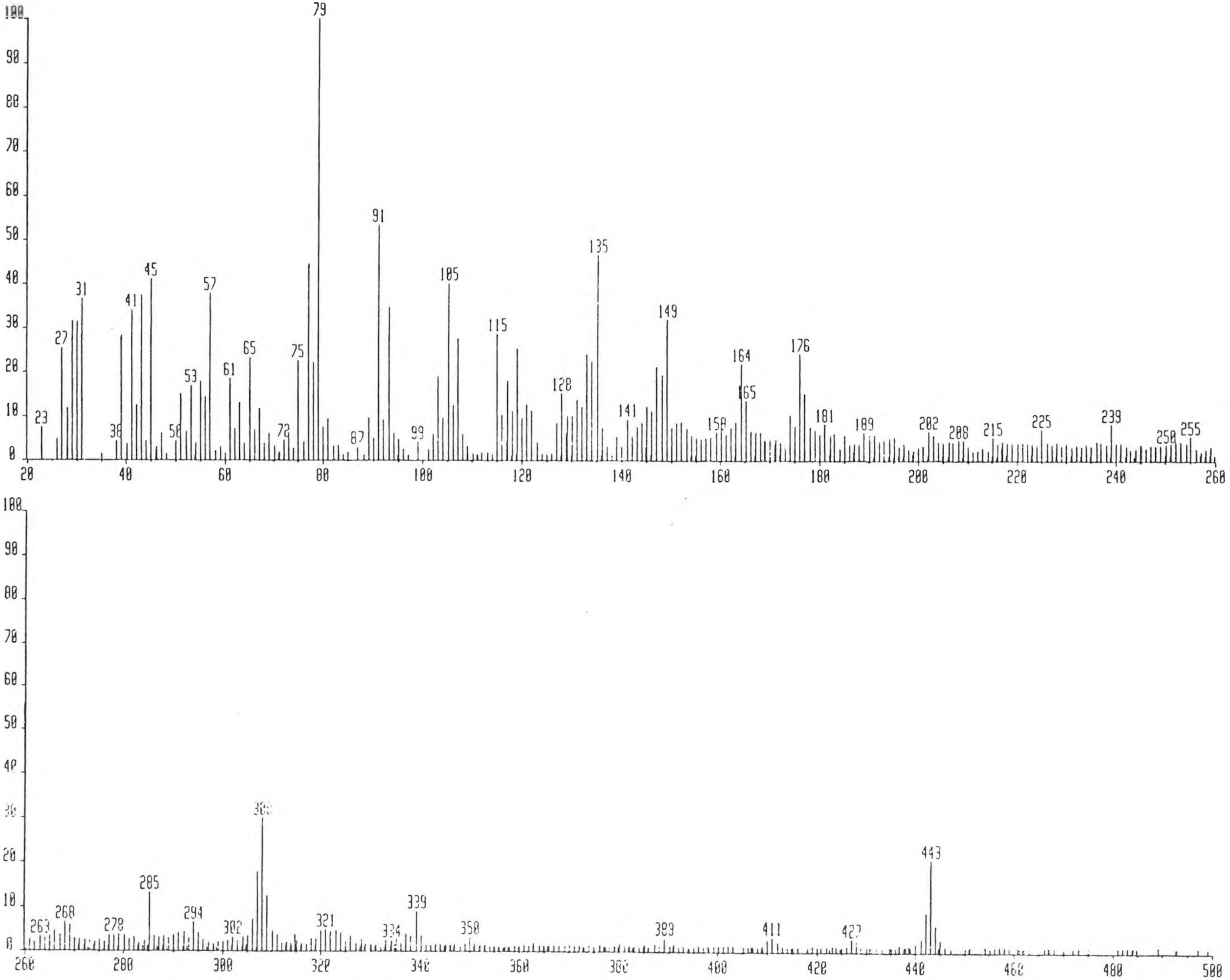


Fig. A.13. Mass spectrum for Fe(ONONO) complex when R = CH_3

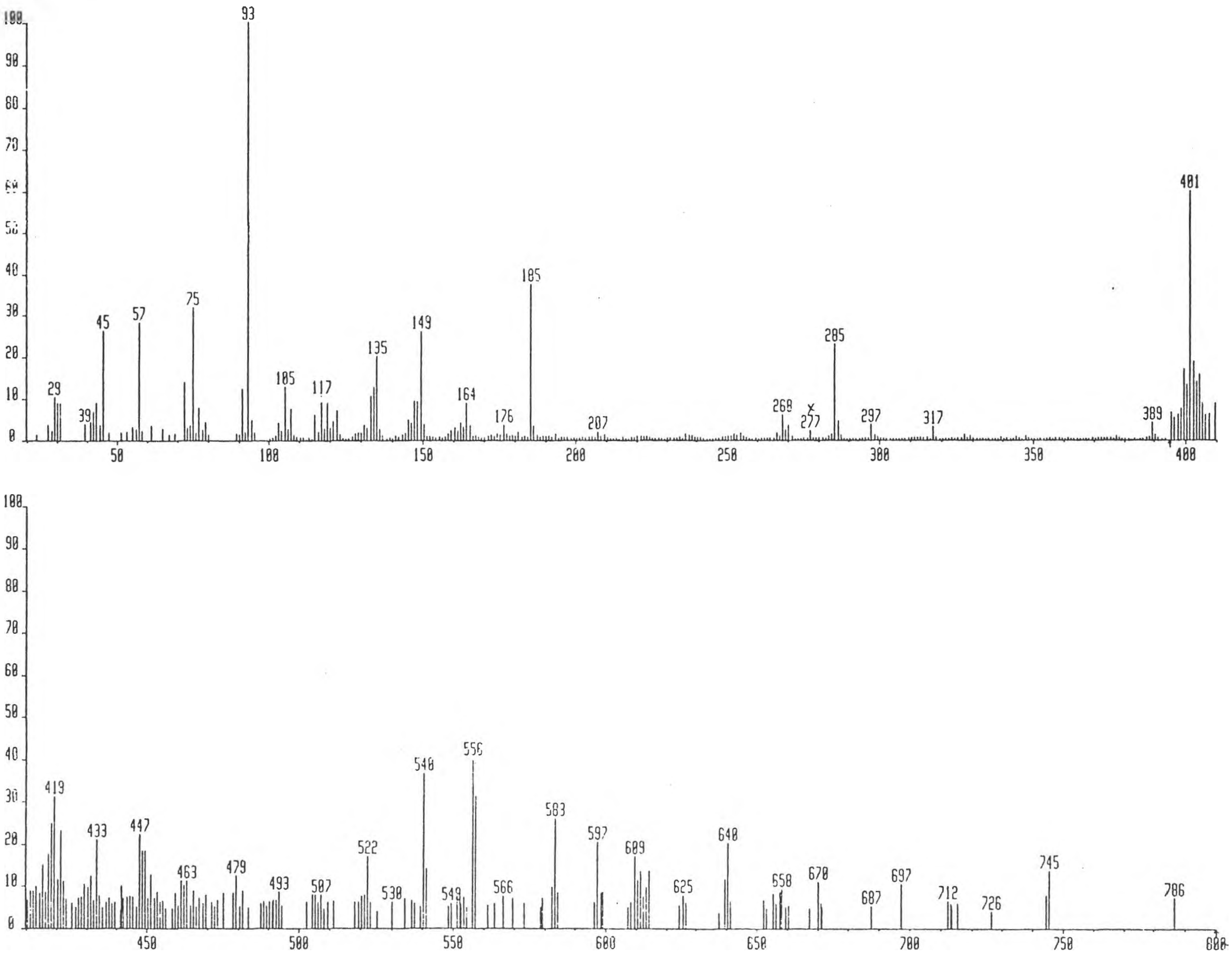


Fig. A. 14. Mass spectrum for UO$_2$(ONONO) complex when R = CH$_3$

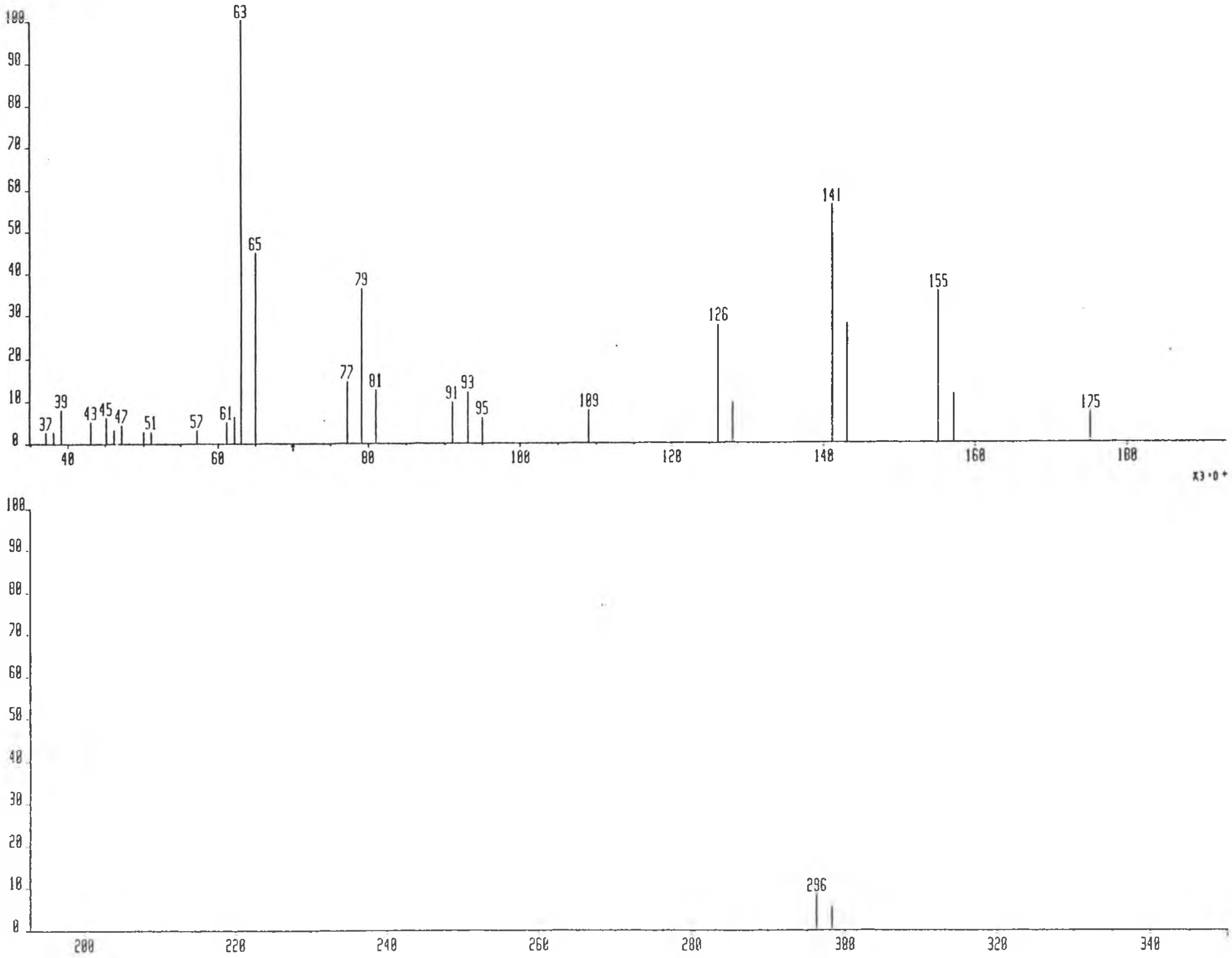


Fig. A.15. Mass spectrum for Cu(ONO) complex.

A3. REFERENCES

1. Curry, J.D., Robinson, M.A. and Busch, D.H., Inorg. Chem., 6, 1570 (1967).

2. Fleischer, E. and Hawkinson, S., J.Amer. Chem. Soc., 89, 720 (1967).

3. Alcock, N.W., Liles, D.C., McPartlin, M. and Tasker; P.A., J.Chem Soc., Chem Commun. 727 (1974).

4. Lindoy, L.F. and Busch, D.H., J.Chem Soc. Chem Commun., 683 (1972).

5. Goedken, V.L. and Christoph, G.G., Inorg. Chem., 12, 2316 (1973).

6. Lindoy, L.F. and Busch, D.H., Inorg. Chem., 13 2494 (1974).

7. Wester, D. and Palenik, G.J., J.Amer. Chem, Soc., 96, 7565 (1974).

8. Wester, D. and Palenik, G.J., J.Amer.Chem.Soc., 95, 6505 (1973).

9. Palenik,G.J. and Wester, D.W., Inorg. Chem., 17, 864 (1978).

10. Gerloch, M., Badarau, I.M. and Audiere, J.P., Inorg. Chem., 18 3220 (1979).

11. Pelizzi, G., Pelizzi, C., Predieri, G. and Resola, S., J.Chem.Soc. Dalton Trans., 1349 (1982).

12. Drew, M.G.B. and Nelson, S.M., Acta Cryst., B. 35, 1594 (1979).

13. Bernal, I., Korp. J.D., Wilson, L.J. and Merrill, C.L., J.Chem.Soc., Daltons., 1951 (1981).

14. Drew, M.G.B., Nelson, S.M., Cairns C., and Nelson. J., J.Chem. Soc., 942 (1981).

15. Robson, R., Aust. J. Chem., 23, 2217 (1970)

16. Robson, R., Inorg. Nucl. Chem., 6, 125 (1970).

17. Hoskins, B.F., Robson, R., Schaap, R., Inorg. Nucl. Chem., 8, 21, (1972).

18. Mc.Fayden, W.D., Robson, R., Schaap, H., Inorg. Chem; 11, 1777 (1972).

19. Dickson, I.E., Robson, R., Ibid., 13, 1301 (1974).

20. Casellato, U., Vigato, P.A., Vidali, M. Coord. Chem. Rev., 23, 31, (1977).

21. Mazurek, W., Berry, K.J., Murray, K.S., Maxwell, J.O., Snaw, M.R. and Wedd, A.G., Inorg. Chem, 21, 3071 (1982).

22. Vince, D.G., Robson, R., Inorg. Chim Acta., 25, 191 (1977).

23. Livingstone, S.E. and Oluka, J.E., Trans. Met. Chem. 5, 77 (1980).

24. Barclay, G.A. and Hoskins, B.F., J.Chem. Soc., 1979 (1965).

25. Kishita, M., Muto, Y and Kubo, M., Aust. J.Chem., 10, 386 (1957).

26. Hatfield, W.E. and Inman, G.W.jr., Inorg. Chem., 8, 1376 (1969).

27. Calvin, M and Barkelew, C.W., J.Amer.Chem.Soc., 68, 2267 (1946).

28. Hatfield, W.E. and Bunger, F.L., Inorg.Chem., 5, 1161 (1966).

29. Ginsberg, A.P., Sherwood, R.C. and Koubek, E., J. Inorg.. Nucl. Chem., 29 353 (1967).

30. Ginsberg, A.P., Koubele, E and Williams, H.J., Inorg.Chem., 5, 1656 (1966).

31. Tokii, T., Muto, Y., Kato, M., Imai, K and Jonassen, H.B., J.Inorg.Nucl.Chem.,34, 3377 (1972).

32. Sinn, E., J.Chem.Soc., Comm., 665 (1975).

33. Bertrand, J.A. and Kelley, J.A., Inorg. Chim. Acta, 4, 203 (1970).

34. Davis, J.A. and Sinn, E., J.Chem.Soc., Daltons, 165 (1976).

35. Bertrand, J.A., Kelley, J.A. and Breece, J.L., Inorg.Chim.Acta., 4, 247 (1970)

36. Ison, K and Kokot, E., Aust. J.Chem. 23, 661 (1970).

37. Theriot, L.J., Carlisle, G.O. and Hu, H.J., J. Inorg. Nucl. Chem 31,2891 (1969).

38. Carlisle, G.O. and Theriot, L.T., J. Inorg.Nucl. Chem. 35, 2093 (1973).

39. Carlisle, G.O., Ganguli, K.K. and Theriot, L.J., J.Inorg.Nucl.Chem.34, 2761 (1972).

40. Dua, S.K., Rastogi, D.K. and Sahni, S.K., J.Inorg. Nucl. Chem., 42, 1711 (1980)

41. Hongwen, H. and Zhuangyu, Z., Chem.J.Chin.Univ., 1, 65 (1984).

42. Openshaw, H.T. and Robinson, R., J.Chem. Soc., 914 (1946).

43. Chiddix, M.E., Hesse, S.H. and Williams, M.R., C.A., 52, 9208C (1958).

44. Koenig, K.E., Helgson, R.C. and Cram, D.J., J.Amer. Chem.Soc., 98, 4020 (1976).

45. Martin, R.W., C.A., 48, 5218g (1954).

46. Parris, C.L., Org. synth., coll Vol. 5, 73 (1973).

47. Parris, C.L. and Christensen, R.M., J.Org.Chem. 25 331 (1960).

48. Sacconi, L. and Bertini, I., Inorg.Chem; 7, 1178 (1968).

49. Sacconi, L. and Speroni, G.P., Inorg.Chem., 7, 295 (1968).

50. Orioli, P.L. and Vaira, M.D., J.Chem.Soc., A, 2078 (1969).

51. Ciampolini, M. and Speroni, G.P., Inorg. Chem., 5, 45 (1966).

52. Ciampolini, M. and Nardi, N., Inorg. Chem., 6, 445 (1967).

53. Don, Z. and Gray, M.B.; J.Am.Chem.Soc., 88 1394 (1966).

54. Lever, A.B.P., "Inorganic electronic spectroscopy, Elsevier, Amsterdam, 1968.

55. Hathaway, B.J. and Tomlinson, A.A.,coord.Chem. Rev., 5 (1970).

56. Hathaway, B.J. and Billing, D.E., coord.Chem.Rev., 5, 143 1970).

57. Sacconi, L., Bertini,I and Morassi, R., Inorg. Chem., 6, 1548 (1968).

58. Tindimubona, A.R., University of Nairobi, Personal Commun.

59. Vidali, M., Vigato, P.A., Casellato, V., Tondello, E. and Traverso, O., J. Inorg.Nucl.Chem., 37, 1715 (1975).

60. Bandoli, G., Clemente, D., Croatto, U., Vidali, M. and Vigato, P.A., Chem.Commun. 1330(1971).

61. Bandoli, G., Clemente, D., Croatto, U., Vidali, M. and Vigato, P.A., J.Chem.Soc., Dalton, 2331 (1973).

62. Bandoli, G., Cattalini, L., Clemente, D.A., Vidali, M. and Vigato, P.A., Chem.Commun., 344 (1972).

63. Halb, D., Rae, A.D. and Waters, T.N., Acta Cryst., 22, 258 (1967).

64. Day, V.W., Marks, T.J. and Wachter, W.A., J.Amer. Chem. Soc., 97 4519 (1975).

65. Graziani, R., Marangoni, G., Paolucci, G. and Forsellini, E., J.Chem.Soc., Dalton, 818 (1978).

66. Alcock, M.W. and Esperas, S., J.Chem.Soc., Dalton, 893 (1977).

67. Akhtar, M.N. and Smith, A.J., Acta Cryst., B29, 275 (1973).

68. Kato, M., Janassen, H.B. and Fanning, J.C., Chem. Rev., 6, 99 (1964).

69. Bertrand, J.A. and Kirkwood, C.E., Inorg.Chim. Acta., 6 248 (1971).

70. Schafer, H.L., Morrow, J.C. and Smith, H.M., J.Chem.Phys., 42, 504 (1965).

71. Sayer, R.S., Williams, R.J. and Watson, W.H., Inorg. Chem., 9, 951 (1967).

72. Bertrand, J.A. and Kelly, J.A., J.Amer.Chem.Soc., 88, 4746 (1966).

73. Kilbourn, B.T. and Dunitz, J.D., Inorg. Chim. Acta., 1, 209 (1967).

74. Bertrand, J.A. and Kelly, J.A., Inorg.Chem., 8, 1982 (1969).

75. Gill, N.S. and Sterns, M., Inorg. Chem., 9 1919 (1970).

76. Bevan, J.A., Graddon, D.P. and McConnell, J.F. Nature, 199, 373 (1963).

77. Casy, A.T., Hoskins, B.F. and Williams, F.D., Chem.Commun., 904 (1976).

78. Bertrand, J.A. and Kelly, J.A., Inorg.Chem. Acta, 4, 526 (1970).

79. Ohta, H., Bull.Chem.Soc.Japan., 33, 202 (1960).

80. Yamada, S., Nakamura, H. and Tsuchida, R., Bull Chem.Soc. Japan., 31, 303 (1958).

81. Kammerer, H. and Lenz, H., Kunststoffe., 51 26 (1961).

82. Rulfs, C.L., De, A.K., Lakritz, J. and Elving, P.J., Anal.Chem., 27, 1802 (1955).

83. Lewis, J. and Wilkins, R.G., "Modern Coordination Chemistry", Interscience., (1960).

84. Foex, G., "Constantes selectionees diamagnetisme et paramagnetisme"., (1957).

85. Beech G., "Fortran IV in Chemistry"., John. Wiley and Sons., 153 (1975).

86. Surman, D.J. and Vickerman, J.C., J.Chem.Soc., Chem. Commun., 324 (1981).

87. Barber, M., Bordoli, R.S., Sedgwick, R.J. and Tyler, A.N., J.Chem.Soc., Chem.Commun., 325 (1981).

88. Fenselau, C., J.Natural Products., 47,Vol:2, 215-225 (1984).