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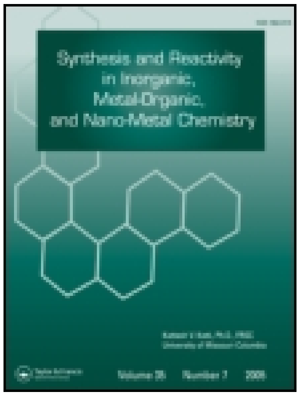

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SCHIFF BASE COMPLEXES DERIVED FROM SALICYLALDEHYDE WITH AMINE, $[Ni(1,2\text{-}pn)_2Cl_2]\cdot 3H_2O$ AND $[Cu(1,2\text{-}pn)_2]SO_4\cdot 2H_2O$, AS COMPLEX LIGANDS

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ABSTRACT

Schiff base complexes known as complex ligands were prepared by the condensation of dichlorobis(1,2-diaminopropane)nickel(II), $[Ni(1,2\text{-}pn)_2Cl_2]\cdot H_2O$, or bis(1,2-diaminopropane)copper(II) sulphate, $[Cu(1,2\text{-}pn)_2]SO_4\cdot H_2O$, with salicylaldehyde producing the Schiff base complex ligands [ML] (M = Ni or Cu). The complex ligands [ML] act as bidentate ligands through the bridged di-μ-phenoxy oxygen atoms. These Schiff base complexes react with transition metal ions yielding homo- and heteronuclear complexes of the types $[MLM'Cl_2]$ or $[(ML)_2M'Cl_2]$, $[(ML)_2M']Cl_2$,

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$[(ML)_2M'](ClO_4)_2$ and $[(ML)_2M'(NO_3)_2](NO_3)_n$, M = Ni or Cu; M′ = Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ce(III) and Th(IV). The complexes were characterized by elemental analyses, thermal analyses, IR, visible and ESR spectra, magnetic susceptibility measurements as well as mass spectra. Magnetic moments were altered by the introduction of additional metal cations besides the one already present in the complex ligands. The M′ cations were linked to the outer phenoxo oxygen atoms in the $[NiL]\cdot\frac{1}{2}H_2O$ and $[CuL]\cdot H_2O$ complex ligands. All homo- and hetero bi- and tri-nuclear complexes show antiferromagnetic interactions which are attributed to inter- or intramolecular interactions of the metal cations. Mass spectra of the complex ligands and selected homo- and hetero bi- and trinuclear complexes support the formula weights of these complexes. Visible and ESR spectra as well as magnetic moments indicated that the parent mononuclear complex ligands [ML] have square-planar geometry. The binuclear and trinuclear complexes have similar or different geometries, octahedral or square-planar. The octahedral configuration is completed by chlorine atoms, nitrate groups and/or solvent molecules.

INTRODUCTION

Multimetallic complexes constitute an important part of modern inorganic chemistry due to the nature of these compounds as active sites in a variety of metalloenzymes[1,2] and play a significant and expanding role in industrial catalysis[3] and materials chemistry[4–7]. The experimental study of multimetallic complexes dates back to 1704 with the discovery of Prussian blue. The synthesis of complexes which contain two or more metal ions each with appropriate complement of external ligands[8] and one or more shared entities are referred to as bridging groups in macrocyclic and macroacyclic[9–12].

One effective method for the synthesis of macrocyclic complexes involves the presence of a metal ion in the cyclization reaction. The metal ion plays an important role in directing the reaction, and this effect has been termed the metal-template effect. This reaction depends on the size of the cation used as a template and the solvent employed in the condensation and its purity[13]. In case of the larger Schiff base macrocycles, transition metal cations are ineffective as templates. Consequently the use of alkaline earth, lanthanides and main group templating agents had enabled the generation of the corresponding transition metal complexes through the transmetallation reaction[14].

In this study, another method is reported for the synthesis of Schiff base complexes from their corresponding amine complexes, known as complex ligands (mononuclear complexes) abbreviated as [ML] where M = Ni(II) or Cu(II), shown in Fig. 1. It was found that the metal ions are bonded to the N_2O_2 sites in the complex ligands. The complex ligands [ML] react with a metal(II) chloride or perchlorate, $M'Cl_2{\cdot}xH_2O$ or $M'(ClO_4)_2{\cdot}6H_2O$, providing various products of homo- and hetero bi- and trinuclear complexes. M′ occupies the O,O sites of the μ-phenoxo oxygen atoms of the ligands and completes the preferred geometry by chloride, nitrate ions and/or solvent molecules.

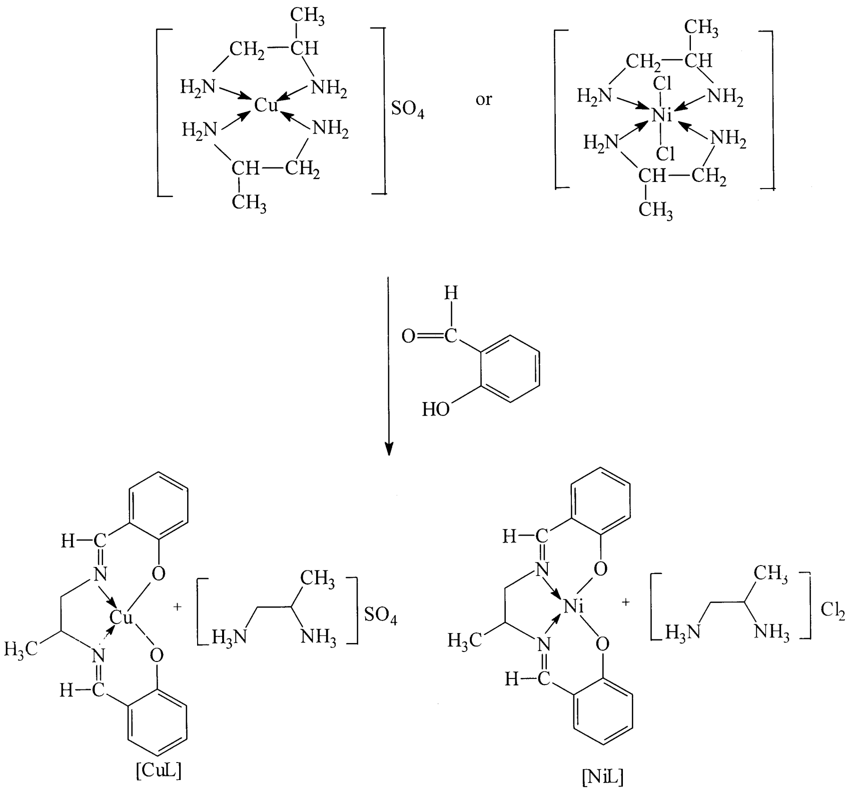


Figure 1. Formation of the complex ligands.

EXPERIMENTAL

Materials

$MnCl_2{\cdot}4H_2O$, $FeCl_3{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$, $CuSO_4{\cdot}5H_2O$, $ZnCl_2$, $Ce(NO_3)_3{\cdot}6H_2O$, $Th(NO_3)_4{\cdot}5H_2O$ and $UO_2(NO_3)_2{\cdot}6H_2O$, 1,2-diaminopropane, salicylaldehyde were BDH, Analar or Merck chemicals. The solvents used were absolute and 95% ethanol, methanol, dimethylformamide (DMF), acetone and diethyl ether. Concentrated hydrochloric and nitric acids were used. These solvents and acids were reagent grade chemicals.

Preparation of the Complex Ligands from Amine Complexes

Complex Ligand $[NiL]{\cdot}\frac{1}{2}H_2O$ (**2**)

A solution of 8.25 g, 67.6 mmol of salicylaldehyde in ethanol was added to 10 g, 33.8 mmol of the blue amine complex, $[Ni(1,2\text{-}pn)_2Cl_2]$ in ethanol[15]. The solution was refluxed for 3 h. The red solid nickel complex was formed. The mixture was allowed to cool slowly to room temperature and collected by filteration, washed with ethanol then ether and finally air-dried. Yield 11.22 g, (95%). The complex is soluble in DMF. The filtrate contained the soluble by-product $(NH_3CH_2\text{-}CH(CH_3)\text{-}NH_3)Cl_2$ as shown in Fig. 1. It was obtained by concentrating the filtrate and filtering the white solid which was then air-dried. Yield 3.1 g, (85.4%).

Complex Ligand $[CuL]{\cdot}H_2O$ (**16**)

A solution of 2.25 g (18.5 mmol) of salicylaldehyde in ethanol was added to 3 g (9.25 mmol) of the blue amine complex, $[Cu(1,2\text{-}pn)_2]SO_4{\cdot}H_2O$, in ethanol[16]. The solution was refluxed for 3 h. The colour of the solution changed from blue to deep violet and a white precipitate appeared. The white precipitate was obtained by filtration and the filterate was evaporated to near dryness then refiltered to obtain the complex ligand, $[CuL]{\cdot}H_2O$, washed with small amounts of ethanol then ether and finally air-dried. The yield was 2.45 g (74%). It was found that the white precipitate is the amine sulphate $(NH_3CH_2\text{-}CH(CH_3)\text{-}NH_3)SO_4$ according to Fig. 1.

Preparation of the Homo- and Heteronuclear Metal Complexes

A solution of the metal chloride, nitrate or perchlorate in ethanol was added to the complex ligand dissolved in ethanol in the molar ratio 1:1. The solutions were refluxed for 2–3 h on a water-bath. The solid metal complexes were precipitated after cooling and collected by filtration, washed with ethanol, then ether and finally air-dried. The products of the reactions using metal perchlorates were washed with water prior to washing with ethanol to insure that the prepared complexes are not contaminated with the starting metal salt.

The following detailed preparation of the complexes are given as examples, the other metal complexes were prepared similarly.

Preparation of $[(NiL)_2Co](ClO_4)_2$ Complex (9)

An ethanolic solution (30 mL) of $Co(ClO_4)_2 \cdot 6H_2O$ (0.54 g, 1.48 mmol) was added to an ethanolic solution (40 mL) of the complex ligand $[NiL] \cdot \frac{1}{2}H_2O$ (1 g, 2.96 mmol). The solution was refluxed for 2 h. On cooling to room temperature, the formed precipitate was filtered, washed several times with water, ethanol then ether and finally air-dried. Yield 1.2 g (87%).

Preparation of $(NiL)_2FeCl_2]Cl \cdot 4H_2O$, Complex (7)

An ethanolic solution (30 mL) of $FeCl_3 \cdot 6H_2O$ (0.399 g, 1.48 mmol) was added to 1.0 g (2.96 mmol) of the complex ligand $[NiL] \cdot \frac{1}{2}H_2O$ dissolved in 40 mL of ethanol. The solution was refluxed for 3 h and a reddish-brown precipitate appeared. The solution was allowed to cool to room temperature. The solid product was obtained by filtration, washed with ethanol then ether and finally air-dried. Yield 0.757 g (56%).

Analyses and Physical Measurements

Electronic spectra of the metal complexes, as DMF solutions, were recorded on a Jasco 550 spectrophotometer. IR spectra of the ligands and their metal complexes, as KBr discs, were recorded on a Perkin-Elmer 598 spectrometer. Polystyrene was used as a calibrant. ESR spectra of the metal complexes were recorded as polycrystalline samples at room temperature on a JEOL microwave unit, JES-FE$_2$XG spectrometer at the Central Laboratories, Tanta University, Tanta, Egypt. The magnetic field was calibrated with a 2,2-diphenyl-1-picrylhydrazyl sample purchased from Aldrich.

Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a model MKI Johnson Matthey, Alfa Products, UK, magnetic susceptibility balance. $Hg[Co(SCN)_4]$ was used as a calibrant. Diamagnetic corrections were calculated from Pascal's constants. Effective magnetic moments were calculated from the expression $\mu_{eff.} = 2.828\ (\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetism of the constituting atoms. Mass spectra of the ligands were recorded on a Hewlett-Packard MS 5988 mass spectrometer at the Microanalytical Center, Cairo University, Giza, Egypt. The fragmentation was carried out at 300 °C and 70 eV. TGA, DTG and DTA measurements were carried out on a Shimadzu-50 thermal analyzer.

Microanalyses of carbon, hydrogen, nitrogen, sulfur and chlorine were carried out at the Microanalytical Center, Cairo University, Giza, Egypt. Analyses of metals were carried out on an Optima 3000 Perkin-Elmer inductivity coupled plasma instrument (ICP).

RESULTS AND DISCUSSION

The complex ligands were synthesized by the condensation of an ethanolic solution of salicylaldehyde with a suspension of the amine complexes, $[Ni(1,2pn)_2Cl_2]\cdot H_2O$ or $[Cu(1,2pn)_2]SO_4\cdot H_2O$, in ethanol.

The reaction of the complex ligands with various metal ions produce a new series of either binuclear complexes such as $[CuLFeCl_3(H_2O)]\cdot 3H_2O$ and $[NiLUO_2(NO_3)]NO_3$ or trinuclear complexes such as, $[(NiL)_2FeCl_2]Cl\cdot 4H_2O$, $[(ML)_2Ce(NO_3)_2]NO_3$, $[MLZn_2Cl_4]\cdot nH_2O$, $[(ML)_2CdCl_2]\cdot nH_2O$, $[(ML)_2Th(NO_3)_2](NO_3)_2\cdot nH_2O$, M = Ni(II) or Cu(II). The elemental analyses correspond to the formulae of the complexes given in Table I. Examples of the reactions of the transition and actinide metal salts with the complex ligands are indicated by the following equations:

$$\begin{aligned}
2[NiL] + MnCl_2\cdot 4H_2O &\rightarrow [(NiL)_2MnCl(H_2O)]Cl\cdot H_2O + 2H_2O\\
2[NiL] + FeCl_3\cdot 6H_2O &\rightarrow [(NiL)_2FeCl_2]Cl\cdot 4H_2O + 2H_2O\\
[CuL] + FeCl_3\cdot 6H_2O &\rightarrow [CuLFeCl_3(H_2O)]\cdot 3H_2O + 2H_2O\\
2[NiL] + 2ZnCl_2 &\rightarrow [NiLZn_2Cl_4]\\
2[NiL] + Ce(NO_3)_3\cdot 6H_2O &\rightarrow [(NiL)_2Ce(NO_3)_2](NO_3) + 6H_2O\\
2[CuL] + CdCl_2\cdot H_2O &\rightarrow [(CuL)_2CdCl_2]\cdot H_2O\\
2[CuL] + Th(NO_3)_4\cdot 5H_2O &\rightarrow [(CuL)_2Th(NO_3)_2](NO_3)_2 + 5H_2O\\
[NiL] + UO_2(NO_3)_2\cdot 6H_2O &\rightarrow [NiLUO_2(NO_3)]NO_3 + 6H_2O
\end{aligned}$$

Table I. Analytical and Physical Data for the Homo- and Heteronuclear Complexes of Complex Ligands $[NiL]\cdot\frac{1}{2}H_2O$ and $[CuL]\cdot H_2O$

						Elemental Analysis, % Found/(Calc.)					
No.	Reactions	Complexes	Yield (%)	Color	M.p. °C	C	H	N	Ni/Cu	M′	Cl
(1)	$NiCl_2\cdot 6H_2O$+1,2-pn 1:2	$[Ni(1,2\text{-}pn)_2Cl_2]\cdot 3H_2O$ $C_6H_{26}N_4OCl_2Ni$, Amine complex	85.0	Blue	80	21.5 (21.6)	7.5 (7.8)	17.2 (16.9)	17.9 (17.8)		21.8 (21.4)
(2)	$[Ni(1,2\text{-}pn)_2Cl_2]\cdot H_2O$+ Salicylaldehyde	$[NiL]\cdot\frac{1}{2}H_2O$ $C_{17}H_{17}N_2O_{21/2}$ Ni, Complex Ligand	95.0	Red	188	58.4 (58.7)	4.8 (4.9)	8.2 (8.1)	16.5 (16.9)		—
(3)	$[NiL]+NiCl_2\cdot 6H_2O$	$[(NiL)_2NiCl_2]\cdot 2H_2O$ $C_{34}H_{36}N_4O_6Ni_3Cl_2$	76.0	Brownish-yellow	276	48.1 (48.4)	4.4 (4.3)	6.5 (6.6)	20.6 (20.9)		8.3 (8.4)
(4)	$[NiL]+Ni(ClO_4)_2\cdot 6H_2O$	$[(NiL)_2Ni](ClO_4)_2$ $C_{34}H_{32}N_4O_{12}Ni_3Cl_2$	73.0	Reddish-brown	—	43.2 (43.6)	3.2 (3.4)	5.8 (6.0)	19.1 (18.8)		7.5 (7.6)
(5)	$[NiL]+CuCl_2\cdot 2H_2O$	$[NiLCuCl_2]\cdot H_2O$ $C_{17}H_{18}N_2O_3NiCuCl_2$	80.0	Reddish-brown	195	41.4 (41.5)	3.6 (3.7)	5.5 (5.7)	11.5 (11.9)	12.7 (12.9)	14.6 (14.4)
(6)	$[NiL]+MnCl_2\cdot 4H_2O$	$[(NiL)_2MnCl_2](H_2O)]2\cdot H_2O$ $C_{34}H_{36}N_4O_6Ni_2MnCl_2$	78.0	Red	> 290	48.6 (48.6)	4.5 (4.3)	6.6 (6.7)	13.7 (14.0)	6.2 (6.5)	8.4 (8.4)
(7)	$[NiL]+FeCl_3\cdot 6H_2O$	$[(NiL)_2FeCl_2]Cl\cdot 4H_2O$ $C_{34}H_{40}N_4O_8Ni_2FeCl_3$	56.0	Reddish-brown	250	44.6 (44.8)	4.3 (4.4)	6.3 (6.1)	13.1 (12.9)	5.9 (6.1)	11.6 (11.7)
(8)	$[NiL]+CoCl_2\cdot 6H_2O$	$[NiLCoCl_2]$ $C_{17}H_{16}N_2O_2$ $NiCoCl_2$	65.0	Reddish-green	> 290	43.8 (43.5)	3.1 (3.4)	5.9 (6.0)	12.6 (12.5)	12.4 (12.6)	15.2 (15.1)
(9)	$[NiL]+Co(ClO_4)_2\cdot 6H_2O$	$[(NiL)_2Co](ClO_4)_2$ $C_{34}H_{32}N_4O_{12}Ni_2CoCl_2$	87.0	Yellowish-green	—	43.2 (43.6)	3.2 (3.4)	6.1 (6.0)	12.4 (12.6)	6.1 (6.3)	7.5 (7.6)
(10)	$[NiL]+Ce(NO_3)_3\cdot 6H_2O$	$[(NiL)_2Ce(NO_3)_2]NO_3$ $C_{34}H_{32}N_7O_{13}Ni_2Ce$	74.0	Yellowish-brown	238	40.9 (40.7)	3.5 (3.2)	9.7 (9.8)	12.1 (11.7)	— (14.0)	—

(*continued*)

Table I. Continued

No.	Reactions	Complexes	Yield (%)	Color	M.p. °C	Elemental Analysis, % Found/(Calc.) C	H	N	Ni/Cu	M′	Cl
(**11**)	$[NiL]+Th(NO_3)_4 \cdot 5H_2O$	$[(NiL)_2Th(NO_3)_2](NO_3)_2 \cdot 4H_2O$ $C_{34}H_{40}N_8O_{20}Ni_2Th$	78.0	Reddish-brown	191	33.2 (33.2)	3.1 (3.2)	9.5 (9.1)	9.2 (9.5)	— (18.9)	—
(**12**)	$[NiL]+ZnCl_2$	$[NiLZn_2Cl_4]$ $C_{17}H_{16}N_2O_2NiZn_2Cl_4$	80.0	Red	> 270	33.6 (33.4)	2.8 (2.6)	4.8 (4.6)	9.5 (9.6)	21.1 (21.4)	23.5 (23.2)
(**13**)	$[NiL]+CdCl_2 \cdot H_2O$	$[(NiL)_2CdCl_2] \cdot 4H_2O$ $C_{34}H_{40}N_4O_8Ni_2CdCl_2$	65.0	Red	> 290	43.9 (43.7)	4.5 (4.3)	6.2 (6.0)	12.4 (12.6)	11.7 (12.0)	7.5 (7.6)
(**14**)	$[NiL]+UO_2(NO_3)_2 \cdot 6H_2O$	$[NiLUO_2(NO_3)]NO_3$ $C_{17}H_{16}N_4O_{10}NiU$	60.0	Yellow	201	28.2 (27.9)	2.4 (2.2)	7.7 (7.6)	8.2 (8.0)	— (32.5)	—
(**15**)	$CuSO_4 \cdot 5H_2O+1,2\text{-pn}$ 1:2	$[Cu(1,2\text{-pn})_2]SO_4 \cdot 2H_2O$ $C_6H_{24}N_4O_6Cu$, Amine complex	90.0	Blue	262	20.6 (20.9)	6.8 (7.0)	16.4 (16.3)	18.2 (18.5)	—	9.7 (9.3)
(**16**)	$[Cu(1,2\text{-pn})_2]SO_4 \cdot H_2O+$ Salicylaldehyde	$[CuL] \cdot H_2O$ $C_{17}H_{18}N_2O_3Cu$, Complex Ligand	74.0	Purple	210	56.5 (56.4)	4.9 (5.0)	8.0 (7.7)	17.5 (17.6)	—	—
(**17**)	$[CuL]+NiCl_2 \cdot 6H_2O$	$[(CuL)_2NiCl_2] \cdot H_2O$ $C_{34}H_{34}N_4O_5Cu_2NiCl_2$	73.0	Gray	185	49.3 (48.9)	4.1 (4.1)	6.7 (6.7)	15.1 (15.2)	6.8 (7.0)	8.3 (8.5)
(**18**)	$[CuL]+Ni(ClO_4)_2 \cdot 6H_2O$	$[(CuL)_2Ni](ClO_4)_2$ $C_{34}H_{32}N_4O_{12}Cu_2NiCl_2$	78.0	Green	—	43.3 (43.2)	3.4 (3.4)	5.8 (5.9)	13.5 (13.4)	6.1 (6.2)	7.4 (7.5)
(**19**)	$[CuL]+CuCl_2 \cdot 2H_2O$	$[(CuL)_2CuCl_2] \cdot 6H_2O$ $C_{34}H_{44}N_4O_{10}Cu_3Cl_2$	60.0	Reddish-brown	200	43.8 (43.9)	4.6 (4.8)	6.1 (6.0)	20.5 (20.5)	—	7.4 (7.6)
(**20**)	$[CuL]+MnCl_2 \cdot 4H_2O$	$[(CuL)_2MnCl_2]$ $C_{34}H_{32}N_4O_4Cu_2MnCl_2$	74.0	Brown	> 270	50.5 (50.2)	4.3 (4.0)	6.8 (6.9)	15.5 (15.6)	6.5 (6.8)	8.9 (8.7)

(**21**)	[CuL]+$FeCl_3 \cdot 6H_2O$	[CuLFe$Cl_3(H_2O)$]$\cdot 3H_2O$	80.0	Black	203	35.6	4.4	4.8	10.8	9.6	18.8
		$C_{17}H_{24}N_2O_6CuFeCl_3$				(35.3)	(4.2)	(4.8)	(11.0)	(9.7)	(18.4)
(**22**)	[CuL]+$CoCl_2 \cdot 6H_2O$	[(CuL)$_2$Co]$Cl_2 \cdot 5H_2O$	86.0	Gray	308	44.8	4.6	6.2	13.9	6.5	7.6
		$C_{34}H_{42}N_4O_9Cu_2CoCl_2$				(44.9)	(4.7)	(6.2)	(14.0)	(6.5)	(7.8)
(**23**)	[CuL]+$Co(ClO_4)_2 \cdot 6H_2O$	[(CuL)$_2$Co]$(ClO_4)_2$	68.0	Reddish-brown	228	43.4	3.3	5.8	13.6	6.1	7.5
		$C_{34}H_{32}N_4O_{12}Cu_2CoCl_2$				(43.2)	(3.4)	(5.9)	(13.4)	(6.2)	(7.5)
(**24**)	[CuL]+$Ce(NO_3)_3 \cdot 6H_2O$	[(CuL)$_2$Ce$(NO_3)_2$]NO_3	83.0	Reddish-brown	225	40.5	3.5	9.4	12.7	—	—
		$C_{34}H_{32}N_7O_{13}Cu_2Ce$				(40.3)	(3.2)	(9.7)	(12.5)	(13.8)	
(**25**)	[CuL]+$Th(NO_3)_4 \cdot 5H_2O$	[(CuL)$_2$Th$(NO_3)_2$]$(NO_3)_2$	76.0	Reddish-brown	>270	35.3	2.8	9.5	11.2	—	—
		$C_{34}H_{32}N_8O_{16}Cu_2Th$				(35.0)	(2.8)	(9.6)	(10.9)	(19.9)	
(**26**)	[CuL]+$2ZnCl_2$	[CuLZn_2Cl_4]$\cdot 3H_2O$	80.0	Reddish-brown	219	30.2	3.6	4.0	9.2	19.4	20.8
		$C_{17}H_{22}N_2O_5CuZn_2Cl_4$				(30.5)	(3.3)	(4.2)	(9.5)	(19.5)	(21.2)
(**27**)	[CuL]+$CdCl_2 \cdot H_2O$	[(CuL)$_2$CdCl_2]$\cdot H_2O$	87	Reddish-brown	>270	45.8	3.6	6.2	14.5	12.3	7.7
		$C_{34}H_{34}N_4O_5Cu_2CdCl_2$				(45.9)	(3.9)	(6.3)	(14.3)	(12.6)	(8.0)

Characterization of the Complex Ligands

Elemental analyses, IR and electronic spectra as well as magnetic moments indicated that the reaction of the amine complexes with salicylaldehyde yielded the complex ligands [ML] (M = Ni(II) or Cu(II)) as shown in Fig. 1.

IR spectra of the amine complexes showed the appearance of the NH_2 stretching vibrations at 3200–3330 cm^{-1} and the NH_2 degenerate deformation (scissor) at 1640–1650 cm^{-1}, these bands disappeared after the condensation with salicylaldehyde and new bands appeared at 1615–1625 cm^{-1} attributed to the stretching vibration of the azomethine group, ν(C=N), in addition to a band at 760–910 cm^{-1} assigned to the α-substituted phenyl ring.

It is worth noting that the reaction of the amine complex $[Cu(1,2pn)_2]SO_4{\cdot}H_2O$ with salicylaldehyde in the molar ratio 1:4 yielded two products, the first is the amine sulphate $(H_3N\text{-}CH_2\text{-}CH(CH_3)\text{-}NH_3)SO_4{\cdot}3H_2O$ which is soluble in cold water. The IR spectrum of this compound shows a broad band at 3400 cm^{-1}, attributed to ν(OH) of water molecules, and another broad band at 1140–1025 cm^{-1} which is assigned to the ionic sulfate group similar to that observed in the starting amine complex, $[Cu(1,2pn)_2]SO_4{\cdot}H_2O$. The second product was the complex ligand $[CuL]{\cdot}H_2O$

The ^{1}HNMR spectrum of the diamagnetic complex ligand $[NiL]{\cdot}\frac{1}{2}H_2O$ did not show a signal due to the phenolic OH group which supports the absence of the ν(OH) frequency in its IR spectrum. These observations support the route of the reaction as shown in Fig. 1 and excluded the condensation of the four amino-groups with salicylaldehyde as previously reported in the case of using 1,3-diaminopropane[17].

Electronic and ESR Spectra and Magnetic Moments of the Complex Ligands

The electronic spectra and the magnetic moments of the parent amine complexes and complex ligands are shown in Table II. The complex ligands showed two bands at 280–415 nm which would be assigned to $\pi \rightarrow \pi^*$ transitions of the aromatic rings overlapping with the absorption due to the azomethine groups.

A square-planar geometry for the Ni(II) and Cu(II) complex ligands, $[NiL]{\cdot}\frac{1}{2}H_2O$ and $[CuL]{\cdot}H_2O$, is suggested. $[NiL]{\cdot}\frac{1}{2}H_2O$ is diamagnetic and showed a band at 542 nm in its visible spectrum similar to that reported for [Ni(acacen)][18] (acacen = N,N′-ethylenebis(acetylacetoneimine). $[CuL]{\cdot}H_2O$ showed a band at 570 nm in its visible spectrum indicative of a square-planar geometry[19] and its magnetic moment is 1.81 B.M. which supports

Table II. UV-Visible Spectra, Magnetic Moments, and Molar Conductivity Data of Homo- and Heteronuclear Metal Complexes

No.	Complexes	UV/Visible (nm)^a, ε ($M^{-1}\,cm^{-1}$)	Magnetic Moments B.M. $\mu_{eff.}$	$\mu_{compl.}$^{c}	Conductance (Ohm^{-1} $cm^2\,mol^{-1}$)
(**1**)	[$Ni(1,2\text{-}pn)_2Cl_2$]·H_2O Amine complex	580	2.61	—	263.0
(**2**)	Complex Ligand [NiL]·$\frac{1}{2}H_2O$	542 (228) 415 (12000) 339 (20000) 281 (25000)	Diamag.		10.0
(**3**)	[$(NiL)_2NiCl_2$]·$2H_2O$	533 (30), 761^b 408 (1370), 424^b 325 (1860)		2.60 (3.2)	10.0
(**4**)	[$(NiL)_2Ni$]$(ClO_4)_2$	533 (374)		2.0	68.0
(**5**)	[$NiLCuCl_2$]·H_2O	567 (235), 848^b,585^b		1.84 (1.90)	54.0
(**6**)	[$(NiL)_2MnCl_2$]·$2H_2O$	534 (340) 435 sh (24000) 406 (35000) 326 (45000)		5.9 (5.9)	40.0
(**7**)	[$(NiL)_2FeCl_2$]Cl·$4H_2O$	500 (2000)		6.1 (5.9)	62.0
(**8**)	[$(NiL)Co$]Cl_2	674 (728), 528 (444)		4.6 (4.8)	56.0
(**9**)	[$(NiL)_2Co$]$(ClO_4)_2$	677 (540), 532 (320)		3.83 (4.8)	100.0
(**10**)	[$(NiL)_2Ce(NO_3)_2$]NO_3	533 (263)		2.14 (2.54)	100.0
(**11**)	[$(NiL)_2Th(NO_3)_2$]$(NO_3)_2$·$4H_2O$	523 (174)		2.68	201.0
(**12**)	[$NiLZn_2Cl_4$]	523 (135)		Diamag.	37.0
(**13**)	[$(NiL)_2CdCl_2$]·$4H_2O$	525 (274)		Diamag.	18.0
(**14**)	[$NiLUO_2(NO_3)$]NO_3	525 (126)		1.34	50.0

(*continued*)

Table II. Continued

No.	Complexes	UV/Visible (nm)[a], ε ($M^{-1} cm^{-1}$)	Magnetic Moments B.M.		Conductance ($Ohm^{-1} cm^2 mol^{-1}$)
			$\mu_{eff.}$	$\mu_{compl.}$[c]	
(**15**)	$[Cu(1,2\text{-}pn)_2]SO_4 \cdot H_2O$ amine complex	546	1.91	—	267.0
(**16**)	$[CuL] \cdot H_2O$	572 (659)	1.81		6.0
(**17**)	$[(CuL)_2NiCl_2] \cdot H_2O$	570 (522)		2.89 (4.2)	21.0
(**18**)	$[(CuL)_2Ni](ClO_4)_2$	570 (800)		3.40 (4.2)	38.5
(**19**)	$[(CuL)_2CuCl_2] \cdot 6H_2O$	570 (550)	1.62	2.81 (3.3)	12.0
(**20**)	$[(CuL)_2MnCl_2]$	570 (411)		7.86 (6.5)	25.0
(**21**)	$[CuLFeCl_3(H_2O)] \cdot 3H_2O$	525 (306), 475 (365)		5.6 (6.2)	11.0
(**22**)	$[(CuL)_2Co]Cl_2 \cdot 5H_2O$	648 (250), 572 (386)		4.94 (6.5)	106.0
(**23**)	$[(CuL)_2Co](ClO_4)_2$	650 (290), 572 (322)		4.1 (6.5)	84.0
(**24**)	$[(CuL)_2Ce(NO_3)_2]NO_3$	572 (409)		2.99 (3.7)	62.0
(**25**)	$[(CuL)_2Th(NO_3)_2](NO_3)_2$	582 (565)		2.51 (2.92)	200.0
(**26**)	$[CuLZn_2Cl_4] \cdot 3H_2O$	568 (252)		1.35 (1.90)	32.0
(**27**)	$[(CuL)_2CdCl_2] \cdot H_2O$	568 (643)		2.86 (2.92)	10.0

[a] In DMF(10^{-3} M).

[b] Reflectance spectrum.

[c] Found (Expected): expected values were calculated on the basis of adding the commonly expected magnetic susceptibilities of the component metal cations.

this geometry and the visible spectral data are similar to that reported for [Cu(acacen)][20]. TGA of the complex ligands, $[NiL]\cdot\frac{1}{2}H_2O$ and $[CuL]\cdot H_2O$, showed that they contain water molecules which were lost at 100–110 °C.

The ESR spectrum of the cystalline copper complex ligand, $[CuL]\cdot H_2O$, (Fig. 5), in the powder form has been recorded at room temperature and exhibits a signal at $g = 1.81$ and a shoulder at 1.84 which indicates that the geometry around the Cu(II) ion is square-planar[21].

Mass Spectra of the Complex Ligands

The mass spectra of the complex ligands showed that the parent peaks compare well with their formula weights. The mass spectrum of the complex ligand $[CuL]\cdot H_2O$ (F.W. = 361.9) is presented in Fig. 2. The parent peak at $m/e = 343$ compares well with the calculated formula weight of the anhydrous complex ligand [CuL] (F.W. = 343.9).

Conductance of the Starting Amine Complexes and Their Complex Ligands

The parent amine complexes showed high values of electrical conductance (Table II). This agrees with the ionic nature of these compounds. The magnetic moment of the parent amine complex, $[Cu(1,2pn)_2]SO_4\cdot H_2O$, is 1.91 B.M. and its visible spectral band at 546 nm agrees with a square-planar geometry of the $[Cu(1,2\text{-}pn)_2]^{2+}$ cation. However, the Ni(II) complex is expected to be octahedral with the two chloride ions coordinated to the metal cation as indicated from the value of the magnetic moment (2.61 B.M.) and its visible spectral band at 580 nm is due to an $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ electronic transition. Its conductance would thus be due to the replacement of the chloride ions by DMF solvent molecules in the complex. The complex ligands, [ML], are non-conducting which agrees with their proposed molecular structures in Fig. 1.

Homo- and Heteronuclear Metal Complexes

The complex ligands $[NiL]\cdot\frac{1}{2}H_2O$ and $[CuL]\cdot H_2O$ have di-μ-phenoxy oxygen bridges which act as O,O coordinating sites. These complex ligands can thus be used as chelating agents toward metal cations such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ce(III), Th(IV) and UO_2(VI). A variety of bi- and trinuclear complexes were prepared.

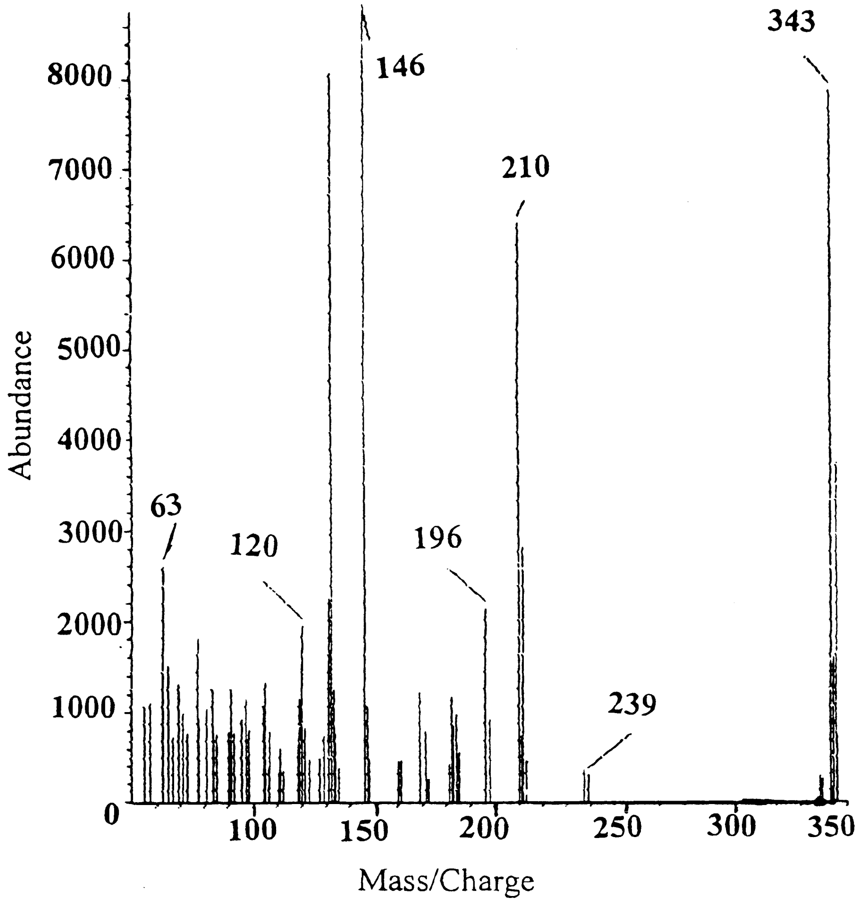
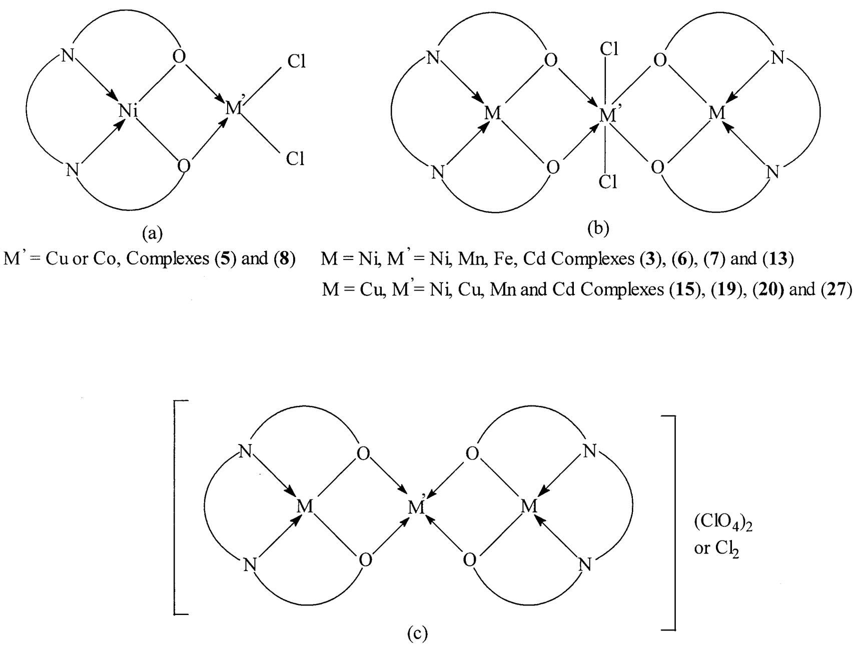


Figure 2. The mass spectrum of the complex ligand [CuL].

The elemental analyses of the metal complexes in Table I are consistent with the proposed structures in Figs. 3, 4 and 5. It was found that the molecular formulas of the products are $[MLM'Cl_2]$, $[(ML)_2M'Cl_2]$, $[(ML)_2M'(NO_3)_2]$ and $[(ML)_2M'](ClO_4)_2$.

IR Spectra

The IR spectra of the homo- and heteronuclear metal complexes showed a shift of the phenolic ν(C-O) to lower frequencies, $\sim 30\,cm^{-1}$, as



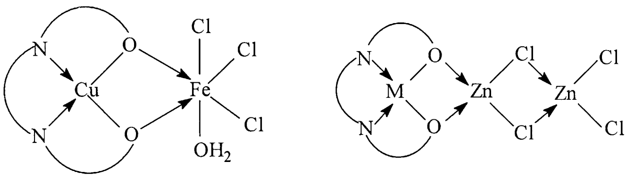
(a)
M' = Cu or Co, Complexes (**5**) and (**8**)

(b)
M = Ni, M' = Ni, Mn, Fe, Cd Complexes (**3**), (**6**), (**7**) and (**13**)
M = Cu, M' = Ni, Cu, Mn and Cd Complexes (**15**), (**19**), (**20**) and (**27**)

(c)

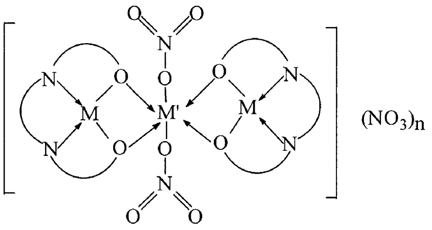
M = Ni, M' = Ni, Co, Complexes (**4**), (**8**) and (**9**)
M = Cu, M' = Ni, Co, Complexes (**18**), (**22**) and (**23**)

Figure 3. The proposed structures of homo- and heteronuclear metal complexes of the complex ligands [ML].



M = Ni or Cu

Figure 4. The proposed structures of the binuclear complex (**21**) and trinuclear complex (**26**).



M = Ni(II) or Cu(II); M' = Ce(III), n = 1 or Th(IV), n = 2

Figure 5. The proposed structures of the heterotrinuclear metal complexes (**10**), (**11**), (**24**) and (**25**).

compared to its location in the parent complex ligands. Such a shift is expected in the case of complexes where μ-phenoxy oxygen atoms bridge other metal cations (M′).

The IR spectra of the complexes (**9**), (**18**) and (**23**) show the characterestic strong and broad absorption band at $1060\,cm^{-1}$ which is attributed to the non-coordinated ClO_4^- ion[22]. The appearance of new bands around $1380–1435\,cm^{-1}$ in the IR spectra of the nitrato complexes confirmed the monodentate nature of this group[22].

The IR spectra of the UO_2(VI) complex (**14**) shows a strong absorption band at $930\,cm^{-1}$ which is assigned to the antisymmetric $\nu_3(O{=}U{=}O)$ vibration.

The IR spectra of the complexes showed broad bands at $3320–3460\,cm^{-1}$ which could be assigned to $\nu(OH)$ of water molecules associated with the complex formation. Also, the existence of new bands at $840–870\,cm^{-1}$ and $630–660\,cm^{-1}$ is attributed to $\delta(H_2O)$ and $\rho(H_2O)$, respectively[22], suggesting the presence of coordinated water molecules to the metal ions.

Electronic and ESR Spectra and Magnetic Moments of the Homo- and Heteronuclear Metal Complexes

Electronic spectra of the homo- and heteronuclear complexes were measured in DMF and are given in Table II. The reflectance spectrum of the homotrinuclear complex $[(NiL)_2NiCl_2]\cdot 2H_2O$ (**3**), shows two bands at 761 and 424 nm. The band at 761 nm is due to the characteristic $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ electronic transition in octahedral geometry for the middle Ni(II) ion (O_2O_2

sites). The magnetic moment of the trinuclear complexes (**3**) at room temperature is 2.6 B.M. supports this geometry and thus lower value may be due to intermolecular interactions. The band at 424 nm assigned to d–d transitions in square-planar geometry for the inner Ni(II) ions (N_2O_2 sites). The magnetic moment of the trinuclear complex (**4**) at room temperature is 2.0 B.M. which is consistent with the value for a combination of low-spin and a high-spin nickel(II) centres. This behaviour is similar to that reported for homodinuclear nickel(II) complexes[23]. The visible spectrum of the heterobinuclear complex $[NiLCuCl_2]\cdot H_2O$ (**5**) shows two bands at 848 and 585 nm due to d–d transitions of Cu(II) ions in a tetrahedral geometry and the Ni(II) ion in a square-planar geometry, respectively. The magnetic moment of this complex (**5**) is 1.84 B.M. due to the unpaired electron of the Cu(II) ion while the nickel ion is spin-paired. These observations are similar to those reported for heteronuclear Cu(II) and Ni(II) Schiff base complexes[24,25].

The visible spectra of the heterotrinuclear complexes (**6**) and (**10**)–(**14**), show one d–d transition band at 523–534 nm which would be due to the Ni(II) cation only similar to that observed for the complex ligand, the other accompanying cations, Mn(II), d^5, Zn(II) and Cd(II) d^{10}, Ce(III), Th(IV) and UO_2(VI), do not interfere. The visible spectrum of the heterotrinuclear complex $[(NiL)_2FeCl_2]Cl\cdot 4H_2O$ (**7**) shows a charge transfer band at 500 nm ($\varepsilon = 2000$) thus masking the Ni(II) absorption band.

The magnetic moment of the complex ligand $[NiL]\cdot\frac{1}{2}H_2O$ is diamagnetic, d^8 system in square-planar geometry, so any magnetic moment of the heteronuclear species should arise from the other coordinated metal ions *via* the di-μ-phenoxo bridges. Based on this assumption, the observed magnetic moments of the heteronuclear complexes Ni(II)-Mn(II) (**6**) and Ni(II)-Fe(III) (**7**), 5.9 and 6.1 B.M., are those expected for an isolated d^5 system in octahedral geometry, Fig. 3(b). Also, the observed magnetic moments of the heteronuclear complexes Ni(II)-Th(IV) (**11**) and Ni(II)-UO_2(VI) (**14**), 2.68 and 1.34 B.M., can be assigned to the distortion of the geometry of Ni(II) from square-planar towards tetrahedral as a result of introducing the large Th(IV) and UO_2(VI) cations.

The visible spectra of the heteronuclear complexes $[(NiL)_2Co]Cl_2$ (**8**) and $[(NiL)_2Co](ClO_4)_2$ (**9**) show two d–d bands at 674 ($\varepsilon = 728$), 528 ($\varepsilon = 444$) and 677 ($\varepsilon = 540$), 532 ($\varepsilon = 320$) nm, respectively. The first band of each complex is attributed to d–d transition of the Co(II) ion in tetrahedral geometry while the second band is due to a d–d transition of the Ni(II) ion in square-planar geometry and similar to that of the complex ligand, $[NiL]\cdot\frac{1}{2}H_2O$. The magnetic moments of the complexes (**8**) and (**9**) are 4.6 and 3.83 B.M., respectively, while the expected values for tetrahedral complexes are 4.4–4.8 B.M. The low value of the magnetic moment of complex (**9**) would point to the fact that the geometry of Co(II) is not purely tetrahedral and may tend towards square-planar which complexes have lower magnetic moments (2.1–2.8 B.M.)[26]. The visible spectra of the heterotrinuclear complexes $[(CuL)_2Co]Cl_2 \cdot 5H_2O$ (**22**) and $[(CuL)_2Co](ClO_4)_2$ (**23**) are 572 ($\varepsilon = 386$), 648 ($\varepsilon = 250$) and 572 ($\varepsilon = 322$), 650 nm ($\varepsilon = 290$), respectively. The first band at 572 nm is similar to that of the parent complex ligand $[CuL] \cdot H_2O$ while the second band at 648–650 nm ($\varepsilon = 250$–290) is due to the Co(II) ion in tetrahedral geometry. It was well known that the electronic spectra in an octahedral Co(II) complexes, which are usually high-spin ones, lead to a weak band ($\varepsilon < 10$) near 500 nm while for tetrahedral complexes a much stronger band ($\varepsilon < 100$) at 600–700 nm is expected[27]. Magnetic moments and ESR spectra support these geometries. The magnetic moments of the two previous complexes are 4.94 and 4.1 B.M., respectively. These values would indicate antiferromagnetic interaction between Cu(II)-Co(II) ions. The ESR spectrum of $[(CuL)_2Co]Cl_2 \cdot 5H_2O$ (**22**) measured at room temperature exhibits a signal with $g = 1.81$, Fig. 6, similar to that observed for the complex ligand $[CuL] \cdot H_2O$ in square-planar geometry and other signals at $g = 1.85$, 1.89, 1.90, 1.91 and a shoulder at 1.93 attributed to Co(II) in tetrahedral geometry. The splitting of the latter signal is due to the interaction between the electrons and the ^{59}Co nuclei which have a nuclear spin $I = 7/2$.

The visible spectra of the homotrinuclear complex (**19**) and the heteronuclear complexes (**20**) and (**24**)–(**27**) show one absorption band which would be due to the d–d transition of the Cu(II) cation as that observed in the case of the complex ligand $[CuL] \cdot H_2O$, the other accomanying cations, Mn(II), d^5, Zn(II) and Cd(II), d^{10}, Ce(III) and Th(IV), do not interfere. The spectrum of $[CuL^3FeCl_3(H_2O)] \cdot 3H_2O$ (**21**) shows bands at 525 and 475 nm, the former band was assigned to the transition of the Cu(II) ion and is consistent with square-planar geometry while the later band was assigned to the d–d transition of a Fe(III) ion in an octahedral geometry[26] (Fig. 4) which is achieved through the chloride ions and a water molecule. The magnetic moment of the complex is 5.6 B.M. which is lower than expected for Cu(II)-Fe(III) ions due to strong antiferromagnetic interactions between the metal ions. The ESR spectrum of the complex exhibits a signal with $g = 1.81$ similar to that observed for the complex ligand $[CuL] \cdot H_2O$ in square-planar geometry and another signal at $g = 1.84$ and a shoulder at $g = 1.85$ which are attributed to Fe(III) ion.

The magnetic moment of the homotrinuclear complex $[(CuL)_2 \cdot CuCl_2] \cdot 6H_2O$ (**19**) is 2.81 B.M., and indicates antiferromagnetic coupling which may be due to intermolecular and/or intramolecular interactions.

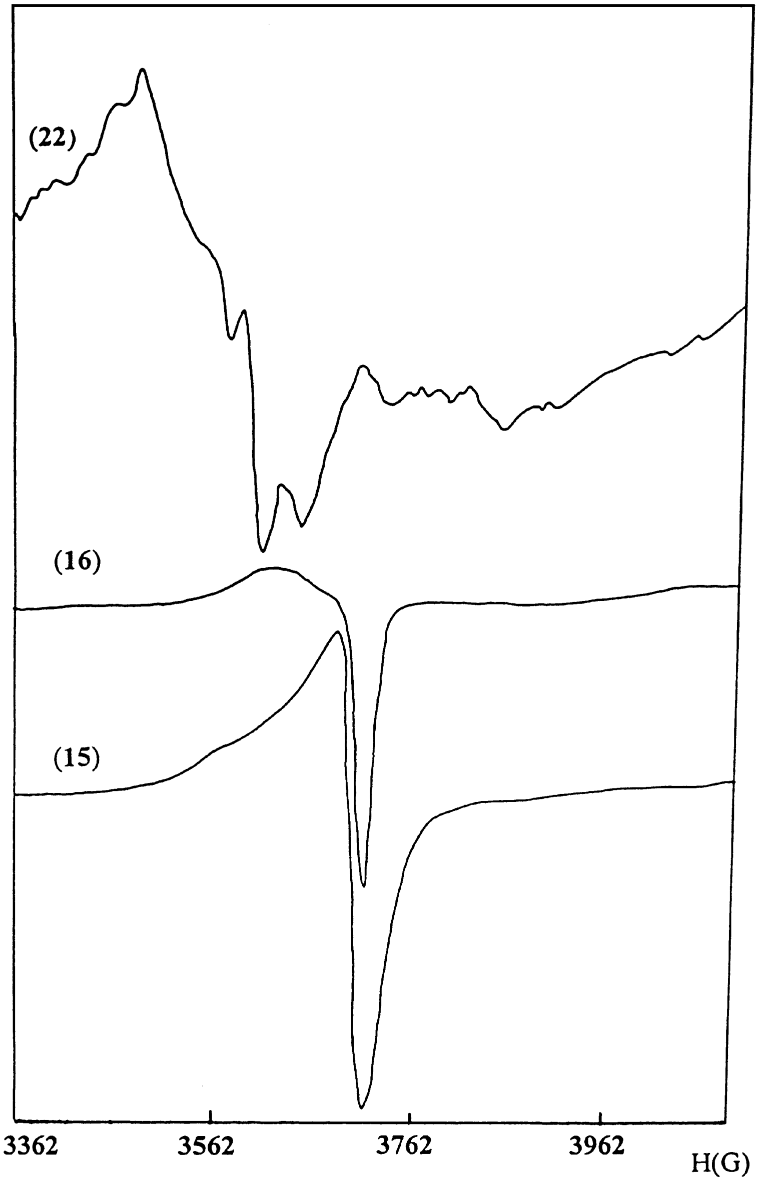


Figure 6. ESR spectra of the parent amine complex, $[Cu(1,2\text{-}pn)_2SO_4]\cdot H_2O$ (**15**); the complex ligand $[CuL]\cdot H_2O$ (**16**) and $[(CuL)_2Co]Cl_2\cdot 5H_2O$ (**22**).

The visible spectra of the heterotrinuclear complexes $[(CuL)_2NiCl_2]\cdot H_2O$ (**17**) and $[(CuL)_2Ni](ClO_4)_2$ (**18**) show a single band at 570 nm due to the overlap of the absorption bands of both Cu(II) and Ni(II) cations in square-planar geometries. The values of the magnetic moments of these complexes are 2.89 and 3.4 B.M., which is higher than the value expected for the Cu(II) ion and suggest that the geometry of the Ni(II) ion is distorted from square-planar towards tetrahedral.

Mass Spectra of Heteronuclear Metal Complexes

The mass spectra of the homo- and heteronuclear complexes provide good evidence for the molecular formulas of these complexes. The heterotrinuclear complexes (**7**), (**22**), (**20**) and (**21**), $[(NiL)_2FeCl_2]Cl\cdot 4H_2O$ (F.W. 912), $[(CuL)_2Co]Cl_2\cdot 5H_2O$ (F.W. 907.7), $[(CuL)_2MnCl_2]$ (F.W. 813.6) and $[CuLFeCl_3(H_2O)]\cdot 3H_2O$ (F.W. 578.1) as representative complexes, are depicted in Figs. 7 and 8. The mass spectra of these complexes showed the highest mass peaks at m/e 850, 817, 811 and 508, respectively, which agree with the formula weights of the anhydrous complexes $[(NiL)_2FeCl_2]Cl$ (F.W. 840), $[(CuL)_2Co]Cl_2$ (F.W. 817.7), $[(CuL)_2MnCl_2]$ (F.W. 813.6) and $[CuLFeCl_3]Cl$ (F.W. 506.1). The fragmentation patterns of the former two complexes show fragments at 338 and 343 due to the complex ligands [NiL] and [CuL], respectively.

Conductance of the Homo- and Heteronuclear Metal Complexes

The molar conductance values (Table II) of the complex ligands measured in DMF solutions lie in the range 6–10 $ohm^{-1}\,cm^{-2}\,mol^{-1}$ suggesting that they are non-electrolytes. The conductivity of the heteronuclear complexes (**7**), (**10**), (**14**) and (**24**) are 62, 100, 50 and 62 $ohm^{-1}\,cm^{-2}\,mol^{-1}$, respectively, which suggest that these complexes are 1:1 electrolytes[28]. The conductivity of the heterotrinuclear Ni(II)-Th(IV) (**11**) and Cu(II)-Th(IV) (**25**) complexes are 201 and 200 $ohm^{-1}\,cm^{-2}\,mol^{-1}$, respectively, suggesting that these complexes are 2:1 electrolytes. These results indicate that the coordination geometry of both Ce(III) and Th(IV) is octahedral (Fig. 4).

Complexes (**4**), (**9**), (**18**) and (**23**) in Table II which contain two perchlorate anions showed lower values of conductivity, 38.5–100 $ohm^{-1}\,cm^2\,mol^{-1}$, than those expected for 2:1 electrolytes. This would be due to the bulky perchlorate anions which would have lower mobilities in their solutions. On the other hand, the complexes that contain two chloride ions, (**8**) and (**22**), are expected to have higher values of conductivity. However, their con-

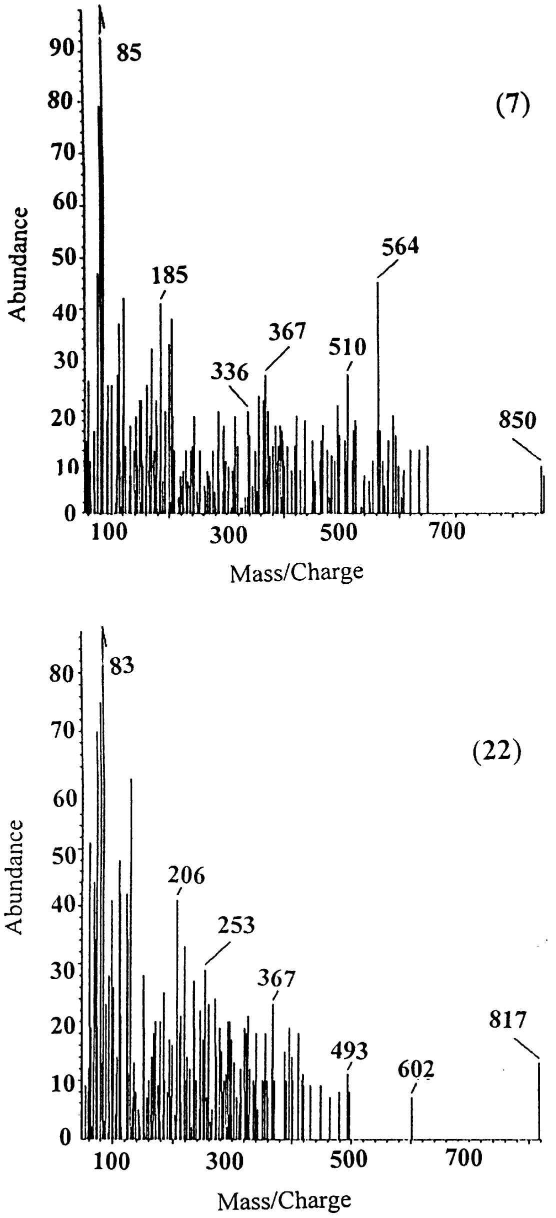


Figure 7. Mass spectra of the heterotrinuclear complexes $[(NiL)_2FeCl_2]Cl{\cdot}4H_2O$ (**7**) and $[(CuL)_2Co]Cl_2{\cdot}5H_2O$ (**22**).

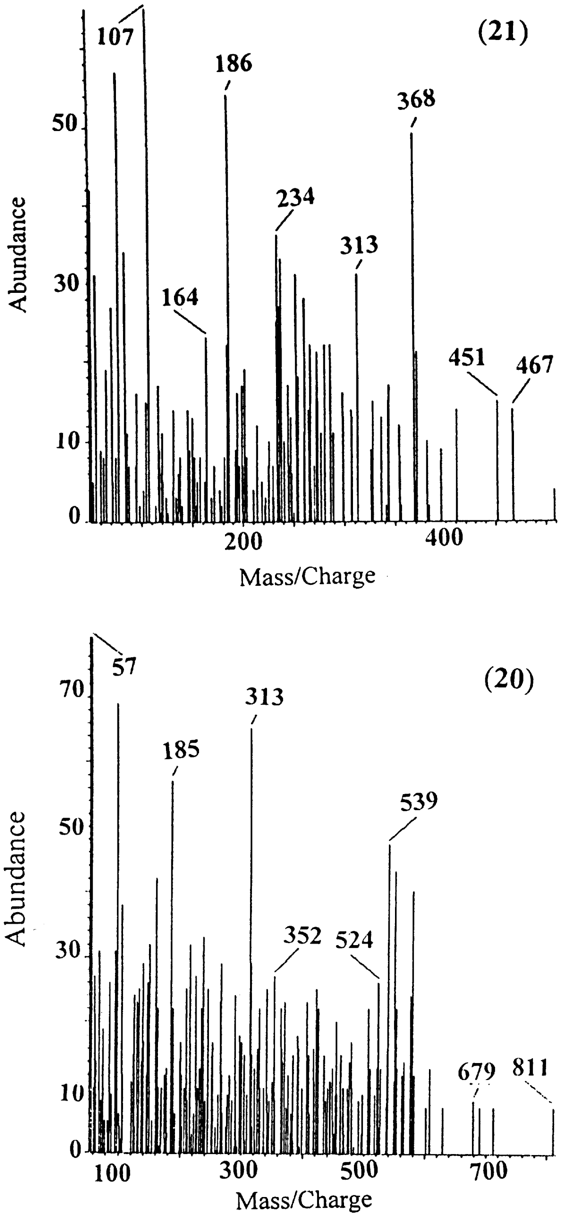


Figure 8. Mass spectra of heterotrinuclear complexes [$(CuL)_2MnCl_2$] (**20**) and [$CuLFeCl_3(H_2O)$]·$3H_2O$ (**21**).

ductivities are 56 and 106 $ohm^{-1} cm^2 mol^{-1}$, respectively, which indicate the formation of ion-pairing in these solutions. The other complexes which contain coordinated chloride ions are non-conducting or show a certain degree of conductivity which would be due to their replacement by DMF solvent molecules. Examples of the latter type are the complexes (**3**), (**5**), (**6**), (**12**), (**13**), (**17**), (**19**), (**20**), (**21**), (**26**), (**27**) in Table II.

Its is worth noting that complex ligands similar to $[NiL]\cdot\frac{1}{2}H_2O$ and $[CuL]\cdot H_2O$ previously have been used as chelating agents towards metal cations[29]. However, the preparations of the present ligands are carried out through a different route and the products of the reactions of these complex ligands with metal chlorides and perchlorates are new and to our knoweldge have not been reported before. In addition, while the two types of complexes in Fig. 2 have been previously reported, those of the type (b), Fig. 2, have not been reported before. Besides, all the variety of the structures of the complexes obtained in this work is quite obvious.

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