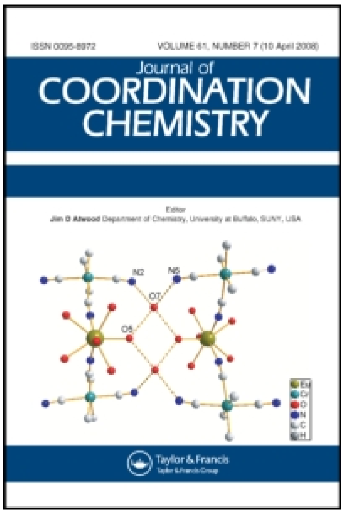

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Khalil, Saied M. E. and Emara, Adel. A.(2002) 'Asymmetric Schiff Base (N 2 O 3) Complexes as Ligands Towards Mn(II), Fe(III) and Co(II), Synthesis and Characterization', Journal of Coordination Chemistry, 55: 1, 17 — 32

To link to this Article: DOI: 10.1080/00958970211871

URL: http://dx.doi.org/10.1080/00958970211871

J. Coord. Chem., 2002, Vol. 55(1), pp. 17–32

ASYMMETRIC SCHIFF BASE (N_2O_3) COMPLEXES AS LIGANDS TOWARDS Mn(II), Fe(III) AND Co(II), SYNTHESIS AND CHARACTERIZATION

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(Received 27 April 2000; In final form 11 October 2000)

Heterobi- and tri-nuclear complexes [LMM′Cl] and $[(LM)_2M']$(M = Ni or Cu and M′ = Mn, Fe or Co) have been synthesised. The heteronuclear complexes were prepared by stepwise reactions using two mononuclear Ni(II) and Cu(II) complexes of the general formula $[HLM]\cdot 1/2H_2O$, as ligands towards the metal ions, Mn(II), Fe(III) and Co(II). The asymmetrical pentadentate (N_2O_3) Schiff-base ligands used were prepared by condensing acetoacetylphenol and ethylenediamine, molar ratio 1 : 1, to yield a half-unit compound which was further condensed with either salicylaldehyde or naphthaldehyde to yield the ligands H_3L^1 and H_3L^2 which possess two dissimilar coordination sites, an inner four-coordinate N_2O_2 donor set and an outer three-coordinated O_2O set. ^1H NMR and IR spectra indicate that the Ni(II) and Cu(II) ions are bonded to the inner N_2O_2 sites of the ligands leaving their outer O_2O sites vacant for further coordination. Different types of products were obtained according to the type of metal ion. These products differ in stoichiometry according to the type of ligand in the parent compound. Electronic spectra and magnetic moments indicate that the structures of the parent Ni(II) and Cu(II) complexes are square-planar while the geometry around Fe(III), Mn(II) and Co(II) in their products are octahedral as elucidated from IR, UV-visible, ESR, ^1H NMR, mass spectrometry and magnetic moments.

Keywords: Heterobi- and tri-nuclear Schiff base complexes; Asymmetric Schiff-base (N_2O_3) complexes

INTRODUCTION

Macrocycle and macroacyclic ligands are used in the synthesis of homo- and hetero-di- and polynuclear and mixed-valence complexes [1–10]

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ISSN: 0095-8972 DOI: 10.1080/00958970290000623

incorporating similar or different metal ions which are of special importance in the field of biochemistry. Recently, much effort has been devoted to modify the macrocycles by introducing potent donor groups on the lateral chains [11 – 13] with the hope of increasing the number of coordination sites or obtaining multinuclear complexes of desired structures. Many proteins can develop their activity in the presence of two or more metal ions [14 – 16]. Some enzymes such as emocyanine contain a dinuclear copper (II) complex which acts as one of the active sites for oxygen activation [14 – 16]. Due to their flexible cavities, penta- and heptadentate ligands with N_3O_2, N_3O_4, N_5O_2 and N_4O_2S coordination sites proved to be the most suitable ones for coordinating transition and non-transition metal cations. Also, hexadentate ligands with N_2O_4 coordinating sites (Fig. 1) have large outer cavities to accommodate large cations such as the uranyl or lanthanide ions, which are further coordinated to solvent molecule (s) to complete the preferred hepta or octa coordination sphere [17 – 23]. The preparations of these heterobinuclear metal complexes are usually preceded by the preparation of the mononuclear Cu(II) or Ni(II) complexes then reacting them with the uranyl salt [19, 20].

In our previous publications [24, 25] a series of asymmetrical pentadentate N_2O_3 Schiff base ligands and mononuclear Cu(II) and Ni(II) complexes were prepared. Further reactions on mononuclear Cu(II) or Ni(II) complexes with transition metal cations or uranyl ions yielded bi- and trinuclear metal complexes of the type [LMM′Cl], [LMM'_2Cl_3] and [$(LM)_2UO_2(OH_2)$], (M′ or M = Cu or Ni) have also been reported.

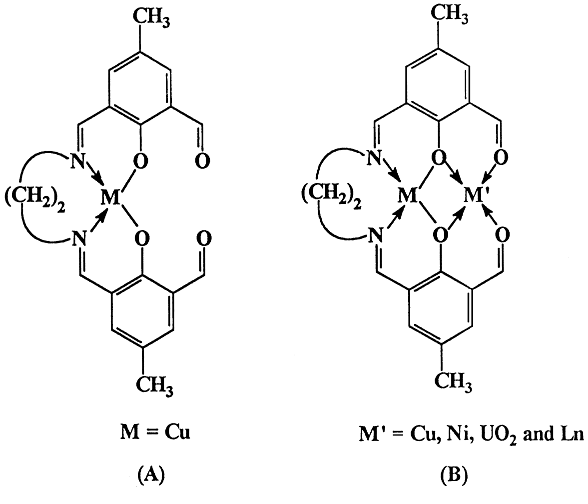


FIGURE 1 Structures of the mononuclear complex(A) and heteronuclear complex(B).

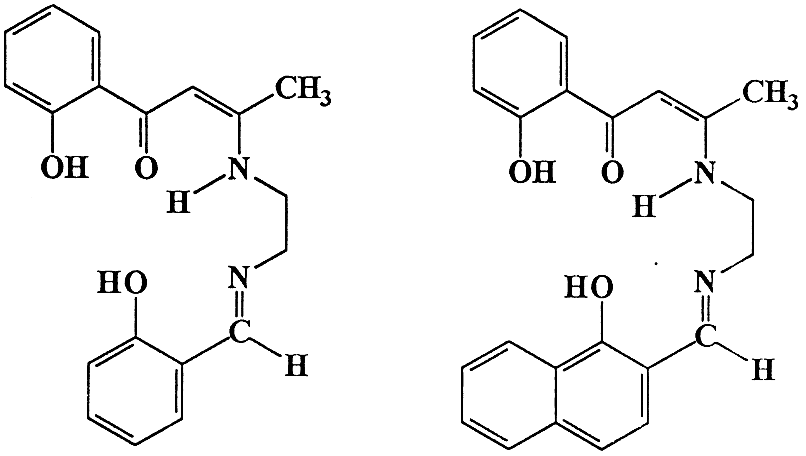
Continuing our studies, the heterobi- and tri-nuclear [LMM′Cl] and [(HLM)$_2$M′](M = Ni or Cu and M′ = Mn, Fe or Co) complexes have been prepared using the mononuclear Ni(II) and Cu(II) complexes as ligands.

PHYSICAL MEASUREMENTS

ESR spectra of the metal complexes were recorded 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-picryl-hydrazyl sample purchased from Aldrich. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alfa Products, Model No. MKI magnetic susceptibility balance. The effective magnetic moments were calculated from the expression $\mu_{\text{eff.}} = 2.828\ (\chi_M \cdot T)^{1/2}$ B.M., where χ_M is the molar susceptibility. Diamagnetic corrections were calculated from Pascal's constants for all atoms in the compounds. ^{1}H NMR spectra of the Schiff base ligand, H_3L^2, and its diamagnetic nickel complex in $CDCl_3$ were recorded on a Bruker WP 200 SY spectrometer at room temperature using TMS as an internal standard. Mass spectra of the metal complexes were recorded on a Hewlett-Packard mass spectrometer model MS-5988. The fragmentation was carried out at 205 – 260°C and 70 eV. IR spectra were recorded with a Perkin-Elmer IR 598 spectrometer (4000 – 200 cm^{-1}) using KBr discs and polystyrene as a calibrant. Electronic spectra of the solutions of the metal complexes in DMF were recorded on a Perkin-Elmer 555 spectrophotometer. Conductivity measurements of solutions of the metal complexes in DMF (10^{-3} M) were carried out using a conductivity meter Mod. LBR 40A, Germany. Microanalyses of carbon, hydrogen, nitrogen and chlorine were carried out at the Microanalysis Centre, Cairo University, Giza, Egypt. Analyses of copper and nickel in the mononuclear complexes followed the dissolution of the solid complex in hot concentrated HCl, then diluting with water and filtering to remove the precipitated ligand. The solution was neutralized with ammonia solution and the metal ions were then titrated with EDTA.

EXPERIMENTAL

All chemicals used were of Merck or BDH grade. The two asymmetric pentadentate Schiff base ligands (Fig. 2) and their mononuclear Ni(II) and Cu(II) complexes were prepared as previously described [25].



H_3L^1 H_3L^2

FIGURE 2 Structures of the asymmetric pentadentate schiff base ligands, H_3L^1 and H_3L^2.

Preparation of the Heteronuclear, [LMM′Cl] and [LM)$_2$M′X$_n$] Metal Complexes, M = Cu or Ni and M′ = Mn(II), Fe(III) and Co(II), X = Cl or H_2O, n = 1, 2

Mn(II), Fe(III) or Co(II) chloride was dissolved in ethanol and added gradually to a hot solution of the parent Cu(II) or Ni(II) complexes dissolved in chloroform. The resulting solution was refluxed for 8 – 10 h on a water bath, precipitation of the products occurred after cooling and were filtered off, washed several times with ethanol, ether and finally air-dried. The solid complexes were preserved in a desiccator over anhydrous $CaCl_2$.

The following detailed synthesis is given as an example, all of the other complexes were prepared similarly.

A solution of 0.354 g (1.311 mmol) of $FeCl_3 \cdot 6H_2O$ in 20 mL ethanol was added to the mixture of 0.5 g (1.312 mmol) of the parent Ni(II) complex of the ligand H_3L^1, $Ni(HL^1) \cdot H_2O$, in 30 mL $CHCl_3$ and $LiOH \cdot H_2O$ in 5 mL methanol. The solution was refluxed for 8 h, a deep brown precipitate appeared, the solution was then allowed to cool to room temperature. The precipitate was separated by filtration, washed with ethanol, then ether and finally air-dried. Yield, 0.46 g (67%).

The complexes were insoluble in water and soluble in DMF only to 10^{-3} M solution. The addition of $LiOH \cdot H_2O$ was not essentials to obtain the heteronuclear complexes.

RESULTS AND DISCUSSION

Macrocyclic and macroacyclic complexes are generally synthesized by different methods such as template and stepwise reactions. Success in template synthesis of macrocyclic complexes depends upon the choice of the template ion [12]. Previous studies suggest that non-transition metal ions such as Pb(II) and Ba(II) can act as efficient template ions for the synthesis of various types of macrocycles. These metal ions are highly adaptable to the coordination cavity even when their ionic radii are not well matched with the size of the cavity [12, 26–28]. Pilkington and Robson first reported the direct template synthesis of a binucleating macrocycle comprised of two molecules of 2,6-diformyl-4-methylphenol and two molecules of 1,3-diaminopropane [29]. In the present ligands, H_3L^1 and H_3L^2, Ni(II) or Cu(II) ions were initially coordinated to the four N_2O_2 inner sites then Mn(II), Fe(III) and Co(II) ions were further coordinated to the outer sites O_2O. Table I shows the chemical analyses of the parent complexes and the products of their reactions with Mn(II), Fe(III) and Co(II) chlorides. Table II shows the UV-visible spectra, magnetic moments and conductivity of the parent and the product complexes. ^{1}H NMR data of the ligands H_3L^1, H_3L^2 and their Ni(II) complexes are given in Table III.

Mononuclear Ni(II) and Cu(II) Complexes

The structures of the two parent Cu(II) and Ni(II)complexes were elucidated by chemical analyses, UV-visible and IR spectra. IR spectra showed that the absorption of the azomethine groups in these complexes are shifted to lower frequencies, 1615 and 1610 cm^{-1} compared to 1635 and 1630 cm^{-1} for H_3L^1 and H_3L^2, respectively, which indicate that these groups participate in coordinating the Ni(II) and Cu(II) cations. A broad absorption band appeared at ≈ 3400 cm^{-1} and is assigned to ν OH of the hydrated water molecules thus masking the ν OH of the remaining phenolic OH group. ^{1}H NMR spectra of the Ni(II) complexes of ligands H_3L^1 and H_3L^2, Table III, showed the absence of the signal assigned to one of the phenolic protons and the imine proton of the ligands which indicate that they are deprotonated on Ni(II) complexation. The signal due to the other phenolic proton is shifted to lower field which was caused by the electron withdrawing effect of the Ni(II) ion [30]. Thus, the ^{1}H NMR data along with IR spectra discussed above support the binding of Ni(II) and Cu(II) ions to the inner N_2O_2 sites of the ligand. The structures of the parent Ni(II) and Cu(II) complexes are also confirmed by determining their magnetic moments and electronic

TABLE I Analytical and physical data for the metal complexes

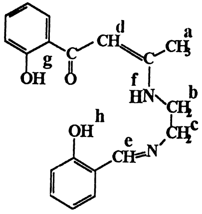
			Yield	*Elemental analyses, % found/(calc.)*				
Reactions	*Complexes*	*Color*	(%)	*C*	*H*	*N*	*M*	*Cl*
(1) $Ni(HL^1)$	$Ni(HL^1)$ $(C_{19}H_{18}N_2O_3Ni)$	Brownish yellow	90	59.5 (59.9)	4.8 (4.8)	7.4 (7.4)	15.5 (15.4)	
(2) $Ni(HL^1)\cdot H_2O + MnCl_2\cdot 4H_2O$	$[NiL^1MnCl(H_2O)_2]$ $(C_{19}H_{21}N_2O_5ClNiMn)$	Reddish Brown	79	45.3 (45.1)	4.1 (4.2)	5.5 (5.5)		7.1 (7.0)
(3) $Ni(HL^1)\cdot H_2O + FeCl_3\cdot 6H_2O$	$[NiL^1FeCl_2(H_2O)]$ $(C_{19}H_{19}N_2O_4Cl_2NiFe)$	Greenish Brown	67	43.5 (43.5)	3.6 (3.6)	5.2 (5.3)		13.7 (13.5)
(4) $Ni(HL^1)\cdot H_2O + CoCl_2\cdot 6H_2O$	$[NiL^1CoCl(H_2O)_2]$ $(C_{19}H_{21}N_2O_5ClNiCo)$	Brick Red	68	44.4 (44.7)	4.2 (4.1)	5.4 (5.5)		6.6 (6.9)
(5) $Cu(HL^1)$	$Cu(HL^1)$ $(C_{19}H_{18}N_2O_3Cu)$	Brown	93	59.1 (59.1)	4.7 (4.7)	7.3 (7.3)	16.4 (16.5)	
(6) $Cu(HL^1)\cdot H_2O + MnCl_2\cdot 4H_2O$	$[CuL^1MnCl(H_2O)_2]$ $(C_{19}H_{21}N_2O_5ClCuMn)$	Pale Brown	72	44.5 (44.5)	4.1 (4.1)	5.3 (5.5)		6.8 (6.9)
(7) $Cu(HL^1)\cdot H_2O + FeCl_3\cdot 6H_2O$	$[CuL^1FeCl_2(H_2O)]$ $(C_{19}H_{19}N_2O_4Cl_2CuFe)$	Deep Brown	73	43.2 (43.1)	3.8 (3.6)	5.3 (5.3)		13.6 (13.4)
(8) $Cu(HL^1)\cdot H_2O + CoCl_2\cdot 6H_2O$	$[CuL^1CoCl(H_2O)_2]$ $(C_{19}H_{21}N_2O_5ClCuCo)$	Yellowish Brown	73	44.4 (44.3)	4.3 (4.1)	5.4 (5.4)		7.0 (6.9)
(9) $Ni(HL^2)\cdot H_2O$	$Ni(HL^2)\cdot H_2O$ $(C_{23}H_{22}N_2O_4Ni)$	Dark brownish yellow	86	61.5 (61.5)	4.9 (4.9)	6.2 (6.2)	13.1 (13.4)	
(10) $Ni(HL^2)\cdot H_2O + MnCl_2\cdot 4H_2O$	$[(NiHL^2)(NiL^2)MnCl(H_2O)]\cdot 2H_2O$ $(C_{46}H_{46}N_4O_9ClNi_2Mn)$	Reddish Brown	41	55.0 (54.9)	4.5 (4.5)	5.5 (5.6)		3.7 (3.5)
(11) $Ni(HL^2)\cdot H_2O + FeCl_3\cdot 6H_2O$	$[(NiHL^2)(NiL^2)FeCl(H_2O)]Cl\cdot 3H_2O$ $(C_{46}H_{48}N_4O_{10}Cl_2Ni_2Fe)$	Brown	52	52.3 (52.1)	4.7 (4.5)	5.1 (5.3)		6.5 (6.7)
(12) $Ni(HL^2)\cdot H_2O + CoCl_2\cdot 6H_2O$	$[(NiHL^2)(NiL^2)CoCl(H_2O)]\cdot H_2O$ $(C_{46}H_{44}N_4O_8ClNi_2Co)$	Deep Red	43	55.5 (55.7)	4.5 (4.4)	5.5 (5.6)		3.5 (3.6)
(13) $Cu(HL^2)$	$Cu(HL^2)$ $(C_{23}H_{20}N_2O_3Cu)$	Dark brown	92	62.9 (63.4)	4.6 (4.6)	6.2 (6.4)	14.6 (14.6)	

(14) $Cu(HL^2) \cdot H_2O + MnCl_2 \cdot 4H_2O$	$[(CuHL^2)(CuL^2)MnCl(H_2O)]$ $(C_{46}H_{42}N_4O_7ClCu_2Mn)$	Pale Brown	45	56.5 (56.5)	4.3 (4.2)	5.5 (5.7)	3.5 (3.6)
(15) $Cu(HL^2) \cdot H_2O + FeCl_3 \cdot 6H_2O$	$[CuL^2FeCl(H_2O)_2]Cl \cdot 3H_2O$ $(C_{23}H_{29}N_2O_8Cl_2CuFe)$	Green	87	42.5 (42.4)	4.5 (4.5)	4.3 (4.3)	10.8 (10.9)
(16) $Cu(HL^2) \cdot H_2O + CoCl_2 \cdot 6H_2O$	$[CuL^2CoCl(H_2O)_2]$ $(C_{23}H_{23}N_2O_5ClCuCo)$	Brown	85	49.1 (48.9)	3.9 (4.1)	5.1 (5.0)	6.2 (6.3)

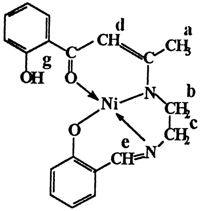
TABLE II Electronic spectra, magnetic moments and molar conductivity data of metal complexes

Complexes	*UV-visible (nm)*	*Magnetic moments (B.M.)*	*Conductance* $Ohm^{-1}\ cm^2\ mol^{-1}$
(1) $Ni(HL^1)$	535, 300, 240	Diamag.	5.0
(2) $[NiL^1MnCl(H_2O)_2]$	570, 518, 440, 400, 322, 266	5.46	25.0
(3) $[NiL^1FeCl_2(H_2O)]$	550, 406, 334, 274	5.76	20.0
(4) $[NiL^1CoCl(H_2O)_2]$	518, 500, 440, 404, 380, 328, 270	4.63	5.0
(5) $[Cu(HL^1)]$	540, 335, 245	1.92	5.0
(6) $[CuL^1MnCl(H_2O)_2]$	544, 424, 336	6.50	18.0
(7) $[CuL^1FeCl_2(H_2O)]$	570	5.45	28.0
(8) $[CuL^1CoCl(H_2O)_2]$	550, 362, 282	4.67	5.0
(9) $[Ni(HL^2)] \cdot H_2O$	530, 295	Diamag.	5.0
(10) $[(NiHL^2)(NiL^2)MnCl(H_2O)] \cdot 2H_2O$	530, 420, 332	5.9	17.0
(11) $[(NiHL^2)(NiL^2)FeCl(H_2O)]Cl \cdot 3H_2O$	530, 420, 330	4.58	80.0
(12) $[(NiHL^2)(NiL^2)CoCl(H_2O)] \cdot H_2O$	524, 420, 332	4.78	7.0
(13) $[Cu(HL^2)]$	515, 285	1.94	5.0
(14) $[Cu(HL^2)(CuL^2)MnCl(H_2O)]$	538, 410, 370, 320	4.10	8.0
(15) $[CuL^2FeCl(H_2O)_2]Cl \cdot 3H_2O$	518, 408, 388, 328	4.86	78.0
(16) $[CuL^2CoCl(H_2O)_2]$	530, 405, 360, 320	3.60	15.0

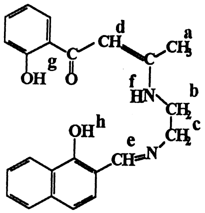
TABLE III The ^{1}H NMR data of the free ligands H_3L^1(I) and H_3L^2(II) and their Ni(II) complexes (III) and (IV), respectively, in $(CD_3)_2SO$



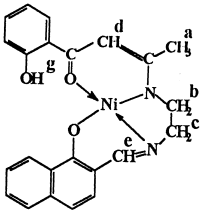
I



II



III



IV

	δ_H (ppm)							
	H^a	H^b and H^c	H^d	H_{ar}	H^e	H^f	H^g	H^h
H_3L^1 (I)	2.02 (s)*	3.67 (m)	5.85 (s)	7.20 – 7.49 (m)	7.9	11.01 (br)*	13.28 (br)	13.28 (br)
$[Ni(HL^1)]$ (II)	2.1 (s)	3.30 (m)	5.85 (s)	6.4 – 7.60 (m)	7.8	–	11.3 (br)	–
H_3L^2 (III)	2.10 (s)	3.75 (m)	5.65 (s)	6.85 – 7.90 (m)	8.95 (s)	11.20 (br)	13.40 (br)	13.9 (br)
$[Ni(HL^2)] \cdot H_2O$ (IV)	2.30 (s)	2.95 (m)	6.05 (s)	6.85 – 8.60 (m)	8.85 (s)	–	12.10 (br)	–

*s = singlet, m = multiplet and br = broad.

spectral data. The parent Ni(II) complexes are diamagnetic while the Cu(II) complexes are paramagnetic and have magnetic moments 1.92 and 1.94 B.M. for ligands H_3L^1 and H_3L^2, respectively. These data coupled with their electronic spectral absorptions 535, 530 nm for Ni(II) complexes and 540, 530 nm for Cu(II) complexes of the ligands H_3L^1 and H_3L^2, respectively, indicate that their geometries are square planar.

Heteronuclear Complexes

Composition and Molar Conductance

On the basis of elemental analyses and physical data, shown in Tables I and II, the reactions of the mononuclear Ni(II) or Cu(II) complexes with Mn(II), Fe(III) or Co(II) chlorides in the molar ratio, 1:1 yielded heterobi- and tri-nuclear complexes. The preparations of these complexes require long reaction times and could be represented by the following equations:

$$[HL^1M] + M'Cl_2{\cdot}6H_2O + LiOH\cdot H_2O \rightarrow [ML^1M'Cl(OH_2)_2] + LiCl + 6H_2O$$

$$(M = \text{Ni or Cu}), (M' = \text{Mn or Co})$$

$$[HL^1M] + FeCl_3\cdot 6H_2O + LiOH\cdot H_2O \rightarrow [ML^1FeCl_2(H_2O)] + LiCl + 7H_2O \quad (M = \text{Ni or Cu})$$

$$2[HL^2Ni] + MnCl_2\cdot 4H_2O + LiOH\cdot H_2O \rightarrow [(HNiL^2)(NiL^2)MnCl(H_2O)]\cdot 2H_2O + LiCl + 3H_2O$$

$$2[HL^2Ni] + CoCl_2\cdot 6H_2O + LiOH\cdot H_2O \rightarrow [(HNiL^2)(NiL^2)CoCl(H_2O)]\cdot H_2O + LiCl + 6H_2O$$

$$2[HL^2Ni] + FeCl_3\cdot 6H_2O + LiOH\cdot H_2O \rightarrow [(HNiL^2)(NiL^2)FeCl(H_2O)]Cl\cdot 3H_2O + LiCl + 4H_2O$$

$$2[HL^2Cu] + MnCl_2\cdot 4H_2O + LiOH\cdot H_2O \rightarrow [(HCuL^2)(CuL^2)MnCl(H_2O)]\cdot 4H_2O + LiCl + H_2O$$

$$[HL^2Cu] + FeCl_3\cdot 6H_2O + LiOH\cdot H_2O \rightarrow [CuL^2FeCl(H_2O)]Cl\cdot 4H_2O + LiCl + 3H_2O$$

$$[HL^2Cu] + CoCl_2\cdot 6H_2O + LiOH\cdot H_2O \rightarrow [CuL^2CoCl(H_2O)_2] + LiCl + 6H_2O$$

The molar conductance values of the heteronuclear complexes 11 and 15 in DMF solution (see Tab. II) fall in the expected range for 1 : 1 electrolytes [31], indicating that one of the chloride ions lies outside the coordination sphere. The other complexes have low molar condutance values, however, the ones which have values ranging from 15 – 28 $\text{Ohm}^{-1}\,\text{cm}^{-2}\,\text{mol}^{-1}$ contain coordinated chloride ions which would exchange with the hydrated water molecules.

IR Spectra

The IR absorption spectra of the heteronuclear complexes revealed no shift of the azomethine groups. Unfortunately, the ν OH of the remaining phenolic group in the parent Ni(II) or Cu(II) complexes is masked by the absorption of the hydrated water molecules, thus there is no direct indication about their replacement by the Mn(II), Fe(III) and Co(II) cations. However the coordination of the Mn(II), Fe(III) and Co(II) cations occurs through the outer vacant sites O_2O, the remaining coordination sites are occupied by chloride or/and water molecules, as indicated from chemical analyses and other spectroscopic data.

Electronic and ESR Spectra and Magnetic Moments

The electronic spectra of the heteronuclear metal complexes, as solutions in dimethylformamide, Table II, show similar absorption spectra. Their spectra show an absorption band in the range (266 – 282 nm and/or another band at (322 – 336 nm). The first band would be assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic rings overlapping with the $n \rightarrow \pi^*$ transition within the C=O, group. The second band would be assigned to the $n \rightarrow \pi^*$ transition within the C=N groups. Other bands appeared at 360 – 388 and 400 – 440 nm. The latter bands in the visible spectra could be assigned to charge transfer transitions. Lower energy bands appearing in the range 500 – 570 nm were assigned to the *d-d* transitions within the metal cations. Mn(II) and Fe(III) cations are d^5 systems and their *d-d* transitions are thus spin-forbidden. However, their hetero-complexes show only the absorption bands due to either the Cu(II) or Ni(II) cations but at shifted wavelengths due to the introduction of other metal cations in the complex which would affect the donating sites. In addition, in the case of heteronuclear complexes containing Co(II) cations, the expected ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition in its visible spectra would be overlapped by the absorption band of either Cu(II) or Ni(II) cations. Best evidence for the proposed structures of the heteronuclear complexes comes from magnetic measurements and ESR spectra, Figure 3. Where the starting Ni(II) complexes of H_3L^1 and H_3L^2 are square-planar d^8 (diamagnetic) and any magnetic moment of the heteronuclear species should arise from occupation of O_2O compartment. On this assumption the observed magnetic moments for the heteronuclear complexes 2, 3, 4, 10, 11 and 12 (Tab. II) are those for isolated d^5 systems, Mn(II) and Fe(III) and d^7 systems, Co(II). Thus, these complexes are ESR-active. Complex 2 $[NiL^1MnCl(H_2O)_2]$ ($\mu_{eff} = 5.46$ B. M. at 294 K), exhibits one broad band with $g = 1.86$, Figure 3. Also, the magnetic moment of complex 10, $[(NiHL^2)(NiL^2)MnCl(H_2O)] \cdot 2H_2O$ ($\mu_{eff} = 5.9$ B. M.) agrees well with an octahedral geometry around the Mn(II) cation. An ESR spectrum of complex 6, $[CuL^1MnCl(H_2O)_2]$ ($\mu_{eff} = 6.5$ B.M.), (Fig. 3) shows two bands with $g = 1.88$, 1.91 and a shoulder at 1.94, where the first value corresponds to the Mn(II) ion similar to the g-value which was observed for complex 2, and the two other values are due to the Cu(II) ion. The magnetic moment of complex 14, $[(CuHL^2)(CuL^2)MnCl(H_2O)]$ was 4.10 B.M. lower than expected for d^9 and d^5 systems, due to antiferromagnetic interactions occurring between the three metal ions. An ESR spectum of complex 3, $[NiL^1FeCl_2(H_2O)]$ exhibits one broad band with $g = 1.89$, (Fig. 3) due to Fe^{+3} (d^5) with a magnetic moment ($\mu_{eff} = 5.76$ B.M.) indicating that the geometry around Fe^{+3} is octahedral. The ESR spectrum of complex 7, $[CuL^1FeCl_2(H_2O)]$ ($\mu_{eff} = 5.45$ B.M.) shows two bands and a shoulder, Figure 3, a broad band at g 1.85 attributed to Fe^{+3} (d^5) and the other band at g 1.91 and a shoulder at 1.95 assigned to the Cu(II) cation. The magnetic moments of heteronuclear complexes 7 and 15, Table II, are lower than those expected for Cu^{+2}-Fe^{+3} ions due to antiferromagnetic interactions occurring between the metal cations. The magnetic moments of the heteronuclear complexes Ni(II)-Co(II), 4 and 12, are 4.63 and 4.78 B.M., respectively, indicating octahedral geometry for Co(II) ions in the complexes (Figs. 4 and 5) while the magnetic moments of the heteronuclear complexes Cu(II)-Co(II), (8 and 16) exhibit a reduced magnetic moment, 4.67 and 3.60 B.M., owing to antiferromagnetic interactions occurring between those metal ions.

Mass Spectra of Heteronuclear Complexes

The mass spectra of the heteronuclear complexes 15 and 16, are shown in Figure 6. Complex 15 showed the parent peak at $m/e = 652$ which compares well with the formula weight of the complex. Complex 16 showed the parent peak at $m/e = 566$ which compares with the formula $[CuL^2CoCl(H_2O)_2 + 1]$.

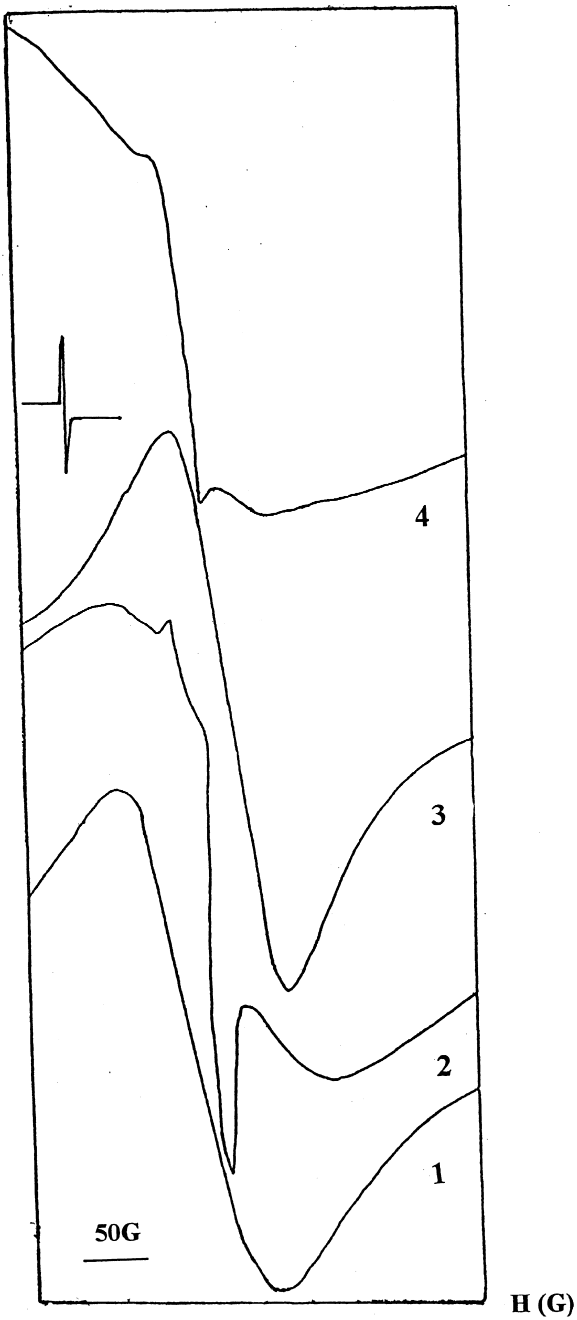
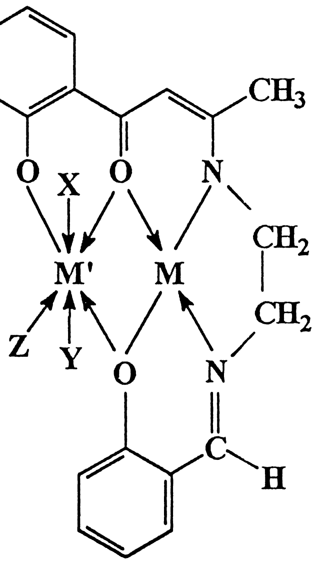
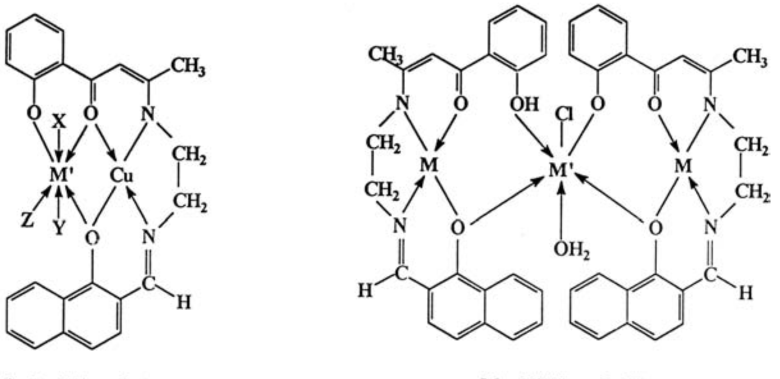


FIGURE 3 ESR powder spectra; X-bands, of the heteronuclear complexes, 1: [NiL^{1}MnCl(H_2O_2)](complex 2), 2: [CuL^{1}MnCl(H_2O)$_2$](complex 6), 3: [NiL^{1}FeCl$_2$(H_2O)](complex 3), and 4: [CuL^{1}FeCl$_2$(H_2O)](complex 7).



M = Ni(II) or Cu(II)
M' = Mn(II) or Co(II), X = Y = H_2O and Z = Cl
M' = Fe(III), X = Y = Cl and Z = H_2O

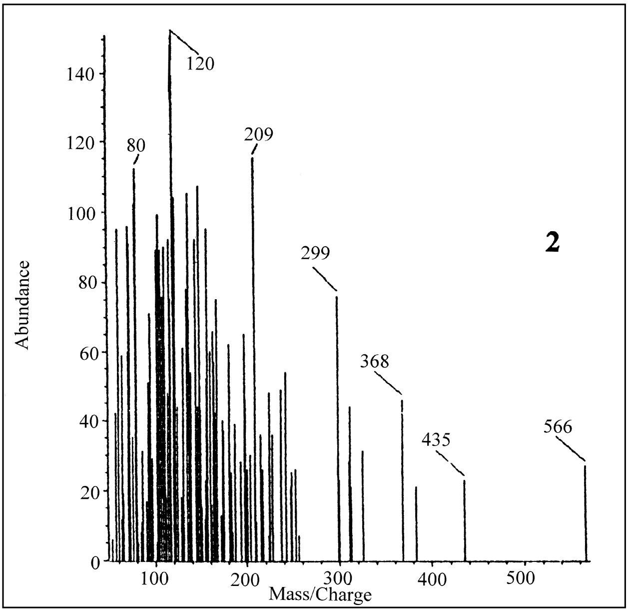
FIGURE 4 Proposed structures of the heteronuclear of the ligand H_3L^1.



M' = Fe(III) or Co(II), X = Y = H_2O and Z = Cl

M = Ni(II) or Cu(II)
M' = Mn(II) or Fe(III) or Co(II)

FIGURE 5 Proposed structures of the heteronuclear of the ligand H_3L^2.



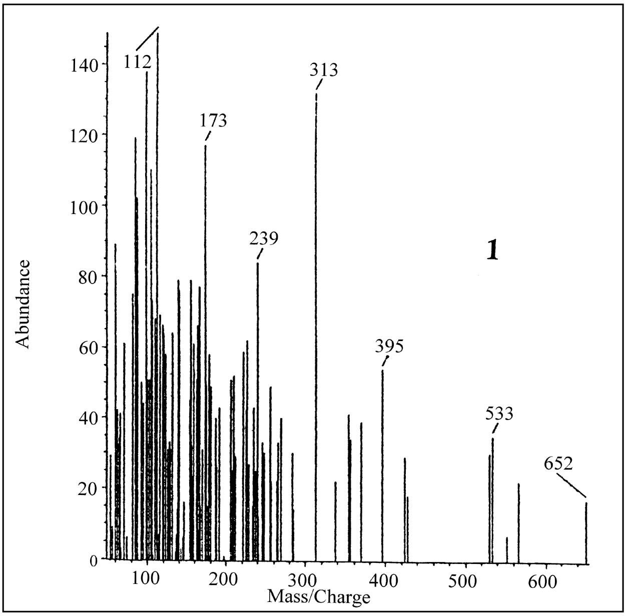


FIGURE 6 Mass spectra of 1: [$CuL^2FeCl(H_2O)_2$]$Cl \cdot 3H_2O$ (complex 15) and 2: [$CuL^2CoCl(H_2O)_2$] (complex 16).

Figures 4 and 5 show the proposed structures of the heteronuclear metal complexes of ligands H_3L^1 and H_3L^2, respectively.

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