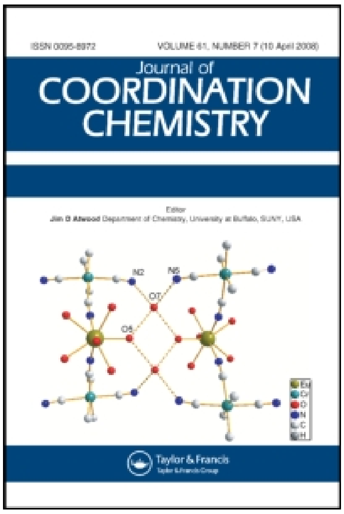

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Bi-, TRI- and Penta-Nuclear Complexes of Chelating Schiff Bases Derived from *o*-Acetoacetylphenol and Amine Complexes, $[Ni(1,2\text{-pn})_2Cl_2]\cdot 3H_2O$ and $[Cu(1,2\text{-pn})_2]SO_4\cdot 2H_2O$

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BI-, TRI- AND PENTA-NUCLEAR COMPLEXES OF CHELATING SCHIFF BASES DERIVED FROM *o*-ACETOACETYLPHENOL AND AMINE COMPLEXES, $[Ni(1,2\text{-}Pn)_2Cl_2]\cdot 3H_2O$ AND $[Cu(1,2\text{-}Pn)_2]SO_4\cdot 2H_2O$

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Two novel macroacyclic Schiff base ligands were prepared by condensation of two diamine metal complexes, $[Ni(1,2\text{-}pn)_2Cl_2]\cdot 3H_2O$ and $[Cu(1,2\text{-}pn)_2]SO_4\cdot 2H_2O$ with *o*-acetoacetylphenol. The ligands $MH_6L(M = \text{Ni}$ or Cu) are hexabasic and contain two O_4 coordination sites. They act as ligands towards transition metal ions yielding homo- and heteronuclear complexes of the type $[NiH_4LCu(H_2O)_2]\cdot 4H_2O$, $[MH_2LM'_2(H_2O)_6]$, $[MLM'_4(H_2O)_8]$, $[MH_2LCe_2(NO_3)_2(H_2O)_2]$ and $[NiLTh_2(NO_3)_2(H_2O)_2]$ ($M = \text{Ni}$ or Cu; $M' = \text{Mn(II)}$, Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ce(III), Th(IV) and UO_2(VI)). The complexes were characterized by elemental analysis, thermogravimetric analysis (TGA), IR, visible and ESR spectra, magnetic susceptibility measurements and mass spectrometry. Magnetic moments were altered by the introduction of metal cations besides the one already present in the complex ligands. The M′ cations were linked to two ketonic oxygen atoms and two phenyl oxygen atoms in $[NiH_6L(H_2O)_2]$ and $[CuH_6L]$ 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 heteronuclear complexes support the formula weights of these complexes. Visible and ESR spectra as well as magnetic moments indicated that the parent mononuclear complex ligands $[MH_6L]$ have an octahedral geometry for Ni(II) and a square-planar geometry distorted towards tetrahedral for Cu(II). The metal cations in bi-, tri- and pentanuclear complexes are octahedral or square-planar. The octahedral configuration is completed by chloride anions and/or solvent molecules.

Keywords: Macroacyclic Schiff-base complexes; Homo- and heteronuclear transition metal complexes

INTRODUCTION

Heterodinuclear metal complexes are of interest because of the unique physicochemical properties that arise from their metal–metal interactions [1–3]. Macrocyclic and macroacyclic ligands, also known as compartmental ligands, are used for the

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generation of complexes with peculiar spectroscopic and magnetic properties [4–7]. Synthesis of these Schiff-base complexes is achieved through the *template* reaction [8–11] or *transmetallation* reactions [12–18] which are used when the transition metal cations are ineffective as templates. These ligands and their metal complexes have different applications in fields such as bioinorganic chemistry, material science, catalysis, separation and encapsulation processes, hydrometallurgy, formation of compounds with unusual properties and metal–metal interactions [19–25].

In this study another method is reported for the synthesis of Schiff-base complexes from corresponding amine complexes, also known as complex ligands and abbreviated as $[MH_6L]$, Scheme 1, where $M = \mathrm{Ni(II)}$ or Cu(II). It was found that the metal ions are bonded to the N_4 sites in $[MH_6L]$ complex ligands. The complex ligands $[\mathrm{MH_6L}]$ react with metal(II) chlorides or nitrates, $M'\mathrm{Cl_2 \cdot H_2O}$ or $M'\mathrm{(NO_3)_2 \cdot 6H_2O}$, providing different products of homo- and hetero- bi-, tri- and penta-nuclear complexes. M' occupies the O_4 sites of $[M\mathrm{H_6L}]$ ligands and complete its preferred geometry by nitrate, chloride ions and/or water molecules.

EXPERIMENTAL

Materials

$\mathrm{MnCl_2 \cdot 4H_2O}$, $\mathrm{FeCl_3 \cdot 6H_2O}$, $\mathrm{CoCl_2 \cdot 6H_2O}$, $\mathrm{NiCl_2 \cdot 6H_2O}$, $\mathrm{CuCl_2 \cdot 2H_2O}$, $\mathrm{CuSO_4 \cdot 5H_2O}$, $\mathrm{ZnCl_2}$, $\mathrm{Ce(NO_3)_3 \cdot 6H_2O}$, $\mathrm{Th(NO_3)_4 \cdot 5H_2O}$ and $\mathrm{UO_2(NO_3)_2 \cdot 6H_2O}$ and 1,2-diaminopropane were BDH, Analar or Merck chemicals. *o*-Acetoacetylphenol was prepared by the Wittig method [26]. The solvents used were absolute and 95% ethanol, methanol, dimethylformamide (DMF), acetone and diethyl ether. Concentrated hydrochloric and nitric acids and the solvents were reagent grade chemicals.

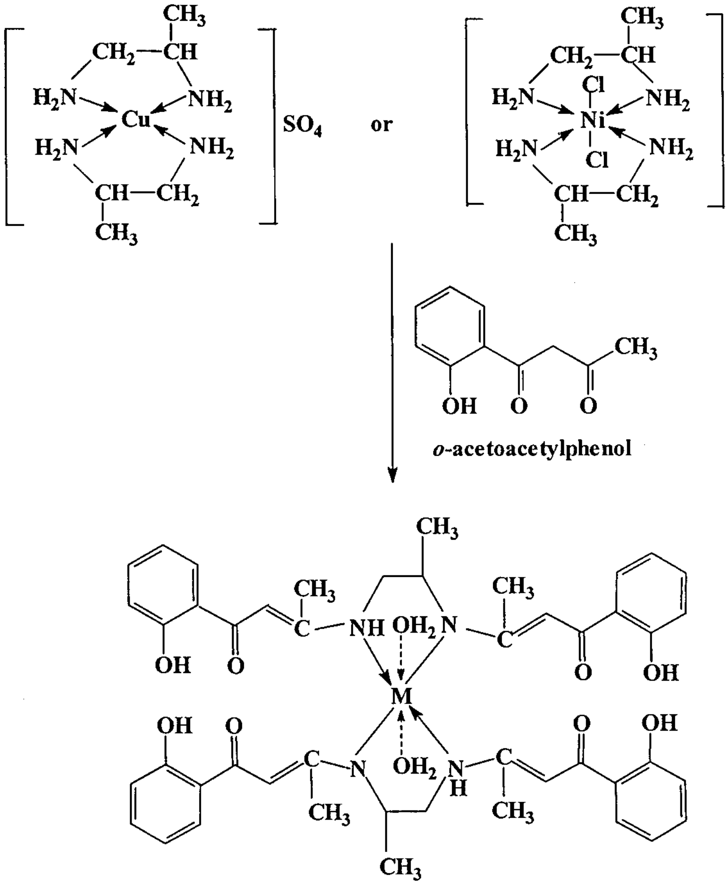
Preparation of the Complex Ligands, [*M*H₆*L*], from Amine Complexes

To a stirred suspension of the amine complex, $\mathrm{[Ni(1,2\text{-}pn)_2Cl_2] \cdot 3H_2O}$ [27] or $\mathrm{[Cu(1,2\text{-}pn)_2]SO_4 \cdot 2H_2O}$ [28], in ethanol was added an ethanolic solution of *o*-acetoacetylphenol at room temperature. A green precipitate appeared, its amount increased continuously and stirring was continued for 10 h. The products were collected by filtration, washed with twice distilled water several times to get rid of the excess parent amine complexes, then washed with ethanol, diethyl ether and finally air-dried. Scheme 1 outlines the synthesis of these complex ligands.

Preparation of the Homo- and Heteronuclear Metal Complexes

A solution of the metal chloride or nitrate in ethanol was added to the complex ligand, $[M\mathrm{H_6}L]$ suspended in ethanol. The solutions were stirred for 8–10 h at room temperature in the presence of $\mathrm{LiOH \cdot H_2O}$ which was used as a deprotonating agent. The solid metal complexes were collected by filtration, washed with ethanol then ether and finally air-dried.

Detailed preparations of the following complexes are given as examples, however, other metal complexes were prepared similarly.



M = Ni, $[NiH_6L(H_2O)_2]$; M = Cu, $[CuH_6L]$
[dotted arrows indicate coordinated water molecules to Ni(II)]

SCHEME 1 Formation of the Complex Ligands

Preparation of $[(NiL)Ni_4(H_2O)_{10}]Cl_2$, complex 3

An ethanolic solution (30 mL) of $NiCl_2 \cdot 6H_2O$ (1.08 g, 4.52 mmol) was added to an ethanolic solution (40 mL) of the complex ligand $[NiH_6L(H_2O)_2]$ (1 g, 1.13 mmol). The solution was stirred for 10 h and the formed green precipitate was filtered, washed several times with ethanol then air-dried. Yield, 0.742 g (50%).

Preparation of $[(NiH_2L)Co_2(H_2O)_2] \cdot 6H_2O$, complex 7

An ethanolic solution (10 mL) of $LiOH \cdot H_2O$ (0.166 g, 3.96 mmol) was added to the complex ligand, $[NiH_6L(H_2O)_2]$ (0.87 g, 0.99 mmol) in (20 mL) ethanol and stirred until complete dissolution of the complex. An ethanolic solution (30 mL) of $CoCl_2 \cdot 6H_2O$ (0.472 g, 1.98 mmol) was added to the previous solution and stirred for 8 h. The formed precipitate was filtered, washed with ethanol then air-dried. Yield 0.677 g (62%).

Preparation of $[(NiH_2L)Ce_2(NO_3)_2(H_2O)_4]$, complex 8

An ethanolic solution (10 mL) of $LiOH \cdot H_2O$, (0.191 g, 4.54 mmol) was added to the complex ligand, $[NiH_6L(H_2O)_2]$, (1.0 g, 1.13 mmol) suspended in (30 mL) ethanol. The solution was stirred till complete dissolution of the complex. An ethanolic solution (30 mL) of $Ce(NO_3)_3 \cdot 6H_2O$, (0.986 g, 2.270 mmol) was added and stirred for 10 h. A reddish-black precipitate was obtained by filtration, washed with ethanol and ether, then air-dried. Yield 0.9 g (63%).

Analysis and Physical Measurements

Electronic spectra of the metal complexes as DMF solutions (10^{-3} M), in certain cases concentrated solutions, were also used. Reflectance spectra of some of the complexes were carried out using $BaSO_4$ discs. The different electronic spectra were recorded on Jasco 550 spectrophotometer. IR spectra of the 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 on a JEOL microwave unit, JES-FE_2XG 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 were measured by the Gouy method at room temperature using Model No. 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 mass spectrometer MS 5988 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 (ICP).

RESULTS AND DISCUSSION

Multinuclear hetero-metal complexes are of interest not only in elucidating the magnetic coupling between different metal ions and developing complex-based magnetic materials [29], but also as model compounds of active sites of multinuclear metalloenzymes [30]. Heterometal polynuclear complexes are still limited by the small number of known and fully characterized compounds and by the relative difficulty of synthesing such new compounds. Two synthetic strategies have been developed for the synthesis of heterometal complexes. One uses a polynucleating ligand providing inequivalent coordination environments for different metal ions [31–34], the other method utilizes "Complex Ligands" such as the ligands prepared in this study, which have available coordination sites for other metal ions [35–38]. This method is successful for the preparation of heteropolynuclear metal complexes in the present work.

The mononuclear Schiff-base complexes, $[MH_6L]$ (M = Ni(II) or Cu(II)) were synthesized by the addition of *o*-acetoacetylphenol to an ethanolic solution of the amine complexes, $[Ni(1,2pn)_2Cl_2]\cdot 3H_2O$ or $[Cu(1,2pn)_2]SO_4\cdot 2H_2O$. The homo- and hetero-, bi-, tri- and penta-nuclear complexes were obtained by reacting the complex ligands with metal chlorides or nitrates. Table I shows the analytical and physical data on the parent amine complexes, the complex ligands and their corresponding homo- and heterometal complexes. Table II shows the electronic spectral data, magnetic moments and molar conductivities of the different types of homo- and heterometal complexes obtained in this study.

Characterization of the Complex Ligands

Elemental analysis, IR, electronic and ESR spectra and magnetic moments indicated that the reaction of the amine complexes with *o*-acetoacetylphenol yielded the complex ligands, $[NiH_6L(H_2O)_2]$ and $[CuH_6L]$.

IR spectra of the amine complexes, Fig. 1, show the appearance of the NH_2 stretching vibrations at 3200–3330 cm^{-1} and NH_2 degenerate deformation (scissor) at 1640–1650 cm^{-1}. The stretching vibrations of the SO_4 group in the complex ligand $[Cu(1,2pn)_2]SO_4\cdot H_2O$ which disappeared after the condensation appeared at 980 cm^{-1} (ν_1, vw), 1120 cm^{-1} (ν_3, vs) and 613 cm^{-1} (ν_4, s) which are characteristic of the ionic sulfate group [39]. New bands appeared in the spectra of the complex ligand at 1615–1620 cm^{-1} attributed to the stretching vibration of the azomethine group, ν(C=N). In addition a band appeared at 870–885 cm^{-1} which is assigned to the α-substituted phenyl ring as shown in Fig. 1. The complex ligands could be represented in both the keto- and enol-forms, Fig. 2, thus their IR spectra showed bands at 1510–1515 cm^{-1} attributed to the νC$\overset{...}{=}$N group from conjugation in the enol-form, Fig. 3. The vibrational band of one ketonic νC=O group appears at lower frequency, 1590 cm^{-1}, due to its conjugation with νC=C bond which could be represented as a C$\overset{...}{=}$O group, Fig. 3. The N–H absorption appears as a broad and medium band at 3190 cm^{-1} due to hydrogen bonding. The phenolic and enolic OH groups and water molecule vibrations appear as a broad band at 3410–3480 cm^{-1}. Two bands at 1350 and 1230–1250 cm^{-1} are attributed to phenolic δ(OH) and ν(C–O), respectively.

Electronic and ESR Spectra and Magnetic Moments of the Complex Ligands

The electronic spectra and the magnetic moments of the complex ligands and their parent amine complexes are shown in Table II. The complex ligands showed bands at 300–380 nm, assigned to $\pi \rightarrow \pi^*$ transitions of the aromatic rings overlapping with absorptions due to the carbonyl and azomethine groups.

Two different geometries of the complex ligands $[NiH_6L(H_2O)_2]$ and $[CuH_6L]$ were suggested. The complex ligand $[NiH_6L(H_2O)_2]$ showed bands at 405 and 632 nm in its reflectance spectrum which correspond to the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ electronic transitions, respectively, and its magnetic moment is 2.63 M.B. which indicates that the complex ligand has octahedral geometry [40]. The low value of the magnetic moment of this complex would be due to the presence of a small percent of molecules with square-planar geometry. The complex ligand $[CuH_6L]$ showed bands at 625 and 448 nm indicative of a square-planar slightly distorted towards tetrahedral

TABLE I Analytical and physical data of complex ligands and their homo- and hetero-nuclear metal complexes

No.	*Reactions*	*Complexes*	*Yield (%)*	*Color*	*m.p.* (°C)	*Elemental Analysis, % Found (Calc.)*					
						C	*H*	*N*	*Ni/Cu*	*M′*	*Cl/S*
1	$NiCl_2 \cdot 6H_2O + (1,2\text{-pn})$ 1 : 2	$[Ni(1,2\text{-pn})_2Cl_2] \cdot 3H_2O$ $C_6H_{26}N_4Cl_2NiO_3$ 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	$[Ni(1,2\text{-pn})_2Cl_2] +$ *o*-acetoacetylphenol (1 : 4)	$[NiH_6L(H_2O)_2]$ $C_{46}H_{54}N_4O_{10}Ni$ Complex ligand	24.0	Green	215	62.4 (62.7)	5.9 (6.2)	6.5 (6.4)	6.7 (6.7)	–	–
3	$[NiH_6L(H_2O)_2] + NiCl_2 \cdot 6H_2O$	$[(NiL)Ni_4(H_2O)_{10}]Cl_2$ $C_{46}H_{64}N_4O_{18}Ni_5Cl_2$	50.0	Green	> 270	41.1 (41.6)	4.7 (4.9)	4.5 (4.2)	21.8 (22.1)	–	5.6 (5.3)
4	$[NiH_6L(H_2O)_2] + CuCl_2 \cdot 2H_2O$	$[(NiH_4L)Cu(H_2O)_2] \cdot 4H_2O$ $C_{46}H_{60}N_4O_{14}NiCu$	35.0	Green	> 270	54.7 (54.4)	5.4 (5.8)	5.6 (5.5)	5.9 (5.8)	6.4 (6.3)	–
5	$[NiH_6L(H_2O)_2] + MnCl_2 \cdot 4H_2O$	$[(NiH_2L)Mn_2(H_2O)_6] \cdot 2H_2O$ $C_{46}H_{62}N_4O_{16}NiMn_2$	48.0	Brown	> 270	50.3 (50.4)	5.4 (5.7)	5.3 (5.1)	5.5 (5.4)	9.7 (10.0)	–
6	$[NiH_6L(H_2O)_2] + FeCl_3 \cdot 6H_2O$	$[(NiL)Fe_2(H_2O)_6] \cdot 4H_2O$ $C_{46}H_{64}N_4O_{18}NiFe$	32.0	Reddish-brown	219	49.1 (48.8)	5.5 (5.7)	5.1 (4.9)	5.4 (5.2)	9.5 (9.9)	–
7	$[NiH_6L(H_2O)_2] + CoCl_2 \cdot 6H_2O$	$[(NiH_2L)CO_2(H_2O)_2] \cdot 6H_2O$ $C_{46}H_{62}N_4O_{16}NiCo_2$	62.0	Greenish-brown	180	49.4 (50.1)	5.9 (5.7)	5.2 (5.1)	5.5 (5.3)	10.2 (10.7)	–
8	$[NiH_6L(H_2O)_2] + Ce(NO_3)_3 \cdot 6H_2O$	$[(NiH_2L)Ce_2(NO_3)_2(H_2O)_4]$ $C_{46}H_{54}N_6O_{18}NiCe_2$	63.0	Gray	> 270	42.5 (41.9)	3.8 (4.1)	6.7 (6.4)	4.9 (4.5)	– (21.3)	–
9	$[NiH_6L(H_2O)_2] + Th(NO_3)_4 \cdot 5H_2O$	$[(NiL)Th_2(H_2O)_2(NO_3)_2]$ $C_{46}H_{48}N_{16}O_{16}NiTh_2$	56.0	Yellowish-green	> 270	38.1 (37.7)	3.3 (3.3)	5.2 (5.7)	4.2 (4.0)	– (31.7)	–
10	$[NiH_6L(H_2O)_2] + ZnCl_2$	$[(NiH_2L)Zn_2(H_2O)_2] \cdot H_2O$ $C_{46}H_{52}N_4O_{11}NiZn_2$	79.0	Brownish-yellow	135	54.0 (53.8)	4.4 (5.1)	5.6 (5.5)	5.9 (5.7)	12.9 (12.7)	–

11	$CuSO_4 \cdot 5H_2O + (1,2\text{-pn})$ (1 : 2)	$[Cu(1,2\text{-pn})_2]SO_4 \cdot 2H_2O$ $C_{16}H_{24}N_4SO_6Cu$ amine complex	90	Blue	262	20.6 (20.9)	6.8 (7.0)	16.4 (16.3)	18.2 (18.5)	–	9.7 (9.3)
12	$[Cu(1,2\text{-pn})_2]SO_4 +$ o-acetoacetylphenol (1 : 4)	$[CuH_6L]$ $C_{46}H_{50}N_4O_8Cu$ Complex ligand	76.0	Green	195	64.7 (65.0)	5.6 (5.9)	6.7 (6.6)	7.6 (7.5)	–	–
13	$[CuH_6L] + NiCl_2 \cdot 6H_2O$	$[(CuL)Ni_4Cl_2(H_2O)6] \cdot 2H_2O$ $C_{46}H_{60}N_4O_{16}CuNi_4Cl_2$	53.0	Green	> 270	42.9 (42.6)	4.7 (4.7)	4.5 (4.3)	5.2 (4.9)	17.7 (18.1)	5.6 (5.5)
14	$[CuH_6L] + CuCl_2 \cdot 2H_2O$	$[(CuH_2L)Cu_2(H_2O)_4] \cdot 3H_2O$ $C_{46}H_{60}N_4O_{15}Cu_3$	84.0	Green	230	50.2 (50.2)	5.8 (5.5)	5.4 (5.1)	17.6 (17.3)	–	–
15	$[CuH_6L] + MnCl_2 \cdot 4H_2O$	$[(CuH_2L)Mn_2(H_2O)_4] \cdot 2H_2O$ $C_{46}H_{58}N_4O_{14}CuMn_2$	45.0	Green	225	51.9 (51.9)	5.7 (5.5)	5.5 (5.3)	6.4 (6.0)	10.8 (10.3)	–
16	$[CuH_6L] + FeCl_3 \cdot 6H_2O$	$[(CuL)Fe_2(H_2O)_4] \cdot 2H_2O$ $C_{46}H_{56}N_4O_{14}CuFe_2$	60.0	Reddish-brown	222	51.8 (51.9)	5.4 (5.3)	5.3 (5.3)	6.2 (6.0)	10.2 (10.5)	–
17	$[CuH_6L] + CoCl_2 \cdot 6H_2O$	$[(CuH_2L)Co_2] \cdot 6H_2O$ $C_{46}H_{58}N_4O_{14}CuCo_2$	30.0	Green	230	51.3 (51.5)	5.5 (5.5)	5.2 (5.2)	6.2 (5.9)	10.6 (11.0)	–
18	$[CuH_6L] + Ce(NO_3)_3 \cdot 6H_2O$	$[(CuH_2L)Ce_2(H_2O)_2(NO_3)_2]$ $C_{46}H_{50}N_4O_{16}CuCe_2$	93.0	Reddish-brown	> 270	42.4 (42.9)	4.1 (3.9)	6.6 (6.5)	4.6 (4.9)	– (21.8)	–
19	$[CuH_6L] + ZnCl_2$	$[(CuH_2L)Zn_2] \cdot 5H_2O$ $C_{46}H_{56}N_4O_{13}CuZn_2$	82.0	Green	205	51.9 (51.8)	5.4 (5.3)	5.4 (5.2)	6.3 (6.0)	12.4 (12.3)	–
20	$[CuH_6L] + UO_2(NO_3)_2 \cdot 6H_2O$	$[(CuH_3L)(UO_2)_2(C_2H_5OH)_2] \cdot NO_3$ $C_{50}H_{59}N_5O_{17}CuU_2$	56.0	Yellowish-brown	195	39.0 (38.9)	3.8 (3.9)	4.6 (4.5)	4.3 (4.1)	– (30.9)	–

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

No.	*Complexes*	*UV–Visible*[a] (nm) (ε)	*Magnetic Moments* (B.M.)		*Conductance* $\Omega^{-1}\,cm^2\,mol^{-1}$
			μ_{eff}	$\mu_{compl.}$[d]	
1	$[Ni(1,2\text{-}pn)_2Cl_2]\cdot 3H_2O$ amine complex	580	2.61	–	263.0
2	$[NiH_6L(H_2O)_2]$ complex ligand	493 (67), 556^b, 632^c 420 (267), 487^b, 405^c 380 (3222) 300 (2644)	2.63		8.0
3	$[(NiL)Ni_4(H_2O)_{10}]Cl_2$	450 (44), 629^b 363 (3289), 488^b 310 (2444)		5.4 (5.7)	157.0
4	$[(NiH_4L)Cu(H_2O)_2]\cdot 4H_2O$	635 (52), 513 (110)		4.1 (3.9)	10.0
5	$[(NiH_2L)Mn_2(H_2O)_6]\cdot 2H_2O$	628^c		9.1 (9.0)	18.0
6	$[(NiL)Fe_2(H_2O)_6]\cdot 4H_2O$	467 (4169), 625^c		8.4 (9.0)	7.0
7	$[(NiH_2L)Co_2(H_2O)_2]\cdot 6H_2O$	620 (285) 583 (285) 405 (3915)		6.0 (7.6)	8.0
8	$[(NiH_2L)Ce_2(NO_3)_2(H_2O)_4]$	452 (4400), 634^c		3.02 (4.8)	50.0
9	$[(NiL)Th_2(H_2O)_2(NO_3)_2]$	520^b		1.75	83.0
10	$[(NiH_2L)Zn_2(H_2O)_2]\cdot H_2O$	448 (194), 568^b, 633^c		3.21	13.0
11	$[Cu(1,2\text{-}pn)_2]SO_4\cdot 2H_2O$ amine complex	546^c	1.91	–	267.0
12	$[CuH_6L]$ complex ligand	625 (65), 448 (108)	1.77	–	8.27
13	$[(CuL)Ni_4Cl_2(H_2O)_6]\cdot 2H_2O$	533 (247), 714^b		3.63 (5.2)	36.0
14	$[(CuH_2L)Cu_2(H_2O)_4]\cdot 3H_2O$	648 (163), 631 (238) 484 (407)		2.30 (3.6)	6.0
15	$[(CuH_2L)Mn_2(H_2O)_4]\cdot 2H_2O$	621^c		5.95 (8.7)	6.0
16	$[(CuL)Fe_2(H_2O)_4]\cdot 2H_2O$	634^c		7.73 (8.7)	10.0
17	$[(CuH_2L)Co_2]\cdot 6H_2O$	700 (62), 585 (250)		8.2 (7.2)	12.0
18	$[(CuH_2L)Ce_2(H_2O)_2(NO_3)_2]$	634^c		3.08 (4.4)	48.0
19	$[(CuH_2L)Zn_2\cdot 5H_2O$	629 (198)		2.17	9.0
20	$[(CuH_3L)(UO_2)_2$ $(C_2H_5OH)_2]\cdot NO_3$	736 (18), 641 (228)		2.46	87.0

[a] In DMF (10^{-3} M);
[b] Concentrated solution;
[c] Reflectance spectrum;
[d] Found/(Expected): expected values were calculated on the basis of adding the commonly expected magnetic susceptibilities of the component metal cations.

geometry [41]. The magnetic moment of this complex ligand is 1.77 B.M. within the range for square-planar geometry. These results are also supported by TG– DTA analysis. Thus TGA and DTA data of the complex ligand $[CuH_6L]$ showed that it does not contain water molecules, while the complex ligand $[NiH_6L(H_2O)_2]$ contains two coordinated water molecules which were eliminated at 169°C. The weight loss is endothermic. The thermal data thus support the fact that the Ni(II) cation is hexacoordinate. On heating the complex ligand $[NiH_6L(H_2O)_2]$, at 170°C in an air oven, undergoes a reversible thermochromism transition from a green complex (octahedral, high spin, $\mu_{eff} = 2.63$ B.M.) to a red complex (square-planar, low spin, $\mu_{eff} = 0$). The reverse change of the thermal product (red) to the parent complex ligand (green) occurred after few minutes of adding water. The thermal product obtained by heating, was characterized by chemical analysis, IR and electronic spectra and magnetic moment measurement. The electronic spectrum of this thermal product exhibits a band at 450 nm, consistent with square-planar geometry. The diamagnetic

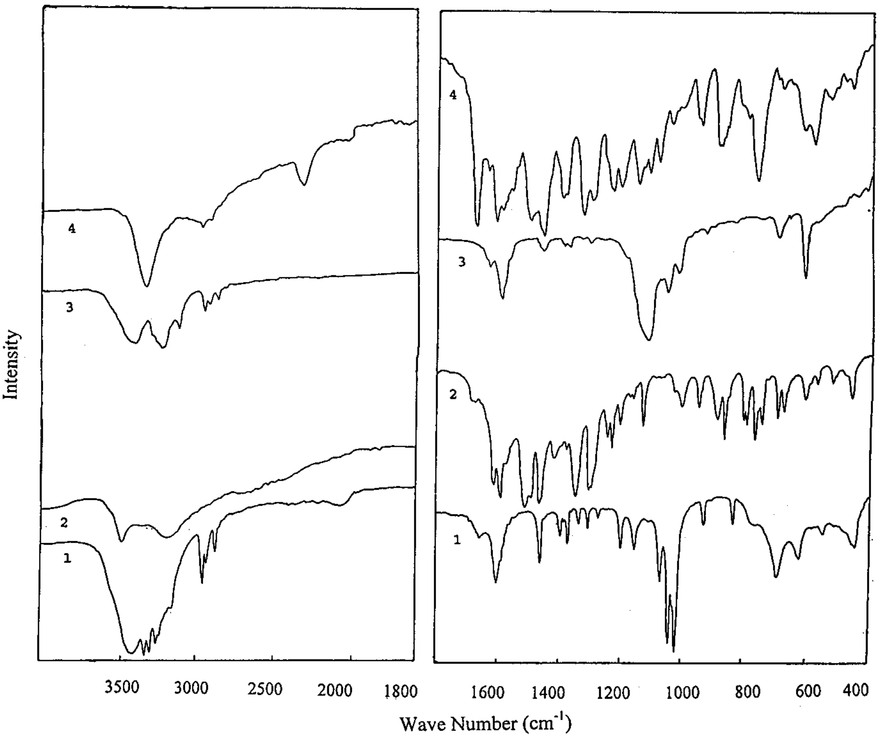


FIGURE 1 IR Spectra of 1 [Ni(1,2-pn)$_2$Cl$_2$]$\cdot$3H$_2$O, 2 [NiH$_6$*L*(H$_2$O)$_2$], 3 [Cu(1,2-pn)$_2$]SO$_4\cdot$2H$_2$O and 4 [CuH$_6$*L*].

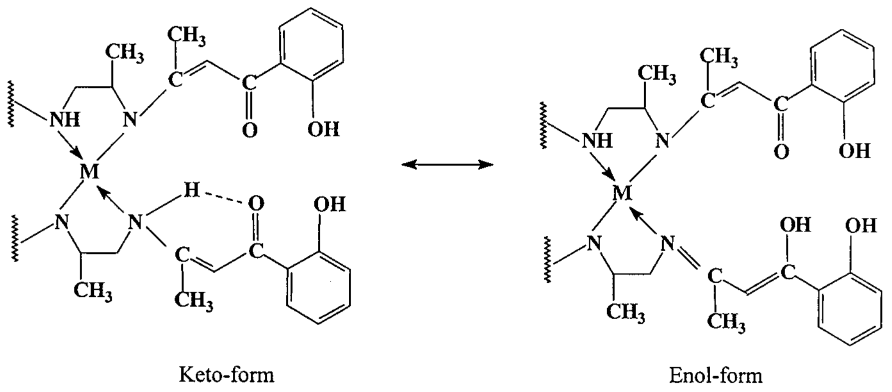


FIGURE 2 Keto-enol tautomers of the complex ligands [MH$_6$*L*] (The right-hand side of the complex ligand is only shown in this figure).

behavior for the obtained thermal product at room temperature, corresponds to a configurational change from octahedral to square-planar geometry.

The ESR spectrum of the crystalline copper complex ligand [CuH$_6$*L*] recorded at room temperature, Fig. 4, shows one broad signal with $g_{eff} = 1.82$ in the powder form and is consistent with a square-planar geometry distorted towards tetrahedral.

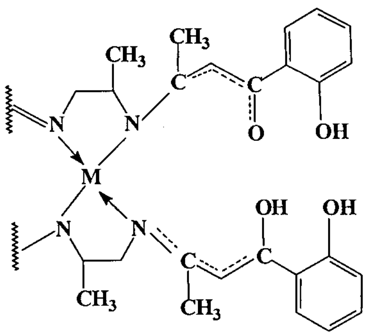


FIGURE 3 Conjugation occurring in the enol-form.

Mass Spectra of the Complex Ligand

The mass spectrum of the complex ligand [CuH_6L], Fig. 5 shows that the parent peak at $m/e = 850$ which compares well with its calculated formula weight (850).

Conductance of the Parent Amine Complexes and their Complex Ligands

The solutions of the parent amine complexes showed high values of electrical conductance (Table II), consistent with the Cu(II) complex having an ionic sulfate group. Its IR spectrum and magnetic moment (1.91 B.M.) also agree with square-planar geometry for the $[Cu(1,2pn)_2]^{2+}$ cation. However, the Ni(II) complex is expected to be octahedral with two chloride ions coordinated to the metal cation. This was indicated from the value of its magnetic moment (2.61 B.M.) and its visible spectral band at 580 nm due to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ electronic transition. Its conductance would thus be due to the replacement of the chloride ions by the DMF solvent molecules. Solutions of the complex ligands are non-conducting consistent with their proposed molecular structures (Scheme 1).

Homo- and Heteronuclear Metal Complexes

The complex ligands $[NiH_6L(H_2O)_2]$ and $[CuH_6L]$ contain two tetradentate O_4 coordination 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 homo- and heteronuclear metal complexes were prepared.

The elemental analysis of the metal complexes, Table I, are consistent with the proposed molecular formulas, $[(NiH_4L)Cu(H_2O)_2]\cdot 4H_2O$, $[(MH_2L)M'(H_2O)_4]$, $[(MH_2L)M'_2(H_2O)_6]$, $[(ML)M'_4(H_2O)_8]Cl_2$, $[(MH_2L)Ce_2(NO_3)_2(H_2O)_2]$ and $[(NiL)Th_2(NO_3)_2(H_2O)_2]$ (M = Ni or Cu; M' = Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ce(III), Th(IV) and UO_2(VI)).

IR Spectra

The IR spectra of the homo- and heteronuclear complexes show a shift of the $\nu C{=}O$ of the ketonic groups to lower frequencies by 5–15 cm^{-1}. This confirms that the chelation

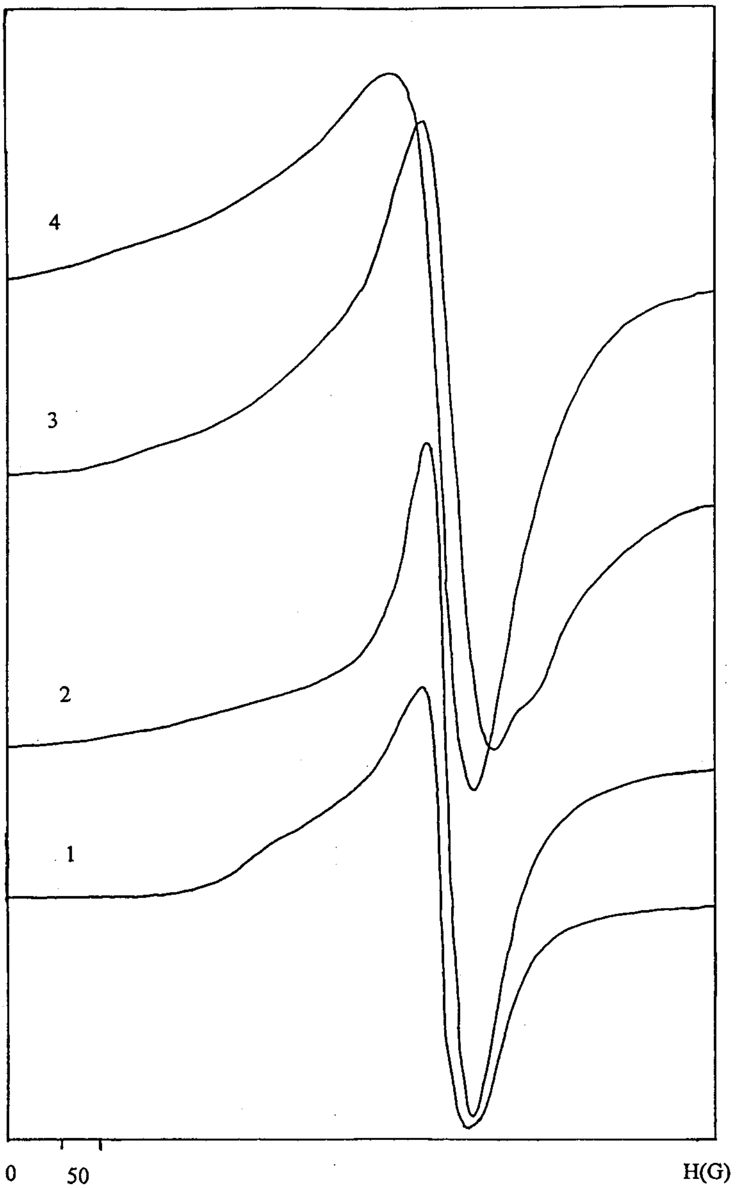


FIGURE 4 ESR powder Spectra; X-bands of the 1 the parent amine complex, $[Cu(1,2pn)_2]SO_4 \cdot 2H_2O$, (complex **11**); 2 the complex ligand $[CuH_6L]$, (complex **12**) 3 the homotrinuclear $[(CuH_2L)Cu_2(H_2O)_4] \cdot 3H_2O$, (complex **14**) and 4 the heterotrinuclear complex, $[(CuH_2L)Co_2] \cdot 6H_2O$, (complex **17**).

of the newly introduced metal ions is through the two oxygen atoms of the ketonic and the phenolic groups, O_4 sites, Fig. 6. The appearance of new bands around 1380–1435 cm^{-1} in the IR spectra of the nitrato complexes confirm the monodentate linkage of this group [39]. The IR spectra of the UO_2(VI), complex **20**, shows a strong absorption band at 910 cm^{-1} which is assigned to the antisymmetric $\nu_3(O{=}U{=}O)$ vibration. The IR spectra of most of the complexes showed a broad band at 3320–3460 cm^{-1}

assigned to ν(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} are attributed to $\delta(H_2O)$ and $\rho(H_2O)$, respectively, and suggest the presence of water molecules coordinated to the metal ions [39].

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

The concentrated DMF solution of the homopentanuclear Ni(II) complex, $[NiLNi_4(H_2O)_{10}]Cl_2$, complex **3**, shows bands at 450, 488 and 629 nm. The band at 629 nm is similar to that of the complex ligand, $[NiH_6L(H_2O)_2]$, at 632 nm indicating that the central Ni(II) cation is coordinated to N_4 sites in an octahedral geometry and corresponds to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ electronic transition. The band at 450 nm would be due to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ electronic transition. The latter two bands would

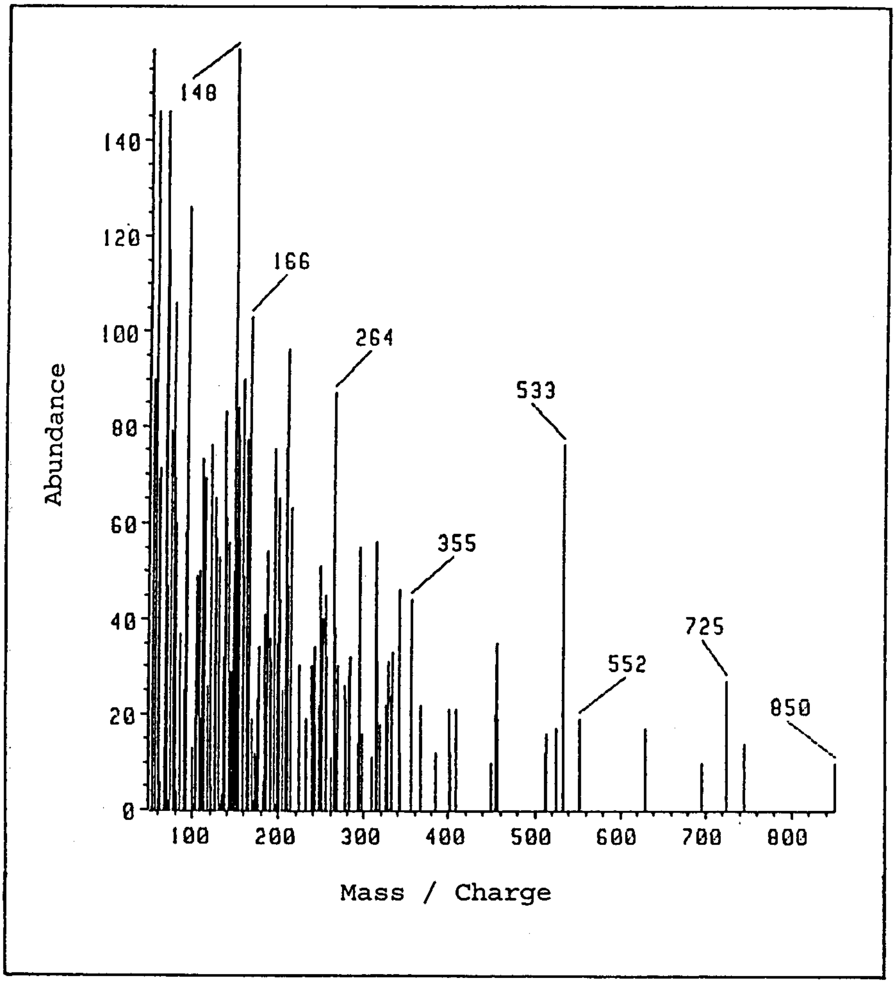
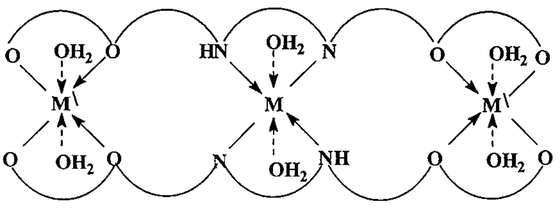


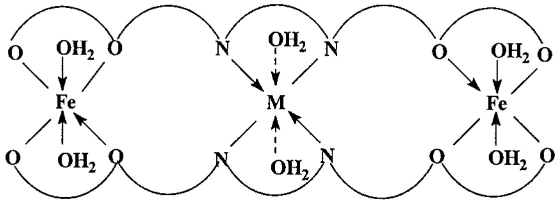
FIGURE 5 Mass Spectrum of the Complex Ligand $[CuH_6L]$.

also overlap with absorptions of both Ni(II) ions which are coordinated to O_4 sites in octahedral geometry. The band at 488 nm would be due to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition which indicate that the two middle Ni(II) cations have a square-planar geometry. The magnetic moment supports these geometries where the magnetic moment of the complex is 5.4 B.M. as expected for three Ni(II) cations in octahedral geometry. The visible spectrum of the heteronuclear complex, $[(NiH_4L)Cu(II)(H_2O)_2] \cdot 4H_2O$, complex **4**, shows bands at 635 and 513 nm, due to the absorptions of both Ni(II) and Cu(II), respectively, and indicate that the geometries around the Ni(II) and Cu(II) cations are octahedral and square-planar, respectively. The magnetic moment of the complex, 4.1 B.M., supports this suggestion. The visible spectrum of the homotrinuclear Cu(II) complex, $[(CuH_2L)Cu_2(H_2O)_4] \cdot 3H_2O$, **14**, shows bands at 631 and 684 nm. The former band is attributed to the distorted square-planar geometry around the central Cu(II) ion coordinated to the N_4 sites and is similar to that of the complex ligand



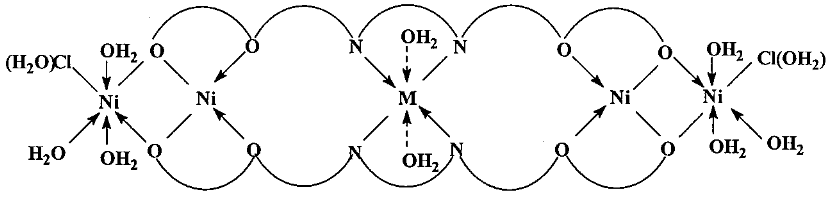
M = Ni(II) or Cu(II), M′= Co(II), Ni(II) and Cu(II)

(A)



M = Ni(II) or Cu(II)

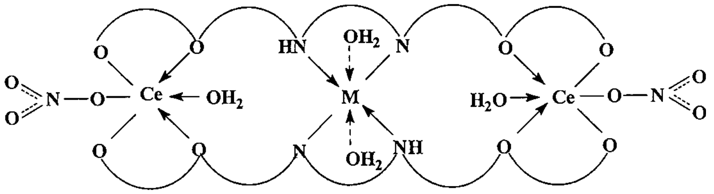
(B)



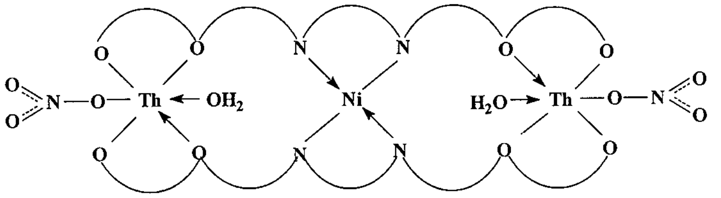
M = Ni(II) or Cu(II)

(C)

FIGURE 6 The proposed structures of homo- and heteronuclear metal complexes (Dotted arrows indicate probable coordination of water molecules to the metal cation).



M = Ni(II) or Cu(II)



(D)

FIGURE 6 (continued)

[CuH_6L]. The latter band would be due to the outer Cu(II) ions which would have octahedral geometry and linked to O_4 sites. ESR spectrum of this complex, Fig. 6, has a signal at $g = 1.82$ which coincides with both the square-planar and distorted octahedral geometries of the central and terminal Cu(II) cations, respectively. The visible spectrum of the heteropentanuclear complex **13**, [$CuLNi_4Cl_2(H_2O)_6$] · $2H_2O$ shows bands at 714 and 533 nm. The band at 714 nm would be due to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ electronic transition of the outer two Ni(II) ions in octahedral geometry and overlaps with the transition of the Cu(II) cation while its geometry would be distorted towards tetrahedral and the band at 533 nm would be due to the electronic transition of the two middle Ni(II) ions in square-planar geometry. The magnetic moments of the latter two homo- and heteronuclear complexes suggest antiferromagnetic interactions between the central Cu(II) cation and the incoming Cu(II) or Ni(II) cations.

The visible spectra of the heterotrinuclear Ni(II)–Co(II) and Cu(II)–Co(II) complexes, [(NiH_2L)$Co_2(H_2O)_2$] · $6H_2O$, **7**, and [(CuH_2L)Co_2] · $6H_2O$, **17**, show bands at 620, 583 and 700, 585 nm, respectively. The band at 620 ($\varepsilon = 285$) nm would be due to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ electronic transition of the Ni(II) ion in octahedral geometry while the band at 700 nm indicates that the Cu(II) cation is tetrahedral and coordinated to N_4 sites. The bands at 583 ($\varepsilon = 285$) and 585 ($\varepsilon = 250$) nm are attributed to Co(II) cations in tetrahedral geometries. It was well known that the electronic spectra in octahedral Co(II) complexes, which are usually high spin, have a weak band ($\varepsilon < 10$) near 500 nm while for tetrahedral complexes a much stronger band ($\varepsilon > 100$) at 600–700 nm is expected [42]. The magnetic moments of these two complexes (Table II) support these geometries and showed slightly antiferromagnetic interactions between adjacent metal cations in the former complex. An ESR spectrum of complex **17**, Fig. 6, shows two bands with g values = 1.82 and 1.80, where the first band corresponds to the Cu(II) ion, similar to the g-value observed for the mononuclear complex ligand, [CuH_6L], and the other would be due to the Co(II) ion.

The spectrum of the heterotrinuclear complex, $[CuH_3L(UO_2)_2(C_2H_5OH)_2]NO_3$, **20**, shows a band at 641 nm ($\varepsilon = 228$) due to the absorption of the Cu(II) cation. However, the increase of the wavelength and the higher magnetic moment (2.46 B.M.) would be interpreted as due to distortion of the square-plane towards the tetrahedral geometry from the larger UO_2(VI) cation. This observation was reported in the literature for Cu(II)–UO_2(VI) or Ni(II)–UO_2(VI) complexes of similar Schiff-basis [43].

The visible spectra of the Ni(II)–Mn(II) and Cu(II)–Mn(II) complexes **5** and **15** show bands at 628 and 621 nm, respectively, similar to those of the parent complex ligands, $[NiH_6L(H_2O)_2]$ and $[CuH_6L]$, and are attributed to the transition energy of the Ni(II) and Cu(II) cations, respectively, while the transitions due to the Mn(II) ion, d^5, are spin-forbidden. The magnetic moment of the former complex 9.1 B.M., agrees well with the expected value (9.0 B.M.) for Ni(II)–2Mn(II), while the magnetic moment of the latter complex 5.95 B.M. is lower than expected (8.7 B.M.) for Cu(II)–2Mn(II) due to antiferromagnetic interactions between metal cations.

The visible spectra of the Ni(II)–Fe(III) and Cu(II)–Fe(III) complexes **6** and **16** show charge transfer bands in their DMF solutions. Complex **6**, $[(NiL)Fe_2(H_2O)_6] \cdot 4H_2O$, shows a charge transfer band in its DMF solution due to the Fe(III) cation at 467 nm ($\varepsilon = 4169$) thus masking the Ni(II) absorption at 493 nm. The visible spectra of the two complexes show bands at 625 and 634 nm in their reflectance spectra, respectively, similar to those observed for their complex ligands, $[NiH_6L(H_2O)_2]$ and $[CuH_6L]$. The magnetic moments of the complexes suggest slightly antiferromagnetic interactions.

The visible spectra of the Ni(II)–Ce(III), Cu(II)–Ce(III), Ni(II)–Zn(II), Cu(II)–Zn(II), complexes **8**, **18**, **10** and **19**, respectively, show a band in their reflectance spectra (Table II), due to *d-d* transition of the Ni(II) and Cu(II) cations and are similar to those observed in the spectra or the corresponding complex ligands. This indicates that each Ni(II) and Cu(II) cation has the same geometry in the heteronuclear complexes. The magnetic moments of the former two complexes suggest antiferromagnetic interactions between adjacent metal cations. As Zn(II) is diamagnetic, the magnetic moments of the two latter complexes 3.21 and 2.17 B.M. are due to the Ni(II) and Cu(II) cations, respectively, and indicate octahedral geometry for the Ni(II) ion and tetrahedral geometry for the Cu(II) ion.

The visible spectrum of the heteronuclear complex **9**, $[(NiL)Th_2(NO_3)_2(H_2O)_2]$ shows a band at 520 nm due to the *d–d* transition of the Ni(II) ion in square-planar geometry. The magnetic moment of the complex is 1.75 B.M. which indicates a partial change of the geometry of the central Ni(II) cation from octahedral towards square-planar due to the introduction of the large Th(IV) ion.

The number of cations added to the complex ligands, $[NiH_6L(H_2O)_2]$ or $[CuH_6L]$ differs from one to four in an unpredictable manner. Thus, complex **4** added only one Cu(II) ion in addition to the central Ni(II) ion. Complexes **5–10** and **14–20** added only two outer cations, while complexes **3** and **13** added four outer cations.

Conductance of the Homo- and Heteronuclear Metal Complexes

Homo- and heteronuclear metal complexes are non-conducting except complexes **3** and **20** which showed molar conductance 157.0 and 87.0 $\Omega^{-1}\,cm^{-2}\,mol^{-1}$, respectively, and indicate that these complexes are 2 : 1 and 1 : 1 electrolytes [44], respectively. The other complexes **8**, **9**, **13** and **18** which contain coordinated chloride or nitrate ions show a certain degree of conductivity which would be due to the replacement of these coordinated ions by DMF solvent molecules.

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