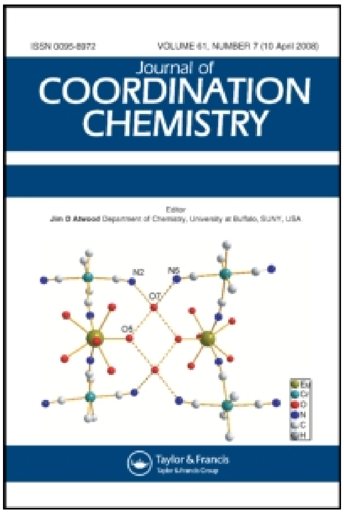

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CHROMOTROPIC CHANGES OF Cu(II) AND Ni(II) COMPLEXES WITH N_2O_2 AND N_3O_2 SCHIFF-BASE LIGANDS IN THE SOLID PHASE

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CHROMOTROPIC CHANGES OF Cu(II) AND Ni(II) COMPLEXES WITH N_2O_2 AND N_3O_2 SCHIFF-BASE LIGANDS IN THE SOLID PHASE

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Four new Schiff-base ligands have been prepared from the condensation of 3-formyl-4-hydroxy-1,8-naphthyridin-2-one with different diamines and a triamine, H_2L_a–H_2L_d. Two series of Ni(II) and Cu(II) complexes with the four ligands were also prepared. The ligands and their metal complexes were characterized by chemical analyses, IR, Far-IR, electronic, ESR and mass spectra as well as magnetic measurements and X-ray diffraction patterns.

Different products for Ni(II) and Cu(II) were obtained in similar reactions with the same metal salt, depending on the nature of the ligand. Different geometries were also obtained depending on the counter anion of metal salt. Thus, violet square-planar Cu(II) complexes were obtained with $Cu(OAc)_2 \cdot H_2O$ and green octahedral ones with $CuCl_2 \cdot 2H_2O$, except the reaction with ligand H_2L_d which gave only an octahedral product whether the anion was acetate, chloride or perchlorate. Electronic and ESR spectra were used to differentiate between the two geometries of the Cu(II) complexes. The green octahedral Cu(II) complexes undergo irreversible thermochromism to the violet square-planar complexes except the copper complex of the ligand H_2L_d which did not not show any color change and retained its octahedral geometry. Based on the magnetic moments and thermal analyses, only one Ni(II) complex of the Schiff-base ligand H_2L_c undergoes reversible thermochromism from green (octahedral) to red (square-planar). The reverse change of the thermal product (red) to the parent complex (green) proceeded on exposure to atmospheric air for a few minutes. On the other hand, Ni(II) complexes of ligands H_2L_a and H_2L_b have stable square-planar geometry and all efforts to add other ligands such as H_2O or pyridine to these complexes failed to yield other products. The corresponding Cu(II) complexes were easily transformed to their octahedral geometry by adding H_2O or pyridine and heating.

Keywords: Chromotropic changes of Cu(II) and Ni(II) complexes;
polydentate Schiff-base ligands

INTRODUCTION

Nickel(II) and Cu(II) complexes provide many examples of thermochromism in the solid phase, which is attributed to changes in their coordination geometry.[1-5] In these complexes, small differences in the electronic properties and steric requirements of the ligand are reflected in the structures that they prefer when heated or cooled. However, systematic knowledge is still lacking as to the factors that decide the preference for certain coordination geometries at different temperatures.

Thermochromic changes of Ni(II) complexes are classified into the following five kinds of isomeric transformations according to their origins:[6] dimer to monomer,[7] square-planar to distorted square-planar,[8] tetragonally distorted octahedral to distorted tetrahedral,[9] octahedral to tetrahedral[10] and square-planar to tetrahedral.[11,12] The isomeric transformation of square-planar to octahedral nickel(II) complexes of substituted ethylenediamines has been previously studied.[13-15] The ease and mode of structural changes observed in these complexes are strongly dependent on the nature and position of the substituent groups in the diamines.

In this work, the 1,8-naphthpyridine nucleus was selected because it is useful in pharmaceutical activities.[16,17] Four Schiff-base ligands were prepared by condensing 3-formyl-4-hydroxy-1,8-naphthpyridin-2-one with different diamines and a triamine, H_2L_a–H_2L_d. The mononuclear Ni(II) and Cu(II) complexes of these Schiff-base ligands were prepared and characterized by chemical analyses, electronic and ESR spectra, magnetic moment measurements and X-ray diffraction patterns.

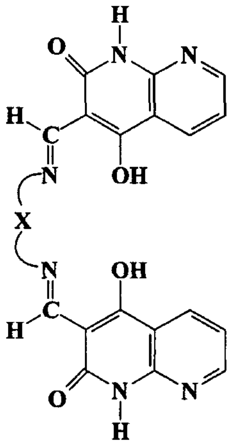
EXPERIMENTAL

Materials

Metal salts, 2-aminopyridine, diethylmalonate, phosphorous oxychloride, 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane and N-(2-aminoethyl)-1,3-propanediamine and DMF were Merck chemicals. Organic solvents were reagent grade and 1,2-diaminoethane and ethanol were distilled before use.

Preparation of the Schiff-Base Ligands

New series of Schiff-base ligands H_2L_a, H_2L_b, H_2L_c and H_2L_d (Figure 1) were prepared by refluxing 3-formyl-4-hydroxy-1,8-naphthpyridin-2-one[18]



X	Ligand
CH_2CH_2	H_2L_a
$\underset{CH_3}{CHCH_2}$	H_2L_b
$CH_2CH_2CH_2$	H_2L_c
$CH_2CH_2\underset{H}{N}CH_2CH_2CH_2$	H_2L_d

FIGURE 1 Structures of the Schiff-base ligands.

and the corresponding diamine, 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane and N-(2-aminoethyl)-1,3-propanediamine, respectively, in ethanol, in the molar ratio 2 : 1 for 4 h. The yellow precipitates were obtained by filtration. The crude ligands were recrystallized from dimethylformamide (DMF) and stored in a desiccator over calcium chloride. The purity of the ligands were established from elemental analyses and mass spectra. Analysis for H_2L_a, $C_{20}H_{16}N_6O_4$, Calc.: C, 59.4; H, 4.0; N, 20.8; *m/e*, 404.4; Found: C, 59.2; H, 3.9; N, 20.8; *m/e*, 404; m.p., 260°C; Yield, 95%; for H_2L_b, $C_{21}H_{18}N_6O_4$, Calc.: C, 60.4; H, 4.3; N, 20.1; *m/e*, 417.4; Found: C, 60.6; H, 4.5; N, 20.0; *m/e*, 417; m.p., 245°C; Yield, 75% ; for H_2L_c, $C_{21}H_{18}N_6O_4$, Calc.: C, 60.4; H, 4.3; N, 20.1; *m/e*, 417.4; Found: C, 60.4; H, 4.3; N, 20.2; *m/e*, 417; m.p., 265°C; Yield, 71% and for H_2L_d, $C_{23}H_{23}N_7O_4$, Calc.: C, 59.9; H, 5.0; N, 21.2; *m/e*, 461.5; Found: C, 59.9; H, 5.1; N, 21.0; *m/e*, 461; m.p., 217°C; Yield, 79%.

Preparation of the Metal Complexes

A solution of nickel(II) or copper(II) acetate, chloride or perchlorate in 30 mL ethanol was added to the corresponding ligand suspended in 40 mL ethanol in the molar ratio 1 : 1 and the solutions were refluxed for 3 h. The solid-metal complexes were precipitated hot, then allowed to cool and collected by filtration, washed with ethanol, ether and finally air-dried. The complexes were insoluble in water and common solvents except the copper complex of the ligand H_2L_d which is soluble in DMF and thus enabled its solution visible spectrum to be determined.

The following detailed preparation of $[L_cNi(OH_2)_2]\cdot 4H_2O$ is given as an example, however, other metal complexes were prepared similarly.

A solution of 1.78 g (7.18 mmol) of $Ni(OAc)_2\cdot 4H_2O$ in 40 mL methanol was added to 3.0 g (7.18 mmol) of ligand H_2L_c suspended in 40 mL methanol. The solution was refluxed for 3 h where a red precipitate appeared. The solution was allowed to cool to room temperature. The red solid product was obtained by filtration, washed with methanol then ether and finally air-dried. The red product changed to green on exposure to air.

Reactions carried out, elemental analyses and physical properties are cited in Table I. Table II shows electronic spectral data and magnetic moments of the metal complexes.

Physical Measurements

IR spectra were recorded on a Perkin-Elmer IR 598 spectrometer (4000–200 cm^{-1}) using KBr discs and polystyrene as a calibrant. Far-IR spectra (650–50 cm^{-1}) were recorded with a Nicolet 20 FFT_1 spectrometer using polyethylene platelets. Electronic spectra of the metal complexes, as Nujol mulls or in DMF solution were recorded on a Perkin-Elmer 555 spectrophotometer. Mass spectra of the four ligands and representative complexes were recorded on a Hewlett-Packard mass spectrometer model MS-5988. The fragmentation was carried out at 300°C and 70 eV. 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 using mercury(II) tetrathiocyanatocobaltate(II) as a calibrant. The effective magnetic moments were calculated from the expression $\mu_{eff} = 2.828\ (\chi_M \cdot T)^{1/2}$ BM, where χ_M is the molar susceptibility. Diamagnetic corrections were calculated from Pascal's constants for all atoms in the compounds. TGA, DTG and DTA measurements were carried out on a Shimadzu-50 thermal analyzer. ESR spectra of the copper(II) complexes were recorded for polycrystalline samples at room temperature 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. X-ray powder diffraction patterns of the ligands and their Cu(II) complexes were recorded on a Philips P M 8203 diffractometer using CuKα radiation and Ni filter.

Microanalyses of carbon, hydrogen and nitrogen were carried out at the Microanalytical Centre, Cairo University, Giza, Egypt. Analyses of the copper and nickel in the complexes followed the dissolution of the solid

TABLE I Elemental analysis and physical properties of the Ni(II) and Cu(II) metal complexes

Reactions	*Metal complexes*	*Yield %*	*Color*	*m.p.* (°C)	*Elemental analyses found* (*Calcd.*)			
					C	*H*	*N*	*M*
1. $H_2L_a + Ni(OAc)_2 \cdot 4H_2O$	$[L_aNi]$ ($C_{20}H_{14}N_6O_4Ni$)	73	Orange	> 300	52.2 (52.1)	3.3 (3.1)	18.1 (18.2)	12.4 (12.7)
2. $H_2L_b + Ni(OAc)_2 \cdot 4H_2O$	$[L_bNi]$ ($C_{21}H_{16}N_6O_4Ni$)	78	Orange	> 300	53.3 (53.1)	3.2 (3.4)	17.7 (17.7)	12.3 (12.4)
3. $H_2L_c + Ni(OAc)_2 \cdot 4H_2O$	$[L_cNi(OH_2)_2] \cdot 4H_2O$ ($C_{21}H_{28}N_6O_{10}Ni$)	90	Green	> 300, at 150°C changes to red	43.2 (43.3)	4.6 (4.8)	14.3 (14.4)	10.2 (10.1)
4. Thermal product of complex 3, $[L_cNi(OH_2)_2] \cdot 4H_2O$	$[L_cNi] \cdot \frac{1}{2}H_2O$ ($C_{21}H_{17}N_6O_{4\frac{1}{2}}Ni$)	86	Red	> 300	52.1 (52.1)	3.6 (3.5)	17.2 (17.4)	12.3 (12.1)
5. $H_2L_d + Ni(OAc)_2 \cdot 4H_2O$	$[L_dNi(OH_2)] \cdot 3H_2O$ ($C_{23}H_{29}N_7O_8Ni$)	80	Green	> 300, at 210°C changes to red	46.8 (46.8)	5.2 (5.0)	16.6 (16.6)	9.9 (10.0)
6. $H_2L_a + Cu(OAc)_2 \cdot H_2O$	$[L_aCu] \cdot 1\frac{1}{2}H_2O$ ($C_{20}H_{17}N_6O_{5\frac{1}{2}}Cu$)	71	Brownish violet	> 300	48.9 (48.7)	3.5 (3.5)	16.8 (17.0)	12.9 (12.9)
7. $H_2L_a + CuCl_2 \cdot 2H_2O$	$[L_aCu(OH_2)_2] \cdot 3\frac{1}{2}H_2O$ ($C_{20}H_{25}N_6O_{9\frac{1}{2}}Cu$)	63	Green	270, at 180°C changes to brownish violet	42.5 (42.5)	4.4 (4.5)	15.1 (14.9)	11.2 (11.2)
8. Thermal product of complex 7, $[L_aCu(OH_2)_2] \cdot 3\frac{1}{2}H_2O$	$[L_aCu]$ · ($C_{20}H_{14}N_6O_4Cu$)	85	Brownish violet	> 300	51.5 (51.6)	3.1 (3.0)	18.2 (18.0)	13.3 (13.5)
9. $H_2L_b + Cu(OAc)_2 \cdot H_2O$	$[L_bCu]$ ($C_{21}H_{16}N_6O_4Cu$)	77	Violet	> 300	52.6 (52.6)	3.3 (3.4)	17.3 (17.5)	13.3 (13.2)
10. $H_2L_b + CuCl_2 \cdot 2H_2O$	$[L_bCu(OH_2)_2] \cdot 3\frac{1}{2}H_2O$ ($C_{21}H_{27}N_6O_{9\frac{1}{2}}Cu$)	88	Green	247, at 190°C changes to brownish violet	43.6 (43.6)	4.8 (4.7)	14.3 (14.5)	11.2 (11.0)
11. $H_2L_c + Cu(OAc)_2 \cdot H_2O$	$[L_cCu] \cdot \frac{1}{2}H_2O$ ($C_{21}H_{17}N_6O_{4\frac{1}{2}}Cu$)	85	Bluish violet	> 300	51.3 (51.6)	3.4 (3.5)	17.1 (17.2)	13.2 (13.0)
12. $H_2L_c + CuCl_2 \cdot 2H_2O$	$[L_cCu(OH_2)_2] \cdot 6H_2O$ ($C_{21}H_{32}N_6O_{12}Cu$)	92	Green	215, at 140°C changes to bluish violet	40.3 (40.4)	5.2 (5.2)	13.8 (13.5)	10.3 (10.2)
13. $H_2L_d + Cu(OAc)_2 \cdot H_2O$	$[L_dCu(OH_2)] \cdot 4\frac{1}{2}H_2O$ $C_{23}H_{32}N_7O_{9\frac{1}{2}}Cu$	79	Green	195	44.2 (44.4)	4.9 (5.2)	15.8 (15.8)	10.2 (10.2)

TABLE II Visible spectra and magnetic moments of the Ni(II) and Cu(II) complexes

Metal complexes	*Visible spectra* (nm)	μ_{eff} (BM)
1. $[L_aNi]$	530	Diamagnetic
2. $[L_bNi]$	535	Diamagnetic
3. $[L_cNi(OH_2)_2]\cdot 4H_2O$	610, 355	2.95
4. $[L_cNi]$*	510	Diamagnetic
5. $[L_dNi(OH_2)]\cdot 3H_2O$	670, 375	3.10
6. $[L_aCu]\cdot 1\frac{1}{2}H_2O$	530, 410	1.66
7. $[L_aCu(OH_2)_2]\cdot 3\frac{1}{2}H_2O$	630, 460	1.79
8. $[L_aCu]$*	535	1.72
9. $[L_bCu]$	548, 380	1.74
10. $[L_bCu(OH_2)_2]\cdot 3\frac{1}{2}H_2O$	650, 500, 370	1.79
11. $[L_cCu]\cdot \frac{1}{2}H_2O$	560	1.72
12. $[L_cCu(OH_2)_2]\cdot 6H_2O$	660, 480	1.86
13. $[L_dCu(OH_2)_2]\cdot 4\frac{1}{2}H_2O$	689	1.87

*A thermal product.

complex in boiling aqua regia, conc. H_2SO_4 was added and boiled to release nitrogen oxide gases, diluting with water and the solution was neutralized with ammonia solution, the metal ions were then titrated with EDTA.

RESULTS AND DISCUSSION

The reaction of Schiff bases with Ni(II) and Cu(II) acetates, chlorides and perchlorates produce complexes with different geometries, square-planar, [LM], and octahedral, $[LM(OH_2)_2]\cdot nH_2O$, $M = Ni$ or Cu, Figure 2, depending on the nature of the ligand and the counter anion of the metal salt. Elemental analyses and mass spectra of Ni(II) and Cu(II) complexes indicate that the formulae of these complexes are as given in Table I.

IR and Far-IR Spectra of the Complexes

In order to determine the mode of chelation in the Schiff-base complexes under investigation, it is necessary to investigate their IR and Far-IR spectra and compare them with those of the free ligands. It was found in all metal complexes that the C=N stretching band of the Schiff-base ligands is shifted by $20\,cm^{-1}$ to lower frequencies, indicating the involvement of the azomethine group in the chelation with the metal ion. The broad band at $3500-3200\,cm^{-1}$ in the spectra of the complexes implies the presence of H_2O molecules (supported from the thermal analysis). The band due to the

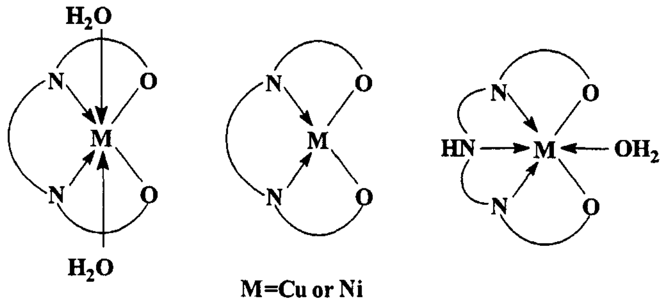


FIGURE 2 The proposed structures of the metal complexes.

bending vibration of H_2O was found at $972-815\,cm^{-1}$, TGA demonstrates the nature of H_2O molecules in the complexes (see later). From Far-IR spectra the new bands observed at 550–470 and $450-380\,cm^{-1}$ are assigned to the M–O and M–N stretching vibrations, respectively. These results indicate that the chelation of the metals is through N_2O_2 coordination sites.

To determine whether such geometry was obtained when the ligands reacted with different metal salts, a series of Ni(II) and Cu(II) complexes have been studied and the structures of the complexes have been proposed on the basis of electronic, ESR and mass spectra, and magnetic measurements.

Electronic, ESR Spectra and Magnetic Moment Data of the Metal Complexes

Based on the electronic spectra and magnetic moments data, Table II, the nickel(II) complexes have two different geometries. The first geometry is square-planar with its characteristic features; the complexes are reddish orange in color, diamagnetic and show electronic spectral bands at 530 and 535 nm for complexes **1** and **2**, assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ transition.[19,20] These complexes were obtained whether the metal : ligand ratio was 1 : 1 or 1 : 2 and the Ni(II) salt was chloride, sulfate, acetate or perchlorate. The complexes are insoluble in polar solvents such as pyridine and water which implies that the coordination bonds in the planar positions are strong enough to prevent the addition of coordinating solvent molecules in axial positions. A similar behavior has been observed in Ni–SALEN complexes.[21,22] The second geometry is octahedral where the complexes are green colored and show the expected magnetic moments, 2.95 and 3.10 BM, for Ni(II) complexes **3** and **5**, respectively. Their electronic spectra showed absorption bands at 610, 355 and 670, 375 nm, respectively, attributed to the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions. These complexes were obtained starting with Ni(II) acetate whether the metal : ligand ratio was 1 : 1 or 1 : 2. The formation of two different geometries is assigned to the diferences in the length of the carbon chain of the diamine, the ligands H_2L_a and H_2L_b form five-membered chelating rings and the ligands H_2L_c and H_2L_d form six-membered chelating rings. Accordingly, the nickel(II) ions in $[L_aNi]$ and $[L_bNi]$ keep the square-planar configuration even in pyridine or water owing to their sufficiently strong ligand field, while complexes $[L_cNi(OH_2)_2] \cdot 4H_2O$ and $[L_dNi(OH_2)] \cdot 3H_2O$ have water molecules coordinated to their apical positions consistent with the decrease in the ligand field caused by an increase in the number of methylene groups.[23] On the other hand, these Ni(II) complexes differ from the Ni–SALEN family in that the latter retain the planar structure even if the number of methylene groups is increased to 3, 4 or 5.[24,25]

Two different geometries of copper(II) complexes were obtained according to the type of the counter anion of the metal salt except for $[L_dCu(H_2O)] \cdot 4\frac{1}{2}H_2O$ which was the only product. Violet colored square-planar, $[LCu] \cdot nH_2O$, complexes were obtained with $Cu(OAc)_2 \cdot 2H_2O$ and green colored distorted octahedral complexes, $[LCu(OH)_2] \cdot nH_2O$, with either $CuCl_2 \cdot 2H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$ as indicated by their visible, ESR spectra and magnetic moments, Table II. The former type of Cu(II) complexes showed a band at 530–560 nm in their visible spectra, which compares well with a value of 545 nm for Cu(acacen),[26] indicative of square-planar geometry and their magnetic moments are 1.66–1.74 BM which support this geometry. The latter type of green complexes have magnetic moments 1.79–1.87 BM and exhibit visible bands at 630–660 and 460–500 nm assigned to the $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively, supporting the distorted octahedral geometry. The difference of the values of the absorption bands of the square-planar complexes **6** and **11**, 530 and 560 nm respectively, are due to the different ligand field strengths exerted by the five- and six-membered rings[23] formed by ligands H_2L_a and H_2L_c, respectively.

The ESR spectra of the Cu(II) complexes **6** and **7** in the polycrystalline state are different, Figure 3, and show one signal for the former complex, $g_{\mathrm{eff}} = 1.91$, characteristic of square-planar complexes, while the latter complex shows two signals in its spectra, $g_{\parallel} = 1.89$ and $g_{\perp} = 1.91$ $[g_{\mathrm{av}} = 1/3(g_{\parallel} + 2g_{\perp}) = 1.90]$. The observed g-values of the latter complex point to the presence of the unpaired electron in the dz^2 orbital with $g_{\parallel} < g_{\perp}$, characteristic of flattened octahedral geometry. The $g_{\parallel}$ obtained for the Cu(II) complexes is less than 2.3 indicating covalent character of the copper–ligand bond.[27,28] The axial symmetry parameter (G) for the Cu(II)

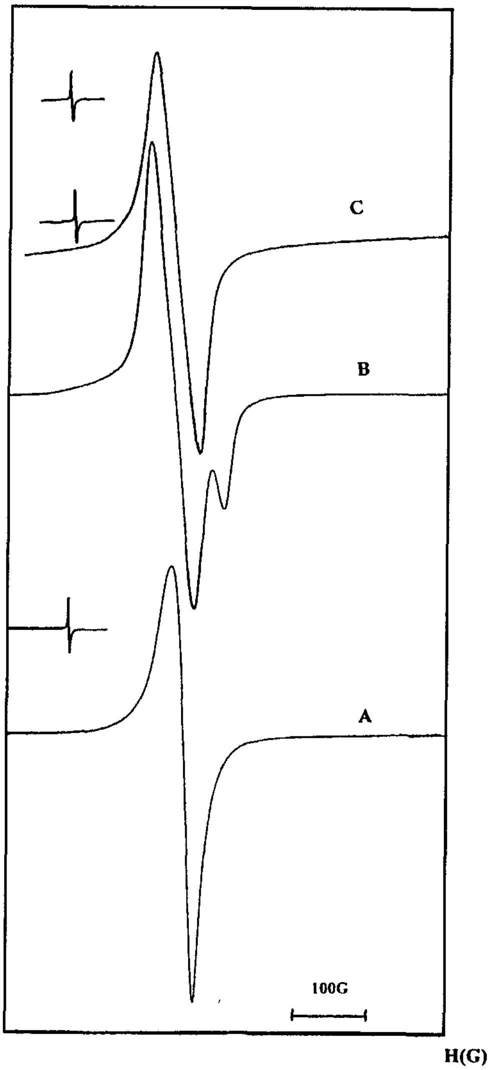


FIGURE 3 ESR powder spectra; X-bands, of the Cu(II) complexes, A: $[L_aCu]\cdot 1\frac{1}{2}H_2O$ (complex **6**), B: $[L_aCu(OH_2)_2]\cdot 3\frac{1}{2}H_2O$ (complex **7**) and C: $[L_dCu(OH)_2)]\cdot 4\frac{1}{2}H_2O$ (complex **13**).

complexes is found to be less than 4 (0.82) indicating the presence of interactions between adjacent copper centers in the solid state.[29] The positions of absorption signals in the ESR spectra of the Cu(II) complexes of both ligands H_2L_b and H_2L_c are similar to those of ligand H_2L_a indicating that the coordination of Cu(II) is similar in all of these complexes.

The Cu(II) complex of the ligand H_3L_d yielded only one type, a green complex $[L_dCu(H_2O)]\cdot 4\frac{1}{2}H_2O$, whether Cu(II) acetate, chloride or perchlorate were used. The ESR spectra of this complex, Figure 3, show one broad signal with $g_{eff} = 1.91$, the magnetic moment of the complex is 1.87 BM and its electronic spectrum shows a band at 689 nm indicative of distorted octahedral geometry originating through a Jahn–Teller effect.[30]

Thermal Studies

TGA of the Ni(II) complexes **1–3** indicated that the first two complexes do not contain water molecules, while complex **3** contains four hydrated water molecules which are eliminated within the temperature range 60–125°C and two coordinated water molecules which were eliminated at 125–160°C. Figure 4 shows the TGA curves of the ligand H_2L_c together with complex **3** and its thermal product, complex **4**, mentioned later. On heating **3**, $[L_cNi(OH_2)_2]\cdot 4H_2O$, at 150°C in an air oven it undergoes a reversible thermochromism from green (octahedral, high spin, $\mu_{eff} = 2.95$ BM) to red (square-planar, low spin, $\mu_{eff} = 0$). The reverse change of the thermal product (red) to the parent complex (green) occurs on standing under atmospheric air for some minutes. Also, the green octahedral Cu(II) complexes **7**, **10** and **12** (Table I) change their colors from green to brownish

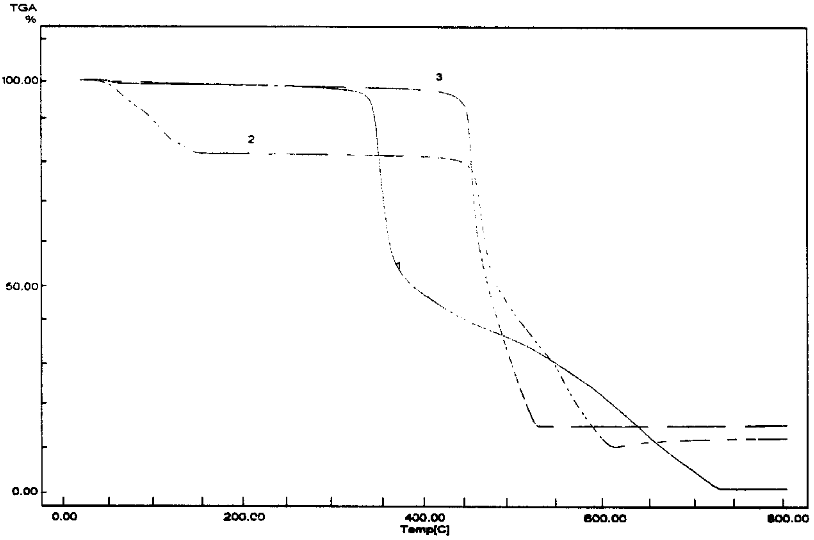


FIGURE 4 TGA curves of the ligand H_2L_c and its Ni(II) complexes, 1: H_2L_c ligand, 2: $[L_cNi(OH_2)_2]\cdot 4H_2O$ (complex 3) and 3: $[L_cNi]\cdot \frac{1}{2}H_2O$ (thermal product of complex 3).

or bluish violet in the temperature range 140–190°C as an irreversible thermochromism step. Complex **13** which maintained its green octahedral geometry was an exception. The thermal products obtained by heating, were characterized by chemical analyses, IR, electronic and mass spectra as well as magnetic measurements. The electronic spectra of these thermal products exhibit bands at 510 and 520–545 nm, respectively, consistent with the square-planar geometry of these products. The magnetic moments for the obtained thermal products at room temperature are given in Table II. The data show changes in the magnetic moments on heating, thus the red product **4** is diamagnetic and the brownish violet product **8** shows a decrease in its magnetic moment corresponding to configurational changes from octahedral to square-planar geometry. On the other hand, the magnetic moment and electronic spectral data indicate that Ni(II) complex **5**, $[L_dNi(OH_2)]\cdot 3H_2O$ did not show any transformation of geometry by heating and maintained its octahedral geometry. This result is due to the ligand H_2L_d being pentadentate, Figure 2, thus preserving the more stable octahedral geometry in both its Cu(II) and Ni(II) complexes.

Mass Spectra of the Metal Complexes

The mass spectra of the Ni(II) and Cu(II) complexes **2**, **3** and **7**, are shown in Figures 5 and 6. Complex **2**, showed its parent peak at $m/e = 475$ which compares well with its formula weight. Complex **3** showed the parent peak at $m/e = 486$ (as shown in the enlarged part of the spectrum) which compares with the formula weight of its thermal product, $[L_cNi]\cdot\frac{1}{2}H_2O$, complex **4** (FW = 484). Complex **7** showed the parent peak at $m/e = 502$ (as shown in the enlarged part of the spectrum) which compares with the formula $[L_aCu(OH_2)_2]$ and also showed another peak of low intensity at $m/e = 466$ which corresponds to the formula weight of its thermal product, $[L_aCu]$, complex **8**.

X-Ray Diffraction Patterns

X-ray diffraction patterns of the ligands, H_2L_b and H_2L_c, their Cu(II) complexes and the parent metal salts, $Cu(OAc)_2\cdot H_2O$ and $CuCl_2\cdot 2H_2O$ were recorded between 4° and 90° (2θ). The interplanar spacing, d (Å) and the relative intensities (I/I^0) of the ligands and their Cu(II) complexes **9–12** were calculated and recorded in Table III. Comparing the X-ray diffraction patterns of each ligand with its corresponding Cu(II) complexes and the parent Cu(II) salts indicated that the interplanar spacing, d (Å) and the

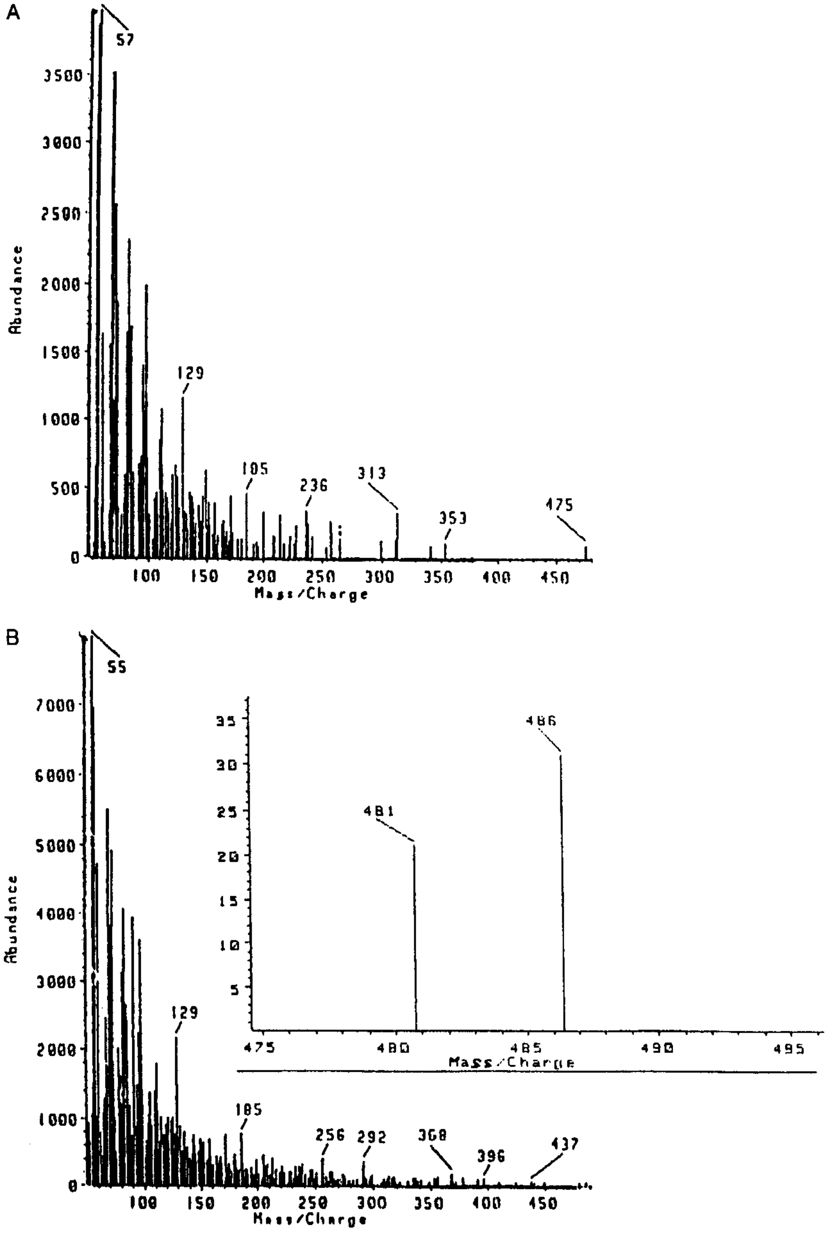


FIGURE 5 Mass spectra of the Ni(II) complexes, A: $[L_bNi]$ (complex 2) and B: $[L_cNi(OH_2)_2] \cdot 4H_2O$ (complex 3).

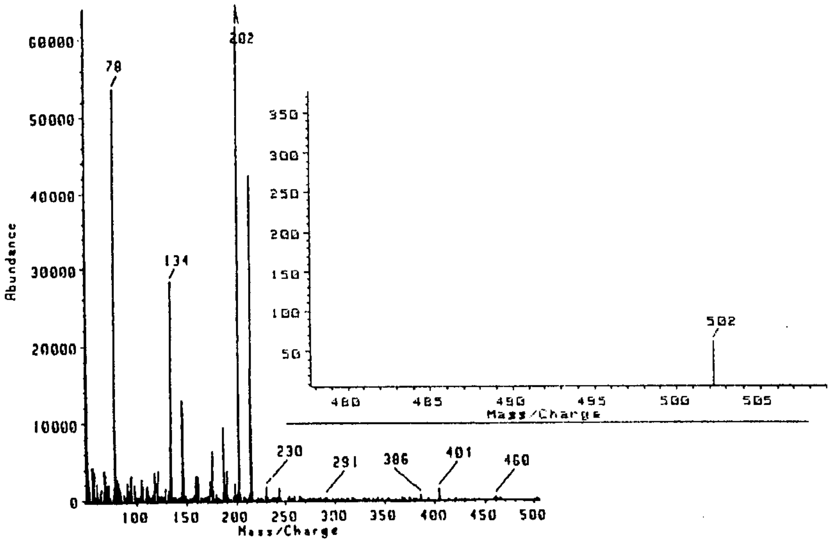


FIGURE 6 Mass spectrum of the Cu(II) complex $[L_aCu(OH_2)_2]\cdot 3\frac{1}{2}H_2O$ (complex 7).

TABLE III X-ray diffraction data of the ligands H_2L_b and H_2L_c and their Cu(II) complexes

H_2L_b		$[L_bCu]$		$[L_bCu](OH_2)_2\cdot 3\frac{1}{2}H_2O$		H_2L_c		$[L_cCu]\cdot \frac{1}{2}H_2O$		$[L_cCu(OH_2)_2]\cdot 6H_2O$	
d(Å)	I/I^0	d(Å)	I/I^0	d(Å)	I/I^0	d(Å)	I/I^0	d(Å)	I/I^0	d(Å)	I/I^0
9.1	95	12.2	53	10.6	70	16.4	30	11.3	100	10.1	49
7.5	100	10.1	94	9.4	62	8.0	50	10.1	78	5.1	37
6.1	12	8.3	64	8.9	47	7.0	100	7.5	98	4.7	27
5.8	28	5.9	40	7.8	20	6.6	31	6.5	19	4.5	38
5.4	65	5.2	17	7.0	32	6.2	23	6.2	46	3.9	26
5.2	9.0	4.9	15	5.8	26	5.5	66	5.7	57	3.2	100
4.8	15	4.6	14	5.2	27	4.1	57	5.3	20	2.8	22
4.3	12	4.3	14	4.9	27	3.8	31	4.8	70	2.7	21
4.1	11	3.6	12	4.7	39	3.6	99	4.7	26	2.5	21
3.7	18	3.4	100	4.6	41	3.4	35	4.4	22	—	—
3.6	17	3.0	11	4.4	26	3.1	55	4.1	21	—	—
3.4	70	2.9	13	4.3	26	2.7	12	3.9	17	—	—
3.3	76	2.8	10	3.8	26	—	—	3.4	99	—	—
3.2	64	2.6	9.0	3.5	26	—	—	3.2	29	—	—
3.0	11	2.5	8.0	3.4	24	—	—	3.0	22	—	—
2.5	9.0	2.4	8.0	3.2	100	—	—	2.9	18	—	—
—	—	2.2	7.0	2.7	18	—	—	2.8	18	—	—
—	—	2.0	9.0	2.6	20	—	—	2.7	19	—	—
—	—	1.9	8.0	—	—	—	—	2.6	18	—	—
—	—	1.7	7.0	—	—	—	—	2.5	16	—	—
—	—	—	—	—	—	—	—	2.3	16	—	—
—	—	—	—	—	—	—	—	2.2	21	—	—

relative intensities (I/I^0) are different which could be attributed to the complex formation.

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