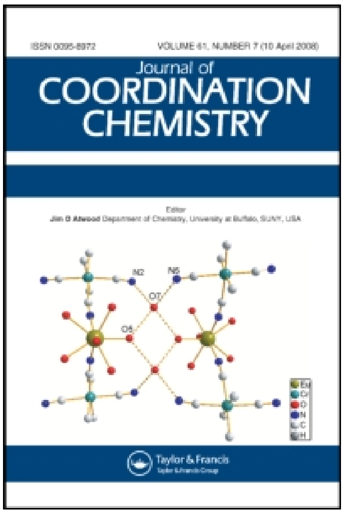

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ESR AND SPECTROSCOPI STUDIES OF METAL COMPLEXES OF NOVEL SCHIFF BASES DERIVED FROM 6-METHYL-3-FORMYL-4-HYDROXY-2-(lH) QUINOLONE AND 1, 3-DIAMINOPROPANE OR N-(2-AMINOETHYL)-l, 3-PROPANEDIAMINE, PART VI

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ESR AND SPECTROSCOPIC STUDIES OF METAL COMPLEXES OF NOVEL SCHIFF BASES DERIVED FROM 6-METHYL-3-FORMYL-4-HYDROXY-2-(1H) QUINOLONE AND 1,3-DIAMINOPROPANE OR N-(2-AMINOETHYL)-1,3-PROPANEDIAMINE, PART VI*

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Two novel dianionic tetradentate (N_2O_2) and pentadentate (N_3O_2) Schiff base ligands and their corresponding Cu(II), Ni(II), Co(II), Mn(II), VO(IV), Fe(III), UO_2(VI), Th(IV), Zn(II) and Cd(II) complexes were prepared and characterized by elemental analyses, IR, visible and ESR spectra, magnetic susceptibility measurements as well as mass spectroscopy. Mononuclear and or dinuclear metal complexes were obtained. The Cu(II) complexes have either square-planar or octahedral geometries. The mononuclear Ni(II) complex show anomalous behavior where both square-planar and octahedral geometries coexist, while its dinuclear complex has an octahedral geometry. Co(II) complexes were either mononuclear or dinuclear and showed five-coordinate trigonal bipyramidal and/or octahedral geometry. These structural geometries were confirmed by the results obtained from the thermal analyses. VO(IV) complexes were octahedral and polymeric. The mononuclear Mn(II) complex of the tetradentate ligand and the dinuclear Fe(III) complex of the pentadentate ligand were the only compounds obtained and showed octahedral geometry. The UO_2(VI) and Cd(II) cations behaved similarly and coordinated to two tetradentate ligand molecules through their outer O–O coordinating sites, while they coordinated to only one molecule of the pentadentate ligand, through their N_3O_2 or N_2O_2 sites, respectively. This reflects the effect of the cavity size of both ligands towards accommodating large cations. Th(IV) cations were coordinated to two bidentate nitrate anions, thus aiding the ligands to accommodate large cations in their cavities and raising their coordination sphere to either eight or nine. Small Zn(II) cations are well accommodated in the cavities of both ligands.

Keywords: Tetra- and pentadentate Schiff bases; transition and actinide metal complexes

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[*] Part V see Ref. [1].

INTRODUCTION

Schiff base complexes of transition metals have many practical applications. Transition metal complexes of N,N-ethylenebis-(salicylideneimine), SALEN, and its derivatives have been used as biomimetric catalysts for oxygen transfer,[2] as catalysts for enantioselective epoxidation[3] and aziridination,[4] as catalysts for mediating redox reactions[5] and as mediators for other oxidative processes.[6] The preparation and characterization of uranyl specific complexing agents "Uranophiles" are also important in the recovery of uranium(VI) cations from sea and waste water.[7,8]

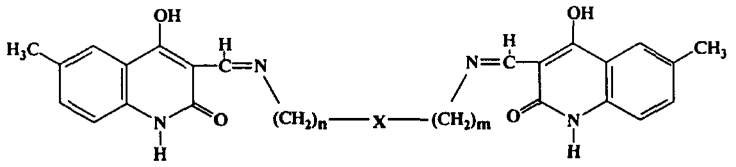
Schiff base ligands derived from 6-methyl-3-formyl-4-hydroxy-2-(1H) quinolone have been previously prepared in our laboratory and were investigated together with their transition metal complexes.[1,9–12] This continuation of our work describes the synthesis of two novel Schiff base ligands derived from the condensation of the above mentioned aldehyde and a di- or a tri-aliphatic amine, Figure 1. Also, their metal complexes have been prepared and characterized.

The aim of this work is to compare the behavior of both tetra- and pentadentate ligands of similar structures towards chelating certain transition, actinide and non-transition metal cations.

EXPERIMENTAL

Materials

p-Toluidine, diethylmalonate, orthophosphoric acid (85%), phosphorous pentaoxide, sodium acetate, sodium hydroxide, hydrochloric acid, nitric acid, sulfuric acid, N,N-dimethylformamide (DMF), 1,3-diaminopropane and N-(2-aminoethyl)-1,3-propanediamine were purchased from Merck. Ethanol, methanol and metal salts were reagent grade chemicals.



H_2L_a, n = m = 1; X = CH_2
H_2L_b, n = 2; m = 3; X = NH

FIGURE 1 Tetra- and pentadentate Schiff-base ligands.

Preparation of the Schiff Base Ligands

6-Methyl-3-formyl-4-hydroxy-2-(1H)quinolone[13] and either 1,3-diaminopropane or N-(2-aminoethyl)-1,3-propanediamine (molar ratio 2 : 1) were refluxed in ethanol for 4 h. The color of the solution changed from red to pale yellow and the precipitated ligands were filtered on cooling, then washed with ethanol. The crude products were recrystallized from DMF. The purity of the ligands were determined by elemental analyses and mass spectra. Yields were 78% and 60%, respectively, and m.p. > 280°C. Analysis for H_2L_a, $C_{25}H_{24}N_4O_4$, Calc.: C, 67.6; H, 5.4; N, 12.6; *m/e*, 444.5; Found: C, 67.8; H, 5.3; N, 12.5; *m/e*, 445 and for H_2L_b, $C_{27}H_{29}N_5O_4$, Calc.: C, 66.6; H, 5.8; N, 14.4; *m/e*, 487.5; Found: C, 66.1; H, 5.6; N, 14.2; *m/e*, 487.

Preparation of the Metal Complexes

A solution of the metal salt in ethanol was added to the ligand suspended in ethanol. In the case of VO(IV) and Th(IV) salts, water was added to ensure complete dissolution of the metal salt. The preparations of uranyl complexes were carried out in methanol as uranyl acetate is more soluble in this solvent. The solutions were refluxed for 2–3 h except for the reactions with Fe(III) and VO(IV) salts which yielded their products by stirring at room temperature thus avoiding oxidation of the vanadyl salt. It was also observed in reactions 7, 8, 9, 17, 18 and 20 that the ligand dissolved completely after addition of the metal salt solution. The solid metal complexes were precipitated in the hot solutions, then allowed to cool slowly and collected by filtration, washed with water, ethanol then ether and finally air-dried. The prepared complexes were insoluble in water and common organic solvents.

Attempts to prepare the Fe(III) complex of ligand H_2L_a were unsuccessful. An yellow oil was always obtained and trials to precipitate a solid product either by cooling or adding different organic solvents failed to yield any product. Also, attempts to prepare the Mn(II) complex of ligand H_2L_b failed to yield product.

The following detailed preparation of $[UO_2L_b] \cdot 6H_2O$ complex is given as an example, however, other metal complexes were prepared similarly:

A solution of 0.6 g (1.23 mmol) of $UO_2(OAc)_2 \cdot 2H_2O$ in 30 mL methanol was added to 0.522 g (1.23 mmol) of ligand H_2L_b suspended in 40 mL methanol. The solution was refluxed for 3 h to give an yellowish orange precipitate. The solution was allowed to cool to room temperature. The solid product was obtained by filtration, washed with methanol then ether and finally air-dried.

Reactions carried out and elemental analyses are given in Table I. Reaction 14 in Table I was carried out in dimethylformamide under reflux

TABLE I Elemental analyses and other data of the metal complexes

	Reactants	*Metal complexes*	*Color*	*Yield* (%)	*Chemical analyses* (%), *Found* (*Calc.*)				
					C	*H*	*N*	*Cl*	*M*
1	$H_2L_a + Cu(OAc)_2 \cdot H_2O$	$[L_aCu] \cdot 2H_2O$ $C_{25}H_{26}N_4O_6Cu$	Pale green	82	55.3 (55.4)	4.7 (4.8)	10.2 (10.3)	—	11.8 (11.7)
2	$H_2L_a + Ni(OAc)_2 \cdot 4H_2O$	$[L_aNi(OH_2)_2] \cdot 1\frac{1}{2}H_2O$ $C_{25}H_{29}N_4O_{7\frac{1}{2}}Ni$	Pale brown	79	52.9 (53.2)	5.4 (5.2)	9.9 (9.9)	—	10.2 (10.4)
3	$H_2L_a + CoCl_2 \cdot 6H_2O$	$[L_aCo(OH_2)] \cdot 2H_2O$ $C_{25}H_{28}N_4O_7Co$	Green	67	53.8 (54.1)	5.1 (5.1)	10.0 (10.0)	—	10.5 (10.6)
4	$H_2L_a + MnCl_2 \cdot 2H_2O$	$[L_aMn] \cdot 2H_2O$ $C_{25}H_{26}N_4O_6Mn$	Deep yellow	67	56.1 (56.3)	4.8 (4.9)	10.5 (10.5)	—	10.0 (10.3)
5	$H_2L_a + VOSO_4 \cdot H_2O$	$[L_a(VO)] \cdot H_2O$ $C_{25}H_{24}N_4O_6V$	Yellow	56	57.0 (56.9)	4.9 (4.9)	10.6 (10.6)	—	—
6	$2H_2L_a + UO_2(OAc)_2 \cdot 2H_2O$	$[(HL_a)_2(UO_2)(OH_2)]$ $C_{50}H_{48}N_8O_{11}U$	Pale yellow	63	51.0 (51.1)	4.1 (4.1)	9.3 (9.5)	—	—
7	$H_2L_a + Zn(NO_3)_2 \cdot 6H_2O$	$[L_aZn] \cdot H_2O$ $C_{25}H_{24}N_4O_5Zn$	Buff	85	56.9 (57.1)	4.6 (4.6)	10.7 (10.7)	—	12.4 (12.4)
8	$2H_2L_a + Cd(NO_3)_2 \cdot 6H_2O$	$[(HL_a)_2Cd] \cdot 3H_2O$ $C_{50}H_{52}N_8O_{11}Cd$	Yellowish brown	71	57.0 (57.0)	4.8 (5.0)	10.5 (10.6)	—	10.7 (10.7)
9	$H_2L_a + Th(NO_3)_4 \cdot 4H_2O$	$[L_aTh(NO_3)_2] \cdot H_2O$ $C_{25}H_{22}N_6O_{10}Th$	Yellowish white	68	36.7 (36.8)	2.8 (2.8)	10.3 (10.3)	—	—
10	$H_2L_b + Cu(OAc)_2 \cdot H_2O$	$[L_bCu(OH_2)] \cdot 2\frac{1}{2}H_2O$ $C_{27}H_{34}N_5O_{7\frac{1}{2}}Cu$	Green	81	53.0 (53.0)	5.4 (5.6)	11.3 (11.5)	—	10.5 (10.4)

11	$H_2L_b + 2Ni(OAc)_2 \cdot 4H_2O$	$[L_bNi_2(OAc)_2(OH_2)_3] \cdot 5H_2O$ $C_{31}H_{49}N_5O_{16}Ni_2$	Pale green	69	43.1 (43.0)	5.6 (5.7)	8.0 (8.1)	—	13.4 (13.6)
12	$H_2L_b + Ni(ClO_4)_2 \cdot 6H_2O$	$[L_bNi]$ $C_{27}H_{27}N_5O_4Ni$	Deep yellow	70	59.4 (59.6)	4.9 (5.0)	12.8 (12.9)	—	10.8 (10.8)
13	$H_2L_b + 2CoCl_2 \cdot 6H_2O$	$[L_bCo_2Cl_2(OH_2)_2] \cdot 4H_2O$ $C_{27}H_{39}N_5O_{10}Cl_2Co_2$	Green	71	41.5 (41.5)	4.8 (5.0)	9.0 (9.0)	9.1 (9.1)	14.8 (15.1)
14	$[L_bCu(OH_2)]_2 \cdot 2\frac{1}{2}H_2O$ $+ CoCl_2 \cdot 6H_2O$	$[L_bCo(OH_2)] \cdot H_2O$ $C_{27}H_{31}N_5O_6Co$	Yellow	60	55.9 (55.9)	5.2 (5.4)	12.0 (12.1)	—	10.2 (10.2)
15	$H_2L_b + VOSO_4 \cdot H_2O$	$[L_bVO] \cdot 3\frac{1}{2}H_2O$ $C_{27}H_{34}N_5O_{8\frac{1}{2}}V$	Greenish yellow	83	52.5 (52.7)	5.4 (5.6)	11.4 (11.4)	—	—
16	$H_2L_b + UO_2(OAc)_2 \cdot 2H_2O$	$[L_bUO_2] \cdot 6H_2O$ $C_{27}H_{39}N_5O_{12}U$	Yellow	76	37.5 (37.6)	4.4 (4.6)	8.1 (8.1)	—	—
17	$H_2L_b + Zn(NO_3)_2 \cdot 6H_2O$	$[L_bZn] \cdot 4H_2O$ $C_{27}H_{35}N_5O_8Zn$	Brown	78	52.1 (52.1)	5.4 (5.5)	11.3 (11.3)		10.4 (10.5)
18	$H_2L_b + Cd(NO_3)_2 \cdot 6H_2O$	$[L_bCd] \cdot 4\frac{1}{2}H_2O$ $C_{27}H_{36}N_5O_{8\frac{1}{2}}Cd$	Pale brown	71	47.7 (47.8)	5.3 (5.3)	10.2 (10.3)	—	16.4 (16.6)
19	$H_2L_b + 2FeCl_3 \cdot 6H_2O$	$[L_bFe_2Cl_4(OH_2)] \cdot 2H_2O$ $C_{27}H_{33}N_5O_7Cl_4Fe_2$	Reddish brown	92	40.9 (40.9)	4.0 (4.2)	8.6 (8.8)	17.7 (17.9)	14.0 (14.1)
20	$H_2L_b + Th(NO_3)_4 \cdot 4H_2O$	$[L_bTh(NO_3)_2] \cdot 3H_2O$ $C_{27}H_{33}N_7O_{13}Th$	Pale yellow	80	36.2 (36.2)	3.7 (3.7)	11.0 (11.0)	—	—

TABLE II Visible spectra and magnetic moments of the metal complexes

	Complex	*Visible spectra* (nm)[a]				*Magnetic moments*	
						μ_{eff}[b] (B.M.)	μ_{compl}[c] (B.M.)
1	$[L_aCu]\cdot 2H_2O$		545			1.99	—
2	$[L_aNi(OH_2)_2]\cdot 1\frac{1}{2}H_2O$	600		470		2.39	—
3	$[L_aCo(OH_2)]\cdot 2H_2O$	655	545		385	3.49	—
4	$[L_aMn]\cdot 2H_2O$		—			4.00	—
5	$[L_aVO]\cdot H_2O$		580			1.84	—
6	$[(HL_a)_2UO_2(OH_2)]$		550		330	—	—
10	$[L_bCu(OH_2)]\cdot 2\frac{1}{2}H_2O$	665	575			2.33	—
11	$[L_bNi_2(OAc)_2(OH_2)_3]\cdot 5H_2O$	670	590	375	340	—	4.64
12	$[L_bNi]$		540	365		Diamag.	—
13	$[L_bCo_2Cl_2(OH_2)_2]\cdot 4H_2O$	612	540	360		—	5.64
14	$[LbCo(OH_2)]\cdot H_2O$		590,540	365		5.49	—
15	$[L_bVO]\cdot 3\frac{1}{2}H_2O$		575	415	350	2.27	—
16	$[L_bUO_2]\cdot 6H_2O$		562	480	—	—	
19	$[L_bFe_2Cl_4(OH_2)]\cdot 2H_2O$		535	435	340	—	7.41

[a] Nujol mull.
[b] μ_{eff} is the magnetic moment of one cationic species in the complex.
[c] μ_{compl} is the magnetic moment of all cations in the complex.

for 3 h. The obtained precipitate was treated as mentioned above. Table II shows the visible spectra and magnetic moments of the obtained complexes.

Analyses and Physical Measurements

Electronic spectra of the metal complexes, as Nujol mulls, were recorded on a Perkin-Elmer 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 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 magnetic susceptibility balance, Johnson Matthey, Alfa products, UK, Model No. MKI. $Hg[Co(SCN)_4]$ was used as a calibrant. Diamagnetic corrections were calculated from Pascal's constants.[14] 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 constituent atoms. Mass spectra of the ligands were recorded on a Hewlett-Packard mass spectrometer MS 5988. The fragmentation was carried out at 300°C and 70 eV. TG-DTA measurements were carried out on a Perkin-Elmer high temperature differential thermal analyzer with 3700 data point resolution.

Microanalyses of carbon, hydrogen and nitrogen were carried out at the Microanalytical Center, Cairo University, Giza, Egypt. Analyses of metals followed dissolution of the solid complexes in boiling aqua regia, conc. H_2SO_4 acid was added and boiled to release nitrogen oxide gases. The diluted solutions were neutralized by ammonia solution and the metal cations were then titrated with EDTA.

RESULTS AND DISCUSSION

Two Schiff-bases were prepared in this study, tetra- and pentadentate (N_2O_2 and N_3O_2) dibasic ligands, Figure 1. The IR spectra of the ligands H_2L_a and H_2L_b showed bands at 3180 and 3205 cm^{-1}, respectively, due to the overlap of the stretching vibrational modes of the heterocyclic NH group and the enolic NH group originating through resonance between the C=N and the OH groups[15] as indicated in Figure 2. In addition the spectrum of the ligand H_2L_b showed a band at 3270 cm^{-1} due to the aliphatic imine group.

The vibration of the C=O group in the heterocyclic ring couples with that of the C=C bond in both spectra and appears as strong absorption bands at 1640 and 1670 cm^{-1} for ligand H_2L_b and at 1635 and 1660 cm^{-1} for ligand H_2L_a. The lowering in the vibration frequencies of the C=N, at 1600 and at 1598 and 1610 cm^{-1} in the spectrum of ligands H_2L_a and H_2L_b, respectively, is due to the tautomeric structures of the ligands, Figure 2, where the C=N group is better designated as C$\overset{..}{-}$N group. Bands due to the stretching vibrations of the phenolic and enolic OH groups appear at 3400 cm^{-1} for ligand H_2L_a and at 3450 cm^{-1} for ligand H_2L_b.

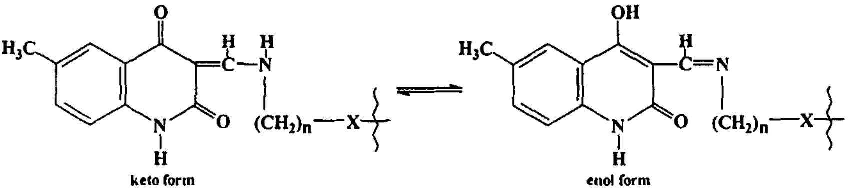


FIGURE 2 Keto–enol tautomers of the Schiff-base ligands.

The mass spectra of the ligands, Figure 3, show peaks at $m/e = 445$ and 487 corresponding to their parent molecular ions. It is worth noting that the C=O group of the heterocyclic ring at the 2-position (cf. Figure 1) is inactive as it does not condense with amines.[16]

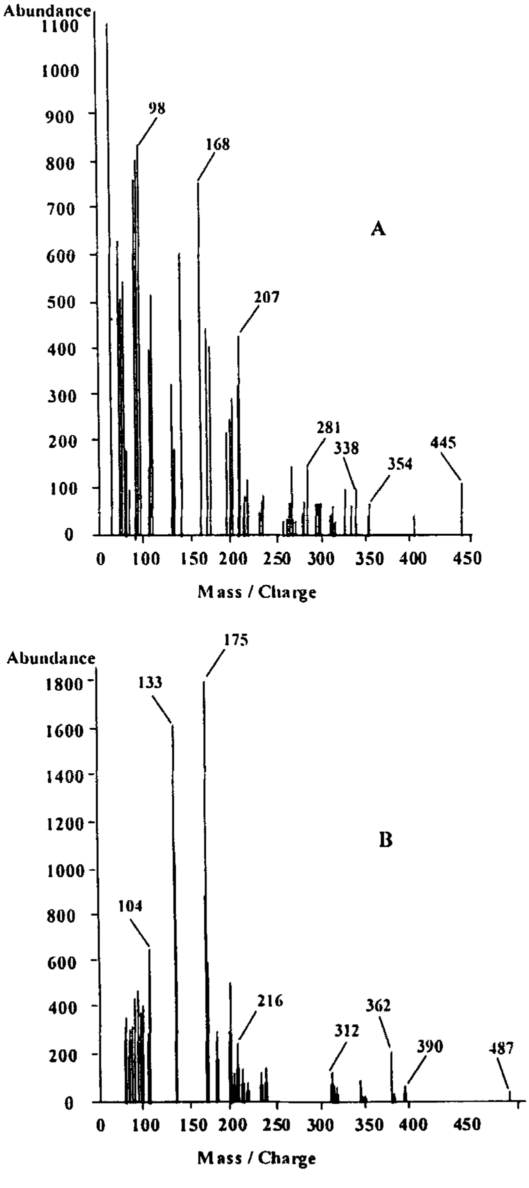


FIGURE 3 Mass spectra of A: H_2L_a and B: H_2L_b ligands at 70 eV and 300°C.

IR Spectra of Metal Complexes

With two exceptions, all the IR spectra of the solid complexes showed a shift of the absorbance of the C=N group to lower frequencies, between 1572 and 1590 cm^{-1}. The exceptions are the IR spectra of UO_2(VI) and Cd(II) complexes of H_2L_a in which no shift was observed. Also, the spectra showed that the phenolic OH band is replaced by water absorption bands between 3490 and 3363 cm^{-1}. These results indicate replacement of the two protons of the phenolic OH groups of the ligand by a metal ion and the involvement of the azomethine groups in metal coordination.

The IR spectra of the two UO_2(VI) complexes of H_2L_a and H_2L_b show strong absorption bands at 915 and 930 cm^{-1}, respectively, which are assigned to the antisymmetric ν_3 (O–U–O) vibration.

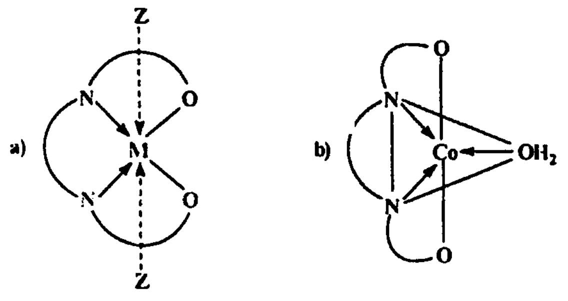
The IR spectra of Th(IV) complexes of H_2L_a and H_2L_b showed absorption bands at 1438, 1400, 1325 and 825 cm^{-1} for the former complex and at 1430, 1386, 1276 and 820 cm^{-1} for the latter complex assigned to the bidentate chelating NO_3^- groups coordinating to the Th(IV) cation and completing its eight- and nine-coordination spheres, respectively.

On the other hand, the appearance of the characteristic bands of the ν (V=O) observed in the IR spectra of VO(IV) complexes of H_2L_a and H_2L_b at 878 and 895 cm^{-1} (strong) and at 950 and 958 cm^{-1} (medium), respectively, with the insolubility of the complexes in organic solvents indicate polymeric structures of these complexes achieved through V=O → V=O bonds.[17,18]

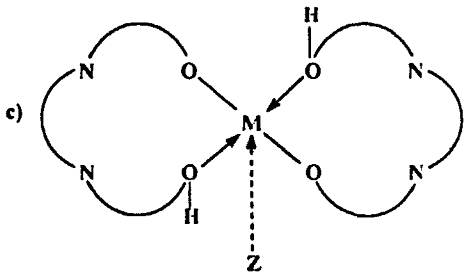
The absorption of the NH group of the heterocyclic ring in the IR spectra of the complexes of H_2L_a and H_2L_b ligands is observed at ≈3180 cm^{-1}, while that of the NH group of the aliphatic chain complexes of ligand H_2L_b is masked by the broad water absorption band. Unfortunately, the acetate absorbance bands of the binuclear Ni(II) complex of H_2L_b ligand were obscured by ligand absorptions.

Electronic, ESR Spectra and Magnetic Measurements of the Metal Complexes

Two different geometries for copper(II) complexes were obtained, a square-planar $[L_aCu]\cdot 2H_2O$ and a distorted octahedral $[L_bCu(OH)_2]\cdot 2\frac{1}{2}H_2O$, Figures 4(a) and 5(a), as indicated by their visible spectra and magnetic moments, Table II. The former complex showed a band at 545 nm in its visible spectrum indicative of square-planar geometry[19] and its magnetic moment is 1.99 B.M. which supports this geometry. The latter complex showed bands at 665 and 575 nm indicative of distorted octahedral geometry



a, M = Ni; Z = H_2O or
M = Mn, VO; Z = oxygen
atom(s) of neighbouring
molecule(s) or
M = Cu, Zn

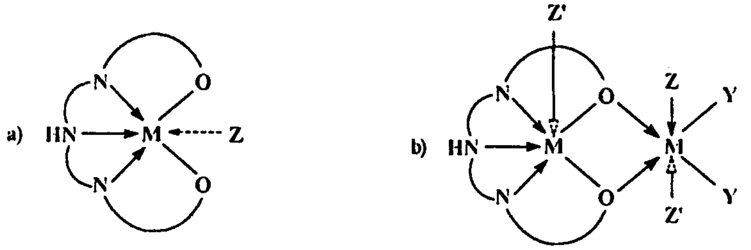


c, M = UO_2; Z = H_2O or
M = Cd

FIGURE 4 Proposed structures of metal complexes of ligand H_2L_a.

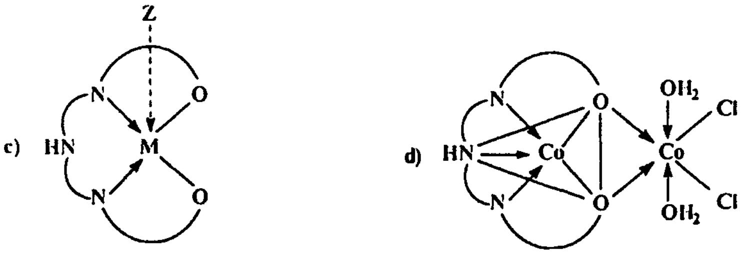
originating through the Jahn–Teller effect.[20] Its magnetic moment is 2.33 B.M. which is higher than expected and could be due to spin-orbit coupling. The ESR spectra of these complexes, Figure 6, are typical of planar or axially distorted Cu(II) ions, and correspond to an axial pattern with $g_{\parallel} > g_{\perp}$. The $g_{\parallel}$ and $g_{\perp}$ values for the first complex are 1.950 and 1.917, $[g_{av} = \frac{1}{3}(g_{\parallel} + 2g_{\perp}) = 1.928]$ and the latter complex are 1.938 and 1.917, $[g_{av} = \frac{1}{3}(g_{\parallel} + 2g_{\perp}) = 1.924]$. However, the parallel feature is less well resolved in the spectra of the former complex compared to that of the latter complex.

The electronic absorption spectra and magnetic moments of Ni(II) complexes, mononuclear $[L_aNi(OH_2)_2] \cdot 1\frac{1}{2}H_2O$ and dinuclear $[L_bNi_2(OAc)_2(OH_2)_3] \cdot 5H_2O$, Table II, indicate octahedral symmetry. The visible spectrum of the dinuclear product shows four absorption bands



a, M = Cu, Co; Z = H_2O or
M = UO_2

b, M = Ni; Z = Z' = H_2O; Y = AcO or
M = Fe; Z = H_2O; Z' = Y = Cl



c, M = VO; Z = oxygen atom
of a neighbouring molecule
M = Ni, Cd, Zn

FIGURE 5 Proposed structures of metal complexes of ligand H_2L_b.

indicating the presence of two different ligand fields around the two Ni(II) cations, Figure 5(b). The higher energy bands at 590 and 340 nm correspond to the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ electronic transitions for the Ni(II) cation surrounded by three nitrogen atoms and three oxygen atoms. The lower energy bands at 670 and 375 nm correspond to the same transitions for the Ni(II) cation surrounded by six oxygen atoms.[21] The third transition of the Ni(II) cations, $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ was not detected owing to the maximum limit of our machine (900 nm). The lower value of the magnetic moment of the former complex, 2.39 B.M., indicates that both octahedral and square-planar geometries exist together.[22,23] The reaction of H_2L_b with $Ni(ClO_4)_2 \cdot 6H_2O$ was carried out to examine the effect of the change of the metal salt on the resultant product. A diamagnetic $[L_bNi]$ product was obtained which reflects the weak coordinating power of the ClO_4^- anion compared to the AcO^- anions. Its visible spectrum showed a band at 540 nm which supports the square-planar geometry of the complex, Figure 5(c).

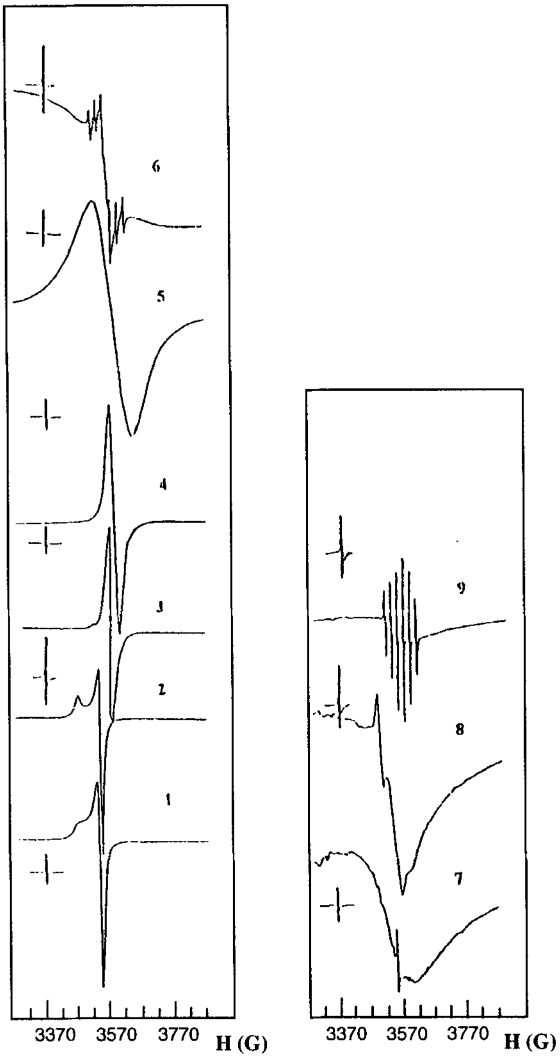


FIGURE 6 ESR powder spectra; X-bands, of $[L_aCu]\cdot 2H_2O$ (1), $[L_bCu(OH_2)]\cdot 2\frac{1}{2}H_2O$ (2), $[L_aVO]\cdot H_2O$ (3), $[L_bVO]\cdot 3\frac{1}{2}H_2O$ (4), $[L_aMn]\cdot 2H_2O$ (5), $[L_bFe_2Cl_4(OH_2)]\cdot 2H_2O$ (6), $[L_aCo(OH_2)]\cdot 2H_2O$ (7), $[L_bCo(OH_2)]\cdot H_2O$ (8), and $[L_bCo_2Cl_2(OH_2)_2]\cdot 4H_2O$ (9) complexes. The signal at $\approx$3370G is due to the dpph field calibrant.

The electronic absorption spectra of the Co(II) complexes, the mononuclear $[L_aCo(OH_2)]\cdot 2H_2O$ and the dinuclear $[L_bCo_2Cl_2(OH_2)_2]\cdot 4H_2O$, complexes showed bands at 655 nm for the former complex and at 612 and 540 nm for the latter complex. The bands at 655 and 612 nm indicate five-coordinate geometry around Co(II) cations[24] and is characteristic of a distorted trigonal bipyramidal structure.[25] The band at 540 nm of the latter complex would be assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition of the outer octahedral Co(II). On the other hand, the magnetic moment of the former complex is 3.49 B.M. which is similar to the previously reported five-coordinated Co(II) Schiff-base complex.[26] This result is supported by TG-DTA analyses. Thus, TGA and DTA data for these complexes indicated that two hydrated water molecules are lost at 101°C and a coordinated water molecule is lost at 155°C in the case of the former complex, also four hydrated water molecules are lost at 103°C and two coordinated water molecules are lost at 142°C for the latter complex. The previous weight losses were endothermic ones. The thermal data indicated that the Co(II) cation in the former complex is pentacoordinate while one of the Co(II) cations in the latter complex is pentacoordinate and the other is hexacoordinate, Figures. 4(b) and 5(d). An ESR spectrum of the former complex, Figure 6, showed a broad band centered at g-value *ca.* 1.883 intersected by a sharp signal at g-value *ca.* 1.907. This indicates that the molecule has axis of symmetry lying on the Z-axis, while the equatorial plane contains inequivalent coordinating atoms. The ESR spectrum of the latter complex, Figure 6, shows splitting which arises from coupling of the inner cobalt(II) ion to the surrounding nitrogen atoms.[27,28]

The mononuclear cobalt(II) complex of the ligand H_2L_b, $[L_bCo(OH_2)] \cdot H_2O$, which was prepared by refluxing the Cu(II) complex of the same ligand, $[L_bCu(OH_2)] \cdot 2\frac{1}{2}H_2O$, with $CoCl_2 \cdot 6H_2O$ in DMF as a solvent showed a magnetic moment of 5.49 B.M. indicating octahedral geometry around the Co(II) cation, Figure 5(a). Besides the band observed at 590 nm in the visible spectrum of the complex which is due to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition, the spectrum also showed a shoulder at 540 nm which could be due to the $^4T_{1g} \rightarrow {}^4A_{2g}$ transition or it may be due to spin–orbit coupling, vibrational broadening, low symmetry components to the ligand field or transitions to doublet states.[21] ESR spectrum of the complex, Figure 6, shows two well characterized signals at 1.936 and 1.914 and a shoulder at 1.899. These absorption bands indicate severe distortion of the octahedral symmetry of the molecules in the solid state where these signals could be assigned to g_z, g_y and g_x values, respectively. The IR spectra of both the parent Cu(II) complex and the product Co(II) complexes are similar indicating the same type of bonding.

The electronic absorption spectra VO(IV) complexes, $[L_aVO] \cdot H_2O$ and $[L_bVO] \cdot 3\frac{1}{2}H_2O$, show *d–d* transition bands at 580 and 575 nm, respectively, indicating octahedral geometry around the VO(IV) cations,[29] Figures 4(a) and 5(c). Magnetic moments of the complexes are 1.84 and 2.27 B.M., respectively. The higher values observed are due to orbital contributions resulting from the polymeric association of the molecules. ESR spectra of the solid complexes at room temperature are similar, Figure 6, and show one strong signal with $g_{\rm eff}$ of 1.901 and 1.900, respectively. Splitting of the bands was not observed as their insolubility in organic solvent hindered observation of the solution spectra. The lack of hyperfine structure might be due to strong spin exchange in the magnetically concentrated samples.

The magnetic moment of the complex, $[L_aMn]\cdot 2H_2O$ is 4.0 B.M. which may indicate anti-ferromagnetic interactions between neighboring Mn(II) cations in the polymeric chains, Figure 4, similar to that observed for VO(IV) complexes. The ESR spectrum of the solid complex at room temperature showed a broad band with $g_{\rm eff}$ of 1.909 (Figure 6). Again, no splitting is observed due to the insolubility of the complex in organic solvents. However, it was cited that polymeric species of Mn(II) complexes show this type of a single broad band in the ESR spectra.[30,31]

The electronic absorption spectrum of the Fe(III) complex, $[L_bFe_2Cl_4(OH_2)]\cdot 2H_2O$, Figure 5(b), showed bands at 535 and 435 due to *d–d* transitions in octahedral geometry.[21] The ESR spectrum of the complex, Figure 6, showed splitting which would be due to the coupling of the inner iron(III) ion to the surrounding nitrogen atoms.[27,28]

The electronic spectral features of UO_2(VI) complexes, $[(HL_a)_2UO_2(OH_2)]$ and $[L_bUO_2]\cdot 6H_2O$ (Table II) exhibit two absorption bands at 330 and 550 nm for the former complex and at 480 and 562 nm for the latter complex. The higher energy bands of both complexes are attributed to electronic transitions from apical oxygens to *f* orbitals of the uranium(VI) ion and the lower energy bands are due to the charge transfer transition from equatorial ligands to the uranium(VI) ion.[32]

It is worth noting that the small cation, Zn(II), was incorporated in the cavities of both ligands while the large cations, Cd(II) and UO_2(VI) were accommodated in the pentadentate cavity of ligand H_2L_b, while the cavity of the tetradentate ligand, H_2L_a, was insufficient to accommodate such cations. Thus, UO_2(VI) and Cd(II) cations are linked only to the outer O–O atoms of two monoanionic HL_a moieties, Figure 4(c), as the N_2O_2 cavity of this ligand is unable to accommodate the large UO_2(VI) and Cd(II) cations, while the N_3O_2 cavity of one ligand is large enough to accommodate the same cations, Figure 5(a) and (c). Similar observations were reported for similar ligands.[33] The pentadentate ligand allowed the UO_2(VI) cation to reach its favorite equatorial pentacoordination while the tetradentate ligand was not able to do so.

Mass Spectra of the Metal Complexes

The mass spectrum of the nickel complex 11, Figure 7 indicates that the complex is binuclear, with the highest mass peak at *m/e* 868 (calculated value 864.2). The fragmentation pattern shown in Scheme 1 agrees with the proposed formula of the complex. Also, the mass spectra of the vanadyl and uranyl complexes of ligand H_2L_b, 15 and 16, Table I, showed their base peaks are at 616 and 864 (calculated values 615.5 and 863.7), respectively, indicating that these complexes are mononuclear.

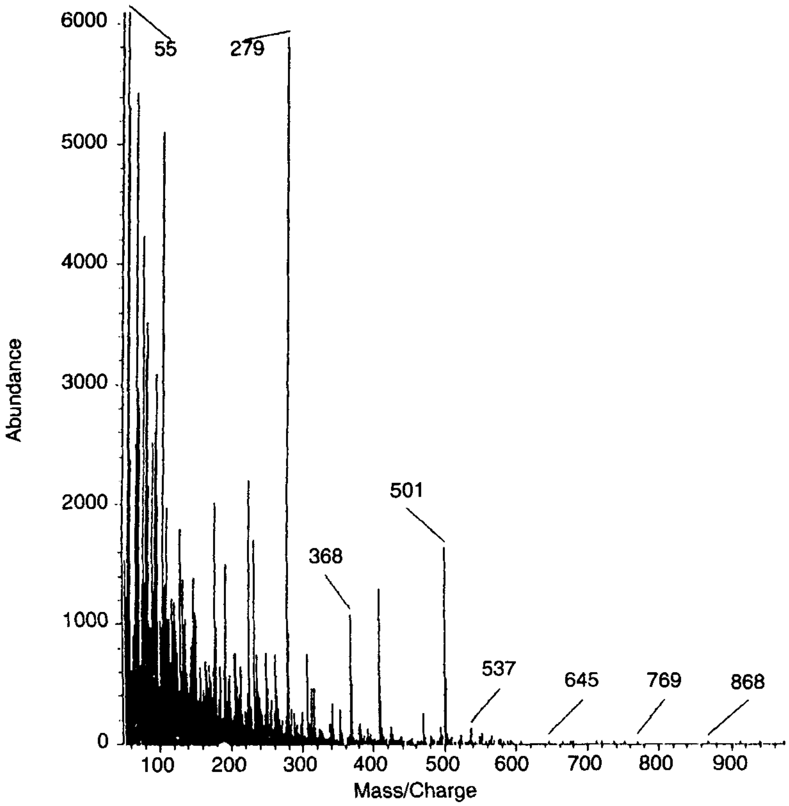
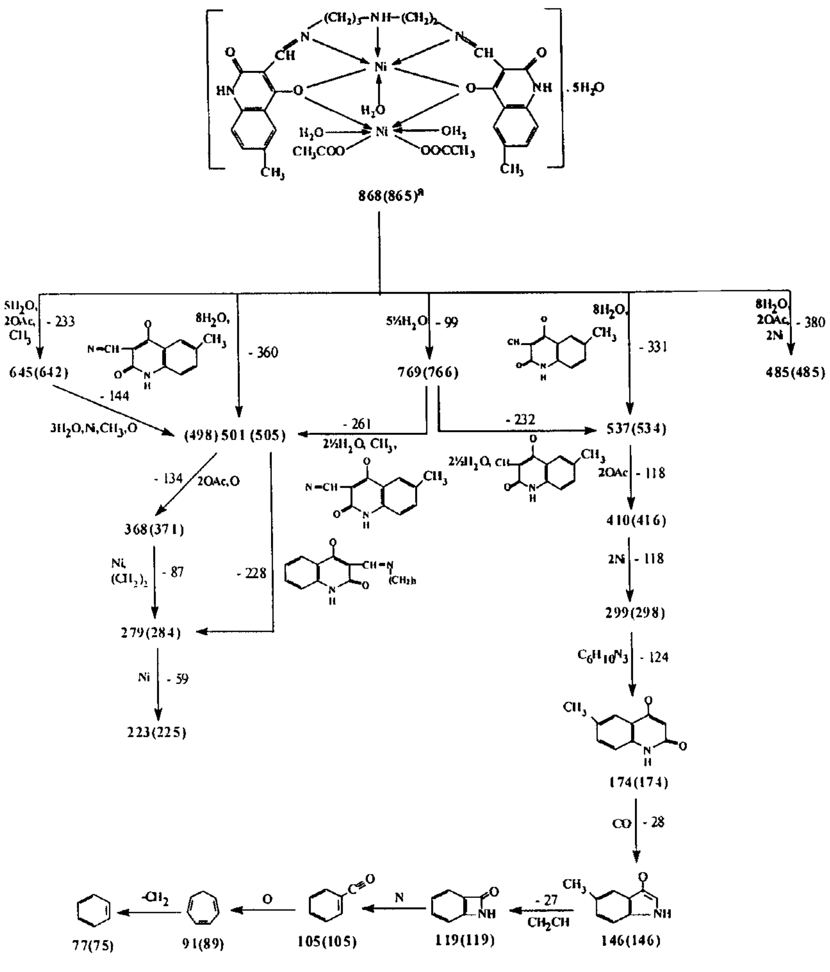


FIGURE 7 Mass spectrum of the dinuclear complex, $[L_bNi_2(OAc)_2(OH_2)_3] \cdot 5H_2O$.



ᵃValues in parenthesis are the calculated m/e

SCHEME 1 Fragmentation pattern of the $[L_bNi_2(OAc)_2(OH_2)_3]\cdot 5H_2O$.

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