Preparation and Characterization of Novel Asymmetrical Schiff-Base Ligands Derived from 2-methyl-7-formyl-8-hydroxyquinoline and their Metal Complexes

Kamal A. R. Salib[a]; Akila A. Saleh[a]; Samy Abu El-Wafa[a]; Hoda F. O. El-Shafiy[a]

[a] Faculty of Education, Department of Chemistry, Ain Sham University, Cairo, Egypt

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

PREPARATION AND CHARACTERIZATION OF NOVEL ASYMMETRICAL SCHIFF-BASE LIGANDS DERIVED FROM 2-METHYL-7-FORMYL-8-HYDROXYQUINOLINE AND THEIR METAL COMPLEXES

KAMAL A.R. SALIB*, AKILA A. SALEH, SAMY ABU EL-WAFA and HODA F.O. EL-SHAFIY

Faculty of Education, Department of Chemistry, Ain Sham University, Roxy, Cairo, Egypt

Two novel asymmetrical Schiff-base ligands, H_2L^1 and H_2L^2, were prepared by reacting two half-unit Schiff-base compounds with 2-methyl-7-formyl-8-hydroxyquinoline. The two half-unit Schiff-base compounds were initially prepared by condensing dimedone with either ethylenediamine or *p*-phenylenediamine, respectively. Both ligands are dibasic and contain two sets of NO coordinating sites. Twelve metal complexes were obtained by reacting both ligands with Cu(II), Ni(II), Co(II), Mn(II), Fe(III), VO(IV) cations. The ligands and their metal complexes were characterized by elemental analysis, IR, UV–Vis, ESR and mass spectra, also magnetic moments of the complexes were determined. Visible spectra of the complexes indicated distorted octahedral geometries around the metal cations. ESR spectra indicated mononuclear and dinuclear structures of the complexes of ligands H_2L^1 and H_2L^2, respectively. Magnetic moments of the complexes were rather low compared with those expected for octahedral geometries and indicated polymeric linkage of the metal complex molecules within their crystal lattices. The insolubility of the metal complexes in most organic solvents support the polymeric structures.

Keywords: Asymmetrical schiff bases; Transition metal complexes; ESR spectra of TM complexes; Magnetic moments of TM complexes

INTRODUCTION

Schiff bases offer versatile and flexible ligands capable of binding with metal cations to yield complexes, some of them have suitable properties for practical applications [1–3].

Quinoline, its derivatives and their metal complexes were also used in therapeutic treatments for diseases [4–6].

The present study deals with the preparation of two asymmetric Schiff-base ligands and their metal complexes. These Schiff-base ligands were prepared by condensing two half-unit compounds with 2-methyl-7-formyl-8-hydroxyquinoline. The two half-unit

---

*Corresponding author. E-mail: ksalib@yahoo.com
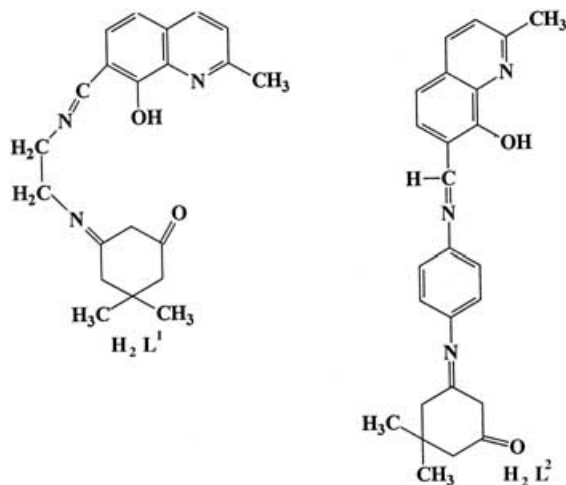
STRUCTURE 1   Structures of the asymmetrical Schiff-base ligands.

compounds were initially prepared by the condensation of dimedone with either ethylenediamine or *p*-phenylenediamine.

   The parent aldehyde, 7-formyl-8-hydroxyquinoline, used in the present study as its 2-methyl derivative for the preparation of the two asymmetrical Schiff-base ligands, was previously used to prepare its own metal complexes [7]. The Co(II), Ni(II) and Cu(II) complexes possess tetrahedral, octahedral and square planar geometries, respectively, and the ligand behaved as a neutral monodentate ligand coordinating only through the oxygen atom of the aldehyde group. The Hg(II) and Cd(II) complexes coordinated to the oxygen atom of the aldehyde group and to the oxygen atom of the phenolic group through the replacement of its hydrogen atom. In the latter complexes, the aldehyde behaved as a monobasic bidentate ligand. It was surprising that the nitrogen atom of the quinoline ring did not participate in coordinating metal cations since 8-hydroxyquinoline itself is an efficient chelating agent through the nitrogen atom of the heterocyclic ring and the oxygen atom of the phenolic group.

   The two asymmetric Schiff-base ligands H_2L^1 and H_2L^2 (Structure 1) reacted with Cu(II), Ni(II), Co(II), Mn(II), VO(IV) and Fe(III) ions to form complexes which differ in their structures as will be shown later.

EXPERIMENTAL

All chemicals used were either BDH, Analar or Merck products. The chemicals used were 8-hydroxy-2-methylquinoline, dimedone, ethylenediamine, *p*-phenylenediamine, copper(II) perchlorate hexahydrate, nickel(II) and cobalt(II) acetate tetrahydrates, manganese(II) chloride tetrahydrate, iron(III) nitrate nonahydrate and vanadium(II) sulfate monohydrate. The mineral acids utilized were perchloric, nitric and hydrochloric acids. The organic solvents used were ethanol, chloroform, ethylacetate, dioxane, dimethylformamide (DMF), dimethylsulfoxide (DMSO), carbon tetrachloride, dichloromethane, benzene and diethylether.

The nickel(II) and cobalt(II) acetate tetrahydrates were converted to their corresponding perchlorate hexahydrate salts through their reaction with perchloric acid.

Preparation of 7-Formyl-8-Hydroxy-2-Methylquinoline

8-Hydroxy-2-methylquinoline (1.59 g, 10 mmol) was added to 8.5 mL (105 mmol) chloroform and 20 ml of an aqueous solution of 15% NaOH. The reaction mixture was heated under reflux for 4 h on a water bath, during which time the color of the solution changed to brown. The excess chloroform was evaporated and the solution was left to cool to room temperature. The pH of the solution was adjusted to 4–5 by dilute hydrochloric acid and the formed precipitate was filtered and washed with twice distilled water then chloroform to remove any traces of the unreacted 8-hydroxy-2-methylquinoline. The color of the product was orange yellow. Anal. Calcd. for $C_{11}H_9NO_2$ (F. W. 187.2) (%): C, 70.6; H, 4.9; N, 7.5. Found: C, 70.8; H, 4.8; N, 7.0; m.p. 214°C, yield 1.31 g (70%).

Preparation of the Half-Unit Schiff Bases

Half-unit Schiff bases were prepared by slow addition of equimolar amounts of ethylenedimine (0.6 g, 10 mmol) or p-phenylenediamine (1.08 g, 10 mmol) dissolved in absolute ethanol to an ethanolic solution of dimedone (1.4 g, 10 mmol). The ethanolic solution was kept at room temperature and stirred for 10 h where ethanol was totally evaporated. The product of dimedone and ethylenediamine (A) was solidified by washing with ethylacetate to which one or two drops of dioxane was added. The product of the p-phenylenediamine (B) was precipitated immediately. Both products were filtered, washed several times with ethanol and dried *in vacuo*. The products were pale yellow. Anal. Calcd. for (A) $C_{10}H_{18}N_2O$ (F. W. 182.3) (%): C, 65.9; H, 10.0; N, 15.4. Found: C, 65.9; H, 9.9; N, 15.3; m.p. > 280°C. Anal. Calcd. for (B) $C_{14}H_{18}N_2O$ (F. W. 230.3) (%): C, 73.0; H, 7.9; N, 12.2. Found: C, 72.8; H, 7.9; N, 12.0; m.p. 175°C. Yields of the half-unit Schiff bases were 60–70%.

Preparation of the Schiff-Base Ligands H_2L^1 and H_2L^2 (Structure 1)

The preparations were carried out by refluxing equimolar amounts of the obtained half-units 1.82 g, 10 mmol of (A) or 2.30 g, 10 mmol of (B) with 1.87 g, 10 mmol of 7-formyl-8-hydroxy-2-methylquinoline for 10 h in a mixture of dioxane and ethanol (1:1 by volume). The resulting solution was left to cool to room temperature and the solids were precipitated by adding a few drops of water. The separated solids were purified by recrystallization from dimethylformamide. The colors of the ligands H_2L^1 and H_2L^2 were greenish yellow and pale brown, respectively. Anal. Calcd. H_2L^1 $C_{21}H_{23}N_3O_2$ (F. W. 349.4) (%): C, 72.2; H, 6.6; N, 12.0. Found: C, 72.1; H, 6.8; N, 12.0. Anal. Calcd. for H_2L^2, $C_{25}H_{25}N_3O_2$ (F. W. 399.5) (%): C, 75.2; H, 6.3; N, 10.5. Found: C, 75.3; H, 6.2; N, 10.5. m.p. > 280 and 200°C, respectively. Yields were 60–65%.

Preparation of the Metal Complexes

LiOH · H_2O was used as a deprotonating agent. LiOH · H_2O (0.082 g, 2 mmol) (or 0.126 g, 3 mmol in the case of the reaction with the Fe(III) salt) dissolved in the least

amount of distilled water (2 mL) was added to a suspension of the ligand (1 mmol) (or 1.5 mmol in the case of Fe(III) ion) in 20 mL ethanol. The mixture was stirred for 1 h, then the metal salt (1 mmol), namely $(Cu(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ or $VOSO_4 \cdot H_2O$, dissolved in the least amount of distilled water was added. The reaction solution was left for 2–4 days at room temperature while stirred occasionally to ensure the complete formation of the metal complexes. The precipitated solid complexes were filtered, washed several times with distilled water followed by ethanol to remove any traces of the unreacted metal salts then washed with diethylether and finally dried in a desiccator over anhydrous $CaCl_2$. The complexes are partially soluble in DMSO, DMF, $CHCl_3$ and ethanol and insoluble in most other common organic solvents viz. benzene, CCl_4 and CH_2Cl_2.

Electronic spectra of the ligands were recorded as solutions in DMSO, DMF, dioxane and $CHCl_3$; the metal complexes as Nujul mulls and as solutions in either DMSO or DMF on a Jasco V-550 UV–Vis spectrophotometer. IR spectra of the compounds were recorded on a Shimadzo IR spectrometer model 470 and a Perkin-Elmer 598 IR spectrometer using KBr discs, polystyrene was used as a calibrant. ESR spectra of the solid metal complexes were recorded on a JEOL microwave unit JES-FE$_2$XG spectrometer at the Central Laboratories of Tanta University, Tanta, Egypt. The magnetic field was calibrated with 2,2-diphenyl-1-picrylhydrazine purchased from Aldrich. Mass spectra of the ligands and one of the complexes was recorded on a Hewlett-Packard mass spectrometer MS 5988 at the Microanalytical Center, Cairo University. The fragmentations were 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 MKI magnetic susceptibility balance, mercury(II) tetrathiocyanate-cobaltate(II) was used as a calibrant. The effective magnetic moments were calculated from the expression $\mu_{eff} = 2.828 (\chi_m T)^{1/2}$ B.M., where χ_m is the molar susceptibility. Diamagnetic corrections were calculated from Pascal's constants.

Microanalyses of carbon, hydrogen and nitrogen were carried out at the Microanalytical Center, Cairo University. Analyses of the metals followed decomposition of their complexes with concentrated nitric acid, the resultant solution was diluted with water and filtered to remove the precipitated ligand. The solution was neutralized with ammonia solution, the metal ions were then titrated with EDTA. Vanadium was estimated by a Perkin-Elmer Atomic Absorption Apparatus Model 3100 HGA 600 at the Faculty of Science, Ain Shams University.

RESULTS AND DISCUSSION

Half-Unit Schiff Bases

Two half-unit Schiff bases were prepared by reacting dimedone with either ethylenediamine or *p*-phenylenediamine (Structure 2).

The mass spectrum of the former half-unit Schiff base (A), Structure 2, indicates that its molecules weight is 182, calculated $= 182$.

The IR spectra of both half-unit Schiff bases showed bands at 3260 and 3080 cm^{-1}, for half-unit (A) and at 3423 and 3340 cm^{-1} for half-unit (B). These bands are assigned to ν_{as} and ν_s vibrations of the NH$_2$ group, respectively. A band due to ν_{NH} group
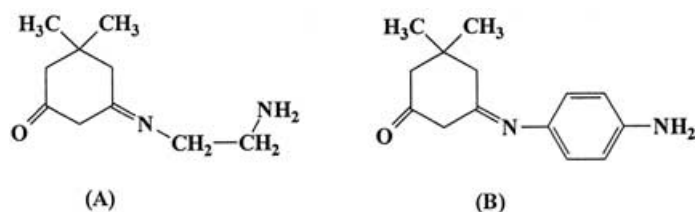
STRUCTURE 2   Ketonic forms of the half-unit Schiff bases.
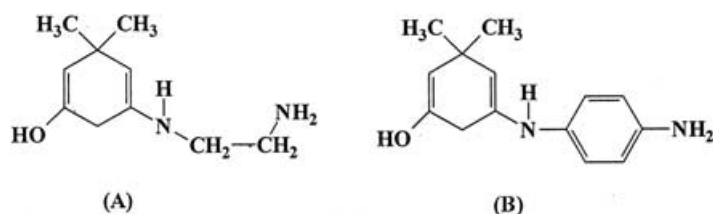
STRUCTURE 3   Enolic form of the half-unit Schiff bases.

originating through resonance of the ketonic form to the enolic forms (Structure 3) of the half-unit compounds appeared at 3080 and 3230 cm^{-1} for half-unit (A) and (B), respectively. However, the former band is overlapping with the ν_s vibration of the NH$_2$ group of half-unit (A). The stretching vibration of the enolic OH group appears as a weak broad band at 3440 and 3450 cm^{-1} for half-unit compounds (A) and (B), respectively. In the parent dimedone compound this band appears at 3460 cm^{-1}. Strong bands in the range 1500–1635 cm^{-1} are assigned to $\nu_{C=O}$, $\nu_{C=C}$ and $\nu_{C=N}$ bonds originating through resonance between the ketonic and enolic forms of the half-unit molecules [8]. Two bands in the range 1240–1280 cm^{-1} are assigned to ν_{C-O} and ν_{C-N} bonds whereas the spectrum of the parent dimedone compounds shows only one band at 1248 cm^{-1} assigned to ν_{C-O} bond.

Asymmetrical Schiff-Base Ligands

Two asymmetrical Schiff-base ligands (Structure 1) were prepared by condensing the parent aldehyde, 2-methyl-7-formyl-8-hydroxyquinoline with the half-unit Schiff bases (A) or (B), Structure 2, to yield the ligands H$_2$L^1 and H$_2$L^2, respectively.

The IR spectra of the ligands are devoid of the bands due to the NH$_2$ group of the half-unit compounds and the band due to the C=O group of the parent aldehyde, which appears at 1685 cm^{-1}, in the spectrum of the free aldehyde, due to condensation of the NH$_2$ and C=O groups to produce the Schiff-base linkage. Instead, the intensity of the band at $\sim$1580 cm^{-1}, due to the heterocyclic C=N group, is enlarged in the case of the ligands due to its overlap with the azomethine group of the Schiff-base linkage. The stretching vibration of the phenolic OH group persists at $\sim$3380 cm^{-1} as for the parent aldehyde. The low values of the latter bands may be attributed to the formation of intramolecular hydrogen bonding between the nitrogen atom of the heterocyclic ring or the azomethine group and the phenolic OH group as shown in Structure 4.

The stretching vibrations of the NH and the enolic OH groups originating through resonance, Structure 5, appear at 3230 and 3335 cm^{-1}, respectively, in the case of

STRUCTURE 4   H-bonding in asymmetric Schiff-base ligands (only one half of the ligand molecule is shown in this figure which contains the quinoline moiety and where H-bonding occurs).

STRUCTURE 5   Resonance occurring in the dimedone moiety of the asymmetric ligands, H_2L^1 and H_2L^2.

H_2L^2 ligand while they are overlapped by the strong and broad absorption band of the phenolic group in the case of ligand H_2L^1. The band due to the remaining C=O group of the dimedone moiety appears as a shoulder at $1635\,cm^{-1}$. The ν_{C-N} of the heterocyclic ring and ν_{C-O} of the phenol moiety appear at 1330 and $1365\,cm^{-1}$, respectively. The δ_{OH} of the phenolic group appears as a doublet at 1265 and $1247\,cm^{-1}$ which would reflect the effect of both types of H-bonding as shown in Structure 4, besides the presence of the enolic OH group, Structure 5.

The UV–Vis spectra of the asymmetrical Schiff-base H_2L^1 shows five bands in the ranges 248–251, 281–286, 330–339, 395–430 and 440–473 nm respectively. The first three bands could be assigned to electronic transitions within the aromatic ring, C=O and C=N groups. The latter two bands can be assigned to an intramolecular charge transfer originating from the quinoline moiety to the azomethine linkage. In the case of ligand H_2L^2, the second and third transitions overlap and appear as a single broad band. Also, only one charge transfer band appears in the region 395–473 nm.

The mass spectra of each of the ligands H_2L^1 and H_2L^2 show a molecular ion peak corresponding to its formula weight. Also, their degradation patterns show some similar fragments which indicate the similarity of their molecular structures.

Metal Complex

Reaction of the two asymmetrical Schiff-base ligands H_2L^1 and H_2L^2 with the transition metal cations Cu(II), Ni(II), Co(II), Mn(II), VO(II) and Fe(III) yielded twelve metal complexes. The metal complexes were characterized by their chemical analyses, IR, UV–Vis and ESR spectra (Tables I and II). Also, the magnetic moments of the complexes were determined.

Magnetic Moments of the Metal Complexes

The values of the magnetic moments of the metal complexes, Tables I and II are rather peculiar, thus our discussion will start with these values. The values of the magnetic moments are generally lower than those expected for known geometries [9,10], Table III. These low values indicate strong antiferromagnetic exchange between

TABLE I Chemical analyses and other data of metal complexes of ligand H_2L^1

Reactants	Metal complexes	M. Wt.	Color	Yield %	M.p. °C	Elemental analyses (%) found/(Calc.)				μ_{eff} B.M.
						C	H	N	M	
1. H_2L^1+Cu(ClO$_4$)$_2$·6H$_2$O	[Cu L^1]·¾ H$_2$O, C$_{21}$H$_{24½}$N$_3$O$_{2¾}$Cu	426.5	Green	71	> 270	59.2 (59.1)	5.6 (5.8)	9.9 (9.9)	14.8 (14.9)	1.72
2. H_2L^1+Ni(ClO$_4$)$_2$·6H$_2$O	[Ni L^1]·¾H$_2$O, C$_{21}$H$_{24½}$N$_3$ O$_{2¾}$ Ni	421.7	Deep green	86	> 270	60.0 (59.8)	5.8 (5.9)	10.0 (10.0)	13.9 (13.9)	2.20
3. H_2L^1+Co(ClO$_4$)$_2$·6H$_2$O	[Co L^1]·2½ H$_2$O, C$_{21}$H$_{28}$N$_3$O$_{4½}$Co	450.4	Bluish green	85	> 270	56.0 (56.0)	6.1 (6.3)	9.2 (9.3)	12.3 (12.4)	3.68
4. H_2L^1+MnCl$_2$·4H$_2$O	[Mn L^1]·2H$_2$O, C$_{21}$H$_{25}$N$_3$O$_3$Mn	422.4	Deep green	77	> 270	59.8 (59.7)	5.9 (5.9)	9.9 (10.0)	12.9 (13.1)	3.26
5. H_2L^1+VOSO$_4$·H$_2$O	[VO L^1]·1¾H$_2$O, C$_{21}$H$_{26½}$N$_3$O$_{4¾}$V	447.9	Brown	64	> 270	56.4 (56.3)	5.9 (6.0)	9.4 (9.4)	11.5 (11.4)	1.30
6. 3H_2L^1+2Fe(NO$_3$)$_3$·9H$_2$O	[Fe(L^1)$_{1½}$]·3½H$_2$O, C$_{31½}$H$_{41½}$N$_{4½}$O$_{6½}$Fe	643.1	Black	64	> 270	58.7 (58.8)	6.3 (6.5)	9.8 (9.8)	8.4 (8.7)	4.17

TABLE II Chemical analyses and other data of metal complexes of ligand H_2L^2

Reactants	Metal complexes	M. Wt.	Color	Yield %	M.p. °C	Elemental analyses (%) found/(Calc.)				μ_{eff}[a] B.M.	μ_{compl}[b] B.M.
						C	H	N	M		
1. H_2L^2+Cu(ClO$_4$)$_2\cdot$6H$_2$O	[Cu$_2$ L^2)$_2$]$\cdot$6H$_2$O C$_{50}$H$_{58}$N$_6$O$_{10}$Cu$_2$	1030.1	Bluish green	75	>270	58.3 (58.3)	5.3 (5.7)	8.0 (8.2)	12.7 (12.3)	1.38	1.94
2. H_2L^2+Ni(ClO$_4$)$_2\cdot$6H$_2$O	[Ni$_2$ (L^2)$_2$]$\cdot$6H$_2$O C$_{50}$H$_{58}$N$_6$O$_{10}$Ni$_2$	1020.5	Green	71	>270	58.7 (58.9)	5.5 (5.7)	8.0 (8.2)	11.0 (11.5)	–	–
3. H_2L^2+Co(ClO$_4$)$_2\cdot$6H$_2$O	[Co$_2$(L^2)$_2$]$\cdot$4H$_2$O C$_{50}$H$_{54}$N$_6$O$_8$Co$_2$	984.9	Greenish black	79	>270	60.6 (61.0)	5.5 (5.5)	8.4 (8.5)	11.8 (12.0)	2.87	4.06
4. H_2L^2+MnCl$_2\cdot$4H$_2$O	[Mn$_2$(L^2)$_2$]$\cdot$6H$_2$O C$_{50}$H$_{58}$N$_6$O$_{10}$Mn$_2$	1012.9	Olive green	71	>270	59.3 (59.3)	5.7 (5.8)	8.1 (8.3)	10.8 (10.9)	4.37	6.18
5. H_2L^2+VOSO$_4\cdot$H$_2$O	[(VO)$_2$ (L^2)$_2$]$\cdot$6H$_2$O C$_{50}$H$_{58}$N$_6$O$_{12}$V$_2$	1036.9	Brown	70	>270	57.6 (57.9)	5.6 (5.6)	8.0 (8.1)	9.6 (9.8)	1.37	1.94
6. 3H_2L^2+2Fe(NO$_3$)$_3\cdot$9H$_2$O	[Fe$_2$ (L^2)$_3$]$\cdot$4H$_2$O C$_{75}$H$_{77}$N$_9$O$_{10}$Fe$_2$	1376.2	Black	63	>270	65.3 (65.5)	5.2 (5.6)	9.2 (9.2)	8.0 (8.1)	2.06	2.91

[a] μ_{eff} is the magnetic moment of one cation in the complex.
[b] μ_{compl} is the total magnetic moment of all cations in the complex.

TABLE III   Comparison between magnetic (B.M.) of the metal complexes and those expected for different symmetries

Metal cation	μ_{eff} for metal complexes		Literature cited values [a]			
	H_2L^1	H_2L^2	Octahedral high spin	5-coordinate	tetrahedral	square-planar
Cu(II)	1.72	1.38	1.70–2.20	–	–	1.70–2.20
Ni(II)	2.20	–	2.90–3.30	3.20–3.40	3.2–4.1	Diamagnetic
Co(II)	3.68	2.87	4.70–5.20	–	4.40–4.80	2.10–2.80
Mn(II)	3.26	4.37	5.90	–	–	–
VO(II)	1.30	1.37	1.70–1.80	–	–	–
Fe(III)	4.17	2.06	5.90	–	–	–

[a][9,10].

adjacent metal cations, probably existing in polymeric structures. The very weak solubility of all metal complexes in organic solvents strongly support this suggestion.

Table III compares the observed magnetic moments of the metal complexes with those expected for octahedral, five-coordinate, tetrahedral and square-planar geometries. The values of the magnetic moments for all metal complexes are generally lower than the cited values for all geometries. However, no regular relation exists for a certain ligand with the different metal cations. The values observed in the case of Co(II) are higher than square-planar geometry and lower than either tetrahedral or octahedral geometries. Also, for the Ni(II) complex of ligand H_2L^1, the value obtained is lower than octahedral, five-coordinate or tetrahedral geometries but it is definitely not square planar as it would be diamagnetic. On the basis of other spectroscopic results, as mentioned later, the octahedral geometry would be favored. The differences in the locations of different metal cations in their different crystal structures would lead to different antiferromagnetic interactions, which in turn would be reflected in the wide differences of their observed magnetic moments.

ESR Spectra of the Metal Complexes

Next, we discuss the ESR spectral data of the metal complexes as they relate to and support the previous magnetic results. The ESR spectra of the metal complexes of ligand H_2L^2, except that of the VO(IV) and Ni(II) complexes, are shown in Fig. 1 together with the Ni(II) complex of ligand H_2L^1. The spectra of the other corresponding metal complexes of ligand H_2L^1 are quite similar and were thus deleted.

Copper (II) complexes of ligands H_2L^1 and H_2L^2 showed a broad signal at g values 1.924 and 1.926 and a shoulder at 1.973 and 1.981, respectively. The former band would be assigned to $g_{\parallel}$ and the latter shoulder to $g_{\perp}$. These results indicate distorted octahedral geometry of the Cu(II) complexes [11]. The apparent broadening of the ESR signals would be due to the interaction between Cu(II) cations present in nonequivalent lattice positions.

Surprisingly, the Ni(II) complex of ligand H_2L^1 showed a sharp signal at g value 1.903, Fig. 1. The Ni(II) ions have an even number of unpaired electrons and the lowest energy state would be nondegenerate and thus ESR silent. However, due to the distortion of the geometry of the complexes, as a result of their polymeric structures, the actual geometry of the Ni(II) ions would have an orbitally degenerate ground state. The degeneracy of the ground state would thus be lifted in the magnetic field
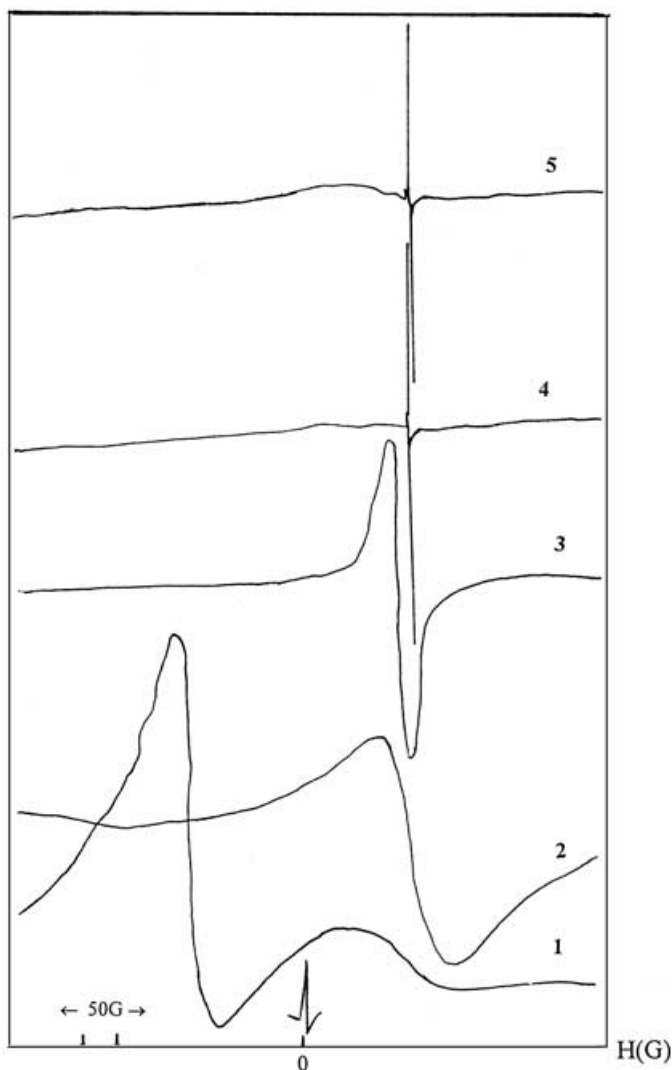
FIGURE 1   ESR powder spectra; X-bands, of $[Fe_2(L^2)_3] \cdot 4H_2O(\mathbf{1})$, $[Mn_2(L^2)_2] \cdot 6H_2O(\mathbf{2})$, $[Cu_2(L_2)^2] \cdot 6H_2O(\mathbf{3})$, $[Ni(L^1)] \cdot 6H_2O(\mathbf{4})$, $[Co_2(L^2)_2] \cdot 4H_2O(\mathbf{5})$ complexes. The signal at ~ 3370 G is due to the dpph field calibrant.

which would allow an ESR signal to be observed. Distorted tetrahedral cores [12] have been shown on the basis of X-ray single crystal studies of Ni(II) Schiff-base complexes containing bulky groups attached to the coordinated azomethine nitrogen atoms.

   Cobalt(II) complexes of both ligands showed a sharp signal at $g = 1.906$, Fig. 1. No splitting was observed which would be expected, due to the interaction of the unpaired electrons with ^{59}Co nuclei which have nuclear spin, $I = 7/2$, as the spectra were carried out at room temperature which would lead to the concentration of the paramagnetic ions.

   Manganese (II) complexes of ligands H_2L^1 and H_2L^2 showed very broad signals at g values 1.909 and 1.906, respectively. It has been previously reported that Mn(II)–Schiff

base chelates with bulkier substituents tend to favor the formation of polymeric species in the solids showing a single broad signal at room temperature [13,14].

Iron (III) complexes showed three signals with $g_x = 1.959$, g_y values in the range 2.115–2.119 and g_z values in the range 2.227–2.234. These results indicate severe distortion of the octahedral geometry in the solid state [15].

The VO(IV) complexes showed multi-line spectra indicating either mononuclear or dinuclear patterns. The vanadyl complex of ligand H_2L^1 showed an eight line pattern and that of ligand H_2L^2 showed fifteen lines pattern, Fig. 2. The g values of the former complex are in the range 1.815–2.079 and the latter complex are in the range 1.809–1.969. The hyperfine structures observed are due to the interaction of the unpaired electron with the ^{51}V nucleus which has a nuclear spin, $I = 7/2$.

It could be concluded from the observed ESR spectra of the vanadyl complexes that the size of the inner cavity of ligand H_2L^1 is suitable for coordinating the vanadyl cation. On the other hand, the structure of ligand H_2L^2 does not allow a mononuclear structure due to the presence of the phenyl group between the two sets of coordinating groups. In the latter case, the dinuclear form would exist where each vanadyl cation
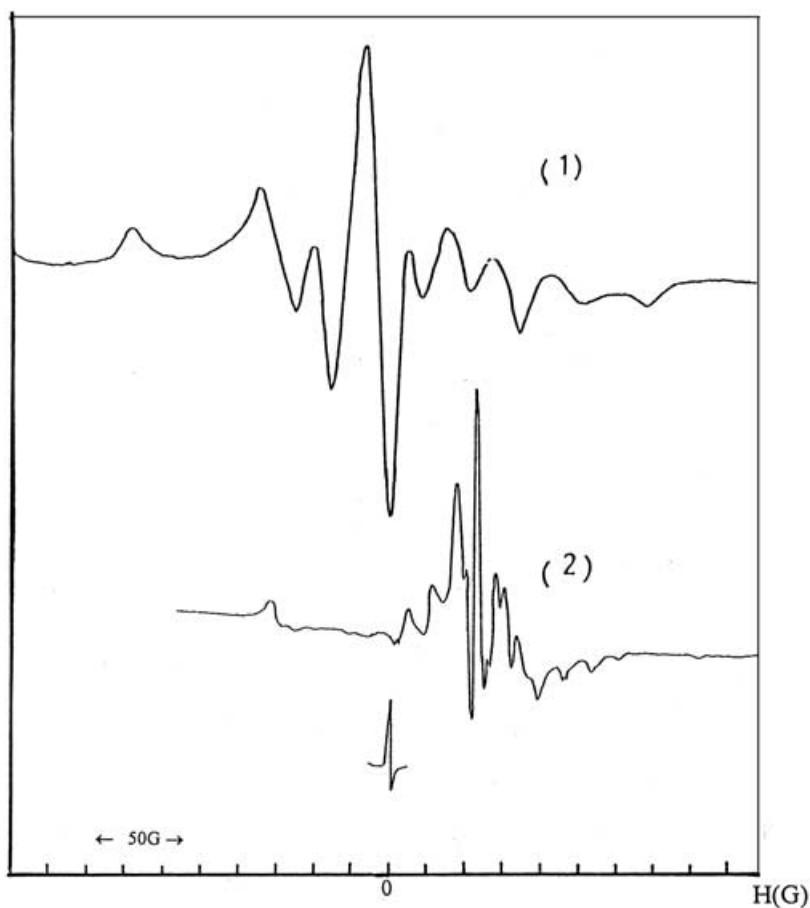

FIGURE 2   ESR powder spectra, X-bands of $[VOL^1]$(1) and $[VOL^2]_2$(2).

links only one azomethine nitrogen atom and a phenolic oxygen atom of each of two adjacent ligand molecules facing each other.

   Comparison between the ESR results and the magnetic moments of the metal complexes indicate that both tools supplement each other. Thus, while the ESR results indicated that the metal complexes of ligand H_2L^1 are mononuclear and those of ligand H_2L^2 are dinuclear, magnetic data indicated that either mononuclear or dinuclear products are further linked in polymeric chains leading to the observed decrease of their magnetic moments.

   Structures 6 and 7 indicate the linkage of either mononuclear or dinuclear complex molecules to each other, through coordination bonds to oxygen atoms from neighboring molecules. Thus, all metal complexes would acquire the distorted octahedral configuration. Also, Fe(III) complexes, which are surrounded by three covalent and three coordinate bonds from three halves of three chelating ligand molecules, would suffer severe distortion of the octahedral geometry as reflected in its ESR spectra.
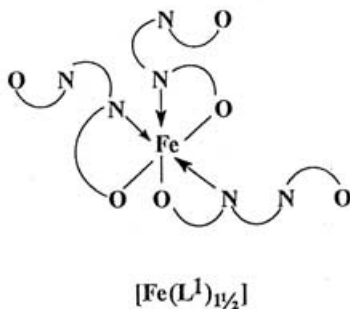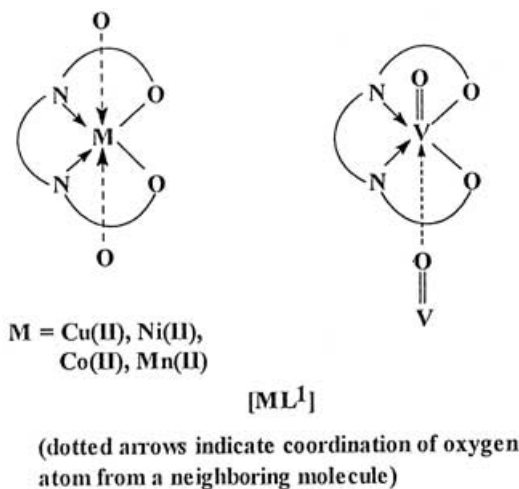
STRUCTURE 6   Suggested structures of metal complexes of the ligand H_2L^1.

$[M_2L^2_2]$
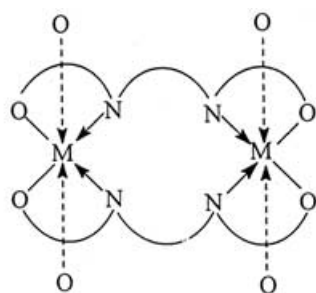
M = Cu(II), Ni(II), Co(II), Mn(II)

$[(VO)_2L^2_2]$

$[Fe_2(L^2)_3]$
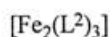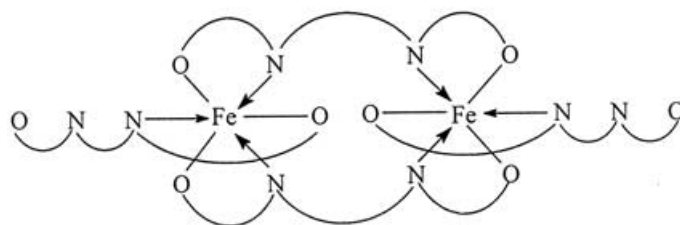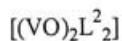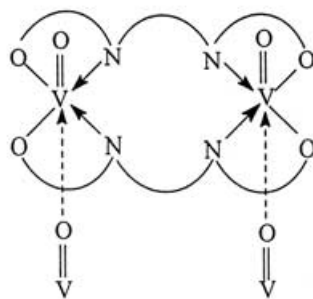
STRUCTURE 7   Suggested structures of metal complexes of the ligand H_2L^2.

IR Spectra of the Metal Complexes

The IR spectra of the metal complexes of a certain ligand are similar. The $\nu_{C=N}$ of the azomethine group is shifted to lower frequencies $\sim 10\,cm^{-1}$ indicating its involvement in coordinating metal cations. The low value of this shift is attributed to the already decreased value of $\nu_{C=N}$ in the parent ligand due to H-bonding between the nitrogen atom of the azomethine group and the hydrogen atom of the adjacent phenolic group, Structure 4, as previously mentioned. Also, the ν_{OH} of the phenolic group is replaced by the ν_{OH} of the hydrated water molecules.

The vanadyl complexes showed two bands; a strong band at 925–930 cm^{-1} and a medium band at 975 cm^{-1}. The location of the former band indicates that the VO(IV) cation is hexacoordinated. The presence of two absorption bands assigned to the VO(IV) cation and the insolubility of the vanadyl complexes in common organic solvents indicate polymerization through V=O → V=O bonds [16,17].

The Visible Spectra of the Metal Complexes

The visible spectra of the metal complexes were carried out as nujol mulls and DMSO or DMF solutions where the metal complexes were sparingly soluble.

The Cu(II) complex of ligand H_2L^1 showed a broad band at 650 nm in nujol mull, also a broad band at 625 nm in its DMSO solution. The Cu(II) complex of ligand H_2L^2 in either nujol mull or DMSO solution showed a broad band at 625 nm. These absorption bands indicate distorted octahedral geometry around the Cu(II) cations [10].

The Ni(II) complexes of both ligands showed a broad band, at 650 nm either as a nujol mull or in its DMF solution. This visible band would be due to $^3A_{2g} \rightarrow {}^3T_{1g}$ transition in octahedral geometry. The $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition is not observed as it is overlapped by ligand absorptions. The $^3A_{2g} \rightarrow {}^3T_{2g}$ transition would be in the near IR region [9].

The Co(II) complexes of ligands H_2L^1 and H_2L^2 showed broad bands at 700 and 550 nm, respectively, in their DMF solutions. In their nujol mulls, they showed broad bands at 670 and 650 nm, respectively, and a shoulder at 700 nm. The energies of these bands would be due to $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition in octahedral geometry [9]. However, their colors are bluish green and greenish black, respectively, which differ from the usual red color of octahedral Co(II) complexes. This could be due to the polymerization of the complexes which would lead to distorted octahedral structures and/or due to charge transfer bands within the ligand molecules.

Mn(II) octahedral complexes are expected to show very weak bands due to spin-forbidden transitions, also show light colors. The Mn(II) complexes of ligands H_2L^1 and H_2L^2 are deep green and olive green colored, respectively. They showed broad absorption bands of measurable intensity at 640 and 660 nm in their nujol mulls, respectively. Also, they showed a broad band at 690 nm in their DMF solutions. The distortion of the octahedral geometry of these complexes, due to polymerization, would be the main reason for shifting the absorbance bands and the increase of their intensities. The colors of the ligands would also contribute to the observed colors of the various complexes.

The VO(IV) complexes are brown with a narrow band at 700 nm in their nujol mulls. This band would be due to $b_2 \rightarrow e$ transition characteristic of octahedral VO(IV) complexes [9]. Only, the VO(IV) complex of ligand H_2L^1 showed a well characterized band at 680 nm in its DMSO solution.

The Fe(III) complexes of ligands H_2L^1 and H_2L^2 are black with narrow bands at 685 and 695 nm, respectively, in their nujol mulls and broad bands at 610 and 650 nm, respectively, in their DMSO solutions. These bands are assigned to the spin-forbidden $^6A_1 \rightarrow {}^4T_2(G)$ transition [9].

All complexes showed charge transfer bands at 400–500 nm in their DMF or DMSO solutions. These bands are similar to those occurring in the parent ligands and can be assigned to the intramolecular charge transfer from the quinoline moiety to the
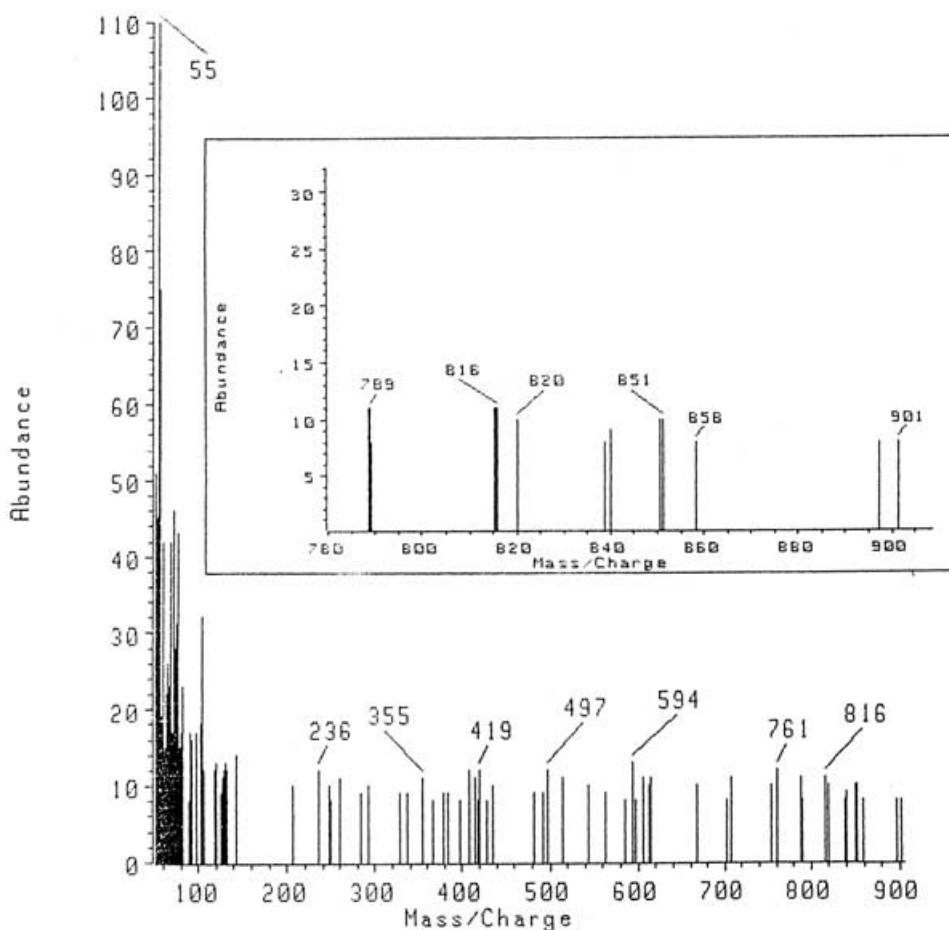
FIGURE 3 The mass spectrum of the Mn(II) complex of the ligand H_2L^2.

azomethine linkage. They are slightly shifted to higher energy than the parent ligands. These bands could also be assigned to ligand $\rightarrow$ metal, or vice versa, change transfer bands. These charge transfer bands would also affect the colors of the metal complexes and lead to their observed deep colors.

Mass Spectra of the Metal Complexes

A representative dimeric complex of the ligand H_2L^2, $[MnL^2]_2 \cdot 6H_2O$, was selected and its mass spectrum, Fig. 3, indicated peaks till $m/e = 901.5$. The m/e of the anhydrous complex is 904.9. Thus, this spectrum supports the dimeric nature of the metal complex.

References

[1] B. Rihter, S. Srihari, S. Hunter and J. Masnovi, *J. Am. Chem. Soc.* **115**, 3918 (1993).
[2] Z. Li, K.R. Conser and E.N. Jacobsen, *J. Am. Chem. Soc.* **115**, 5326 (1993).
[3] A.J. Fry and P.F. Fry, *J. Org. Chem.* **58**, 3496 (1993).

[4] E. Proffit and G. Buchmann, *Arznemittel Forsch* **10**, 181 (1960).
[5] D.R. Williams, *Chem. Rev*. **72**, 203 (1972).
[6] M.R. Mahmoud, A. Awad, A.M. Hamman and H. Saber, *Ind. J. Chem*. **19A**, 1131 (1980).
[7] A.A. El-Asmy, A.Z. El-Sonbati and A.A. Ba-Issa, *Transition Met. Chem*. **15**, 222 (1990).
[8] J.P. Costes and D.E. Fenton, *J. Chem. Soc.*, *Dalton Trans*. 2235 (1983).
[9] J.C. Bailar, H.J. Emeleus, R. Nyholm and A.F. Trotman-Dickenson (Eds.), Comprehensive Inorg. Chem. (Pergamon Press, Oxford, 1975) Vol. 3, pp. 517, 1049, 1089, 1092, 1154, 1155, 1157.
[10] F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry. (Interscience Publishers, New York, 1972) 3rd Edn., pp. 538.
[11] B.J. Hathaway and A.A.G. Tomlinson, *Coord. Chem. Rev*. **5**, 1 (1970).
[12] C.H. Wei and J.R. Einstein, *Acta Cryst*. **B28**, 2591 (1972).
[13] W.C. Potter and L.T. Taylor, *Inorg Chem*. **15**, 1329 (1976).
[14] R.D. Dowsing, J.F. Gibson, M. Goodgame and R.J. Hayward, *J. Chem. Soc. (A)* **187** (1969).
[15] E.A.V. Ebsworth, D.W.H. Rankin and S. Cradok, Structural methods in Inorganic Chemistry. (Blackwell, USA, 1987) 1st Edn., p. 111.
[16] D.E. Hamilton, *Inorg. Chem*. **30**, 1670 (1991).
[17] S.A. Fairhurst, D.L. Hughes, U. Kleinkes, G.L. Heigh, J.R. Sanders and J. Weisner, *J. Chem. Soc. Dalton Trans*. **321** (1995).