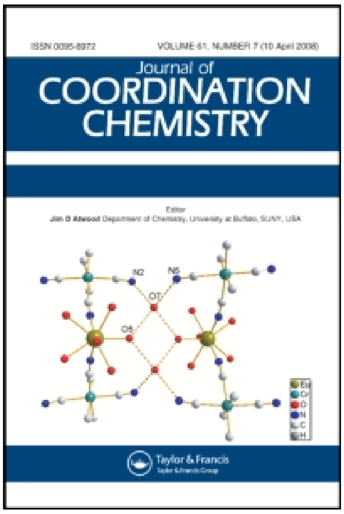
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Synthesis and spectroscopic studies on ternary bis-Schiff-base complexes having oxygen and/or nitrogen donors

Azza A. A. Abu-Hussen[a]
[a] Department of Chemistry, Girl's College for Art, Science and Education, Ain Shams University, Cairo, Egypt

To cite this Article Abu-Hussen, Azza A. A.(2006) 'Synthesis and spectroscopic studies on ternary bis-Schiff-base complexes having oxygen and/or nitrogen donors', Journal of Coordination Chemistry, 59: 2, 157 — 176
To link to this Article: DOI: 10.1080/00958970500266230
URL: http://dx.doi.org/10.1080/00958970500266230

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Coordination Chemistry
Vol. 59, No. 2, January 2006, 157–176

Taylor & Francis
Taylor & Francis Group

Downloaded At: 12:35 23 January 2011

Synthesis and spectroscopic studies on ternary bis-Schiff-base complexes having oxygen and/or nitrogen donors

AZZA A. A. ABU-HUSSEN*

Department of Chemistry, Girl's College for Art, Science and Education,
Ain Shams University, Cairo, Egypt

(*Received 16 September 2004; revised 3 January 2005; in final form 19 July 2005*)

The bis-Schiff-base of N_2O_2 donor dibasic ligand, H_2L, is synthesized by the reaction of 4,6-diacetylresorcinol with ethylamine in molar 1 : 2 ratio. The ligand is characterized using IR, UV-Vis, ^{1}H NMR and mass spectroscopy. The ^{1}H NMR spectrum of the ligand shows the presence of phenolic coordinating groups. Several new mixed ligand complexes of the Schiff-base ligand (H_2L) and (L′) where (L′) = deprotonated 8-hydroxyquinoline (8-HQ), 2,2′-bipyridine (2,2′-Biby) and 1,10-phenanthroline (1,10-Phen) with different metal ions such as Co(II), Ni(II), Cu(II) and UO_2(VI) are synthesized. Elemental analyses, infrared, ultraviolet-visible, electron spin resonance and thermal analysis, as well as conductivity and magnetic susceptibility measurements, are used to elucidate the structures of the newly prepared metal complexes. The complexes are isolated as binuclear and confirmed by ESR spectra. Thermal degradation studies for some complexes show that the final product is the metal oxide. In addition, thermal gravimetric analysis (TGA) is used as a tool to detect that the water molecules associated with the complexes are either coordinated or crystalline. An octahedral geometry is suggested for the Co(II), Ni(II), Cu(II) (for 2,2′-Biby and 1,10-Phen), and UO_2(VI) complexes, square planar for Cu(II) (for 8-HQ) complexes and their calculated field parameters agree with their proposed geometry.

Keywords: bis-Schiff-base complexes; ESR; ^{1}H NMR; UV-vis; Thermal analysis

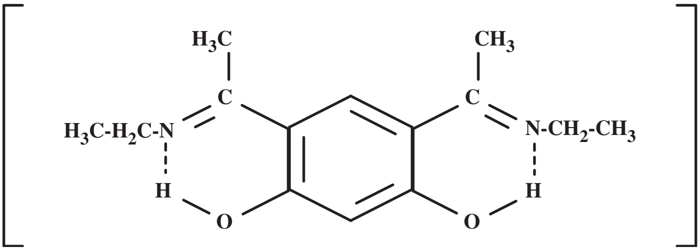
1. Introduction

Transition metal Schiff-base complexes are important stereochemical models in coordination chemistry due to their preparative accessibility and structural diversity [1–3]. A comprehensive review on cyclic and acyclic Schiff-bases and related derivatives appeared recently, particularly dealing with the development of synthetic procedures for the preparation of mono-, di- and polynuclear Schiff-base complexes and their reduced analogues [4]. Some Schiff-base complexes show catalytic properties [5], or act as oxygen carriers [6] and antifungal agents increased by the presence of hydroxyl groups in the ligands [7–11].

---

*Email: azza_aly2000@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500266230



Scheme 1. The Schiff-base ligand, H_2L.

This work aims to synthesize and characterize new ternary binuclear Co(II), Ni(II), Cu(II) and UO_2(VI) complexes of a Schiff-base ligand, H_2L, derived from condensation of 4,6-diacetylresorcinol with ethylamine, Scheme 1. The complexes are characterized by elemental analysis, IR, UV-visible, ^{1}H NMR and ESR spectra and studied using thermal analysis, conductivity measurements and magnetic moments.

2. Experimental

2.1. *Materials*

The nitrate salts of Co(II), Ni(II), Cu(II), and UO_2(VI), resorcinol, acetic anhydride, 8-hydroxyquinoline (8-HQ), 2,2′-bipyridine (2,2′-Bipy) and 1,10-phenanthroline (1,10-Phen) are Merck chemicals. Organic solvents are reagent grade chemicals.

2.2. *Physical measurements*

UV-vis spectra of the metal complexes in DMF were recorded on a Jasco 550 Spectrophotometer. IR spectra of the ligands and their metal complexes, as KBr discs, were recorded on a Perkin–Elmer 1430 Spectrometer. ^{1}H NMR spectra of the ligand and its UO_2(VI) complexes, in DMSO-d_6, were recorded on a Bruker WP 200 SY Spectrometer at room temperature using TMS as internal standard. Mass spectra were recorded at 300°C and 70 eV on a Hewlett–Packard Mass Spectrometer model MS-5988. Magnetic susceptibilities of the complexes were measured at room temperature using Johnson Matthey, Alfa Products, and Model MKI magnetic susceptibility balance [12]. The effective magnetic moments were calculated from the expression $\mu_{\text{eff}} = 2.828(\chi_M \cdot T)^{1/2}$ B.M., where χ_M is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds [13]. ESR spectra of the copper complexes were recorded on a JEOL microwave unit, JES-FE_2XG Spectrophotometer. The magnetic field was calibrated with 2,2-diphenyl-1-picrylhydrazyl. Molar conductivity of 10^{-3} M solutions of the complexes in DMF were measured on the Corning conductivity meter NY 14831 model 441. Thermal analyses have been carried out by using Schimadzu (TGA-50H) from room temperature to 500°C under heating rate of 50°C min^{-1}. Analyses of the metals were carried out by dissolving the complexes in concentrated nitric acid, neutralizing the diluted aqueous solutions with ammonia and titrating the metal solutions with EDTA except UO_2(VI).

Downloaded At: 12:35 23 January 2011

2.3. *Preparation of the Schiff-base ligand, H_2L*

The ligand H_2L was prepared in two steps. The first step involved the acetylation of resorcinol (5.00 g, 45.5 mmol) with acetic anhydride (9.28 g, 91.0 mmol) in the presence of zinc chloride (10.0 g) at 140°C in paraffin oil. The yield was 6.88 g, 78%. The second step involved the addition of a solution of ethylamine (2.06 g, 22.8 mmol) to 4,6-diacetylresorcinol (4.43 g, 22.8 mmol) in ethanol (40 mL). The solution was refluxed for 3 h. A yellow solid formed on cooling the solution slowly to room temperature and the precipitate was collected by filtration, washed with ethanol then diethyl ether, and finally air-dried. The yield was 4.86 g, 75%, figure 1.

2.4. *Preparation of the metal complexes*

An ethanolic solution of the metal salt (20 mL) was gradually added to an ethanolic (30 mL) solution of the ligand in 2 : 1 molar ratio and the solution was stirred for 1 h. The uranyl complex was prepared in methanol. An ethanolic solution of the other ligands L′; L′ = 8-HQ, 2,2′-Bipy or 1,10-Phen, was then added to the previous solution in the molar ratio 2 : 1. The solution was continuously stirred for 4 h, during which the metal complexes precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complexes are air stable in the solid state and soluble in DMF and/or DMSO. A general chemical reaction is formulated as follows:

$$H_2L + 2M(NO_3)_2 \cdot \text{hydrate} + 2L' \longrightarrow [M_2L(L'_2)(NO_3)_Y(H_2O)_Z] \cdot 2A \cdot XH_2O$$

Downloaded At: 12:35 23 January 2011

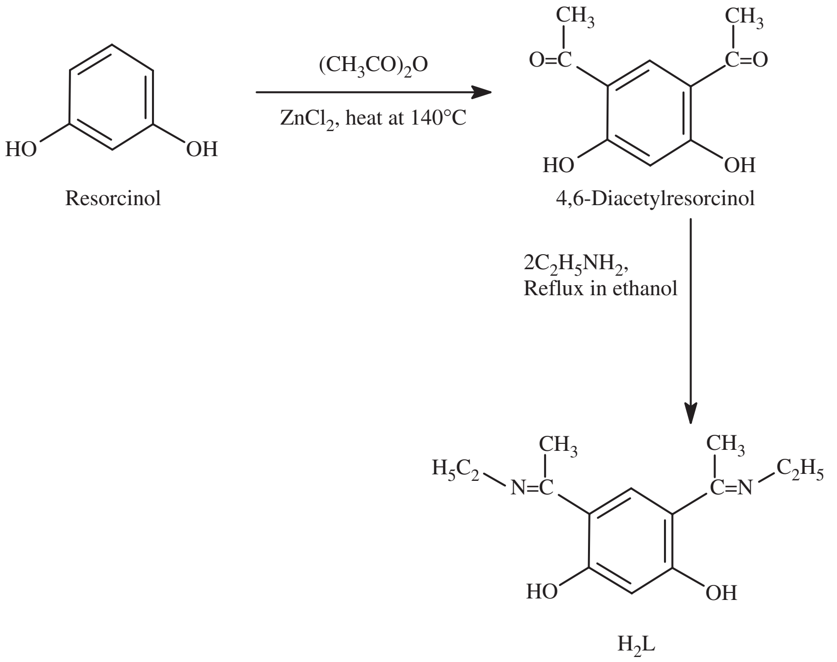


Figure 1. Preparation of the Schiff-base ligand, H_2L.

where

M	A	X	Y	Z	L′
Co(II)	–	–	2	2	2,2′-Biby
Ni(II)	–	–	2	2	2,2′-Biby
Cu(II)	–	–	–	4	8-HQ
Cu(II)	NO_3^-	2	–	–	2,2′-Bipy
Cu(II)	NO_3^-	6	–	–	1,10-Phen
UO_2(VI)	–	–	2	2	2,2′-Biby

The following detailed preparations are given as examples and the other complexes were obtained similarly.

2.4.1. Preparation of complex 9: $[Cu_2(L)(1,10\text{-Phen})_2](NO_3)_2 \cdot 6H_2O$. An ethanolic solution (20 mL) of $Cu(NO_3)_2 \cdot 2.5H_2O$ (1.20 g, 2.4 mmol) was added gradually to an ethanolic solution (40 mL) of the ligand, H_2L (0.60 g, 2.4 mmol). The solution was stirred for 1 h, then an ethanolic solution (30 mL) of 1,10-Phen (0.96 g, 2.4 mmol) was added to the previous solution. The solution was continuously stirred for 3 h, during which the solid complex precipitated. The precipitate was filtered off, washed with ethanol then diethyl ether and finally air-dried. The yield is 2.53 g, 67.3%. The complex is insoluble in water but soluble in DMF to 10^{-3} M.

Downloaded At: 12:35 23 January 2011

2.4.2. Preparation of complex 11: $[(UO_2)_2(L)(2,2'\text{-Bipy})_2(NO_3)_2(H_2O)_2]$. A methanolic solution (20 mL) of $UO_2(NO_3)_2 \cdot 6H_2O$ (1.20 g, 1.19 mmol) was added gradually to a methanolic solution (40 mL) of the ligand, H_2L (0.29 g, 1.18 mmol). The solution was stirred for 1 h, then an ethanolic solution (30 mL) of 2,2′-Bipy (0.37 g, 1.18 mmol) was added. The solution was continuously stirred for 3 h and the complex precipitated. The precipitate was filtered off, washed with methanol then diethyl ether and finally air-dried. The yield is 1.32 g, 71%. The complex is insoluble in water but soluble in DMF and DMSO.

3. Results and discussion

The reactions of the Schiff-base, H_2L, with different metal ions in the presence of coordinating ligands L′, L′ = 8-HQ, 2,2′-Bipy and 1,10-Phen, produce a new series of binuclear metal complexes, M = Co(II), Ni(II), Cu(II) and UO_2(VI). The analytical and physical data of the metal complexes are listed in table 1.

3.1. *Characterization of the ligand, H_2L*

Mass spectroscopy was performed on the H_2L ligand to determine its molecular weight and fragmentation pattern. The molecular ion peak was observed at $m/e = 248$, confirming its formula weight (FW) = 248. The schematic fragmentation of the ligand is depicted in figure 2. The ^{1}H NMR spectrum of H_2L in DMSO-d_6 (table 2) showed signals at δ (ppm) 1.34 (3H, CH_3^a), 3.74 (3H, CH_3^b), 2.67 (2H, CH_2^c), 5.82 (^{1}H, Ar–H^e), 8.24 (^{1}H, Ar–H^f), and 12.17 (^{1}H-OH-phenolic^d). Figure 3 shows the ^{1}H NMR spectra of the ligand in DMSO-d_6 before deuteration by the addition

Downloaded At: 12:35 23 January 2011

Table 1. Analytical and physical data of the metal complexes.

							Elemental analysis, % Found/(Calcd)			
Ligand or complex		Formula	M.F.	Color	Yield (%)	m.p. (°C)	C	H	N	M
I	$[H_2L]$	$C_{14}H_{20}N_2O_2$	248.326	Yellow	75	130	67.86 (67.65)	8.26 (8.11)	10.93 (11.28)	–
1	$[Co_2(L)(8\text{-}HQ)_2(H_2O)_4]$	$C_{32}H_{38}N_4O_8Co_2$	724.536	Reddish brown	70	>300	53.08 (53.04)	5.23 (5.28)	7.65 (7.73)	16.29 (16.26)
2	$[Co_2(L)(2,2'\text{-}Bipy)_2(NO_3)_2(H_2O)_2]$	$C_{34}H_{38}N_8O_{10}Co_2$	836.590	Deep brown	85	>300	48.64 (48.81)	4.53 (4.57)	13.27 (13.39)	13.78 (14.08)
3	$[Co_2(L)(1,10\text{-}Phen)_2(NO_3)_2(H_2O)_2]$	$C_{38}H_{38}N_8O_{10}Co_2$	884.635	Pale brown	76	>300	51.35 (51.59)	4.04 (4.32)	12.23 (12.66)	13.63 (13.32)
4	$[Ni_2(L)(8\text{-}HQ)_2(H_2O)_4]$	$C_{32}H_{38}N_4O_8Ni_2$	724.096	Green	74	>300	53.10 (53.08)	5.23 (5.28)	7.71 (7.73)	16.19 16.21
5	$[Ni_2(L)(2,2'\text{-}Bipy)_2(NO_3)_2(H_2O)_2]$	$C_{34}H_{38}N_8O_{10}Ni_2$	836.144	Green	60	>300	48.51 (48.84)	4.48 (4.58)	13.78 (13.40)	13.86 (14.04)
6	$[Ni_2(L)(1,10\text{-}Phen)_2(NO_3)_2(H_2O)_2] \cdot 2H_2O$	$C_{38}H_{42}N_8O_{12}Ni_2$	920.218	Green	83	>300	49.24 (49.59)	4.51 (4.60)	11.84 (12.17)	12.88 (12.76)
7	$[Cu_2(L)(8\text{-}HQ)_2(H_2O)_4]$	$C_{32}H_{38}N_4O_8Cu_2$	733.756	Deep green	73	>300	52.40 (52.38)	5.19 (5.22)	7.59 (7.63)	17.36 (17.31)
8	$[Cu_2(L)(2,2'\text{-}Bipy)_2] \cdot (NO_3)_2 \cdot 2H_2O$	$C_{34}H_{38}N_8O_{10}Cu_2$	845.664	Pale brown	86	>300	47.51 (48.29)	4.30 (4.52)	13.17 (13.25)	14.73 (15.01)
9	$[Cu_2(L)(1,10\text{-}Phen)_2] \cdot (NO_3)_2 \cdot 6H_2O$	$C_{38}H_{46}N_8O_{14}Cu_2$	965.768	Pale brown	67	>300	47.66 (47.25)	4.38 (4.80)	11.46 (11.60)	13.53 (13.14)
10	$[(UO_2)_2(L)(8\text{-}HQ)_2] \cdot 4H_2O$	$C_{32}H_{38}N_4O_{12}U_2$	1146.677	Orange	82	>300	33.46 (33.51)	3.31 (3.34)	4.85 (4.88)	–
11	$[(UO_2)_2(L)(2,2'\text{-}Bipy)_2]\ (NO_3)_2 \cdot 2H_2O$	$C_{34}H_{38}N_8O_{14}U_2$	1258.720	Orange	71	>300	32.13 (32.44)	3.21 (3.04)	8.67 (8.90)	–
12	$[(UO_2)_2(L)(1,10\text{-}Phen)_2]\ (NO_3)_2 \cdot 2H_2O$	$C_{38}H_{38}N_8O_{14}U_2$	1306.769	Orange	78	>300	34.63 (34.92)	2.66 (2.93)	8.28 (8.57)	–

Downloaded At: 12:35 23 January 2011

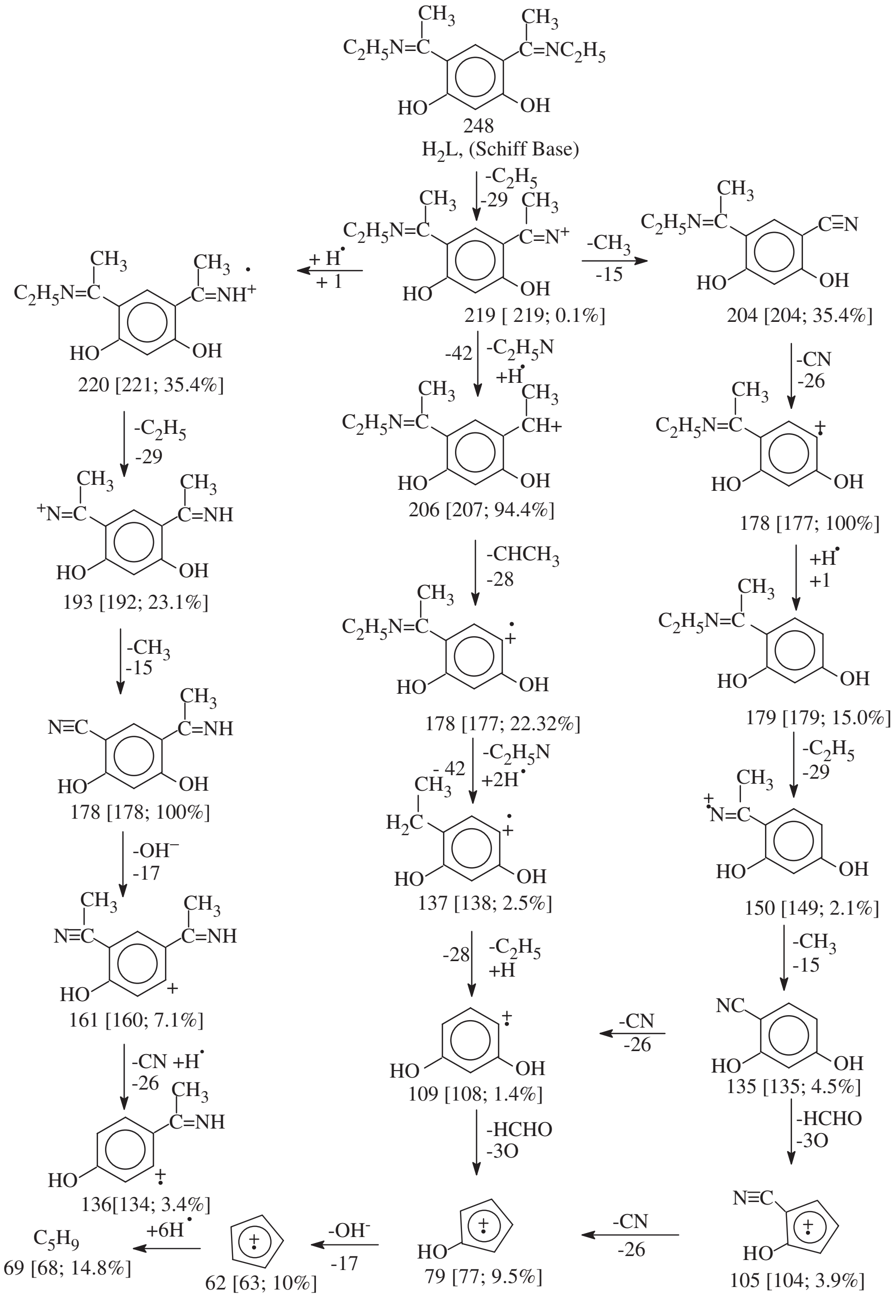
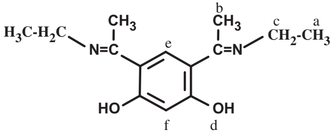


Figure 2. The schematic fragmentations of H_2L ligand, where the values under each fragment denoted as calculated [found; intensity].

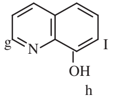
of D_2O. It is observed that the signal due to the proton (12.17, phenolic-OH^d) completely disappeared on adding D_2O, while the other signals still exist at their expected positions. The IR spectrum of the ligand shows a broad band at 3430 cm^{-1} due to the stretching vibrations of phenolic hydroxyl groups. The broadness is due to

Downloaded At: 12:35 23 January 2011

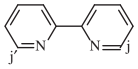
Table 2. ^1H NMR data of H_2L and L′; (L′= 8-HQ, 2,2′-Bipy or 1,10-Phen) and their UO_2(VI) complexes (**10**, **11** and **12**).



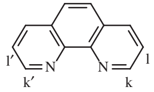
I H_2L



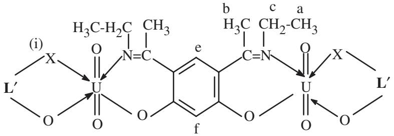
II 8-HQ



III 2,2′-Bipy



IV 1,10-Phen



UO_2(VI) Complexes (**10**, **11** and **12**)

	Chemical shifts, δ_H (ppm) (ii),(iii)					Complexes		
Assignment	**I** (H_2L)	**I** (H_2L), D_2O	**II** 8-HQ	**III** 2,2′-Bipy	**IV** 1,10-Phen	**10**	**11**	**12**
H^a	1.34 (3H,t)	1.34 (3H,t)	–	–	–	1.30 (3H,t)	1.14 (3H,t)	1.20 (3H,t)
H^b	3.74 (3H,s)	3.70 (3H,s)	–	–	–	3.60 (3H,s)	3.16 (3H,s)	3.24 (2H,s)
H^c	2.67 (2H,q)	2.33 (2H,q)	–	–	–	2.38 (2H,m)	2.45 (2H,m)	2.22 (2H,s)
H^d	12.17 (1H,s,br)	–	–	–	–	–	–	–
H^e	5.82 (1H,s)	5.80 (1H,s)	–	–	–	5.44 (1H,s)	5.22 (1H,s)	5.95 (1H,s)
H^f	8.24 (1H,s)	8.23 (1H,s)	–	–	–	(iv)	(iv)	(iv)
H^g	–	–	7.46 (1H,s,br)	–	–	–	–	–
H^h	–	–	8.45 (1H,s,br)	–	–	–	–	–
H^I	–	–	9.08 (1H,s)	–	–	–	–	–
$H^{j,\,j'}$	–	–	–	8.70 (2H,d)	–	–	7.45 (2H,d)	–
$H^{k,k'}$	–	–	–	–	9.20 (2H,d)	–	–	9.02 (2H,m,br)
$H^{l,l'}$	–	–	–	–	7.70 (2H,d)	–	–	7.32 (2H,m,br)

(i) X = N or O and L′ = (8HQ, 2,2′-Biby or1,10-Phen).
(ii) Values obtained from the spectra in DMSO-d_6.
(iii) t: triplet, d: doublet, q: quartet, s: singlet, br: broad and m: multiplet.
(iv) The chemical shift of the signal (the aromatic region is overlapped with the ligands, L′).

Downloaded At: 12:35 23 January 2011

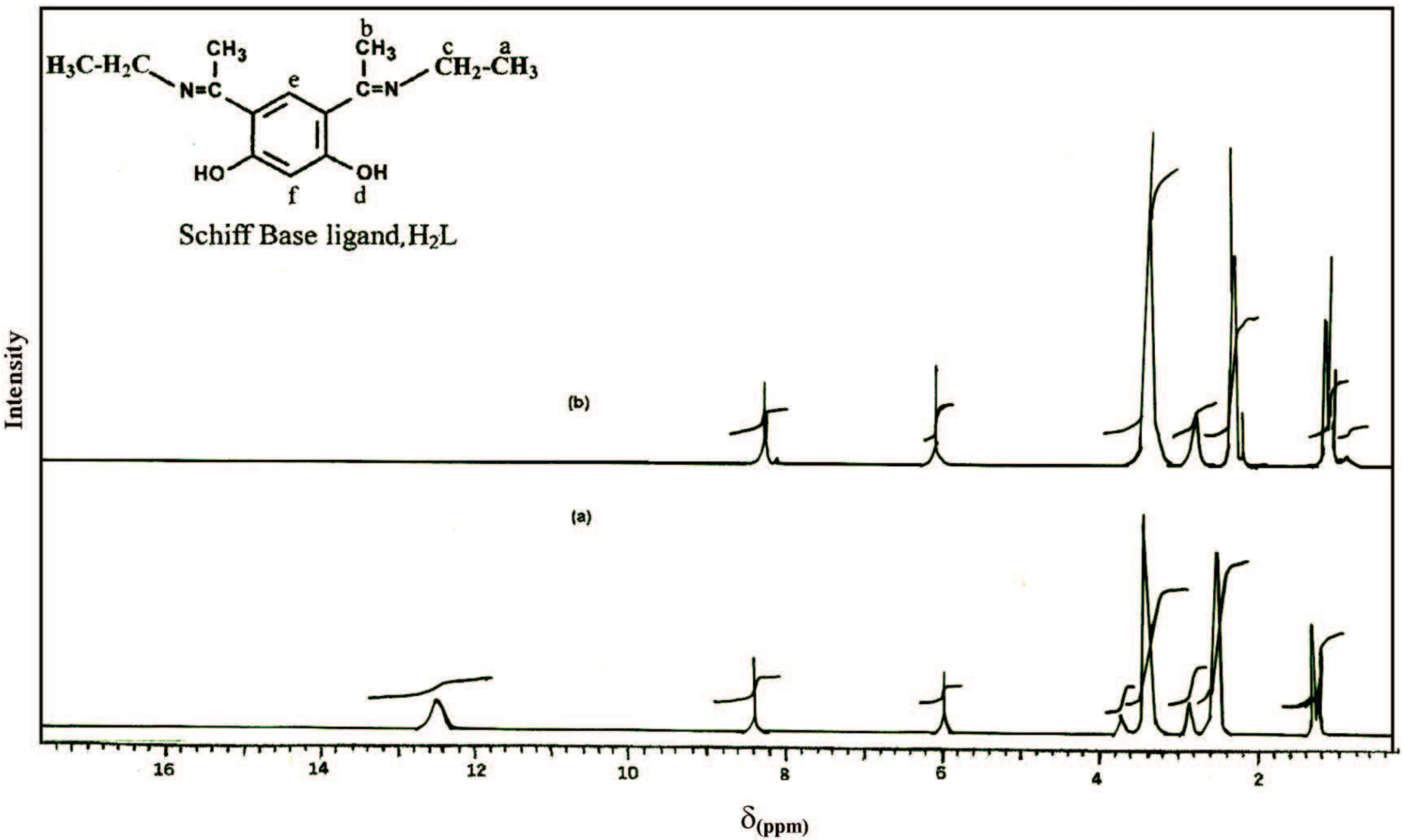


Figure 3. ^{1}H NMR spectra of the Schiff base H_2L (a) in d-DSMO, $\delta_{(ppm)}$ and (b) after the addition of D_2O, $\delta_{(ppm)}$.

intermolecular hydrogen bonding between the phenolic groups and the azomethine groups (figure 4). The band at $1236\,\mathrm{cm}^{-1}$ is ascribed to the ν(C–O) stretching vibrations, where the strong band observed at $1680\,\mathrm{cm}^{-1}$ is assigned to the stretching vibrations of the azomethine group (table 3). The electronic spectrum of the ligand H_2L (10^{-3} M in DMF), shows mainly three bands at 210, 242 and 370 nm due to ($^1L_a \rightarrow {}^1A_1$) and ($^1L_b \rightarrow {}^1A_1$) transitions of the phenyl ring and π–π* transition within the C=N group. In addition, a broad band at 410 nm is due to the n–π * transition which is overlapping with the intermolecular CT from the phenyl ring to the azomethine group (table 4) [14].

3.2. *Characterization of the complexes*

3.2.1. Infrared spectroscopy. The characteristic bands of the infrared spectra of H_2L, L′; L′ = 8-HQ, 2,2′-Bipy and 1,10-Phen, and the metal complexes are listed in table 3. The infrared spectra of H_2L and some of its metal complexes **3**, **4** and **11** are shown in figure 4. The IR spectra of complexes (**1**–**12**) exhibit a broad band around $3200–3463\,\mathrm{cm}^{-1}$ assigned to ν(OH) of water molecules associated with the complex, which are also confirmed by elemental and thermal analyses. The IR spectra of the complexes show a shift of the ν(C=N) band towards lower wavenumbers of $1635–1665\,\mathrm{cm}^{-1}$ compared with the free ligand band at $1680\,\mathrm{cm}^{-1}$. This shift indicates coordination of the two azomethine groups to the metal ions [15]. Coordination through the phenolic oxygen after deprotonation is revealed by the appearance of a band due to ν(C–O) at much lower frequencies ($1205–1225\,\mathrm{cm}^{-1}$) in all the complexes compared to that of H_2L ($1236\,\mathrm{cm}^{-1}$) [16, 17], suggesting that the hydroxyl groups of the Schiff-base coordinate with the metal ions. The IR spectra of the UO_2(VI) complex displays two bands at 905–915 and $810–820\,\mathrm{cm}^{-1}$, which are assigned to the $\nu_{as}(UO_2)$ and $\nu_s(UO_2)$ modes, respectively. This observation suggests that the ν(O=U=O) moiety is virtually linear in these complexes [18, 19]. New bands in the $416–503\,\mathrm{cm}^{-1}$ and $348–390\,\mathrm{cm}^{-1}$ ranges are tentatively assigned to ν(M–O) and ν(M–N), respectively, supporting bonding of the ligand to the metal ions by the phenolic oxygen atoms and the azomethine nitrogen atoms of the ligand. It is difficult to assign the band corresponding to ν(M–N) for 2,2′-Bipy complexes under the experimental conditions, since their ν(M–N) vibrations are in the range $180–290\,\mathrm{cm}^{-1}$ [20, 21].

The infrared spectra of the free ligands L′; L′ = 8-HQ, 2,2′-Bipy and 1,10-Phen, have been compared with those after coordination. The spectrum of the free 8-hydroxyquinoline shows a strong band at $1586\,\mathrm{cm}^{-1}$ due to the stretching vibrations of the (C=N) group [22]. This band is shifted to a higher wavenumber on coordination for complexes **1**, **4**, **7** and **10** suggesting that the lone pair on nitrogen is involved in the formation of a bond with metal. Moreover, the broad stretching vibration at $3242\,\mathrm{cm}^{-1}$ due to –O–H group of the free 8-HQ ligand [22] was found to be absent in the latter complexes, suggesting the formation of an M–O bond with 8-hydroxyquinolate. Thus, 8-hydroxyquinolinate in all the complexes is a bidentate chelating ligand. Changes are observed in the infrared spectrum of 2,2′-Bipy when it is coordinated with the metal centres. The characteristic band of the C=N group in complexes **2**, **5**, **8** and **11** are shifted to higher wavenumber compared with the free ligand at $1570\,\mathrm{cm}^{-1}$ [23]. This suggests that both nitrogens of 2,2′-Bipy are coordinated to the metal ion [24]. Similar behaviour has been observed for the C=N vibration of 1,10-Phen, which has a band

Downloaded At: 12:35 23 January 2011

Downloaded At: 12:35 23 January 2011

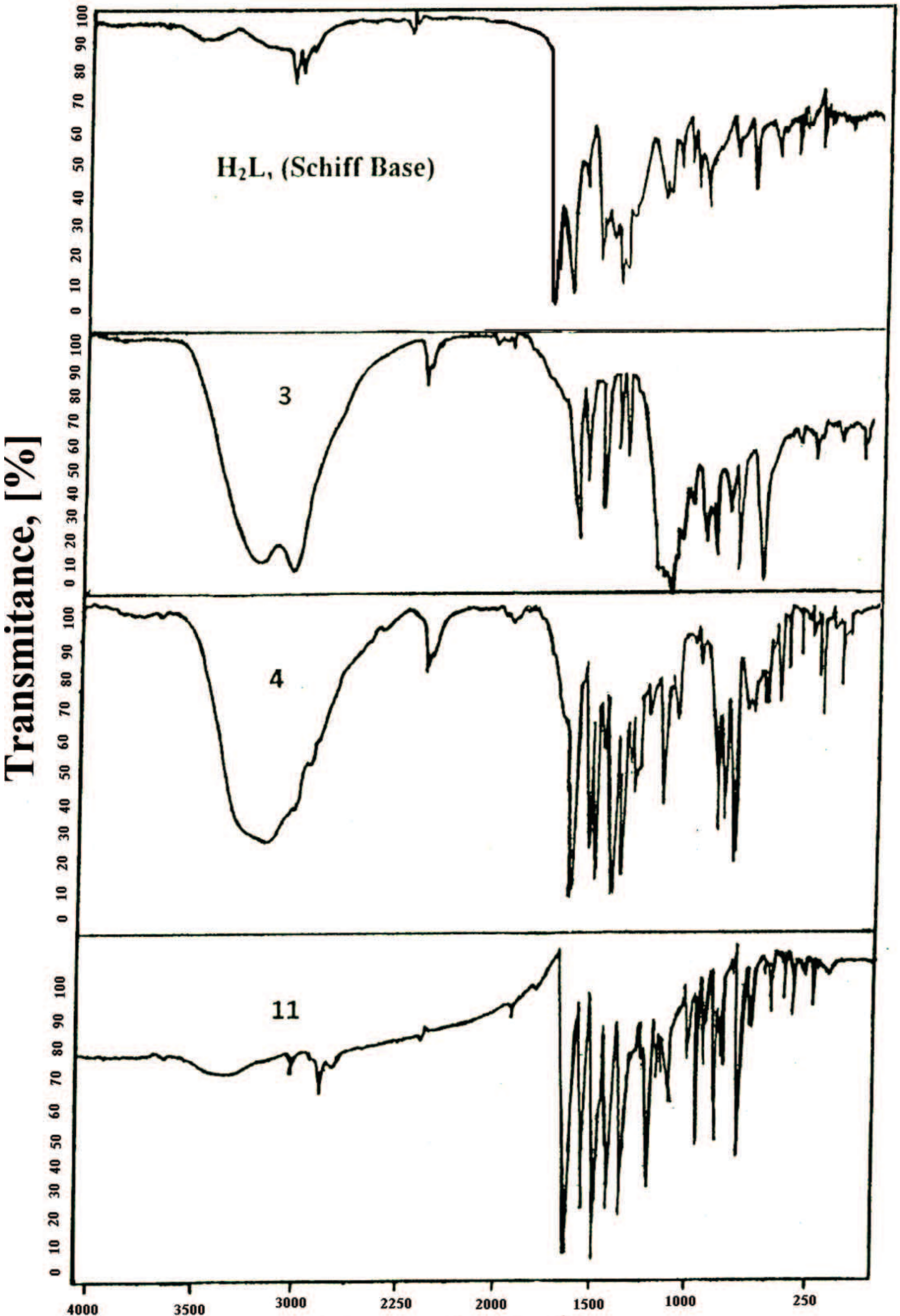


Figure 4. IR-spectra of the Schiff base ligand, H_2L and the complexes, **3**: $[Co_2(L)(1,10\text{-Phen})_2(NO_3)_2(H_2O)_2]$; **4**: $[Ni_2(L)(8\text{-HQ})_2(H_2O)_4]$ and **11**: $[(UO_2)_2(L)(2,2'\text{-Biby})_2](NO_3)_2 \cdot 2H_2O$.

Downloaded At: 12:35 23 January 2011

Table 3. The characterization bands of the infrared spectrum of H_2L, L′; (L′ = 8-HQ, 2,2′-Bipy and 1,10-Phen) and their transition metal complexes.

Ligand or complex		ν_{OH} (Phenolic or crystalline)	ν(C=N)	ν(C–O)	$\nu(NO_3)$			ν(M–O)	ν(M–N)	ν_3(O=U=O)
					ν_s	$\nu_{s'}$	ν_{as}			
I	$[H_2L]$	3430,3237br	1680s	1236 m	–	–	–	–	–	–
II	8-HQ	3242br	1586s	1090 m	–	–	–	–	–	–
III	2,2′-Bipy	–	1570s	–	–	–	–	–	–	–
IV	1,10-Phen	–	1560s	–	–	–	–	–	–	–
1	$[Co_2(L)(8\text{-}HQ)_2(H_2O)_4]$	3200br	1645s	1213s, 1220m	–	–	–	503m	348m	–
2	$[Co_2(L)(2,2'\text{-}Bipy)_2(NO_3)_2(H_2O_2)_2]$	3243m	1652s	1218m	1364s	1050m	990w	416m	–	–
3	$[Co_2(L)(1,10\text{-}Phen)_2(NO_3)_2(H_2O)_2]$	3238br	1655s	1215m	1355m	1060m	992m	480m	370w	–
4	$[Ni_2(L)(8\text{-}HQ)_2(H_2O)_4]$	3240br	1654s	1210m, 1225m	–	–	–	558m	390w	–
5	$[Ni_2(L)(2,2'\text{-}Bipy)_2(NO_3)_2(H_2O)_2]$	3370br	1660s	1222m	1347s	1053m	985w	467m	–	–
6	$[Ni_2(L)(1,10\text{-}Phen)_2(NO_3)_2(H_2O)_2] \cdot 2H_2O$	3380br	1640s	1210m	1360m	1073w	995w	495m	372w	–
7	$[Cu_2(L)(8\text{-}HQ)_2(H_2O)_4]$	3463br	1635s	1205m, 1220w	–	–	–	467m	370w	–
8	$[Cu_2(L)(2,2'\text{-}Bipy)_2] \cdot (NO_3)_2 \cdot 2H_2O$	3433br	1653s	1208m	1380s	–	–	465m	–	–
9	$[Cu_2(L)(1,10\text{-}Phen)_2] \cdot (NO_3)_2 \cdot 6H_2O$	3430br	1645s	1210m	1380s	–	–	455m	374w	–
10	$[(UO_2)_2(L)(8\text{-}HQ)_2] \cdot 4H_2O$	3430s	1650s	1213m, 1220w	–	–	–	–	365w	905s, 820m
11	$[(UO_2)_2(L)(2,2'\text{-}Bipy)_2]\ (NO_3)_2 \cdot 2H_2O$	3420br	1665s	1215m	1338m	1061m	995w	–	372w	915s, 814m
12	$[(UO_2)_2(L)(1,10\text{-}Phen)_2]\ (NO_3)_2 \cdot 2H_2O$	3224br	1642s	1205m	1345m	1056w	997w	–	370w	910s, 810m

s = Strong, w = weak, m = medium and br = broad.
ν_s: A single degenerate state which is symmetrical about the principle axis.
$\nu_{s'}$: A symmetrical state with respect to the three C_{2v} axes.
ν_{as}: Antisymmetrical state with respect to the three C_{2v} axes.

Downloaded At: 12:35 23 January 2011

Table 4. Electronic spectral data of the ligands and their metal complexes, magnetic moments and molar conductivities.

		Electtronic absorption bands, nm, and their assignment[a]			Ligand field parameters					
	Ligand or complex	π–π^* C=N	$n \rightarrow \pi^*$ and CT	d–d	B (cm^{-1})	β	10Dq (cm^{-1})	μ_{comp}[b] (B.M)	μ_{eff}[c] (B.M.)	(Λ^d) $Ohm^{-1} cm^2 mol^{-1}$
I	[H_2L]	370 (1.07)	410 (1.56)	–	–	–	–	–	–	–
II	8-HQ	363 (1.23)	400 (1.45)	–	–	–	–	–	–	–
III	2,2′-Bipy	373 (1.54)	390 (1.51)	–	–	–	–	–	–	–
IV	1,10-Phen	363 (1.58)	410 (1.61)	–	–	–	–	–	–	–
1	$[Co_2(L)(8\text{-}HQ)_2(H_2O)_4]$	365 (2.98)	412 (4.31)	550 (6.30), 650 (5.96)	479	0.800	8569	5.25	4.41	15
2	$[Co_2(L)(2,2'\text{-}Bipy)_2(NO_3)_2(H_2O_2)_2]$	360 (5.26)	–	515 (4.03), 550 (1.06)	802	0.826	9624	4.64	4.52	165
3	$[Co_2(L)(1,10\text{-}Phen)_2(NO_3)_2(H_2O)_2]$	355 (2.97)	430 (3.02)	570 (2.84), 610 (5.01)	725	0.747	8703	4.50	4.39	148
4	$[Ni_2(L)(8\text{-}HQ)_2(H_2O)_4]$	360 (3.80)	410 (2.42)	473 (3.89), 675 (1.23)	786	0.755	8260	4.76	3.26	12
5	$[Ni_2(L)(2,2'\text{-}Bipy)_2(NO_3)_2(H_2O)_2]$	365 (1.14)	410 (1.86)	470 (3.51), 760 (4.32)	928	0.890	5010	4.16	3.11	158
6	$[Ni_2(L)(1,10\text{-}Phen)_2(NO_3)_2(H_2O)_2] \cdot 2H_2O$	365 (2.13)	410 (2.21)	475 (3.24), 670 (5.20)	769	0.739	9230	4.90	3.34	154
7	$[Cu_2(L)(8\text{-}HQ)_2(H_2O)_4]$	364 (3.22)	410 (2.33)	520 (5.22)	–	–	–	2.66	1.51	16
8	$[Cu_2(L)(2,2'\text{-}Bipy)_2] \cdot (NO_3)_2 \cdot 2H_2O$	365 (1.84)	410 (5.37)	594 (3.28)	–	–	–	2.72	1.49	158
9	$[Cu_2(L)(1,10\text{-}Phen)_2] \cdot (NO_3)_2 \cdot 6H_2O$	350 (3.52)	415 (2.15)	586 (4.32)	–	–	–	2.21	1.48	165
10	$[(UO_2)_2(L)(8\text{-}HQ)_2] \cdot 4H_2O$	345 (3.15)	–	600 (4.54)	–	–	–	–	–	20
11	$[(UO_2)_2(L)(2,2'\text{-}Bipy)_2]\ (NO_3)_2 \cdot 2H_2O$	362 (2.56)	–	560 (1.58)	–	–	–	–	–	135
12	$[(UO_2)_2(L)(1,10\text{-}Phen)_2]\ (NO_3)_2 \cdot 2H_2O$	360 (3.50)	–	610 (3.47)	–	–	–	–	–	126

[a] Values of molar absorptivity ε_{max} are in parenthesis and multiplied by 10^3 (mol^{-1} L).

[b] μ_{comp}: the total magnetic moment of the complex.

[c] μ_{eff}: where calculated for one metal ion in the complex.

[d] Conductances in DMF, 10^{-3} M.

at 1560 cm^{-1}. This band shifts on coordination to higher wavenumber in complexes **3**, **6**, **9** and **12**, respectively, presumably because of coordination to the metal [25].

The coordination behavior of NO_3^- groups was investigated. The NO_3^- ions are coordinated to the metal ions as unidentate ligands for complexes **2**, **3**, **5**, **6**, **11** and **12**. Unidentate nitrate groups show C_{2V} symmetry, with three non-degenerate modes of vibration (ν_s, $\nu_{s'}$ and ν_{as}), where $\nu_s(NO_3^-)$ is in the range 1345–1364 cm^{-1}, $\nu_{s'}(NO_3^-)$ 1050–1073 cm^{-1} and $\nu_{as}(NO_3^-)$ 985–997 cm^{-1} [26]. The $\nu_s(NO_3^-)$ of the unidentate NO_3^- is markedly shifted to lower frequency compared to that of the free nitrate (1384 cm^{-1}) [27] providing a measure of the covalent bond strength due to transfer of electron density from NO_3^- to the metal ion. For the non- coordinated nitrate in complexes **8** and **9**, a very strong band at 1380 cm^{-1} has been observed. Complexes of 8-HQ (**1**, **4**, **7** and **10**) do not show bands assigned to the nitrate groups; this result is confirmed by elemental analysis and the observed molar conductance for the complexes suggesting non-electrolytic nature of these complexes (tables 1 and 3).

3.2.2. Spectroscopic, magnetic moment studies and molar conductivity. The electronic spectral data for a DMF solution of H_2L, L′; and the binuclear metal complexes are listed in table 4. The spectra of the ligands I–IV showed four absorption bands in the range 210–226 nm, 232–268 nm, 363–373 nm and 390–410 nm. The former two bands are assigned to the absorption of ($^1L_a \rightarrow {}^1A_1$) and ($^1L_b \rightarrow {}^1A_1$) of the phenyl ring, while the third band is assigned to ($\pi \rightarrow \pi^*$) transition of the azomethine group, which is shifted to lower wavelength on coordination, as a result of the participation of the two azomethine nitrogens in coordination. The latter broad band is assigned to the intermolecular CT and *n*–π^* transition from the ligand to the metal ions.

The electronic spectra of the complexes showed several absorption bands, including absorption bands of the ligands and d–d transitions of the metal ions. Spectra of the complexes, which reveal maxima at the wavelength of the first band of the ligands (210–226 nm), are independent of complexation. The second band for the complexes lies in the range 270–287 nm, markedly different for the second band of the free ligands, and there is a great increase of absorption. These changes can be attributed to absorption of free NO_3^-, superimposed on the spectra of the ligand. The NO_3^- anion strongly absorbs in the indicated range and also demonstrates a maximum at 310 nm [26, 28]. The nitrate anion possesses one bonding π-molecular orbital and it is reasonable to assume that, on complexation, electron density transfers from the occupied π orbital of NO_3^- to the free orbital of metal contributing to covalent bonding between the two species. The third band is ascribed to π–π^* transitions involving the azomethine found at 345–365 nm [29]. The band at 390–430 nm is assigned to charge transfer transition. Lower energy bands in the range 515–760 nm are assigned to d–d transitions of the metal cations [30].

The spectra of the brown Co(II), complexes **1**, **2** and **3** (table 4) show two d–d transition bands in the 515–650 nm region for complexes **1**, **2** and **3**. The two bands are assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g} \rightarrow {}^4T_{1g}(F)$ transitions of octahedral geometry [31, 32]. The colour agrees well with the proposed geometry. The ligand field parameters for the investigated complexes (B, β and 10Dq), were calculated and found in the ranges reported for the suggested structure. The B values were found in the range 46.0–62.0% that of the free ion ($B^\circ = 971\ cm^{-1}$), indicating considerable covalent cobalt-ligand bond character [29]. The β values are less than unity indicating strong M–L covalent bonds. Based on the 10Dq values, the type of base has a great influence

Downloaded At: 12:35 23 January 2011

on the energy of transition and the order is tentatively suggested to be as follows: 2,2′-Bipy > 1,10-Phen > 8-HQ. This order indicates the ability of cobalt ion to coordinate with nitrogen donor ligands over oxygen donor ligands. The magnetic moments of these complexes (5.25, 4.64 and 4.50 B.M.) are calculated for two Co(II) complexes and the values are less than expected, which agree with the binuclear complexes (table 4).

The molar conductance values of the complexes in DMF (10^{-3} M) are 15, 165 and 148 $\mathrm{Ohm^{-1}\,cm^2\,mol^{-1}}$. The higher observed values for complexes **2** and **3** indicate that these complexes are 1 : 2 electrolytes due to displacement of the coordinated nitrate ions by DMF [33, 34]. The conductance measurements confirm the electrolytic nature of the related complexes of 2,2′-Bipy and 1,10-Phen, **2**, **3**, **5**, **6**, **8**, **9**, **11** and **12**. On the other hand, the value of the molar conductance of complex **1**, $[Co(L)(8\text{-}HQ)_2(H_2O)_4]$, suggests non-electrolytic nature of this complex [35]. Similar behaviour has been observed for the other complexes of 8-HQ (**4**, **7** and **10**) (table 4).

The visible spectra of the green Ni(II) complexes (**4**, **5** and **6**) show three bands. The most intense band at ~470 nm is assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition in complexes **4**, **5** and **6** at the same region. The latter transition is a less intense peak at 670–760 nm, assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition due to the existence of octahedral environment [36]. The B, β and 10Dq values for these complexes are calculated (table 4) and the 10Dq values suggest that the bases follow the order: 1,10-Phen > 8-HQ > 2,2′-Biby. The β values are larger than those calculated for Co(II) complexes, indicating that the complexes of Ni(II) have more ionic character than Co(II). The total magnetic moments for the Ni(II) complexes are in the range 4.16–4.92 B.M., in agreement with two Ni(II) ions in octahedral geometry. The molar conductance of the complexes in DMF (10^{-3} M) are 12, 158 and 154 $\mathrm{Ohm^{-1}\,cm^2\,mol^{-1}}$, indicating that complex **4** is non-electrolyte, while **5** and **6** are 1 : 2 electrolytes (table 4). From the electronic spectra and the magnetic moments of Ni(II) complexes, it is possible to conclude that the two Ni(II) ions have octahedral geometry [37].

All Cu(II) complexes exhibit five absorption maxima. The first three maxima in the range 210–365 nm were ascribed previously to the ligands, while the fourth maximum lies in the range 410–415 nm and is probably due to the ligand–metal charge transfer transition. The absorption maxima at 520, 594 and 586 for complexes **7**, **8** and **9**, respectively, are due to the d–d transition to ($^2E_g \rightarrow {}^2T_{2g}$) for the octahedral complex **7** and to ($^2B_{1g} \rightarrow {}^2A_{1g}$) for the square planar complexes **8** and **9** [38, 39]. Best evidence for the proposed structure of the binuclear complexes comes from the magnetic measurements and ESR spectra. The ESR spectra of Cu(II) complexes (**7**, **8** and **9**) are shown in figure 5. Complex **7**, $[Cu_2(L)(8\text{-}HQ)_2(H_2O)_4]$, exhibits two g_{eff} ($g_{\|} = 2.3081$ and $g_{\perp} = 2.1823$) with ($g_{av} = 1.6900$), which indicates that this complex is octahedral or distorted octahedral geometry around the Cu(II) ions. Complex **8**, $[Cu_2(L)(2,2'\text{-}Biby)_2]\cdot(NO_3)_2\cdot 2H_2O$, and complex **9**, $[Cu_2(L)(1,10\text{-}phen)_2]\cdot(NO_3)_2\cdot 6H_2O$, showed intense broad bands with $g_{eff} = 2.3360$ and 2.3583 for **8** and **9**, respectively. The value of g_{eff} and the shape of the ESR signals of the Cu(II) complexes suggest square-planar coordination around the Cu(II) ions [40]. The positive contribution of the g_{eff} values over the free electron value (2.0023), indicates an increase in the covalency between the ligand and the Cu(II) ions in the complexes. The magnetic moment for complexes **7**, **8** and **9** are $\mu_{eff} = 1.51$, 1.49 and 1.48, respectively, at room

Downloaded At: 12:35 23 January 2011

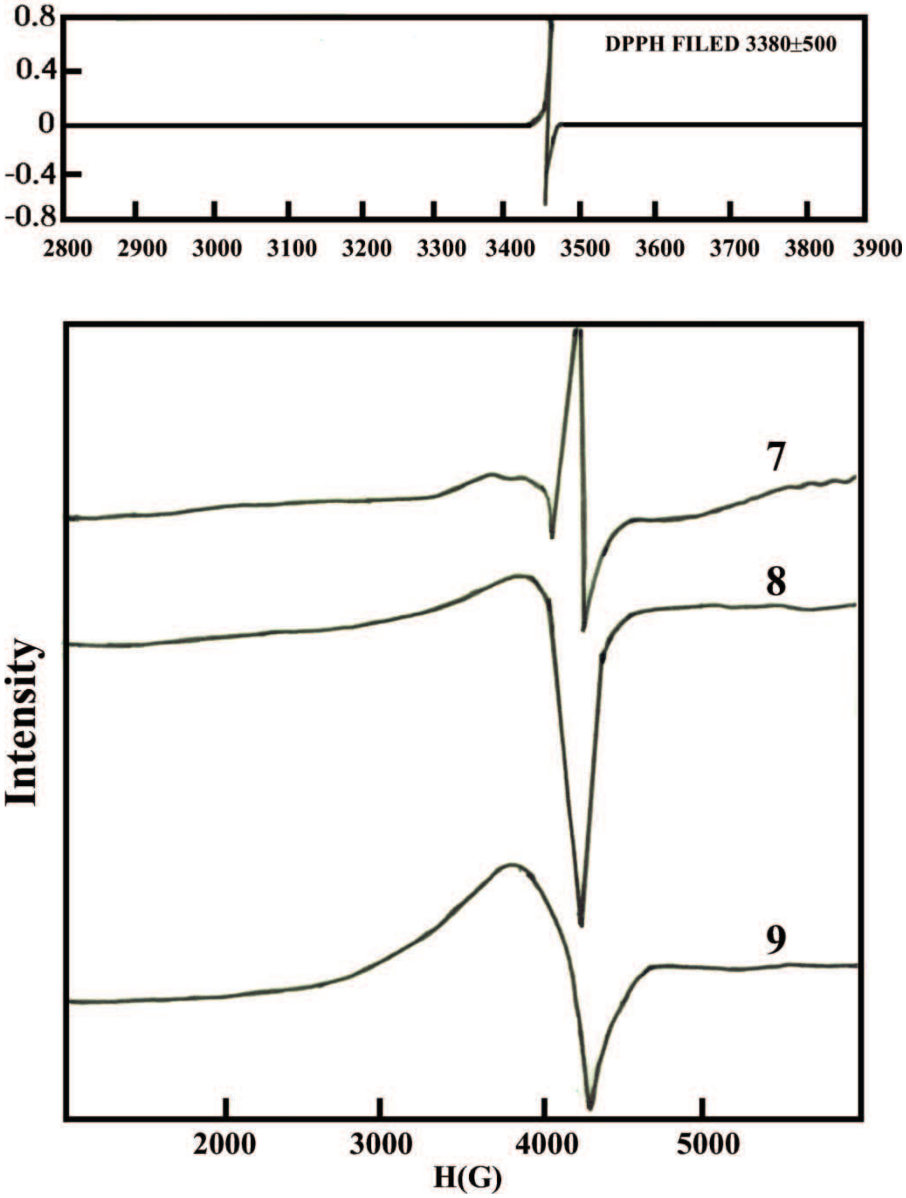


Figure 5. ESR spectra of the complexes, **7**: $[Cu_2(L)(8\text{-}HQ)_2(H_2O)_2]$, **8**: $[Cu_2(L)(2,2'\text{-}Biby)_2] \cdot (NO_3)_2 \cdot 2H_2O$ and **9**: $[Cu_2(L)(1,10\text{-}Phen)_2] \cdot (NO_3)_2 \cdot 6H_2O$.

Downloaded At: 12:35 23 January 2011

temperature. The calculated μ_{eff} values of the magnetic moments may be due to the antiferromagnetic interaction between the two electrons in the two adjacent Cu(II) ions. The Cu(II) ions achieve octahedral or square planar coordination geometry through the addition of other ligands L′, nitrate or water molecules. The molar conductance of the Cu(II) complexes in DMF (10^{-3} M solution) are 16 [35], 158 and 165 $\text{Ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ (table 4) [33, 34].

The electronic spectra of the orange, UO_2(VI) complexes (table 4) exhibit a charge transfer band around 560–610 nm for the complexes **10**, **11** and **12**, respectively. These complexes are diamagnetic. The high energy band of the UO_2(VI) complexes is attributed to an electronic transition from the apical oxygen to *f* orbitals of the uranium(VI) ion or due to a charge transfer transition from ligands to the uranium(VI) ion [41].

The ^{1}H NMR spectral data of the UO_2(VI) complexes (**10**, **11** and **12**) were recorded in DMSO-d_6 solution and are presented with assignments in table 2. The absence of the phenolic (OH) proton signal at (12.17 ppm) of the ligand in all the complexes of the UO_2(VI), indicates coordination by phenolic oxygen to the metal ion after deprotonation [19, 42]. Moreover, the spectra of the complexes showed new signals due to the participation of the aromatic protons of 8-HQ, 2,2′-Bipy and 1,10-Phen, suggesting that these ligands are involved in complex formation. The signal due to the hydroxy proton of the free ligand 8-HQ, of H^h (8.45 ppm) [22] disappeared on complexation, suggesting formation of a M–O bond by deprotonation of 8-HQ [43]. This was confirmed by disappearance of the hydroxyl group band of the phenolic group in the infrared spectra and also by the non-electrolytic nature of 8-HQ complexes. For complex **11**, the signal of $H^{j,j'}$ (8.70 ppm) protons for 2,2′-Bipy is shifted up-field to 7.45 ppm suggesting involvement of the 2,2′-Bipy ring through chelation [44, 45]. The ^{1}H NMR spectrum of complex **12**; $[(UO_2)_2(L)(1,10\text{-Phen})_2(NO_3)_2(H_2O)_2]$, is compared to the free 1,10-Phen ligand. The phenanthroline molecule contains four pairs of equivalent protons ($H^{k,k'}$ and $H^{l,l'}$), which resonate within the range of 7.60–9.20 ppm [14, 28]. The complexation gives rise to substantial changes in the positions of the spectral patterns, which lie in the range 7.32–9.02 ppm. All the signals are shifted upfield and become broadened, suggesting that 1,10-Phen is complexed. The molar conductance of the complexes in DMF solutions are 20, 135 and 156 $\text{Ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ (table 4) indicating that complex **10** is non-electrolytic [35] while **11** and **12** are 1 : 2 electrolytes [33, 34].

3.2.3. Thermal analysis. Thermal decomposition of complex **6** has been investigated using thermal gravimetric analysis (TGA) and DrTGA (figure 6). The TGA-curve of complex 6, $[Ni_2(L)(Phen)_2(NO_3)_2(H_2O)_2]\cdot 2H_2O$, shows that the first stage with 5.12% loss of the total weight is due to the removal of two lattice water molecules between 50–120°C [46]. The second stage at 120–230°C corresponds to the loss of 4.34%, due to the removal of the two coordinated water molecules [47]. The third stage of decomposition corresponds to the loss of 15.30% at 250–300°C due to loss of two NO_3^- groups. The last stage at 300–460°C, the loss of 57.82% of the total weight, is due to the decomposition of the complex and formation of nickel oxide at 500°C (table 5). The DrTGA curve of the complex shows a peak at 110°C, corresponding to lattice rearrangement while the strong peak at 280–320°C can be assigned to decomposition of the anhydrous complex through loss of the organic molecule

Downloaded At: 12:35 23 January 2011

Downloaded At: 12:35 23 January 2011

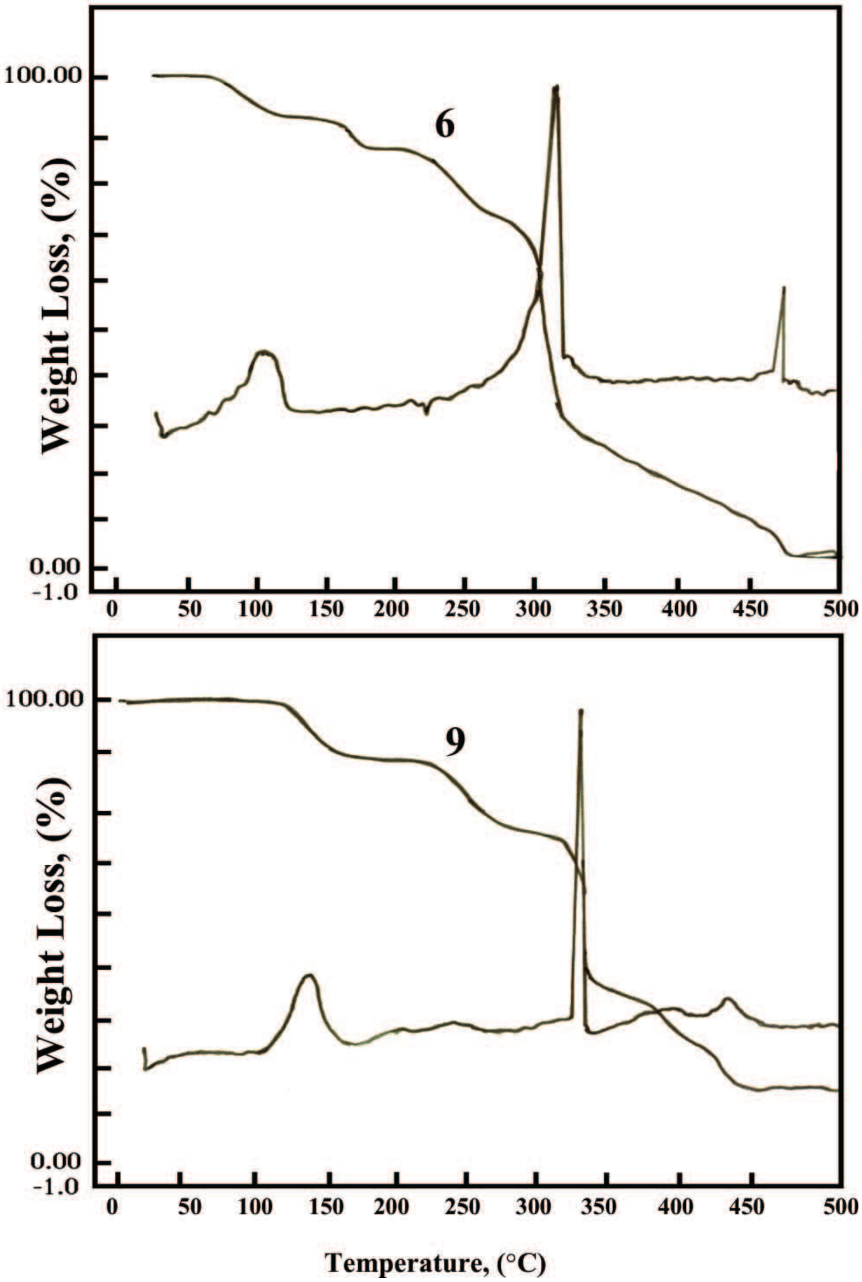


Figure 6. TGA and DrTGA of the complexes, **6**: $[Ni(L)(1,10\text{-}Phen)_2(NO_3)_2(H_2O)]\cdot 2H_2O$ and **9**: $[Cu_2(L)(1,10\text{-}Phen)_2]\cdot(NO_3)_2\cdot 6H_2O$.

Downloaded At: 12:35 23 January 2011

Table 5. Thermogravimetric analysis (TGA) of complexes **6** and **9**.

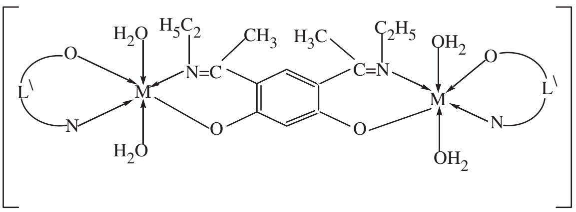
Complex	Loss in weight % Found (Calcd)	Assignment	Temperature range (°C)
6 $[Ni_2L(1,10\text{-Phen})_2\,(NO_3)_2(H_2O)_2]\cdot 2H_2O$	5.12 (4.14)	Loss of two lattice H_2O	50–120
	4.34 (4.14)	Loss of two coordinated H_2O	120–230
	15.30 (14.22)	Loss of two NO_3 groups	250–300
	57.82 (61.26)	Decomposition of the complex	300–460
	17.42 (16.24)	NiO (residue)	460–500
9 $[Cu_2L(1,10\text{-Phen})_2]\cdot(NO_3)_2\cdot 6H_2O$	10.12 (11.19)	Loss of six crystalline water molecules	50–210
	13.35 (12.84)	Loss of two NO_3 groups	210–320
	60.78 (59.50)	Decomposition of the complex	320–440
	15.75 (16.47)	CuO (residue)	440–500

and formation of metal oxide at 500°C (figure 6). The thermal decomposition is suggested to proceed as follows:

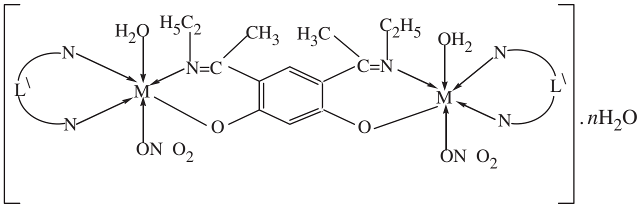
$$
\begin{aligned}
&\textbf{(6)}\qquad [Ni_2(L)(1,10\text{-Phen})_2(NO_3)_2(H_2O)_2]\cdot 2H_2O\\
&\xrightarrow[50\text{–}85^\circ C]{-2H_2O,\ \text{crystalline}} [Ni_2(L)(1,10\text{-Phen})_2(H_2O)_2].\\
&\xrightarrow[100\text{–}230^\circ C]{-2H_2O,\ \text{coordinated}} [Ni_2(L)(1,10\text{-Phen})_2(NO_3)_2]\\
&\xrightarrow[250\text{–}300^\circ C]{-2(NO_3)} [Ni_2(L)(1,10\text{-Phen})_2]^{+2}\\
&\xrightarrow[310\text{–}460^\circ C]{\text{decompostition of the complex}} NiO\ (500^\circ C)
\end{aligned}
$$

The TGA curve of $[Cu_2(L)(1,10\text{-Phen})_2]\cdot(NO_3)_2\cdot 6H_2O$ shows three stages (figure 6). The first with loss of 10.12% of the total weight of the complex is due to the loss of six crystalline water molecules at 50–210°C. The second stage corresponds to the loss of 13.35% is assigned to the loss of two nitrate groups at 210–320°C. The last stage corresponds to the loss of 60.78% at 320–440°C due to decomposition of the complex. The residue was 15.75% of the total molecular weight that can be ascribed to the formation of copper oxide at 500°C. The decomposition at 440–500°C confirms the partial oxidation of the oxide (table 5). The DrTGA curve of the hydrated chelate exhibits two peaks. The first peak at 140°C is probably due to loss of water while the second peak at 335°C corresponds to the melting of the anhydrous complex. The decomposition of the complex occurs in the range 440–500°C (figure 6).

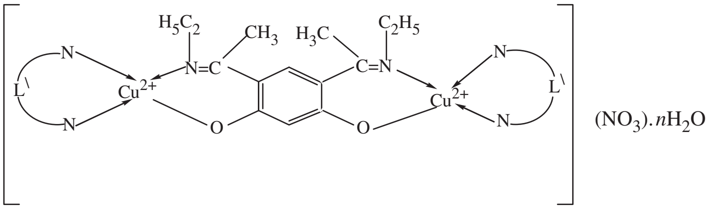
$$
\begin{aligned}
&\textbf{(9)}\qquad [Cu_2(L)(1,10\text{-Phen})_2]\cdot(NO_3)_2\cdot 6H_2O\\
&\xrightarrow[50\text{–}150^\circ C]{-6H_2O\ [\text{crystalline water molcules}]} [Cu_2(L)(1,10\text{-Phen})_2](NO_3)_2\\
&\xrightarrow[160\text{–}320^\circ C]{-2(NO_3)} [Cu_2(L)(1,10\text{-Phen})_2]^{2+}\\
&\xrightarrow{440\text{–}500^\circ C} CuO\ (500^\circ C)
\end{aligned}
$$



Complexes 1,4,7 and 10 where, M = Co(II), Ni(II),Cu(II), UO_2(VI) and L\ = 8-HQ (in case of UO_2(VI) complex, the $4H_2O$ molecules are out of coordination).



Complexes 2, 3, 5, 6, 11 and 12, where M = Co(II), Ni(II), Cu(II), UO_2(VI) and L\ = 1,10-phen or 2,2′-Biby. For all of these complexes n = 0 except for 6, 11 and 12 complexes where, n = 2 (in case of UO_2(VI) complexes 11 and 12 the NO_3^- ions and water molecules are out of coordination)



Complexes 8 and 9 where, L\ = 1,10-phen or 2,2′-Biby and n = 2 for complex 8 and 6 for complex 9

Figure 7. Representative structures of the ternary complexes.

On the basis of elemental analyses and the discussed physical measurements (tables 1–5) a tentative structure is proposed for the binuclear complexes as shown in figure 7.

References

[1] R. Hernandez-Molina, A. Mederos. In *Comprehensive Coordination Chemistry III*, A.B.P. Lever (Ed.), Elsevier (2003).

[2] A.D. Garnovskii, B.I. Kharisov. *Synthetic Coordination and Organometallic Chemistry*, Marcel Dekker, New York (2003).

[3] A.D. Garnovskii, I.S. Vasilchenko. *Russ. Chem. Rev.*, **71**, 943 (2002).

[4] P.A. Vigato, S. Tamburini. *Coord. Chem. Rev.*, **248**, 1717 (2004).

[5] W. Zeng, J. Li, Z. Mao, Z. Hong. S. Qin. *Advcd Synth. Catalysis*, **346**, 1385 (2004).

[6] K. Kuraoka, T. Yazawa, Y. Chujo. *Chem. Commun.*, **24**, 2477 (2000).

[7] Z.H. El-Wahab, A. Mashaly, M. Mahmoud, A.A. Salman, B.A. El-Shetary, A.A Faheim. *Spectrochimica Acta*, **60**A, 2861 (2004).

[8] El-Tabl, A. Saad, El-Enein, S. Abdou. *J. Coord. Chem.*, **57**, 281 (2004).

[9] P. Nagpal, R.V. Singh. *App. Organomet. Chem.*, **18**, 221 (2004).

[10] M. Yildiz, B. Duelger, S.Y. Koyuncu, B.M. Yapici. *J. Indian Chem. Soc.*, **81**, 7 (2004).

Downloaded At: 12:35 23 January 2011

[11] N.N. Majeti, R. Kumar. *Reactive Funct. Polymers*, **46**, 1 (2000).

[12] A.B.P. Lever. *Comprehensive Coordination Chemistry II, Volume 2: Fundamentals: Physical Methods, Theoretical Analysis and Case Studies*, Elsevier, Oxford (2004).

[13] F.E. Mabbs, D.J. Machin. *Magnetism and Transition Metal Complexes*, Chapman and Hall, London (1973).

[14] E. Pretsch, J. Seibl, W. Simon, T. Clerc. *Tables of Spectral Data for Structure Determination of Organic Compounds*, Spring-Verlag, Berlin (1983).

[15] U.B. Gangadharmath, V.K. Revankar, V.B. Mahale. *Spectrochimica Acta*, **58A**, 2651 (2002).

[16] M.H. Mashaly, T.H. Ismail, S.B. El-Maraghy, H.A. Habib. *J. Coord. Chem.*, **56**, 15 (2003).

[17] A.A. Saleh, A.M. Tawfik, S.M. Abu-El-Wafa, H.F. Osman. *J. Coord. Chem.*, **57**, 1191 (2004).

[18] U. Casellato, S. Tamburini, P. Tomasin, P.A. Vigato. *Inorg. Chim. Acta*, **341**, 118 (2002).

[19] R.C. Maurya, P. Patel, S. Rajput. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 801 (2003).

[20] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York (1997).

[21] J.R. Ferraro. *Low-frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York (1971).

[22] A. Dhammani, R. Bohra, R.C. Mohrotra. *Polyhedron*, **17**, 163 (1998).

[23] P.G. Bradley, N. Kress, B.A. Hornberger, R.F. Dallinger, W.H. Woodruff. *J. Am. Chem. Soc.*, **103**, 7441 (1981).

[24] K. Iftikar, M. Sayeed, N. Ahmed. *Inorg. Chem.*, **21**, 80 (1982).

[25] J. Yang, J.-F. Ma, Y.-M. Zhang, E. Leroi, F.-F. Li, J.-F. Liu. *J. Coord. Chem.*, **56**, 1409 (2003).

[26] R.L. Carter. *Molecular Symmetry and Group Theory*, John Wiley & Sons, New York (1977).

[27] M.S. Atanassova, G.D. Dimitravo. *Spectrochimica Acta*, **59A**, 1655 (2003).

[28] G.D. Dimitrov, M.S. Atanassova. *Z. Anorg. Allg. Chem.*, **629**, 12 (2003).

[29] A.P. Lever. *Inorganic Electronic Spectroscopy*, Elsevier, Amesterdam (1984).

[30] S.F.A. Kettle. *Coordination Compounds Spectroscopy*, Elsevier, Amsterdam (1984).

[31] A. Chadghan, J. Pons, A. Caubet, J. Casabo, J. Ros, A. Larena, J. Piniella. *Polyhedron* **19**, 885 (2000).

[32] S.M. Khlil, A.A Emara. *J. Coord. Chem.*, **55**, 17 (2002).

[33] J.V. Quagliano, J. Fujita, G. Franz, P.J. Phillips, J.A. Walmesley, S.Y. Tyree. *J. Am. Chem. Soc.*, **83**, 3770 (1956).

[34] V.V. Savant, C.C. Patel. *J. Inorg. Nucl. Chem.*, **31**, 231 (1969).

[35] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).

[36] Z. Smekal, P. Thorntn, Z. Sindelar, R. Klicka. *Polyhedron*, **17**, 1631 (1998).

[37] G.V. Prabhu, D.Venkapya. *Ind. J. Chem.*, **33A**, 830 (1994).

[38] M.N. Patel. *Synth. React, Inorg. Met.-Org. Chem.*, **34**, 553 (2004).

[39] B.N. Figgis. *Introduction to Ligand Field*, John Wiley & Sons, New York (1970).

[40] A. Taha. *Spectrochimica Acta*, **59A**, 1373, (2003).

[41] D. Boghaei, S. Mohebi. *Tetrahedron*, **58**, 5357 (2002).

[42] B.V. Agarwala, S. Hingorn, V. Puri, C.L. Khetrapal, G.A. Naganagowda. *Transition Metal Chem.*, **19**, 25 (1994).

[43] B.C. Baker, D.T. Sawyer. *Anal. Chem.*, **40**,1945 (1968).

[44] H.A. Hussain, A.A. Ansari, K. Iftikar. *Spectrochimica Acta*, **60A**, 873 (2004).

[45] G.E. Matsubayashi, T. Tanaka. *J. Organometallic Chem.*, **120**, 347 (1976).

[46] J.W. Dodd, K.H. Tonge. *Thermal Methods: Analytical Chemistry by Open Learning*, John Wiley & Sons, New York (1987).

[47] D.K. Dwivedi, B.V. Agarwala, A.K. Dey. *Bull. Soc. Chim. Belg.*, **96**, 431 (1987).

Downloaded At: 12:35 23 January 2011