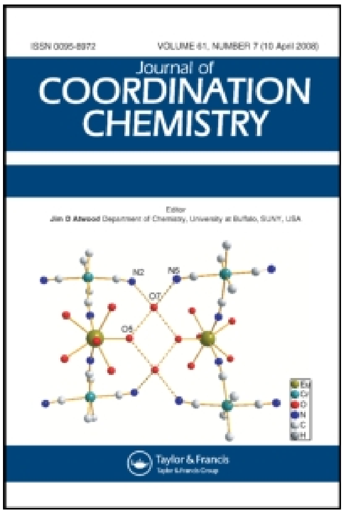

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Mononuclear and homobinuclear cobalt(II), nickel(II) and copper(II) complexes with mono and bis-azocompounds derived from 2,7-dihydroxynaphthalene and anthranilic acid or *o*-aminophenol

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MONONUCLEAR AND HOMOBINUCLEAR COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES WITH MONO AND BIS-AZOCOMPOUNDS DERIVED FROM 2,7-DIHYDROXYNAPHTHALENE AND ANTHRANILIC ACID OR *o*-AMINOPHENOL

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Two new series of mononuclear and homobinuclear Co(II), Ni(II) and Cu(II) complexes with mono- and bis-azo compounds derived from 2,7-dihydroxynaphthalene and anthranilic acid or *o*-aminophenol are prepared and characterized by elemental and thermal analyses, conductance, IR, electronic, ESR spectra and magnetic moment measurements. The ligand field splitting parameters and Racah constant are calculated. The spectral and magnetic results obtained are utilized to determine the geometries around the metal(II) ion. The geometry of the complex formed depends on the structure of the ligand and the type of metal(II) ion. The mode of bonding of the ligand with the metal ions is deduced from IR spectra.

Keywords: Cobalt(II); Nickel(II); Copper(II); Dihydroxynaphthalene; Anthranilic acid

INTRODUCTION

Interest in mono- and bis-azo transition metal(II) complexes incorporating a naphthalene moiety arises from their wide applications in industry and biological systems [1–7]. Transition metal azo complexes have played an important role in the development of coordination chemistry. The mode of bonding and structure of such complexes has been investigated using different physico chemical methods [8–11]. Also many azo compounds have been used as chromogenic agents for the determination of metal ions [12–15], and in pharmaceutical analysis [16,17] as reagents for the spectrophotometric analysis of drugs in pure and dosage forms, due to the formation of ion-pair or charge transfer complexes. Although many studies have been carried out on the spectral behavior of mono- and bis-azo compounds and their metal chelates,

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studies on azo compounds derived from 2,7-dihydroxynaphthalene as the chelating agent have so far been unsatisfactory [18–20].

Herein we report the stoichiometry and molecular structure of cobalt(II), nickel(II) and copper(II) complexes with mono- and bis-azo ligands derived from 2,7-dihydroxynaphthalene and anthranilic acid or *o*-aminophenol determined by conductance, elemental and thermal analyses, magnetic studies and different spectroscopic techniques.

EXPERIMENTAL

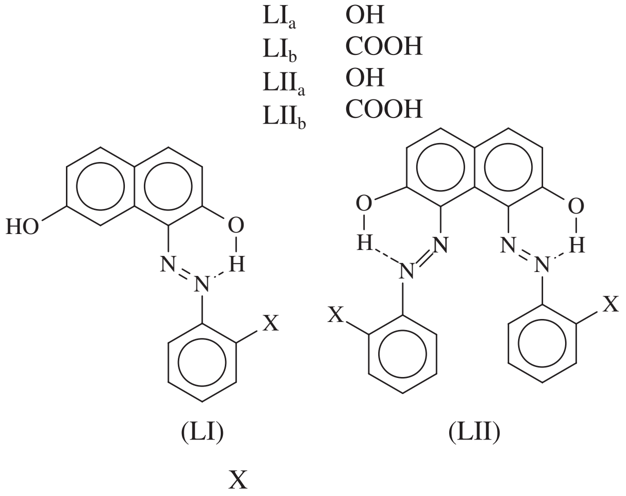
All compounds and solvents used in the present investigation were pure grade BDH or Prolabo chemicals. The ligands (LI and LII) were prepared according to the previously reported method [21]. The purity of the ligands was determined by IR, ^{1}HNMR spectroscopy and elemental analysis. The ligands used in the present investigation are shown in Scheme 1.

Preparation of the Mononuclear and Homobinuclear Complexes

The solid complexes were prepared by mixing a hot solution of the metal(II) acetate (0.001 M) or (0.002 M) in (50% V/V) aqueous ethanol with a saturated ligand solution (0.001 M) in ethanol. The mixture was then refluxed in a water bath for at least 10 h, and allowed to cool, whereupon the solid complex separated. The complexes were filtered off, washed with ethanol and then dried over silica gel.

The complexes thus prepared were stored over P_2O_5. The structures of the solid cobalt(II), nickel(II) and copper(II) complexes were determined by elemental and thermal analyses, conductance, IR, electronic, ESR spectra and by magnetic susceptibility studies.

The apparatus and procedures are the same as described previously [22,23].



SCHEME 1

TABLE I Elemental analysis, magnetic, conductance and ESR spectral data of monoazo mononuclear and homobinuclear bisazo complexes

	Complex	*Elemental analysis*[a]				μ_{eff}[b]	Λ[c]	*ESR*		
		%C	*%H*	*%N*	*%M*			$g_{\parallel}$	$g_{\perp}$	g_{eff}
1	$[NiLI_a(H_2O)]\cdot 3H_2O$	46.94	4.40	6.85	14.43	–	8.20	–	–	–
		(46.15)	(4.30)	(6.22)	(14.15)					
2	$[NiLI_b(H_2O)]\cdot 3H_2O$	46.68	4.12	6.41	13.40	–	15.30	–	–	–
		(46.30)	(4.30)	(6.15)	(13.89)					
3	$[CoLI_a(H_2O)]\cdot 3H_2O$	46.24	4.40	6.85	14.43	1.97	9.20			1.518
		(46.51)	(4.22)	(6.72)	(14.20)					
4	$[CoLI_b(H_2O)]\cdot 3H_2O$	46.68	4.12	6.41	13.50	1.96	17.80			1.5231
		(46.50)	(4.08)	(6.22)	(12.95)					
5	$[CuLI_a(H_2O)]\cdot 3H_2O$	46.42	4.35	6.77	15.39	2.03	10.12	1.790	1.654	1.7233
		(46.38)	(4.22)	(6.18)	(15.77)					
6	$[CuLI_b(H_2O)]\cdot 3H_2O$	46.19	4.08	6.34	14.41	1.78	13.10	1.755	1.648	1.702
		(46.38)	(3.90)	(6.18)	(14.14)					
7	$[Ni_2LII_a(H_2O)_2]\cdot 2H_2O$	46.05	3.42	9.57	20.00	–	11.30	–	–	–
		(46.90)	(3.70)	(10.03)	(20.22)					
8	$[Ni_2LII_b(H_2O)_2]\cdot 4H_2O$	46.40	3.86	8.24	17.27	–	12.15	–	–	–
		(46.08)	(3.03)	(8.02)	(17.10)					
9	$[Co_2LII_a(H_2O)_2]\cdot 2H_2O$	45.05	3.41	9.56	20.14	2.15	10.22			1.599
		(45.38)	(3.15)	(10.01)	(19.85)					
10	$[Co_2LII_b(H_2O)_2]\cdot 4H_2O$	42.37	3.85	8.24	17.33	2.10	7.28			1.6732
		(42.16)	(3.22)	(8.15)	(17.15)					
11	$[Cu_2LII_a(H_2O)_2]\cdot 2H_2O$	44.37	3.36	9.40	21.38	1.45	9.09	1.839	1.648	1.7461
		(45.02)	(3.15)	(9.13)	(20.98)					
12	$[Cu_2LII_b(H_2O)_2]\cdot 4H_2O$	41.92	3.8	8.13	18.43	1.40	13.17	1.834	1.722	1.779
		(41.72)	(3.31)	(8.02)	(18.16)					

[a]Calculated (found); [b]BM/M^{2+} ion; [c]10^{-3} M in DMF, $\Omega^{-1}cm^{-2}mol^{-1}$.

RESULTS AND DISCUSSION

The stoichiometry of the solid complexes was confirmed by elemental analyses, Table I, of the isolated chelates. The data show satisfactory agreement with the proposed formulae. All the solid complexes are soluble in DMF but insoluble in common organic solvents and do not have sharp melting points but decompose on heating above 350°C.

The molar conductance values of the complexes (10^{-3} M DMF solution) were found to be in the range 7.28–17.80 $\Omega^{-1}cm^{-2}mol^{-1}$. These values indicate that the complexes are non-electrolytes [24]. The conductometric titration curves for the mono- and bis-azo compounds indicate the probable formation of 1 : 1 and 2 : 1 complexes (M : L), respectively. The steady increase in equivalent conductance–molar ratio curves is attributed to the liberation of H^+ through formation of covalent bonding between the oxygen atom of the hydroxyl group (either phenolic or carboxylic OH) and the metal ion to give a five or six-membered ring, respectively.

Figure 1 shows the thermogravimetric and differential thermal analysis curves for some selected Ni(II) and Cu(II) complexes. The DTA curves show endothermic peaks in the range 50–120°C which are due to the removal of water molecules from the crystal lattice. Removal of coordinated water molecules is represented by endothermic peaks within the range 180–250°C. The strong exothermic peaks at 380–600°C are due to the phase transformation taking place during decomposition of the anhydrous complex leading to the formation of NiO or CuO as final products from which the metal

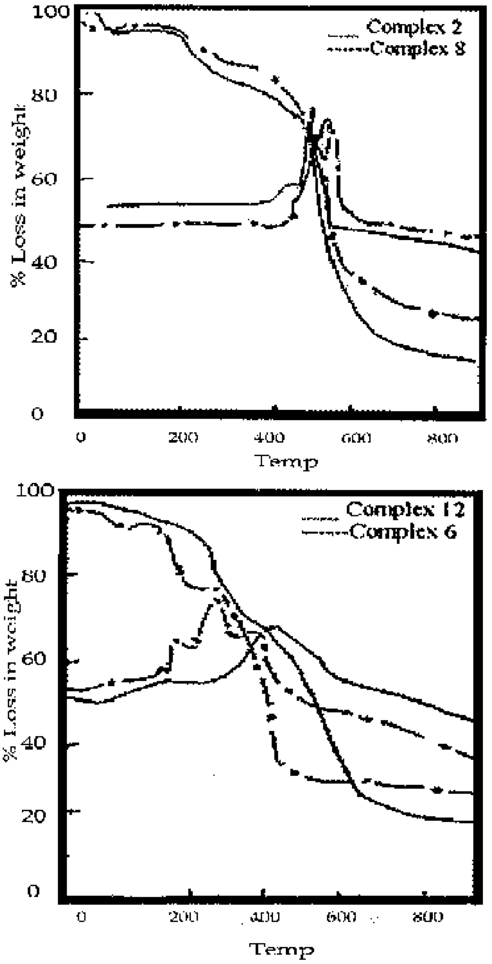
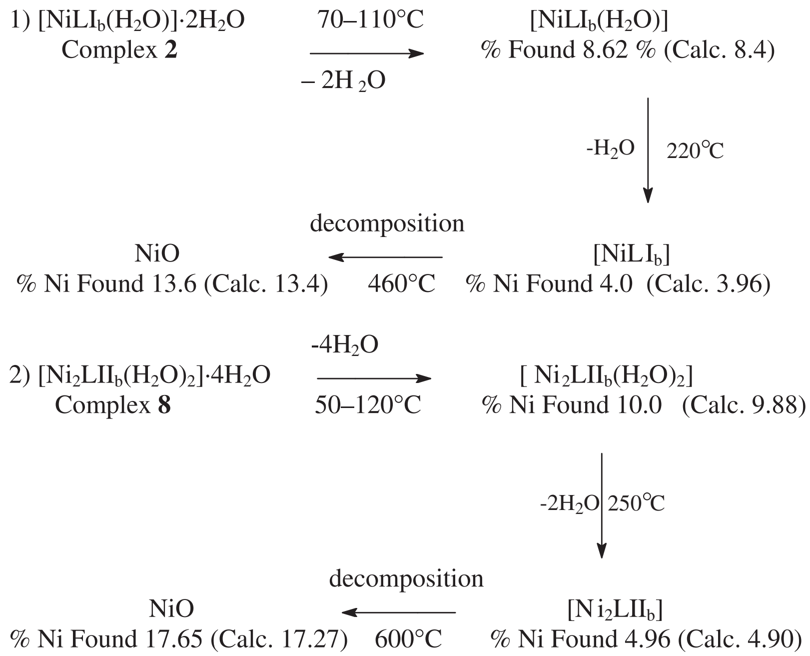


FIGURE 1 TGA-DTA analysis for mononuclear and homobinuclear Ni(II) and Cu(II) complexes.

content was estimated and confirmed from elemental analysis. The thermal decomposition of the mononuclear and homobinuclear Ni(II) or Cu(II) complexes **2** and **6**, **8** and **12**, respectively with ligands LI_b and LII_b is shown in Scheme 2.

Thus, the bisazo binuclear complex is more stable than the mononuclear one. The thermal stability runs in the order: complex **8** > complex **12** > complex **2** > complex **6**.

The IR spectra of the solid mono and homobinuclear chelates have been studied and compared with those of the free ligands, and the following points are to be noted: (a) Disappearance of the weak broad band at $\sim 2930\,cm^{-1}$ due to the intramolecularly hydrogen bonded OH group [25]. The absence of this weak broad band in the IR spectra of the complexes indicates the participation of the *o*-OH in complex formation through proton displacement. (b) In mononuclear complexes **1**–**6**, the presence of the broad band at 3155 and $3220\,cm^{-1}$ for ligands LI_a and LI_b, respectively is attributed to υ_{OH} in position 7 indicating that in complexes **1**–**6** the second hydroxy group (in position 7) does not contribute to complex formation. This conclusion is further



SCHEME 2

supported by comparing the IR spectra of the free ligands with those of dehydrated complexes where there are shifts in δ_{OH} and $\upsilon_{C\text{–}OH}$ at 1279 and 1265 cm^{-1}, respectively, by 10–20 and 15–25 cm^{-1} to lower wavenumber in the spectra of complexes **1**–**6**. The intensity of these bands also decreases to one half relative to neighboring bands. The shift in δ_{OH} and $\upsilon_{C\text{–}OH}$ and decrease in intensity indicate participation of the other two OH groups (phenolic and carboxyl groups) in complex formation of mononuclear azo chelates. (c) The IR spectra of the free ligands LI$_b$ and LII$_b$ exhibit $\upsilon_{C=O}$ bands at 1653 and 1655 cm^{-1} bands attributed to υ_{COO} at 1593 and 1605 cm^{-1}, respectively. The band shifts of 5–10 cm^{-1} to lower wavenumbers in the spectra of the complexes indicates participation of the carboxyl group in chelate formation. (d) In the homobinuclear bisazochelates (**7**–**12**) the δ_{OH} and $\upsilon_{C\text{–}OH}$ bands disappear indicating deprotonation of all phenolic or carboxylic OH groups in the formation of the metal chelates. (e) The presence of coordinated water molecules is indicated by the observation of a double peak around 3300 cm^{-1} corresponding to υ_{OH}, and further confirmed by the γ_{OH} band at 840–820 cm^{-1} [26] while the band at 1255–1240 cm^{-1} is assigned to the bending vibration δ_{H_2O}. (f) The participation of the N=N group in chelation for complexes (**1**–**12**) is evident from the shift of $\upsilon_{N=N}$ from 1410–1425 cm^{-1} in the spectra of the free ligands to lower wave number by 5–15 cm^{-1} in the spectra of the complexes. The two new bands within the ranges 510–465 and 420–380 cm^{-1}, which are absent in the spectra of free ligands, are assigned to $\upsilon_{M\text{–}O}$ and $\upsilon_{M\text{–}N}$, respectively [27].

Magnetic moments at room temperature (300 K) for the monoazo mononuclear and bisazo homobinuclear Co(II) and Cu(II) complexes are listed in Table I. The electronic spectral data together with the ligand field parameters (10Dq) and Racah parameter are calculated and listed in Table II.

TABLE II IR and electronic spectral data

Compound	*IR* (cm^{-1})						*Electronic spectral* (cm^{-1}) *parameters*		
	ν_{OH}	ν_{CO}	$\nu_{N=N}$	δ_{OH}	ν_{M-O}	ν_{M-N}	*d–d Transition*	*10Dq*	β
LI_a	3200 3155	–	1425	1270	–	–	–	–	–
1 $[NiLI_a(H_2O)]\cdot 3H_2O$	3300 3150	–	1420	1245	510	380	32 787 20 202	1120	680
3 $[CoLI_a(H_2O)]\cdot 3H_2O$	3300 3150	–	1415	1255	505	385	28 169 18 692	2137	432
5 $[CuLI_a(H_2O)]\cdot 3H_2O$	3300 3150	–	1410	1245	500	385	26 316 19 048		
LI_b	3300 3220	1653	1415	1279	–	–	–	–	–
2 $[NiLI_b(H_2O)]\cdot 3H_2O$	3300 3220	1593	1410	1260	485	390	32 258 20 000	1178	637
4 $[CoLI_b(H_2O)]\cdot 3H_2O$	3200 3155	1596	1405	1255	465	395	23 809 18 868	2015	512
6 $[CuLI_b(H_2O)]\cdot 3H_2O$	3300 3220	1598	1405	1260	470	395	25 575 20 491	–	–
LII_a	3200 3155	–	1410	1275	–	–	–	–	–
7 $[Ni_2LII_a(H_2O)_2]\cdot 2H_2O$	3300	–	1405	1250	490	410	32 363 19 418	1205	518
9 $[Co_2LII_a(H_2O)_2]\cdot 2H_2O$	3300	–	1405	1255	495	415	24 631 18 660	2078	425
11 $[Cu_2LII_a(H_2O)_2]\cdot 2H_2O$	3300	–	1405	1260	500	415	28 974 19 120	–	–
LII_b	3400 3220	1655	1420	1270	–	–	–	–	–
8 $[Ni_2LII_b(H_2O)_2]\cdot 4H_2O$	3300	1600	1410	1245	505	420	32 363 20 202	1433	615
10 $[Co_2LII_b(H_2O)_2]\cdot 4H_2O$	3300	1605	1415	1249	510	415	24 390 18 692	2008	415
12 $[Cu_2LII_b(H_2O)_2]\cdot 4H_2O$	3300	1605	1410	1250	500	415	28 794 20 366	–	–

The electronic spectra of Co(II) complexes **3**, **4**, **9** and **10** show two broad bands within the range 18 868–18 660 and 28 169–23 805 cm^{-1} corresponding to $^4T_{1g}\rightarrow{}^4A_{2g}$ (υ_2) and $^4T_{1g}\rightarrow{}^4A_{1g}$ (υ_3) transitions [28–30], indicating square-planar geometry. This is also supported by the values of magnetic moments in the range 1.96–2.15 BM/Co^{2+} ion expected for low spin square planar geometry around Co(II) ions [31].

On comparing the splitting energy field parameters of Co(II) ions with different ligands (10Dq) it can be seen that the values are in the order: $LI_a > LII_a > LI_b > LII_b$, i.e., ligand LI_a gives the highest splitting energy value.

The electronic spectra of nickel(II) complexes **1**, **2**, **7** and **8** show two bands within the range 19 418–20 202 and 32 758–32 787 cm^{-1} assigned to $^3A_{2g}\rightarrow{}^3T_{1g}$ (F) and $^3A_{2g}\rightarrow{}^3T_{1g}$ (P) transitions, respectively. The nickel(II) complexes show diamagnetic [30,32] character, suggesting square planar geometry. The (10Dq) values are in the following order: $LII_b > LII_a > LI_b > LI_a$.

The Cu(II) complexes **5**, **6**, **11** and **12** have magnetic moments 2.03, 1.78, 1.45 and 1.40 BM/Cu^{2+}, respectively. The decrease in the magnetic moment for complexes **11** and **12** is due to copper–copper antiferromagnetic interactions. The electronic spectra of the Cu(II) complexes show two broad bands within the ranges 19 048–20 491 and

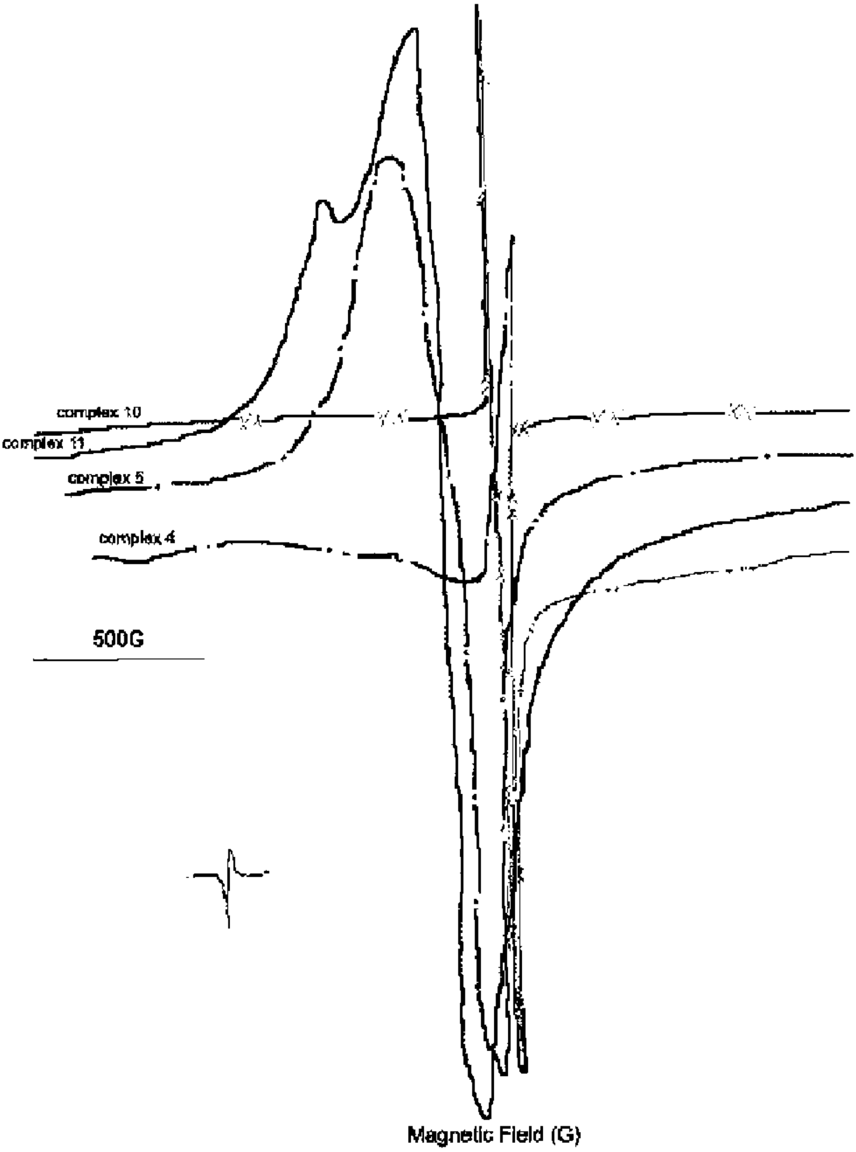
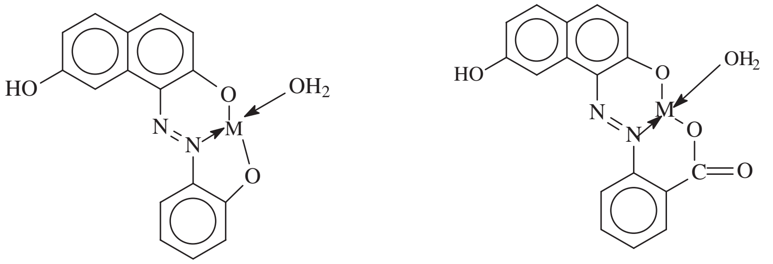


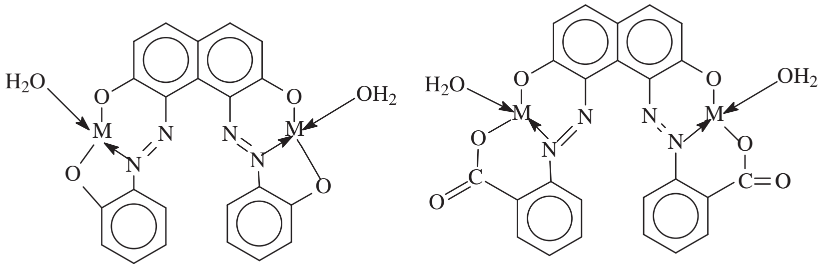
FIGURE 2 X-band ESR spectra of Co(II) or Cu(II) monoazo mononuclear or bisazo homobinuclear complexes.

28 974–25 575 cm^{-1}, which can be assigned to $^2T_{2g}\rightarrow{}^2E_g$ and charge transfer (M→L or L→M) interactions in distorted tetrahedral configurations [28,29].

The X-Band ESR spectra of Co(II) complexes **3**, **4**, **9** and **10** and Cu(II) complexes **5**, **6**, **11** and **12** were obtained in the solid state at 300 K in order to confirm the geometries around Co(II) and Cu(II). Figure 2 shows the ESR spectra of some of the complexes; the shape of the signals and the g_{eff} values (Table I) are very similar to low-spin, square-planar Co(II) complexes and distorted tetrahedral Cu(II) ions [33].



Complexes **1**, **3** and **5** Complexes **2**, **4** and **6**



Complexes **7**, **9** and **11** Complexes **8**, **10** and **12**

SCHEME 3 M = Ni(II), Co(II) or Cu(II).

Our studies show the bonding of the metal(II) ions in monoazo monouclear and homobinuclear bisazo complexes can be formulated as shown in Scheme 3.

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