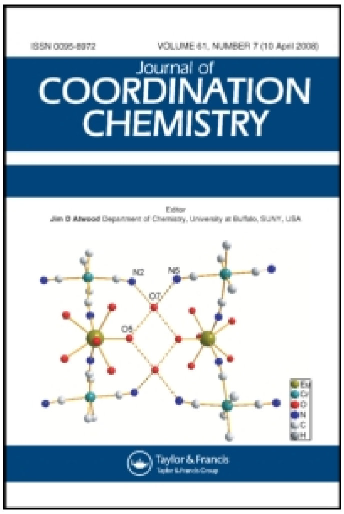

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Formation of novel mono- and multi-nuclear complexes of Mn(II), Co(II) and Cu(II) with bis azo-dianils containing the pyrimidine moiety: Thermal, magnetic and spectral studies

S. M. Abu-El-Wafa[a]; N. A. El-Wakiel[a]; R. M. Issa[a]; R. A. Mansour[a]
[a] Chemistry Department, Faculty of Science, Tanta University, Egypt

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Formation of novel mono- and multi-nuclear complexes of Mn(II), Co(II) and Cu(II) with bis azo-dianils containing the pyrimidine moiety: Thermal, magnetic and spectral studies

S. M. ABU-EL-WAFA*, N. A. EL-WAKIEL, R. M. ISSA and R. A. MANSOUR

Chemistry Department, Faculty of Science, Tanta University, Egypt

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A novel series of Mn(II), Co(II) and Cu(II) complexes with some bisazo-dianils (compounds having two N=N and two HC=N groups) containing the pyrimidine moiety were prepared and characterized by elemental and thermal analyses, molar conductance and magnetic moment determination as well as IR, electronic absorption and ESR spectra. The data revealed different geometries around the metal ions, depending on both the ligand and metal ion.

Keywords: Multinuclear complexes; Biazodianil complexes containing the pyrimidine moiety; Thermal; Magnetic and spectral studies

1. Introduction

The interest in azo-azomethine metal complexes with transition metal ions arises from their wide applications in industrial and biological systems [1–8]. Despite the importance of azo-azomethine derivatives and their metal chelates, little has appeared in the literature [9–11] and no systematic studies have been carried out concerning complex formation between azo-azomethines containing the pyrimidine moiety and transition metal ions.

The present investigation synthesizes mono- and multi-nuclear complexes of bisazo-dianils containing two pyrimidine moities in the molecule with Mn(II), Co(II) and Cu(II) ions. Complexes of these ions with azo compounds were found to be better dyeing agents than the free azo dye [12], also azomethine complexes readily function as catalysts in photochemical [13] and oxidation reactions of organic compounds [14]. The complexes obtained were characterized by elemental and thermal analyses, molar conductance and magnetic moment measurements as well as IR, electronic absorption and ESR spectra.

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*Corresponding author. Email: abuelwafa_1@hotmail.com

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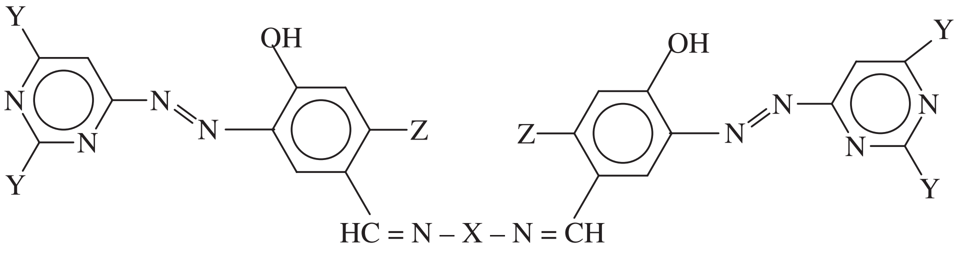
2. Experimental

All compounds used in the present investigation were pure laboratory grade chemicals from BDH or Aldrich.

2.1. *Preparation of the bisazo-dianil ligands*

The ligands used in the present investigation were prepared according to recommended methods [10,15,16] and the purity was tested by elemental analysis, IR and ^{1}H-NMR spectra. The bisazo-dianils of pyrimidine have the following structural formulas:



	L_{I}	L_{II}	L_{III}	L_{IV}	L_{V}
X	$(CH_2)_3$	$(CH_2)_3$	$(CH_2)_6$	$(CH_2)_6$	$(CH_2)_3$
Y	OH	CH_3	CH_3	CH_3	OH
Z	OH	OH	OH	H	H

2.2. *Preparation of the solid metal ion complexes*

A hot ethanolic solution of the ligand (1 mmol) dissolved in 50 mL hot ethanol was mixed with a hot ethanolic solution of the metal chloride (1–4 mmol). The reaction mixture was refluxed on a water bath for at least 10 h then allowed to cool. The separated solid complexes were then filtered off, washed with small portions of hot ethanol three times, then dried in vacuum. Table 1 illustrates the conditions of preparation of the metal complexes. The dry complexes were then characterized.

The elemental analyses were carried out at the microanalytical units of Cairo and Tanta universities. Thermal analysis (TGA) was performed on a Shimadzu TA50 WSI.

The IR spectra were recorded as KBr discs within the range 4000–200 cm^{-1} on a Perkin Elmer 1430 spectrophotometer. The UV/Vis spectra of the complexes as Nujol mull and in DMF solutions were obtained on a Shimadzu 240 UV-Vis spectrophotometer. ESR spectra were obtained on a JOEL JES-FEZ XG spectrometer supplied with E101 Unit.

Magnetic moment determination was carried out at room temperature by the Gouy method using 20 kilo Gauss, magnetic suceptibility balance (Johnson Matthey Wayne PA 19087 USA) at 60 Hz. Diamagnetic corrections were carried out using Pascal's constants.

Table 1. Data for the preparation of the complexes.

Complex no.	No. and Wt. of ligand	Metal chloride formula and Wt.	Ligand : Metal ratio
1	1.0 mmol L_I, 0.595 g	$MnCl_2 \cdot 4H_2O$ 0.593 gm = 3 mmol	1 : 3
2	L_I, 0.595 g	$CuCl_2 \cdot 2H_2O$ 0.512 gm = 3 mmol	1 : 3
3	L_{II}, 0.617 g	$MnCl_2 \cdot 4H\ _2O$ 0791 g = 4 mmol	1 : 4
4	L_{II}, 0.617 g	$CuCl_2 \cdot 2H_2O$ 0.341 g = 2 mmol	1 : 2
5	L_{III}, 0.659 g	$CoCl_2 \cdot 6H_2O$ 0.238 g = 1 mmol	1 : 1
6	L_{IV}, 0.627 g	$CuCl_2 \cdot 2H_2O$ 0.341 g = 2 mmol	1 : 2
7	L_V, 0.627 g	$MnCl_2 \cdot 4H_2O$ 0.395 g = 2 mmol	1 : 2
8	L_V, 0.605 g	$CoCl_2 \cdot 6H_2O$ 0.476 g = 2 mmol	1 : 2

% yield for all complexes (70–75%).

Molar conductivity was performed for 10^{-3} M DMF solution using a JENWAY model 4070 conductance meter.

3. Results and discussion

The formulas of the complexes were suggested on the basis of the analytical data (table 2). The calculated and found values are in good agreement. The number of metal ions present in any one complex was found to depend on the ligand and metal ion forming the complex. The complexes were soluble in DMF, partly soluble in ethanol or methanol but insoluble in benzene.

The molar conductance values of the complexes in DMF (table 2) revealed that complexes **1** and **4** were 1 : 1 electrolytes, complexes **2**, **6**, **7** and **8** existed as 1 : 2 electrolytes, and **3** was a 1 : 4 electrolyte. The conductance values indicated that Cl^- was not involved in coordination with the metal ions. Complex **5** was a non-electrolyte [17], deprived of chloride ions.

3.1. *Thermal analysis*

The TGA curves for some complexes are shown in figure 1, stoichiometric calculations and thermal decomposition patterns are collected in table 3. The results indicate:

(i) The lattice water or ethanol molecules in the complexes were evaporated within the temperature range 70–100°C, while coordinated water molecules were removed at 115–200°C. The number of water or ethanol molecules in the complex was determined from the weight loss on the thermogram. The results are in satisfactory agreement with the data obtained from elemental analysis and dehydration experiments (table 2).

Table 2. Elemental analysis, molar conductance, magnetic moments and ESR $g_{eff.}$ values of solid chelates.

			Microanalysis results[a]										
No.	Complex	Color	%C	%H	%N	%Cl	%M	%H_2O	Λ^b_m	$\mu^c_{eff.}$	$g_\perp$	g_{II}	$g_{eff.}$
1	$[Mn_3H_3L_I(H_2O)_6(OH)_2] \cdot 11H_2OCl$	Brown –	26.6 (26.5)	5.1 (5.2)	12.4 (12.4)	3.1 (2.8)	14.6 (14.8)	28.9 (29.2)	52.12 –	5.01 –	– –	– –	1.9 –
2	$[Cu_3H_4L_I(H_2O)_7] \cdot 13H_2O \cdot 2Cl$	Brown –	24.8 (24.6)	4.6 (4.2)	– –	6.0 (5.4)	15.7 (15.9)	29. 0 (28.6)	91.39 –	1.1 –	1.75 –	1.65 –	1.7 –
3	$[Mn_4L_{II}(H_2O)_8] \cdot 18H_2O \cdot 4Cl$	Brown –	23.7 (23.6)	5.7 (5.5)	10.9 (10.8)	10.0 (9.4)	15.5 (16.0)	30.4 (29.8)	240 –	2.1 –	– –	– –	1.7 –
4	$[Cu_2HL_{II}(H_2O)_6] \cdot 4H_2O \cdot Cl$	Brown –	36.7 (36.1)	5.0 (4.6)	– –	3.9 (4.1)	13.7 (14.2)	19.5 (19.5)	55.16 –	1.05 –	2.04 –	1.94 –	1.99 –
5	$[CoH_3L_{III}(H_2O)_3(OH)] \cdot 18H_2O$	Dark Brown	35.2 (34.8)	6.9 (6.2)	– –	– –	5.7 (6.1)	33.9 (34.2)	7.0 –	3.3 –	2.22 –	2.17 –	2.20 –
6	$[Cu_2L_{IV}(H_2O)_4] \cdot 35H_2O \cdot 2Cl$	Brown –	25.9 (25.4)	6.3 (5.4)	– –	4.8 (5.4)	8.9 (8.59)	48. 4 (48.5)	112.0 –	0.98 –	2.05 –	1.74 –	1.9 –
7	$[Mn_2L_{IV}(H_2O)_4] \cdot 11H_2O \cdot 2Cl$	Brown –	36.8 (36.5)	5.5 (5.3)	10.6 (10.2)	6.8 (7.0)	11.5 (11.5)	25.8 (25.2)	93.5 (25.2)	2.1 –	– –	– –	1.7 –
8	$[Co_2L_V(H_2O)_2(EtOH)_2] \cdot 2Cl$	Brown –	45.8 (45.3)	5.0 (4.8)	– –	8.2 (8.3)	13.6 (14.5)	4. 0 (3.9)	110 –	– –	– 2.08	2.14 –	2.11 –

[a]%C (%F); [b]$Ohm^{-1}cm^2$; [c]B.M/M ion.

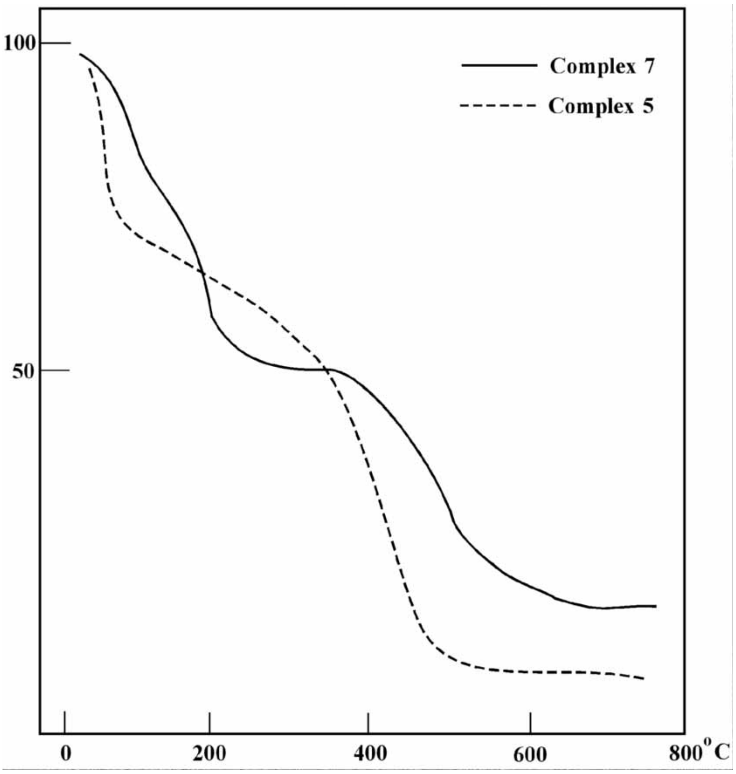


Figure 1. The TGA curves for complex **7** (most stable) and complex **5** (less stable).

(ii) For complexes **1**–**4**, **6**, **7** and **8**, the Cl^- ions were lost within the temperature range 150–250°C. Complexes heated in an oven at 270–300°C were found to be without chloride ions.

(iii) The last step in the decomposition reaction took place at a temperature higher than 400°C, involving combustion of the organic ligand leading to the formation of the metal oxides as the final decomposition product. The metal content was calculated from the weight of the final residue. The results were in agreement with those of chemical analysis.

(iv) The thermal stability of the complexes can be arranged in the following order:

$$\mathbf{7} > \mathbf{2} > \mathbf{1} > \mathbf{4} > \mathbf{3} > \mathbf{6} > \mathbf{8} > \mathbf{5}$$

Thus complex **7** was the most stable while **5** was least stable.

3.2. *Infrared spectra*

On comparing the IR spectra of the solid complexes with those of the corresponding ligands [18], the following can be pointed out:

(i) The spectra of all complexes exhibited intense broad bands at 3200–3500 cm^{-1} due to ν_{OH} of lattice and coordinated water or ethanol molecules. The IR spectra of the

Table 3. Results of thermogravametric analysis (TGA) of metal chelate complexes.

No.	Complex	Temp. °C	% loss in weight %C (% F)	Assignment
1	$[Mn_3H_3L_I(H_2O)_6(OH)_2] \cdot 11H_2OCl$	21–90	16.6 (16.90)	Loss of 11 lattice water molecules.
	$[Mn_3H_3L_I(H_2O)_6(OH)_2]Cl$	97–190	12.1 (12.30)	Loss of 6 coordinated water molecules and 2$^-$OH anions.
	$[Mn_3H_3L_I]Cl$	200	3.1 (2.6)	Loss of HCl molecule.
	$Mn_3H_3L_I$	210–350	–	Thermal stability.
	MnO	355–600	–	Decomposition and formation of MnO.
2	$[Cu_3H_4L_I(H_2O)_7] \cdot 13H_2O \cdot 2Cl$	27–100	18.6 (18.2)	Loss of 13 lattice water molecules.
	$[Cu_3H_4L_I(H_2O)_7]Cl_2$	120–230	10.1 (9.8)	Loss of 7 coordinated water molecules.
	$[Cu_3H_4L_I]Cl_2$	235	5.8 (5.3)	Loss of 2HCl molecules.
	$Cu_3H_4L_I$	240–390	–	Thermal stability.
	CuO	400–610	–	Decomposition and formation of CuO.
3	$[Mn_4L_{II}(H_2O)_8] \cdot 18H_2O \cdot 4Cl$	30–90	21.6 (21.9)	Loss of 18 lattice water molecules.
	$[Mn_4L_{II}(H_2O)_8]Cl_4$	95–125	11.4 (11.6)	Loss of 8 coordinated water molecules.
	$[Mn_4L_{II}]Cl_4$	125–135	10.0 (9.4)	Loss of 4HCl coordinated molecules.
	Mn_4L_{II}	140–280	–	Thermal stability.
	MnO	285–500	–	Decomposition and formation of MnO.
4	$[Cu_2HL_{II}(H_2O)_6] \cdot 4H_2O \cdot Cl$	30–90	7.8 (7.8)	Loss of 4 lattice water molecules.
	$[Cu_2HL_{II}(H_2O)_6]Cl$	100–170	11.7 (11.7)	Loss of 6 coordinated water molecules.
	$[Cu_2HL_{II}]Cl$	180–220	2.5 (2.6)	Loss of HCl molecule.
	Cu_2HL_{II}	230–290	–	Thermal stability.
	CuO	300–555	–	Decomposition and formation of CuO.
5	$[CoH_3L_{III}(H_2O)_3(OH)] \cdot 18H_2O$	25–90	27.7 (27.9)	Loss of 18 lattice water molecules.
	$[CoH_3L_{III}(H_2O)_3(OH)]$	100–180	6.2 (6.2)	Loss of 6 coordinated water molecules and $^-$OH anions.
	CoH_3L_{III}	190–290	–	Thermal stability.
	CoO	300–525	–	Decomposition and formation of CoO.
6	$[Cu_2L_{IV}(H_2O)_4] \cdot 35H_2O \cdot 2Cl$	30–105	43.4 (43.5)	Loss of 35 lattice water molecules.
	$[Cu_2L_{IV}(H_2O)_4]Cl_2$	115–170	5.0 (5.0)	Loss of 4 coordinated water molecules.
	$[Cu_2L_{IV}]Cl_2$	180–200	5.3 (5.6)	Loss of 2HCl molecule.
	Cu_2L_{IV}	210–275	–	Thermal stability.
	CuO	280–625	–	Decomposition and formation of CuO.
7	$[Mn_2L_{IV}(H_2O)_4] \cdot 11H_2O \cdot 2Cl$	25–80	18.9 (18.5)	Loss of 11 lattice water molecules.
	$[Mn_2L_{IV}(H_2O)_4]Cl_2$	90–150	6.9 (6.7)	Loss of 4 coordinated water molecules.
	$[Mn_2L_{IV}]Cl_2$	160–200	7.2 (7.0)	Loss of 2HCl molecule.
	Mn_2L_{IV}	250–390	–	Thermal stability.
	MnO	400–630	–	Decomposition and formation of MnO.
8	$[Co_2L_V(H_2O)_2(EtOH)_2]Cl_2$	100–110	10.6 (11.2)	Loss of 2 coordinated water molecules.
	$[Co_2L_V(EtOH)_2]Cl_2$	110–135	8.9 (8.5)	Loss of 2 coordinated ethane molecules.
	$[Co_2L_V]Cl_2$	140	–	Loss of 2HCl molecules.
	Co_2L_V	145–255	–	Thermal stability.
	CoO	260–620	–	Decomposition and formation of CoO.

dehydrated complexes indicated the disappearance of the OH-bands from the spectra of complexes **3**, **6** and **7** due to displacement of all phenolic protons by metal ions. The IR spectrum for complex **4** showed a shift and decrease in the intensity of the OH-bands (to almost half value), indicating partial removal of protons from the OH-groups.

(ii) The IR spectra of all complexes showed a shift of the –N=N-bands at 1500–1537 cm^{-1} (asym. $\nu_{N=N}$) and 1388–1480 cm^{-1} (sym. $\nu_{N=N}$) to lower wavenumbers by 50–55 cm^{-1} indicating coordination of a nitrogen atom of the azo-group to the metal ion.

(iii) The bands due to $\nu_{C=N}$ in the spectra of ligands L_{III}, L_{IV} and L_V were observed at the same positions in the spectra of the metal complexes **5**, **6**, **7** and **8** showing that the C=N group in these complexes did not participate in complex formation.

(iv) The $\nu_{C=N}$ bands in the spectra of ligands L_I and L_{II} lying at 1667–1657 cm^{-1}, displayed a shift of 20–30 cm^{-1} to lower wavenumbers in the spectra of complexes **1**, **2**, **3** and **4** indicating that the C=N nitrogen atom coordinates to the metal ion in these complexes.

(v) The spectra of all complexes exhibited two new bands at 589–500 cm^{-1} and 389–363 cm^{-1} which can be assigned to ν_{M-O} and ν_{M-N}.

Based on the results of IR spectral investigation of the complexes it can be concluded that the bonding of the ligands to the metal ions in complexes **1**, **2**, **3** and **4** involved the azo and azomethine nitrogens in addition to the OH-groups. For complexes **5, 6**, **7** and **8** the azo groups and the ortho OH-groups were involved in complex formation.

3.3. *Electronic absorption spectra*

The electronic absorption spectra of complex **1** displayed two bands while those of the complexes **2**–**8** exhibited only one broad maximum. The values of λ_{max} in nujol mull and DMF solutions, the corresponding electronic transitions and geometries are collected in table 4. From these results, the following can be pointed out:

(i) For complex **1**, the Mn(II) ion exhibited square-pyramidal geometry while the Mn(III) had octahedral geometry. In the other manganese(II) complexes **3** and **7** the metal ion was tetrahedral.

(ii) Cobalt(II) complex **8** exhibited tetrahedral geometry while complex **5** was octahedral.

(iii) For complex (**2**) the geometry of Cu(II) was square pyramidal, for complex **4** it was octahedral, and for complex **6** it was tetrahedral.

The geometries of the solid complexes can find support from the results of magnetic measurements and ESR spectra as discussed below.

On comparing the results of the electronic absorption spectra as nujol mulls with those in DMF solutions, shifts are observed.

Table 4. The electronic spectral data of metal chelates.

		d–d transitions					
		Nujol mull		DMF			
Complex no.	Ion	λ_{max}	$\nu\,cm^{-1}$	λ_{max}	$\nu\,cm^{-1}$	Assignment	Geometry
1	Mn(III)	540	18480	541	18484	$^6A_{1g} \rightarrow {}^4T_{1g}$	Octahedral
	Mn(II)	560	17725	560	17725	$^6T_{1g} \rightarrow {}^4A_{1g}$	Square pyramid
2	Cu(II)	610	16400	540	18550	$^2E_g \rightarrow {}^2T_{2g}$	Square pyramid
3	Mn(II)	510	19530	535	18690	$^6T_{1g} \rightarrow {}^4T_{1g}$ (G)	Tetrahedral
4	Cu(II)	615	16200	540	18480	$^2T_{2g} \rightarrow {}^2E_g$	Octahedral
5	Co(II)	450	21700	510	19850	$^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$	Octahedral
6	Cu(II)	520	19120	530	18900	$^2B_{2g} \rightarrow {}^2T_{2g}$	Distorted tetrahedral
7	Mn(II)	460	21800	450	22100	$^6T_{1g} \rightarrow {}^4T_{2g}$ (G)	Distorted tetrahedral
8	Co(II)	660	15000	680	14650	$^4A_2 \rightarrow {}^4T_1$ (P)	Tetrahedral

(i) The small shifts obtained with complexes **6** and **8** indicate the geometry are not changed. The shifts in band positions can be explained on the basis of changes in the refractive index of the medium or its dielectric constant on going from the solid state to DMF solution.

(ii) The obvious shifts observed for complexes **2**, **3**, **4** and **8** indicate a change in geometry in DMF solution, originating from coordination of solvent molecules to the metal ion forming octahedral geometry.

3.4. *Magnetic measurements*

Bulk magnetic susceptibilities of solid complexes were determined at room temperature using the Gouy method, from which the corresponding magnetic moments were calculated. The data thus obtained are given in table 2; these results indicated:

(i) The Mn(II) complexes **3** and **7** had μ_{eff} values quite close to that of the spin-only value for one electron revealing low spin Mn(II) in these complexes. For **1**, the observed magnetic moment is lower than the spin only value of d^5 and higher than the d^4 state, consistent with mixed Mn(II) and Mn(III), with some antiferromagnetic interactions. Actually Mn(II) is readily oxidized to Mn(III) in air when allowed to react with N_2O_2 tetradentate Schiff bases [19]. The existence of Mn(III) and Mn(II) in this complex was confirmed by DC polarographic and CV measurements. The DC polarogram at the dropping mercury electrode (DME) (in 0.01 M KCl 50% v/v DMF) showed two waves, in addition to the waves of the ligand. The first is a sine wave with small height compared to the second one with $E_{1/2}$ at -1.7 V. The first wave is due to the reduction of Mn(III) to Mn(II) while the second represents reduction of Mn(II) to the metal. The ratio of wave heights was 1 : 6 indicating the consumption of one electron at the first wave and six electrons at the second:

$$\mathrm{Mn^{3+} + e \rightarrow Mn^{2+}}$$

$$\mathrm{3Mn^{2+} + 6e \rightarrow 3Mn^{0}}$$

(ii) The cyclic voltammogram of complex **1** at hanging mercury drop electrode (HMDE) displayed two peaks for the reduction of the manganese ions, a small peak with $E_P = -0.01$ V and a large broad peak with $E_P = -1.85$ volt. This supports the existence of two oxidation states of manganese in this complex. For complexes **3** and **7** only one peak at more negative potentials was observed indicating that manganese in these complexes is divalent.
The cobalt(II) complexes **5** and **8** had magnetic measurements lower than the spin only values of d^3 system which can be ascribed to some antiferromagnetic interactions between adjacent Co(II) ions [20,21].

(iii) The observed magnetic moments for the Cu(II) complexes **2**, **4** and **6** were much lower than the spin only value of one unpaired electron and indicated strong antiferromagnetic interaction between adjacent Cu(II) ions [20,21].

3.5. *Electron spin resonance spectra*

The X-band ESR spectrum of the solid complexes are represented in figure 2; the g_{eff} values are recorded in table 1. These results indicate:

(i) For complex **1**, the ESR signal is broad, indicating interaction between Mn(II) ions in non-equivalent lattice positions [22,23]. The other manganese complexes **3** and **7**, gave ESR spectra with a sharp signal characteristic of low spin Mn(II). The shape of the ESR spectrum together with the g_{eff} values indicate square-pyramid geometry (for the terminal Mn(II)) for complex **1** and square-planar geometry for complexes **3** and **7**.

(ii) The ESR spectrum of complex **8** showed a broad signal in the low field region (~3000 G), indicating spin-exchange interactions between cobalt(II) ions [24,25]. This metal-metal interaction is attributed to the *quasi*-orthogonality between the S and P orbitals of the ligands and the d-orbital on the cobalt(II) that contains the unpaired spin [26]. The ESR spectra of four-coordinate complex ***8*** shows axial symmetry, *g*-component, ($g\| > g\perp$) with $dx^2 - dy^2$ ground state for species having tetrahedral structures while the spectra of complex **5** had sharp signals, g-components ($g\perp > g\|$) showing axial symmetry with a dz^2 ground state from elongated tetragonal octahedral [27] structures. The ESR pattern and g_{eff} values indicated octahedral geometry for complex **5** and tetrahedral for **8**.

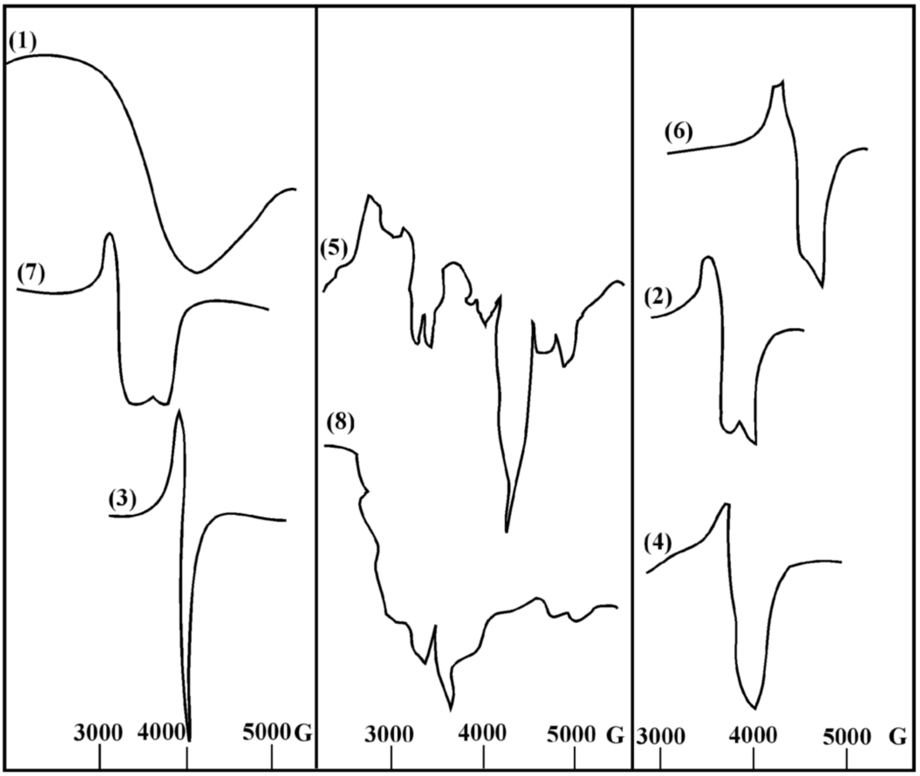


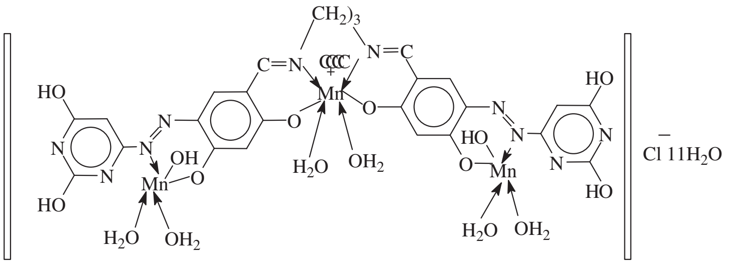
Figure 2. X-band ESR spectra of metal chelates complexes.

The ESR spectra of the Cu(II) complexes display sharp signals characteristic of axial symmetry indicating dipolar interaction between copper(II) ions. According to the Jahn–Teller theorem, tetragonal distortion reduces the symmetry and is expected for all copper(II) complexes under investigation. This results in an anisotropy of the g-tensor; the g_{eff} values for the reported copper(II) complexes are in agreement with an orbitally nondegenerate state [28]. The shape of the signals and g_{eff} values indicate square pyramidal geometry for complex **2**, octahedral for **4** and tetrahedral for **6**.

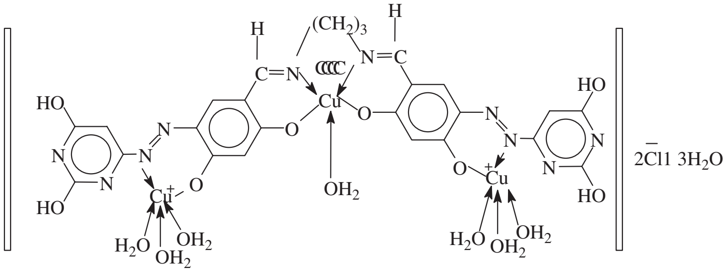
According to Kivelson and Neiman [29], the g_{eff}-values for the complexes indicate considerable mixed ionic–covalent bonding character.

Based on the results of elemental and thermal analyses, the IR, UV/Vis and ESR spectra, magnetic moment determination, and molar conductance measurements, the complexes involved in the present study can be formulated as follows:

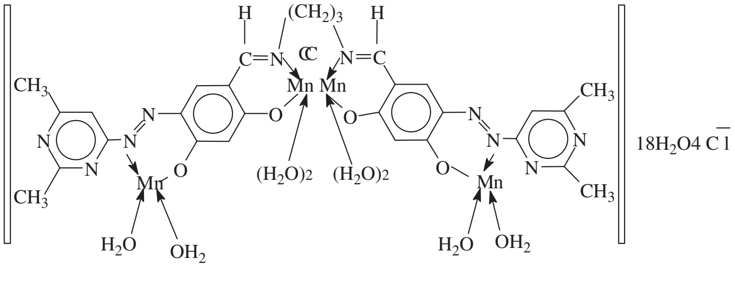
Complex 1



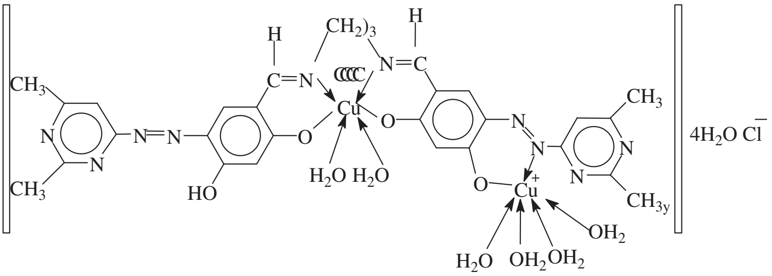
Complex 2:



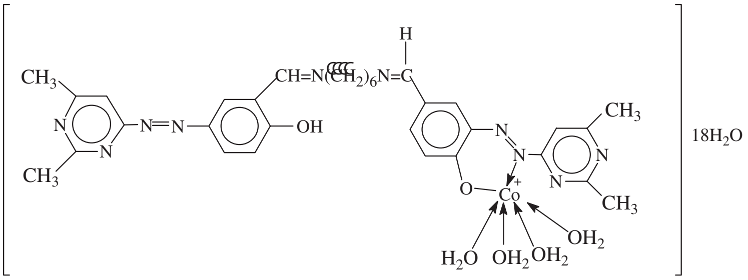
Complex 3:



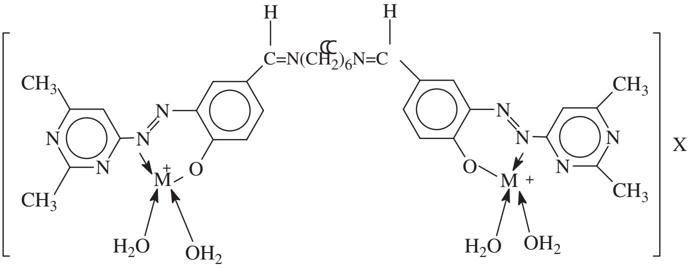
Complex 4:



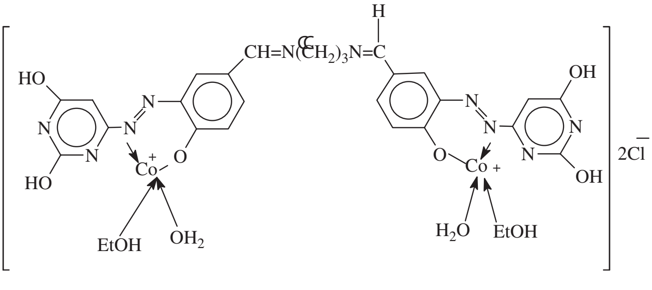
Complex 5:



Complexes 6,7:



For complex (6)	***For complex (7)***
M = Cu	***M = Mn***
X = 35H_2O.2Cl^-	***X = 11H_2O.2Cl^-***



4. Conclusion

Formation of novel mono and homopolynuclear complexes of Mn(II), Co(II) and Cu(II) with the new bisazodianil ligands containing the pyrimidine moiety are reported.

For manganese, the Mn(II) ions retain their valency when the ions are coordinated to the azo centers; manganese ion bonded to the dianil part (azomethine) are oxidized to the trivalent state, a behavior common for such compounds [26,27] . This finds further support from the results of magnetic moment and electrochemical reduction (DC polarography and CV). Manganese(II) complexes **3** and **7** are low spin with square-planar geometry consistent with magnetic moment values UV/Vis and ESR spectra.

Cobalt(II) forms mono and homobinuclear complexes **5** and **8** with octahedral and tetrahedral geometry, respectively. Copper(II) ions formed homo bi-nuclear, complexes **4** and **6**, which have tetrahedral geometry and trinuclear complex **2**, which has square-pyramidal geometry.

In all complexes the chloride ions do not coordinate with the metal ions as indicated by molar conductivity and absence of M-Cl bands in the spectra of all complexes.

Thermal studies of the complexes denoted that the complexes lose their water content in the first decomposition step while the chloride ions are eliminated in the second one. The third step is the decomposition of the complex to the metal oxide, the quantity of metal oxide formed is in agreement with the results of metal content determined by analytical procedures.

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