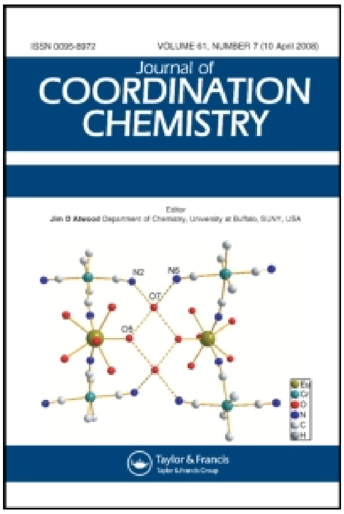

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Hetero-binuclear chelates of Mn(II), Co(II) and Cu(II) *o*-cresolphthalein complexonates with other metal ions

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HETERO-BINUCLEAR CHELATES OF Mn(II), Co(II) AND Cu(II) *o*-CRESOLPHTHALEIN COMPLEXONATES WITH OTHER METAL IONS

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Heterobinuclear metal chelates of Mn^{2+}, Co^{2+} or Cu^{2+} and some transition metal ions with *o*-cresolphthalein complexone have been prepared and characterized. Elemental analyses are in agreement with proposed formulae. Thermal analyses (TGA and DTA) were used to determine the degradation products; some thermodynamic parameters were calculated. IR and UV-Vis spectra identified the mode of bonding between the metal ions and the ligand as well as its geometry. Magnetic moment determination and ESR spectra of the heterobinuclear complex revealed some antiferromagnetic interaction between the metal ions, which depends mainly on the two metal ions forming the chelate. Electrochemical studies of the complexes [DC-polarography and cyclic voltammetry (CV)] confirmed the existence and the nature of the metal ions in the chelate.

Keywords: Mixed metal complexes; *o*-Cresolphthalein complexone; Mn(II), Co(II); Cu(II) complexes

INTRODUCTION

o-Cresolphthalein complexone (*o*-CPC) is known to function as a reagent for the spectrophotometric determination of some metal ions based on its ability to form colored chelates [1–5]. In a previous study, the mononuclear and homobinuclear chelates of Co(II), Ni(II) and Cu(II) with *o*-CPC were characterized in solution and in the solid state [6]. Also, the formation constants of metal complexes with *o*-CPC were determined using pH titration method [7].

It has been stated in some articles [8–10] that heterobinuclear metal complexes exhibit unique physicochemical properties owing to the existence of metal–metal interactions. It was also reported that some heteronuclear complexes of Schiff bases had applications in bioinorganic reactions, catalysis and hydrometallurgy, as well as being a class of metal complexes with obvious metal–metal interactions [11–13].

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The present article reports the preparation of new groups of heterobinuclear *o*-CPC chelates of Mn(II), Co(II) and Cu(II) with some other metal ions. These heterobinuclear chelates have been characterized by elemental and thermal analyses, IR, UV-Vis and ESR spectroscopy, magnetic moment determination, DC-polarography and cyclic voltammetry (CV).

EXPERIMENTAL

The compounds and solvents used were of the highest purity grade available from BDH and Aldrich.

Mononuclear complexes of Mn(II), Co(II) and Cu(II) were prepared as reported earlier [6]. To a solution of *o*-CPC, (0.005 mol in 50 cm^3 ethanol), Mn(II), Co(II) or Cu(II) chloride (0.005 mol) in 50% (v/v) water–ethanol (50 cm^3) was added dropwise with continuous stirring. Both solutions were freed from oxygen by bubbling pure nitrogen for 30 min. The mixture was further stirred for 20 min and then the volume of the reaction mixture was reduced to about 50 cm^3. The heteronuclear complexes were obtained by adding a solution of the second metal chloride [0.005 mol in 50% (v/v) water–ethanol (50 cm^3)] dropwise with continuous stirring to the solution of the mononuclear Mn(II), Co(II) or Cu(II)–*o*-CPC chelate. After mixing was complete, the reaction mixture was further stirred for 20 min and the volume of solvent was reduced to about 25 cm^3. The mixture was allowed to cool to room temperature and the solid heterobinuclear complexes were formed. The solids that separated were filtered off and purified by crystallization from pure ethanol, with precipitation by addition of ether when necessary. The solids obtained were filtered off and dried in vacuum. The purity of the heterobinuclear complexes was confirmed by elemental analyses and thin-layer chromatography (TLC). For TLC experiments, only one symmetrical spot was obtained from each complex, indicating the existence of a single compound. The purified chelates were characterized, using the techniques and apparatus reported previously [14,15].

RESULTS AND DISCUSSION

The results of elemental analyses given in Table I are in good agreement with the formulae. The complexes contain four to eleven water molecules depending on the metal ions present.

Thermal Analysis

Some complexes were subjected to thermal analyses (TGA and DTA). The results obtained are collected in Table II and represented in Fig. 1. The essential features of the solid-state decompositions are: (1) the destruction of the crystal lattice of the complexes, (2) the breaking and redistribution of chemical bonds and (3) the formation of the crystal lattice of the reaction products. In view of these aspects and our experimental observations, a mechanism consistent with the thermal decomposition

TABLE I Elemental analysis and magnetic moment data of the complexes

Complex	*Formula*	*Color*	*Elemental analysis (%)*					μ_{eff} *(BM)*
			C	*H*	*N*	*M_1*	*M_2*	
1	$[MnL(H_2O)_3]\cdot H_2O$	Beige	51.0 (50.5)	4.7 (5.0)	3.5 (3.7)	6.9 (7.2)	–	5.80
2	$[MnVOL(H_2O)_5]\cdot H_2O$	Green	45.3 (44.5)	4.1 (4.6)	3.2 (3.3)	6.6 (6.4)	5.8 (6.0)	–
3	$[MnCoL(H_2O)_4]\cdot 6H_2O$	Purple	42.8 (41.5)	4.7 (5.1)	2.9 (3.0)	6.0 (5.9)	6.2 (6.4)	9.3
4	$[MnNiL(H_2O)_4]\cdot 4H_2O$	Violet	43.0 (43.2)	4.6 (4.9)	2.8 (3.1)	6.6 (6.2)	6.9 (6.16)	4.39
5	$[MnCuL(H_2O)_4]\cdot 4H_2O$	Faint green	42.7 (42.9)	4.4 (4.9)	2.8 (3.1)	5.8 (6.2)	8.0 (7.1)	5.80
6	$[MnUO_2L(H_2O)_4]\cdot 2H_2O$	Purple	35.5 (36.1)	3.5 (3.8)	2.7 (2.6)	5.4 (5.2)	22.1 (22.3)	5.60
7	$[CoL(H_2O)]\cdot 3H_2O$	Bluish green	52.4 (52.6)	4.8 (4.8)	3.8 (3.9)	7.6 (8.1)	–	4.14
8	$[CoVOL(H_2O)_3]\cdot 3H_2O$	Dark violet	41.9 (42.5)	4.8 (4.9)	2.9 (3.1)	6.8 (5.6)	5.8 (6.5)	–
9	$[CoNiL(H_2O)_2]\cdot 8H_2O$	Dark purple	41.0 (41.3)	5.5 (5.3)	2.8 (3.0)	6.0 (6.35)	6.1 (6.24)	–
10	$[CoCuL(H_2O)_2]\cdot 9H_2O$	Dark violet	40.0 (40.35)	5.20 (5.6)	2.7 (2.95)	6.0 (6.2)	6.5 (6.7)	4.8
11	$[CoMoOL(H_2O)_2]\cdot 4H_2O$	Bluish green	42.8 (43.0)	5.0 (4.4)	3.2 (3.1)	6.3 (6.6)	10.0 (10.7)	–
12	$[CoUO_2L(H_2O)_2]\cdot 2H_2O$	Red orange	38.0 (37.8)	3.8 (3.4)	3.0 (2.8)	6.4 (5.8)	22.9 (23.5)	4.0
13	$[CuL(H_2O)]\cdot 3H_2O$	Pale green	53.2 (53.6)	4.3 (4.5)	3.9 (3.9)	8.6 (8.9)	–	1.74
14	$[CuVO(H_2O)_3]\cdot 4H_2O$	Deep grey	43.1 (43.2)	4.2 (4.7)	3.0 (3.15)	6.9 (7.2)	6.1 (5.7)	2.4
15	$[CuNiL(H_2O)_2]\cdot 5H_2O$	Dark purple	44.0 (44.6)	4.4 (4.6)	3.4 (3.3)	6.9 (7.4)	6.8 (6.7)	–
16	$[CuMoOL(H_2O)_2]\cdot 4H_2O$	Dark green	41.9 (42.8)	4.4 (4.3)	3.3 (3.1)	10.46 (10.7)	6.92 (7.1)	4.60
17	$[CuUO_2L(H_2O)_2]\cdot 4H_2O$	Grey green	35.8 (35.8)	3.4 (3.7)	2.3 (2.6)	5.7 (5.9)	21.8 (22.2)	1.70

TABLE II Results of thermal (TG and DT) analyses of some complexes

Complex	*TGA*				*DTA*					
	Step	*Temp range (°C)*	*Wt. loss (%)*[a]	*Part removal*[b]	*Peak*	*T(K)*	ΔH^{d}	ΔG^{d}	ΔS^{d}	*Log* $K \times 10^{4}$
3	a	30–70	3.6(3.88)	$H_2O(l)$	1	369	−5.52	−1.143	−0.018	1.62
	b	125–179	15.8(16.18)	$H_2O(c)$	2	457	7.71	−1.091	−0.018	1.25
	c	190–323	38.54(37.80)		3	522	2.10	−0.096	−0.0042	0.096
	d	327–710	16.25(15.09)		4	811	16.40	−3.26	−0.016	2.10
9	a	17–103	19.83(19.35)	$H_2O(l+c)$						
	b	206	7.77(8.0)							
	c	457	26.1(25.94)							
10	a	30–133	20.2(20.79)	$H_2O(l)$ +	1	376	−4.07	0.45	0.012	0.627
	b	208	13.04(13.78)	$H_2O(c)$	2	463	6.65	−0.82	−0.016	0.917
	c	291	20.64(20.06)		3	522	3.52	−0.240	−0.0072	0.24
	d	675	17.61(17.30)		4	628	2.93	−0.252	−0.0051	0.211
14					5	790	8.29	−1.432	−0.0132	0.95
	a	30–104	9.01(9.02)	$H_2O(l)$ +	1	456	23.45	−21.798	0.0992	25.0
	b	150	30.56(30.13)	$H_2O(c)$	2	249	2.51	−0.095	0.005	0.095
	c	277	33.78(33.65)		3	617	1.05	−0.125	0.0019	0.165
	d	799			4	552	6.27	−0.857	−0.0086	0.54
					5	734	−3.48	0.25	0.0037	0.13
15	a	30–70	12.55(12.27)							
	b	168	7.56(7.73)							
	c	432	44.7(43.08)							
	d	513	23.85(21.7)							
16					1	48	5.73	−0.96	−0.015	0.000
					2	263	−6.70	1.045	0.014	0.000
					3	344	4.27	−0.571	−0.008	0.005
					4	391	−1.92	0.216	0.003	0.002
					5	621	−11.22	1.523	0.014	0.005
					6	735	−1.48	0.147	0.002	0.007

[a]Found (calcd.). [b]*l* = lattice; *c* = coordinated. [c]kJ mol^{-1}. [d]kJ/mol.

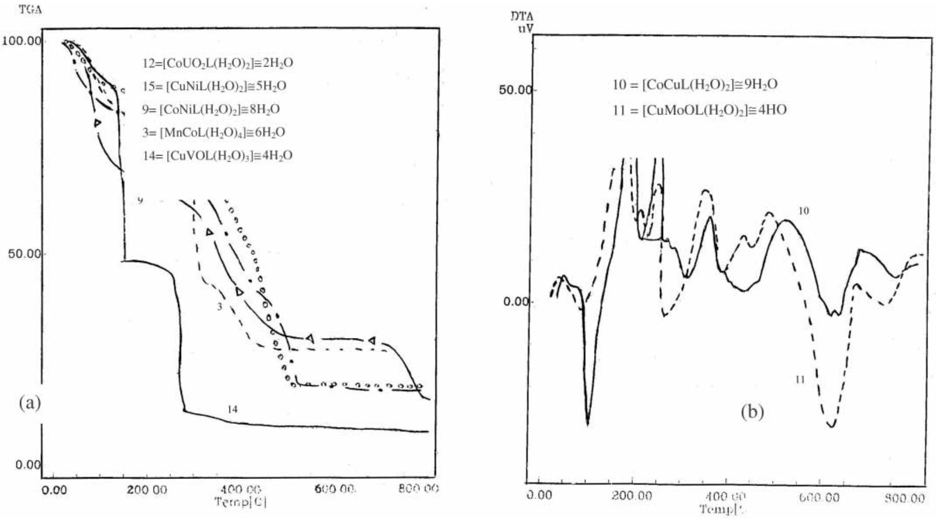
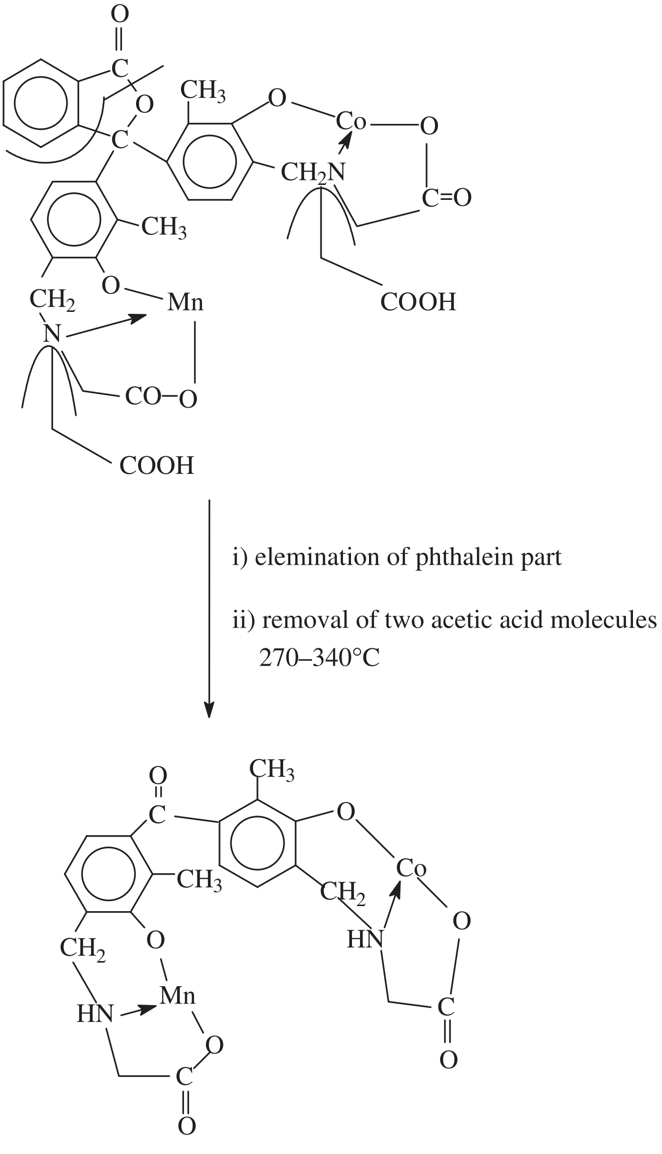


FIGURE 1 TGA (a) and TDA (b) results for some heterobinuclear *o*-CPC complexes.

can be suggested. It involves the following stages:
The first stage: elimination of water molecules associated with complex formation i.e. dehydration of the complex:

$$[\mathrm{MnCoL(H_2O)_8}]\cdot 2\mathrm{H_2O}\xrightarrow[\substack{-2\mathrm{H_2O}\\ \text{lattice water}}]{30-70^\circ\mathrm{C}} > [\mathrm{MnCoL(H_2O)_8}]\xrightarrow[\substack{-8\mathrm{H_2O}\\ \text{coordinated water}}]{125-179^\circ\mathrm{C}} > [\mathrm{MnCoL}]$$

In Complex **9**, [CoNiL $\cdot$ 10H_2O], only one dehydration step was observed but in Complexes **3**, **10**, **14** and **15** water of crystallization and coordinated water molecules were lost separately.



i) elemination of phthalein part

ii) removal of two acetic acid molecules
270–340°C

The anhydrous complexes showed thermal stability up to 180–370°C, after which they lost a part of the organic ligand as follows:
This second stage may take place in a single step as for Complexes **3** and **14** or, as in the case of Complexes **9** and **10**, may involve two steps.

The final stage is the decomposition of the rest of the organic molecule with formation of mixed metal trioxalates as the final products. These are thermally stable up to 800°C.

The DTA curves show two endothermic peaks for dehydration of the complexes and two exothermic peaks for decomposition of the anhydrous heterobinuclear complexes. The activation energy (E_a) for each step was estimated from the DTA curves according to the literature method [16]. The E_a values were used to calculate some thermodynamic parameters of the thermal decomposition reaction.

The following conclusions can be drawn about the degradation of the complexes from the thermal analyses:

(1) The mechanism and the thermodynamic parameters (ΔH, ΔG, ΔS and log K) cited in Table II show that the decomposition stages are affected by the nature or type of metal ions in the mixed-metal complexes.
(2) Negative values for the entropy of activation observed for the dehydration step can be attributed to the formation of more ordered anhydrous complexes.
(3) Activation-energy values and the maximum temperature of the decomposition of the mixed complexes indicated the following order of the stabilities of the mixed Complexes: **9** > **15** > **16** > **3** > **10** > **14**.

IR Spectra

The IR spectra of the heterobinuclear metal complexes of *o*-CPC (Table III) display strong broad bands within the range 3500–3300 cm^{-1} with maxima within the range

TABLE III Spectral data for the complexes

Complex	*IR – Spectra (ν,cm^{-1})*							*Electronic Spectrum λ_{max} (nm)*	*ESR g_{eff}*
	ν_{OH}	$\nu_{C=O}$	$\nu_{C=O}$	$\nu_{C=O}$	γ_{H_2O}	ν_{M-O}	ν_{M-N}		
L	3430, 3250	1750	1660	1640					
1	3400	1700	1610	1585	805	480	375	390, 590	1.9513
2	3400	1730	1620	1600	810	480	370		1.9875
3	3390	1740	1620	1600	805	475	370	335, 390, 520	2.0053
4	3400	1710	1610	1590	805	475	375		2.0053
5	3400	1700	1600	1590	805	470	380		
6	3390	1700	1600	1585	805	465	380	340, 390, 510	
7	3400, 3200	1745	1660	1590	805	465	370	570	
8	3390	1700	1610	1590	810	470	370		
9	3390	1700	1620	1600	810	475	375	310, 375, 560	
10	3400	1700	1600	1585	805	470	380	325, 380	2.0683
11	3400	1710	1610	1600	805	470	375	350, 415, 560	
12	3410	1700	1610	1600	810	480	385	348, 400, 560	
13	3370	1710	1610	1585	810	480	375	385, 585	2.1413
14	3380	1710	1620	1600	810	475	370	340, 380, 520	2.0269
15	3390	1700	1610	1590	810	465	380	340, 400, 520	2.0207
16	3390	1730	1610	1600	805	465	385	310, 415, 560	
17	3360	1710	1610	1590	805	460	375		2.068 (b)

b: broad.

3410–3360 cm^{-1}. The presence of the γ_{H_2O} band at 810–805 cm^{-1} confirms the presence of coordinated water molecules.

Comparison of the spectra of the metal complexes with that of the free ligand reveals the following:

(1) The δ_{OH} bands of the phenolic groups at 1220 cm^{-1} in the spectra of the ligand disappear in the spectra of the complexes, denoting displacement of the phenolic protons by the metal ions on complex formation.

(2) The $\nu_{C=O}$ bands at 1750, 1660 and 1640 cm^{-1} for the free ligand change to a group of bands at 1740–1700, 1620–1600 and 1600–1585 cm^{-1}. This change results from the contribution of some acetate carboxyl groups to complexation through proton displacement by the metal ion.

(3) The ν_{C-N} band at 1310 cm^{-1} in the spectrum of *o*-CPC is shifted to lower wavenumbers, indicating coordination of the amine nitrogen atom to the metal ion. This bonding is essential for complex formation since it leads to two stable six- and five-membered rings.

(4) The spectra of all complexes exhibit two new bands at 480–460 and 385–370 cm^{-1}, which can be ascribed to the stretching mode of the M–O and M–N bonds formed on complexation of the metal ions with *o*-CPC. There is a new band situated at 980–930 cm^{-1} which can be ascribed to $\nu_{M=O}$ in Complexes **2**, **6**, **8**, **11**, **12**, **14** and **16**.

UV/Vis Absorption Spectra

The electronic absorption spectra of the heterobinuclear metal-(*o*-CPC) complexes correspond to an overlap of the spectra of the individual 1:1 metal ion-(*o*-CPC) complexes with some slight shifts in their positions, Fig. 2. This behavior can be taken as evidence that the metal ions in the mixed metal ion complexes retain the same geometry as in the 1:1 metal complexes. Accordingly, the geometry of the

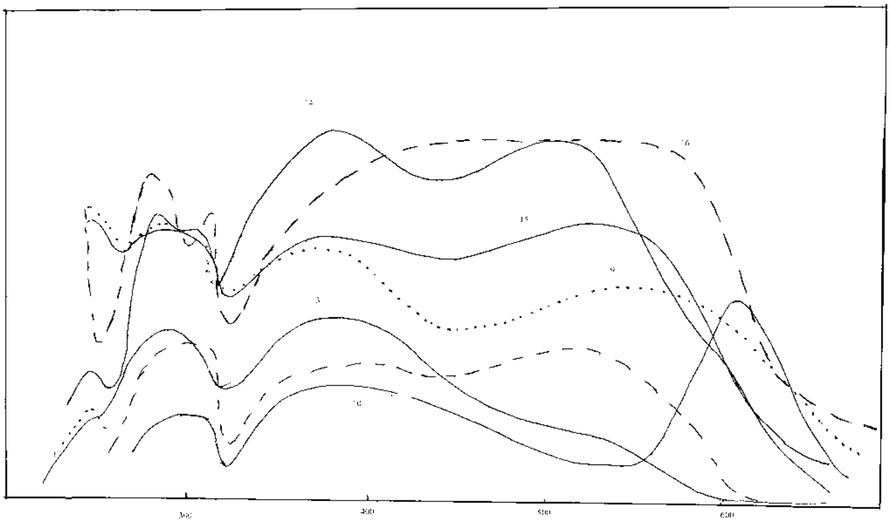


FIGURE 2 Electronic absorption spectra of heterobinuclear complexes with *o*-CPC.

metal ions in the heterobinuclear complexes can be given as follows: VO^{2+}, MoO, UO_2 and Mn^{2+} (octahedral), Co^{2+}, Ni^{2+}, Cu^{2+} (tetragonal).

Magnetic Measurements

The magnetic moment values for Complexes **1**, **3**, **7**, **10**, **12**–**14**, **16** and **17** of the heterobinuclear complexes under study are collected in Table I. The values obtained are obviously lower than the additive magnetic moments of the individual 1:1 complexes. The lowering of the values is larger when the two metal ions are paramagnetic. The lowering of the magnetic moment values reflect antiferromagnetic interactions between the two metal ions [17,18]. The small effect of the $UO_2{}^{2+}$ ion on the magnetic moment denotes a low antiferromagnetic interaction with this ion. This can be ascribed to the absence of d or f electrons from the uranyl ion.

ESR Spectra

X-band ESR spectra of the powdered heterobinuclear complexes of *o*-CPC measured at room temperature are shown in Fig. 3. The *g*-values are listed in Table III. Comparison of the ESR spectra of the heterobinuclear complexes with those of mononuclear complexes of *o*-CPC shows the following features:

(1) Six isotropic signals are observed for Complex **1** (mononuclear Mn(II) complex), but on formation of the heterobinuclear complexes we notice the following:
   (a) For complexes **4** and **6**, the number of signals is not affected whether there is a Ni(II) or a $UO_2{}^{+}$ ion; although the pattern and the shape of signals in complexes **4** and **6** still have the same characteristics as the ESR signal of Mn(II) there is an obvious change in the g_{eff} values for the heterobinuclear complexes.
   (b) The number of ESR signals for Complexes **2** and **3** (15–16 signals) depends on the nature and the type of the second metal ion present (Co^{2+} or VO^{2+}). The pattern and shape of each metal ion in the heterobinuclear complexes still have the same characteristics (Mn, Co) or (Mn, VO) as in the individual mononuclear complexes, but a number of signals overlap with an obvious change in the g_{eff} values for the heterobinuclear complexes.

(2) For mononuclear $CuL \cdot 4H_2O$ (Complex **13**), three anisotropic signals are observed but in its heterobinuclear complexes, (**10**, **14**, **15** and **16**) the number of signals increases and their positions are affected by the presence of metal–metal interactions. The pattern and the shape of the signals are the same and have the same characteristics of paramagnetic ions Mn^{2+}, Co^{2+}, Ni^{2+} or VO^{2+} as the individual mononuclear complexes. Complex **15** exhibits 13 line signals, corresponding to a complete change of the ESR spectra of the individual ions Cu^{2+} (d^9 ESR active) or Ni^{2+} (d^8 ESR silent). The appearance of 13 lines suggests that the antiferromagnetic interaction taking place between (Cu^{2+} d^9 and Ni^{2+} d^8) leads to an obvious change of the ESR spectra of heterobinuclear Complex **15**, although for Complex **17**, the number of signals is not affected by the second metal ion (UO^{2+}) because UO^{2+} is diamagnetic. The shape and number of ESR signals and the g_{eff} values are affected by the presence of the second metal ion whether paramagnetic or diamagnetic.

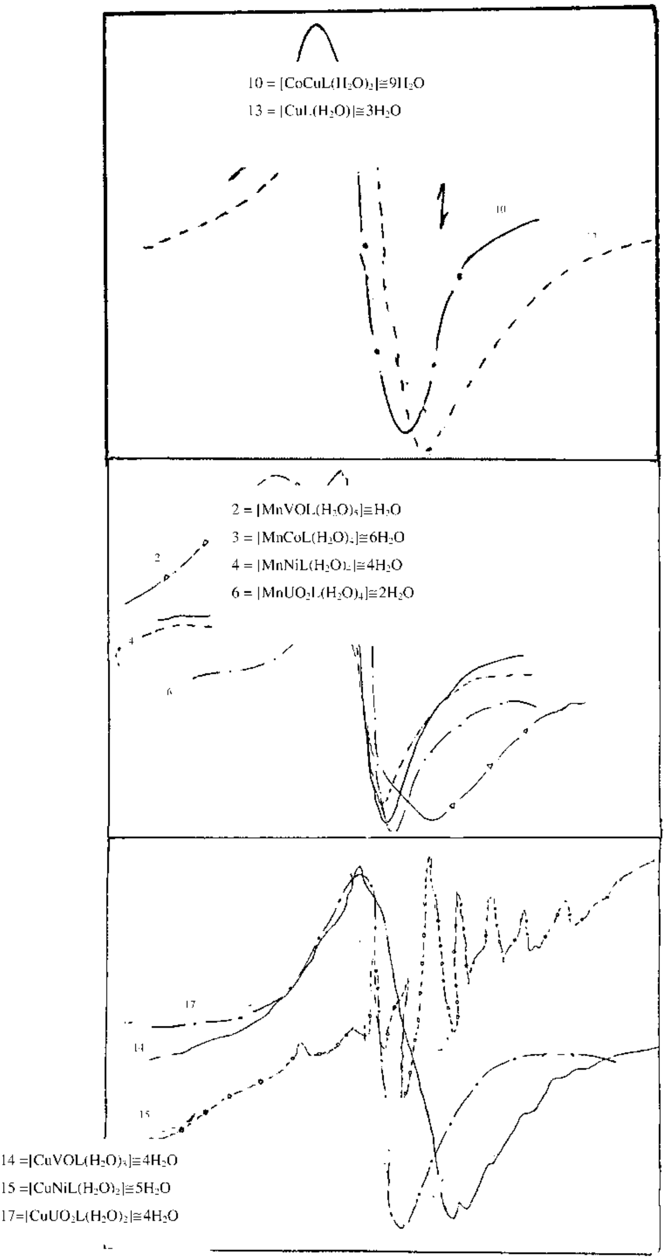
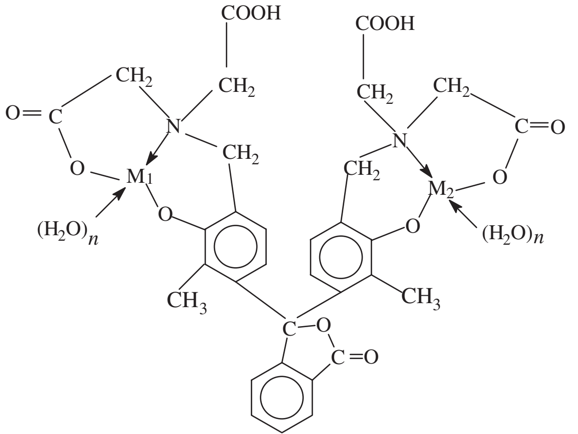


FIGURE 3 X-band ESR spectra of some heterobinuclear *o*-CPC complexes.

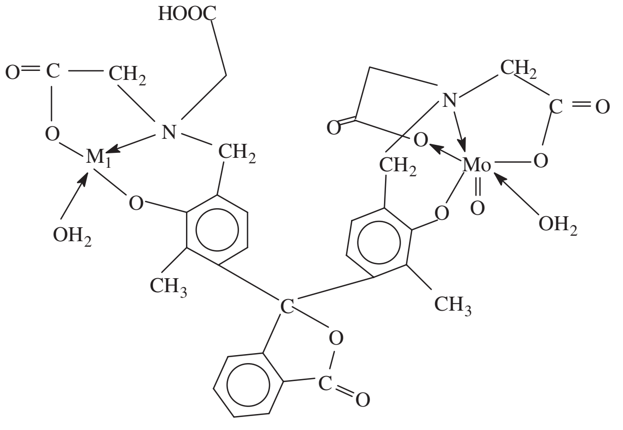
(3) The g_{eff} values of Complexes **5**, **10**, **13**, **14**, **15** and **17** are more positive than the value for the free electron, $g = 2.0023$. This may be ascribed to covalent bonding between *o*-CPC and the two metal ions forming the heterobinuclear complex. The g_{eff} values of the other mixed metal complexes are more negative than the value for the free electron, indicating a decrease in the covalent nature of the bond between *o*-CPC and the two metal ions.

Based on the above results of analytical and thermal analyses, IR, visible and ESR spectra as well as magnetic susceptibilities of the heterobinuclear complexes, the following structures are suggested for the complexes:



$M_1 = Mn^{2+}(H_2O)$
$Co^{2+}(H_2O)$
$Cu^{2+}(H_2O)$

$M_2 = VO^{2+}(H_2O)_2$
$Co^{2+}(H_2O)$
$Ni^{2+}(H_2O)$
$Cu^{2+}(H_2O)$
$UO_2^{2+}(H_2O)$



$MoO(H_2O)$

Complex **11** or **16**

Electrochemical Studies

The electroreduction of five complexes (**3**, **4**, **5**, **9** and **15**) in 0.1 M KCl containing 20% (v/v) DMF was studied by DC polarography. The $E_{1/2}$ values are listed in Table IV. The polarographs of each complex showed two cathodic waves corresponding to reduction of the two metal ions involved. The $E_{1/2}$ values are observed at more

TABLE IV Electrochemical reduction data

Complex	$E_{1/2}{}^{a}(V)$	$E_P\ (V)$			*Metal ion*	*v*	E_P	$I_P(V)$
		(1)	*(2)*	*(3)*				
3	−1.23	1.17	1.19	1.20	Mn^{2+}	200	1.08	2.4
	−0.91	1.04	1.06	1.08	Co^{2+}	100	1.06	1.14
						50	1.04	0.64
						20	1.02	0.4
4	−1.52	1.41	1.44	1.46	Mn^{2+}			
	−1.04	0.90	0.92	0.94	Ni^{2+}			
5	−1.31	1.11	1.14	1.16	Mn^{2+}			
	−0.23	0.32	0.34	0.36	Cu^{2+}			
9	−1.25	1.2	1.22	1.24	Co^{2+}			
	−1.05	0.90	0.91	0.92	Ni^{2+}			
15	−1.05	0.95	0.97	0.99	Ni^{2+}			
	−0.21	0.31	0.34	0.35	Cu^{2+}			
						200	1.16	0.6
						100	1.14	0.36
						50	1.11	0.28

[a]Measured relative to SCE. [b]Measured relative to SCE. Three separate results are shown for each complex.

negative values than the potentials of the free metal ions. Analysis of the waves showed that the reactions proceed irreversibly and involve the uptake of two electrons per metal ion in the complex. The existence of the two waves is a good indication of two metal ions in the complexes. The electrode reaction was found to be governed mainly by diffusion, with some contribution from adsorption.

The cyclic voltammetric studies using an HMDE (hanging mercury drop electrode) showed two cathodic peaks for each complex; however, no anodic peaks were observed except for copper. For copper the anodic wave occurs at more positive potentials than the cathodic peak. The results indicate that the electrode reaction is irreversible. The irreversible nature of the reduction reaction is further supported by the shift of the peak potential to more negative values with increasing scan rate. The plot of E_p *vs.* $\sqrt{v}$ is a linear relationship indicating that the reduction process is mainly controlled by diffusion.

The appearance of the anodic peak for the complex containing Cu^{2+} can be attributed to the formation of Cu/Hg amalgam on reduction of Complex **15**, the copper amalgam readily undergoing anodic dissolution of Cu from the drop surface.

The CV results are in good agreement with those of DC polarography, supporting the existence of the two metal ions in the heterobinuclear complexes of *o*-CPC.

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