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MONONUCLEAR AND HOMOBINUCLEAR VANADIUM(IV), CHROMIUM(III), MOLYBDENUM(III), AND URANIUM(VI) CHELATES WITH *ORTHO*-CRESOLPHTHALEIN COMPLEXONE

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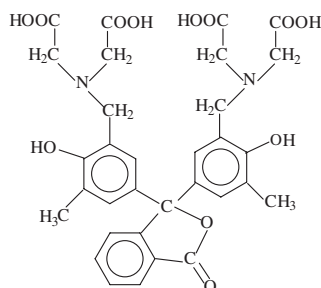
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Mononuclear and homobinuclear *o*-cresolphthalein complexone complexes with VO²⁺, Cr³⁺, MoO⁺, and UO₂²⁺ have been prepared and their structures investigated. The empirical formulas, the mode of bonding, and the geometry of the complexes were obtained from elemental and thermal analyses, IR, electronic and ESR spectra, magnetic moment determinations, DC and CV polarographic studies.

Keywords: Mononuclear complexes; Homobinuclear complexes; *o*-Cresolphthalein complexonates; Chelates of VO²⁺, Cr³⁺, MoO⁺, and UO₂²⁺

INTRODUCTION

o-Cresolphthalein complexone (*o*-CPC) [trade name phthalein purple] (Scheme 1) is a good chromogenic reagent for spectrophotometric determination of a number of metal ions [1–5].



SCHEME 1. Structure of the ligand (*o*-CPL or H₆L).

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In a previous investigation we studied the reaction of *o*-CPC with Co^{2+} , Ni^{2+} , and Cu^{2+} ions in solution. Solid mononuclear and binuclear complexes were prepared and characterized [6]. The acid–base properties of (*o*-CPC) and its reaction with some metal ions were also studied by potentiometric titration [7].

No detailed study of complexes of *o*-cresolphthalein complexone with other transition metal ions has been carried out. Accordingly, we have extended our studies of *o*-CPC to complexes of vanadyl, chromic, molybdenum, and uranyl ions.

Bi- or polynuclear complexes of these metal ions have important roles in biochemical reactions. Emocyanine enzyme contains a binuclear copper(II) complex considered to be the active site for oxygen activation [8]. Metal complexes containing two or more metal ions per molecule find wide applications in catalysis and materials science [9–11]. Such complexes can also display peculiar spectroscopic and magnetic properties [12–14].

The present study investigates mono- and homobinuclear complexes of vanadium(IV), chromium(III), molybdenum(III), and uranium(VI) with (*o*-CPC). Solid complexes were prepared and characterized by elemental and thermal analyses, IR, UV–Vis and ESR spectra, magnetic moment determinations, polarographic and cyclic voltammetry measurements.

EXPERIMENTAL

All chemicals were of the purest grade available from BDH and Aldrich, or fine pure chemicals.

Preparation of the Solid Complexes

For vanadium(IV) and molybdenum(III) complexes, where the ions are susceptible to oxidation, the solutions of *o*-CPC (5 mmol in 50 cm³ ethanol) and metal ion [5 mmol in 50 cm³ water–ethanol mixture (50% v/v) for mononuclear complexes and 12 mmol in 100 cm³ water–ethanol mixture (50% v/v) for homobinuclear complexes] were freed from oxygen by bubbling pure nitrogen for 30 min and then mixed by dropwise addition. The reaction mixture was stirred for about 30 min, and the volume was reduced to about 25 cm³ by evaporation. The solid complexes thus separated were filtered off, purified by dissolution in ethanol and reprecipitated by addition of ether. The purified solids were filtered off and dried *in vacuo*.

For the preparation of the chromium(III) and uranium(VI) complexes, the same procedure was followed but without bubbling nitrogen through the solutions since these ions do not undergo air oxidation.

The pure metal complexes were characterized by elemental analysis (carried out at the Microanalytical Unit Laboratory, Cairo University, Cairo, Egypt), thermal analysis (TGA and DTA), and IR, UV–Vis, and ESR spectroscopy. The magnetic moments of the paramagnetic complexes were also determined.

The methods of investigation and apparatus used were as described in the literature [15–18].

A pen recording polarograph model 4001 SARGENT-WELCH was used for studying the polarographic behavior of the complexes under investigation. A cell described by Meites [19] was used for the polarographic studies with a dropping mercury elec-

trode (DME) ($m = 1.03 \text{ mg s}^{-1}$, $t = 3.3 \text{ s}$ at mercury height $h = 60 \text{ cm}$) and a saturated calomel electrode (SCE) as a reference electrode, supplied by SARGENT-WELCH.

Cyclic voltammograms of the complexes were recorded using a potentiostat Model 264 A (from EG&G). The 303 A electrode assembly was supplied by EG&G, with a hanging mercury drop electrode (area = $2.6 \times 10^{-2} \text{ cm}^2$) as a working electrode, Pt wire as a counter electrode and (Ag/AgCl/KCl₃) as a reference electrode.

RESULTS AND DISCUSSION

Elemental Analysis

The elemental analyses (Table I) agree with calculated values for the suggested formulas. The recommended methods of analysis [20] were used for determination of the metal content of the complexes. The complexes contained varied numbers of water molecules depending on the nature and number of metal ions in the complex.

Thermal Analysis

Mononuclear and homobinuclear Cr(III) and UO₂(II) complexes were subjected to TGA and DTA. The data obtained are collected in Tables II–IV.

The TGA curves indicate loss of waters of crystallization within the temperature range 70–120°C while the coordinated water molecules were eliminated within the temperature range 100–180°C but the two steps interacted. Mono- and homobinuclear Cr³⁺ complexes showed a decrease in weight of 4.00 and 7.00% respectively, corresponding to loss of one and two chloride ions within the temperature range 240–390°C.

TABLE I Elemental analysis, magnetic moment measurements and ESR spectra of the complexes

Complex No.	Empirical formula	Color (Formula wt.)	Found (calcd.) (%)				μ_{eff}^a	g_{eff}^a
			C	H	N	M		
1	[VO(H ₄ L)(H ₂ O) ₂] · 3(H ₂ O) [C ₃₂ H ₄₀ N ₂ O ₁₈ V]	Purple (791.62)	48.9 (48.6)	5.3 (5.1)	3.2 (3.5)	5.9 (6.4)	1.75	1.9896
2	[(VO) ₂ (H ₂ L)(H ₂ O) ₄] · 11(H ₂ O) [C ₃₂ H ₅₈ N ₂ O ₂₉ V ₂]	Purple (1036.71)	36.9 (37.1)	5.1 (5.6)	2.5 (2.7)	9.9 (9.8)	1.60	2.0000
3	[Cr(H ₄ L)Cl(H ₂ O) ₂] · 7(H ₂ O) [C ₃₂ H ₄₈ ClCrN ₂ O ₂₁]	Green (883.59)	43.2 (43.5)	5.4 (5.5)	3.3 (3.2)	5.8 (5.9)	3.28	1.6672
4	[Cr ₂ (H ₂ L)Cl ₂ (H ₂ O) ₄] · 3(H ₂ O) [C ₃₂ H ₄₂ Cl ₂ Cr ₂ N ₂ O ₁₉]	Green (933.60)	40.9 (41.2)	4.7 (4.5)	3.2 (3.0)	11.3 (11.1)	6.45	1.7382
5	[Mo(H ₄ L)(H ₂ O)] · 2(H ₂ O) [C ₃₂ H ₃₆ MoN ₂ O ₁₅]	Green (784.59)	48.8 (49.0)	4.3 (4.6)	3.3 (3.6)	11.8 (12.2)	3.70	1.9893
6	[Mo ₂ (H ₂ L)(H ₂ O) ₂] · 4(H ₂ O) [C ₃₂ H ₄₀ Mo ₂ N ₂ O ₁₈]	Dark green (932.58)	41.6 (41.2)	3.8 (4.3)	2.7 (3.0)	20.8 (20.6)	3.40	1.9735
7	[UO ₂ (H ₄ L)(H ₂ O)] · 1.5(H ₂ O) [C ₃₂ H ₃₅ N ₂ O _{16.5} U]	Orange (933.67)	40.3 (40.5)	3.5 (3.7)	2.8 (3.0)	25.0 (25.1)	d	d
8	[(UO ₂) ₂ (H ₂ L)(H ₂ O) ₂] · 2(H ₂ O) [C ₃₂ H ₃₆ N ₂ O ₂₀ U ₂]	Red orange (1244.72)	30.4 (30.9)	3.0 (2.9)	2.5 (2.3)	38.0 (38.3)	d	d

All the synthesized complexes decompose without melting above 300°C.

The reaction yield was 70–75%.

^ad = Diamagnetic.

TABLE II Thermogravimetric analyses of some complexes

Complex No.	Complex Mol. Wt.	Process	Temperature range ($^{\circ}\text{C}$)	Product	Mass (% loss)	
					Found	Calcd.
3	$[(\text{H}_4\text{L})\text{Cr}(\text{H}_2\text{O})_2\text{Cl}] \cdot 7\text{H}_2\text{O}$ (883.59)	Loss of water of hydration	30–120	$7\text{H}_2\text{O}$	14.00	14.27
	$[(\text{H}_4\text{L})\text{Cr}(\text{H}_2\text{O})_2\text{Cl}]$ (757.48)	Loss of coordinated water	120–180	$2\text{H}_2\text{O}$	3.50	4.08
	$[(\text{H}_4\text{L})\text{CrCl}]$ (721.45)	Loss of chloride ion	180–240	HCl	4.00	4.01
	$[(\text{H}_4\text{L})\text{Cr}]$ (686.00)	Loss of amine part and two methyl groups	240–480	Amine part, $2\text{CH}_4, \text{H}_2\text{O}$	20.40	19.92
Degradation of the whole molecule and formation of chromium oxalate as final product ($480\text{--}760^{\circ}\text{C}$)						
4	$(\text{H}_2\text{L})\text{Cr}_2(\text{H}_2\text{O})_4\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (933.60)	Loss of water of hydration	30–70	$3\text{H}_2\text{O}$	6.00	5.79
	$[(\text{H}_2\text{L})\text{Cr}_2(\text{H}_2\text{O})_4\text{Cl}_2]$ (879.56)	Loss of coordinated water	70–170	$4\text{H}_2\text{O}$	7.50	7.72
	$[(\text{H}_2\text{L})\text{Cr}_2\text{Cl}_2]$ (807.50)	Loss of chloride ions	170–390	2HCl	7.00	7.59
	$[(\text{H}_2\text{L})\text{Cr}_2]$ (736.59)	Loss of phthalein part and two acetate groups	390–610	Phthalein part, $2\text{CH}_3\text{COOH}$	26.50	26.78
Degradation of the whole molecule and formation of chromium oxalate as final product ($610\text{--}640^{\circ}\text{C}$)						
7	$(\text{H}_4\text{L})(\text{UO}_2)(\text{H}_2\text{O}) \cdot 1.5\text{H}_2\text{O}$ (950.01)	Loss of water of hydration	30–70	$1.5\text{H}_2\text{O}$	2.98	2.84
	$[(\text{H}_4\text{L})(\text{UO}_2)(\text{H}_2\text{O})]$ (922.99)	Loss of coordinated water	70–115	H_2O	1.92	1.90
	$[(\text{H}_4\text{L})(\text{UO}_2)]$ (904.97)	Loss of amine part and two methyl groups	115–340	Amine part, $2\text{CH}_4, \text{H}_2\text{O}$	18.97	18.53
Degradation of the whole molecule and formation of uranium oxalate as final product ($340\text{--}480^{\circ}\text{C}$)						
8	$(\text{H}_2\text{L})(\text{UO}_2)_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (1244.72)	Loss of water of hydration	30–70	$2\text{H}_2\text{O}$	3.00	2.90
	$[(\text{H}_2\text{L})(\text{UO}_2)_2(\text{H}_2\text{O})_2]$ (1208.69)	Loss of coordinated water	70–100	$2\text{H}_2\text{O}$	3.00	2.90
	$[(\text{H}_2\text{L})(\text{UO}_2)_2]$ (1172.66)	Loss of phthalein part and two acetate groups	100–440	Phthalein part, $2\text{CH}_3\text{COOH}$	21.10	21.21
Degradation of the whole molecule and formation of uranium oxalate as final product ($446\text{--}550^{\circ}\text{C}$)						

Formation of metal oxalates as final product was confirmed by IR spectra [21].

Mononuclear Cr^{3+} and UO_2^{2+} complexes showed a weight loss of 20.40 and 18.97% respectively, within the temperature range 340–480°C owing to loss of the amine and two methyl groups. Homobinuclear Cr^{3+} and UO_2^{2+} complexes showed a weight loss of 26.50 and 21.10% respectively, within the temperature range 440–610°C, corresponding to loss of phthalein and two acetate groups. The last step involved complete decomposition of the ligand and formation of metal oxalate as the final product. The final product was examined by IR spectroscopy, showing bands characteristic of the oxalate ion at 1670–1630 [$\nu(\text{C}=\text{O})$], 1420–1360 [$\nu(\text{C}-\text{O})$] and 520–470 cm^{-1} [ring deformation + $\delta(\text{O}-\text{C}=\text{O})$] characteristic of the metal oxalates [21]. Further support for this conclusion is gained from the elemental analysis of the remaining residue of the chromium(III) complexes which gave the following results (calculated values in parentheses):

- For the mononuclear complex (%): C 19.3 (19.6), H nil (nil), N nil (nil) and Cr 27.8 (28.3).
- For the binuclear complex (%): C 19.2 (19.6), H nil (nil), N nil (nil) and Cr 28.1 (28.3).

The found and calculated values are in good agreement, confirming the formation of metal oxalate as the final product.

Thermodynamic parameters of the thermal decomposition reactions were determined from TGA curves [22]. The values depicted in Table III indicate two clear points. The first is that the thermodynamic parameters (E^* , ΔH^* , ΔG^* , and ΔS^*) of the decomposition steps are affected by the nature and ratio of the metal ion in the formed complex. The second point is that the entropy of activation observed with respect to the dehydration step has small negative values. This can be explained on the premise that the first degradation step involves two simultaneous processes; the first is volatilization of the water molecules from the solid complex with positive ΔS^* and the second is the formation of more ordered anhydrous complexes with negative ΔS^* . The determined values result from both processes.

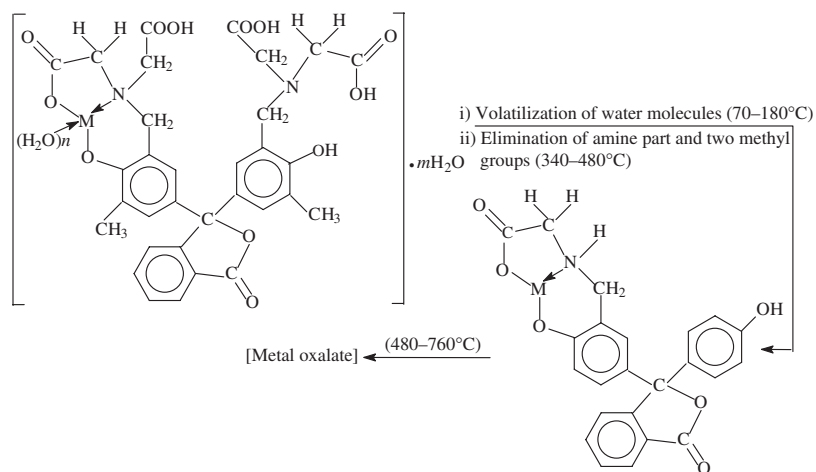
TABLE III Thermodynamic parameters (kJ mol^{-1}) of the thermal decomposition of some complexes

Complex No.	Peak No.	T (K)	E	ΔH	ΔG	ΔS
3	1	348	33.6809	30.7876	97.4644	-0.1916
	2	428	32.1887	28.6303	125.1773	-0.2256
	3	483	72.6474	68.6317	140.5643	-0.1489
	4	633	29.3049	24.0421	183.6846	-0.2522
	5	893	200.3042	192.8798	255.1147	-0.0697
4	1	323	70.6578	67.9724	91.4955	-0.0728
	2	393	14.5422	11.2748	114.0395	-0.2615
	3	553	19.0096	14.4120	166.9242	-0.2758
	4	773	52.0336	45.6069	223.5639	-0.2302
	5	898	425.5820	418.1160	251.4618	0.01856
7	1	323	43.0561	40.3707	94.2315	-0.1668
	2	365.5	20.7225	17.6837	107.2533	-0.2451
	3	500.5	34.2189	30.0577	146.2771	-0.2322
	4	683	18.9085	13.23	197.5717	-0.2699
8	1	323	37.6010	34.9156	93.1735	-0.1804
	2	358	32.6408	29.6644	103.4747	-0.2062
	3	548	14.2635	9.7074	161.3461	-0.2767
	4	768	64.5790	58.1939	226.2669	-0.2189

The DTA curves exhibited two endothermic peaks below 152°C corresponding to volatilization of the lattice and coordinated water molecules. Mononuclear Cr³⁺ and UO₂²⁺ complexes displayed an exothermic peak between 253 and 443°C due to loss of amine and two methyl groups. The exothermic peak at 248–399°C (for the binuclear Cr(III) and UO₂(II) complexes) represented decomposition of the phthalein ring and two acetate groups. The last exothermic peak occurred within the temperature range 404–790°C, corresponding to decomposition of the remainder of the complexes and formation of a metal-oxalato complex.

Based on the thermal analyses, decomposition of mononuclear and binuclear complexes can be represented as follows:

(a) For mononuclear complexes:



(ii) For binuclear complexes:

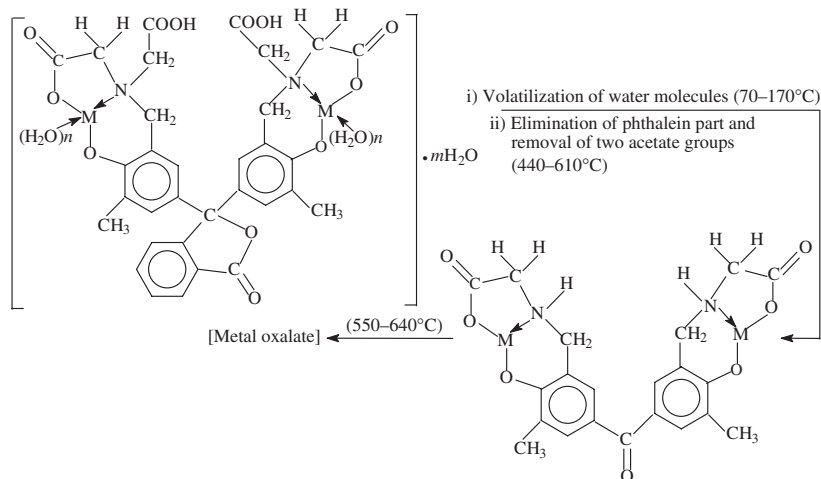


TABLE IV DTA peaks and their assignments of some complexes

Complex No.	DTA peak ($^{\circ}\text{C}$)		Assignment
	Endo	Exo	
3	75		Dehydration process
	137		Thermal dissociation of coordinated water
	186		Removal of chloride ion
		443	Decomposition of the amine part and loss of two methyl groups
		790	Decomposition of complex
4	64		Dehydration process
	137		Thermal dissociation of coordinated water
	260		Removal of chloride ion
		399	Decomposition of the phthalein part and two acetate groups
		676	Decomposition of complex
7	73		Dehydration process
	141		Thermal dissociation of coordinated water
		253	Decomposition of the amine part and loss of two methyl groups
		429	Decomposition of complex
4	80		Dehydration process
	152		Thermal dissociation of coordinated water
		248	Decomposition of the phthalein part and two acetate groups
		404	Decomposition of complex

TABLE V Spectral data of the complexes

Complex No.	IR spectra (cm^{-1}) ^a						Electronic spectra ^{a,b}	
	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{O})$	$\delta(\text{OH})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	λ_{max} nm (Absorbance)
H₆L	3430 br,s	1750 m	1660 s	1640 w	—	—	—	235 280 (2.00) (0.68)
1	3250 m							260, —, 380, 500
	3400 br,s	1740 w	1610 m	1600 m	805 s	465 m	380 w	
2	3210 m							
	3390 br,s	1710 m	1600 m	1590 s	810 s	485 m	375 w	270, —, 340, 590
3	3250 m							
	3423 br,s	1751 m	1631 s	1590 w	815 s	510 m	380 w	280, 310, 400, 580
4	3250 w							
	3443 br,s	1696 m	1662 s	1631 s	853 w	520 m	403 w	260, 305, 420, 585
5	3200 w							
	3390 br,s	1700 m	1600 s	1590 w	810 m	480 w	380 w	280, 355, 410, 555
6	3210 w							
	3380 br,s	1690 w	1600 m	1585 m	805 s	475 m	375 m	270, 300, 360, 580
7	3210 w							
	3400 br,s	1720 m	1610 s	1600 w	810 m	470 m	370 w	278, 300, 380, 500
8	3200 w							
	3370 br,s	1710 m	1600 s	1590 w	805 s	465 w	w	270, 300, 360, 520
	3210 w							

^abr = broad, s = strong, m = medium, w = weak.

^bElectronic spectral data for 1×10^{-4} M of ligand and Nujol mull for complexes.

IR Spectra

The IR spectra of the complexes (Table V) compared to that of the ligand display new strong broad bands within the range $3443\text{--}3370\text{ cm}^{-1}$, due to $\nu(\text{OH})$ of water. This is supported by bands within the $853\text{--}805\text{ cm}^{-1}$ range corresponding to $\gamma(\text{H}_2\text{O})$ of the coordinated water molecules [15,16].

The band due to the deformation of the phenolic OH group at 1220 cm^{-1} in the spectrum of the ligand strongly decreased in intensity relative to neighboring bands in the spectra of mononuclear complexes and vanished completely from the spectra of binuclear complexes. The $\nu(\text{C}=\text{O})$ bands of the carboxylate groups at 1750 , 1660 , and 1640 cm^{-1} in the spectrum of the ligand turned to peaks at 1751 – 1690 , 1662 – 1600 , and 1585 cm^{-1} in the spectra of the complexes, indicating bonding of one carboxylate group to each metal ion. The $\nu(\text{C}-\text{N})$ bands at 1310 cm^{-1} for the ligand shift 10 – 20 cm^{-1} to lower wave numbers. The IR spectra of the complexes indicate that the metal ion is bonded to the ligand through covalent links with the phenolic and carboxylic groups with proton displacement and a coordination bond with the nitrogen atom. This finds support in the appearance of two new bands at 520 – 465 and 403 – 370 cm^{-1} assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ [21].

UV-Vis Absorption (Transmittance) Spectra

The electronic absorption spectra of the ligand in ethanol displays two bands at 235 and 280 nm corresponding to the π – π^* transitions within the aromatic rings. The ligand spectrum does not exhibit any absorption bands in the visible region.

The electronic absorption spectra of the complexes under study as Nujol mulls (Table V) display three bands within the range 260 – 600 nm . The bands below 300 nm are those due to π – π^* transitions of the ligand. The bands at 300 nm or above are due to ligand–metal charge transfer and d–d transitions of the metal ions, since the ligand has no absorption bands within this region (Fig. 1). Comparing the electronic absorption spectra of mononuclear and homobinuclear complexes of *o*-CPC some obvious shifts in the positions of the bands are observed, reflecting the metal ion–metal ion interactions. The small shifts in band positions denote that the metal ions in the homobinuclear complexes retain the same geometry as in the mononuclear complexes. The wavelengths and magnetic moment values indicate that all complexes are octahedral.

Magnetic Measurements

Magnetic moment values were determined by the Gouy method (Table I); correction for diamagnetic atoms was carried out using Pascal's constants. The value for the mononuclear VO^{2+} complex lies within those for the spin-only value for one electron. The value for the homobinuclear complex is lower than for the mononuclear one denoting a possible antiferromagnetic interaction. The values for the chromium and molybdenum complexes are 3.3 , 3.2 , 3.8 and 3.4 BM per metal atom for Complexes **3**, **4**, **5**, and **6**, respectively. This indicates that each chromium or molybdenum ion contains three unpaired electrons. The values of the Cr^{3+} and Mo^{3+} complexes displayed the same trend as VO^{2+} , showing antiferromagnetic interaction in the homobinuclear complex. The uranyl complexes are diamagnetic as expected for hexavalent uranium.

ESR Spectra

X-band ESR spectra of Complexes **1**, **2**, **3**, **4**, **5** and **6** at room temperature (Fig. 2 and Table I) exhibit the following characteristics:

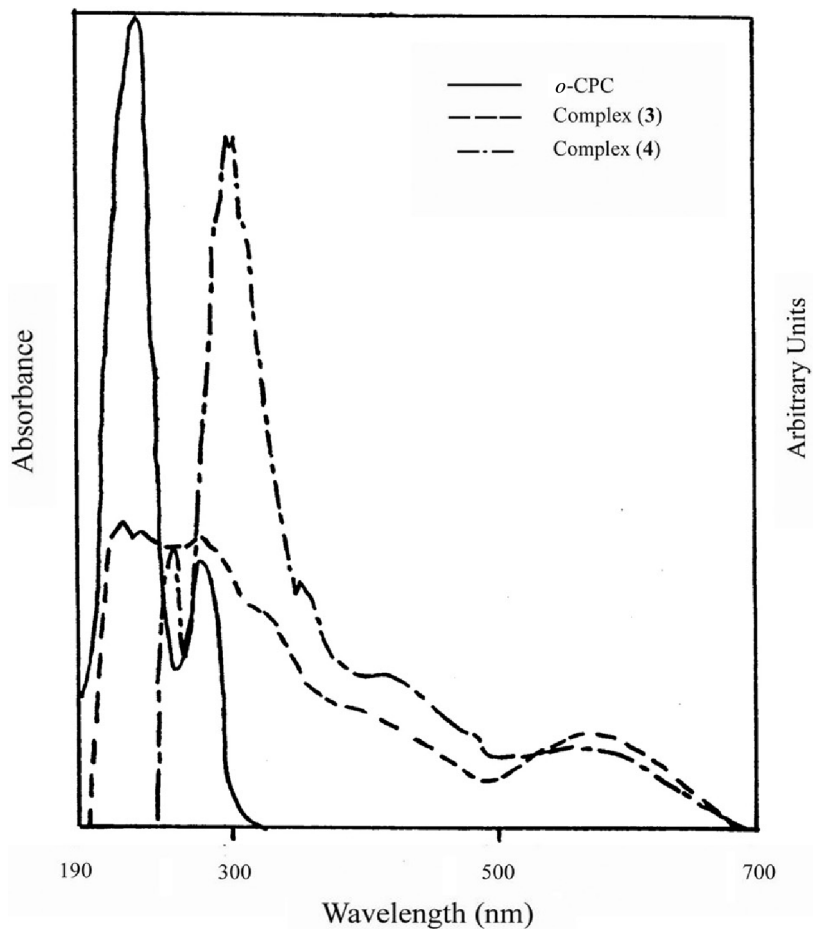


FIGURE 1 The electronic absorption spectra of the ligand *o*-CPC and its Cr(III) complexes.

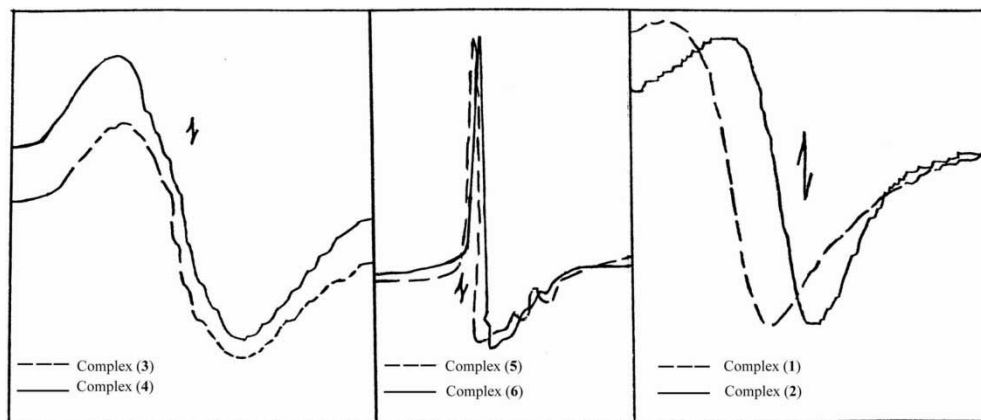


FIGURE 2 The room temperature X-band ESR spectra of the solid V(IV), Cr(III), and Mo(III) complexes.

- (a) For oxovanadium(IV) complex **1**, eight lines are observed with average hyperfine splitting 55 G and intensity ratio 1:2:3:5:7:3:2:1. The eight-line spectrum $g_{\text{eff}}=1.9932$ is characteristic of oxovanadium(IV). For the homobinuclear oxovanadium (IV) complex **2**, fifteen lines were observed with average hyperfine splitting 27 G and intensity ratio 1:3:4:5:7:9:10:13:11:6:5:3:2:2:1. The $g_{\text{eff}}=1.9632$ is due to the coupling of two interacting ^{51}V nuclei. Comparison of the spectra of Complexes **1** and **2** reveals that the fine structural features are more closely spaced for Complex **2** than for the mononuclear complex. This results from the greater number of possible transitions for a homobinuclear complex than for the mononuclear one [23,24]. For systems that have weak coupling between identical nuclei, the hyperfine interval is A/n , where A is the observed single nuclei coupling constant and n is the number of coupled nuclei. Thus, the A value of Complex **2** should be half the value for Complex **1**. This prediction was observed experimentally in the two VO^{2+} complexes.
- (b) For mono- and homobinuclear Cr(III) complexes **3** and **4**, the ESR spectra exhibit an isotropic broad signal with six lines for Complex **3** and fourteen lines for Complex **4**. The g_{eff} values are 1.6672 and 1.7382 respectively. Comparison of the ESR spectra of Complexes **3** and **4** shows that the fine structures of the binuclear complex are more closely spaced than for Complex **3**.
- (c) In the case of mono- and homobinuclear Mo(III) complexes **5** and **6**, the ESR spectra exhibit an isotropic, sharp signal with four lines. The g_{eff} values are 1.9352 and 1.9436 respectively. The ESR spectra obtained are completely different from those reported by previous authors [25] for Mo(III)–Schiff-base complexes.

The g_{eff} values of Complexes **1**, **2**, **3**, **4**, **5**, and **6** have a negative contribution from the value of the free electron, $g=2.0023$ which may be due to a decrease in covalent bonding between *o*-CPC and oxovanadium(IV), chromium(III), or Mo(III) ions [26].

Electrochemical Investigations

Electroreduction of the complexes was carried out using DC polarography at the dropping mercury electrode (DME) and cyclic voltammetry (CV) at the hanging mercury drop electrode (HMDE).

The VO^{2+} complexes yielded one reduction wave at the DME with height corresponding to two electrons per vanadyl ion. The height for Complex **1** was almost half that for Complex **2**. The half-wave potential ($E_{1/2}$) values [-0.75 V (SCE)] were not much different, denoting that in such dilute solutions no interaction occurred between the vanadyl ions. The waves were found to be diffusion controlled and the electrode reduction was irreversible as indicated from analysis of the reduction waves.

The Mo^{3+} and Cr^{3+} complexes did not show any reduction at DME denoting that the reduction of such ions does not take place at potentials less positive than that for H^+ reduction.

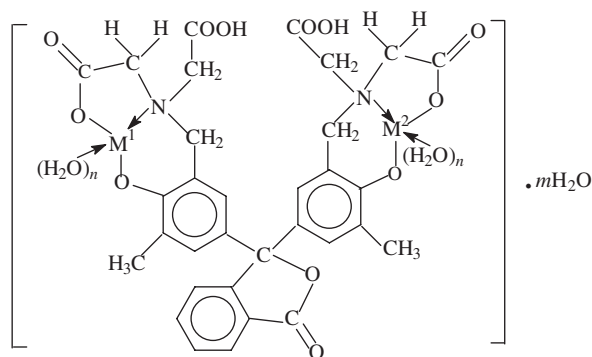
For the uranyl complexes, two waves of almost equal height were obtained. These waves with $E_{1/2}$ at -0.24 and -0.82 V vs. SCE represent the reduction of UO_2^{2+} to UO_2^+ then UO^{2+} . The reduction waves were found to be irreversible and diffusion controlled.

CV of VO^{2+} complexes gave a single cathodic peak with E_p at -0.13 V vs. sat. Ag/AgCl reference electrode but only weak anodic peaks were obtained. The peak potential shifted slightly to a more negative potential and the peak current (I_p) increased with increased scan rate. This behavior suggests the irreversible diffusion-controlled character of the reduction process.

For the uranyl complexes, two cathodic peaks were observed with E_p at -0.77 and -1.13 V vs. sat. Ag/AgCl electrode, but very weak anodic peaks appeared. The peak potential shifted somewhat to a more negative potential and peak current increased with increasing scan rate. This behavior indicates irreversible diffusion-controlled reduction reactions.

CONCLUSION

Based on the results obtained from analytical and thermal analyses, IR, UV-Vis and ESR spectra, magnetic moment determinations, cyclic and polarographic studies, the bonding of the ligand to the metal ions under investigation can be represented as follows:



$M^1 = \text{VO}^{2+}$, Cr^{3+} , MoO^+ , or UO_2^{2+} , $M^2 = \text{H}$ for 1:1 complexes and $M^1 = M^2$ for 1:2 (L:M) complexes, n = number of water molecules coordinated to the metal ion and m = number of water molecules outside the coordination sphere (Table I).

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