

Synthesis, Spectral and Thermal Studies of VO(IV) and UO₂(VI) Complexes with N,N'-Triethylenediamine-bis(3-carboxypropenamide)

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The complexes of VO(IV) and UO₂(VI) with N,N'-triethylenediamine-bis(3-carboxypropenamide) (TEBCPH₂) have been synthesized and characterized by chemical analysis, conductance, magnetic, infrared spectral and thermal studies. On the basis of the above studies it is concluded that the ligand acts as hexadentate in dioxouranium(VI) complex whereas in the oxovanadium(IV) complex the ligand shows tetradentate nature. The VO(IV) and UO₂(VI) complexes have been assigned the formulae [VO(TEBCP)]·2H₂O and [UO₂(TEBCP)] respectively.

Key Words: Oxovanadium, Dioxouranium, N,N'-Triethylenediamine-bis(3-carboxypropenamide), Spectral, Thermal.

INTRODUCTION

Studies of metal complexes of polydentate ligands containing amide groups have been reported in literature¹. In continuation of the earlier studies, the present communication reports the synthetic, structural and thermal aspects of the complexes of the polydentate ligand, triethylenediamine-bis(3-carboxypropenamide) [TEBCPH₂] with VO²⁺ and UO₂²⁺ ion^{2,3}. For the complex [VO(TEBCP)]·2H₂O the kinetic parameters of thermal decomposition such as energy of activation (E), pre-exponential factor (A) and entropy of activation (ΔS) have been determined by Coates-Redfern equation.

EXPERIMENTAL

The chemicals used were of AR grade or pure quality. The solvents were double distilled before use.

The ligand TEBCPH₂ was prepared by literature method^{1,2}. Maleic anhydride (0.1 mol) was dissolved in glacial acetic acid (50 mL) and to this triethylenetetramine (0.05 mol) was added dropwise with constant stirring under ice-cold conditions. The white solid formed was filtered, washed several times with acetone and then recrystallized from aqueous ethanol (m.p. 176°C).

Preparation of the complexes

The complexes were prepared by refluxing an alcoholic solution of TEBCPH₂ and an alcoholic solution of the metal salt [VOSO₄/UO₂(CH₃COO)₂] in 1 : 1 ratio

for about 2–3 h. The resulting solution was concentrated to half of its volume, the precipitated complex was filtered, washed with ethanol and dried over anhydrous calcium chloride in a desiccator.

The complexes were crystalline solid, stable at room temperature and nonhygroscopic. Both the complexes were soluble in DMF and DMSO. The metal contents of the complexes were determined by standard methods⁴. The molar conductivities of the complexes in DMF were determined at room temperature ($28 \pm 2^\circ\text{C}$). Magnetic susceptibilities of the complexes were determined at room temperature by Gouy method. Molecular masses of the complexes were determined by Rast method using biphenyl as solvent⁵. The infrared spectra of the complexes were recorded in the range $4000\text{--}400\text{ cm}^{-1}$. The TG and DTG curves of the complexes were recorded on a thermal analyzer from ambient to 700°C . The mass percentage vs. temperature curves obtained were redrawn in appropriate scales. Independent pyrolysis experiment in air was carried out for both the complexes and loss of mass determined in each case was compared with that obtained from TG.

Thermal decomposition kinetics of the VO(IV) complex was studied and the kinetic parameters were evaluated.

RESULTS AND DISCUSSION

The analytical results (Table-1) indicate a 1 : 1 (M : L) stoichiometry for the complexes. The molar conductivities (Table-2) of the complexes in DMF and in nitrobenzene were in the ranges corresponding to those of nonelectrolytes.

TABLE-1
ANALYTICAL DATA OF VO(IV) and UO₂(VI) COMPLEXES OF TEBCPH₂

Complex	Colour	M : L ratio	Molar mass	Metal percentage
[VO(TEBCP)]·2H ₂ O	Grey	1 : 1	448	11.26 (11.51)
[UO(TEBCP)]	Yellow	1 : 1	618	38.91 (39.02)

Calculated values are given within parentheses.

TABLE-2
MOLAR CONDUCTANCE DATA OF VO(IV) and UO₂(VI) COMPLEXES

Complex	Concentration $\times 10^3\text{ M}$	Molar conductance, $\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$	
		In DMF	In nitrobenzene
[VO(TEBCP)]·2H ₂ O	1.03	3.1	4.2
[UO(TEBCP)]	1.00	2.3	3.4

The magnetic moment of the complex, [VO(TEBCP)]·2H₂O is found to be 1.79 B.M., which is very close to the spin-only value of 1.73. The dioxouranium complex was found to be diamagnetic in nature. This can be explained on the basis of the electronic configuration of the central metal ion. The central metal ion, U⁶⁺ does not possess any unpaired electron and has the inert gas configuration.

The infrared spectra of the complexes were compared with that of the free ligand. In the infrared spectrum of the ligand, the $\nu(\text{N—H})$ mode of secondary amine appears at 3320 cm^{-1} . The shifting of this band to a lower region (3282 cm^{-1}) in the spectrum of the complex, $[\text{VO}(\text{TEBCP})]\cdot 2\text{H}_2\text{O}$, indicates the involvement of secondary amino nitrogen in coordinate bond formation with the metal ion. The amide N—H stretching frequency observed at 3300 cm^{-1} in the spectrum of the ligand is left unchanged in the spectrum of the oxovanadium complex. This shows the non-participation of the amide nitrogen on coordination. The amide carbonyl stretching frequency observed at 1620 cm^{-1} remains unaltered indicating its non-participation in coordinate bond formation with the metal ion. The infrared spectrum of the ligand showed a medium band at 3100 cm^{-1} which is assigned to $\nu(\text{O—H})$ of carboxylic acid group⁶. This group is hydrogen bonded with the carbonyl group of the amide. The disappearance of this band in the infrared spectrum of the complex indicates the deprotonation of carboxyl group and coordination through the oxygen atom. This is further supported by the disappearance of the strong band at 1700 cm^{-1} which is due to the stretching frequency of C=O of carboxylic acid and the appearance of two new bands at 1539 and 1337 cm^{-1} . These are assigned to the asymmetric and symmetric stretching of coordinated carboxylate group. A strong band at 919 cm^{-1} is assigned to the V=O stretching frequency of VO^{2+} unit. This complex shows an additional band around 3450 cm^{-1} , indicating the presence of water of hydration⁷. Further the absence of a characteristic absorption band around 800 cm^{-1} indicates that the water molecules are not coordinated⁸. In addition to these absorptions, two new bands observed at 540 and 485 cm^{-1} may be due to $\nu(\text{M—N})$ and $\nu(\text{M—O})$ respectively⁷.

In the infrared spectrum of the complex, $[\text{UO}_2(\text{TEBCP})]$, the medium band around 3320 cm^{-1} in the ligand which is due to $\nu(\text{N—H})$ of the secondary amino group is shifted to a lower frequency, 3290 cm^{-1} . This shows the participation of the secondary amino group in complex formation. The amide N—H stretching frequency observed at 3300 cm^{-1} in the spectrum of the ligand is shifted to 3250 cm^{-1} in the spectrum of the complex indicating the involvement of amide-nitrogen in coordination^{9,10}. The amide carbonyl group stretching frequency observed at 1620 cm^{-1} remains unaltered indicating its non-participation in coordinate bond formation with the metal ion. The infrared spectrum of the ligand showed a medium band at 3100 cm^{-1} which is due to $\nu(\text{O—H})$ of carboxylic acid group. This group is hydrogen bonded with the carbonyl group of the amide. This band disappears in the spectrum of the complex. This shows the deprotonation of the acid group and its coordination through the hydroxyl-oxygen. The band at 1700 cm^{-1} disappears on complexation and gives two new bands at 1546 cm^{-1} due to the asymmetric stretching of coordinated carboxylate group and at 1384 cm^{-1} due to the symmetric stretching of coordinated carboxylate group. The asymmetric stretching frequency of dioxouranium(VI) ion is observed at 920 cm^{-1} in the complex. Two additional bands at 535 cm^{-1} and at 481 cm^{-1} may be due to $\nu(\text{M—N})$ and $\nu(\text{M—O})$ vibrations. IR spectral data are given in Table-3.

TABLE-3
IR SPECTRAL DATA (cm^{-1}) OF THE LIGAND AND THE COMPLEXES

TEBCPH ₂ (Ligand)	[VO(TEBCP)]·2H ₂ O	[UO ₂ (TEBCP)]	Tentative assignments
—	3450 (m)	—	v(O—H) of lattice water
3320 (m)	3282 (w)	3290 (w)	v(N—H) of 2° amine
3300 (m)	3300 (w)	3250 (m)	v(N—H) of 2° amide
3100 (m)	—	—	v(O—H) of COOH group
2940 (m)	2940 (m)	2940 (w)	v(C—H)
1700(m)	—	—	v(C=O) of COOH
1660(m)	1660(w)	1660 (m)	v(C=C)
1620(s)	1621 (s)	1623 (s)	v(C=O) of 2° amide
—	1539(s)	1546(s)	v(C=O) of coordinated COO ⁻ (asym)
1502(s)	1501 (s)	1500(s)	v(C—N)
—	1337 (s)	1384(s)	v(C=O) of coordinated COO ⁻ (sym)
—	—	920 (m)	Stretching frequency of UO ₂ (VI)
—	919 (m)	—	Stretching frequency of V=O
—	540 (m)	535 (m)	v(M—N)
—	485 (w)	481 (w)	v(M—O)

Thermal studies were conducted on the complexes, [VO(TEBCP)]·2H₂O and [UO₂(TEBCP)]. Independent pyrolysis experiment in air was also carried out. For this, a known amount of the complex was heated in a porcelain crucible up to 750°C for *ca.* 1 h. From the mass of the residue, the loss of mass was calculated in each case, which was compared with the percentage loss of mass obtained from the experiment.

For the complex, [VO(TEBCP)]·2H₂O, the TG plateau up to 468 K shows its stability and the complex starts decomposition after this temperature. The first stage of decomposition is from 468 K. The weight loss at this stage is about 8%. The peak temperature at this stage is 361 K. This stage corresponds to the loss of two water molecules from the complex. The loss of water molecules at this low temperature indicates that they are lattice held^{11, 12}. The second stage of decomposition ranges from 409 to 591 K. During this stage a weight loss of 34% occurs. The summit temperature as given by DTG curve is 567 K. The third stage of decomposition extends from 591 to 691 K. The weight loss during this interval is only 17%. The peak is obtained at 651 K. The fourth stage of decomposition is in between 691 and 748 K. The peak temperature from the DTG curve is 712 K. The TG curve exhibits a second plateau after 748 K indicating the completion of decomposition. The last three stages of decomposition are attributed to the complete removal of the ligand from the complex. The residue is due to the stable metal oxide.

For the dioxouranium complex, [UO₂(TEBCP)], the TG plateau is up to 465 K indicating that the complex is stable up to 465 K. The DTG curve has two peaks at 571 and 782 K showing that the complex undergoes decomposition in two

stages. The TG curve exhibits a second plateau after 850 K indicating the completion of decomposition. The complex shows a weight loss of 24.2% at 574 K. The complex decomposes rapidly at 574 K due to breaking up of the organic moiety of the complex. Decomposition continues with a gradual decrease in weight and a constant weight due to the formation of stable U₃O₈ is obtained at ca. 850 K corresponding to a weight loss of 54.21%.

The Coats-Redfern plots of $\log [g(\alpha)/T^2]$ vs. $1/T$ of oxovanadium(IV) complex at different stages of decomposition were drawn and are given in Figs. 1-4. Values were obtained from the TG curves. The data used to evaluate the kinetic parameters are given in Tables 4-7. The values given in Table 8 were calculated by assuming the order parameter (n) as unity. The activation energy E, pre-exponential factor A and entropy of activation ΔS were evaluated. The negative values of ΔS indicate that the activated complex is more ordered than the reactants.

TABLE-4
DATA USED TO EVALUATE KINETIC PARAMETERS
FOR DECOMPOSITION OF [VOL].2H₂O: Stage I

α	$g(\alpha)$	T (K)	$(1/T) \times 10^3$	$\log [g(\alpha)/T^2]$
0.1176	0.1252	343	2.9155	-5.9731
0.2215	0.2503	363	2.7548	-5.7213
0.3235	0.3909	383	2.6110	-5.5744
0.4876	0.6687	403	2.4813	-5.3854
0.6521	1.0558	423	2.3641	-5.2291
0.8236	1.7350	443	2.2573	-5.0535
0.9117	2.4274	463	2.1598	-4.9460
0.9706	3.5275	483	2.0704	-4.8204

TABLE-5
DATA USED TO EVALUATE KINETIC PARAMETERS
FOR DECOMPOSITION OF [VOL].2H₂O: STAGE II

α	$g(\alpha)$	T (K)	$(1/T) \times 10^3$	$\log [g(\alpha)/T^2]$
0.0129	0.0131	519	1.9268	-7.3169
0.0390	0.0397	529	1.8903	-6.8477
0.1039	0.1097	539	1.8553	-6.4229
0.2078	0.2329	549	1.8215	-6.1119
0.3377	0.4120	559	1.7889	-5.8799
0.6104	0.9426	569	1.7575	-5.5359
0.8571	1.9459	579	1.7271	-5.2362
0.9610	3.2447	589	1.6977	-5.0291

TABLE-6
DATA USED TO EVALUATE KINETIC PARAMETERS
FOR DECOMPOSITION OF [VOL]-2H₂O: STAGE III

α	$g(\alpha)$	T (K)	$(1/T) \times 10^3$	$\log [g(\alpha)/T^2]$
0.1569	0.1707	601	1.6638	-6.3256
0.1905	0.2113	611	1.6367	-6.2472
0.2857	0.3365	621	1.6103	-6.0592
0.4048	0.5188	631	1.5849	-5.8851
0.4762	0.6466	641	1.5600	-5.8031
0.5952	0.9045	651	1.5360	-5.6708
0.6905	1.1727	661	1.5129	-5.5712
0.8095	1.6582	671	1.4903	-5.4338
0.8824	2.1404	681	1.4684	-5.3358

TABLE-7
DATA USED TO EVALUATE KINETIC PARAMETERS
FOR DECOMPOSITION OF [VOL]-2H₂O: STAGE IV

α	$g(\alpha)$	T (K)	$(1/T) \times 10^3$	$\log [g(\alpha)/T^2]$
0.2727	0.3185	701	1.4265	-6.1884
0.5636	0.8293	711	1.4065	-5.7850
0.7475	1.3764	721	1.3870	-5.5771
0.9091	2.3979	731	1.3680	-5.3480
0.9636	3.3141	741	1.3495	-5.2193

TABLE 8
KINETIC PARAMETERS FOR THE THERMAL
DECOMPOSITION OF [VOL]-2H₂O

Stage of decomposition	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
I	25.85740	8.42867×10^2	-287.217170
II	191.34761	2.46179×10^{17}	-13.077596
III	99.30205	2.61264×10^7	-205.158680
IV	236.98702	1.04543×10^{17}	-22.056017

On the basis of the above experimental evidences, it may be concluded that the ligand TEBCPH₂ acts as hexadentate in the dioxouranium(VI) complex. Two additional coordination sites of central uranium are occupied by the two uranyl oxygen atoms. Thus, the coordination number of the central metal ion is eight. The infrared spectral analysis indicates the tetradentate nature of the ligand in the

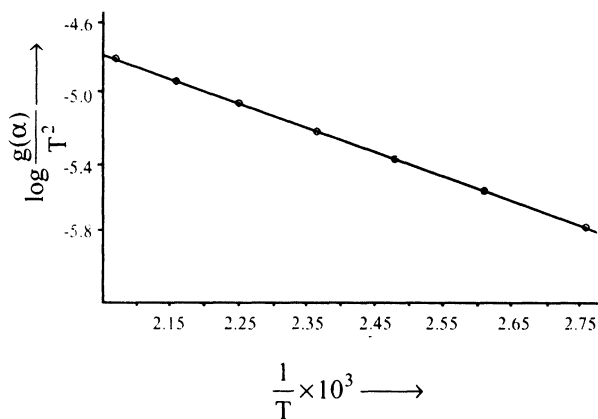


Fig. 1. Stage I of [VOL]·2H₂O

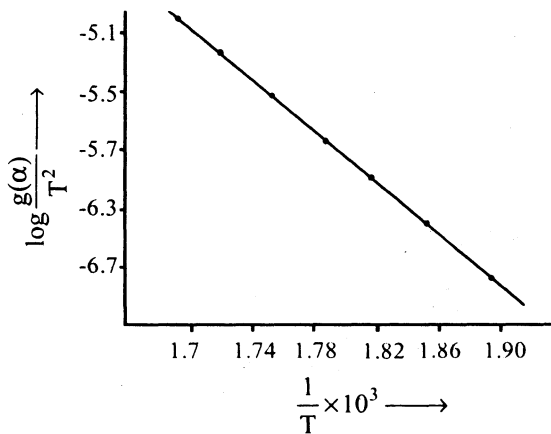


Fig. 2. Stage II of [VOL]·2H₂O

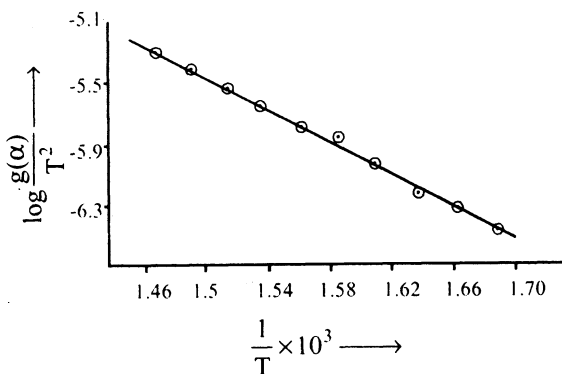


Fig. 3. Stage III of [VOL]·2H₂O

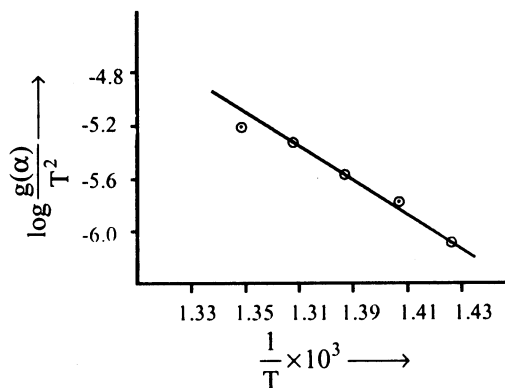


Fig. 4. Stage IV of [VOL]·2H₂O

oxovanadium(IV) complex. The two secondary amino nitrogen atoms and the two carboxylate oxygen atoms act as the four donor sites. One of the coordination sites of vanadium is occupied by vanadyl oxygen atom. Thus, the coordination number of vanadium is five in this complex. The spectral and thermal studies indicate the presence of lattice water in the oxovanadium(IV) complex.

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