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Synthesis and Characterization of VO(IV) and UO_2(VI) Complexes with Nitrogen and Oxygen Donor Ligands

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A few complexes of VO(IV) and UO_2(VI) with two nitrogen and oxygen donor ligands, N,N′-diethylenediamine-bis(3-carboxypropenamide) [$DEBCPH_2$] and N,N′-propylenediamine-bis(3-carboxypropenamide) [$PBCPH_2$] have been synthesized and characterized by chemical analysis, conductance, magnetic, thermal and infrared spectral studies. On the basis of the above studies it is concluded that $PBCPH_2$ acts as tetradentate in both the oxo- vanadium(IV) and dioxouranium(VI) complexes. The complexes have been assigned the formulae $[VO(PBCP)]\cdot 2H_2O$ and $[UO_2(PBCP)]$ respectively. On the other hand, $DEBCPH_2$ acts as tetradentate in the oxovanadium(IV) complex whereas in the dioxouranium(VI) complex it shows pentadentate nature. Thus, these two complexes have been assigned the formulae $[VO(DEBCP)]\cdot 2H_2O$ and $[UO_2(DEBCP)]$ respectively.

Key Words: Synthesis, VO(IV), UO_2(VI) complexes.

INTRODUCTION

Synthesis and characterization of complexes of polydentate ligands containing amide groups have been reported in literature[1]. In continuation of the earlier studies[2–4], the present communication reports the synthetic, structural and thermal aspects of the complexes of two polydentate ligands, $PBCPH_2$ and $DEBCPH_2$ with VO^{2+} and UO_2^{2+} ions.

EXPERIMENTAL

All the chemicals used were of AR grade or pure quality. The solvents were double distilled before use. The ligands N,N′-diethylenediamine-bis(3-carboxypropenamide) [$DEBCPH_2$] and N,N′-propylenediamine-bis(3-carboxypropenamide) [$PBCPH_2$] were pepared by literature method[2].

Preparation of the complexes: The complexes were prepared by refluxing an alcoholic solution of the ligand, $PBCPH_2$/$DEBCPH_2$ and an alcoholic solution of the metal salt 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.

Oxovanadium(IV) sulphate and dioxouranium(VI) acetate were the metal salts used for the preparation of the complexes.

All the complexes were crystalline, stable at room temperature and non-hygroscopic. The complexes are soluble in DMF and DMSO. The metal contents of the complexes were determined by standard methods[5]. The molar conductivities of the complexes in DMF and nitrobenzene were determined at room temperature (28 ± 2)°C. Magnetic susceptibilities of the complexes were determined at room temperature by Gouy method. Molar masses of the complexes were determined by Rast method by using biphenyl as solvent[6]. The infrared spectra of the complexes were recorded in the range 4000–400 cm^{-1}. The TG and DTG curves of the complexes were recorded on a thermal analyzer from ambient to 800°C. 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.

RESULTS AND DISCUSSION

The analytical data given in Table-1 indicate a 1 : 1 (M : L) stoichiometry for the complexes. The molar conductivities of the complexes (Table-2) in DMF and nitrobenzene were in the range corresponding to those of non-electrolytes.

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Complex	M : L ratio	Molar mass	Metal percentage
$[VO(DEBCP)]\cdot 2H_2O$	1 : 1	416 (400)	12.91 (12.75)
$[VO(PBCP)]\cdot 2H_2O$	1 : 1	390 (371)	13.89 (13.74)
$[UO_2(DEBCP)]$	1 : 1	581 (567)	42.14 (41.98)
$[UO_2(PBCP)]$	1 : 1	552 (538)	44.45 (44.24)

Calculated values are given in parentheses.

TABLE-2
MOLAR CONDUCTANCE DATA OF THE COMPLEXES IN DMF AND IN NITROBENZENE

Complex	Concentration × 10^{-3} M	Molar conductance (ohm^{-1} cm^2 mol^{-1})	
		DMF	Nitrobenzene
$[CO(DEBCP)]\cdot 2H_2O$	1.02	4.1	4.8
$[VO(PBCP)]\cdot 2H_2O$	1.01	3.4	4.3
$[UO_2(DEBCP)]$	1.02	2.4	2.9
$[UO_2(PCBP)]$	1.01	2.8	2.7

The magnetic moment of the complexes $[VO(DEBCP)]\cdot 2H_2O$ and $[VO(PBCP)]\cdot 2H_2O$ were found to be 1.78 and 1.77 B.M. respectively which are very close to the spin only value of 1.73 corresponding to one unpaired electron[7]. The dioxouranium complexes were found to be diamagnetic in nature. This may be explained on the basis of the electronic configuration of the central metal ion. The central metal ion, U^{6+}, does not possess any unpaired electron and has the inert gas configuration of radon.

The infrared spectrum of the ligands exhibits a stretching frequency of amide[8] NH at 3300 cm^{-1}. A medium band at 3100 cm^{-1} is assigned to ν(O—H) of the carboxylic acid group which is hydrogen bonded with carbonyl group of amide[9]. The band at 1700 cm^{-1} is due to the stretching frequency of carbonyl group of carboxylic acid. The amide carbonyl stretching frequency[10] is observed at 1620 cm^{-1}. The band at 3320 cm^{-1} in the spectrum of the ligand DEBCPH$_2$ is assigned to the NH stretching frequency of secondary amino group.

The proton NMR spectrum of the ligand, PBCPH$_2$ in DMSO, shows a total of six signals indicating the presence of six types of H-atoms. A singlet at 8 ppm (2H) indicates the OH groups. A quartet at 3.6 ppm (4H) is given by the methylene protons near to secondary amide groups. A quintet at 2.05 ppm is given by the methylene protons in between the above mentioned methylene groups. A triplet at 6.4 ppm (2H) is due to two amide protons. A doublet of doublet at 6.1 ppm is due to —C=CH—[8,9]. The proton NMR spectrum of the ligand, DEBCPH$_2$, shows signals at 4.5 (8H, CH$_2$), 8.4 (2H, amide NH), 5.8–6.1 (doublet 4H, CH=CH), 5.1 (singlet 1H, secondary amino group) and a sharp singlet at 9.1 ppm (2H, COOH).

The mass spectrum of DEBCPH$_2$ shows molecular ion peak at 299 and a base peak at M/z 183 due to $[C_8N_3O_2H_{13}]^+$ ion. From these data the following structure may be assigned to the ligands.

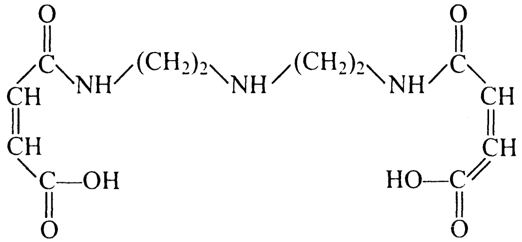

Fig. 1. Structure of N,N′-diethyleneaminebis(3-carboxypropenamide)

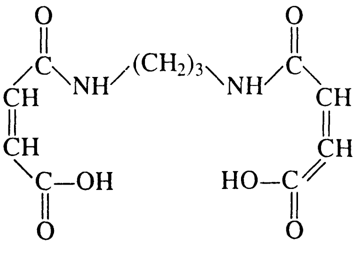

Fig. 2. Structure of N,N′-propylene-bis(3-carboxypropenamide)

The infrared spectra of the complexes were compared with those of the ligands. In the spectrum of dioxouranium(VI) complex of $DEBCPH_2$ the band around 3320 cm^{-1} is shifted to lower region (3284 cm^{-1}). This indicates the involvement of secondary amino group in coordinate bond formation. However, the ν(N—H) mode of secondary amine observed at 3320 cm^{-1} in the spectrum of the ligand is left unchanged in the spectrum of oxovanadium(IV) complex showing the non-participation of the secondary amino-nitrogen in coordination. The amide N—H stretching frequency observed at 3300 cm^{-1} in the spectrum of $DEBCPH_2$ is shifted to a lower frequency around 3250 cm^{-1} in the spectra of both dioxouranium(VI) and oxovanadium(IV) complexes indicating the involvement of amide nitrogen in coordination[11, 12]. The amide carbonyl stretching frequency observed at 1620 cm^{-1} remains unaltered in the spectra of both the oxovanadium(IV) and dioxouranium(VI) complexes of $DEBCPH_2$. This indicates the non-participation of amide carbonyl group in coordination. The IR spectra of the ligand showed a medium band at 3100 cm^{-1} which is assigned to ν(O—H) of carboxylic acid group. This is hydrogen bonded with the carbonyl group of the amide. The disappearance of this band in the infrared spectra of the complexes indicates the deporotonation 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 1542–1540 and 1345–1340 cm^{-1}. These are assigned to the asymmetric and symmetric stretching of coordinated carboxylate group. A strong band at 918 cm^{-1} in oxovanadium complex is assigned to V=O stretching frequency of VO^{2+} unit. The oxovanadium complex shows an additional band around 3450 cm^{-1}, indicating the presence of water of hydration[13]. Further, the absence of a characteristic absorption band around 800 cm^{-1} indicates that the water molecules are not coordinated[14]. In the spectrum of the dioxouranium(VI) complex with $DEBCPH_2$ a band observed at 920 cm^{-1} is assigned to asymmetric stretching frequency of O=U=O group. In addition to these absorptions, two new bands observed at 540–535 and 485–481 cm^{-1} may be due to ν(M—N) and ν(M—O) respectively.

In the infrared spectrum of the dioxouranium(VI) and oxovanadium(IV) complexes of $PBCPH_2$, the amide N—H stretching freqeuncy observed at 3304 cm^{-1} in the sepctrum of the ligand is shifted to a lower frequency around 3250 cm^{-1}. This indicates the involvement of the amide nitrogen in coordination. 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 3102 cm^{-1} which is due to ν(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 showing the deprotonation of the acid group and its coordination through the hydroxyl oxygen. The band at 1700 cm^{-1} vanishes and gives two new bands at 1545–1540 cm^{-1}, due to the asymmetric stretching of coordinated carboxylate group and at 1382–1380 cm^{-1} due to the symmetric stretching of coordinated carboxylate group. The asymmetric stretching frequency of O═U═O group is observed at 921 cm^{-1} in the complex. A strong band at 918 cm^{-1} is assigned to the V═O stretching frequency of VO^{2+} unit. The oxovanadium complex shows an additional band around 3450 cm^{-1} indicating the presence of water of hydration[13]. The absence of absorption band around 800 cm^{-1} shows that the water molecules are not coordinated[14]. In addition to these absorptions, two new bands observed at 543–540 and 484–482 cm^{-1} may be due to ν(M—N) and ν((M—O) respectively[13].

TABLE-3

IR SPECTRAL (cm^{-1}) DATA OF DEBCPH$_2$ AND THE COMPLEXES

DEBCPH$_2$	[VO(DEBCP)]·2H$_2$O	[UO$_2$(DEBCP)]	Tentative assignments
—	3450 (m)	—	ν(O—H) of lattice water
3320 (m)	3320 (w)	3284 (w)	ν(N—H) of 2° amine
3300 (m)	3250 (m)	3252 (m)	ν(N—H) of 2° amide
3100 (m)	—	—	ν(O—H) of COOH
2940 (m)	2940 (m)	2940 (w)	ν(C—H)
1700 (m)	—	—	ν(C—O) of COOH
1660 (m)	1660 (w)	1660 (m)	ν(C═C)
1620(s)	1622 (s)	1624 (s)	ν(C═O) of 2° amide
—	1540 (s)	1542 (s)	ν(C—O) of coordinated COO$^-$ (asy)
1502 (s)	1502 (s)	1500 (s)	ν(C—N)
—	1340 (s)	1345 (s)	ν(C═O) of coordinated COO$^-$ (sy)
—	—	920 (s)	Stretching frequency of UO$_2$(VI)
—	918 (s)	—	Stretching frequency of V═O
—	540 (m)	535 (m)	ν(M—N)
—	486 (w)	482 (w)	ν(M—O)

s = strong, m = medium, w = weak, sy = symmetric, asy = asymmetric

TABLE-4

IR SPECTRAL (cm^{-1}) DATA OF $PBCPH_2$ AND THE COMPLEXES

$PBCPH_2$	$[CO(PBCP)]·2H_2O$	$[UO_2(PBCP)]$	Tentative assignments
—	3450 (m)	—	ν(O—H) of lattice water
3304 (m)	3250 (m)	3249 (w)	ν(N—H) of 2° amide
3100 (m)	—	—	ν(O—H) of COOH group
2940 (m)	2940 (m)	2940 (m)	ν(C—H)
1700 (m)	—	—	ν(C=O) of COOH
1660 (m)	1660 (w)	1660 (m)	ν(C=C)
1620 (s)	1621 (s)	1622 (s)	ν(C=O) of 2° amide
—	1540 (s)	1545 (s)	ν(C=O) of coordinated COO^- (say)
1500 (s)	1502 (s)	1501 (s)	ν(C—N)
—	1380 (s)	1382 (s)	ν(C=O) of coordinated COO^- (sy)
—	—	921 (m)	Stretching frequency of UO_2(VI)
—	918 (s)	—	Stretching frequency of V=O
—	540 (m)	543 (m)	ν(M—N)
—	484 (w)	482 (w)	ν(M—O)

s = strong, m = medium, w = weak, sy = symmetric, asy = asymmetric

Thermal studies were conducted on all the complexes. Independent pyrolysis experiments in air were also carried out. For this a known amount of the complex was heated in a porcelain crucible up to 800°C for about 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 $[UO_2(DEBCP)]$ the TG plateau is up to 476 K indicating that the complex is stable up to 476 K. The DTG curve has two peaks at 498 and 762 K showing that the complex undergoes decomposition in two stages. The TG curve shows a second plateau after 800 K indicating the completion of decomposition. The complex shows a weight loss of 25.15% at 498 K. The complex decomposes rapidly at 498 K due to the breaking 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 U_3O_8 at about 762 K with a weight loss of 49.28% (theoretical 50.5%).

For the uranyl complex $[UO_2(PBCP)]$, the TG plateau up to 463 K shows its stability and the complex starts decomposition after this temperature. There are two decomposition stages as indicated by the DTG peaks at 487 and 748 K. The TG curve exhibits a second plateau after 780 K. This shows the completion of decomposition. The independent pyrolysis shows that the final decomposition product is U_3O_8 in conformity with the mass loss data obtained from TG. The total weight loss observed is 48.1% (theoretical 47.83%).

The complex, $[VO(TEBCP)]\cdot 2H_2O$, is found to be stable up to 323 K. The complex decomposes after 323 K in four stages. The first stage of decomposition is from 323 to 490 K. The weight loss is about 9.5% within a temperature interval of 167 K. The peak temperature at this stage is 392 K. This stage corresponds to the loss[15, 16] of two water molecules from the complex. The loss of water molecules at this low temperature indicates that they are lattice held. The second stage of decomposition ranges from 490 to 592 K. A weight loss of 27% occurs during this stage. The summit temperature as given by the DTG curve is 568 K. The third stage of decomposition extends from 592 to 680 K. The peak temperature at this stage is 662 K and the weight loss is 13.8%. The fourth stage of decomposition is from 680 to 736 K. The peak temperature from the DTG curve is 728 K. The TG curve exhibits a second plateau after 736 K showing the completion of decomposition. The last three stages of decomposition are attributed to the complete removal of the ligand from the complex. The residual mass of 24.28% (theoretical 24.52%) shows that the final decomposition product is the stable metal oxide.

For the complex, $[VO(DEBCP)]\cdot 2H_2O$, the TG plateau is up to 340 K indicating that this complex is stable up to 340 K. The complex decomposes in four stages. The first stage of decomposition is from 340 to 470 K. The peak temperature at this stage is 385 K. The mass loss at this stage is about 9% which corresponds to the loss of water molecules from the complex. The loss of water molecules at this low temperature shows that they are lattice held. The second stage of decomposition is from 470 to 581 K. The summit temperature at this stage is 523 K and the mass loss is 29.5%. The third stage of decomposition is from 581 to 670 K. The mass loss during this interval is only 14.8%. The peak temperature from the DTG curve is 638 K. The fourth stage of decomposition is in between 670 and 722 K. The peak temperature from the DTG curve is 703 K. The TG curve shows a second plateau after 722 K indicating the completion of decomposition. The independent pyrolysis shows that the final decomposition product is the stable metal oxide.

Conclusion

From the above experimental evidences, it may be concluded that the ligand $DEBCPH_2$ acts as a pentadentate ligand in dioxouranium(VI) complex. Two additional coordination sites of central uranium were occupied by the two uranyl oxygen atoms. Thus, the coordination number of the central metal ion is seven. In the oxovanadium(IV) complex $DEBCPH_2$ acts as a tetradentate ligand with the two secondary amide nitrogen atoms and the two carboxylate oxygen atoms as 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 ligand $PBCPH_2$ acts as a tetradentate ligand in dioxouranium(VI) and oxovanadium(IV) complexes with the two amide nitrogen atoms and the two carboxylate oxygen atoms as donor sites. In the dioxouranium(VI) complex, two additional sites of central uranium are occupied by the two uranyl oxygen atoms. As a result, the coordination number of the central metal ion is six in the complex of dioxouranium(VI) with $PBCPH_2$. In the case of oxovanadium(IV) complex, 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 infrared spectral and thermal studies reveal the presence of lattice water in the oxovanadium(IV) complexes with both $PBCPH_2$ and $DEBCPH_2$.

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