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Synthesis and Characterization of Some Mixed Ligand Complexes of Thorium(IV) and Dioxouranium(VI) with 1-Carbamido-3-Methylpyrazol-5-One and Various Anions

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A series of 10 mixed ligand complexes of two actinide metal ions, *viz.*, Th(IV) and UO_2(VI) with 1-carbamido-3-methylpyrazol-5-one (CMP) and various anions such as nitrate, acetate, thiocyanate, oxalate and sulphate have been synthesised and characterized on the basis of elemental analysis, molecular mass, molar conductance, IR spectra, TG and DTG data. These complexes have the general formulae $[(Th(CMP)_2(a)_4)]$, $[(Th(CMP)_2(aa)_2)]$, $[(UO_2(CMP)_2(a)_2)]$ and $[(UO_2(CMP)_2(aa))]$, where a = monovalent anions such as acetate, nitrate and thiocyanate and aa = divalent anions such as oxalate and sulphate. In these complexes, CMP acts as a neutral bidentate ligand, the anions such as acetate, nitrate and thiocyanate act as monovalent unidentate ligands, and the anions such as oxalate and sulphate act as divalent bidentate ligands.

INTRODUCTION

1-Carbamido-3-methylpyrazol-5-one (CMP) forms stable complexes with thorium(IV) nitrate.[1] From the literature it seems that CMP has not been used as a ligand for the uranyl species. Moreover, the coordination behaviour of CMP towards Th(IV) and UO_2(VI) ions in presence of various coordinating anions has not been studied so far. Therefore, it is interesting to synthesize some mixed ligand complexes of these two actinide ions with CMP and certain anions with a view to examine the coordination behaviour of CMP towards these actinide ions in presence of different coordinating anions.

The ligand, CMP ,has four potential donor atoms, *viz.*, the ring carbonyl oxygen, side carbonyl oxygen, amino nitrogen of the carbamido part and imino nitrogen of the ring. It is not likely that all the four donor atoms would be utilized by a particular metal ion in a complex. Therefore, the present investigation is to ascertain the nature of coordination of CMP with two actinide ions in presence of certain coordinating anions. The structure of the ligand can be represented as shown in Fig. 1.

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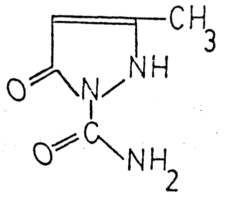

Fig. 1. 1-Carbamido-3-methylpyrazol-5-one (CMP).

EXPERIMENTAL

The ligand CMP was prepared by the literature method.[2] Equimolar quantities of semicarbazide hydrochloride and ethyl acetoacetate were mixed together in methanol and stirred well to get the crystals of CMP. The ligand formed was recrystallized from hot water.

On refluxing the respective nitrates of Th(IV) and UO_2(VI) with CMP in the mole ratio 1 : 2 in acetonitrile, the corresponding nitrato complexes were formed. The complexes have to be dried *in vacuo* over phosphorus(V) oxide to get non-hydrated products. From these nitrato complexes, other mixed ligand complexes have been prepared by substituting other anions for nitrate ions All the 10 complexes prepared are non-hygroscopic crystalline solids with varying colours. They are sparingly soluble in benzene, ethanol and methanol and insoluble in petroleum ether and chloroform.

The TG and DTG curves of these complexes were recorded simultaneously on a thermal analyser from ambient to 700°C. The mass % *vs.* temperature curves obtained were redrawn in appropriate scales. Independent pyrolysis experiment in air was also carried out for each of the complexes studied, and loss of mass determined in each case was compared with that obtained from TG.

The metal contents of the complexes were obtained by oxalate oxide method. The molar conductivities of the complexes in acetonitrile, methanol, and nitrobenzene (*ca* 10^{-3} M soultions) were measured at room temperature (28 ± 2°C) using an ELICO conductivity bridge type CM82T with a dip-type cell having Pt electrodes (cell constant = 1.64 cm^{-1}). The electronic spectra of the ligand and the complexes were recorded in acetonitrile. (*ca* 10^{-3} M solutions) in the range 185–900 nm. The IR spectra of the ligand and the complexes were recorded in KBr in the range 4000–400 cm^{-1}. Molecular masses of the complexes were determined by Rast method using biphenyl as the solvent.[4] The TG and DTG curves of the complexes were recorded on a thermal analyser from ambient to 700°C.

RESULTS AND DISCUSSION

From the analytical, molecular mass and conductance data (Tables 1 and 2) the complexes have the general formulae $[Th(CMP)_2a_4]$, $[Th(CMP)_2(aa)_2]$, $[UO_2(CMP)_2(a)_2]$ and $[UO_2(CMP)_2(aa)]$, where 'a' and 'aa' represent the monovalent and divalent anions, *viz.*, NO_3^-, OAc^-, NCS^-, SO_4^{2-}, $C_2O_4^{2-}$. Molar conductance values of the complexes in acetonitrile, methanol and nitrobenzene are in the ranges corresponding to those of non-electrolytes in these solvents. The conductance values suggest that all the anions act as additional ligands in these complexes, and, therefore, all the complexes are neutral.

TABLE-1
ANALYTICAL AND MOLECUALR WEITGHT DATA OF Th(IV) AND UO_2(VI) COMPLEXES OF CMP AND VARIOUS ANIONS

Complex	Colour	Molecular mass Found (Calcd.)	% Analysis, found (calcd.)	
			Metal	Anion
$[Th(CMP)_2(NO_3)_4]$	Yellow	758 (762)	31.40 (31.20)	31.86 (32.53)
$[UO_2(CMP)_2(NO_3)_2]$	Yellow	671 (676)	35.30 (35.20)	18.98 (18.34)
$[Th(CMP)_2(NCS)_4]$	Yellow	728 (746)	29.90 (31.10)	30.24 (31.09)
$[UO_2(CMP)_2(NCS)_2]$	Yellow	653 (668)	35.90 (35.60)	16.54 (17.36)
$[Th(CMP)_2(C_2O_4)_2]$	Reddish brown	678 (690)	27.80 (27.80)	24.87 (25.50)
$[UO_2(CMP)_2(C_2O_4)]$	Yellow	638 (640)	30.10 (30.50)	14.34 (13.75)
$[Th(CMP)_2(SO_4)_2]$	Pink	696 (706)	32.60 (32.90)	28.93 (27.19)
$[UO_2(CMP)_2(SO_4)]$	Yellow	642 (648)	36.60 (36.70)	13.58 (14.81)
$[Th(CMP)_2(OAc)_4]$	Yellow	736 (750)	30.10 (30.00)	C = 30.10 (28.80)* H = 3.01 (3.46) N = 10.80 (11.20)
$[UO_2(CMP)_2(OAc)_2]$	Yellow	658 (670)	29.50 (29.30)	C = 26.13 (25.07) H = 3.48 (2.98) N = 13.46 (12.53)

*CHN data since estimation of acetate ion could not be done

TABLE-2
MOLAR CONDUCTANCE DATA AND YIELDS OF COMPLEXES

Complex	Molar conductance in ohm^{-1} cm^2 mol^{-1}			Yield (%)
	Acetonitrile	Methanol	Nitrobenzene	
$[Th(CMP)_2(NO_3)_4]$	8.10	9.00	0.50	79
$[Th(CMP)_2(OAc)_4]$	14.80	6.10	0.20	66
$[Th(CMP)_2(NCS)_4]$	33.80	47.20	1.50	62
$[Th(CMP)_2(C_2O_4)_2]$	71.20	73.20	2.30	63
$[Th(CMP)_2(SO_4)_2]$	6.70	8.10	0.50	65
$[UO_2(CMP)_2(NO_3)_2]$	6.80	7.30	0.20	83
$[UO_2(CMP)_2(OAc)_2]$	2.10	7.20	0.80	76
$[UO_2(CMP)_2(NCS)_2]$	46.80	45.30	1.10	73
$[UO_2(CMP)_2(C_2O_4)]$	68.30	71.20	2.10	74
$[UO_2(CMP)_2(SO_4)]$	4.30	9.60	0.20	72

The electronic spectra of the ligand and the complexes were recorded in acetonitrile. Important electronic spectral bands and their tentative assignments are presented in Table-3. The spectrum of the ligand shows two absorption maxima at 33.33 and 45.45 kK, which are assigned respectively to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In the spectra of the complexes these bands are slightly red shifted and they appear at 31.25 and 41.66 kK along with an additional band at 47.61 kK. The bands at 41.66 and 47.61 kK are the split bands of the $\pi \rightarrow \pi^*$ transition in the complexes. The spectra of all the complexes are almost similar to that of the ligand suggesting that the electronic transitions are mainly localised on the ligand moiety.

TABLE-3
ELECTRONIC SPECTRAL BANDS* OF CMP AND THE COMPLEXES

CMP	Complexes of Th(IV)					Complexes of UO_2(VI)					Assignments
	NO_3^-	OAc^-	NCS^-	$C_2O_4^{2-}$	SO_4^{2-}	NO_3^-	OAc^-	NCS^-	$C_2O_4^{2-}$	SO_4^{2-}	
33.33	31.25	31.25	31.25	31.25	31.25	31.25	31.25	31.25	31.25	31.25	$n \rightarrow \pi^*$
45.45	41.66	41.66	41.66	41.66	41.66	40.00	41.66	41.66	41.66	41.66	$n \rightarrow \pi^*$
—	47.61	47.61	47.61	47.61	47.61	47.61	47.61	45.45	47.61	47.61	$n \rightarrow \pi^*$

*$\bar{\nu}_{max}$ in kK.

Important IR spectral bands of the ligand and the complexes are presented in Tables 4 and 5. The spectrum of the ligand exhibits two strong bands at 3400 and 3300 cm^{-1}, which are attributed to the stretching vibrations of the NH_2 group. In the spectra of all the complexes, these two bands are observed without any change in position indicating that the NH_2 group is not participated in coordination. The spectrum of the ligand also exhibits strong bands at 1720 and at 1640 cm^{-1}, which are assigned to $\nu(C{=}O)$ modes of the side carbonyl of the amide part and the ring carbonyl group, respectively. In the spectra of the complexes both these bands are shifted to lower wave number regions at 1680 and at 1610 cm^{-1}, respectively. These shifts suggest that both the carbonyl oxygen atoms of CMP take part in coordination in the present complexes. The bands corresponding to $\nu(CH)_3$ and pyrazolone ring and other modes of CMP molecule are presented in the same region in the spectra of the ligand and the complexes. Hence, CMP acts as a neutral bidentate ligand bonding through the oxygen atoms of both the carbonyl groups with the formation of a six-membered ring, which imparts stability to the complexes.

The IR spectra of the nitrato complexes exhibit three additional bands at 1440, 1320 and 1010 cm^{-1}, which are assigned respectively to ν_4, ν_1 and ν_2 modes of the coordinated nitrate ions. The magnitude of separation between the split bands ν_4 and ν_1 is of the order of *ca.* 120 cm^{-1} indicating that the nitrate ions are coordinated to the metal ions unidentately. This is further confirmed by the conductivity values of these nitrato complexes.

TABLE-4

INFRATED SPECTRAL BANDS (cm^{-1}) OF CMP AND THE COMPLEXES OF Th(IV) WITH CMP AND VARIOUS ANIONS

CMP (Ligand)	NO$_3^-$ Complex	OAc$^-$ Complex	NCS$^-$ Complex	C$_2$O$_4^{2-}$ Complex	SO$_4^{2-}$ Complex	Assignments
3400 s	3400 br	3400 s	3400 s	3400 s	3400 s	ν(N—H)
3300 s	3300 br	3300 br	3300 br	3300 s	3300 s	
2940 m	2940 m	2940 m	2940 m	2940 m	2940 m	ν(CH$_3$)
—	—	—	2050 s	—	—	ν(CN) of NCS$^-$
1720 s	1680 s	1680 s	1680 s	1680 s	1680 s	ν(C=O) (amide)
—	—	1660 s	—	1660 s	—	ν_{asym}(OCO) of COO$^-$
1640 s	1610 s	1610 vs	1610 vs	1610 vs	1610 vs	ν(C=O) (ring carbonyl)
1590 s	1590 s	1590 s	1590 s	1590 s	1590 s	Stretching of pyrazolone ring
1480 s	1480 s	1480 s	1480 s	1480 s	1480 s	ν(C—N)
—	1440 s	—	—	—	—	ν_4(NO$_3^-$)
1400 w	1400 w	1400 w	1400 w	1400 w	1400 w	ν(CH$_3$)
—	—	1380 vs	—	1380 vs	—	ν_s (OCO) of COO$^-$
—	1320 m	—	—	—	—	ν_1(NO$_3^-$)
—	—	—	—	—	1210 s	ν_3(OSO$_3$) of SO$_4^{2-}$
—	—	—	—	—	1140 s	
—	—	—	—	—	1080 s	ν_3(OSO$_3$) of SO$_4^{2-}$
—	1010 s	—	—	—	—	ν_2(NO$_3^-$)
—	—	—	—	—	970 s	ν_1(OSO$_3$) of SO$_4^{2-}$
—	—	—	860 s	—	—	ν(CS) of NCS$^-$
—	—	—	480 s	—	—	ν(NCS) of NCS$^-$

The spectra of the acetato complexes exhibit two bands at 1660 and 1380 cm^{-1}, which are not present in the spectrum of the ligand. These bands are assignable respectively to ν_{asym}(OCO$^-$) and ν_{sym}(OCO$^-$) modes of the coordinated carboxylate group. In the spectra of the complexes the position of ν_{asym}(OCO$^-$) is shifted to higher region than the position in the spectrum of the free acetate at 1560 cm^{-1}, and ν_{sym}(OCO$^-$) mode is shifted to a lower region than that of the free acetate at 1416 cm^{-1}. These shifts indicate that the acetate ion is coordinated to the metal ions in a unidentate fashion.[6–8] Molar conductance values of these complexes support the involvement of these ions in coordination in the present complexes.

The spectra of the thiocyanato complexes exhibit three bands at 2050, 800, 480 cm^{-1}, which are assigned respectively to ν(CN), ν(CS) and δ(NCS) modes of the coordinated thiocyanate. Since ν(CN) mode is lower than 2100 cm^{-1} and ν(CS) vibration is greater than 720 cm^{-1}, the thiocyanate ions are coordinated to the metal ions through nitrogen atom in a unidentate fashion.[9–11]

In the spectra of the oxalato complexes there are two bands at 1660 and 1380 cm^{-1}, which are assigned to ν_{asym}(OCO$^-$) and ν_{sym}(OCO$^-$) modes of the bidentately coordinated dicarboxylate ion.[12] Hence, oxalate ion is coordinated bidentately to the metal ions with a chelate structure, which is supported by the non-electrolytic behaviour of their complexes in solution.

TABLE-5

INFRARED SPECTRAL BANDS (cm^{-1}) OF CMP AND THE COMPLEXES OF UO_2(VI) WITH CMP AND VARIOUS ANIONS

CMP (Ligand)	NO_3^- Complex	OAc^- Complex	NCS^- Complex	$C_2O_4^{2-}$ Complex	SO_4^{2-} Complex	Tentative assignments
3400 s	3400 br	3400 s	3400 s	3400 s	3400 s	ν(N—H)
3300 s	3300 br	3300 s	3300 s	3300 s	3300 s	
2940 m	2940 m	2940 m	2940 m	2940 m	2940 m	$\nu(CH_3)$
—	—	—	2050 s	—	—	ν(CN) of NCS^-
1720 s	1680 s	1680 s	1680 w	1680 s	1680 s	ν(C=O) (amide)
—	—	1660 s	—	1660 w	—	ν_{asym}(OCO) of COO^-
1640 vs	1610 vs	1610 vs	1610 vs	1610 vs	1610 vs	ν(C=O) (ring carbonyl)
1590 s	1590 s	1590 s	1590 s	1590 s	1590 s	Stretching of pyrazolone ring
1480 s	1480 s	1480 s	1480 s	1480 s	1480 s	ν(C—N)
—	1440 s	—	—	—	—	$\nu_4(NO_3^-)$
1400 w	1400 w	1400 w	1400 w	1400 w	1400 w	$\nu(CH_3)$
—	—	1380 vs	—	1380 vs	—	ν_{sym} (OCO) of COO^-
—	1320 m	—	—	—	—	$\nu_1(NO_3^-)$
—	—	—	—	—	1210 s	$\nu_3(OSO_3)$ of SO_4^{2-}
—	—	—	—	—	1140 s	
—	—	—	—	—	1080 w	
—	1010 s	—	—	—	—	$\nu_2(NO_3^-)$
—	—	—	—	—	970 s	$\nu_1(OSO_3)$ of SO_4^{2-}
—	940 vs	940 vs	940 vs	940 vs	940 vs	ν_3(O=U=O)
—	—	—	860 s	—	—	ν(CS) of NCS
—	—	—	480 w	—	—	ν(NCS) of NCS

The sulphato complexes of Th(IV) and UO_2(IV) with CMP exhibit three IR bands at 1210, 1140, and 1080 cm^{-1}. These are the split bands of ν_3 mode of the bidentately coordinated sulphate ion.[13, 14] Therefore, sulphate ion is coordinated to the metal ions through oxygen atom in a bidentate fashion in the present complexes. The non-electrolytic behaviour of these complexes in acetonitrile, methanol and nitrobenzene supports the coordination of sulphate ion.

The spectra of all the UO_2(VI) complexes have an additional strong band in the region 940 cm^{-1}, which has no parallel band in the spectrum of the free ligand or in the spectra of Th(IV) complexes. This band is attributed to

ν_{asym}(O=U=O) mode of the UO_2^{2+} group. Since there is no band corresponding to ν_{sym}(O=U=O) mode, it is assumed that the oxygen atoms of the UO_2(VI) are in *trans* position in these complexes.

Thermal studies were conducted on each of the representative complexes of Th(IV) and UO_2(VI). The two complexes chosen are the nitrato complexes of Th(IV) and UO_2(VI) of CMP, *viz.*, $[Th(CMP)_2(NO_3)_4]$ and $[UO_2(CMP)_2(NO_3)_2]$. The thermal decomposition data including the plateau in TG, peak temperature and peak width in DTG are given in Table-6. Independent pyrolysis experiment in air was also carried out for each of the complexes studied. For this a known amount of the complex was heated in a porcelain crucible up to *ca.* 700°C for 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.

TABLE-6
THERMAL DECOMPOSITION DATA OF THE NITRATO COMPLEX

Complex	Plateau in TG (°C)	Peak in DTG (°C)	Peak width in DTG (°C)	Final residue	Final mass loss		
					TG (%)	Independent pyrolysis (%)	Theotetical (%)
$[Th(CMP)_2(NO_3)_4]$	upto 200	260	200–300	ThO_2	66.10	65.80	65.30
	above 425	305	300–425				
$[UO_2(CMP)_2(NO_3)_2]$	upto 250	275	250–340	U_3O_8	59.40	58.80	58.50
	above 525	375	340–410				

The m *vs.* T curves (TG curves) and Δm/ΔT *vs.* T curves (DTG curves) of the two complexes studied are presented in Figs. 2 and 3. For the complexes, $[Th(CMP)_2(NO_3)_4]$ the TG plateau up to *ca.* 200°C shows that the complex starts decomposition after this temperature. There are two decompostion stages as indicated by the DTG peaks at 260°C and 305°C. The TG curve exhibits a second plateau after 425°C. This shows the completion of the decomposition. The independent pyrolysis experiment shows that the final decomposition product is ThO_2 in conformity with the mass loss data obtained from TG.

For the uranyl complex, $[UO_2(CMP)_2(NO_3)_2]$ the TG plateau is up to 250°C indicating that this complex is stable up to *ca.* 250°C. The DTG curve has three peaks at 275, 375 and 460°C, showing that this complex undergoes decomposition in three stages unlike the thorium complex. The TG curve exhibits a second plateau after 525°C, indicating the completion of decomposition. The independent pyrolysis experiment shows that a final decomposition product is U_3O_8 which is in conformity with the mass loss data obtained from TG and independent pyrolysis.

On the basis of the observations and discussion it can be concluded that the primary ligand, CMP, acts as neutral bidentate ligand towards both Th(IV) and UO_2(VI) in presence of secondary anionic ligands In all these complexes, nitrate, acetate and thiocyanate ions act as monovalent unidentate ligands, whereas oxalate and sulphate ions act as divalent bidentate ligands. Thus a coordination number 8 is assigned to both the metal ions in these complexes.

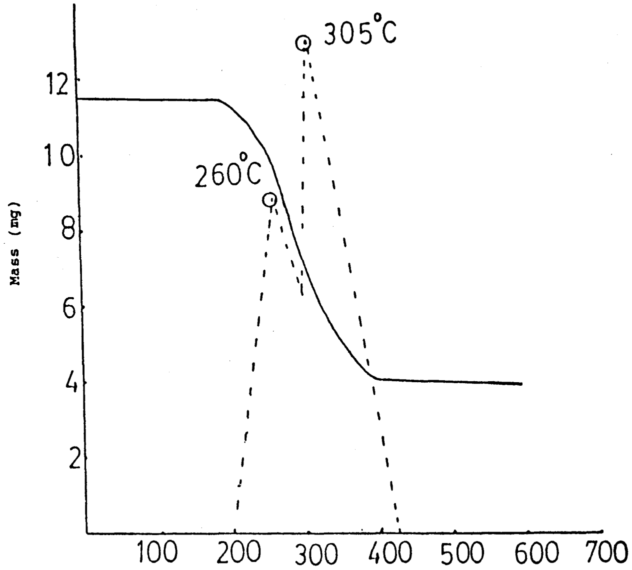

Fig. 2. TG and DTG curves of $[Th(CMP)_2(NO_3)_4]$ in AIR.

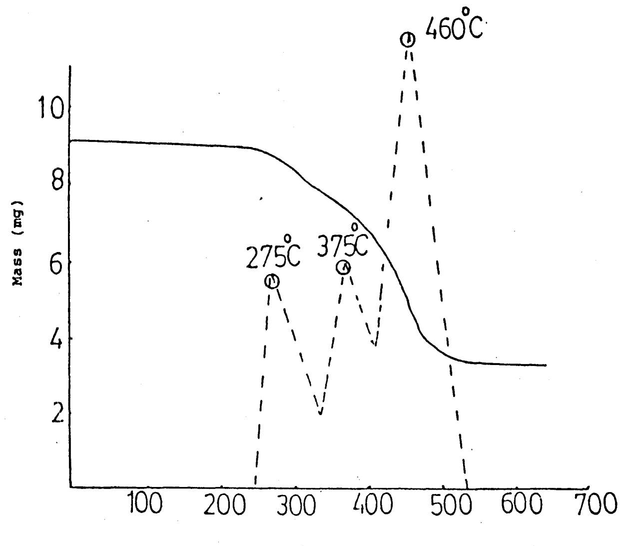

Fig. 3. TG and DTG curves of $[UO_2(CMP)_2(NO_3)_2]$in AIR.

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