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Synthesis and Characterization of Mixed Ligand Complexes of Thorium(IV) and Dioxouranium(VI) with Schiff Base of *p*-Anisidine and Dimethyl Sulphoxide

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A series of six mixed ligand complexes of the actinide metal ions, *viz.*, Th(IV) and UO_2(VI) with a Schiff base of *p*-anisidine and dimethyl sulphoxide and various anions such as acetate, nitrate, sulphate and thiocyanate have been synthesized and characterized. The analytical data include elemental analysis, molecular weight determinations, conductivity, spectral and thermal studies. The composition of these complexes are $[Th(DMDA)_4(DMSO)_2(a)_4]$, $[Th(DMDA)_4(DMSO)_2(aa)_2]$, $[UO_2(DMDA)_2(DMSO)_2(a)_2]$ and $[UO_2(DMDA)_2(DMSO)_2(aa)]$, where DMDA = 4,4′-dimethyl diphenyl azomethine, a = monovalent anion such as acetate, nitrate and thiocyanate and aa = divalent anion such as sulphate. In these complexes schiff base of *p*-anisidine acts as a neutral monodentate ligand, DMSO and monovalent anion acts as unidentate ligand and divalent sulphate ion acts as a bidentate ligand

INTRODUCTION

From literature it seems that the coordination behaviour of the Schiff base 4,4′-dimethoxy diphenyl azomethine (DMDA) towards Th(IV) and UO_2(VI) ions in presence of dimethyl sulphoxide (DMSO) and various coordinating anions has not been studied so far. Therefore, we prepared some mixed ligand complexes of these two actinide ions with the Schiff base of *p*-anisaldehyde and dimethyl sulphoxide in presence of coordinating anions such as acetate, nitrate, sulphate and thiocyanate.

The ligand Schiff base has three potential coordination sites, *viz.*, two methoxy-oxygen and one imino-nitrogen. All the three donor atoms cannot be utilized by the metal ions in a complex. The present investigation is to ascertain the coordination behaviour of this polydentate Schiff base in presence of coordinating DMSO and various anions.

The structures of the lignd can be represented as in Fig. 1.

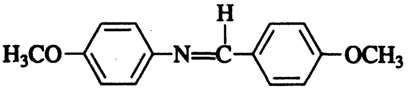

Fig. 1 4,4′-Dimethoxy diphenyl azomethine (DMDA)

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EXPERIMENTAL

The ligand DMDA was prepared by literature method. An ethanolic solution of *p*-anisidine and *p*-anisaldehyde in the molar ratio 1 : 1 was mixed and refluxed in a water bath for about 2 h. The resulting solution was concentrated by evaporation in a water bath. Cooled to get solid crystals of Schiff base (DMDA). Filtered, washed with ether and dried *in vacuo* over phosphorus(V) oxide and the melting point was noted.

The nitrato complex of thorium was prepared by mixing equal volumes (20 cm^3) of solutions of thorium nitrate, Schiff base and DMSO in acetone solvent in the molar ratio 1 : 4 : 2 and refluxed on a water bath for about 4 h. The resulting solution was concentrated to get a brown viscous liquid. It was extracted with benzene and then with diethyl ether to get a brown coloured solid complex. It was dried *in vacuo* over phosphorous(V) oxide.

The acetato complex of uranium is prepared by refluxing equal volumes of the solution of uranyl acetate, Schiff base and DMSO in the molar ratio 1 : 2 : 2 in acetone. It is concentrated and extracted with benzene and diethyl ether to get the brown coloured solid complex. Melting point of this complex was recorded. The other anionic complexes were prepared from these nitrato and acetato complexes by substituting other anions (SCN^- and SO_4^{2-}) for nitrate or acetate ions. All the complexes are non-hygroscopic crystalline brown solids. They are sparingly soluble in benzene, ethanol and methanol and insoluble in pertroleum ether and chloroform.

The TG and DTG curves of these complexes were recorded on a thermal analyser from ambient to 700°C. The mass percentage *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 content of the complexes was obtained by oxalate oxide method. The molar conductivities of the complex in acetonitrile, methanol and nitrobenzene were measured at room temperature. The IR spectra of the ligand and complexes were recorded in KBr in the range 4000–400 cm^{-1}. Molecular masses of complexes were determined by Rast method using biphenyl as solvent.[1] The anion content was estimated gravimetrically.

RESULTS AND DISCUSSION

From the analytical data (Tables 1 and 2) the complexes have the general formulae: $[Th(DMDA)_4(DMSO)_2x_4]$ and $[UO_2(DMDA)_2(DMSO)_2x_2]$ where $x = NO_3^-, OAc^-, SCN^-, 0.5\ SO_4^{2-}$.

Molar conductivity values of the complexes in acetonitrile, methanol and nitrobenzene were in the ranges corresponding to those of non-electrolytes in these solvents. The conductance values suggest that the anions were coordinated to the metal ions and hence the anions act as additional ligands.

TABLE-1

Complex	Colour	Molecular mass	% Analysis	
			Metal	Anion
$[Th(DMDA)_4(DMSO)_2(NO_3)_4]$	Dark brown	1601.55	14.23 (14.48)	14.90 (15.48)
$[Th(DMDA)_4(DMSO)_2(SCN)_4]$	Brown	1285.55	17.99 (18.05)	17.60 (18.04)
$[Th(DMDA)_4(DMSO)_2(SO_4)_2]$	Brown	1545.55	14.99 (15.01)	11.80 (12.42)
$[UO_2(DMDA)_2(DMSO)_2(OAc)_2]$	Dark brown	1026.88	23.74 (23.17)	CHN data taken
$[UO_2(DMDA)_2(DMSO)_2(SCN)_2]$	Brown	946.75	25.01 (25.13)	11.81 (12.25)
$[UO_2(DMDA)_2(DMSO)_2(SO_4)]$	Brown	1004.88	23.44 (23.68)	9.10 (9.55)

TABLE-2

Complexes	Molar conductance in ohm^{-1} cm^2 mol^{-1}			Yield (%)
	Acetonitrile	Methanol	Nitrobenzene	
$[Th(DMDA)_4(DMSO)_2(NO_3)_4]$	5.8	9.2	0.10	73
$[Th(DMDA)_4(DMSO)_2(SCN)_4]$	12.1	4.8	0.38	80
$[Th(DMDA)_4(DMSO)_2(SO_4)_2]$	2.1	3.2	0.15	78
$[UO_2(DMDA)_2(DMSO)_2(OAc)_2]$	8.9	5.3	0.20	70
$[UO_2(DMDA)_2(DMSO)_2(SCN)_2]$	6.7	7.8	0.15	81
$[UO_2(DMDA)_2(DMSO)_2(SO_4)]$	4.1	8.1	0.50	78

TABLE-3

Bacteria	$[UO_2(DMDA)_2(DMSO)_2(OAc)_2]$	$[Th(DMDA)_4(DMSO)_2(NO_3)_4]$
Pseudomonas aeruginosa	14 mm	12 mm
Staphylococcus aureus	16 mm	No inhibition
Enterobacter agglomerans	No inhibition	No inhibition
Klebsiella pneumoniae	No inhibition	14 mm

The IR spectrum of the ligand exhibits a strong band at 1633 cm^{-1} which is attributed to the stretching vibrations of C═N group. In the spectrum of the complexes this band is shifted to lower wave number region at 1607 cm^{-1}. This shift suggests that C═N group of the ligand takes part in coordination in the present complexes. The band at 1250 cm^{-1} in the spectrum of ligand is that of stretching vibration of C—O of methoxy group which is retained in the spectra of complexes without any change in position. This indicates that OCH_3 group of the ligand was not involved in bonding. The bands corresponding to $\nu(CH_3)$, phenyl ring and other modes of the ligand molecules are present in the same region in the spectra of the complexes. Hence DMDA acts as a neutral monodentate ligand bonding through the nitrogen atom of azomethine group.

The lowering in stretching frequencies of the order of 80 cm^{-1} observed in the complexes at 1020 cm^{-1} is indicative of the bonding from the oxygen atom of the sulphoxide.[2] The nitrato complexes show new bands at 1476, 1400 and 1282 cm^{-1} which are assigned respectively to ν_4, ν_1 and ν_2 modes of the coordinated nitrate ion. The magnitude of separation between the split bands is of the order of 76 cm^{-1} indicating that the nitrate ions are coordinated to the metal ion unidentately. This is further confirmed by the conductivity values.

The spectra of acetato complexes exhibit two bands at 1662 cm^{-1} and 1256 cm^{-1} which are not present in the spectra of the ligand. These bands are assignable to $\nu_{asym}(OCO^-)$ and $\nu_{sym}(OCO^-)$ modes of coordinated carboxylate group. The large separation between these two bands confirms the unidentate coordination of carboxylate ion.[3–5] Molar conductance values support the involvement of these ions in coordination.

The bands due to the coordinated nitrate ion and carboxylate ion disappear in its thiocyanate and sulphate complexes. Both the sulphate complexes show three new absorption bands around 1247, 1177 and 1086 cm^{-1} which are not observed in the spectra of ligands or other complexes. These are assigned to ν_3 of chelating bidentate sulphato group. The spectra of the thiocyanate complexes exhibit two bands at 2050 and 800 cm^{-1} which are assigned to $\nu(CN)$ and $\nu(CS)$ modes of the coordinated thiocyanate. Since $\nu(CN)$ mode is lower than 2100 cm^{-1} and $\nu(CS)$ vibration is greater than 720 cm^{-1}, the thiocyanate ions are coordinated to the metal ion through nitrogen atom in a unidentate fashion.[6–8] In all the uranyl complexes there is one more band appearing in between 922–910 cm^{-1} which is attributable to the asymmetric stretching vibration ν_3 of the O=U=O group.

The magnetic data agree well with the theoretical diamagnetic values expected for a $5f^0$ system.

Thermal studies were conducted on $[Th(DMDA)_4(DMSO)_2(NO_3)_4]$ and $[UO_2(DMDA)_2(DMSO)_2(OAc)_2]$ complexes. 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 750°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.

For the complex $[Th(DMDA)_4(DMSO)_2(NO_3)_4]$ the TG plateau up to 195°C shows its stability and the complex starts decomposition after this temperature. There are two decomposition stages as indicated by the DTG peaks at 210°C and 450°C. The TG curve exhibits a second plateau after 500°C. This shows the completion of the decomposition. The independent pyrolysis shows that the final decomposition product is ThO_2 in conformity with the mass loss data obtained from TG.

For the uranyl complex $[UO_2(DMDA)_2(DMSO)_2(OAc)_2]$ the TG plateau is up to 190°C indicating that this complex is stable up to 190°C. The DTG curve has two peaks at 204°C and 550°C showing that this complex undergoes decomposition in two stages. The TG curve exhibits a second plateau after 570°C indicating the completion of decomposition. The complex shows a weight loss of 33.71% at 204.3°C. The complex decomposes rapidly at 204.3°C due to the 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 U_3O_8 at about 550°C with a weight loss of 62.5% (theoretical 62.2%).

All these studies confirm the structure of the complexes as $[UO_2(DMDA)_2(DMSO)_2(x)_2]$ and $[Th(DMDA)_4(DMSO)_2(x)_4]$, where $x = OAc^-, NO_3^-, SCN^-$. For sulphato complexes the structure was found to be $[UO_2(DMDA)_2(DMSO)_2(x)]$ and $[Th(DMDA)_4(DMSO)_2(x)_2]$, where $x = SO_4^{2-}$. Thus a coordination number of 8 is assigned to uranium in all the three uranyl complexes and 10 for thorium.

The antimicrobial activities of compounds were tested by plate diffusion method as described in Indian Pharmacopoeia.[9] It may be observed that the compounds indicate mutually antagonistic or synergistically promoting antimicrobial effect.

Compounds $[Th(DMDA)_4(DMSO)_2(NO_3)_4]$ and $[UO_2(DMDA)_2(DMSO)_2(OAc)_2]$ were tested against different bacteria like *Pseudomonas aeruginosa, Staphylococcus aureus, Enterobacter agglomerans, Klebsiella pneumoniae* and *Escherichia coli* using filter paper disc method.[10] The filter paper discs soaked in 4% solution of the compounds in acetone were placed at the centre of organism seeded agar plates (petridishes). The petridishes were incubated at 28°C for 16 h. The activities were noted by measuring the diameters of inhibition zones in mm. The results obtained are summarised in Table-3.

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