

Kinetic and Antimicrobial Studies on Some Novel Mixed Ligand Complexes of Thorium(IV) and Dioxouranium(VI) Ions

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A new series of mixed ligand complexes of Th(IV) and UO₂(VI) with a Schiff base derived from vanillin and *p*-anisidine (HMBAMB), dimethyl sulphoxide (DMSO) and various anions have been synthesized. These complexes were characterized by various physico-chemical data such as CHN, metal ion contents, spectral, magnetic and molar conductivities. The thermal stability along with the kinetic parameters were determined by mechanistic and non-mechanistic equations applicable to thermal decomposition studies. The mechanisms of different decomposition stages were proposed from the kinetic data. Antimicrobial activity of the ligand and the complexes against different bacteria was studied. From these experimental observations compositions of the complexes were ascertained to be [UO₂(HMBAMB)₄(DMSO)₂a₂], [UO₂(HMBAMB)₄(DMSO)₂(aa)], [Th(HMBAMB)₄(DMSO)₂(a)₄] and [Th(HMBAMB)₄(DMSO)₂(aa)₂] where HMBAMB is representing the ligand, 4N(4'-hydroxy-2'-methoxy-benzalidene)aminomethoxy benzene, a = monovalent anions such as acetate, nitrate and thiocyanate and aa = divalent anion, viz., sulphate. In these complexes, the primary ligands, viz., schiff base and DMSO act as neutral monodentate and the coordinating anions viz; acetate, nitrate, thiocyanate as monodentate and the sulphate ion as bidentate.

Key Words: Th(IV) and UO₂(VI) complexes, Kinetic, Antimicrobial.

INTRODUCTION

Coordination behaviour of the Schiff base 4N(4'-hydroxy-2'-methoxy benzalidene)aminomethoxy benzene (HMBAMB) towards thorium(IV) and dioxouranium(VI) in presence of DMSO and various anions were not reported so far. Hence an attempt is made to synthesize these complexes and to ascertain the coordination geometry, antibacterial activity and thermal stability of these complexes. Structural investigation of the complexes was done by various physico-chemical studies such as conductance, spectral and magnetic studies, CHN analysis and metal estimation.

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EXPERIMENTAL

The Schiff base 4-N(4'-hydroxy-2'-methoxy benzalidene)aminomethoxy benzene is synthesized by literature method¹. It was prepared by the condensation reaction of *p*-anisidine and vanillin. Equimolar methanolic solutions of *p*-anisidine (0.2 M) and vanillin (0.2 M) were refluxed on a water bath for about 2 h. The resulting mixture was concentrated and cooled to get the solid component. It was filtered, washed with ether and dried *in vacuo*. Recrystallized from methanol and tested the purity by noting the melting point.

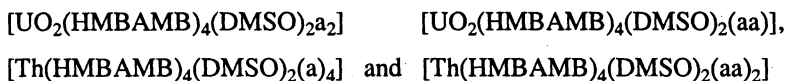
Acetato complex of uranium was prepared by mixing the acetic solutions of uranyl acetate (0.2 mmol), HMBAMB (0.8 mmol) and DMSO (0.4 mmol) and refluxing on a water bath for about 4 h. The brown liquid obtained was concentrated on a water bath and crystallized. The solid complex was filtered, washed repeatedly with benzene and then extracted with diethyl ether. It was dried *in vacuo* over phosphorus(V) oxide to get nonhygroscopic crystals. To prepare the nitrate complex of Th(IV) the same procedure was employed as before. The yield and melting point of the complexes were noted. The cyanato and sulphato complexes were prepared from acetato and nitrate complexes of uranium and thorium by substitution methods². Acetic solutions of acetato or nitrate complexes were refluxed with stoichiometric quantity of the respective anionic salts such as ammonium thiocyanate or lithium sulphate dissolved in aqueous acetone (50% v/v)

All the complexes were analysed for the metal content by oxalate-oxide method³. TG and DTG curves of the acetato complex were recorded on a thermal analyzer at a heating rate of 10°C/min. Elemental analyses of a few complexes were carried out (Table-1). IR Spectra of the ligand and all the complexes were recorded on a Perkin-Elmer-397 spectrophotometer using KBr disc technique at a range of 4000-400 cm⁻¹. The conductivities of all the complexes were measured in three solvents such as methanol, nitrobenzene and acetonitrile using a direct reading Elico conductivity bridge. Magnetic susceptibilities of acetato and nitrate complexes were recorded at room temperature. Molecular masses of all the complexes were determined by Rast's method using biphenyl as solvent. Antibacterial activity of the parent complexes against six different bacteria such as *Klebsiella pneumoniae*, *Proteus mirabilis*, *Enterobacter agglomerans*, *Pseudomonas aeruginosa*, *Escherichia coli*, *Staphylococcus aureus* were assessed.

RESULTS AND DISCUSSIONS

All the complexes are brown or black coloured and possess high melting point. They are nonhygroscopic, moderately soluble in acetone, methanol and acetonitrile and insoluble in benzene and diethyl ether. Analytical data of the complexes are presented in Table-1. CHN analysis data of the complexes were found to be in good agreement with the theoretical values. Molar conductivities of all these complexes in the three solvents such as nitrobenzene, acetonitrile and methanol are found to be in the range corresponding to that of nonelectrolytes (Table-1). The conductance values suggest that all the anions are coordinated to the central metal ion. Magnetic susceptibilities of the parent complexes were measured and

found to be diamagnetic as expected for a $5f^0$ system. From all these analytical results the complexes can be formulated as



where $\text{a} = \text{NO}_3^-$, OAc^- , SCN^- and $\text{aa} = \text{SO}_4^{2-}$

TABLE 1
ANALYTICAL DATA

Complexes	% Analysis, Found (Calcd.)			Conductance ($\text{ohm}^{-1} \text{cm}^{-1} \text{mol}^{-1}$)			Molecular mass, Found (Calcd.)
	C	H	N	Nitro- benzene	Methanol	Aceto- nitrile	
$[\text{UO}_2(\text{HMBAMB})_4(\text{DMSO})_2(\text{AC})_2]$	52.01 (51.86)	5.12 (4.99)	3.31 (3.56)	5.29	10.2	8.9	1565.20 (1573.50)
$[\text{Th}(\text{HMBAMB})_4(\text{DMSO})_2(\text{NO}_3)_4]$	46.43 (46.11)	4.44 (4.36)	6.99 (6.72)	4.30	3.5	14.2	1654.90 (1665.55)
$[\text{UO}_2(\text{HMBAMB})_4(\text{DMSO})_2(\text{SO}_4)]$	49.90 (49.50)	4.63 (4.55)	3.41 (3.61)	5.12	4.1	8.9	1539.86 (1551.50)
$[\text{Th}(\text{HMBAMB})_4(\text{DMSO})_2(\text{SO}_4)_2]$	47.89	4.62	3.19	4.01	8.9	13.2	1613.83 (1609.55)
$[\text{UO}_2(\text{HMBAMB})_4(\text{DMSO})_2(\text{SCN})_2]$	50.78	4.72	5.18	8.10	12.3	17.2	1555.20 (1571.50)
$[\text{Th}(\text{HMBAMB})_4(\text{DMSO})_2(\text{SCN})_4]$	49.9 (49.47)	4.43 (4.39)	6.62 (6.79)	3.20	8.1	6.3	1632.32 (1649.55)

The IR spectrum of the ligand exhibits a strong band at 1625 cm^{-1} , This is attributed to the stretching vibration of azomethine group. A corresponding band is observed in all the complexes with a downward shift of $20\text{-}25 \text{ cm}^{-1}$. This confirms the coordination of 'N' atom of $\text{C}=\text{N}$ group to the central metal ion⁴. A broad band was observed around $3432\text{-}3407 \text{ cm}^{-1}$ in all the complexes due to the stretching of intermolecularly hydrogen bonded $-\text{OH}$ group. Another strong band-observed at 1020 cm^{-1} in all the complexes shows the presence of coordinated $\text{S}=\text{O}$ moiety of DMSO in the complexes. There is no parallel band at this region in the ligand. The lowering in stretching frequency of DMSO is of the order of 80 cm^{-1} indicative of the bonding from 'O' atom of sulphoxide⁵. The ligand exhibits two bands around 2828 cm^{-1} and 1445 cm^{-1} which are retained in all its complexes indicating the non-participation of $-\text{OCH}_3$ group in coordination.

The nitrate complex of thorium exhibited three new bands at 1476 , 1390 and 1290 cm^{-1} which are absent in the spectrum of the ligand or in other anionic complexes. These are assigned respectively to ν_4 , ν_3 , 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 90 cm^{-1} indicating that the nitrate ions are coordinated unidentately to the metal ions. The acetato complex of uranium exhibited two additional bands at 1650 and 1250 cm^{-1} due to asymmetric and symmetric vibrations of COO^- groups. Since the difference between ν_a and ν_s is at a range of 400 cm^{-1} , a value far greater than that for ionic complexes, acetate ion is coordinated to the metal ion in a unidentate fashion⁶. In sulphate complexes of both Th(IV) and $\text{UO}_2(\text{VI})$, three bands are observed around 1240 , 1174 and 1084 cm^{-1} which are assigned to the stretching frequency of chelated bidentate sulphate ions. In both the thiocyanato complexes a sharp band is observed at 2050 cm^{-1} . This is attributed to the stretching vibration of NCS^- ion. Since this value is lower than 2100 cm^{-1} , the coordination through nitrogen atom of NCS^- ions is revealed. All the methyl complexes exhibited a strong band around $920\text{--}930\text{ cm}^{-1}$ corresponding to the ν_a ($\text{O}=\text{U}=\text{O}$) modes of UO_2^{2+} group. The band observed at 840 cm^{-1} is assigned to the symmetric stretching vibration of the uranyl ion. This indicates that the linearity of the $\text{O}=\text{U}=\text{O}$ is retained in the complexes.

TG and DTG curves for the acetato complex of uranium have been recorded. It undergoes a two stage decomposition as indicated by the DTG peaks at 225 and 507°C . A plateau up to 198°C in the TG curve indicates that the compound is stable up to this temperature and it shows the absence of coordinated water or other solvent molecules. The first stage decomposition starts at 198°C and gets completed at 257°C . The mass loss corresponds to the dissociation of two coordinated DMSO molecules. In the second stage of decomposition a plateau up to 435°C and after that the mass loss occurs up to 572°C . The mass of the final residue corresponds to the formation of the stable oxide U_3O_8 . The formation of the first decomposition product and final residue is substantiated by the agreeable results obtained from the mass loss data of TG and independent pyrolysis experiments.

Kinetic parameters such as energy of activation (E), pre-exponential factor (A) and entropy of activation (Δs) of each decomposition stage was calculated by applying nonmechanistic equations such as Coats-Redfern equation⁹, MKN equation¹², MacCallum-Tanner and Horowitz-Metzger¹¹ equation and values were compared (Table-2) ' α ' and ' T ' values for the computation of kinetic parameters are also presented in table-2. Kinetic parameters calculated are agreeable in the case of Coats-Redfern, MKN and MacCallum-Tanner equations. But a higher value is obtained in the case of Horowitz-Metzger equation due to the inherent error involved in deriving the equation. A negative value of entropy of activation for these two decomposition stages suggests that the activated complex has more ordered configuration than the reactant and the reaction in these cases may be described as slower than normal¹³.

Using nine mechanistic equations the values of E and A were calculated. It was found that for both decomposition stages Mampel equation gave the highest value for correlation coefficient (Table-3). Hence the rate controlling processes for these decompositions are random nucleation with one nucleus on each particle. A and E values calculated from mechanistic equations are also comparable with

the values obtained from non-mechanistic equation such as Coats-Redfern. Thus the proposed mechanism is acceptable.

TABLE 2
KINETIC PARAMETERS FOR THE THERMAL DECOMPOSITION OF
(UO₂(HMBAMB)₄(DMSO)₂(AC)₂ USING NON-MECHANISTIC EQUATIONS

	Stage I	Stage II	Stage I		Stage II		
			α	T	α	T	
n	1.1	1.04	0.1818	481	0.0860	713	
CR	108.94	128.74	0.2270	486	0.1300	723	
E	MKN	109.17	129.12	0.3727	496	0.2170	743
(kJ mol ⁻¹)	MT	109.86	132.41	0.4549	501	0.3040	753
	HM	115.98	144.98	0.5727	506	0.3010	763
	CR	1.26 × 10 ⁹	1.35 × 10 ⁶	0.6636	511	0.4780	773
A	MKN	1.42 × 10 ⁹	1.56 × 10 ⁶	0.7273	516	0.5652	783
(S ⁻¹)	MT	6.94 × 10 ⁸	1.33 × 10 ⁶	0.8182	521	0.6521	793
	HM	3.28 × 10 ¹⁰	1.73 × 10 ⁷			0.7391	803
	CR	-75.58	-135.54			0.9261	813
Δ_s	MKN	-73.91	-134.35			0.8695	823
(K ⁻¹ mol ⁻¹)	MT	-76.91	-135.69			0.9565	833
	HM	-57.85	-114.34				
	CR	0.9983	0.9983				
r	MKN	0.9989	0.9983				
	MT	0.9991	0.9986				
	HM	0.9988	0.9970				

CR: Coats-Redfern equation⁹

MT: MacCallum-Tanner equation¹⁰

T: Temperature (K)

MKN: Madhusudan-Krishnan-Ninan equation¹²

IBM: Horowitz-Metzger equation¹¹

r: Correlation coefficient

TABLE 3
Antibacterial activity of HMBAMB and [UO₂(HMBAMB)₄(DMSO)₂(AC)₂

Bacteria	Inhibition zones (mm)	
	HMBAMB	[UO ₂ (HMBAMB) ₄ (DMSO) ₂ (AC) ₂
<i>Klebsiella pneumoniae</i>	12	17
<i>Proteus mirabilis</i>	No inhibition	No inhibition
<i>Enterobacter agglomerans</i>	8	14
<i>Pseudomonas aeruginosa</i>	13	18
<i>Escherichia coli</i>	No inhibition	No inhibition
<i>Staphylococcus aureus</i>	13	17

The ligand and the parent complexes were screened for their antibacterial activity by plate-diffusion method. They were active against four strains and inactive towards the remaining two strains (Table-4). These results show that chelation has increased the antibacterial activity of the ligands¹⁴.

From these investigations it is concluded that all the complexes are neutral and each one of them contains four molecules of the Schiff base (HMBAMB), and two molecules of DMSO. Both thorium and uranium exhibited a coordination number of '10' in all the six complexes.

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