

## Note

### **THERMAL BEHAVIOUR OF URANIUM(VI) AND CERIUM(IV) COMPLEXES OF 1-(2'-HYDROXYBENZYL)-2-(2'-HYDROXYPHENYL)-BENZIMIDAZOLE**

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Derivatives of benzimidazoles play an extremely important part in the structure and function of a number of biologically significant molecules, generally by virtue of their being coordinated to a metal ion. Very few systems are reported in the literature showing the linear relationship between thermal stability of metal chelates and structure of chelating agents [1]. Thermal properties of metal chelates with various ligands have been studied earlier [2–7]. The chelating ligands used in these cases are mostly oximes. The renewed interest of the authors in the Schiff's base compounds is due to their high stability and their effective use in chemical separations [8,9]. Uranyl compounds with various nitrogen and oxygen donors have been extensively reviewed [10–16]. Though the synthesis and characterization of complexes of uranium(VI) and cerium(IV) with HBHPB have been reported earlier [17], we have not attempted to study the thermal behaviour of these complexes. Hence we report the thermal behaviour of the complexes of HBHPB with uranium(VI) and cerium(IV).

#### APPARATUS

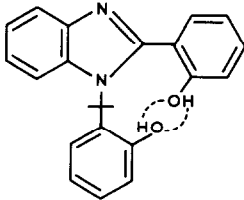
TGA and DTA were recorded on an Ulvac Sinku TA-1500 thermal analyser at the Indian Institute of Science, Bangalore.

#### SYNTHESIS AND CHARACTERISTICS OF THE LIGAND

1-(2'-Hydroxybenzyl)-2-(2'-hydroxyphenyl)-benzimidazole was prepared according to Subbarao and Ratnam [18], by refluxing 1,2-phenylene diamine with salicylaldehyde (1:3) in glacial acetic acid. The white product that separated was recrystallized from methanol.

The IR spectrum measured in KBr pellets showed a peak at  $1480\text{ cm}^{-1}$  which can be assigned to (C=N) stretching. A peak at  $3500\text{--}3700\text{ cm}^{-1}$

corresponding to the free phenolic  $-OH$  is not observed, instead a peak at  $3300\text{ cm}^{-1}$ , confirms the intramolecular hydrogen bonding of the two  $-OH$  groups [19–21]. Based on the above observations the structure of the ligand can be represented as:



	C	H	N
Calculated	75.94	5.61	8.86
Experimental	75.80	5.76	8.72

#### PREPARATION OF SOLID COMPLEXES

The complexes were prepared by refluxing methanolic solutions of the ligand and corresponding metal salts at  $70\text{--}80^\circ\text{C}$ . The solution containing the complex was evaporated in vacuo until the solid crystallized. The precipitates were filtered off and washed with aqueous methanol. The product was dried in vacuo for 24 h.

#### THERMAL PROPERTIES

All of the hydrated chelates showed weight losses below  $150^\circ\text{C}$  in the thermograms, indicative of the hydrous nature. The experimental amount of water in the chelates determined from weight losses in the thermograms approached the theoretical amount for di- to tetrahydrates. All the anhydrous compounds are stable upto  $150^\circ\text{C}$  except uranyl sulphate which starts to decompose at  $120^\circ\text{C}$ . The anions in the complexes decompose from  $150\text{--}250^\circ\text{C}$ . The maximum decomposition occurs in the temperature range  $250\text{--}300^\circ\text{C}$ , and the process is complete around  $380\text{--}450^\circ\text{C}$ . The thermal properties of the chelates are presented in Table 1.

Extrapolation of the fairly linear portions of the pyrolysis curves at high and low temperatures, and taking the intersection as the decomposition temperature leads to the following thermal stability:  $\text{CeL}_2(\text{NO}_3)_4 > \text{CeL}_2(\text{SO}_4)_2$  and  $(\text{UO}_2\text{LOAc})_2 = \text{UO}_2\text{L}_2(\text{NO}_3)_2 > \text{UO}_2\text{L}_2\text{Cl}_2 > (\text{UO}_2\text{L}_2\text{SO}_4)_2$ .

TABLE I  
Thermal analysis data

Complex	% of H <sub>2</sub> O		% of Anions		% of Ligand		% of Metal		Initial decomposition		Inflection	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Temp., T <sub>a</sub> , TG (°C)	Temp., T <sub>b</sub> , TG (°C)	Temp., T <sub>a</sub> , TG (°C)	Temp., T <sub>b</sub> , TG (°C)
(UO <sub>2</sub> LOAc) <sub>2</sub> ·4H <sub>2</sub> O	4.89	5.03 ( <140)	16.00	17.05 (140-250)	43.90	42.50 (320-350)	32.00	33.90	150	150	380	310
UO <sub>2</sub> L <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	4.95	5.00 (100-150)	11.48	11.00 (150-350)	58.51	71.00 (350-490)	22.03	12.38	150	150	490	410
(UO <sub>2</sub> L <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	2.60	2.90 (100-150)	9.30	8.90 (150-350)	61.00	70.13 (350-480)	23.21	18.17	120	120	490	370
UO <sub>2</sub> L <sub>2</sub> Cl <sub>2</sub> ·4H <sub>2</sub> O	6.89	7.00 ( <150)	6.79	7.06 (150-280)	60.53	70.25 (280-400)	22.77	14.00	140	140	400	380
CeL <sub>2</sub> (NO <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O	6.50	5.00	5.86	6.00 17.58 <sup>a</sup> (180-400)	57.89	57.00 (400-480)	12.82	20.00	180	180	480	410
CeL <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	6.94	6.00 (100-160)	9.22	8.89 18.54 <sup>b</sup> (160-220)(220-340)	61.00	54.98 (340-450)	13.51	24.00 ( > 450)	160	160	450	390

<sup>a</sup> Corresponding to three remaining anions.

<sup>b</sup> Corresponding to one remaining anion.

## Residues

The residues from the thermogravimetric runs of the compounds were weighed and compared to the weight that would be obtained if the residue were a metal oxide. It was found that in all cases, the percentage of metal found (experimental) is less than the theoretical, whereas the sum percentage of metal and ligand from the thermogram equals the theoretical value. Hence it was concluded that during the process of decomposition some of the metal volatilizes and escapes along with the ligand.

## Differential thermal analysis

The first endotherm obtained in all hydrated compounds below 150°C except with uranyl acetate compound may be associated with the loss of water of hydration as borne out by the TGA curve. Since no sharp exothermic peaks are observed in the 250–430°C range, it can be concluded that reduction of the metal does not take place. The temperature ( $T_{\max}$ ) of the decomposition peak maximum, was used in determining the relative thermal stability of chelates. The order of thermal stability is ceric(IV) nitrate > ceric(IV) sulphate and uranyl nitrate > uranyl chloride > uranyl sulphate > uranyl acetate. A comparison of thermal stabilities from DTA ( $T_{\max}$ ) and TGA [(procedural decomposition temperature) showed that they are in good agreement with each other].

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