Thermochimica Acta, 125 (1988) 17–22
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION BEHAVIOUR OF THORIUM(IV) COMPLEXES WITH FURFURYLIDENE ARYLAMINE SCHIFF BASE LIGANDS

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(Received 28 April 1987)

ABSTRACT

Thorium(IV) nitrate and thiocyanate react with bidentate Schiff base ligands, furfurylidenearylamines, forming violet coloured non-electrolytic solids of composition $Th(SB)_nX_4$ (SB = furfurylidenearylamine; X = NO_3, $n = 2$; X = NCS, $n = 2, 3$), characterised by analytical data and IR spectra. Thermogravimetric studies of these complexes reveal the formation of intermediate decomposition species, whose stoichiometry and mechanism of formation are discussed. The complexes start losing weight around 80 ° C, but lose the ligands in a stepwise manner beyond 170 ° C finally forming ThO_2 as the ultimate end product above 650 ° C. These complexes are shown to be thermally less stable than the analogous dioxouranium(VI) complexes.

INTRODUCTION

As a part of our continuing programme on the chemistry of actinides involving the formation with multidentate Schiff base ligands of compounds with a wide range of higher coordination numbers from six to twelve [1–5], we report here the thermogravimetric characteristics of some thorium(IV) complexes involving bidentate heterocyclic Schiff bases derived from furfural and aromatic amines. The special significance of some heterocyclic Schiff bases and enhancement of their biochemical activities on coordination to metal ions have been reported [6,7]. An earlier paper from this laboratory [8] reported the thermogravimetric behaviour of dioxouranium(VI) chloride and thiocyanate complexes with the furfural based Schiff base ligands, the furfurylidene arylamines. The present work, therefore, enables a comparison to be made of the thermal behaviours of the complexes of dioxouranium(VI) and thorium(IV).

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EXPERIMENTAL

Materials

Hydrated thorium tetranitrate, furfural and the amines were obtained from either BDH or LOBA and were used without any further purification. The thorium thiocyanate, $\mathrm{Th(CNS)_4}$, was prepared by metathesis of $\mathrm{Th(NO_3)_4 \cdot 5H_2O}$ and KCNS in EtOH.

Synthesis of $\mathrm{Th(SB)_n X_4}$ *complexes (SB = furfurylidenearylamine;* $X = \mathrm{NO_3}$, $\mathrm{CNS^-}$; $n = 2$ *or 3)*

The thorium nitrate and thiocyanato complexes were synthesised by a common general procedure analogous to that of the corresponding dioxouranium(VI) complexes [8]. Equimolar proportions of the aromatic amines (3 mmol) and freshly distilled 2-furancarboxaldehyde (furfural) were made to react with continuous stirring in EtOH in cold conditions (ca. 10 ° C) for 30 min when the colour changed to red. The ligands were not isolated and were used as obtained. To this red ligand solution an ethanolic solution of the thorium salt (1 mmol) was added with continuous vigorous stirring. The reaction was allowed to proceed at room temperature for a

TABLE 1

Thermal decomposition parameters of thorium(IV) nitrato complexes

Compound [a]	TG data			Species formed	DTA peak (° C)
	Temperature range (° C)	Weight loss (%)			
		Observed	Calculated		
$\mathrm{Th(FA)_2(NO_3)_4}$	40–195	6.63	5.20	$\mathrm{Th(FA)_{1.75}(NO_3)_4}$	
	195–220	14.59	15.61	$\mathrm{Th(FA)_{1.25}(NO_3)_4}$	220 (exo)
	220–225	48.43	49.17	$\mathrm{Th(NO_3)_4}$	225 (exo)
	225–650	68.66	67.92	$\mathrm{ThO_2}$	380 (exo)
$\mathrm{Th(F}p\mathrm{Tol)_2(NO_3)_4}$	40–210	9.12	10.88	$\mathrm{Th(F}p\mathrm{Tol)_{1.5}(NO_3)_4}$	210 (exo)
	210–215	37.19	37.75	$\mathrm{Th(F}p\mathrm{Tol)_{0.25}(NO_3)_4}$	
	215–395	50.62	50.85	–	375 (exo)
	395–700	69.17	68.95	$\mathrm{ThO_2}$	
$\mathrm{Th(F}p\mathrm{Anis)_2(NO_3)_4}$	40–160	5.46	5.70	$\mathrm{Th(F}p\mathrm{Anis)_{1.75}(NO_3)_4}$	
	160–170	44.81	45.60	$\mathrm{Th(NO_3)_4}$	170 (exo)
	170–650	72.78	70.08	$\mathrm{ThO_2}$	
$\mathrm{Th(F}p\mathrm{Phen)_2(NO_3)_4}$	40–190	5.03	5.90	$\mathrm{Th(F}p\mathrm{Phen)_{1.75}(NO_3)_4}$	190 (exo)
	190–200	53.40	54.08	–	
	200–700	71.44	71.00	$\mathrm{ThO_2}$	310 (exo)

[a] FA, furfurylideneaniline; FTol, furfurylidenetoluidine; FAnis, furfurylideneanisidine; FPhen, furfurylidenephenetidine, *p*, para.

TABLE 2

Thermal decomposition parameters of thorium(IV) thiocyanato complexes

Compound [a]	TG data			Species formed	DTA peak (°C)
	Temperature range (°C)	Weight loss (%)			
		Observed	Calculated		
$\mathrm{Th(FA)_3(NCS)_4}$	40–200	4.72	4.37	$\mathrm{Th(FA)_{2.75}(NCS)_4}$	
	200–270	30.25	30.64	$\mathrm{Th(FA)_{1.25}(NCS)_4}$	215 (exo)
	270–455	43.69	43.86	$\mathrm{Th(FA)_{0.5}(NCS)_4}$	422 (exo)
	455–800	73.94	72.99	$\mathrm{ThO_2}$	495 (exo)
$\mathrm{Th(F}o\mathrm{Tol)_3(NCS)_4}$	40–165	4.98	4.54	$\mathrm{Th(F}o\mathrm{Tol)_{2.75}(NCS)_4}$	
	165–200	14.36	13.62	$\mathrm{Th(F}o\mathrm{Tol)_{2.25}(NCS)_4}$	
	200–285	27.93	27.24	$\mathrm{Th(F}o\mathrm{Tol)_{1.5}(NCS)_4}$	
	285–465	43.99	45.40	$\mathrm{Th(F}o\mathrm{Tol)_{0.5}(NCS)_4}$	
	465–800	75.43	74.10	$\mathrm{ThO_2}$	490 (exo)
$\mathrm{Th(F}m\mathrm{Tol)_3(NCS)_4}$	40–210	5.30	4.54	$\mathrm{Th(F}m\mathrm{Tol)_{2.75}(NCS)_4}$	
	210–260	28.53	27.24	$\mathrm{Th(F}m\mathrm{Tol)_{1.5}(NCS)_4}$	220 (exo)
	260–450	39.82	40.86	$\mathrm{Th(F}m\mathrm{Tol)_{0.75}(NCS)_4}$	
	450–552	61.02	60.17	-	490 (exo)
	552–800	75.00	74.10	$\mathrm{ThO_2}$	
$\mathrm{Th(F}o\mathrm{Anis)_2(NCS)_4}$	40–165	6.10	5.80	$\mathrm{Th(F}o\mathrm{Anis)_{1.75}(NCS)_4}$	
	165–280	27.90	29.02	$\mathrm{Th(F}o\mathrm{Anis)_{0.75}(NCS)_4}$	
	280–520	58.79	59.82	-	350 (exo)
	520–800	70.79	69.53	$\mathrm{ThO_2}$	

[a] Abbreviations as in Table 1; *o*, ortho; *m*, meta.

further period of 10–12 h in order to ensure the completion of the reaction. The deep-violet solid compound so obtained was collected on a glass frit, washed with a minimum volume of EtOH followed by small aliquots of diethyl ether and finally dried in vacuo.

Thermal measurements

The thermal measurements were carried out using a Shimadzu DT-30 thermal analyser in static air. The equipment records T, TG, DTA and DTG simultaneously. The rate of heating was 10 °C min^{-1}. The thermal parameters for the decomposition of the complexes are presented in Tables 1 and 2.

RESULTS AND DISCUSSION

All the furfurylidenearylamine complexes reported in this work are intense violet in colour with high melting points and are very sparingly soluble in most of the common organic solvents. These compounds have been characterised [9] by elemental analyses, melting point, conductivity and IR spectral studies. The stoichiometry of the coordination complexes formed between thorium(IV) nitrate or thorium(IV) thiocyanate and the Schiff bases employed, generally correspond to $Th(SB)_2X_4$ ($X = NO_3$, CNS), except with the ligands furfurylideneaniline and furfurylidene *o*-, *m*-, and *p*-toluidine, where 1 : 3 complexes of the type $Th(SB)_3(NCS)_4$ are formed. These complexes are essentially non-electrolytes in dilute solutions of DMF and nitromethane.

The IR spectra

The IR spectra of these complexes provide no evidence for the presence of ionic nitrate and thiocyanate or for the coordinated or lattice water. The IR spectra of the solid Schiff bases have a fairly intense band around the 1625 cm^{-1} [10] region due to the $\nu(C{=}N)$ that shifts in these complexes to about 1630–1600 cm^{-1} providing evidence for the coordination of the azomethine group [11]. The furan oxygen seems to be coordinated to the central metal ion and examples of such ring oxygen and ring sulphur coordination of the furfural and thiophene-2-aldehyde are known [12]. In the thiocyanato complexes, the $\nu(C{\equiv}N)$ appears at 2060–2030 cm^{-1} as an intense sharp band and the $\nu(C{-}S)$ at 840–820 cm^{-1} showing the coordination of the ambidentate thiocyanate ion through its hard N-end [13]. For the nitrato complexes the bands obtained around 1535, 1300, 1030 and 810 cm^{-1} agree very closely with the known bands of $Th(NO_3)_4 \cdot 5H_2O$ [14], suggesting the bidentate coordination of the nitrato groups.

Thermal decomposition studies

Thermogravimetric analyses of the synthesised thorium(IV) complexes have been carried out from ambient temperature to 1000 °C and the salient features are collected in Tables 1 and 2. These observations further confirm some of the IR observations regarding the absence of water molecules in these complexes. As is quite clear, these complexes are fairly stable at room temperature and can be stored unchanged for prolonged periods.

The thermogravimetric analyses of the nitrato complexes show interesting decomposition patterns. The initial decomposition temperature indicates their stability at about room temperature. The decomposition process initially starts at around 60 °C followed by the loss of the Schiff base ligands in discrete steps as temperature rises, ultimately leaving the stable ThO_2 as the end product. In general, these complexes show a drastic loss of the organic ligand at about 160–225 °C. The sharp DTG peaks and the exothermic DTA peaks in this temperature range provide unequivocal confirmation for this phenomenon.

The thermogram of the furfurylideneaniline complex of thorium(IV) nitrate, $Th(FA)_2(NO_3)_4$ (Fig. 1) shows the beginning of decomposition at

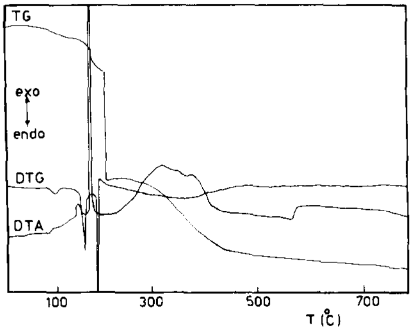

Fig. 1. Thermogram of the thorium(IV) nitrato complex, $Th(FA)_2(NO_3)_4$.

70 °C and the loss of the ligands in a stepwise manner with one or more intermediate products up to 220 °C. In fact, the major loss of ligands is almost complete at about 220–225 °C. Accordingly, the sharp DTG and the strong exothermic DTA peaks are observed at this point. The decomposition process continues thereafter forming ThO_2 as the final end product at ~ 650 °C. Thus, these complexes although stable at room temperature, become unstable at elevated temperatures.

The parameters for the thermal decomposition of the thiocyanato complexes are presented in Table 2 and a representative thermogram is shown in Fig. 2. A comparison between the nitrato and the thiocyanato complexes indicates the substantial difference in their decomposition patterns. A close look at Figs. 1 and 2 makes the comparison quite evident. The thiocyanato complexes are indeed much more stable than the corresponding nitrato complexes, and they start decomposing at a substantially higher temperature. The decomposition again proceeds in discrete steps with the loss of the Schiff base ligands. The decomposition process continues through the formation of the intermediate species, the stoichiometries of which have

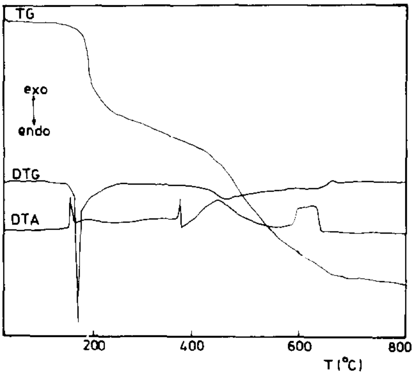

Fig. 2. Thermogram of the thorium(IV) thiocyanato complex, $Th(FA)_3(NCS)_4$.

been determined. ThO_2 is also formed as the stable end product beyond 650 °C.

CONCLUSION

All complexes reported here are stable at room temperature. The thiocyanato complexes are more stable than the nitrato complexes. In addition, considering the initial decomposition temperature as a rough criterion for the thermal stability of the complexes, the furfurylidenearylamine complexes of thorium(IV) appear to be less stable than the corresponding dioxouranium(VI) complexes reported by us earlier [8]. Further, on the basis of the initial decomposition temperatures, the order of stability for the reported thorium(IV) complexes is shown to be $Th(FmTol)_3(NCS)_4 > Th(FA)_2(NO_3)_4 \simeq Th(FpTol)_2(NO_3)_4 \simeq Th(FpPhen)_2(NO_3)_4 > Th(FA)_3(NCS)_4 \simeq Th(FoTol)_3(NCS)_4 > Th(FoAnis)_2(NCS)_4 \simeq Th(FpAnis)_2(NO_3)_4$.

ACKNOWLEDGEMENTS

Grateful thanks are due to the Council of Scientific and Industrial Research (CSIR), New Delhi for supporting the work. One of the authors (V.C.) thanks the CSIR for the award of a Research Associateship and K.C.D. is thankful to the University Grants Commission (UGC), New Delhi for the award of a National Fellowship.

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