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SPECTRAL AND THERMOGRAVIMETRIC STUDIES ON THORIUM(IV) COMPLEXES WITH BIDENTATE HETEROCYCLIC SCHIFF BASES

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ABSTRACT

Thorium(IV) nitrate and thiocyanate react with the bidentate heterocyclic aldimines (PyAlA) and heterocyclic ketimines (AcPyA) to form yellow-, brown- or violet-coloured complexes $[Th(SB)X_4]$ (SB = PyAlA or AcPyA; X = NO_3, NCS). The thiocyanato complexes contain N-bonded isothiocyanato groups and are six-coordinated. The nitrato complexes contain bidentate nitrato groups and are ten-coordinated. All the complexes have been characterised by analytical data, conductivity in non-aqueous media, IR spectra and thermogravimetric studies. From the thermogravimetric measurements of these complexes, it is seen that the thiocyanato complexes are comparatively more stable at higher temperature. Most of the nitrato complexes undergo rapid exothermic decomposition around 200 °C in a single step, whereas the isothiocyanato complexes decompose in a stepwise manner ultimately forming stable ThO_2 as the end product.

INTRODUCTION

The Schiff bases and hydrazones of 2-pyridine carboxaldehyde [1–3] and thiosemicarbazones of 2-acetyl pyridine [4,5] form an interesting class of chelating agents for transition elements. The chemotherapeutic properties of these compounds have also been studied [6,7]. Although a number of complexes of these ligands have been reported with the transition metal ions [1,8,9], the chemistry of heterocyclic Schiff bases with actinides have attracted less attention. Previous work from this laboratory dealt with the coordination behaviour of a series of multidentate Schiff bases [10–13] and bidentate heterocyclic Schiff bases [14,15] with the actinides, and a wide range of compounds with varying coordination numbers from six to twelve were reported. A recent work from this laboratory [16] also reported the formation and thermal decomposition behaviour of dimeric dioxouranium(VI) complexes with the bidentate Schiff base ligands, heterocyclic

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aldimines (PyAlA) (derived from the condensation of 2-pyridine carboxaldehyde and aryl amines) and heterocyclic ketimines (AcPyA) (derived from the condensation of 2-acetylpyridine and aryl amines). As a continuation of the studies on the interaction of heterocyclic Schiff bases with actinide ions and to allow a comparison to be made between the dioxouranium(VI) complexes already reported [16] and their thorium(IV) analogues, we report here several thorium(IV) complexes with the bidentate heterocyclic aldimines (PyAlA) and ketimines (AcPyA).

EXPERIMENTAL

Materials

$Th(NO_3)_4 \cdot 5H_2O$ was obtained from BDH, England. $Th(NCS)_4$ was prepared by metathesis of $Th(NO_3)_4 \cdot 5H_2O$ and KCNS in EtOH. 2-Pyridine carboxaldehyde (Fluka, Switzerland), 2-acetylpyridine (Koch-Light, England) and amines (BDH, England) were reagent grade and were used as supplied.

Analysis and physical measurements

Thorium was estimated by decomposition of the complexes with concentrated HNO_3 followed by direct heating to ThO_2 at 750 °C. The C, H and N microanalyses were carried out by the Central Drug Research Institute, Lucknow. Sulphur was estimated by decomposing the complex by oxidative fusion with Na_2O_2 and NaOH, followed by extraction with water, acidification by dilute HCl and then precipitation as $BaSO_4$ by addition of $BaCl_2$. The analytical data are presented in Tables 1 and 2.

IR spectra of the complexes were recorded in the 4000–400 cm^{-1} region as Nujol mulls in a Perkin Elmer 377 grating spectrometer. 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 Table 3.

Synthesis of the complexes

All the thorium complexes $Th(SB)X_4$ (SB = aldimines (PyAlA) or ketimines (AcPyA); A = aniline; *o*-, *m*-, *p*-toluidine; *o*-, *p*-anisidine; *p*-phenetidine or *o*-, *m*-chloroaniline; X = NO_3^-, SCN^-) were prepared by the interaction of required quantities of the metal salt and the ligand in a suitable solvent following a general procedure as detailed below.

TABLE 1

Analytical and other characterising data of thorium(IV) aldimine complexes

Compound	Empirical formula (Molecular weight)	Colour	Melting point (°C)	Element found (calc.) (%)					Λ_M in DMF (Ω^{-1} cm^2 mol^{-1})
				Th	C	H	N	S	
Th(PyAlAnil)(NO$_3$)$_4$	ThC$_{12}$H$_{10}$N$_6$O$_{12}$	Yellow	200	35.3	21.7	1.2	12.9	–	124.89
	(662)			(35.0)	(21.7)	(1.5)	(12.7)		
Th(PyAl*o*-Tol)(NO$_3$)$_4$	ThC$_{13}$H$_{12}$N$_6$O$_{12}$	Yellow green	210	33.9	23.1	1.6	12.2	–	129.56
	(676)			(34.3)	(23.1)	(1.8)	(12.4)		
Th(PyAl*m*-Tol)(NO$_3$)$_4$	ThC$_{13}$H$_{12}$N$_6$O$_{12}$	Yellow	205	34.0	22.9	1.8	12.0	–	107.34
	(676)			(34.3)	(23.1)	(1.8)	(12.4)		
Th(PyAl*p*-Tol)(NO$_3$)$_4$	ThC$_{13}$H$_{12}$N$_6$O$_{12}$	Yellow green	220	34.5	22.8	1.5	12.4	–	110.79
	(676)			(34.3)	(23.1)	(1.8)	(12.4)		
Th(PyAl*o*-Anis)(NO$_3$)$_4$	ThC$_{13}$H$_{12}$N$_6$O$_{13}$	Brown	215	33.5	22.4	1.8	12.0	–	119.13
	(692)			(33.5)	(22.5)	(1.7)	(12.1)		
Th(PyAl*p*-Anis)(NO$_3$)$_4$	Th$_{13}$H$_{12}$N$_6$O$_{13}$	Brown	200	33.3	22.6	1.8	12.3	–	120.23
	(692)			(33.5)	(22.5)	(1.7)	(12.1)		
Th(PyAl*p*-Phen)(NO$_3$)$_4$	ThC$_{14}$H$_{14}$N$_6$O$_{13}$	Dark green	195	32.7	23.7	1.9	11.9	–	130.54
	(706)			(32.8)	(23.8)	(2.0)	(11.9)		
Th(PyAl*m*-ClAnil)(NO$_3$)$_4$	ThC$_{12}$H$_9$N$_6$O$_{12}$Cl	Reddish yellow	195	33.0	20.2	1.3	11.8	–	124.62
	(696.7)			(33.3)	(20.6)	(1.3)	(12.1)		
Th(PyAlAnil)(NCS)$_4$	ThC$_{16}$H$_{10}$N$_6$S$_4$	Dark violet	215	35.8	29.9	1.6	12.8	19.5	97.48
	(646)			(35.9)	(29.7)	(1.5)	(13.0)	(19.8)	65.90 [a]
Th(PyAl*o*-Tol)(NCS)$_4$	ThC$_{17}$H$_{12}$N$_6$S$_4$	Dark violet	220	34.9	31.0	1.7	12.9	19.1	110.75
	(660)			(35.1)	(30.9)	(1.8)	(12.7)	(19.4)	45.31 [a]
Th(PyAl*m*-Tol)(NCS)$_4$	ThC$_{17}$H$_{12}$N$_6$S$_4$	Dark violet	210	35.3	30.7	1.6	12.5	19.4	177.98
	(660)			(35.1)	(30.9)	(1.8)	(12.7)	(19.4)	52.35 [a]
Th(PyAl*p*-Tol)(NCS)$_4$	ThC$_{17}$H$_{12}$N$_6$S$_4$	Dark violet	210	35.0	30.8	1.5	12.7	19.5	109.24
	(660)			(35.1)	(30.9)	(1.8)	(12.7)	(19.4)	68.47 [a]
Th(PyAl*o*-Anis)(NCS)$_4$	ThC$_{17}$H$_{12}$N$_6$OS$_4$	Dark violet	205	34.2	30.3	1.8	12.4	18.5	129.65
	(676)			(34.3)	30.2)	(1.8)	(12.4)	(18.9)	34.31 [a]
Th(PyAl*p*-Anis)(NCS)$_4$	ThC$_{17}$H$_{12}$N$_6$OS$_4$	Dark violet	190	34.3	29.9	1.9	12.1	18.7	107.27
	(676)			(34.3)	(30.2)	(1.8)	(12.4)	(18.9)	72.72 [a]
Th(PyAl*p*-Phen)(NCS)$_4$	ThC$_{18}$H$_{14}$N$_6$OS$_4$	Dark violet	195	33.7	30.9	2.0	12.3	18.5	112.50
	(690)			(33.6)	(31.3)	(2.0)	(12.2)	(18.5)	55.37 [a]

[a] Measurements in MeOH. Anil = aniline; Tol-toluidine; Anis = anisidine; Phen = phenetidine; ClAnil = chloroaniline.

TABLE 2

Analytical and other characterising data of thorium(IV) ketimine complexes

Compound [a]	Empirical formula (Molecular weight)	Colour	Element found (calc.) (%)				Λ_M in DMF (Ω^{-1} cm^2 mol^{-1})
			Th	C	H	N	
Th(AcPyAnil)$(NO_3)_4$	$ThC_{13}H_{12}N_6O_{12}$ (676)	Yellowish white	34.0 (34.3)	23.2 (23.1)	1.7 (1.8)	12.1 (12.4)	115.25
Th(AcPy*o*-Tol)$(NO_3)_4$	$ThC_{14}H_{14}N_6O_{12}$ (690)	Pale yellow	33.8 (33.6)	24.0 (24.3)	2.2 (2.0)	12.0 (12.2)	108.20
Th(AcPy*m*-Tol)$(NO_3)_4$	$ThC_{14}H_{14}N_6O_{12}$ (690)	Pale yellow	33.5 (33.6)	24.4 (24.3)	2.0 (2.0)	12.3 (12.2)	112.5
Th(AcPy*p*-Tol)$(NO_3)_4$	$ThC_{14}H_{14}N_6O_{12}$ (690)	Brownish yellow	33.6 (33.6)	24.0 (24.3)	2.3 (2.0)	12.2 (12.2)	105.35
Th(AcPy*o*-Anis)$(NO_3)_4$	$ThC_{14}H_{14}N_6O_{13}$ (706)	Yellowish white	32.7 (32.8)	23.9 (23.8)	1.7 (2.0)	11.9 (11.9)	97.58
Th(AcPy*p*-Anis)$(NO_3)_4$	$ThC_{14}H_{14}N_6O_{13}$ (706)	Yellow	32.5 (32.8)	23.8 (23.8)	2.0 (2.0)	11.7 (11.9)	76.90
Th(AcPy*p*-Phen)$(NO_3)_4$	$ThC_{15}H_{16}N_6O_{13}$ (720)	Brownish yellow	32.1 (32.2)	25.0 (25.0)	2.0 (2.2)	11.6 (11.7)	89.32
Th(AcPy*o*-ClAnil)$(NO_3)_4$	$ThC_{13}H_{11}N_6O_{12}Cl$ (710.7)	Light yellow	32.3 (32.6)	21.7 (21.9)	1.3 (1.5)	11.9 (11.8)	103.75
Th(AcPy*m*-ClAnil)$(NO_3)_4$	$ThC_{13}H_{11}N_6O_{12}Cl$ (710.7)	Light yellow	32.5 (32.6)	21.7 (21.9)	1.4 (1.5)	11.7 (11.8)	95.5

[a] All compounds have melting points greater than 250 °C.

TABLE 3

Thermal decomposition parameters of some aldimine complexes of thorium(IV) thiocyanate

Compound	Initial decomp. temp. (°C)	TG data			Species formed	DTA peak (°C)
		Temp. range (°C)	Weight loss (%)			
			Obser-ved	Calcu-lated		
$Th(L^1)(NCS)_4$ [a]	45	45–170	6.05	7.04	$Th(L^1)_{0.75}(NCS)_4$	
		170–320	23.22	21.13	$Th(L^1)_{0.25}(NCS)_4$	
		320–505	45.40	46.13	–	435 (endo)
		505–700	60.82	59.13	ThO_2	660 (exo)
$Th(L^2)(NCS)_4$ [b]	40	40–180	7.50	7.42	$Th(L^2)_{0.75}(NCS)_4$	
		180–300	13.56	14.85	$Th(L^2)_{0.5}(NCS)_4$	285 (exo)
		300–400	21.2	22.27	$Th(L^2)_{0.25}(NCS)_4$	
		400–650	61.25	60.00	ThO_2	640 (exo)
$Th(L^3)(NCS)_4$ [c]	45	40–185	6.52	7.42	$Th(L^3)_{0.75}(NCS)_4$	
		185–340	22.87	22.27	$Th(L^3)_{0.25}(NCS)_4$	310 (exo)
		340–500	46.92	47.27	–	
		500–700	60.82	60.00	ThO_2	620 (exo)
$Th(L^4)(NCS)_4$ [d]	45	40–200	6.84	7.84	$Th(L^4)_{0.75}(NCS)_4$	
		200–330	14.53	14.68	$Th(L^4)_{0.5}(NCS)_4$	300 (exo)
		330–420	22.90	23.52	$Th(L^4)_{0.25}(NCS)_4$	410 (exo)
		420–700	62.45	60.94	ThO_2	
$Th(L^5)(NCS)_4$ [e]	40	40–190	8.56	8.19	$Th(L^5)_{0.75}(NCS)_4$	
		190–340	22.87	24.56	$Th(L^5)_{0.25}(NCS)_4$	290 (exo)
		340–500	48.27	49.56	–	490 (endo)
		500–700	60.81	61.73	ThO_2	600 (exo)

[a] Molecular weight = 646; L^1 = PyAlAnil (molecular weight = 182). [b] Molecular weight = 660; L^2 = PyAl*o*-Tol (molecular weight = 196). [c] Molecular weight = 660; L^3 = PyAl*p*-Tol (molecular weight = 196). [d] Molecular weight = 676; L^4 = PyAl*p*-Anis (molecular weight = 212). [e] Molecular weight = 690; L^5 = PyAl*p*-Phen (molecular weight = 226).

Amine (4 mmol) and 2-pyridine carboxaldehyde or 2-acetyl pyridine (4 mmol) in 10 ml anhydrous ethanol were stirred for 15 min and then refluxed for a further 60 min to ensure the completion of reaction. The reaction mixture was then brought to room temperature. Thorium salt solution (2 mmol) in 5 ml anhydrous ethanol was added to the stirred ligand solution. In about 5 min, a dark violet or yellowish-white precipitate appeared. It was then stirred for 60 min to ensure the completion of reaction. The resulting compound was collected on a frit, washed repeatedly with small volumes of EtOH followed by Et_2O and finally dried in vacuo.

RESULTS AND DISCUSSION

The isolated complexes of thorium(IV) nitrate and thiocyanate with the aldimines (PyAlA) are reported in Table 1 and those of thorium(IV) nitrate with the ketimines (AcPyA) are reported in Table 2, together with their analytical data, molecular formulae, melting points, colour and molar conductivity values. Nitrato and thiocyanato complexes of the aldimines are dark violet in colour and decompose at about 200°C, whereas the yellow-coloured nitrato complexes of the ketimines have higher melting points.

Electrical conductivity and infrared measurements

The limited solubility of these complexes in suitable organic solvents precluded the determination of molecular weights. However, the molar conductance measurements could be carried out in dilute solutions ($\sim 10^{-4}$ M) of DMF and MeOH and all compounds behave essentially as non-electrolytes in these solvents [17]. The higher molar conductivities in DMF may be rationalised by the fact that DMF is a more strongly coordinating solvent than MeOH and displacement of the coordinated anions may be taking place [18]. The measurements in MeOH, however, show their non-electrolytic nature, which is further substantiated on the basis of IR measurements in the solid state, where evidence for uncoordinated NO_3^- and CNS^- are clearly absent (see below).

The IR spectra of these complexes provide evidence not only of the absence of ionic nitrate and thiocyanate, but also of the coordinated or lattice water. The ionic NO_3^- with a D_{3h} symmetry exhibits bands at 831, 1390 and 790 cm^{-1} due to the $\nu_2(A_2)$, $\nu_3(E)$ and $\nu_4(E')$ modes, with the band 1350–1400 cm^{-1} ($\nu_4(E')$) being the most characteristic [19]. The coordinated NO_3^- with a C_{2v} symmetry invariably exhibits bands at 1530–1480 cm^{-1} due to the $\nu_4(B_1)$ mode, at 1290 cm^{-1} due to the $\nu_1(A_1)$ mode, and at 1030, 810, 740 and 731 cm^{-1} due to the $\nu_2(A_1)$, $\nu_5(B_2)$, $\nu_3(A_1)$ and $\nu_6(B_1)$ modes. In all our nitrato complexes prominent vibrational bands were obtained at 1530, 1300, 1030 and 808 cm^{-1} corresponding to the presence of bidentate nitrato groups. These values agree very closely with the known bands for $Th(NO_3)_4 \cdot 5H_2O$ [20], where the bidentate character of the nitrato groups is established on the basis of X-ray crystal structure [21]. In all the thiocyanate complexes with the aldimines $\nu(C{\equiv}N)$ was observed in the 2070–2030 cm^{-1} region and $\nu(C-S)$ in the range 820–800 cm^{-1} suggesting the coordination of the ambidentate CNS^- ligand through the N end [22], in agreement with the hard acid character of thorium(IV) [23]. The Schiff base ligand bands were observed at 1620 cm^{-1} and at 1170–1175 cm^{-1}, corresponding to $\nu(C=N)$ and $\nu(C-N)$, respectively, in all the thorium(IV) complexes. The $\nu(Th-N)$ bands were observed invariably in the 580 cm^{-1} region. These bands clearly indicate the coordination of azomethine nitrogen [8,24]. All these results show that thorium(IV) is ten-coordinated in the nitrato complexes and six-coordinated in the isothiocyanato complexes.

Thermogravimetric analysis

The thermal decomposition patterns of the nitrato complexes of heterocyclic aldimines and heterocyclic ketimines seem to be interesting although quite complex in nature. All the complexes start decomposing at about 40 ° C, and at about 200 ° C a major loss of the ligand is observed with a sharp exothermic peak. No intermediate decomposition species are observed for these complexes. This major weight loss of the compound is calculated to be 80%, whereas the formation of thoria (ThO_2) would require a weight loss of about 60%. The complexes seem to be extremely unstable at higher temperatures, where the evolution of a large amount of heat may result in the decomposition of the compound, producing a major weight loss (Fig. 1). This behaviour is also confirmed by heating the complexes at about 200 ° C and calculating the total loss in weight.

The thermogravimetric decomposition patterns of the isothiocyanato complexes are quite different from those of the nitrato complexes, and indicate the greater stability of the isothiocyanato complexes at higher temperature. All the isothiocyanato complexes start decomposing at 40 ° C with the loss of the ligand molecule in descrete steps (often involving the loss of fractional ligand molecules giving rise to one or more intermediate products). The stoichiometries of the intermediate products have been calculated and are presented in Table 3. For these complexes, the ultimate end product is found to be ThO_2, formed at about 800 ° C (Fig. 2). The

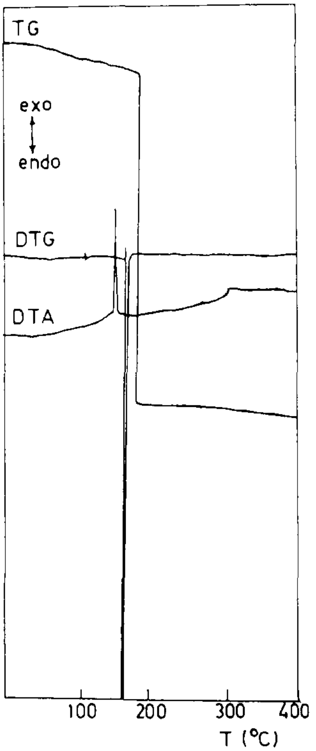

Fig. 1. TG, DTG and DTA curves for [Th(AcPyAnil)$(NO_3)_4$] complex.

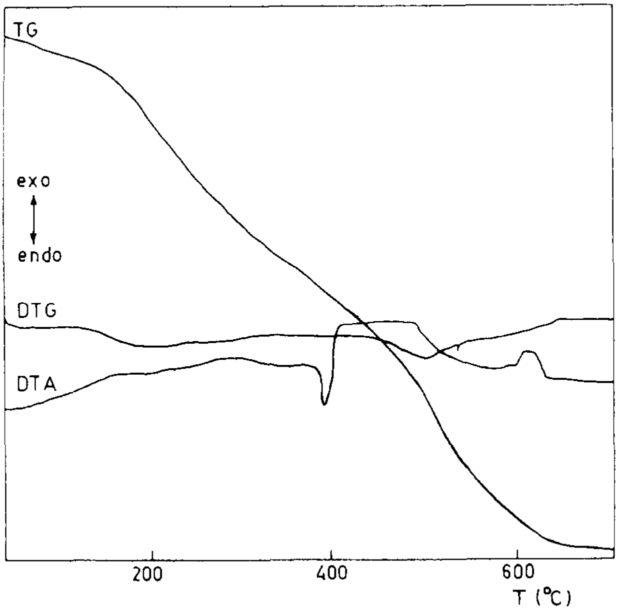

Fig. 2. TG, DTG and DTA curves for [Th(PyAlAnil)(NCS)$_4$] complex.

thermal analyses of the complexes also indicate the absence of water molecules and no endothermic peaks in the temperature range 45–200 °C were observed. This provides additional support for the absence of water molecules (either coordinated or present as water of crystallisation).

CONCLUSION

In contrast with the dimeric dioxouranium(VI) complexes of the type [UO$_2$(OH)(PyAlA)Cl]$_2$ and [UO$_2$(OH)(H$_2$O)AcPyA)$_{0.5}$Cl]$_2$ [16], the thorium complexes [Th(PyAlA)X$_4$] and [Th(AcPyA)X$_4$] (X = NO$_3$, CNS) are monomeric. Furthermore, while the coordination number of uranium in these complexes is seven, for the thorium(IV) complexes the coordination number is six for isothiocyanato and ten for nitrato complexes. A comparative thermal study of the nitrato and the isothiocyanato complexes of thorium(IV) has established the higher thermal stability of the isothiocyanato complexes. The representative thermograms of the nitrato (Fig. 1) and isothiocyanato (Fig. 2) complexes show that their decomposition patterns differ considerably. The decomposition of isothiocyanato complexes follows a definite pattern with a stepwise degradation, finally forming thoria (ThO$_2$). The nitrato complexes show a major loss at about 200 °C.

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