Preparation and characterization of $TlM^{III}(SO_4)_2 \cdot 4H_2O$ (M(III) ≡ Pu, Sm to Dy)

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Abstract

The thallium, plutonium and lanthanide double sulphate tetrahydrates $TlM^{III}(SO_4)_2 \cdot 4H_2O$, (M(III) ≡ Pu, Sm to Dy) were synthesized and characterized by chemical, thermal, IR and X-ray powder diffraction methods. The X-ray data showed that the crystals are monoclinic, of space group $P2_1/c$, with four formula units per unit cell and that the plutonium and the lanthanide compounds are structurally isomorphous to $RbLn(SO_4)_2 \cdot 4H_2O$ reported in the literature. The IR spectra coupled with the X-ray data showed that the trivalent metal ion is coordinated to nine oxygen atoms. The heats of dehydration were calculated from measurements of peak areas under the differential thermal analysis curve recorded during thermal dehydration of all $TlLn(SO_4)_2 \cdot 4H_2O$ compounds.

Keywords: Thallium; Plutonium(III); Lanthanides; Sulphates; X-ray powder diffraction

1. Introduction

The lanthanides and to some extent Pu(III) form a number of hydrated double sulphates with alkali metals and ammonium ions. To the extent structural information is available, the hydrated double sulphates of Pu(III), with sodium and ammonium are isomorphous to the corresponding lanthanide compounds [1–4]. Investigations on the hydrated double sulphates of thallium(I) with plutonium and lanthanides were undertaken, in view of the structural isomorphism of alkali metal double sulphates of Pu(III) with that of lanthanides. To date, only the results of preliminary studies obtained during the early days of plutonium chemistry are available on thallium Pu(III) double sulphate [5]. For the lanthanides, compounds of the type $TlLn(SO_4)_2 \cdot 2H_2O$, where Ln ≡ La to Pr has been prepared and characterized by X-ray structure analysis of the typical compound $TlPr(SO_4)_2 \cdot 2H_2O$ [6]. The present paper deals with the synthesis and characterization by chemical, thermal, IR and X-ray powder diffraction methods of the compounds, $TlPu(SO_4)_2 \cdot 4H_2O$ and $TlLn(SO_4)_2 \cdot 4H_2O$ (Ln ≡ Sm to Dy).

2. Experimental details

2.1. $TlPu(SO_4)_2 \cdot 4H_2O$

A solution of Pu(III) was prepared by electrolytic reduction of Pu(IV) in 1 M H_2SO_4 medium. The quantitative reduction of Pu(IV) to Pu(III) was established by redox titration of an aliquot of the solution against $K_2Cr_2O_7$ to an amperometric end point [7]. The freshly prepared Pu(III) solution was mixed with a solution containing about 10% excess of Tl_2SO_4 over that required for the formation of the compound from stoichiometric ratios of the components. The compound $TlPu(SO_4)_2 \cdot 4H_2O$ was precipitated by the addition of absolute alcohol with continuous stirring. The light-blue solid settled to the bottom of the vessel, leaving a clear supernate. The precipitate was washed with an equal volume mixture of absolute alcohol and 0.1 M H_2SO_4, finally with absolute alcohol, filtered through a fine porosity filter funnel and dried overnight under flowing helium. The preparations were carried out on a 500 mg scale. The spectrum of the solution of the compound in 1 M H_2SO_4 medium was recorded using a Beckman DU-7 recording spectrophotometer. The absorption maxima at 665, 600 and 560 nm established

that the plutonium in the compound is in the trivalent state [8].

2.2. $TlLn(SO_4)_2 \cdot 4H_2O$ (Ln ≡ Sm to Dy)

The lanthanide sulphate octahydrates were prepared from the corresponding oxides of 99.9% purity. About 2 g of the respective lanthanide sulphate octahydrate was dissolved in 0.2 M H_2SO_4 and mixed with a solution containing 10% excess of Tl_2SO_4 (99.5% purity) over that required for the formation of $TlLn(SO_4)_2 \cdot 4H_2O$. The solution was left to stand in air under ambient conditions (22 ± 2 °C) for crystallization of the compound. The crystalline thallium lanthanide sulphate tetrahydrate separated after 2–4 weeks and was filtered using a medium porosity filter funnel, washed with distilled water and then with absolute alcohol and dried in air. The yield of the compound was about 1.5–2 g. Attempts to prepare similar compounds of La to Nd and Ho to Lu under the above conditions were not successful.

The plutonium and lanthanide compounds were analysed by chemical and thermal methods. The Pu(III) content of $TlPu(SO_4)_2 \cdot 4H_2O$ was analysed by redox titration of a solution containing a known mass of the solid in 1 M H_2SO_4 [7]. The quantity of Pu(III) thus obtained agreed with the calculated quantity on the basis of mass taken for analysis and its chemical composition. This confirmed that the plutonium was in the 3+ oxidation state. The lanthanides were determined by precipitation of the hydroxide followed by ignition to the oxide. The total sulphate content of all the compounds was determined gravimetrically as $BaSO_4$ after separating cations (thallium, plutonium and lanthanides in dilute HNO_3 medium) using Dowex-50X4. Water of crystallization was obtained from the mass loss recorded during the thermal dehydration of the compounds. Thallium was determined gravimetrically as thallous chromate.

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of $TlPu(SO_4)_2 \cdot 4H_2O$ were recorded using narrow long platinum crucibles of volume 0.8 ml with a helium flow rate of 100 ml min^{-1} in a Mettler thermoanalyser TA-1, enclosed in a glove-box. The TGA and DTA curves of $TlLn(SO_4)_2 \cdot 4H_2O$ were recorded in a model TGD-7000 thermobalance, using platinum crucibles of 0.5 ml volume and an air flow rate of 100 ml min^{-1}. Pre-heated alumina was used as reference material for the DTA measurements. The area under the DTA peak (ABCD in Fig. 2 given later) was obtained by a graphical method. The sum of the number of squares of 0.05 cm^2 were taken with proper weight being given to each fractional division. This area was then converted into the heat of dehydration through a calibration constant for the heat of fusion of $KClO_4$. The instrumental parameters were kept identical for all DTA measurements. A model PU 9500 IR spectrophotometer was used to record the spectra with the sample dispersed in Nujol for $TlPu(SO_4)_2 \cdot 4H_2O$ and KBr disc for the $TlLn(SO_4)_2 \cdot 4H_2O$. An X-ray diffractometer supplied by Diano Corporation, Woburn, USA, was used to record the X-ray powder diffraction patterns with Cu Kα radiation (mean λ = 1.541 78 Å).

3. Results and discussion

The analytical results for $TlM^{III} (SO_4)_2 \cdot 4H_2O$ are given in Table 1. They show satisfactory agreement for the above compositions. The compositions of the compounds were also confirmed by TGA and DTA measurements carried out using 100 mg samples from 25 to 1200 °C. The curves obtained for $TlPu(SO_4)_2 \cdot 4H_2O$ and a typical compound $TlSm(SO_4)_2 \cdot 4H_2O$ are shown in Figs. 1 and 2.

The plutonium compound showed two endothermic dehydration peaks, indicating a two-step dehydration process. However, only one inflection was observed in the mass loss curve, which could be attributed to the small temperature difference (about 10 °C) between the first-step loss of three and second-step loss of one water molecules. In $TlLn(SO_4)_2 \cdot 4H_2O$ compounds, two distinct endothermic peaks and two inflections in the mass loss curve indicated the loss of three water molecules and one water molecule respectively. The com-

Table 1
Analytical results on $TlM^{III}(SO_4)_2 \cdot 4H_2O$

Metal	Thallium (%)		Metal (%)		Sulphate (%)		H_2O (TGA) (%)	
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
Pu	28.90 (±0.5)	28.89	33.78 (±0.5)	33.79	27.54 (±0.5)	27.14	9.78 (±0.4)	10.18
Sm	24.43 (±0.5)	24.30	32.94 (±0.5)	33.03	31.02 (±0.5)	31.03	11.61 (±0.2)	11.64
Eu	24.50 (±0.5)	24.50	32.88 (±0.5)	32.95	30.97 (±0.5)	30.95	11.60 (±0.2)	11.61
Gd	25.18 (±0.5)	25.14	32.17 (±0.5)	32.67	30.77 (±0.5)	30.69	11.48 (±0.2)	11.51
Tb	25.33 (±0.5)	25.33	32.17 (±0.5)	32.64	30.99 (±0.5)	30.61	11.46 (±0.2)	11.48
Dy	25.65 (±0.5)	25.76	32.34 (±0.5)	32.39	30.42 (±0.5)	30.43	11.39 (±0.2)	11.41

Table 2
Thermoanalytical results on Tl $M^{III}(SO_4)_2 \cdot 4H_2O$

Compound	DTA peak temperature (°C)	TGA temperature range (°C)	Mass loss (%)		Reaction step based on percentage mass loss observed
			Observed	Calculated	
$TlPu(SO_4)_2 \cdot 4H_2O$	155	135–200	9.80	10.18	$TlPu(SO_4)_2 \cdot 4H_2O \longrightarrow TlPu(SO_4)_2 \cdot H_2O$
	165				$TlPu(SO_4)_2 \cdot H_2O \longrightarrow TlPu(SO_4)_2$
	705	600–750	17.54	17.62	$TlPu(SO_4)_2 \longrightarrow Tl_2SO_4 + PuO_2$
		750–1000	48.59	48.22	$Tl_2SO_4 + PuO_2 \longrightarrow PuO_2$
$TlSm(SO_4)_2 \cdot 4H_2O$	125	80–160	8.58	8.73	$TlSm(SO_4)_2 \cdot 4H_2O \longrightarrow TlSm(SO_4)_2 \cdot H_2O$
	190	160–230	3.27	3.19	$TlSm(SO_4)_2 \cdot H_2O \longrightarrow TlSm(SO_4)_2$
		800–1000	60.68	60.79	$TlSm(SO_4)_2 \longrightarrow Sm_2O_2SO_4$

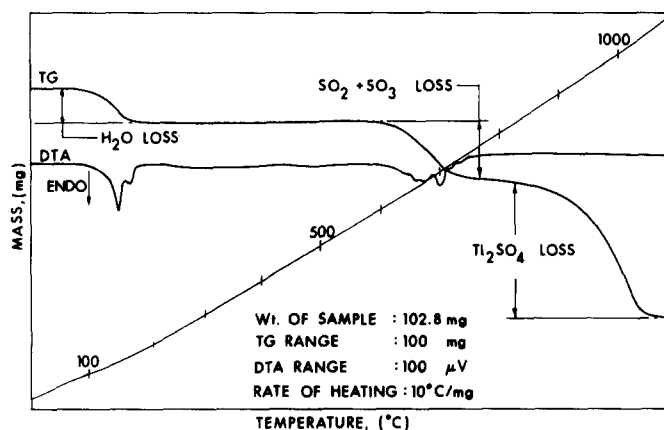
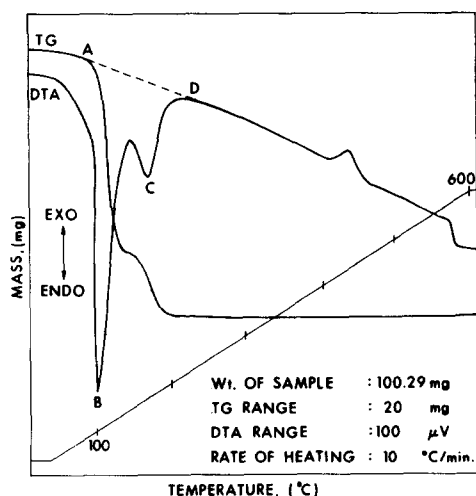Fig. 1. DTA and TG curves of $TlPu(SO_4)_2 \cdot 4H_2O$ in helium.

Fig. 2. DTA and TG curves for $TlSm(SO_4)_2 \cdot 4H_2O$.

Table 3
Differential thermal analysis temperature range and heat of dehydration of $TlLn(SO_4)_2 \cdot 4H_2O$

Compound	DTA temperature range (°C)	Heat of dehydration (kJ mol^{-1})
$TlSm(SO_4)_2 \cdot 4H_2O$	80–230	267.0 ± 6.7
$TlEu(SO_4)_2 \cdot 4H_2O$	70–240	268.9 ± 7.2
$TlGd(SO_4)_2 \cdot 4H_2O$	70–240	271.6 ± 6.5
$TlTb(SO_4)_2 \cdot 4H_2O$	65–245	276.6 ± 7.6
$TlDy(SO_4)_2 \cdot 4H_2O$	60–250	270.4 ± 8.2

Table 4
IR absorption frequencies in the 4000–400 cm^{-1} range for $TlGd(SO_4)_2 \cdot 4H_2O$

Assignment	Observed frequency (cm^{-1})	Assignment	Observed frequency (cm^{-1})
H_2O	3530 b	ν_1-SO_4	995 s
	3350 b		
δ-H_2O	1670 vs	ν_4-SO_4	652 s
	1627 vs		615 s
			565 m, b
ν_3-SO_4	1200 w	ν_2-SO_4 + M–OH_2 wag	475 w, b
	1150 b, w		
	1112 b, w	M–OH_2 stretch	430 w, s
	1170 s		

vs, very sharp; s, sharp; m, medium; w, weak, b, broad.

pounds $TlPu(SO_4)_2$ decomposed to Tl_2SO_4 and PuO_2 between 600 and 800 °C, followed by the loss of Tl_2SO_4 above 800 °C. The anhydrous $TlLnSO_4$ decomposed with the loss of Tl_2SO_4 and formation of $Ln_2O_2SO_4$ above 800 °C. That the final product was PuO_2 in the case of $TlPu(SO_4)_2 \cdot 4H_2O$ and $Ln_2O_2SO_4$ in the case of $TlLn(SO_4)_2 \cdot 4H_2O$ was confirmed from their X-ray powder patterns [9]. The observed and calculated mass losses based on stepwise decomposition reactions, the DTA temperature range for the plutonium and a typical lanthanide compound are summarized in Table 2.

The DTA trace was used to calculate the heat of dehydration of all the $TlLn(SO_4)_2 \cdot 4H_2O$ compounds. The calibration constant for the instrument was derived from the peak area recorded during the fusion of $KClO_4$ and using the value of 103.47 ± 1.26 J g^{-1} for its heat of fusion [10]. This calibration constant was used to calculate the heat of dehydration of $BaCl_2 \cdot 2H_2O$ and

Table 5
Indexed powder data on TlPu(SO$_4$)$_2$·4H$_2$O

hkl	d_{obs} (Å)	d_{calc} (Å)	I/I_0
020	9.508	9.494	75
021	6.371	6.411	30
11$\bar{1}$	5.258	5.266	5
031	5.126	5.117	3
040	} 4.770	4.747	} 35
12$\bar{1}$		4.747	
130	4.534	4.540	70
002	4.353	4.336	5
041	4.164	4.167	18
131	3.917	3.914	8
140	3.827	3.837	24
10$\bar{2}$	3.795	3.794	2
032	} 3.584	3.583	} 30
14$\bar{1}$		3.589	
102	3.461	3.460	20
112	3.399	3.403	25
150	3.278	3.281	15
060	3.164	3.165	100
15$\bar{1}$	3.132	3.122	30
14$\bar{2}$	2.963	2.964	40
211	2.925	2.919	38
230	2.892	2.896	10
221	} 2.823	2.821	} 25
23$\bar{1}$		2.824	
20$\bar{2}$	} 2.739	2.741	} 20
16$\bar{1}$		2.741	
161	2.667	2.671	2
152	} 2.557	2.558	} 5
062		2.559	
241	2.508	2.508	5
123	2.469	2.467	3
16$\bar{2}$	} 2.429	2.430	} 15
17$\bar{1}$		2.431	
24$\bar{2}$	} 2.377	2.374	} 100
080		2.374	
260	2.270	2.270	15
180	} 2.227	2.230	} 12
15$\bar{3}$		2.228	

NH$_4$Lu(SO$_4$)$_2$·2H$_2$O from the DTA peak areas measured during their thermal dehydration. The value of 120.4 kJ mol^{-1} of BaCl$_2$·2H$_2$O and 133±2.5 kJ mol^{-1} for NH$_4$Lu(SO$_4$)$_2$·2H$_2$O showed satisfactory agreement

with the respective values of 118.46 kJ mol^{-1} [11] and 137.64 kJ mol^{-1} [12] reported in the literature. The heats of dehydration of all TlLn(SO$_4$)$_2$·4H$_2$O compounds were calculated from their respective peak areas and the average of three such measurements are given in Table 3. These values are almost identical within the precision of the measurements and indicate the similarity of the metal ion water bonding in these compounds. The heat of dehydration values for TlPu(SO$_4$)$_2$·4H$_2$O could not be measured because of the slow oxidation of the compound when stored in the glove-box atmosphere and difficulty in calibrating the instrument enclosed in the glove-box.

The structural similarity of all TlLn(SO$_4$)$_2$·4H$_2$O compounds was indicated by the occurrence of IR absorption bands in the same region. The maxima observed for the absorption frequencies in the case of a typical compound TlGd(SO$_4$)$_2$·4H$_2$O are listed in Table 4. The presence of water of crystallization in the structure is confirmed by the absorption bands around 3500 cm^{-1} for the O–H stretch mode and sharp bands at 1670 and 1627 cm^{-1} for the H–O–H bend mode. The double band for H–O–H indicates that both coordinated and lattice water may exist in the structure [13]. In the case of TlPu(SO$_4$)$_2$·4H$_2$O the bands due to the H–O–H bend mode occur at 1600 cm^{-1} and as a shoulder at 1620 cm^{-1}, confirming the structural similarity to TlLn(SO$_4$)$_2$·4H$_2$O. The presence of M–OH$_2$ wagging bands indicate that at least some of the four water molecules are coordinated to the trivalent metal ion, although the M–OH$_2$ wagging band is mixed with $\bar{y}_2$ vibrations of the sulphate group. The high symmetry T$_d$ of the sulphate group is lowered to C$_{3v}$ if unidentate or C$_{2v}$, if bidentate or bridged. The observed absorption bands at 1200–1070 cm^{-1} show that the bridging bidentate sulphate group exists in the structure [14]. The assignment of the low frequency bands of the sulphate group is in accordance with that reported for lanthanide sulphate hydrates [15].

The X-ray powder diffraction patterns confirmed the isostructural nature of TlPu(SO$_4$)$_2$·4H$_2$O and all TlLn(SO$_4$)$_2$·4H$_2$O compounds. The powder data could be indexed on a monoclinic unit cell. The indexed

Table 6
Crystal data of TlM^{III}(SO$_4$)$_2$·4H$_2$O space group $P2_1/c$ and $Z=4$

Metal	a (Å)	b (Å)	c (Å)	β (Å)	V (Å^3)	Density (g cm^{-3}) Obs	Cal
Pu	6.546(3)	18.990(7)	8.735(5)	95.72(4)	1080.5(9)	–	–
Sm	6.581(3)	18.970(3)	8.730(6)	95.76(5)	1085.6(9)	3.77(4)	3.80
Eu	6.560(3)	18.907(8)	8.716(4)	95.83(3)	1075.2(7)	–	–
Gd	6.557(4)	18.866(7)	8.702(7)	95.87(7)	1070.8(8)	3.84(4)	3.88
Tb	6.523(3)	18.851(8)	8.676(4)	96.06(4)	1061.0(8)	–	–
Dy	6.464(3)	18.841(6)	8.666(3)	96.11(4)	1049.4(7)	3.95(5)	3.99

powder data for $TlPu(SO_4)_2 \cdot 4H_2O$ are given in Table 5. The space group was deduced to be $P2_1/c$ from the systematically absent reflections, $h0l$ with l odd and $0k0$ with k odd. The crystal data for all the compounds are summarized in Table 6. The crystal data and space group indicate that the compounds are isomorphous to $RbLn(SO_4)_2 \cdot 4H_2O$ in which the geometry of the nine-coordinated trivalent metal ion is a distorted tricapped trigonal prism [16]. The nine coordination of the metal ion is satisfied by the two crystallographically independent tridentate sulphate groups and oxygen from three water molecules. From the IR evidence indicating coordination of water oxygens to the metal ion and structural isomorphism to $RbLn(SO_4)_2 \cdot 4H_2O$, it can be deduced that the Pu^{3+} and Ln^{3+} ions in $TlPu(SO_4)_2 \cdot 4H_2O$ and $TlLn(SO_4)_2 \cdot 4H_2O$ are in ninefold coordination. As in $RbLn(SO_4)_2 \cdot 4H_2O$ the oxygen atom of the fourth water molecule, which is not coordinated to the trivalent metal ion, can be considered to be coordinated to thallium to form the coordination polyhedron of 13 vertices around the thallium in the present series of compounds. The observed decrease in cell volumes of these compounds is in accordance with ionic radii, 1.132 Å for Sm and 1.083 Å for Dy reported in the literature for nine coordination [17].

Acknowledgements

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