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Four thallium(I) uranates(VI), their preparation, structure and properties

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Abstract

Four thallium(I) uranates(VI), Tl_4UO_5, Tl_2UO_4, $Tl_2U_2O_7$ and $Tl_2U_3O_{10}$, were prepared and their IR, and, for the first time, their Raman, electronic and X-ray absorption (EXAFS) spectra have been measured. These uranates are thermally stable under nitrogen up to 660 °C but above this temperature they decompose and their uranium content increases, due to loss of Tl_2O. The thermal stability of these uranates increases with decreasing thallium content. Comparison with the reported values for the standard enthalpies of formation of the corresponding alkali metal uranates, which are essentially cation independent, allows suggested values for the above uranates, respectively, of −2437, −1900, −3182, and $-4437\ \mathrm{kJ\ mol^{-1}}$. Structural information and atom arrangements were obtained from analysis of powder XRD and EXAFS spectroscopy measurements. U–O distances, both primary and secondary, were obtained from EXAFS measurements and these were essentially identical with those calculated from vibrational IR spectra.

1. Introduction

We have previously reported the electronic and vibrational spectra of a range of pure lithium, sodium, potassium, rubidium and caesium uranates(VI) [1–3]. Another monovalent cation is thallium and thallium(I) chemistry resembles that of the alkali metals and silver. Although the practical significance of thallium uranates is limited and thallium is not a fission product, understanding the chemistry and structure of uranate compounds containing heavy cations is important for developing our knowledge of ternary oxide phases containing uranium that are formed in spent ceramic nuclear fuels. Thallium uranates(VI) can be prepared by reacting thallium carbonate with uranium oxide (U_3O_8 or UO_3) in air or under nitrogen, and the following mono- and polyuranates have been reported, Tl_4UO_5, $Tl_2U_xO_{3x+1}$ (x = 1 to 7) [4–7]. Additionally, several thallium uranates containing uranium in the lower oxidation state have been prepared [8–12]. Spectroscopic studies of thallium uranates are however limited to some infrared spectra in the earliest report [5].

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For the present study samples of thallium mono- and polyuranates(VI), Tl_4UO_5, Tl_2UO_4, $Tl_2U_2O_7$ and $Tl_2U_3O_{10}$, were prepared and their infrared, Raman and electronic spectra recorded. Additional structural information was obtained using EXAFS (extended X-ray absorption fine structure) spectroscopy and X-ray powder diffraction. Little thermodynamic data have been reported for the alkali metal uranates and the thermal stability of these thallium uranates has been measured using thermogravimetric analysis in order to assess trends and offer possible predictions.

2. Experimental

The thallium uranates were prepared by the original general procedure [5,6] and, like the heavier alkali monouranates, thallium monouranate was very hygroscopic and readily changed to diuranate.

Vibrational spectra were recorded using an Equinox 55 FTIR Raman spectrometer (Bruker). Infrared spectra were measured using KBr discs and Nujol mulls. Raman spectra were only obtained for Tl_2UO_4 (yellow-orange), $Tl_2U_2O_7$ (red-orange) and $Tl_2U_3O_{10}$ (red) uranates using the 1064 nm NdYAG laser line. The brown colour of Tl_4UO_5 prevented the measurement of a Raman spectrum of acceptable quality. Diffuse reflectance spectra of the thallium uranates were recorded at ambient and −196 °C, (Ocean Optics SD2000 fibre optic spectrophotometer) as described earlier [13]. X-ray powder spectra (Philips PW 1710 diffractometer) agreed well with those reported by Giridharan et al. [5,6] for Tl_4UO_5, Tl_2UO_4 and $Tl_2U_2O_7$. That for the triuranate agreed with that for the $Tl_2O.2.33UO_3$–$Tl_2O.6UO_3$ series [5]. Cell parameters are given (Table 1). Thallium mono- and diuranate have been reported as isostructural with the corresponding potassium compounds [5]. Thermograms, obtained using a TGA/SDTA851 Mettler Toledo instrument and heating under nitrogen to 950 °C at 5° min^{-1}, are shown in Fig. 1 for our four uranates. Tl_4UO_5 is stable under N_2 to ca. 660 °C, when it undergoes a two-step decomposition, losing 31% of its mass between 660 and 790 °C and a further 12% between 790 and 950 °C. This is contrary to Giridharan et al. [6], who reported decomposition commencing just above 380 °C under an inert atmosphere. Thallium monouranate, Tl_2UO_4, starts decomposing above 680 °C, gradually losing weight, 18% between 680 and 950 °C. Thallium diuranate, $Tl_2U_2O_7$, is more stable and loses only 2.8% of its mass between 600 and 950 °C. Thallium triuranate, $Tl_2U_3O_{10}$, is the most stable of those studied here, the weight loss between 700 and 950 °C being only 0.8%. The increased uranium content of the final red powders indicates that the weight loss observed was due to loss of thallium.

Table 1
Cell parameters of thallium uranates determined from X-ray powder diffraction analysis

Uranate	Symmetry system	Cell parameters (nm)
Tl_4UO_5	Orthorhombic	*a*, 0.342(1); *b*, 0.892(1); *c*, 1.235(1)
Tl_2UO_4	Tetragonal	*a*, 0.450(2); *c*, 1.352(2)
$Tl_2U_2O_7$	Orthorhombic	*a*, 0.706(1); *b*, 0.868(1); *c*, 2.003(1)
$Tl_2U_3O_{10}$	Tetragonal	*a*, 0.342(1); *c*, 1.418(1)

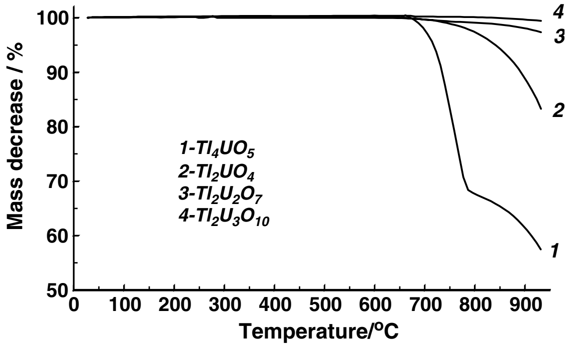

Fig. 1. Thermal stability of thallium uranates. Heating rate, 5° min^{-1}; atmosphere, N_2.

Single crystals of thallium uranates for structural studies cannot be grown due to their insolubility in solvents at room temperature and their thermal instability, but X-ray absorption spectroscopy can be used to obtain their atom arrangements. The uranium *L*(III)-edge X-ray absorption spectra were recorded in transmission mode at the CLRC Daresbury radiation source, (beam current 150 mA, energy 2 GeV, monochromated with a Si 220 double crystal). Solid samples of pure thallium uranates were diluted with boron nitride. The spectra were summed, calibrated and their background subtracted using the Daresbury Laboratory programs EXCALIB and EXBACK and then fitted, using their simulation program EXCURV98.

3. Results and discussion

3.1. Thermodynamic properties

A detailed analysis of the effect of temperature upon the alkali metal uranates is included in a recent review on the high temperature oxidation of uranium oxides in molten salts and in the solid state to form alkali metal uranates and their composition and properties by Griffiths and Volkovich [14]. The chemistry of thallium(I) is often compared with that of potassium and rubidium, since they are the nearest cations in size. As with heavier alkali metals, thallium monouranate is highly hygroscopic. According to our EXAFS spectroscopy results, the atom arrangement in $Tl_2U_2O_7$ resembles that in $Rb_2U_2O_7$ but the vibrational spectrum of thallium diuranate is closer to the spectra of sodium and caesium diuranates rather than potassium and rubidium. Vibrational (IR and Raman) spectra of thallium monouranate are also closer to α-sodium and caesium uranate. Lithium triuranate is the best-characterised triuranate compound. Thallium triuranate is structurally very close to the corresponding lithium uranate and the vibrational spectra reported here of Tl_2UO_{10} are also very similar to the corresponding spectra of Li_2UO_{10}.

The decomposition behaviour of the alkali metal uranates varies with both cation and the uranate type involved: the various authors also do not always agree [14]. There are three basic reaction types. First, evolution of oxygen and the formation of another uranate; second, as before, but with the additional formation of U_3O_8: these apply to the higher uranates. Third, and most common, is the formation of alkali metal oxides. The thermal stability of alkali metal mono- and diuranates decreases with increasing cation radius and the volatility of the oxides. In air lithium monouranate is thermally stable and does not change its composition after 60 h heating at 1300 °C, but it does decompose under vacuum. Sodium and potassium monouranates are less stable and decompose in air at 1200–1300 °C, yielding diuranates. Their pure diuranates are reported stable up to 1300 °C, the maximum temperature so far investigated. Rubidium monouranate loses alkali metal oxide at ca. 1000–1200 °C, producing the corresponding diuranate, $Rb_2U_2O_7$, whereas caesium monouranate, above 900 °C, loses not only caesium oxide but also oxygen, producing, together with $Ca_2U_2O_7$, the black oxygen-deficient tetrauranate, $Cs_2U_4O_{13-x}$. Rubidium monouranate diuranate is thermally stable, but caesium diuranate, above 600 °C in an inert atmosphere, also loses oxygen, yielding $Cs_2U_4O_{12}$ [14].

Thus the black product observed formed here during DTA measurements could be one, or a combination, of three possibilities. First, it could be the black compound UO_2 or UO_{2+x}, but this is least likely since only the yellow uranium oxide, U_3O_8, has been observed previously. Second, it could be an oxygen-deficient uranate, the black colour arising from an intervalence transition (also the feature of UO_{2+x}). Third, and most likely, it could be Tl_2O. This black compound melts at 596 °C and has appreciable vapour pressure above its melting point, 40 mm Hg at 700 °C, rising to 55 mm Hg at 800 °C, 125 mm Hg at 900 °C and 260 mm Hg at 1000 °C [15]. Thus it would be partially removed and deposited in cooler regions by the sweeping action of a gentle stream of nitrogen during the TGA measurements. To date, we have not analysed the black product or the material remaining after TGA measurements.

The published standard enthalpies of formation of the alkali metal uranates at 25 °C, ΔH_f^0, see [14], allow us to suggest values for the thallium uranates studied here. For the monouranates, for which there are the most values reported, there is no apparent trend and the average value is -1893 ± 42 kJ mol^{-1}: we propose that -1900 ± 40 kJ mol^{-1} is a realistic value for Tl_2UO_4. Standard enthalpies have only been reported for the diuranates of sodium, rubidium and caesium, but since their average is -3182 ± 34 kJ mol^{-1} this is an acceptable proposition for ΔH_f^0 for $Tl_2U_2O_7$. For the triuranates, only one value has been reported, for $Li_2U_3O_{10}$, of -4438 kJ mol^{-1}, and similarly for Na_4UO_5, a value of -2457 kJ mol^{-1}: similar values for $Th_2U_3O_{10}$ and Th_4UO_5 might thus be expected.

3.2. Structural analysis

The known structures of the alkali metal uranates are collated and referenced in our review [14]. Of the various uranates that can be prepared the best structurally characterised are the monovalent monouranates. Each uranium is surrounded by six oxygen atoms, two axial (primary) at a shorter distance than the remaining four equatorial (secondary) oxygens. The equatorial oxygens are shared by neighbouring uranium atoms, forming either infinite layers or chains. Layers occur in Li_2UO_4, β-Na_2UO_4 and K_2UO_4, and chains in α-Na_2UO_4. Thallium monouranate was said to be isostructural with K_2UO_4 [5] and the symmetry and cell parameters determined here (Table 1) concur. X-ray absorption spectroscopy also provided the atom arrangement around uranium. The Tl_2UO_4 EXAFS spectrum is given in Fig. 2 and the results of the fit in Table 2. For comparison, the spectra of lithium, potassium and rubidium monouranates were also here measured and in all these compounds uranium is surrounded by six oxygen atoms, two primary (axial) at shorter distances than the remaining four secondary (equatorial). In addition, there are four uranium atoms at around 4 Å and this is consistent with a layer structure, since in the chain structure (as in α-Na_2UO_4) there are two U atoms in the surroundings of each uranium.

Diuranates are structurally similar to monouranates, except that in this case axial 'uranyl' units consist of O–U–O–U–O groups and each U is additionally bound to four equatorial oxygen atoms. EXAFS analysis confirmed this and showed that the atom arrangement in $Tl_2U_2O_7$ resembles that in $Rb_2U_2O_7$. Structures of triuranate compounds are more complex and for lithium triuranate its structure consists of $(UO_2)O_4$ octahedra and $(UO_2)O_5$ pentagonal bipyramids linked by bridging oxygen atoms [16]. The EXAFS data for $Tl_2U_3O_{10}$ (Table 2) were satisfactorily fitted using the description of the structure for $Li_2U_3O_{10}$ [16]. Similarly, the best fit

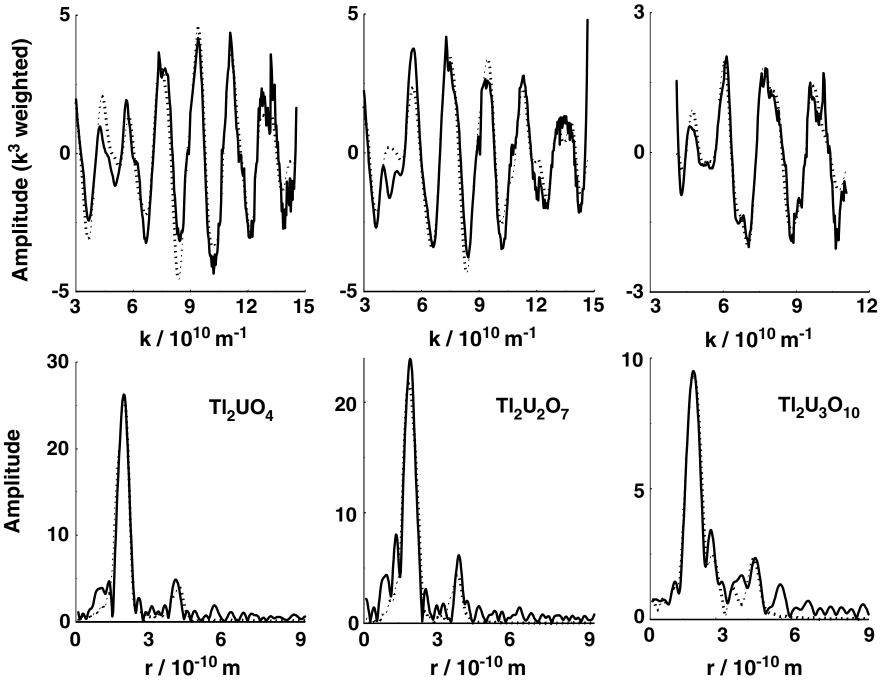

Fig. 2. EXAFS spectra and corresponding Fourier-transforms for thallium uranates. Experimental data, solid lines; best fit, dashed lines.

Table 2
Structural parameters from EXAFS curve fitting of thallium(I) uranates(VI) and (in parentheses) their calculated bond distances from their vibrational spectra

Compound	Shell (U–X) and coord. number	U–X distance, nm[a]	Debye–Waller factor ($2\sigma^2$), nm	*R*
Tl_2UO_4	U–O, 2	0.190 (0.187)	0.0005	32.74
	U–O, 4	0.221 (0.219)	0.0008	
	U–U, 4	0.416	0.0019	
$Tl_2U_2O_7$	U–O, 2	0.187 (0.184–0.189)	0.0006	35.25
	U–O, 4	0.225 (0.218–0.221)	0.0016	
	U–U, 1	0.379	0.0008	
$Tl_2U_3O_{10}$	U–O, 2	0.181 (0.180–0.183)	0.0019	29.89
	U–O, 4	0.214 (0.222–0.223)	0.0022	
	U–O, 2	0.316	0.0021	
	U–O, 6	0.388	0.0036	
	U–O, 12	0.477	0.0023	
Tl_4UO_5	U–O, 4	0.202 (0.201)	0.0048	39.18
	U–O, 2	0.221 (0.222)	0.0012	
	U–Tl, 4	0.431	0.0033	
	U–Tl, 8	0.457	0.0026	

[a] U–O distances determined from the U–O asymmetric stretching frequencies in the IR spectra are given in parenthesis.

of EXAFS data for Tl_4UO_5 was obtained using the structure of Li_4UO_5 [17].

Fig. 3 shows our recorded vibrational spectra of the four thallium uranates. The IR spectra of Tl_2UO_4 and Tl_4UO_5 are similar to the spectra described by Girigharan et al. [5,6]. The IR spectrum of $Tl_2U_3O_{10}$ has common features with that of $Tl_6U_7O_{24}$ [5] and resembles closely the spectrum of $Li_2U_3O_{10}$ [2]. The IR spectrum of $Tl_2U_2O_7$ measured here exhibits more peaks than reported previously [5] and resembles more closely the

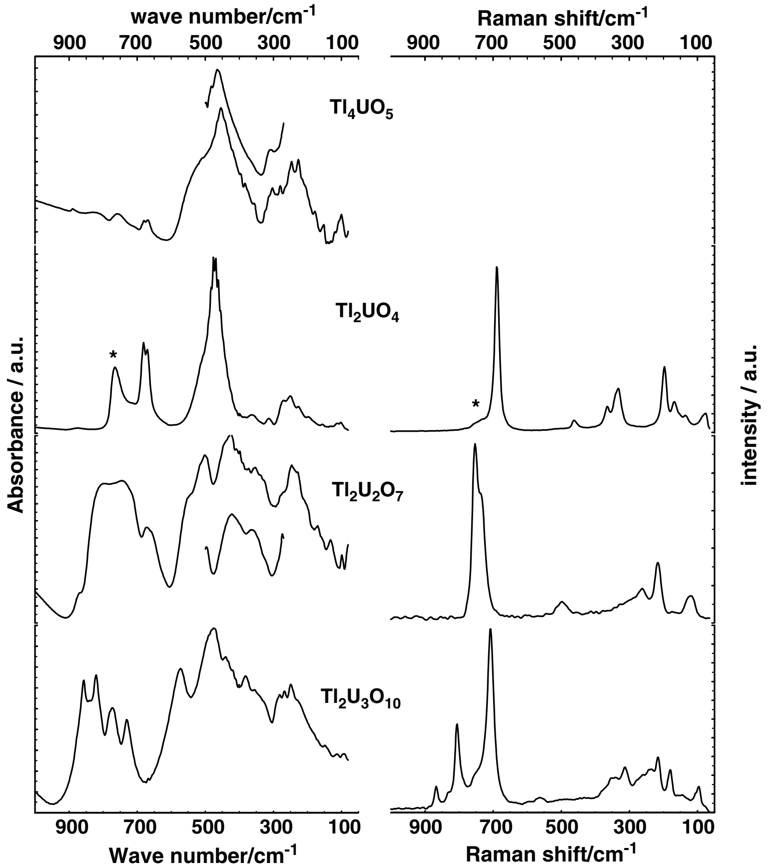

Fig. 3. Spectra of thallium(I) uranates(VI), vibrational, IR left and Raman right.

corresponding spectra of $Na_2U_2O_7$ [2] and $Cs_2U_2O_7$ [3], rather than that of $K_2U_2O_7$ as had been previously suggested [5].

The lengths of primary and secondary U–O bonds can be calculated from the vibrational frequencies of U–O stretching modes using the following equations derived for the uranate-type compounds [18]:

$$R_{\text{U–O(I)}} = 74.75(\nu_{\text{as}})^{-2/3} + 0.975, \quad (1)$$

$$R_{\text{U–O(II)}} = \left(81/R^2_{\text{U–O(I)}}\right)^{1/4}, \quad (2)$$

where $R_{\text{U–O}}$ is the length of U–O bond; ν_{as} is the asymmetric stretching frequency and (I) and (II) refer to primary and secondary U–O bonds, respectively.

The values so calculated are included in Table 2 and agree very well with the parameters obtained from EXAFS spectroscopy measurements, thus providing additional direct confirmation of the above equations. For Tl_4UO_5, the 'primary' U–O bonds are longer than the secondary, but even in this case the bond lengths calculated using Eqs. (1) and (2) correspond well with the results of XAS. This shows directly that elongation of the secondary U–O bonds in the uranates leads to shortening of the primary bonds and the average geometric value of the U–O interatomic distance is preserved. This condition for six-coordinated uranium is reflected by Eq. (2) [18].

3.3. Electronic absorption spectra

Measuring the electronic absorption spectra at different temperatures allows differentiation between species with and without a centre of symmetry. The spectra recorded here (by diffuse reflectance) at room temperature and at −196 °C are shown in Fig. 4. (Band maxima of diffuse reflectance spectra are considerably sharpened at liquid nitrogen temperature.) Compared to our diffuse reflectance spectra of the alkali metal (Li, Na, K, Rb and Cs) mono- and diuranates [1], the spectra of the corresponding thallium compounds are relatively featureless and even at low temperatures do not exhibit clear maxima that can be associated with individual electronic transitions. From the effect of temperature on the thallium spectra we can conclude that thallium mono- and

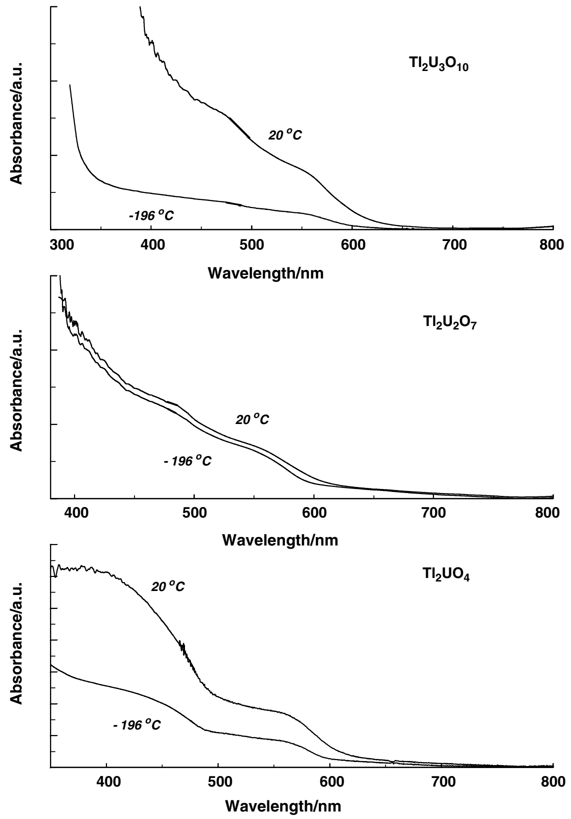

Fig. 4. Diffuse reflectance spectra of thallium uranates at room temperature and −196 °C.

triuranates belong to centrosymmetrical point groups whereas the diuranate probably do not possess a centre of symmetry.

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