

Structure of Thallium Tricarbonatodioxouranate(VI)

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Abstract. $\text{Tl}_4[\text{UO}_2(\text{CO}_3)_3]$, $M_r = 1267.5$, monoclinic, $C2/c$, $a = 10.684$ (2), $b = 9.309$ (2), $c = 12.726$ (3) Å, $\beta = 94.95$ (2)°, $V = 1261.0$ (3) Å³, $Z = 4$, $D_x = 6.676$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 636$ cm⁻¹, $F(000) = 2088$, $T = 295$ K, final $R = 0.037$ for 841 observed reflections. $\text{Tl}_4[\text{UO}_2(\text{CO}_3)_3]$ is isostructural with the corresponding salts of K and NH₄. The Tl atoms are nine coordinated by O atoms, Tl—O = 2.82 (1)–3.27 (1) Å, and do not show significant steric effects of the electron lone pair.

Introduction. A wide variety of crystalline salts of the tricarbonatodioxouranium(VI) anion has been reported (*Gmelin Handbook of Inorganic Chemistry*, 1983). Among the salts with exclusively monovalent cations (Li, Na, K, Rb, Cs, NH₄, Tl, Ag) the title compound stands out because it is almost insoluble in H₂O, but in spite of that crystallizes quite well and, therefore, was used for microdetermination of uranium. In order to learn whether the low solubility of the salt is connected with the steric effects of the Tl coordination, the present X-ray study was carried out during related work (Mereiter, 1986).

Experimental. 0.7 g $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 50 ml H₂O were slowly added at $T \approx 330$ K to 2 g $\text{Tl}_2(\text{CO}_3)_2$ in 200 ml H₂O. The precipitate consisted mainly of stubby prisms (≤ 0.3 mm) and small amounts of acicular and tabular crystals, all yellow in colour and identical in X-ray powder patterns. Single crystal ca 0.015 × 0.028 × 0.24 mm. Philips PW 1100 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Unit-cell dimensions from 19 reflections, $5 < \theta < 25^\circ$. Intensities measured using ω scans, scan width 1°, scan rate 0.6° min⁻¹; three standard reflections, $\pm 2\%$ variation. 1113 unique reflections measured, θ : 2–25°, h : -12–12, k : 0–11, l : 0–15; 841 with $I > 2.5 \sigma(I)$ used; absorption correction by Gaussian integration, transmission factors 0.19–0.39. Unit-cell dimensions and space group indicated isomorphism with the corresponding NH₄ and K salts. Initial atomic parameters from $(\text{NH}_4)_4[\text{UO}_2(\text{CO}_3)_3]$ (Graziani, Bombieri & Forsellini, 1972) gave $R = 0.28$. Least-squares refinement on F , anisotropic temperature factors only for Tl and U, scattering factors for neutral atoms from

Table 1. Atomic coordinates and isotropic temperature factors (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Tl(1)	0.6833 (1)	0.3441 (1)	0.3524 (1)	2.38 (3)†
Tl(2)	0.6033 (1)	0.8207 (1)	0.5468 (1)	2.46 (3)†
U	0.5	0.6925 (1)	0.25	1.06 (3)†
C(1)	0.5	0.9988 (28)	0.25	3.8 (6)
C(2)	0.6150 (11)	0.5412 (15)	0.0897 (12)	1.9 (3)
O(1)	0.5422 (8)	0.9225 (10)	0.1740 (8)	2.7 (2)
O(2)	0.5979 (8)	0.6748 (10)	0.0851 (8)	2.0 (2)
O(3)	0.5615 (8)	0.4735 (10)	0.1643 (8)	2.1 (2)
O(4)	0.5	1.1327 (17)	0.25	3.5 (4)
O(5)	0.6776 (9)	0.4701 (12)	0.0269 (9)	3.4 (3)
O(6)	0.6546 (8)	0.6914 (10)	0.3187 (8)	2.2 (2)

$$\dagger B_{\text{eq}} = \frac{2}{3}\pi^2(U_{11} + U_{22} + U_{33}).$$

SHELX76, isotropic extinction parameter (final value 0.46×10^{-3}), weights $w = [\sigma^2(F_o) + 0.0006F_o^2]^{-1}$, 15 strong reflections down-weighted because of extinction effects. Final $R = 0.037$, $wR = 0.040$, $(\Delta/\sigma)_{\text{max}} < 0.01$, $\Delta\rho_{\text{max}} = 2.5 \text{ e \AA}^{-3}$ near Tl(1). All calculations were carried out with *SHELX76* (Sheldrick, 1976).

Discussion. Atomic parameters are given in Table 1.* The title compound is isostructural with $(\text{NH}_4)_4[\text{UO}_2(\text{CO}_3)_3]$ (Graziani, Bombieri & Forsellini, 1972) and $\text{K}_4[\text{UO}_2(\text{CO}_3)_3]$ (Anderson, Chung Chieh, Irish & Tong, 1980). Table 2 provides a comparison of the cell dimensions and bond lengths of the three compounds. Differences between the crystal structures are moderate and restricted mainly to the dimensions of the M^+ coordination ($M = \text{Tl}, \text{NH}_4, \text{K}$) and of the unit cells. In each of the three structures the two cation sites $M(1)$ and $M(2)$ have to be regarded as nine coordinated because a large gap in the M —O distances occurs only after the ninth-nearest O-atom neighbours (gap ≥ 0.6 Å). For the potassium compound this finding is at variance with that of Anderson *et al.* (1980), who stated K(2) to be eight coordinated and overlooked K(2)—O(1^v) = 2.87 Å. The coordination

* Lists of structure factors, anisotropic thermal parameters, bond angles, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43148 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

figures of the M cations are irregular (Fig. 1). Similar trends in Ti-O , $\text{NH}_4\text{-O}$ and K-O distances and the lack of exceptionally short Ti-O bonds reveal that Ti^+ in the title compound behaves essentially as 'ionic', *i.e.* does not show significant steric effects of the lone pair. Compounds showing this effect, *e.g.* Ti_2CO_3 (Marchand, Piffard & Tournoux, 1975) or Ti_2HPO_4 (Odden, Vignalou, Tranquard & Pépe, 1979), have Ti-O bonds as short as 2.67 (2) and 2.51 (3) Å, respectively, and clearly one-sided Ti coordination. The only remarkably short $M\text{-O}$ distance is not observed in the title compound but found in the K salt, where $\text{K-O}(5^{\text{vii}}) = 2.67$ Å appears to be forced by packing effects.

The shape and environment of the $[\text{UO}_2(\text{CO}_3)_3]$ unit in the title compound are outlined in Fig. 1. Eighteen Ti atoms surround the unit in a way which essentially reflects its approximately $D_{3h}\text{-}\bar{6}m2$ symmetry (actual

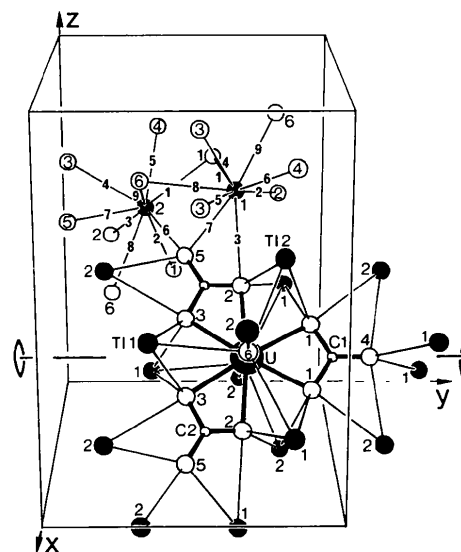


Fig. 1. Environment of the $[\text{UO}_2(\text{CO}_3)_3]$ unit in $\text{Ti}_4[\text{UO}_2(\text{CO}_3)_3]$. Two TiO_6 coordinations are also shown in detail. Small bold-face numbers on bonds to these Ti atoms correspond to the sequence of $M\text{-O}$ bonds in Table 2.

Table 2. Comparison of $\text{Ti}_4[\text{UO}_2(\text{CO}_3)_3]$, $(\text{NH}_4)_4\text{-}[\text{UO}_2(\text{CO}_3)_3]$ and $\text{K}_4[\text{UO}_2(\text{CO}_3)_3]$ bond lengths (Å)

	M represents Ti, NH_4 , and K.		
	Ti (This work)	NH_4 (Graziani <i>et al.</i> , 1972)	K (Anderson <i>et al.</i> , 1980)
a (Å)	10.684 (2)	10.68 (1)	10.247 (3)
b (Å)	9.309 (2)	9.38 (1)	9.202 (2)
c (Å)	12.726 (3)	12.85 (1)	12.226 (3)
β (°)	94.95 (2)	96.45 (9)	95.11 (2)
V (Å ³)	1261	1279	1148
$M(1)\text{-O}(1^{\text{iv}})$	3.07 (1)	3.19 (2)	2.93 (1)
$\text{-O}(2^{\text{iv}})$	2.87 (1)	2.86 (2)	2.75 (1)
$\text{-O}(2^{\text{iii}})$	3.18 (1)	3.22 (2)	3.03 (1)
$\text{-O}(3^{\text{i}})$	2.89 (1)	2.85 (2)	2.75 (1)
$\text{-O}(3^{\text{ii}})$	2.87 (1)	2.94 (2)	2.80 (1)
$\text{-O}(4^{\text{iv}})$	2.99 (1)	2.90 (2)	2.83 (1)
$\text{-O}(5^{\text{iii}})$	2.82 (1)	2.85 (2)	2.76 (1)
$\text{-O}(6^{\text{iv}})$	3.23 (1)	3.32 (2)	3.03 (1)
$\text{-O}(6^{\text{i}})$	3.27 (1)	3.39 (2)	3.24 (1)
Mean	3.02	3.06	2.90
$M(2)\text{-O}(1^{\text{v}})$	2.99 (1)	2.99 (2)	2.87 (1)
$\text{-O}(1^{\text{ii}})$	3.23 (1)	3.11 (2)	3.06 (1)
$\text{-O}(2^{\text{ii}})$	2.94 (1)	2.92 (2)	2.80 (1)
$\text{-O}(3^{\text{iii}})$	3.17 (1)	3.32 (2)	3.10 (1)
$\text{-O}(4^{\text{v}})$	2.93 (0)	3.06 (1)	2.83 (0)
$\text{-O}(5^{\text{vi}})$	2.95 (1)	2.92 (2)	2.67 (1)
$\text{-O}(5^{\text{iii}})$	2.84 (1)	2.95 (2)	2.90 (1)
$\text{-O}(6^{\text{viii}})$	2.98 (1)	2.96 (2)	2.81 (1)
$\text{-O}(6^{\text{i}})$	3.23 (1)	3.15 (2)	3.07 (1)
Mean	3.03	3.04	2.90
$\text{U-O}(6^{\text{iv}})$	1.80 (1)	1.79 (1)	1.80 (1)
$\text{-O}(1^{\text{iv}})$	2.41 (1)	2.46 (1)	2.43 (1)
$\text{-O}(2^{\text{iv}})$	2.43 (1)	2.44 (1)	2.43 (1)
$\text{-O}(3^{\text{iv}})$	2.43 (1)	2.46 (1)	2.43 (1)
$\text{C}(1)\text{-O}(1^{\text{iv}})$	1.31 (2)	1.34 (2)	1.32 (1)
$\text{-O}(4^{\text{i}})$	1.25 (3)	1.22 (3)	1.25 (1)
$\text{C}(2)\text{-O}(2^{\text{i}})$	1.26 (2)	1.33 (2)	1.32 (1)
$\text{-O}(3^{\text{i}})$	1.31 (2)	1.29 (2)	1.30 (1)
$\text{-O}(5^{\text{i}})$	1.27 (2)	1.25 (3)	1.23 (1)

Symmetry code: none or (i) x, y, z ; (ii) $1-x, y, \frac{1}{2}-z$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $x, 2-y, \frac{1}{2}+z$; (vi) $1-x, y-1, \frac{1}{2}-z$; (vii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $\frac{3}{2}-x, \frac{3}{2}-y, 1-z$.

symmetry is $C_{2v}\text{-}2$, however). All O atoms of the unit are involved in Ti-O bonds, three to four in number. Bond distances and angles within the unit are similar to the corresponding figures for the NH_4 and K salts. However, the wave-like deformation of the $\text{U}(\text{CO}_3)_3$ entity is less pronounced than in the K salt, but yet larger than in the NH_4 salt. While the terminal carbonate O(5) atom deviates in the K salt by 0.55 (1) Å from the LS plane through the six equatorial O ligands of U, it deviates in the title compound by 0.38 (1) Å and in the NH_4 salt by 0.31 (2) Å from the corresponding planes.* Even these latter deformations are relatively large in comparison with other tricarbonatodioxouranates(VI) (*e.g.* Mereiter, 1982, 1986) and indicate that the $[\text{UO}_2(\text{CO}_3)_3]$ unit in the title compound and its analogues is exposed to considerable distortion from its environment. In $\text{K}_3\text{Na}[\text{UO}_2(\text{CO}_3)_3]\cdot\text{H}_2\text{O}$ [structure according to Mazzi & Rinaldi (1961); chemical formula according to Walenta (1972)] 17 alkali ions surround the $[\text{UO}_2(\text{CO}_3)_3]$ unit in a fashion resembling Fig. 1, but the $\text{U}(\text{CO}_3)_3$ entity is exactly planar.

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* See deposition footnote.

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Single-Crystal Structure of Lead Uranate(VI)

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Abstract. PbUO₄, $M_r = 509.2$, orthorhombic, *Pbcm*, $a = 5.536$ (1), $b = 7.968$ (2), $c = 8.212$ (3) Å, $Z = 4$, $V = 362.24$ Å³, $D_x = 9.34$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 889.1$ cm⁻¹, $F(000) = 824$, $T = 298$ K, $R = 0.048$ for 530 unique observed reflections having $I \geq 2\sigma(I)$. As in the case of BaUO₄, PbUO₄ forms a layered structure of (UO₂O₄)_∞²⁻ sheets, with the divalent cations in approximate seven coordination sandwiched between the layers. The uranyl groups are in typical octahedral coordination.

Introduction. Several previous studies have been performed to determine the structures of uranates in general (e.g. Gebert, Hoekstra, Reis & Peterson, 1978; Kovba, Polunina, Simanov & Ippolitova, 1961; Peters, 1967) and lead uranate in particular (Frondel & Barnes, 1958; Sterns, 1967). Although until now no single-crystal diffraction study has been performed that yielded atomic positions, X-ray powder diffraction has shown the structure of PbUO₄ to be isomorphous with BaUO₄ (Frondel & Barnes, 1958; Reis, Hoekstra, Gebert & Peterson, 1976; Samson & Sillén, 1947). The present structure confirms the powder studies and has yielded precise atomic positional parameters for PbUO₄.

Experimental. Lead uranate (PbUO₄) was prepared from a melt by adding 2.5 g of PbClF to 0.25 g U(MoO₄)₂ (Cremers, Eller, Penneman & Herrick, 1983) and heating overnight at 823 K. Orange crystals were recovered from the solidified melt. The crystals are

tabular on {100}, and bounded by prominent {011} and minor {001} and {010} faces. Good cleavage is present perpendicular to each of the crystallographic axes. The refractive indices exceed 1.700, and the optical orientation is $a = Z$, $b = Y$, $c = X$ with no distinctive pleochroism. The crystals are biaxial positive with a large angle and strong $r > v$ axial dispersion.

A crystal (0.028 × 0.090 × 0.082 mm) in the form of a square tablet was chosen for X-ray diffraction and mounted perpendicular to the {100} face. The data set was collected by θ - 2θ scans ($2\theta_{\text{max}} = 70^\circ$) on a Picker automated diffractometer using Mo *K* α radiation and a graphite monochromator. Precession photographs were used to verify the Laue symmetry and to obtain initial cell constants. The least-squares-refined cell dimensions based on twelve diffractometer-centered reflections ($40 \leq 2\theta \leq 53^\circ$) are $a = 5.536$ (1), $b = 7.968$ (2) and $c = 8.212$ (3) Å. The space group as determined from systematically absent reflections was *Pbc2*, or *Pbcm*, and *Pbcm* was chosen on the basis of the subsequent successful refinement in the centrosymmetric cell. Reflections in a hemisphere with Miller indices h 0–8, k 0±12, and l 0±13 were collected to yield 846 symmetry-independent reflections. Two standard reflections monitored approximately every 2 h. Analytical absorption corrections based on the indexed faces (max. transmission = 0.127, min. = 0.016) and corrections for Lorentz–polarization factors were performed. Equivalent reflections were averaged, yielding 530 reflections with $I \geq 2\sigma(I)$ and an *R* factor on *F* of 6%. The structure was solved using standard Patterson methods and refined by full-matrix least squares employing the Los Alamos Crystal Structure Codes

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