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# Structure of Dicaesium Tetrachlorodioxouranium(VI)

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**Abstract.** $Cs_2UO_2Cl_4$, $M_r = 667{\cdot}65$, monoclinic, $C2/m$, $a = 11{\cdot}929\,(2)$, $b = 7{\cdot}704\,(2)$, $c = 5{\cdot}816\,(2)$ Å, $\beta = 100{\cdot}02\,(4)^\circ$, $V = 525{\cdot}98$ Å$^3$, $Z = 2$, $D_x = 4{\cdot}27$ g cm$^{-3}$, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7109$ Å, $\mu = 223{\cdot}7$ cm$^{-1}$, $F(000) = 568$, $T = 293$ K, $R = 0{\cdot}0237$, $wR = 0{\cdot}0355$ for 1131 reflections. The structure was redetermined in order to rectify some ambiguities and errors in an earlier determination. While the structure is essentially similar to that previously reported, there are small differences in the cell and atomic parameters, and hence in the interatomic distances.

**Introduction.** The structure of $Cs_2UO_2Cl_4$ was originally determined by Hall, Rae & Waters (1966). There are some obvious errors in this paper. First, the table of atom coordinates almost superimposes the caesium and oxygen atoms. Second, the bond lengths and bond angles are only reported as labels in a diagram, without indications of precision. None of these values are consistent with the table of atomic coordinates, but can be obtained if it is assumed that the authors used a monoclinic angle $\beta = 94{\cdot}67^\circ$, rather than the reported experimental value $\beta = 99{\cdot}67^\circ$.

$Cs_2UO_2Cl_4$ provides one of the simplest examples of the structure of the uranyl ion $UO_2^{2+}$. The linearity of this species and its remarkable chemical stability has excited considerable theoretical and experimental work (Denning, 1991), aimed at understanding the nature of the bonding. In particular it is clear that the length of the U—O bond is sensitive to the nature of the ligands bound in the equatorial plane. A structural survey (Denning, 1982) shows reported U—O distances between 1·52 and 2·00 Å. In most examples of the complex anion $[UO_2Cl_4]^{2-}$ the distance appears to be about 1·75 Å, but reported values range from 1·58 to 1·94 Å. Several structures contain organic cations, some of which can form hydrogen bonds, so the relative simplicity of $Cs_2UO_2Cl_4$ should provide the best guide to the bond length. The value reported by Hall *et al.* (1966), 1·81 Å, is unusually long, while the value of 1·73 Å obtained from their table of atom coordinates appears short. Neither of these is consistent with an estimate based on vibrational frequencies and Badger's rule (Bartlett & Cooney, 1989), using data from 31 compounds, which predicts 1·78 Å.

According to Hall *et al.* $Cs_2UO_2Cl_4$ has only one molecule per primitive unit cell and it is this feature which is responsible for its use in comprehensive studies of the optical spectrum (Barker, Denning & Thorne, 1987) of the uranyl ion, and as the basis for measurements of the electronic energy transfer between these ions (Thorne, Denning, Barker & Grimley, 1985). The structural data are vital to the arguments used in the development of both of these areas of study, and it is in this light that we have undertaken a redetermination of the structure.

**Experimental.** Single crystals of $Cs_2UO_2Cl_4$ were grown by adding stoichiometric quantities of caesium chloride to an aqueous solution of uranyl chloride, and recrystallizing the precipitate from dilute hydrochloric acid. The larger crystals required for optical work (Barker *et al.*, 1987) were grown by slow evaporation of the same solutions. Fine acicular

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Table 1. *Positional parameters and* $U_{eq}$ *values* (Å$^2$)

$U_{eq} = (U_1U_2U_3)^{1/3}$.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| U(1) | 0·0000 | 0·0000 | 0·0000 | 0·0253 |
| Cs(2) | 0·16530 (3) | 0·5000 | 0·32254 (6) | 0·0369 |
| Cl(3) | −0·10105 (9) | −0·2513 (1) | 0·2057 (2) | 0·0384 |
| O(4) | 0·1162 (4) | 0·0000 | 0·2362 (8) | 0·0387 |

and larger tabular crystals were formed. Samples of the acicular crystals, chosen because of their more favourable absorption effects, all gave oscillation photographs showing layer lines consisting of wide (5°) bands of reflection. Careful examination of some of the longer needles showed that they were either curved or parts of spirals. All the samples used for optical measurements had been cut from large tabular crystals. A relatively small one of these ($0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}25$ mm) gave good oscillation and Weissenberg photographs, and was used for data collection on an Enraf–Nonius CAD-4F diffractometer using Mo $K\alpha$ radiation.

1893 reflections were measured in the range $1{\cdot}0 < \theta < 35{\cdot}0°$, with $-19 < h < 19$, $-1 < k < 12$, $-1 < l < 9$. This yielded 1229 unique reflections of which 1131 had $I > 3\sigma(I)$. The Sheldrick merging $R$ factor was 2·43%. Absorption profiles were measured for the 060 and 0,10,0 reflections, giving minimum:maximum corrections of 2·35:1 on $F$. The structure was refined isotropically to 10% when the *DIFABS* absorption correction (Walker & Stuart, 1983) was applied to the uncorrected data, giving minimum:maximum corrections of 2·51:1. Anisotropic refinement including a Larson isotropic extinction correction (Larson, 1970) and using a three-term Chebyshev weighting scheme (Carruthers & Watkin, 1979) converged at $R = 2{\cdot}37$, $wR = 3{\cdot}55\%$, $S = 1{\cdot}20$; $(\Delta/\sigma)_{\max} = 0{\cdot}004$, maximum and minimum heights in final difference Fourier synthesis 0·21 and $-0{\cdot}17$ e Å$^{-3}$. All computations were performed with the *CRYSTALS* program (Watkin, Carruthers & Betteridge, 1985). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Table 2. *Anisotropic temperature factors* (Å$^2$)

$$T = \exp[-2\pi^2(h^2a^*)U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| U(1) | 0·0256(1) | 0·0246(1) | 0·0253(1) | 0·0000 | 0·00301(8) | 0·0000 |
| Cs(2) | 0·0357(2) | 0·0395(2) | 0·0368(2) | 0·0000 | 0·0088(1) | 0·0000 |
| Cl(3) | 0·0439(5) | 0·0338(5) | 0·0441(5) | 0·0053(4) | 0·0158(4) | −0·0022(3) |
| O(4) | 0·037(2) | 0·046(2) | 0·033(2) | 0·0000 | −0·000(2) | 0·0000 |

Table 3. *Interatomic distances* (Å) *less than* 4 Å *and selected interbond angles* (°)

| | | | |
|---|---|---|---|
| U(1)—O(4) | 1·774 (4) | U(1)—Cl(3) | 2·671 (1) |
| Cs(2)—O(4) | 3·324 (4) | Cs(2)—O(4) | 3·9154 (8) |
| Cs(2)—Cl(3) | 3·538 (1) | Cs(2)—Cl(3) | 3·555 (1) |
| Cs(2)—Cl(3) | 3·589 (1) | Cs(2)—Cl(3) | 3·671 (1) |
| Cl(3)—O(4) | 3·198 (4) | Cl(3)—O(4) | 3·215 (4) |
| Cl(3)—O(4) | 3·811 (4) | Cl(3)—O(4) | 3·910 (4) |
| Cl(3)—Cl(3) | 3·681 (2) | Cl(3)—Cl(3) | 3·829 (2) |
| Cl(3)—Cl(3) | 3·832 (2) | Cl(3)—Cl(3) | 3·872 (2) |
| Cl(3)—Cl(3) | 3·924 (2) | O(4)—O(4) | 3·547 (9) |
| | | | |
| Cl(3)—U(1)—O(4) | 90·3 (1) | Cl(3)—U(1)—O(4) | 89·7 (1) |
| Cl(3)—U(1)—Cl(3) | 92·91 (5) | Cl(3)—U(1)—Cl(3) | 87·09 (5) |

**Discussion.** Table 1 lists the atomic coordinates and Table 2 the anisotropic temperature factors.* Table 3 shows interatomic distances less than 4 Å, as well as the interbond angles at uranium. The $b$-axis projection is, apart from the values for bond lengths and angles, similar to that of Hall *et al.* (1966). The $c$-axis projection in Fig. 1 shows the plane containing the four chlorine atoms, with oxygen almost perpendicularly above and below the plane. The angle subtended at uranium by two chlorine atoms, 92·9°, is less than that reported by Hall *et al.* 95°, but nonetheless, not a right angle.

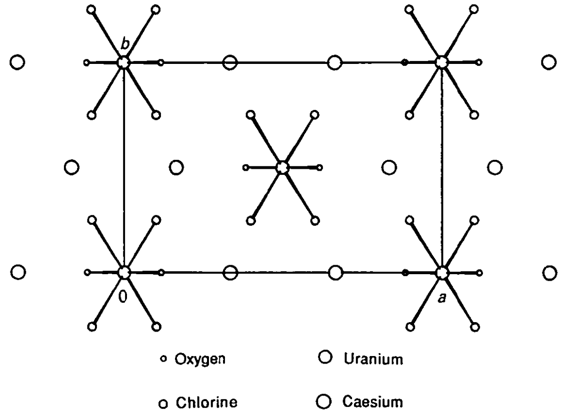

Fig. 1. The $c$-axis projection of the structure of $Cs_2UO_2Cl_4$.

The structure is effectively the same as that described by Hall *et al.* (1966), but their reporting errors have been clarified, and the precision of the determination is much improved. The U—O distance of 1·774 (4) Å is now in good agreement with the prediction of 1·78 Å based on vibrational data (Bartlett & Cooney, 1989). The basis of the optical spectroscopic studies (Barker *et al.*, 1987; Thorne *et al.*, 1985) is established as secure.

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54338 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Time-of-Flight Powder Neutron Diffraction Study of the Structure of $Ba_2PbO_4$

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**Abstract.** Dibarium lead(IV) tetraoxide, $M_r = 545{\cdot}88$, tetragonal, $I4/mmm$, $Z = 2$. $T = 5$ K: $a = 4{\cdot}29650$ (2), $c = 13{\cdot}2285$ (1) Å, $V = 244{\cdot}196$ (4) Å$^3$, $D_x = 7{\cdot}424$ g cm$^{-3}$. $T = 298$ K: $a = 4{\cdot}30241$ (1), $c = 13{\cdot}26070$ (5) Å, $V = 245{\cdot}466$ (2) Å$^3$, $D_x = 7{\cdot}386$ g cm$^{-3}$. Rietveld refinement using time-of-flight powder neutron diffraction data [TOF 30000–103000 μs, 184 contributing reflections, 5 K; TOF 35000–110000 μs, 122 contributing reflections, 298 K] resulted in $R_{wp} = 2{\cdot}6$ ($R_{\rm exp} = 2{\cdot}1$), $\chi^2 = 1{\cdot}5$ at 5 K and $R_{wp} = 5{\cdot}1$ ($R_{\rm exp} = 3{\cdot}0$), $\chi^2 = 3{\cdot}0$ at 298 K. Our results confirm the room-temperature structure determined earlier by X-ray work and show the lack of structural distortions down to 5 K. They also permit a very precise determination of the geometry of the $PbO_6$ octahedra, showing that the tetragonal distortion had been overestimated before by at least a factor of 10. The implication of this result for recent band-structure calculations is stressed.

**Introduction.** The barium lead bismuthate system was one of the first superconducting oxide systems with $T_c = 12$ K for $BaPb_{0{\cdot}75}Bi_{0{\cdot}25}O_3$ (Sleight, Gillson & Bierstedt, 1975). The parent oxide $BaPbO_3$ is a black perovskite whose semimetallic properties are due to overlap of the Pb 6*s* band with the non-bonding O 2*p* states, arising from the 2*p* orbitals perpendicular to the Pb—O bonds (Mattheiss & Hamann, 1982). $BaPbO_3$ may be considered as the $n = \infty$ member of the homologous series of oxides $Ba_{n+1}Pb_nO_{3n+1}$. The $n = 1$ member of this series $Ba_2PbO_4$ is known (Weiss & Faivre, 1959) and a powder X-ray determination of the crystal structure indicated that it adopted the $K_2NiF_4$ structure with an unusual compressed geometry for the $PbO_6$ octahedron [$r$(Pb—O$_{\rm eq}$) = 2·14, $r$(Pb—O$_{\rm ax}$) = 2·06 Å] (Weiss & Faivre, 1959). In view of this and the possible analogies with the layered cuprate systems, such as $La_2CuO_4$, characterized by low symmetry distortions, a high-resolution powder neutron diffraction study of $Ba_2PbO_4$ at ambient and low temperatures was undertaken.

**Experimental.** Preparative techniques based on solid-state reactions of PbO or $PbO_2$ with $BaCO_3$ at high temperatures were found to be unsatisfactory, leading to the loss of PbO and phase separation. A low-temperature preparative route using the citrate sol–gel method (Rosseinsky, Prassides & Day, 1989) often led to the presence of $BaPbO_3$ as an impurity. High purity samples were prepared by an adaptation of the method of Vidyasagar, Gopalakrishnan & Rao (1985). Stoichiometric quantities of barium and lead nitrates are dissolved in the minimum quantity of distilled water. The nitrate solution is added dropwise into rapidly stirred ice-cold concentrated nitric acid, and a white precipitate forms immediately. The $Ba_2Pb(NO_3)_6$ precipitate is filtered, dried at 393 K overnight and decomposed at 1273 K in air in an alumina crucible for 12 h. The product is a red-orange solid and was characterized by powder X-ray diffraction.

Powder neutron data were then collected at both ambient temperature and 5 K at the 1 m position at the High-Resolution Powder Diffractometer

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