INORGANIC COMPOUNDS

Dirubidium Tetrachlorodioxouranium(VI)–Water (1:2)

Christopher E. Anson, Osama Al-Jowder,† Upali A. Jayasooriya* and Anne K. Powell

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England

Abstract

The title compound, $Rb_2[UO_2Cl_4].2H_2O$, has a $[UO_2Cl_4]^{2-}$ anion, with close to D_{4h} ($4/mmm$) symmetry, a U—O distance of 1.751 (9) Å and U—Cl distances of 2.644 (3) and 2.650 (4) Å. The compound is confirmed to be the dihydrate; the degree of hydration had been controversial.

Comment

Because of its high symmetry (D_{4h}, $4/mmm$), the tetrachlorodioxouranium(VI) anion and, in particular, its alkali-metal salts have been the subject of many vibrational spectroscopic studies (Phan Dinh Kien, Kovrikov & Komyak, 1973; Ohwada, 1975, 1978, 1979, 1980; Flint & Tanner, 1981; Bartlett & Cooney, 1989). However, the interpretation of the vibrational data has remained in part ambiguous since only the structure of the caesium salt has been determined. Even here, the ambiguity has not been totally removed, the structure having been solved and refined in space group $C2/m$ (Hall, Rae & Waters, 1966), Pc (Tutov, Solomonov, Solntseva & Fundamenskii, 1981), $C2/m$ again (Watkin, Denning & Prout, 1991) and Cm (Tutov, Plakhtii, Usov, Bublyaev & Chernenkov, 1991). A further uncertainty concerns the degree of hydration of the rubidium, potassium and ammonium salts (see references 3–18 in Flint & Tanner, 1981). Our serendipitous preparation of crystals of the rubidium salt suitable for X-ray analysis thus allowed both structural data for the $[UO_2Cl_4]^{2-}$ complex anion and the degree of hydration in the rubidium salt to be determined.

The structure of the $[UO_2Cl_4]^{2-}$ anion is as expected, with distances U—O(1) 1.751 (9), U—Cl(1) 2.644 (3) and U—Cl(2) 2.650 (4) Å. The only significant deviation from the idealized D_{4h} symmetry concerns the Cl(1)—U—Cl(2) angle which has a value of 90.8 (1)°. The bond lengths can be compared with the U—O and

U—Cl distances found in the caesium salt, *i.e.* 1.774 (4) and 2.671 (1) Å, respectively (Watkin, Denning & Prout, 1991), and 1.780 (4) and 1.780 (5) Å, and 2.644 (2) and 2.688 (2) Å (Tutov, Solomonov, Solntseva & Fundamenskii, 1991). The U—O and U—Cl distances in the caesium salt are significantly longer than those found here and the D_{2h} distortion of the anion is also greater in the caesium salt, with the Cl—U—Cl angle at 92.91 (5)° (Watkin, Denning & Prout, 1991).

The U—O(1) vector is closely aligned with the a axis, making an angle of only 2.0° with it (Fig. 1). There is indeed a fair degree of pseudo-symmetry in the structure reported here; if the $[UO_2Cl_4]^{2-}$ anions alone are considered, they form a close approximation to a C-centred monoclinic cell. However, the Rb^+ ion and O(2) atom do not conform to monoclinic symmetry, and the values for α and γ in this pseudo-centred cell differ significantly from 90° [91.96 (5) and 88.19 (5)°, respectively].
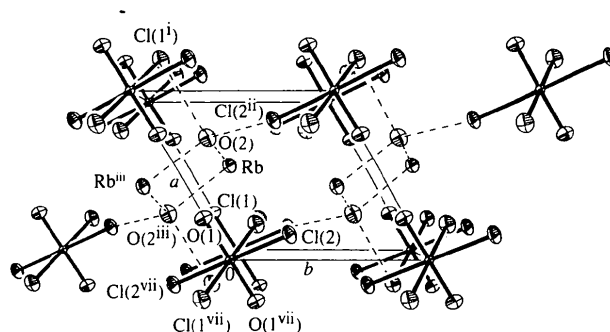

Fig. 1. The unit cell of $Rb_2[UO_2Cl_4].2H_2O$ viewed along the c axis, showing the orientation of the $[UO_2Cl_4]^{2-}$ anions and the Rb_2-(μ-OH$_2$)$_2$ dimeric units. The displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: as given in Table 2 and (vii) $-x, -y, -z$.]

This study also shows that the rubidium salt of the $[UO_2Cl_4]^{2-}$ anion is a dihydrate, contrary to a differential scanning calorimetric study (Ohwada, 1978) which appeared to show it to be a monohydrate. Furthermore, the water molecules are not coordinated to the U atoms (Phan Dinh Kien *et al.*, 1973; Ohwada, 1978) but to the rubidium cations (Ohwada, 1979). The Rb^+ cations and water molecules form $Rb_2(\mu$-OH$_2)_2$ units in the crystal, with each water molecule also making two hydrogen bonds to Cl^- ions (Fig. 1). The O···Cl distances [3.335 (10) and 3.392 (10) Å] indicate weak hydrogen bonding, which is consistent with the vibrational spectra in which the ν(OH) and δ(OH$_2$) modes are rather sharp. Overall, the environment of the water O atom forms a distorted tetrahedron.

The coordination environment of the rubidium cation is best described as approximating to a tricapped trigonal prism, with four O atoms (two from water and two from $[UO_2Cl_4]^{2-}$ anions) and five Cl^- ions making up the coordination shell.

Experimental

Solutions of $RbNO_3$ and $UO_2(NO_3)_2.6H_2O$ in 'concentrated nitric acid' were mixed together and left overnight to give well formed greenish yellow crystals. Surprisingly, the IR spectrum of these crystals showed none of the absorptions expected for nitrate ions, coordinated or otherwise, and the microanalysis of the crystals found no detectable nitrogen. Subsequent investigation of the 'nitric acid' showed that although it was so labelled by the supplier, it was, in fact, concentrated hydrochloric acid. The formulation of the crystals as $Rb_2[UO_2Cl_4].xH_2O$ was indicated by Cl and Rb analysis, and consequent comparison of their IR and Raman spectra with those of previously published structures (Ohwada, 1978, 1979; Flint & Tanner, 1981) established their identity.

Crystal data

$Rb_2[UO_2Cl_4].2H_2O$	Mo $K\alpha$ radiation
$M_r = 618.80$	$\lambda = 0.71069$ Å
Triclinic	Cell parameters from 15
$P\bar{1}$	reflections
$a = 6.795\,(5)$ Å	$\theta = 5.9-13.7°$
$b = 6.929\,(5)$ Å	$\mu = 21.92$ mm^{-1}
$c = 7.457\,(4)$ Å	$T = 300$ K
$\alpha = 91.96\,(5)°$	Block
$\beta = 102.13\,(5)°$	$0.53 \times 0.49 \times 0.29$ mm
$\gamma = 118.82\,(6)°$	Greenish yellow
$V = 296.8\,(3)$ Å^3	
$Z = 1$	
$D_x = 3.48$ Mg m^{-3}	

Data collection

Nicolet Siemens $P3/V$	1304 observed reflections
diffractometer	$[F_o \geq 6\sigma(F_o)]$
ω scans	$R_{int} = 0.0593$
Absorption correction:	$\theta_{max} = 27.5°$
refined from ΔF	$h = -8 \rightarrow 8$
($DIFABS$; Walker &	$k = -9 \rightarrow 9$
Stuart, 1983)	$l = 0 \rightarrow 9$
$T_{min} = 0.489$, $T_{max} =$	2 standard reflections
1.000	monitored every 50
1397 measured reflections	reflections
1336 independent reflections	intensity decay: 8%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.024$
$R = 0.0510$	$\Delta\rho_{max} = 3.04$ e Å^{-3}
$wR = 0.0507$	(1.04 Å from U)
$S = 2.79$	$\Delta\rho_{min} = -3.32$ e Å^{-3}
1304 reflections	Atomic scattering factors
52 parameters	from Cromer & Waber
$w = 1/[\sigma^2(F) + 0.0005F^2]$	(1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($\mathring{A}^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
U	0	0	0	0.0110 (3)
O(1)	0.2519 (16)	−0.0093 (18)	−0.0048 (12)	0.032 (5)
O(2)	0.7405 (19)	0.2290 (19)	0.4210 (13)	0.039 (6)
Cl(1)	0.2030 (6)	0.2240 (6)	0.3413 (4)	0.031 (2)
Cl(2)	0.1624 (6)	0.3766 (5)	−0.1406 (4)	0.030 (1)
Rb	0.5652 (2)	0.2465 (2)	0.7403 (2)	0.0267 (7)

Table 2. *Selected geometric parameters* (Å, °)

Within the $[UO_2Cl_4]^{2-}$ anion

U—O(1)	1.751 (9)	U—Cl(1)	2.644 (3)
U—Cl(2)	2.650 (4)		
O(1)—U—Cl(1)	89.5 (3)	O(1)—U—Cl(2)	89.5 (3)
Cl(1)—U—Cl(2)	90.8 (1)		

About the O(2) atom

O(2)···Cl(1^i)	3.335 (10)	O(2)···Cl(2^{ii})	3.392 (10)
O(2)···Rb	2.901 (9)	O(2)···Rb^{iii}	2.949 (9)

About the Rb atom

Rb···O(1^{iii})	3.049 (9)	Rb···O(1^{iv})	3.095 (9)
Rb···Cl(1)	3.385 (3)	Rb···Cl(1^{vi})	3.361 (3)
Rb···Cl(2^{iv})	3.527 (3)	Rb···Cl(2^{vi})	3.412 (3)
Rb···Cl(2^v)	3.601 (9)	Rb···O(2)	2.901 (9)
Rb···O(2^{iii})	2.949 (9)		

Symmetry codes: (i) $1+x, y, z$; (ii) $1-x, 1-y, -z$; (iii) $1-x, -y, 1-z$; (iv) $x, y, 1+z$; (v) $1+x, y, 1+z$; (vi) $1-x, 1-y, 1-z$.

The U and Rb atoms were located from a Patterson vector map using *SHELXS86* (Sheldrick, 1990). The Cl and O atoms were located from $\Delta\rho$ maps following least-squares refinement of the metal atoms. However, ghost peaks from the U atom were observed in the difference maps. In order to refine the structure fully, it was necessary to make allowances for the strong absorption of the crystal. Because of the poor crystal morphology and hardware problems, it was only possible to allow for absorption using the empirical method of Walker & Stuart (*DIFABS*; 1983). This method did indeed permit successful refinement of all the non-H atoms in the structure. *DIFABS* does not estimate transmission factors in the conventional manner but rather gives an indication of the maximum and minimum corrections applied to the raw data, which multiplied by the overall scale factor results in the T_{max} and T_{min} values given above. All non-H atoms were then refined anisotropically and all refinements were carried out using *SHELX76* (Sheldrick, 1976). The H atoms were not located.

References

Bartlett, J. R. & Cooney, R. P. (1989). *J. Mol. Struct.* **193**, 295–300.
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2A, 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Flint, C. D. & Tanner, P. A. (1981). *Mol. Phys.* **44**, 411–425.
Hall, D., Rae, A. D. & Waters, T. N. (1966). *Acta Cryst.* **20**, 160–162.

Ohwada, K. (1975). *Spectrochim. Acta Part A*, **31**, 973–977.

Ohwada, K. (1978). *J. Inorg. Nucl. Chem.* **40**, 1369–1374.

Ohwada, K. (1979). *J. Inorg. Nucl. Chem.* **41**, 1145–1147.

Ohwada, K. (1980). *Appl. Spectrosc.* **34**, 327–331.

Phan Dinh Kien, Kovrikov, A. & Komyak, A. (1973). *J. Appl. Spectrosc.* **18**, 336–343.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Cambridge, England.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Tutov, A. G., Plakhtii, V. P., Usov, O. A., Bublyaev, P. A. & Chernenkov, Yu. P. (1991). *Kristallografiya*, **36**, 1135–1138.

Tutov, A. G., Solomonov, Y. F., Solntseva, L. V. & Fundamenskii, V. S. (1981). *Sov. Phys. Solid State*, **23**, 900–901.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Watkin, D. J., Denning, R. G. & Prout, K. (1991). *Acta Cryst.* C**47**, 2517–2519.

high temperatures (973–1073 K), synthesis of the title compound, $Re_6Te_4Cl_{10}$, required only 773 K.

The title compound is isostructural with $Re_6S_4Cl_{10}$ and $Re_6Se_4Cl_{10}$. These compounds contain an Re_6 octahedron surrounded by a cube of four Te atoms and four Cl atoms. The Te and Cl atoms are randomly distributed over the eight corners of the cube. The remaining six Cl atoms ($Cl_{terminal}$) are coordinated to the Re atoms at the apices of the octahedron. As expected (Table 2), the Re—Re and Re—$Cl_{terminal}$ distances in $Re_6Te_4Cl_{10}$ agree well with those of the S and Se analogues, and the Re—Te/Cl distances [2.530(3)–2.679(2) Å] are slightly longer [Re—S/Cl 2.401(3)–2.447(3) Å, Re—Se/Cl 2.49–2.51 Å]; bond angles are as expected.

Hexachlorotetra-μ_3-chloro-tetra-μ_3-telluro-octohexarhenium(III)

Yuri V. Mironov, Jason A. Cody and James A. Ibers

Department of Chemistry, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208-3113, USA. E-mail: ibers@chem.nwu.edu

Abstract

The title compound, $Re_6Te_4Cl_{10}$, was obtained by reaction of $ReCl_5$ with elemental Te in an evacuated sealed fused silica tube at 773 K. The structure contains two independent Re_6 octahedral clusters, each with a crystallographic center of symmetry. The Re atoms are coordinated by four μ_3-Te atoms and four μ_3-Cl ligands that are equally distributed over the faces of the metal polyhedron. The remaining six Cl atoms are terminal ligands coordinated to the apices of the Re_6 octahedron. Distance ranges are: Re—Re 2.618(1)–2.638(1), Re—μ_3-L 2.530(3)–2.679(2), Re—$Cl_{terminal}$ 2.325(6)–2.353(5) Å (L is 50% Te and 50% Cl).

Comment

Octahedral Re_6 clusters are well known (Perrin & Sergent, 1988; Yaghi, Scott & Holm, 1992; Long, Williamson & Holm, 1995). The clusters $Re_6X_4Y_{10}$, with X = S, Se, Y = Cl, Br (Leduc *et al.*, 1985; Fedorov *et al.*, 1985; Gabriel, Boubekeur & Batail, 1993) and X = Te, Y = Br (Opalovskii, Fedorov, Lobkov & Erenburg, 1971) have been reported. Only the compounds with X = S, Se and Y = Cl have been characterized by single-crystal X-ray techniques. Whereas the syntheses of the single crystals used in earlier structural studies involved
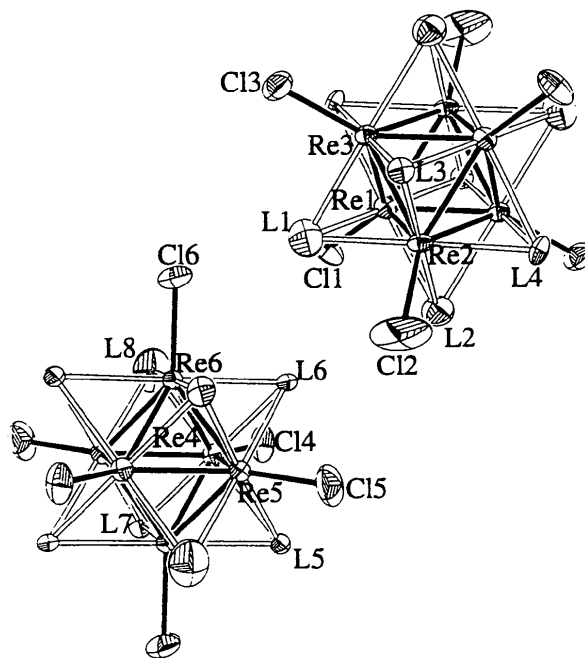

Fig. 1. Molecular structure showing 75% probability displacement ellipsoids. Unique atoms are labeled; each molecule has a crystallographic center of inversion. Atoms labeled L are 50% Te and 50% Cl.
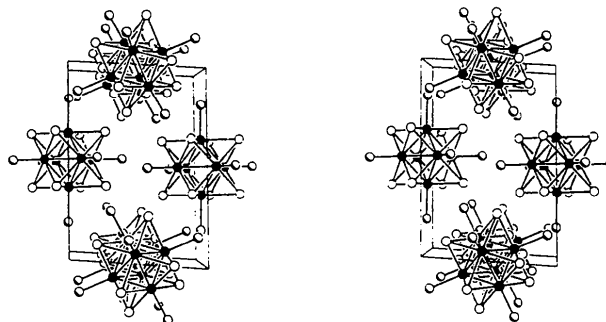

Fig. 2. Stereoview down the b axis of the unit cell of $Re_6Te_4Cl_{10}$. The Re atoms are drawn as filled circles, capping atoms as open circles, and $Cl_{terminal}$ atoms as shaded circles.