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Octaaquabromouranium(IV) Tribromide Monohydrate, [UBr(H_2O)$_8$]Br_3.H_2O

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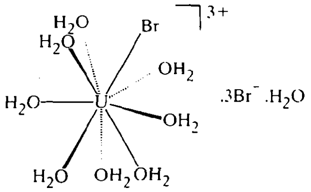
Abstract

The cationic uranium complex, $[U(H_2O)_8Br]^{3+}$, presents a tricapped trigonal prismatic structure in the solid state, with U—O distances (at T = 150 K) in the range 2.379 (8)–2.455 (8) Å and a U—Br bond length of 2.885 (2) Å, in addition to an extended network of intermolecular hydrogen-bonding interactions. The title compound is the first octaaqua complex to be structurally characterized for an actinide element.

Comment

Aqua complexes of uranium are not rare, but the vast majority of them are uranium(VI) derivatives that contain central uranyl (UO_2^{2+}) groups. Only a handful of aqua complexes of uranium that are not based upon the ubiquitous uranyl fragment are known, *e.g.* $[U(C_2O_4)_4(H_2O)]^{4-}$ (Spirlet *et al.*, 1987), $[U(pdc)_2(H_2O)_3]$ (where pdc is 2,6-dipicolinato-*N,O,O′*; Haddad *et al.*, 1987), $[U(NCS)_4(H_2O)_4]$ (Charpin *et al.*, 1977), $[U(MeCN)_2(H_2O)_5Br_2]^+$ (Zych *et al.*, 1993) and $[U(H_2O)_4Cl_4]^-$ (Karbowiak *et al.*, 1996). We report herein the single-crystal X-ray structure of the uranium(IV) derivative $[U(H_2O)_8Br]Br_3.H_2O$, (I), the first example of an octaaqua actinide complex. The structure of a related thorium heptaaqua complex, $[Th(H_2O)_7Cl_2]^{2+}$, was reported a few years ago (Rogers, 1989), and some octaaqua complexes of Y, Gd and Lu are also known (Rogers & Kurihara, 1986, 1987).



(I)

The nine-coordinate complex $[U(H_2O)_8Br]Br_3.H_2O$ displays a central U atom in direct contact with a Br ligand and the eight O atoms of eight water molecules. The overall geometry can be regarded as that of a tricapped trigonal prism, with O2, O4 and O7 capping the three rectangular faces O1/O3/O5/Br1, O1/O3/O6/O8 and O5/O6/O8/Br1, respectively (Fig. 1). The U—O bond distances [range 2.379 (8)–2.455 (8) Å] are similar to those observed in other aqua complexes of U^{IV}, 2.373 (12)–2.488 (6) Å (Haddad *et al.*, 1987; Charpin *et al.*, 1977), and rule out the presence of a dioxo (uranyl) complex, for which the characteristic U=O bond lengths are *ca* 1.76 Å (Rebizant *et al.*, 1987;

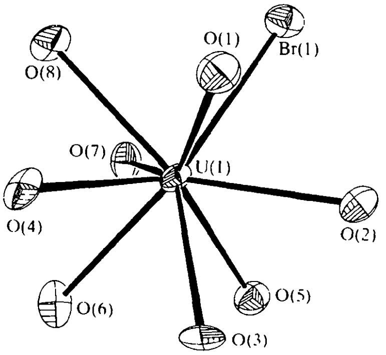


Fig. 1. A view of the $[U(H_2O)_8Br]^{3+}$ cation drawn with 40% displacement ellipsoids.

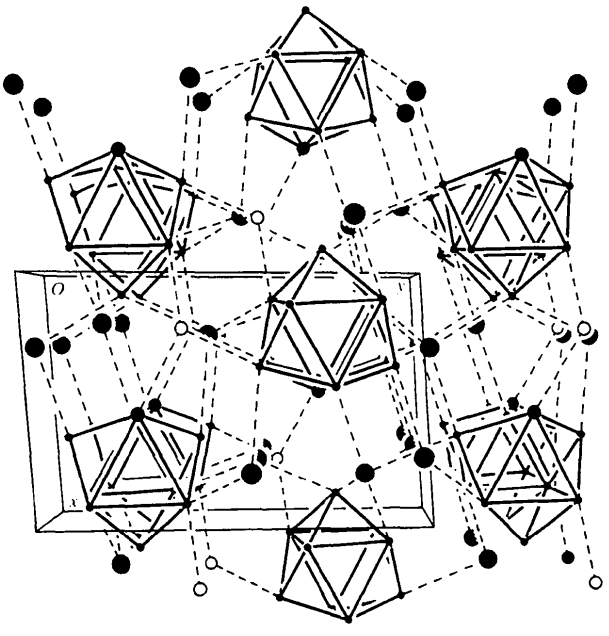


Fig. 2. Unit-cell view of the title compound parallel to the c axis, with $[U(H_2O)_8Br]^{3+}$ cations drawn as polyhedra (U center omitted). Large and medium solid spheres are Br, small spheres are coordinated water and open spheres are lattice water of crystallization. Dashed lines denote the extended hydrogen-bonding network.

Burns *et al.*, 1992). The U—Br distance [2.885 (2) Å] is slightly longer than the corresponding values observed in other uranium(IV) complexes containing terminal U—Br groups, *e.g.* 2.820 (2) Å in Cp_3UBr (Spirlet *et al.*, 1989), 2.8397 (14) and 2.8293 (14) Å in $[Li(thf)_4]_2[U(C_2B_9H_{11})_2Br_2]$ (where thf is tetrahydrofuran; Rabinovich *et al.*, 1996) and 2.795 (6)–2.831 (7) Å in $[UBr_4(OAsPh_3)_2]$ (de Wet & Caira, 1986). The packing of the $[U(H_2O)_8Br]^{3+}$ cations within the unit cell is pseudo-face-centered, as shown in Fig. 2. Layers of cations nearly parallel to (110) exhibit an **abc** stacking arrangement (similar to that observed in cubic close packing). More significantly, the cations are interconnected by an extended network of hydrogen-bonding interactions that involve the three Br^- counter-ions and an additional water molecule of crystallization. The observed contact distances between water ligands attached to the uranium and lattice Br^- counter-anions are relatively short (*ca* 3.1–3.3 Å), while nearest-neighbor contacts between uranium-bound H_2O and the water molecule of crystallization are as close as 2.68 (1) Å (O7···O9). One close contact [3.317 (5) Å] is observed between the Br ligand bound to the uranium and the water molecule of crystallization.

Experimental

Crystals of $[U(H_2O)_8Br]Br_3.H_2O$ used in this structure determination were obtained at 243 K from a concentrated solution of $UBr_4(NCMe)_4$ in 1,2-dimethoxyethane, presumably containing trace amounts of water.

Crystal data

$[UBr(H_2O)_8]Br_3.H_2O$
$M_r = 719.82$
Triclinic
$P\bar{1}$
$a = 8.234 (4)$ Å
$b = 12.781 (7)$ Å
$c = 7.168 (2)$ Å
$\alpha = 97.76 (3)°$
$\beta = 98.36 (2)°$
$\gamma = 85.38 (4)°$
$V = 738.1 (5)$ Å^3
$Z = 2$
$D_x = 3.238$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 23.6–24.7°$
$\mu = 21.877$ mm^{-1}
$T = 150$ K
Plate
0.11 × 0.09 × 0.04 mm
Green

Data collection

Rigaku AFC-7*R* diffractometer
$\omega–2\theta$ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
$T_{min} = 0.09$, $T_{max} = 0.42$
2463 measured reflections
2244 independent reflections

2087 reflections with $F > 4\sigma(F)$
$R_{int} = 0.028$
$\theta_{max} = 25°$
$h = 0 \rightarrow 8$
$k = -15 \rightarrow 15$
$l = -8 \rightarrow 8$
3 standard reflections every 100 reflections intensity decay: 6.2%

Refinement

Refinement on *F*
$R = 0.051$
$wR = 0.078$
$S = 1.07$
2087 reflections
128 parameters
$w = 1/[\sigma^2(F) + 0.005F^2]$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 4.70$ e Å^{-3}
$\Delta\rho_{min} = -3.60$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 0.0011 (2)
Scattering factors from Cromer & Waber (1974)

Table 1. *Selected bond lengths (Å)*

U1—Br1	2.885 (2)	U1—O5	2.447 (7)
U1—O1	2.379 (8)	U1—O6	2.447 (8)
U1—O2	2.431 (8)	U1—O7	2.402 (8)
U1—O3	2.394 (7)	U1—O8	2.428 (7)
U1—O4	2.455 (8)		

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-H-atom displacement parameters were refined anisotropically. The largest maximum and minimum difference Fourier map peaks were located 1.1 and 1.0 Å, respectively, from U1. All O-atom displacement parameters were refined anisotropically, however, their thermal motion appears to be strongly affected by large uncertainties and/or the close proximity of the heavy U center. No H atoms were located or included in the refinements.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXTL-Plus* (Sheldrick, 1990). Molecular graphics: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1209). Services for accessing these data are described at the back of the journal.

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K_3TaS_4

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Abstract

The reaction of K_2S_3, Ta and S yields single crystals of tripotassium tetrathiotantalate, K_3TaS_4. The compound crystallizes with the K_3VS_4-type structure [van den Berg & de Vries (1964). *Proc. K. Ned. Akad. Wet. Ser. B*, **67**, 178–180]. The structure is based on discrete tetrahedral TaS_4^{3-} anions, which are connected *via* K^+ cations.

Comment

We obtained new ternary alkali niobium chalcogenides with structures that contain the $Nb_2S_{11}^{4-}$ anion as a subunit, *e.g.* $K_4Nb_2S_{11}$, *via* the reaction of niobium in alkali-polychalcogenide fluxes (Bensch & Dürichen, 1996). Attempts to prepare the analogous tantalum chalcogenides yielded single crystals of the title compound, for which lattice parameters only have been reported (Latroche & Ibers, 1990). K_3TaS_4 is isotypic with K_3NbS_4, K_3NbSe_4 and K_3TaSe_4 (Latroche & Ibers, 1990), as well as with Cs_3NbSe_4 and Cs_3TaSe_4 (Yun *et al.*, 1988).

The crystal structure of K_3TaS_4 is based on discrete tetrahedral TaS_4^{3-} anions which are connected by K^+ cations. The Ta—S distances range from 2.264 (3) to 2.269 (2) Å [average 2.266 (3) Å] and the S—Ta—S angles are between 108.48 (9) and 111.43 (12)°.

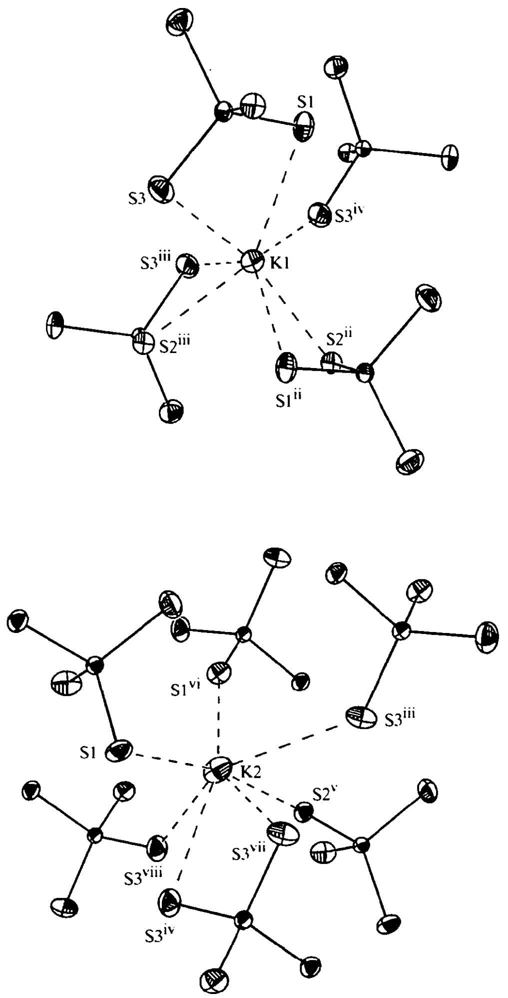

Fig. 1. The coordination spheres of the K^+ cations with the coordinating S atoms labelled; displacement ellipsoids are drawn at the 50% probability level.