INORGANIC COMPOUNDS

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Ammonium Uranyl Hydrogenselenite Selenite

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Abstract

Ammonium uranyl(2+) hydrogenselenate(1−) selenate(2−), $(NH_4)[UO_2(HSeO_3)(SeO_3)]$, has a layered structure with only hydrogen bonding provided by the NH_4^+ ion and (probably) the protonated O atom of the hydrogenselenite ion connecting the layers. The U atom is surrounded by a pentagonal bipyramidal arrangement of O atoms.

Comment

The structures of the selenite compounds of dioxouranium(VI) UO_2SeO_3, $UO_2Se_2O_5$ and $UO_2(HSeO_3)_2.H_2O$ have been characterized previously (Loopstra & Brandenburg, 1978, Trombe, Gleizes & Galy, 1985; Mistryukov & Mikhailov, 1983), as have the structures of some rare uranyl–selenite minerals (Ginderow & Cesbron, 1983*a*,*b*).

In the presence of ammonium ions, within the pH range 4–7, the compound $(NH_4)_2UO_2(SeO_3)_2.0.5H_2O$ crystallizes (Koskenlinna, Mutikainen, Leskelä & Leskelä, 1996). We have found that at a lower pH another type of ammonium uranyl selenite can be crystallized. We now report the structure of that compound.

The structure of the title compound is layered, with no covalent bonds between the layers. The layers are parallel to the (101) plane. The coordination polyhedron of O atoms around the U^{VI} atom in the title compound is a pentagonal bipyramid, as in $UO_2(HSeO_3)_2.H_2O$ and $UO_2Se_2O_5$ (Trombe, Gleizes & Galy, 1985; Mistryukov & Mikhailov, 1983). The two short U—O bonds [1.771 (7) and 1.779 (6) Å] to the uranyl O atoms form an angle of 175.9 (3) Å and the U—O bonds in the pentagonal plane range between 2.325 (6) and 2.417 (6) Å, which makes the geometry the same as those of the coordination polyhedra in the other two compounds.

Each O atom of the pentagonal plane is contributed by a different anion (three selenite ions and two hydrogenselenite ions), each of which acts as a monodentate bridging ligand. All three O atoms of the selenite ion and two of the three O atoms of the hydrogenselenite ion are coordinated to a different U^{VI} ion. The protonated O atom of the hydrogenselenite ion is not coordinated to a metal atom. All O atoms in the pentagonal plane appear within bonding distance from only one metal atom. As Fig. 2 shows, each uranyl ion is connected by the ligands to five others, thus forming a two-dimensional network.

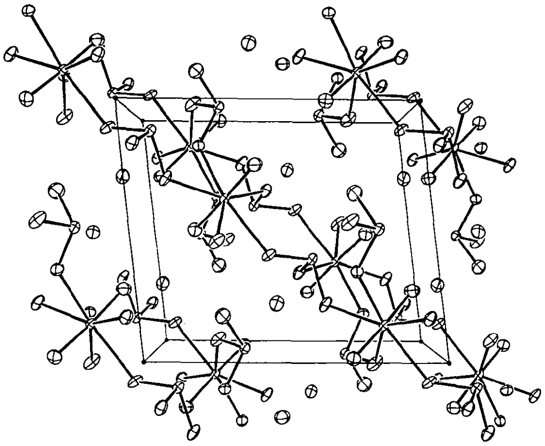

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the unit cell with displacement ellipsoids shown at the 50% probability level. The *a* axis is approximately vertical and the *c* axis horizontal. Atoms without bonds are ammonium N atoms.

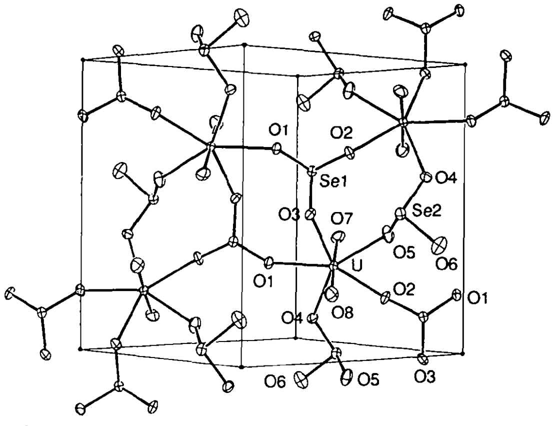

Fig. 2. An *ORTEP*II (Johnson, 1976) drawing of a layer in the unit cell with displacement ellipsoids shown at the 50% probability level. The *b* axis is vertical.

The H atom of the hydrogenselenite ion was not detected in the difference Fourier maps, but the Se—O bond length and the lack of a coordinated atom

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make O6 a likely candidate as the protonated O atom. The Se—O bond lengths and angles between bonds in the hydrogenselenite ion and in the selenite ion are within the normal ranges, although the Se—OH bond length, 1.743 (8) Å, is slightly shorter than usually found in hydrogenselenites. It is, nevertheless, still in the range frequently detected for Se—OH, for example in $Sm(HSeO_3)(SeO_3).2H_2O$, where Se—OH is 1.75 (2) Å (Koskenlinna, Mutikainen, Leskelä & Niinistö, 1994)

Each selenite ion connects three uranyl ions and each hydrogenselenite ion connects two. The hydrogenselenite ion in $UO_2(HSeO_3)_2.H_2O$ is also a bidentate bridging ligand (Mistryukov & Mikhailov, 1983). The protonated O6 atom of the hydrogenselenite ion is at a distance of 2.738 (9) Å from O1$(x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2})$ in an adjacent layer. As there are no other O6···O distances less than 3 Å between different selenite ions, O1 probably acts as an acceptor to the proton, forming a hydrogen bond between the layers. In $Zn(HSeO_3)_2.2H_2O$, the distance between the protonated O atom and the acceptor O atom is 2.793 Å (Kondrashev, Nozik, Fykin & Shibanova, 1979).

The N atom is found to reside between the layers. None of the ammonium H atoms was located. Four N···O distances in the range usually found for hydrogen bonds, ranging between 2.851 (12) and 2.908 (12) Å, are found: N···O1, N···O4, N···O5 and N···O7. The first three of these O atoms are part of one layer and the fourth is part of an adjacent layer. O1 is thus proposed to be the acceptor O atom for an N—H···O hydrogen bond, in addition to the O—H···O bond described above. The assumption is supported by the elongation of the U—O1 bond length, which is the longest in the pentagonal plane. However, no such elongation is detected in the Se—O1 bond length. All distances are in the same range as found in $(NH_4)H_3(SeO_3)_2$, where the N···O distances in the hydrogen-bonding scheme are between 2.881 (3) and 3.063 (3) Å (Tellgren & Liminga, 1974).

Experimental

$(NH_4)[UO_2(HSeO_3)(SeO_3)]$ was prepared by first precipitating an amorphous uranyl selenite from a solution of uranyl sulfate using selenous acid. The precipitate was separated from the solution, dissolved in an aqueous solution of SeO_2 and the pH of the solution was adjusted to between 1 and 3 by the addition of nitric acid. After this, a slight excess over the stoichiometric amount of NH_4^+ in form of aqueous NH_3 was added. The pH was checked to be in the range 1–3 and the solution was allowed to stand at 370 K. Small prisms of the title compound crystallized within a few days.

Crystal data

$(NH_4)[UO_2(HSeO_3)(SeO_3)]$
$M_r = 542.99$
Monoclinic
$P2_1/n$
$a = 8.348 (2)$ Å
$b = 10.326 (2)$ Å
$c = 9.929 (2)$ Å
$\beta = 97.06 (2)°$
$V = 849.4 (3)$ Å^3
$Z = 4$
$D_x = 4.25$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6–15°$
$\mu = 26.621$ mm^{-1}
$T = 294$ K
Prism
0.10 × 0.05 × 0.05 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ-scan (North, Phillips & Mathews, 1968) and spherical
$T_{min} = 0.128$, $T_{max} = 0.190$
2605 measured reflections

2605 independent reflections
1761 observed reflections
$[I > 3.0\sigma(I)]$
$\theta_{max} = 29.96°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 14$
$l = -13 \rightarrow 13$
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
$R = 0.028$
$wR = 0.032$
$S = 0.503$
1761 reflections
110 parameters
H atoms not included
$w = 1/[\sigma^2(F) + (0.02F)^2 + 1.00]$ (Killean & Lawrence, 1969)
$(\Delta/\sigma)_{max} = 0.005$

$\Delta\rho_{max} = 1.26$ e Å^{-3}
$\Delta\rho_{min} = -1.26$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.26×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^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	0.86998 (4)	0.20433 (3)	0.18670 (3)	0.0133 (1)
Se1	0.6112 (1)	0.37437 (8)	0.40524 (8)	0.0157 (3)
Se2	0.4870 (1)	0.02086 (9)	0.18009 (8)	0.0164 (3)
O1	0.5952 (7)	0.3018 (7)	0.5554 (6)	0.020 (3)
O2	0.7934 (8)	0.3143 (7)	0.3761 (6)	0.024 (3)
O3	0.6690 (8)	0.5259 (6)	0.4565 (6)	0.020 (3)
O4	0.4610 (8)	−0.1079 (6)	0.2777 (7)	0.024 (3)
O5	0.6514 (8)	0.0918 (7)	0.2639 (7)	0.023 (3)
O6	0.3476 (9)	0.1240 (8)	0.2418 (8)	0.032 (4)
O7	0.9930 (8)	0.1079 (7)	0.3067 (7)	0.023 (3)
O8	0.7354 (8)	0.2937 (7)	0.0700 (7)	0.026 (3)
N	0.7771 (10)	0.0626 (10)	0.5450 (9)	0.029 (4)

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

U—O1^{i}	2.417 (6)	Se1—O3	1.697 (6)
U—O2	2.352 (7)	Se2—O4	1.675 (7)
U—O3^{ii}	2.325 (6)	Se2—O5	1.683 (6)
U—O4^{iii}	2.399 (7)	Se2—O6	1.743 (8)

U—O5	2.369 (7)	N···O1	2.908 (12)
U—O7	1.779 (6)	N···O4^{iv}	2.851 (12)
U—O8	1.771 (7)	N···O5	2.875 (10)
Se1—O1	1.688 (6)	N···O7^{v}	2.874 (11)
Se1—O2	1.700 (7)		
O1—Se1—O2	99.1 (3)	O4—Se2—O5	102.4 (3)
O1—Se1—O3	101.2 (3)	O4—Se2—O6	98.2 (4)
O2—Se1—O3	99.2 (3)	O5—Se2—O6	95.7 (3)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $1-x, -y, 1-z$; (v) $2-x, -y, 1-z$.

Because of the high absorption, both ψ-scan (North, Phillips & Mathews, 1968) and spherical absorption corrections were applied (*International Tables for X-ray Crystallography*, 1967, Vol. II, Table 5.3.6B). For the ψ-scan correction $T_{\max}$ was 0.999 and $T_{\min}$ was 0.779, and for the spherical correction $T_{\max}$ was 0.190 and $T_{\min}$ was 0.165. The maximum and minimum residual electron densities in the final difference Fourier map are located near the U atom at distances less than 0.7 Å.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *MULTAN*11/82 (direct methods) (Main *et al.*, 1982). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetracaesium Ytterbium Heptachloride with Partly Disordered Chloride Ions

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Abstract

The structure of the title compound, Cs_4YbCl_7, consists of layers of composition Cs_2YbCl_6 containing isolated $YbCl_6^{3-}$ octahedra, separated from each other by layers of composition Cs_2Cl containing sixfold disordered Cl ions. Similarities and differences with the cubic elpasolite structure and some of its distortional variants are discussed. The compound decomposes at *ca.* 520 K into the neighbouring phases CsCl and Cs_3YbCl_6.

Comment

In the $CsCl/LnCl_3$ systems, decreasing Ln ionic radii are associated with an increasing number of compounds and structural modifications. Recently, we found a new distortional variant of the cubic elpasolite structure for Cs_3NdCl_6 (Reuter & Frenzen, 1995) and have since shown that this low-temperature phase occurs for all lanthanides from Nd to Yb (Reuter, Roffe & Seifert, 1996). Apart from the 3:1, 2:1 and 1:2 compounds, an enneachloride $Cs_3Ln_2Cl_9$ exists for Ln = Ho, Tm, Yb and Lu (Meyer & Schönemund, 1980). During the course of our studies of the preparation of anhydrous compounds in these systems from aqueous solution, we found a new phase, Cs_4LnCl_7, for Ln = Ho, Er, Yb and Y. These compounds were not observed when preparation from melts was attempted, since they decompose above 520 K into CsCl and Cs_3LnCl_6, as shown by differential scanning calorimetry (DSC) and X-ray powder diffraction measurements. Because of their low decomposition temperatures, the compounds cannot be prepared by annealing the neighbouring phases CsCl and Cs_3LnCl_6 just below this temperature, even for months. This paper presents the crystal structure of the title compound, Cs_4YbCl_7.

The structure contains isolated, nearly regular $YbCl_6^{3-}$ octahedra [Yb—Cl1 2.594 (4) Å, Cl1—Yb1—Cl1 180, 88.96 (12), 91.04 (12)°]. All octahedra are oriented in the same way. They are arranged parallel to the *ab* plane showing a threefold axis of symmetry in projection along the *c* axis and a twofold axis in projection normal to this plane. Regarding the octahedra as isolated entities, they are cubic close packed. Thus, the stacking period of the octahedra layers is three.

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