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A uranyl sulfate cluster in $Na_{10}[(UO_2)(SO_4)_4](SO_4)_2 \cdot 3H_2O$

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Decasodium uranyl hexasulfate trihydrate, $Na_{10}[(UO_2)(SO_4)_4](SO_4)_2 \cdot 3H_2O$, contains an unusual uranyl sulfate cluster with the composition $[(UO_2)(SO_4)_4]^{6-}$. The cluster is composed of a uranyl pentagonal bipyramid and four sulfate tetrahedra. Three sulfate tetrahedra are linked to the uranyl pentagonal bipyramid by the sharing of vertices, and the other shares an equatorial edge of the uranyl pentagonal bipyramid. The uranyl sulfate clusters occur in layers parallel to (010). The structure also contains two isolated symmetrically distinct sulfate tetrahedra, which also occur in layers parallel to (010). The uranyl sulfate clusters and isolated sulfate tetrahedra are linked through bonds to Na^+ cations, and by hydrogen bonding involving the water molecules.

Comment

Uranyl sulfates constitute an important group of minerals that are fairly widespread, although they are not abundant. Owing to the presence of uranium and sulfate in some ground waters, uranyl sulfate minerals may be important for determining the mobility of uranium in natural systems. We have undertaken a systematic study of the structures of natural and synthetic uranyl sulfates, and have grown crystals of the novel title sodium uranyl sulfate, (I), which contains the second known example of an unusual uranyl sulfate cluster.

The structure of (I) contains one symmetrically distinct U^{6+} cation that is strongly bonded to two O atoms, forming an approximately linear $(UO_2)^{2+}$ uranyl ion (designated Ur), with an average $U-O_{Ur}$ bond length of 1.777 Å. The uranyl ion is coordinated by five O atoms, located at the equatorial vertices of a pentagonal bipyramid, the bipyramid being capped by the O_{Ur} atoms. The mean $U-O_{eq}$ (eq is equatorial) bond length of 2.363 Å is in excellent agreement with the average bond length of 2.37 (9) Å for uranyl polyhedra determined from numerous well refined structures (Burns *et al.*, 1997).

There are six unique S^{6+} cations in the structure of (I), each of which is tetrahedrally coordinated by O atoms, with S—O bond lengths in the range 1.436 (4)–1.524 (3) Å. The structure contains ten symmetrically distinct Na^+ cations that are coordinated by between five and eight ligands, with mean bond lengths ranging from 2.356 to 2.617 Å.

The sums of the bond valences incident upon each site in the structure of (I) were calculated using the parameters for $^{[7]}U^{6+}-O$ given by Burns *et al.* (1997), and the parameters for $S^{6+}-O$ and Na—O from Brese & O'Keeffe (1991). The sum at the U^{6+} site is 6.09, which is consistent with the assignment of all U as U^{6+}. The sums at the S^{6+} and Na sites range from 5.97 to 6.32 and from 0.90 to 1.19, respectively. Excluding the contributions of the H atoms, the sums at the O-atom positions range from 1.85 to 2.19 for atoms O1 to O26, and from 0.28 to 0.41 for atoms O27, O28 and O29, which correspond to H_2O groups.

The projection of the structure of (I) along [100] shows that it contains finite clusters of uranyl and sulfate polyhedra, as well as isolated sulfate tetrahedra (Fig. 1). The uranyl sulfate cluster is shown in Fig. 2 and involves the UrO_5 pentagonal bipyramid, which is linked to four sulfate tetrahedra, three by the sharing of equatorial vertices of the bipyramid and one by the sharing of an equatorial edge with the S1 tetrahedron. The sharing of a tetrahedral edge with the bipyramid results in a relatively short U1···S1 distance of 3.092 (1) Å. This is only the second occurrence of this uranyl sulfate cluster; the first was recently reported in the structure of $Na_6(UO_2)(SO_4)_4(H_2O)_2$ (Hayden & Burns, 2001). It is only the third example of an inorganic uranyl compound that involves the sharing of the edge of a uranyl polyhedron with a tetrahedron that contains a hexavalent cation; the other example is the structure of $K_4[(UO_2)(SO_4)_3]$ (Mikhailov *et al.*, 1977).

The uranyl sulfate clusters in (I) are aligned parallel to (010), and occur in layers that are also parallel to (010) (Fig. 1). The orientations of the uranyl sulfate clusters within the layer are identical. The structure also contains two sulfate tetrahedra (S4 and S5) that are not components of the uranyl

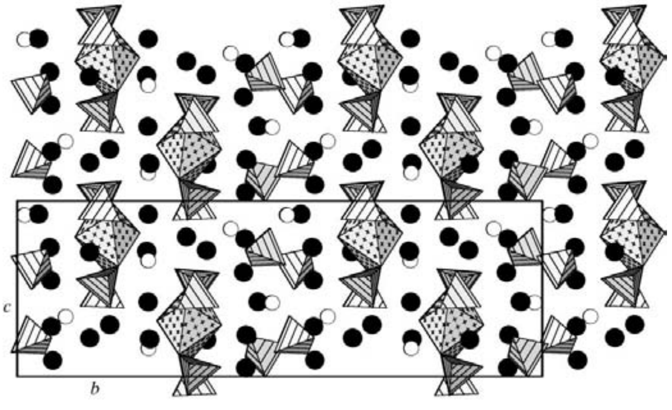

Figure 1
A polyhedral representation of the structure of (I) projected along [100]. Uranyl pentagonal bipyramids and sulfate tetrahedra are shown shaded with crosses and parallel lines, respectively. The positions of the Na^+ cations and H_2O groups are shown as solid and open circles, respectively.

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sulfate cluster. These tetrahedra occur in layers parallel to (010), between the layers of uranyl sulfate clusters. The uranyl sulfate clusters, as well as the S4 and S5 tetrahedra, are connected only through bonds to the Na^+ cations, and by hydrogen bonding to the three symmetrically distinct H_2O groups that are bonded to the Na^+ cations.

The structure of (I) is classed with those uranyl compounds containing isolated clusters of polyhedra of high bond valence, owing to the presence of the uranyl sulfate clusters as well as the isolated sulfate tetrahedra (Burns *et al.*, 1996). This structural class is relatively rare in uranyl compounds, which tend to be dominated by sheets of uranyl polyhedra and other polyhedra of high bond valence.

Although the sharing of an equatorial edge of a uranyl polyhedron with a sulfate tetrahedron is rare in uranyl compounds, it is possibly rather common in solutions containing uranyl and sulfate. Using a combination of EXAFS (extended X-ray absorption fine structure) and NMR spectroscopy, Moll *et al.* (2000) characterized the structures of uranyl sulfate complexes in acidic solutions. They found several complexes that involve the sharing of edges between uranyl pentagonal bipyramids and sulfate tetrahedra, as indicated by U$\cdots$S distances in the range 3.10–3.14 Å, which are in excellent agreement with the value of 3.092 (1) Å found in (I).

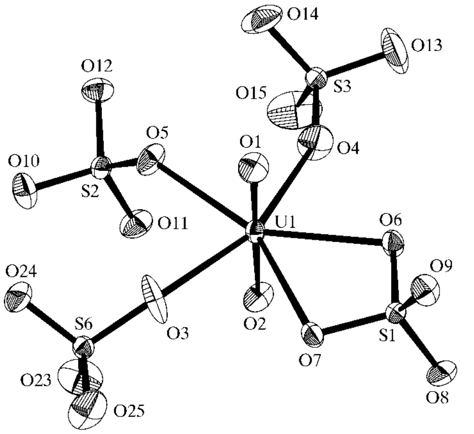

Figure 2
The uranyl sulfate cluster in the structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

The Flack parameter (Flack, 1983) of 0.439 (2) indicates that racemic twinning may be present. The final cycles of the refinement included racemic twinning, which reduced the value of R_1 from 0.041 to 0.019.

Experimental

A uranyl sulfate solution was prepared by dissolving UO_3 (5.78 g; Alfa Aesar) in a solution containing ultrapure water (40 ml) and concentrated sulfuric acid (5.2 ml). A small quantity (5 ml) of the solution was placed in a test tube and the pH adjusted to 4.0 using sodium hydroxide. The resulting solution was placed in a Fisher Scientific Isotemp oven at 343 K until evaporation was complete. Amongst the products, acicular light-yellow crystals of (I) up to 0.5 mm in length were recovered.

Crystal data

$Na_{10}[(UO_2)(SO_4)_4](SO_4)_2 \cdot 3H_2O$
$M_r = 1130.34$
Monoclinic, *Cc*
$a = 9.3072$ (5) Å
$b = 28.7064$ (14) Å
$c = 9.6152$ (3) Å
$\beta = 93.4010$ (10)°
$V = 2564.4$ (2) Å^3
$Z = 4$
$D_x = 2.928$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 9368 reflections
$\theta = 4.6$–68.9°
$\mu = 7.11$ mm^{-1}
$T = 293$ (2) K
Irregular fragment, yellow
0.24 × 0.14 × 0.12 mm
0.08 mm (radius)

Table 1
Selected geometric parameters (Å, °).

U1—O1	1.776 (2)	Na3—O5^{v}	2.622 (3)
U1—O2	1.779 (2)	Na3—O6	2.780 (3)
U1—O3	2.281 (3)	Na4—O18	2.359 (3)
U1—O4	2.315 (3)	Na4—O12	2.454 (3)
U1—O5	2.317 (2)	Na4—O7	2.466 (3)
U1—O6	2.424 (2)	Na4—O15^{viii}	2.533 (5)
U1—O7	2.480 (2)	Na4—O25	2.652 (4)
S1—O8	1.448 (3)	Na4—O16	2.862 (4)
S1—O9	1.463 (3)	Na4—O14^{viii}	2.950 (5)
S1—O7	1.495 (2)	Na5—O19^{ix}	2.336 (3)
S1—O6	1.501 (2)	Na5—O17	2.354 (3)
S2—O10	1.455 (3)	Na5—O15^{viii}	2.364 (4)
S2—O11	1.455 (3)	Na5—O11^{viii}	2.563 (3)
S2—O12^{i}	1.464 (3)	Na5—O21^{vii}	2.672 (5)
S2—O5	1.524 (3)	Na5—O2^{viii}	2.749 (4)
S3—O13	1.436 (4)	Na5—O20^{vii}	2.763 (4)
S3—O14	1.440 (3)	Na6—O16	2.290 (3)
S3—O15	1.451 (3)	Na6—O20^{x}	2.298 (3)
S3—O4	1.495 (3)	Na6—O17^{xi}	2.353 (4)
S4—O16	1.461 (3)	Na6—O21^{xii}	2.387 (4)
S4—O17	1.462 (3)	Na6—O2	2.707 (3)
S4—O18	1.473 (3)	Na7—O22^{xii}	2.388 (3)
S4—O19	1.475 (3)	Na7—O29^{xii}	2.400 (4)
S5—O20	1.462 (3)	Na7—O27^{v}	2.502 (3)
S5—O21	1.464 (3)	Na7—O18^{vii}	2.507 (3)
S5—O22	1.465 (3)	Na7—O26^{vii}	2.510 (4)
S5—O23	1.476 (3)	Na7—O8	2.678 (3)
S6—O24	1.443 (3)	Na7—O25^{vii}	2.899 (5)
S6—O25	1.450 (3)	Na8—O21^{vii}	2.320 (3)
S6—O26	1.455 (3)	Na8—O22^{xii}	2.349 (3)
S6—O3	1.496 (3)	Na8—O15^{viii}	2.388 (5)
Na1—O13^{ii}	2.331 (5)	Na8—O8	2.418 (3)
Na1—O25^{iii}	2.377 (5)	Na8—O16	2.491 (4)
Na1—O9^{iv}	2.476 (4)	Na8—O27^{v}	2.858 (3)
Na1—O27	2.477 (3)	Na8—O17	2.948 (4)
Na1—O12^{iii}	2.508 (5)	Na9—O26	2.299 (4)
Na1—O1	2.609 (3)	Na9—O19^{xi}	2.306 (3)
Na1—O10^{v}	2.772 (5)	Na9—O29^{xi}	2.373 (3)
Na2—O14^{ii}	2.299 (4)	Na9—O23^{i}	2.394 (3)
Na2—O24	2.385 (3)	Na9—O11	2.410 (3)
Na2—O9^{iv}	2.444 (3)	Na10—O23^{x}	2.374 (3)
Na2—O28^{vi}	2.526 (4)	Na10—O10^{vii}	2.409 (3)
Na2—O10	2.558 (3)	Na10—O6	2.420 (3)
Na2—O5	2.590 (3)	Na10—O24^{vii}	2.680 (4)
Na3—O24^{vii}	2.260 (3)	Na10—O26^{vii}	2.726 (4)
Na3—O14^{v}	2.313 (4)	Na10—O4	2.738 (4)
Na3—O12^{iii}	2.436 (3)	Na10—O13	2.783 (5)
Na3—O9	2.483 (3)	Na10—O20^{x}	2.807 (4)
Na3—O28	2.534 (4)		
O1—U1—O2	178.20 (14)		

Symmetry codes: (i) $x, y, 1+z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $1+x, y, z$; (vii) $x-1, y, z$; (viii) $x, y, z-1$; (ix) $x, -y, z-\frac{1}{2}$; (x) $x-1, y, 1+z$; (xi) $x, -y, \frac{1}{2}+z$; (xii) $x-1, -y, \frac{1}{2}+z$.

Data collection

Bruker Apex CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.260$, $T_{\max} = 0.426$
25 908 measured reflections
10 449 independent reflections
10 066 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 34.5°$
$h = -14 \rightarrow 14$
$k = -45 \rightarrow 44$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R(F) = 0.019$
$wR(F^2) = 0.052$
$S = 1.05$
10 449 reflections
416 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.93$ e Å^{-3}
$\Delta\rho_{\min} = -1.24$ e Å^{-3}
Absolute structure: Flack (1983), with 5006 Friedel pairs
Flack parameter = 0.439 (2)

As is typical for compounds containing uranium, it was not possible to locate the positions of the H atoms in the difference Fourier maps, so their positions were excluded from the refinement.

Data collection: *SMART–NT* (Bruker, 1998); cell refinement: *SAINT–NT* (Bruker, 1998); data reduction: *SAINT–NT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1383). Services for accessing these data are described at the back of the journal.

References

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Bruker (1997). *SHELXTL.* Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1998). *SMART–NT* and *SAINT–NT* (Versions 5.00), and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
Burns, P. C., Ewing, R. C. & Hawthorne, F. C. (1997). *Can. Mineral.* **35**, 1551–1570.
Burns, P. C., Miller, M. L. & Ewing, R. C. (1996). *Can. Mineral.* **34**, 845–880.
Dowty, E. (2000). *ATOMS.* Version 5.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hayden, L. A. & Burns, P. C. (2001). *J. Solid State Chem.* **163**, 313–318.
Mikhailov, Y. N., Kikh, L. A., Kuznetsov, V. G., Grevtseva, T. G., Sokol, S. K. & Ellert, G. V. (1977). *Koord. Khim.* **3**, 508–513.
Moll, H., Reich, T., Hennig, C., Rossberg, A., Szabo, Z. & Grenthe, I. (2000). *Radiochim. Acta*, **88**, 559–565.