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A monoclinic polymorph of uranyl dinitrate trihydrate, $[UO_2(NO_3)_2(H_2O)_2]\cdot H_2O$

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Diaquadinitratouranyl(VI) monohydrate is monoclinic (space group $P2_1/c$), in contrast to its triclinic polymorph. The main building block of the structure is the finite non-centrosymmetric $[UO_2(NO_3)_2(H_2O)_2]$ cluster, which is a uranyl hexagonal bipyramid that shares two non-opposite equatorial edges with the nitrate triangles, such that the two water molecules are at neighbouring equatorial vertices. There is an interstitial water site in the structure, which is located between adjacent $[UO_2(NO_3)_2(H_2O)_2]$ clusters.

Comment

Single crystals of the monoclinic polymorph of $[UO_2(NO_3)_2(H_2O)_2]\cdot H_2O$ were obtained by evaporation of nitric acid in a platinum crucible with a uranyl borate glass during attempts to synthesize novel uranyl borate compounds. The crystal structures of five uranyl nitrate compounds are known, *viz.* $[UO_2(NO_3)_2(H_2O)_2]$ (Dalley *et al.*, 1971), triclinic $[UO_2(NO_3)_2(H_2O)_2]\cdot H_2O$ (Hughes & Burns, 2003), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (Taylor & Mueller, 1965), $[(UO_2)_2(NO_3)_2(H_2O)_3(OH)_2]\cdot H_2O$ (Perrin, 1976) and $[(UO_2)_3O(H_2O)_6(OH)_3](NO_3)\cdot 4H_2O$ (Aberg, 1978). All of these structures involve finite clusters formed by uranyl polyhedra and nitrate groups, with hydrogen bonding between neigboring clusters occurring *via* water molecules. The composition and geometric configuration of the clusters is related to the proportion of U and N atoms in the structure, as well as to the hydration state. $[UO_2(NO_3)_2(H_2O)_2]$, $[UO_2(NO_3)_2(H_2O)_2]\cdot H_2O$ and $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ all have a U:N ratio of 1:2 and they differ chemically only in their hydration states. Each compound contains the same cluster, $[UO_2(NO_3)_2(H_2O)_2]$, formed by a uranyl hexagonal bipyramid that shares two opposite equatorial edges with the nitrate groups. In this cluster, the remaining opposite equatorial vertices of the uranyl hexagonal bipyramid correspond to the water molecules (Fig. 1*a*). In the crystal structure of $[(UO_2)_2(NO_3)_2(H_2O)_3(OH)_2]\cdot H_2O$, which has a U:N ratio of 1:1, two uranyl bipyramids of different shape (pentagonal and hexagonal) share an equatorial edge involving two OH groups, thus forming the $[(UO_2)_2(NO_3)_2(H_2O)_3(OH)_2]$ cluster (Fig. 1*b*). The crystal structure of $[(UO_2)_3O(H_2O)_6(OH)_3](NO_3)\cdot 4H_2O$, which has a U:N ratio of 3:1, also contains uranyl bipyramids that share edges *via* OH groups and a central O atom, thus forming the $[(UO_2)_3O(H_2O)_6(OH)_3]$ triuranyl cluster (Fig. 1*c*). Water molecules are located at the unshared equatorial vertices of the uranyl bipyramids, and the nitrate group and the remaining water molecules are located in the interstitial space between the triuranyl clusters.

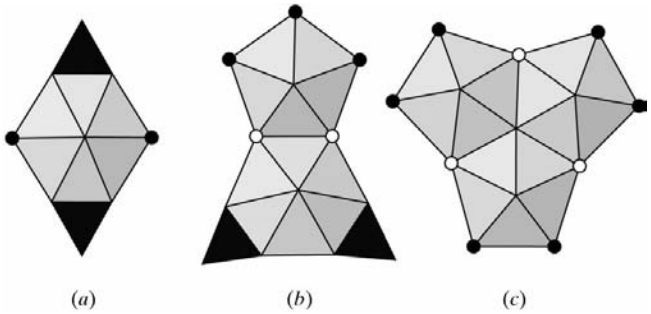

Figure 1
Finite clusters in the crystal structures of uranyl nitrate hydrates, *viz.* (*a*) $[UO_2(NO_3)_2(H_2O)_2]$ (Taylor & Mueller, 1965; Dalley *et al.*, 1971; Hughes & Burns, 2003), (*b*) $[(UO_2)_2(NO_3)_2(H_2O)_3(OH)_2]$ (Perrin, 1976) and (*c*) $[(UO_2)_3O(H_2O)_6(OH)_3]$ (Aberg, 1978). Uranyl polyhedra are shown in gray, nitrate triangles are shown in black, O atoms of OH groups are shown as unfilled circles and O atoms of water molecules are shown as filled circles.

In this paper, we report the crystal structure of the monoclinic polymorph of $[UO_2(NO_3)_2(H_2O)_2]\cdot H_2O$. The U atom in this structure is part of a nearly linear uranyl ion, UO_2^{2+}, which is coordinated by four O atoms and two water molecules arranged at the equatorial vertices of a hexagonal bipyramid, such that the two water molecules in the equatorial plane occupy neighboring vertices. The two symmetrically distinct nitrate triangles each share an edge with the uranyl hexagonal bipyramid, thus forming the finite $[UO_2(NO_3)_2(H_2O)_2]$ cluster (Fig. 2) and causing a distortion of the equa-

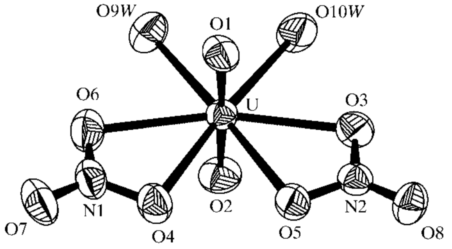

Figure 2
The finite $[UO_2(NO_3)_2(H_2O)_2]$ cluster in the crystal structure of monoclinic $[UO_2(NO_3)_2(H_2O)_2]\cdot H_2O$. Displacement ellipsoids are shown at the 50% probability level.

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torial arrangement of the uranyl ion. Both nitrate chelate bite angles are ~50°, as expected for a four-membered chelate ring. The other O—U—O angles around the equatorial plane range between 61.7 (1) and 68.5 (2)° (Table 1). The $[UO_2(NO_3)_2(H_2O)_2]$ cluster is non-centrosymmetric, unlike the centrosymmetric cluster of the same composition in the crystal structure of triclinic $[UO_2(NO_3)_2(H_2O)_2]\cdot H_2O$ [Fig. 1*a* and Hughes & Burns (2003)]. There is one interstitial water molecule in the monoclinic structure, which is located in the interstitial space between the uranyl nitrate clusters (Fig. 3).

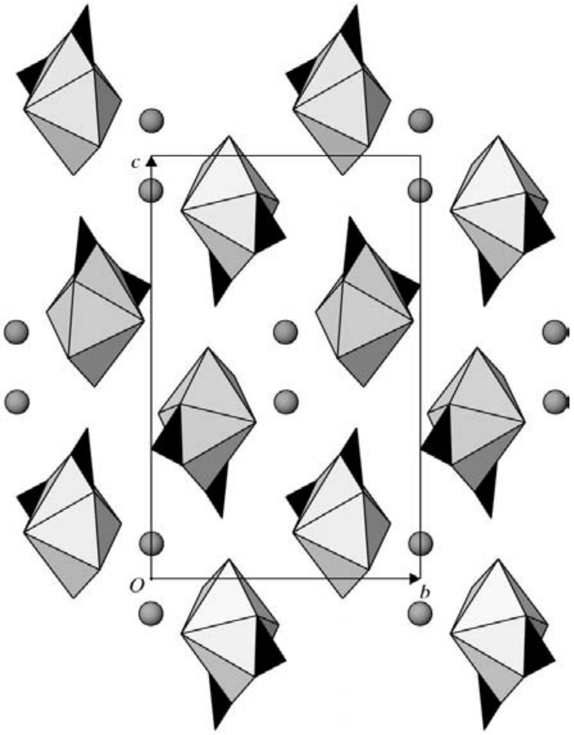

Figure 3
The crystal structure of monoclinic $[UO_2(NO_3)_2(H_2O)_2]\cdot H_2O$, projected parallel to the (100) plane. Uranyl polyhedra are shown in gray, nitrate triangles are shown in black and O atoms of interstitial water molecules are shown as gray spheres.

Bond-valence analysis was perfomed using the parameters of Burns *et al.* (1997) for $^{[8]}U^{6+}$ and Brese & O'Keeffe (1991) for N^{5+}. The bond-valence sums at the U, N1 and N2 sites are 6.00, 4.89 and 4.91 valence units (v.u.), respectively, which are consistent with the formal valences of the corresponding ions. The bond-valence sums for atoms O9*W*, O10*W* and O11*W* range from 0 to 0.45 v.u., which is consistent with their assignment as water molecules. The bond-valence sums for the remaining O atoms range from 1.69 to 1.97 v.u. On the basis of the analysis of interatomic distances around the O atoms of the water molecules, possible hydrogen-bond acceptors for the O9*W*-donor sites are atoms O11*W*^{i} and O7; for atom O10*W*, possible acceptors are atoms O11*W*^{iii} and O8^{i}; and for atom O11*W*, possible acceptors are atoms O2^{iv} and O7 (see Table 1 for symmetry codes).

Experimental

A uranyl borate glass of undetermined composition was prepared by heating a mixture of $NaBO_2(H_2O)_4$ and UO_3 in the molar ratio 100:1 in a platinum crucible at 1366 K for 15 h. Concentrated nitric acid (69.2%) was added to the crucible after cooling to 293 K. Small pale-yellow crystals were recovered from the crucible walls after complete evaporation of the nitric acid at room temperature.

Crystal data

$[UO_2(NO_3)_2(H_2O)_2]\cdot H_2O$
M_r = 448.1
Monoclinic, $P2_1/c$
a = 7.1797 (15) Å
b = 8.954 (3) Å
c = 14.301 (4) Å
β = 99.401 (7)°
V = 907.1 (4) Å^3
Z = 4
D_x = 3.281 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2067 reflections
θ = 2.7–25.4°
μ = 17.95 mm^{-1}
T = 293 (2) K
Plate, pale yellow
0.20 × 0.10 × 0.06 mm

Data collection

Bruker APEX CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*XPREP*; Bruker, 1997)
T_{min} = 0.171, T_{max} = 0.375
9795 measured reflections
3706 independent reflections
2219 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 34.4°
$h = -6 \rightarrow 11$
$k = -13 \rightarrow 14$
$l = -20 \rightarrow 22$

Refinement

Refinement on F^2
$R(F)$ = 0.030
$wR(F^2)$ = 0.059
S = 1.00
3706 reflections
128 parameters
H-atom parameters not defined
$w = 1/[\sigma^2(F_o^2) - 1.0571P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.79 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00110 (6)

The positions of the U atoms and most of the O atoms were determined by direct methods. The remaining O and N atoms were located in difference Fourier maps during structure refinement. In the final cycle of refinement, the maximum difference Fourier peaks were

Table 1
Selected geometric parameters (Å, °).

U—O1	1.738 (3)	N1—O4	1.267 (7)
U—O2	1.778 (4)	N2—O8	1.223 (7)
U—O9*W*	2.450 (5)	N2—O5	1.268 (6)
U—O10*W*	2.481 (4)	N2—O3	1.271 (6)
U—O3	2.482 (5)	O9*W*—O11*W*^{i}	2.746 (5)
U—O4	2.494 (4)	O9*W*—O7^{ii}	2.921 (6)
U—O5	2.509 (4)	O10*W*—O11*W*^{iii}	2.705 (6)
U—O6	2.516 (4)	O10*W*—O8^{i}	3.028 (5)
N1—O7	1.230 (6)	O11*W*—O2^{iv}	3.007 (6)
N1—O6	1.265 (6)	O11*W*—O7	3.272 (7)

O1—U—O2	178.6 (2)	O3—U—O5	50.45 (12)
O1—U—O3	90.87 (17)	O4—U—O5	61.70 (14)
O2—U—O3	90.45 (17)	O4—U—O6	50.32 (14)
O1—U—O4	89.77 (15)	O9*W*—U—O6	65.86 (14)
O2—U—O4	90.25 (15)	O9*W*—U—O10*W*	68.51 (15)
O1—U—O5	89.11 (18)	O10*W*—U—O3	63.18 (15)
O2—U—O5	92.17 (17)	O7—N1—O6	125.3 (6)
O1—U—O6	89.30 (16)	O7—N1—O4	120.1 (6)
O2—U—O6	89.60 (17)	O6—N1—O4	114.6 (5)
O1—U—O9*W*	91.26 (17)	O8—N2—O5	122.6 (5)
O2—U—O9*W*	87.44 (17)	O8—N2—O3	123.5 (5)
O1—U—O10*W*	92.23 (15)	O5—N2—O3	113.9 (6)
O2—U—O10*W*	87.87 (15)		

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

0.22 and 0.70 Å, respectively, from the U-atom position. H atoms were not included in the refinement. However, the electron-density distribution of the final difference Fourier map shows peaks of 0.55–0.71 e Å^{-3} that could be assigned to H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; structure solution: *SHELXTL* (Bruker, 1998); structure refinement: *SHELXTL*; molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXTL* and *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1015). Services for accessing these data are described at the back of the journal.

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