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Uranyl dinitrate trihydrate, $UO_2(NO_3)_2(H_2O)_3$

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The structure of the title compound, which has been synthesized by evaporation at 294 K, consists of centrosymmetric uranyl hexagonal bipyramids that share opposite equatorial edges with two nitrate triangles, resulting in two distinct finite clusters of composition $[(UO_2)(H_2O)_2(NO_3)_2]$. There are two unique symmetrically independent U^{VI} positions and two unique nitrate groups.

Comment

$UO_2(NO_3)_2(H_2O)_3$ was first obtained as a by-product in a synthesis experiment intended to produce uranyl carbonates by room-temperature evaporation of a solution containing uranyl nitrate with various carbonates and nitrates. Subsequently, large single crystals of $UO_2(NO_3)_2(H_2O)_3$ were obtained from a solution of $UO_2(NO_3)(H_2O)_6$, K_2CO_3 and $Cu(NO_3)_2(H_2O)_3$ at ambient temperature and pressure. The structures are known or estimated for the chemically related compounds $UO_2(NO_3)_2(H_2O)_2$ (Taylor & Mueller, 1965), $UO_2(NO_3)_2(H_2O)_6$ (Dalley *et al.*, 1971) and $UO_2(NO_3)_2(H_2O)_3$ (Vdovenko *et al.*, 1963). Each contains the $[(UO_2)(H_2O)_2(NO_3)_2]$ finite cluster. These compounds crystallize in space groups $Cmc2_1$, $P2_1/c$ and $P1$, respectively. Whereas $UO_2(NO_3)_2(H_2O)_2$ and $UO_2(NO_3)_2(H_2O)_6$ differ from $UO_2(NO_3)_2(H_2O)_3$ in their hydration state and space group, the structure published by Vdovenko *et al.* (1963) corresponds to that for $UO_2(NO_3)_2(H_2O)_3$. However, the structure published earlier was incomplete, as only the U and O atoms were located. The refined structure including the N-atom positions is given herein.

There are two symmetrically distinct U^{VI} atoms, positioned on centers of symmetry, both of which are part of linear $(UO_2)^{2+}$ uranyl ions and which are coordinated by six equatorial O atoms, forming hexagonal bipyramids (Fig. 1). Two opposite equatorial edges of each hexagonal bipyramid share edges with NO_3 groups, giving the $[(UO_2)(H_2O)_2(NO_3)_2]$ cluster. Two H_2O groups correspond to equatorial ligands of the uranyl polyhedra. One H_2O group is located between the $[(UO_2)(H_2O)_2(NO_3)_2]$ clusters (Fig. 2).

Bond-valence sums were calculated for each ion using the method of Brese & O'Keeffe (1991). The U bond-valence sums (Burns *et al.*, 1997) are 6.18 and 6.12 for the two unique U positions. The N bond-valence sums are 5.29 and 5.07. For the O-atom positions O1, O3, O4, O5, O7, O8, O9 and O10, the bond-valence sums are within the normal range (1.80–2.07). For atoms O2, O6 and O11, values consistent with H_2O were obtained (0.44, 0.46 and 0.00, respectively).

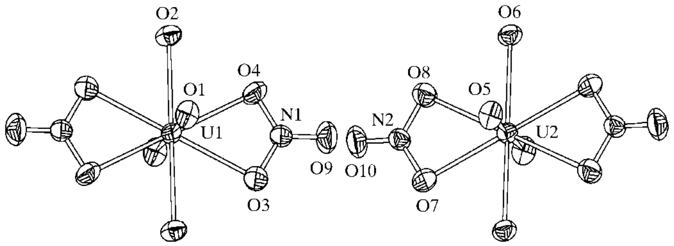

Figure 1
Views of the two $UO_2(NO_3)_2$ clusters in $UO_2(NO_3)_2(H_2O)_3$, shown with 50% probability displacement ellipsoids.

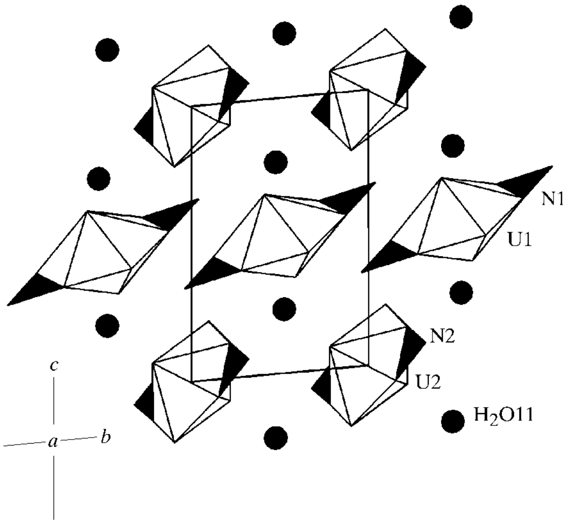

Figure 2
The crystal structure of $UO_2(NO_3)_2(H_2O)_3$, projected along [100]. Uranyl hexagonal bipyramids are shown in white, nitrate triangles in black and free H_2O as black spheres.

Experimental

Transparent yellow crystals of $UO_2(NO_3)_2(H_2O)_3$ of up to 1 mm in maximum dimension were synthesized from a solution containing $Cu(NO_3)_2(H_2O)_3$, $UO_2(NO_3)_2(H_2O)_6$ and K_2CO_3, in a 2:5:1 molar ratio, of in water (50 ml). Following evaporation in an open vessel for 14 d at 294 K and under ambient pressure, crystals were recovered from the vessel walls.

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Crystal data

$UO_2(NO_3)_2(H_2O)_3$
$M_r = 448.08$
Triclinic, $P\bar{1}$
$a = 7.0359$ (15) Å
$b = 7.1730$ (15) Å
$c = 10.084$ (2) Å
$\alpha = 81.697$ (4)°
$\beta = 82.041$ (4)°
$\gamma = 63.642$ (4)°
$V = 449.64$ (16) Å^3
$Z = 2$
$D_x = 3.31$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3612 reflections
$\theta = 3$–34.5°
$\mu = 18.10$ mm^{-1}
$T = 298$ (2) K
Block, yellow
0.12 × 0.11 × 0.10 mm

Data collection

Bruker PLATFORM CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SHELXL*97; Sheldrick, 1997)
$T_{\min} = 0.098$, $T_{\max} = 0.164$
9093 measured reflections
3614 independent reflections
2138 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.090$
$\theta_{\max} = 34.5°$
$h = -10 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R(F) = 0.043$
$wR(F^2) = 0.109$
$S = 1.01$
3614 reflections
130 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.022P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.08$ e Å^{-3}
$\Delta\rho_{\min} = -1.34$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

U1—O1	1.738 (6)	U2—O5	1.745 (6)
U1—O2	2.453 (6)	U2—O6	2.440 (7)
U1—O3	2.485 (7)	U2—O7	2.473 (7)
U1—O4	2.490 (7)	U2—O8	2.539 (6)

The locations of the highest peak and deepest hole in the difference Fourier map are 0.79 Å from U2 and 0.86 Å from U1, respectively. H-atom positions were not included in the refinement.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SHELXTL-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1396). Services for accessing these data are described at the back of the journal.

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