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Tetra-*n*-butylammonium di-μ-hydroxo-bis[dinitratodioxouranate(VI)]

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Key indicators

Single-crystal X-ray study
T = 299 K
Mean σ(C–C) = 0.015 Å
R factor = 0.052
wR factor = 0.101
Data-to-parameter ratio = 20.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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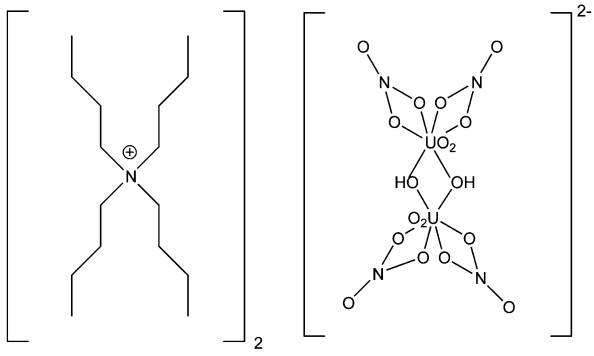
From an aqueous solution of uranyl nitrate hexahydrate and tetra-*n*-butylammonium nitrate, single crystals of the title compound, $(C_{16}H_{36}N)_2[U_2(NO_3)_4(OH)_2O_4]$, were obtained. The structure features a dimeric hydroxo-bridged tetranitratodihydroxobis[dioxouranate(VI)] dianion.

Comment

The coordination chemistry of the uranyl ion, UO_2^{2+}, exhibits a wealth of different structural motifs, due to the ability of the cation to accept almost all kinds of ligands and to form mono-, bi- and polynuclear complexes, particularly with polydentate ligands that can act as bridging ligands between different uranyl species.

In our investigation of the uranyl/nitrate/*n*-alkylammonium system, we obtained crystals of the title compound, (I), which features a binuclear complex anion, tetranitratodihydroxobisdioxouranate(VI), together with an *n*-butylammonium cation (Figs. 1 and 2). The anion is formed by two $UO_2(NO_3)_2(OH)$ groups and sits on an inversion centre, with the two hydroxy groups acting as bridging ligands between the uranyl ions.



(I)

The geometry of the ion is unexceptional with regard to the U—O distances: U1—O9 2.309 (5) and U1—O9^{i} 2.303 (5) Å (bridging O), and U1—O3 2.525 (6), U1—O4 2.521 (6), U1—O6 2.520 (6) and U1—O7 2.518 (6) Å (nitrate O) [symmetry code: (i) $-x+1, -y+1, -z$]. The O—U—O angles in the plane perpendicular to the O═U═O group deviate by approximately 10° from the ideal value of 60°.

The $[UO_2(NO_3)_2(OH)]_2$ group (and close relatives) are not uncommon in the coordination chemistry of the uranyl ion. The hydroxy complex can be found in compounds such as the cholinium complex (Viossat *et al.*, 1983), the 4,4′-bipyridinium compound (Alcock & Flanders, 1987), the crown ether complex [$(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][(μ-

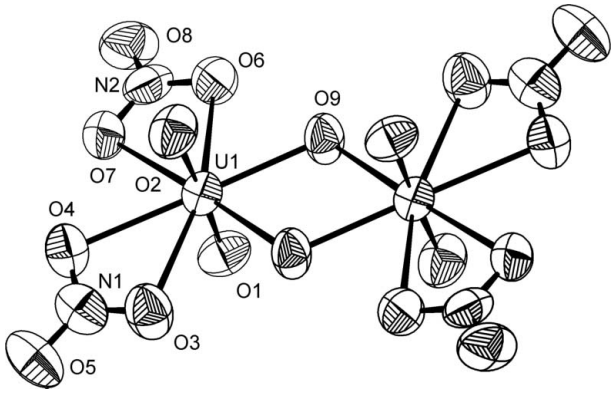


Figure 1
The anion in (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The hydroxo H atoms were not located.

OH)$_2${UO$_2$(NO$_3$)$_2$}$_2$] (Evans *et al.*, 2002) and the cryptand complex dihydro[2.2.2]cryptand di-μ-hydroxo-bis[bis(nitrato-κ^2O,O')dioxouranate(VI)] monohydrate (Thuéry & Masci, 2002).

In some of these compounds, hydrogen bonding was observed, with the bridging OH groups acting as donors. In (I), no H atoms could be located on the hydroxo O atoms. However, an investigation of the O···O distances gave no evidence of possible hydrogen bonding between the OH groups and suitable acceptors. The absence of hydrogen bonds may be explained by the bulky cations, which lead to the formation of a sheet structure with alternating layers of cations and anions (Fig. 3).

Experimental

An aqueous solution of 0.05 m*M* uranyl nitrate hexahydrate (Merck, p.a.) and 0.5 m*M* tetra-*n*-butylammonium nitrate (Fluka, >97%) was left in the dark for slow evaporation. After three months, single crystals of (I) had formed.

Crystal data

$(C_{16}H_{36}N)_2[U_2(NO_3)_4(OH)_2O_4]$	D_x = 1.811 Mg m^{-3}
M_r = 1307.02	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 58 reflections
a = 12.8335 (13) Å	θ = 4.6–18.4°
b = 13.217 (2) Å	μ = 6.82 mm^{-1}
c = 14.148 (3) Å	T = 299 K
β = 94.239 (11)°	Fragment, yellow
V = 2393.1 (7) Å^3	0.25 × 0.22 × 0.20 mm
Z = 2	

Data collection

Bruker Nonius KappaCCD area-detector diffractometer	5427 independent reflections
φ and ω scans	3712 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (*HABITUS*; Herrendorf & Bärnighausen, 1997)	R_{int} = 0.061
T_{min} = 0.390, T_{max} = 0.498	θ_{max} = 27.5°
25561 measured reflections	$h = -15 \rightarrow 16$
	$k = -17 \rightarrow 17$
	$l = -18 \rightarrow 18$

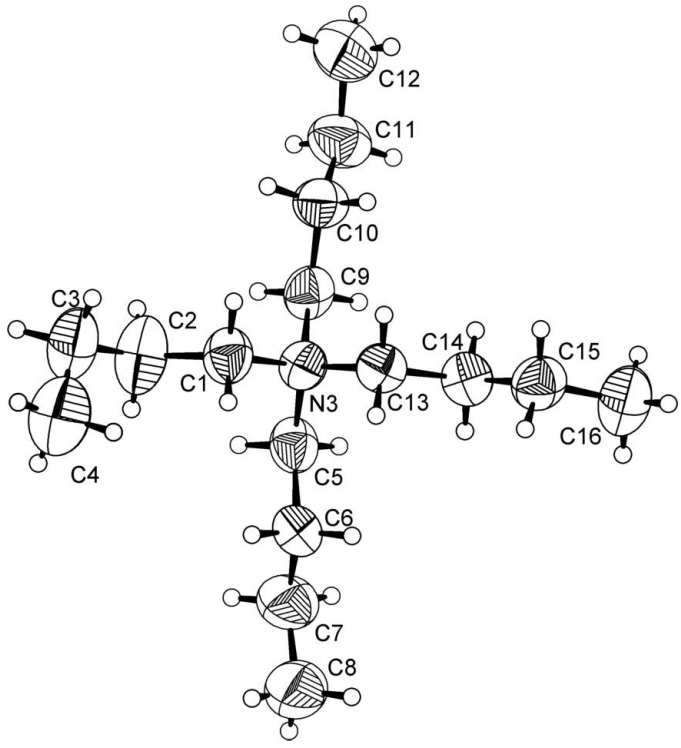


Figure 2
The tetra-*n*-butylammonium ion in (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.005P)^2 + 11.1326P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.052	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.101	$\Delta\rho_{max}$ = 1.06 e Å^{-3}
S = 1.27	$\Delta\rho_{min}$ = −0.81 e Å^{-3}
5427 reflections	
262 parameters	
H-atom parameters constrained	

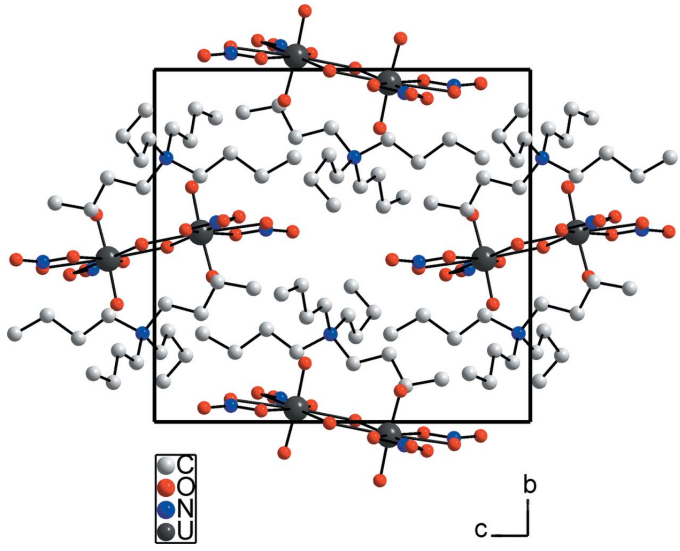


Figure 3
The sheet-like packing of cations and anions in (I). H atoms have been omitted.

The H atoms were found in difference maps and refined as riding on their carrier C atoms in their as-found relative positions, with $U_{iso}(H) = 1.2U_{eq}(C)$. The location of the maximum of electron density is 1.30 Å from atom O7 and 1.34 Å from U1.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *MAXUS* (Mackay *et al.*, 1999).

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