Crystal structure of bis(dimethylsulfoxide) dinitrato dioxo uranium(VI), $\text{UO}_2(\text{NO}_3)_2[(\text{CH}_3)_2\text{SO}]_2$

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Received December 17, 1999, CCDC-No. 1267/374

Discussion

In the monoclinic structure, the uranium atoms are at the centrosymmetric 4c sites being coordinated by eight oxygen atoms. The two O atoms of the linear uranyl group are nearly perpendicularly orientated to the plane of the remaining O atoms forming a hexagonal bipyramid around the uranium atom. Altogether the hexagon is composed of four oxygen atoms of the two equivalent bidentate nitrate groups and two oxygen atoms of the equivalent dimethyl sulfoxide molecules. The bond lengths and angles in the dimethyl sulfoxide group are in good agreement with average values for O bonded uranium and other metal sulfoxides [1] and with vibrational frequencies of the UO_2^{2+} unit in relation to Gutman's donor numbers [2]. The U—O (UO_2^{2+}) distances (1.744(7) Å), however, are too crude in order to reflect the change of the strength of the U—O bonds. The shortest intermolecular C...O distances are C1 to O5 (C1...O5 3.36(3) Å) and C2 to O4 (C2...O4 3.35(3) Å). Therefore weak C—H...O hydrogen bonds [3] to the NO_3^- ligands (O5) and the sulfoxide group (O4) must be taken in consideration despite the very weak hydrogen bond acceptor capability of NO_3^- ions [4]. The co-ordination of O bonded metal ions in sulfoxides can be stereochemically defined by the torsion angles ψ_1 (M—O—S—C1) and ψ_2 (M—O—S—C2) [1]. For the title compound, ψ_1 is $-147.2(5)^\circ$ and ψ_2 is $109.9(6)^\circ$ showing a *trans-trans* conformation.

Abstract

$C_{4}H_{12}N_{2}O_{16}S_{2}U$, monoclinic, $C12/c1$ (No. 15), $a = 17.781(8)$ Å, $b = 5.974(3)$ Å, $c = 15.361(8)$ Å, $\beta = 117.78(4)^{\circ}$, $V = 1443.7$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.036$, $wR_{\text{ref}}(F^2) = 0.086$, $T = 293$ K.

Source of material

Single crystals were prepared by solving a stoichiometric mixture of uranyl nitrate hexahydrate and dimethyl sulfoxide in diethyl ether. Within one day the compound crystallizes. The crystals are filtered off and dried at air.

Experimental details

Because of the presence of uranium atoms satisfactory refinement of the hydrogen positions was not possible.

Table 1. Data collection and handling.

Crystal:	light yellow prism, size $0.08 \times 0.10 \times 0.20$ mm
Wavelength:	Mo K_{α} radiation ($0.71069 \text{ \AA}$)
μ :	115.77 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, ω
$2\theta_{\text{max}}$:	49.92°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	4774, 1265
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 893
$N(\text{param})_{\text{refined}}$:	89
Programs:	SHELXS-86 [5], SHELXL-93 [6], ATOMS [7]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
U	4c	1/4	1/4	0	0.0283(3)	0.0334(3)	0.0241(3)	−0.0031(2)	0.0073(2)	−0.0005(2)
O(1)	8f	0.1974(4)	0.023(1)	0.0184(5)	0.034(3)	0.047(4)	0.055(4)	−0.006(3)	0.027(3)	0.003(4)
O(2)	8f	0.1114(4)	0.444(1)	−0.1072(5)	0.043(4)	0.070(5)	0.034(4)	0.012(4)	0.008(3)	0.001(4)
O(3)	8f	0.1589(4)	0.500(1)	0.0462(5)	0.051(4)	0.053(4)	0.038(4)	0.013(4)	0.009(3)	−0.003(4)
O(4)	8f	0.3090(4)	0.342(1)	0.1681(5)	0.038(4)	0.054(4)	0.032(4)	−0.008(3)	0.010(3)	−0.008(3)
O(5)	8f	0.0396(5)	0.652(2)	−0.0577(7)	0.042(5)	0.062(5)	0.074(6)	0.017(4)	0.015(4)	−0.003(5)
S	8f	0.3838(2)	0.4983(5)	0.2294(2)	0.032(1)	0.050(1)	0.033(1)	−0.002(1)	0.0113(9)	−0.004(1)
N	8f	0.1009(5)	0.539(1)	−0.0406(7)	0.040(5)	0.036(5)	0.049(6)	0.002(4)	0.015(4)	0.002(4)
C(1)	8f	0.4312(8)	0.372(2)	0.3480(9)	0.068(8)	0.043(7)	0.040(7)	0.001(6)	−0.013(6)	0.008(5)
C(2)	8f	0.3345(9)	0.731(2)	0.254(1)	0.061(8)	0.051(7)	0.064(8)	0.011(5)	0.021(7)	−0.014(6)

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