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Unexpected oxidation of *cis*-1,3-dithiane-1,3-dioxide (*cis*-DTSO₂) during the preparation of the uranyl nitrate complex

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Abstract

During the preparation of the complex of hydrated uranyl nitrate with the ligand *cis*-DTSO₂ in ethanolic solution at 50°C, a molecule of the ligand suffered an unexpected oxidation giving rise to propanedisulfonate which acts both as bidentate ligand and as counterion. The uranium atom, the water molecule and the propanedisulfonate moiety are sited on a two-fold axis. The uranium atom is hepta-coordinated, in a pentagonal–bipyramidal fashion, to the uranyl oxygen atoms, one water molecule, two monodentate *cis*-DTSO₂ moieties and the bidentate propanedisulfonate. The water molecule is hydrogen bonded to the *cis*-DTSO₂ molecules. The supramolecular arrangement is made through a C–H...O interaction, giving rise to columns of complexes parallel to the *b*-axis.

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1. Introduction

The uranyl ion (UO₂²⁺) has a linear structure, with the uranium(VI) placed between two oxygen ions. The hydrated uranyl nitrate forms yellow crystals with two, three or six water molecules. This salt has the structure [UO₂(NO₃)₂(H₂O)₂] · xH₂O where *x* = 0, 1 and 4. The uranium is octa-coordinated, and the linear uranyl ion is coordinated to two water molecules and two bidentate nitrate ions. Other water molecules are linked by hydrogen bonding [1]. An important property of this salt is its high solubility in many organic solvents, permitting the solvent extraction of uranium from aqueous solutions [2]. Among the uranyl applications, it can be cited for its use as actinometers, solar collectors and photocatalyst [3].

This work describes the synthesis, characterization and X-ray structure determination of an uranyl complex obtained by reaction of the ligand *cis*-1,3-dithiane-1,3-dioxide (*cis*-DTSO₂) with hydrated uranyl nitrate.

2. Experimental

The ligand *cis*-DTSO₂ was prepared by oxidation of 1,3-dithiane-1-oxide [4,5] with 3-chloroperoxybenzoic acid in dichloromethane and separated by recrystallizations from the *trans*-isomer [6,7]. A 10 mmol DTSO solution in 50 mL of dichloromethane at 0°C was treated dropwise at low temperature, under stirring, with a 10 mmol solution of the oxidant, during 30 min. The solvent was then completely removed and the solid washed with 200 mL of ethyl ether. The insoluble *cis*-compound was separated from the soluble *trans*-compound by treatment with ethanol. The isomers were purified by washings and recrystallization cycles and then characterized by CHN elemental analyses, melting range, IR spectra and ¹H and ¹³C NMR spectra. The crystal-structure of the complex was determined by single-crystal X-ray diffraction.

The uranyl complex was synthesized by reaction of an ethanolic solution of hydrated uranyl nitrate with *cis*-DTSO₂ in the same solvent, at 50°C (molar ratio 1:3). The resulting solution was allowed to stand at room temperature, and after ten days orange crystals were obtained. The crystals were separated, washed with

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cold ethanol and maintained under vacuum over anhydrous calcium chloride.

CHN microanalytical procedures were performed using a Perkin–Elmer 240 elemental analyzer. The S content was determined by combustion in a Shöniguer flask [8]. Melting range was determined in a Quimis model Q.340.21/3 apparatus. IR spectra were recorded on a Nicolet FTIR-8100 spectrometer using KBr pellets. Proton and ^{13}C NMR spectra were recorded on a DRX-500 MHz Bruker.

3. Crystal structure determination

X-ray crystallographic data were recorded on an Enraf-Nonius CAD-4 Mach3 diffractometer in the $\omega/2\theta$ scan mode at 293 K, using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). During data collection the intensities of three standard reflections were monitored every 30 min during the X-ray exposure time; showing no significant decay. Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by the standard Patterson heavy atom method, followed by normal difference Fourier techniques. H-atoms were refined with fixed geometry, each riding on a carrier atom, with an isotropic displacement parameter amounting to 1.2 times the values of the equivalent isotropic displacement parameters of the atoms they are attached to. Data processing and computation were carried out using SHELXS-86 [9], SHELXL-97 [10] and ZORTEP [11].

4. Results and discussion

The C, H and S contents found in the complex are in agreement with the stoichiometry $[\text{UO}_2(\text{C}_3\text{H}_6\text{S}_2\text{O}_6)(\text{C}_4\text{H}_8\text{S}_2\text{O}_2)_2(\text{H}_2\text{O})]$, where $\text{C}_3\text{H}_6\text{S}_2\text{O}_6$ is the bivalent anion propanedisulfonate and $\text{C}_4\text{H}_8\text{S}_2\text{O}_2$ is the ligand *cis*-DTSO₂.

According to IR spectra, shifts of νSO of the free ligand (1055 and 1011 cm^{-1}) to lower frequencies in the complex (1048 and 1003 cm^{-1}) indicate that the *cis*-DTSO₂ is coordinated to the uranium atom through the oxygen. The UO_2^{2+} symmetric stretching band was found at 918 cm^{-1} . Bands attributed to the nitrate ions were not found. The sulfonate group bands were found at 1477 and 1317 s, cm^{-1} . The distances $\text{S}(3)\text{--O}(32\text{S})$ and $\text{S}(3)\text{--O}(33\text{S})$ are shorter than $\text{S}(3)\text{--O}(31\text{S})$, indicating that the non-coordinated SO groups have stronger bands than those coordinated to the uranyl ion. The stretching frequencies, in this case, will be shifted to higher energies, reaching 1477 and 1317 s, cm^{-1} for the antisymmetric and symmetric stretches, respectively.

The structure of the uranyl complex was determined by single-crystal X-ray analysis. Table 1 presents a

summary of data collection and refinement. Table 2 presents selected bond lengths and angles. Table 3 presents the atomic coordinates. Fig. 1 shows the structure of the complex.

Table 1
Crystallographic data and details of the structure refinement

Empirical formula	$\text{C}_{11}\text{H}_{24}\text{O}_{13}\text{S}_6\text{U}$
Formula weight	794.70
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	20.082(1)
b (Å)	11.434(1)
c (Å)	12.361(1)
β (deg)	126.54(1)
Volume (Å ³)	2280.2(3)
Molecules per cell, Z	4
Calculated density, D_c , (g cm^{-3})	2.315
Absorption coefficient, μ (mm^{-1})	7.728
$F(000)$	1528
Crystal size (mm)	$0.30 \times 0.25 \times 0.20$
θ range for data collection (deg)	2.18 – 25.47
Reflections collected	2157
Reflections collected/unique	7283/2097 [$R_{\text{int}} = 0.0320$]
Data/restraints/parameters	2097/0/142
Goodness-of-fit (S) on F^2	1.048
Limiting indices	$0 \leq h \leq 24, -13 \leq k \leq 0, -14 \leq l \leq 12$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0311, wR_2 = 0.0652$
R indices (all data)	$R_1 = 0.0656, wR_2 = 0.0733$

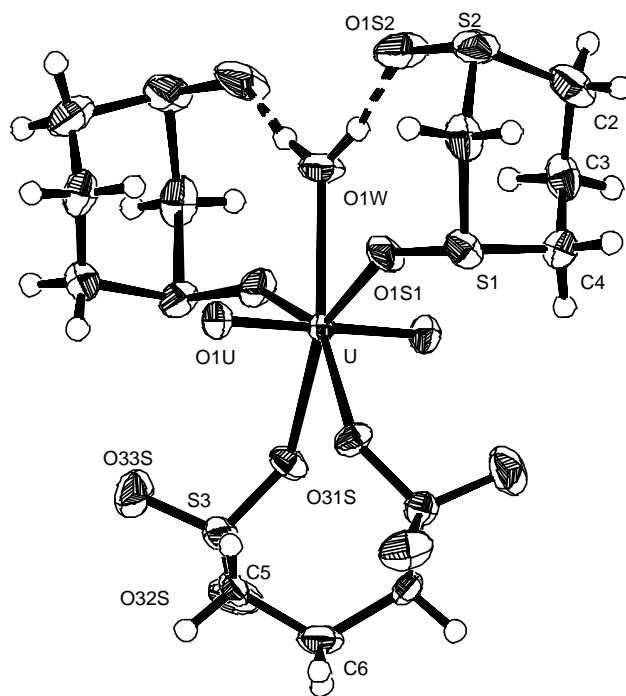


Fig. 1. Structure of the uranyl complex $[\text{UO}_2(\text{C}_3\text{H}_6\text{S}_2\text{O}_6)(\text{C}_4\text{H}_8\text{S}_2\text{O}_2)_2(\text{H}_2\text{O})]$.

Table 2
Bond lengths (Å) and angles (deg)

U–O(1U)	1.768(4)
U–O(31S)	2.351(4)
U–O(1S1)	2.355(5)
U–O(1W)	2.425(7)
S(1)–O(1S1)	1.529(5)
S(1)–C(1)	1.773(8)
S(1)–C(4)	1.788(8)
S(2)–O(1S2)	1.492(6)
S(2)–C(2)	1.800(9)
S(2)–C(1)	1.809(8)
S(3)–O(32S)	1.442(5)
S(3)–O(33S)	1.445(5)
S(3)–O(31S)	1.491(5)
S(3)–C(5)	1.765(7)
C(2)–C(3)	1.516(11)
C(3)–C(4)	1.506(10)
C(5)–C(6)	1.530(8)
O(1U)#1–U–O(31S)	86.4(2)
O(1U)–U–O(31S)	93.8(2)
O(31S)–U–O(31S)#1	74.6(2)
O(31S)–U–O(1S1)#1	74.41(16)
O(31S)#1–U–O(1S1)#1	148.50(17)
O(1S1)#1–U–O(1S1)	136.9(2)
O(1U)–U–O(1W)	89.82(16)
O(31S)–U–O(1W)	142.68(11)
O(1S1)–U–O(1W)	68.46(12)
O(1S1)–S(1)–C(1)	103.9(3)
O(1S1)–S(1)–C(4)	107.1(3)
C(1)–S(1)–C(4)	100.8(4)
O(1S2)–S(2)–C(2)	107.4(4)
O(1S2)–S(2)–C(1)	108.3(4)
C(2)–S(2)–C(1)	97.9(4)
O(32S)–S(3)–O(33S)	114.6(3)
O(32S)–S(3)–O(31S)	109.9(3)
O(33S)–S(3)–O(31S)	110.0(3)
O(32S)–S(3)–C(5)	109.0(3)
O(33S)–S(3)–C(5)	107.3(3)
O(31S)–S(3)–C(5)	105.6(3)
S(1)–O(1S1)–U	145.6(3)
S(3)–O(31S)–U	139.1(3)
S(1)–C(1)–S(2)	120.4(4)
C(3)–C(2)–S(2)	114.4(6)
C(4)–C(3)–C(2)	111.5(7)
C(3)–C(4)–S(1)	114.7(5)
C(6)–C(5)–S(3)	114.6(4)
C(5)–C(6)–C(5)#1	119.1(8)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2, y, -z+\frac{1}{2}$.

From these data it can be seen that the uranium is hepta-coordinated, with the linear uranyl ion coordinated to two monodentate *cis*-DTSO₂, a bidentate propanedisulfonate ion, and one water molecule, in a pentagonal-bipyramidal geometry. The water molecule is also hydrogen bonded to the non-coordinated oxygen atoms of the *cis*-DTSO₂ molecules.

The orange color of the crystals indicated that change in the coordination sphere of the uranyl ion occurred. Unexpected oxidation of *cis*-DTSO₂ to propanedisulfonate was evidenced by the resolution of crystal structure. This is in accordance with elemental analyses and the

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U(eq)</i> ^a
U	10000	2253(1)	2500	20(1)
S(1)	12014(1)	2962(2)	3141(2)	32(1)
S(2)	11919(1)	5671(2)	2886(3)	49(1)
S(3)	8944(1)	−311(2)	2487(2)	29(1)
O(1U)	10301(3)	2258(4)	4166(5)	33(1)
O(1S1)	11306(3)	3009(4)	3276(5)	34(1)
O(1S2)	11200(4)	5727(5)	2950(8)	66(2)
O(31S)	9130(3)	618(4)	1854(5)	29(1)
O(32S)	8246(3)	−999(5)	1456(6)	46(2)
O(33S)	8851(3)	203(5)	3458(6)	50(2)
C(1)	12496(4)	4349(7)	3727(8)	39(2)
C(2)	11524(5)	5260(7)	1197(9)	50(2)
C(3)	11019(5)	4141(7)	704(8)	40(2)
C(4)	11560(5)	3082(7)	1387(8)	37(2)
C(5)	9833(4)	1209(6)	3383(7)	28(2)
C(6)	10000	−1887(9)	2500	41(3)
O(1W)	10000	4374(6)	2500	40(2)
H(1A)	12975	4347	3717	47
H(1B)	12703	4413	4662	47
H(2A)	11181	5891	592	60
H(2B)	11987	5167	1151	60
H(3A)	10609	4174	881	48
H(3B)	10727	4073	−261	48
H(4A)	12001	3100	1280	45
H(4B)	11231	2387	933	45
H(5A)	10312	−724	4004	33
H(5B)	9773	−1764	3914	33
H(6A)	9527	−2392	1914	50
H(6B)	10473	−2392	3086	50
H(1W)	10409	4828	2536	48

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

disappearance of nitrate bands and presence of sulfonate bands.

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