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Crystal Structures of Three UO_2^{2+} Complexes with S-Donors*

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Information concerning the bonding between heavy elements and sulphur donor atoms is very limited and in particular, there is little structural information available on complexes involving U–S bonds. To date, the crystal structure of only one complex containing UO_2 coordinated to 6 S-atoms has been reported, and this only briefly [1]. In contrast, there is a substantial amount of information available on complexes which utilize U–O and U–N bonds. This difficulty in preparing sulphur complexes is a result of hard/soft–acid/base interactions, plus the effect of increased steric constraints. We have synthesized and determined the crystal structures of three dithiocarbamates of general formula: $[Et_2N][UO_2(Dtc)_3]$, with ligands $C_5H_8NS_2$ (1) (Fig. 1), $C_7H_{10}NS_2$ (2) (Fig. 2) and $C_3H_6NS_2$ (3) (Fig. 3).

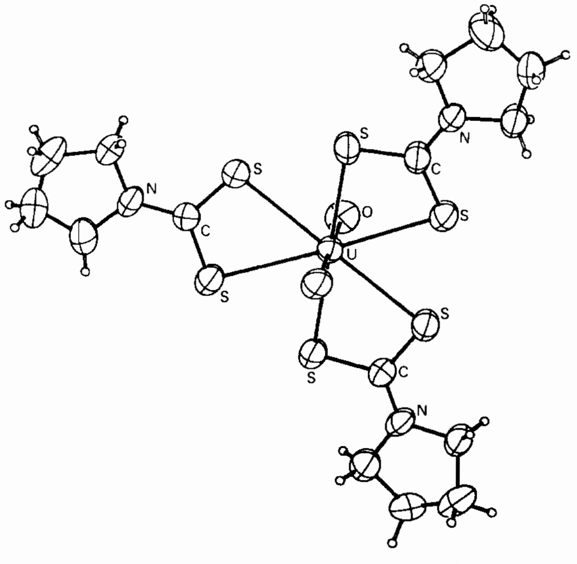

Fig. 1. View of the anion of tetraethylammoniumdioxotris(*N*-pyrrolidinedithiocarbamato)uranium(VI) (1) $[Et_4N][UO_2(C_4H_8NCS_2)_3]$; monoclinic, $P2_1/c$, $a = 10.228(4)$, $b = 18.287(4)$, $c = 17.323(3)$ Å, $\beta = 99.68(2)°$, $Z = 4$, $R = 0.038$ for 3970 reflections.

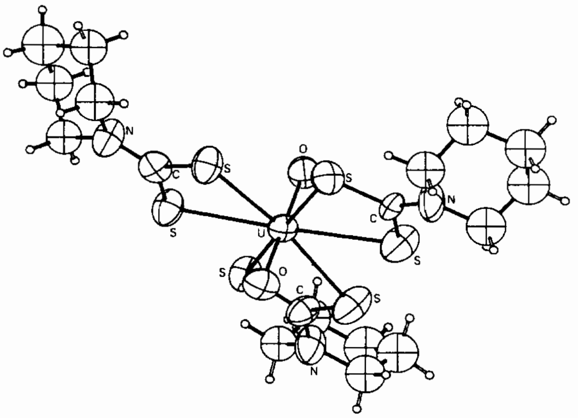

Fig. 2. View of the anion of tetraethylammoniumdioxotris(*N*-piperidinedithiocarbamato)uranium(VI) (2) $[Et_4N][UO_2(C_5H_{10}NCS_2)_3]$; triclinic, $P\bar{1}$, $a = 11.499(2)$, $b = 15.079(4)$, $c = 22.556(5)$ Å, $\alpha = 81.33(2)$, $\beta = 85.09(2)$, $\gamma = 77.89(1)°$, $Z = 4, R = 0.057$ for 5729 reflections.

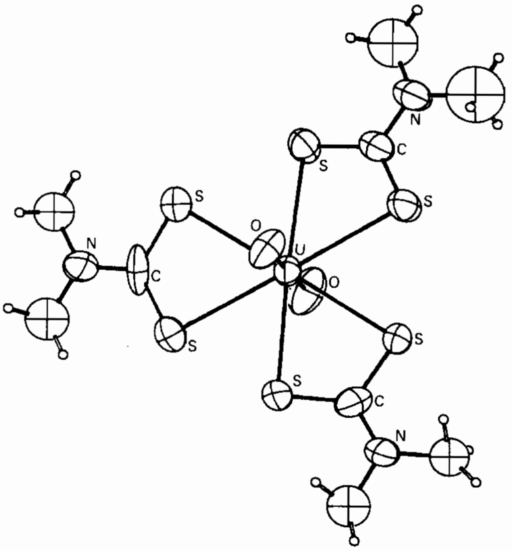

Fig. 3. View of the anion of tetraethylammoniumdioxotris(*N,N*-dimethyldithiocarbamato)uranium(VI) (3) $[Et_4N][UO_2(Me_2CNS_2)_3]$; orthorhombic, *Pbca*, $a = 20.563(5)$, $b = 22.448(6)$, $c = 24.899(5)$ Å, $Z = 8$, $R = 0.054$ for 3722 reflections.

All three complexes were prepared by the same general method. This involved preforming the dithiocarbamate ligand as the potassium salt by reaction of the amine with CS_2/KOH in water and adding this to a solution of uranyl acetate. Metathesis with tetraethylammonium bromide, followed by recrystallization from methanol gave crystals which were suitable for structural investigation.

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All three complexes exhibit hexagonal bipyramidal geometry about the central atom, involving three bidentate dithiocarbamate molecules coordinating to uranium in the equatorial plane. U–O (UO_2^{2+}) bond lengths are in the range 1.743(11)–1.767(11) Å, and there is little deviation from linearity of the uranyl group, the O–U–O bond angles lying in the range 178.3(3)–179.1(5)°. Average U–S distances for each complex are 2.946(2) Å (**1**); 2.926(6) Å (**2**); and 2.935(6) Å (**3**). There is a substantial amount of puckering of the equatorial plane; out of plane deviations are in the range −0.179(2) Å to +0.139(2) Å for **1**, −0.251(5) Å to +0.177(5) Å in **2**, and −0.279(4) Å to +0.284(6) Å in **3**. The larger this degree of puckering, the closer the uranyl group approaches linearity. In contrast, six oxygen donor atoms have been shown to be coplanar, in for example $NaUO_2(OAc)_3$ [2]. Intramolecular S–S distances (ligand bite) range from 2.862(4) to 2.889(5) Å, with intermolecular S–S contact distances in the range 2.911(4)–3.109(4) Å (**1**), 2.959(5)–3.035(4) Å (**2**) and 2.985(5) to 3.050(6) Å (**3**).

In **1**, the pyrrolidine rings lie above and below the mean equatorial plane. All of the piperidine rings of **2** adopt the chair conformation with carbon atoms displaced from the mean planes by −0.271(4) to +0.261(2) Å. In one anion of **3** the Me_2N–C moieties of the dithiocarbamate ligand are to one side of the equatorial plane, but in the other they lie on both sides.

References

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2 W. H. Zachariasen and H. A. Plettinger, *Acta Crystallogr.*, *12*, 526 (1959).