metal-organic compounds

Actinide interactions with microbial chelators: the dioxobis[pyridine-2,6-bis(monothiocarboxylato)]uranium(VI) ion

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The title complex, bis(tetraphenylphosphonium) dioxobis(pyridine-2,6-dicarbothioato-O,N,O')uranium(VI), $(C_{24}H_{20}P)_2$-$[UO_2(C_7H_3NO_2S_2)_2]$, was prepared by reacting two equivalents of pyridine-2,6-bis(monothiocarboxylate) (pdtc) with uranyl nitrate. The geometry of the eight-coordinate U atom is hexagonal bipyramidal, with the uranyl O atoms in apical positions. This is the first reported complex in which this ligand binds a metal through the O and not the S atoms. Principal bond lengths include uranyl lengths of 1.774 (2) Å, U—O distances of 2.434 (2) and 2.447 (3) Å, and two U—N distances of 2.647 (3) Å. The anion lies on an inversion centre.

Comment

First identified as a bacterial metabolite (Ockels *et al.*, 1978), pyridine-2,6-bis(monothiocarboxylate) (pdtc) has been isolated from several strains of *Psuedomonas* and is produced as an extracellular reducing agent (Lee *et al.*, 1999). This reductant has been proven to be a necessary component in carbon tetrachloride decomposition and its production varies with environmental conditions. In the course of our studies of the interactions of extracellular microbial chelators with

(I)
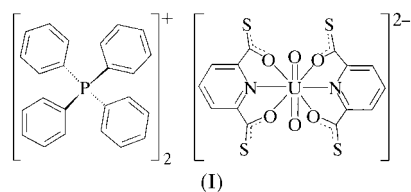
actinides, we isolated the complex of pdtc bound to the dioxouranium(VI) (uranyl) ion. When pdtc is combined with hard metal ions such as Fe^{III} or U^{VI}, one of two structures forms, either a polymeric or a monomeric species. The monomeric species is generally isolated if there is an excess of metal, otherwise the very insoluble polymeric species is favoured. The complexes are sparingly soluble in aqueous solution and small crystallites precipitate rapidly. To slow down crystallization and to improve the solubility of the complex in organic solvents, the bis(tetraphenylphosphonium)
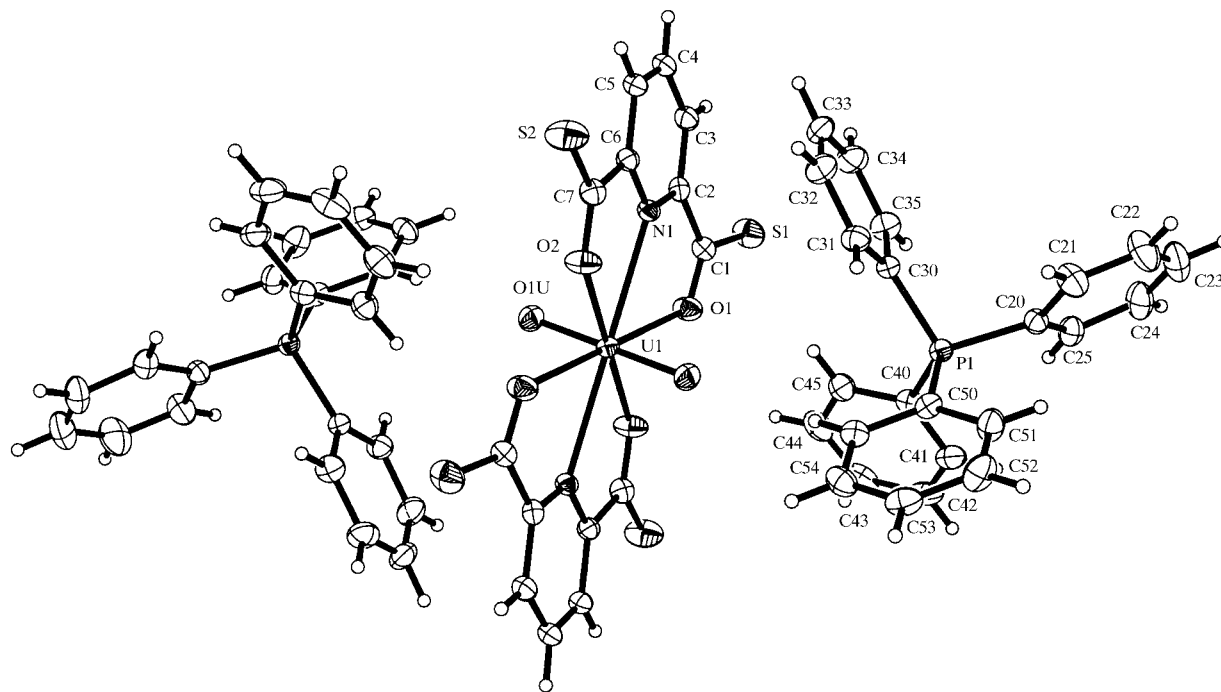

Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 40% probability level and H atoms are drawn as small spheres of arbitrary radii. The labelled and unlabelled cations shown are derived from the coordinates in the CIF by the symmetry operations $(1 + x, y, z)$ and $(3 - x, 1 - y, 2 - z)$, respectively. Atom U1 lies on an inversion centre at $(1, \frac{1}{2}, 1)$ and the unlabelled atoms in the anion are derived by use of the symmetry operation $(2 - x, 1 - y, 2 - z)$.

salt of pdtc was used, giving the title complex, (I). By using acetonitrile/water (80/20) as the solvent, large yellow blocks were isolated from the reaction. The crystals were harvested after 50% of the solvent had evaporated. When the complex was prepared in pure acetonitrile, a plate-like crystal morphology was observed, but the structure was the same as that of the block crystals. X-ray quality crystals of the polymeric species have not yet been obtained, but efforts to isolate them and complexes of this ligand with other actinides are ongoing.

The unit cell of (I) contains two tetraphenylphosphonium cations, with the $[UO_2(pdtc)_2]^{2-}$ anion sitting on an inversion centre. Fig. 2 shows a view down the a axis of the unit cell, illustrating the stacking of the tetraphenylphosphonium cations and the relative orientation of the cations and the anion. The coordination environment of the U atom is hexagonal bipyramidal, with two axial O atoms, and with two tridentate pdtc ligands bound through four carbonyl O atoms and two pyridine N atoms in the equatorial plane. This is the first example of a metal being bound through the O and not the S atoms of this ligand. Previous structures of metal complexes of pdtc include structures with Pd^{II} (Espinet *et al.*, 1994), Ni^{II}, Ni^{III} and Co^{III} (Krüger & Holm, 1990), and the hard ion Fe^{III} (Hildebrand *et al.*, 1984). In all these cases, the ligand is tridentate, as in (I), but binds to the metal in an NS_2 fashion.

For the non-sulfur-containing ligand pyridine-2,6-dicarboxylate (pdc), the uranyl structures for two monomers (Marangoni *et al.*, 1974; Cousson *et al.*, 1991) and a polymer (Immirzi *et al.*, 1975) are known. The repeat unit of the polymer consists of a linear uranyl group equatorially surrounded by five ligand atoms: two carboxylate O atoms and the N atom of one pdc ion, an O atom of an adjacent pdc ligand and one water molecule. The bridging carboxylate
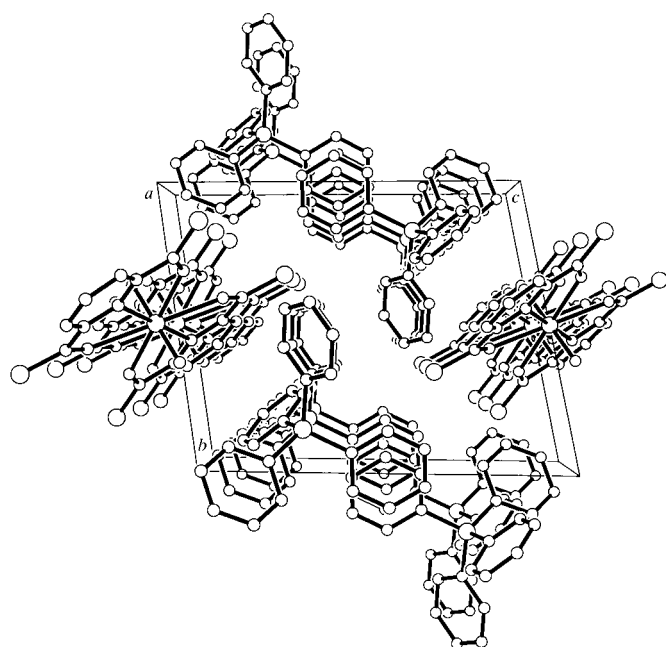
group gives rise to a polymeric structure in the form of a single helix. The uranyl group binds two axial O atoms at 1.76 (2) Å, a pyridine N atom at 2.51 (2) Å, two carboxylate O atoms at 2.36 (1) and 2.42 (2) Å, another carboxylate O atom from an adjacent pdc unit at 2.33 Å and a bound water at 2.42 (2) Å. One of the monomer structures (Marangoni *et al.*, 1974) contains two axial O atoms and two tridentate ligands, at bond lengths of U—N = 2.73 (2) Å, and U—O = 2.37 (2) and 2.42 (3) Å. The longer bond lengths to the tridentate ligand in the monomer studied by Marangoni *et al.* (1974) and the current structure are consistent with a coordination number of 6 in the equatorial plane, *versus* 5 for the polymer.

Experimental

The pdtc used in the preparation of (I) was synthesized according to the method of Hildebrand *et al.* (1983). A solution of [pdtc][PPh$_4$]$_2$ (8.47 mg, 0.010 mmol) dissolved in acetonitrile (5 ml) was added slowly to an aqueous solution (1 ml) of uranyl nitrate (12 mg, 0.0304 mmol). The resulting solution was not stirred and was allowed to stand, loosely capped, in a fume hood for 96 h. Yellow block-shaped crystals were harvested by decanting the mother liquor and coating the crystals with mineral oil. The synthesis of the monomeric species is quantitative based on the ligand.

Crystal data

$(C_{24}H_{20}P)_2[UO_2(C_7H_3NO_2S_2)_2]$	$Z = 1$
$M_r = 1343.22$	$D_x = 1.655$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.2351$ (7) Å	Cell parameters from 4192
$b = 11.607$ (1) Å	reflections
$c = 13.807$ (1) Å	$\theta = 1.51–23.29°$
$\alpha = 77.891$ (1)°	$\mu = 3.28$ mm^{-1}
$\beta = 81.46$ (1)°	$T = 293$ (2) K
$\gamma = 69.14$ (1)°	Block, yellow
$V = 1347.7$ (2) Å^3	$0.32 \times 0.25 \times 0.20$ mm

Data collection

Siemens $P4/PC$ CCD area-detector diffractometer	5605 independent reflections
ω scans	5485 reflections with $I > 2\sigma(I)$
Absorption correction: empirical	$R_{int} = 0.031$
($SADABS$ in $SHELXL$97;	$\theta_{max} = 28.45°$
Sheldrick, 1997)	$h = -11 \rightarrow 11$
$T_{min} = 0.31$, $T_{max} = 0.52$	$k = -14 \rightarrow 15$
9541 measured reflections	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.030$	$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2]$
$wR(F^2) = 0.073$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
5605 reflections	$\Delta\rho_{max} = 1.21$ e Å^{-3}
349 parameters	$\Delta\rho_{min} = -1.95$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

U1—O1U	1.774 (2)	S1—C1	1.675 (4)
U1—O2	2.434 (2)	S2—C7	1.676 (4)
U1—O1	2.447 (3)	O1—C1	1.268 (5)
U1—N1	2.647 (3)	O2—C7	1.263 (4)
O1U—U1—O2	92.16 (11)	O1U—U1—N1	84.96 (10)
O1U—U1—O1	93.26 (10)	O2—U1—N1	59.75 (9)
O2—U1—O1	118.42 (9)	O1—U1—N1	59.77 (9)

Figure 2
The view down the *a* axis of the unit cell of (I).

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H atoms were placed in ideal positions and refined as riding (C—H 0.93 Å), with displacement parameters fixed at $1.2U_{eq}$ of their parent atoms. The final difference Fourier map contained a peak of 1.21 e Å^{-3} located 0.8 Å from the U1 atom.

Data collection: *SMART* (Siemens, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1565). Services for accessing these data are described at the back of the journal.

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