

Chloroheptakis(dimethyl sulfoxide)-
uranium(IV) trichlorideWarren J. Oldham,^{a*} Brian L. Scott,^b Kent D. Abney,^c
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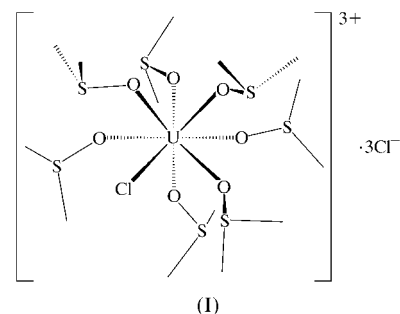
In the title complex, $[\text{UCl}(\text{C}_2\text{H}_6\text{OS})_7]\text{Cl}_3$, the uranium metal center is coordinated in a distorted bicapped trigonal prism geometry by seven O atoms from dimethyl sulfoxide ligands and by a terminal chloride ligand. Charge balance is maintained by three outer-sphere chloride ions per uranium(IV) metal center. Principle bond lengths include U—O 2.391 (2)–2.315 (2) Å, U—Cl 2.7207 (9) Å, and average S—O 1.540 (5) Å.

Comment

Uranium tetrachloride readily dissolves in anhydrous dimethyl sulfoxide (DMSO) to give deep-green solutions from which well formed emerald green crystals can be isolated. Pristine crystals are reported to correctly analyse for $\text{UCl}_4 \cdot 7\text{DMSO}$, but may be converted to $\text{UCl}_4 \cdot 5\text{DMSO}$ or $\text{UCl}_4 \cdot 3\text{DMSO}$ upon washing with carbon tetrachloride or on prolonged exposure to vacuum (Bagnall *et al.*, 1968). Available evidence demonstrates that $\text{UCl}_4 \cdot 3\text{DMSO}$ adopts an auto-ionized structure, $[\text{UCl}_2(\text{dmsO})_6][\text{UCl}_6]$, in both solution and the solid state, composed of discrete eight-coordinate uranium cations and six-coordinate uranium anions (Bombieri & Bagnall, 1975; Sakurai *et al.*, 1980). The central member of the series, $\text{UCl}_4 \cdot 5\text{DMSO}$, probably adopts the ionic $[\text{UCl}_3(\text{dmsO})_5]\text{Cl}$ structure, which is supported by spectroscopic evidence and by analogy to unpublished structural data cited for the thorium analog (Alvey *et al.*, 1973). Based on its relative thermal stability, the solid-state structure of the title complex, (I), has been suggested to consist of $[\text{UCl}_3(\text{dmsO})_5]\text{Cl}$, with two additional DMSO molecules weakly held in the crystal lattice (Bagnall *et al.*, 1968; Davies & Miller, 1983). However, we now find that $\text{UCl}_4 \cdot 7\text{DMSO}$ crystallizes as $[\text{UCl}(\text{dmsO})_7]\text{Cl}_3$.

Complex (I) crystallizes in space group $P2_1/n$ with no unusual intermolecular contacts. The geometry around the

eight-coordinate uranium(IV) metal center is best described as a distorted bicapped trigonal prism when evaluated by the shape parameters δ' and φ , where δ' is the angle of intersection between pairs of faces along the type *b* edges and φ is the torsion angle of the *BAAB* trapezoidal atoms ($\delta' = 12.4, 19.7, 45.0$ and 47.3° , and $\varphi = 15.4$ and 17.3° ; Porai-Koshits & Aslanov, 1972; Muettetries & Guggenberger, 1974). The vertices of the trigonal prism are defined by five DMSO O atoms and by a terminal chloride ligand, *i.e.* O1, O2, O3, Cl1, O4 and O7. The two face-capping vertices are defined by atoms O5 and O6. Charge balance is maintained by three outer-sphere chloride ligands per uranium(IV) metal center.



The δ' and φ analyses require that dodecahedral *A* and *B* site labels be imposed on the eight-coordinate structure. Using this formalism, the chloride ligand of the title complex occupies one of the less sterically encumbered *B* sites, as is generally observed for the related dodecahedral complexes. The U—Cl bond length of 2.7207 (9) Å is within the range of values reported in other seven- and eight-coordinate uranium(IV) structures, *e.g.* 2.813 (4) Å in $[\text{UCl}(\text{OPMe}_3)_6]^{3+}$ (Bombieri *et al.*, 1976), 2.62 (2) and 2.72 (4) Å in $[\text{UCl}_3(\text{EtC-ONeEt}_2)_4]^+$ (Bagnall *et al.*, 1982), an average of 2.597 (3) Å in $\text{UCl}_4(\text{thf})_3$ (Van Der Sluys *et al.*, 1993), 2.665 (5) Å in

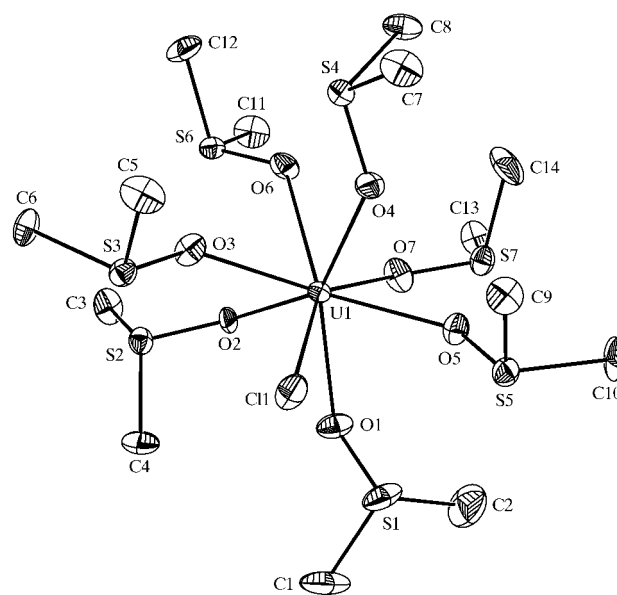


Figure 1

Displacement ellipsoid plot (50% probability) showing the molecular structure of $[\text{UCl}(\text{C}_2\text{H}_6\text{OS})_7]\text{Cl}_3$ and the atom-numbering scheme used in Table 1.

[UCl(dmf)₇]³⁺ (Kepert *et al.*, 1983), 2.70 (2) Å in [UCl₂(dms₆)₆]²⁺ (Bombieri & Bagnall, 1975), 2.624 (4) Å in [UCl₄(NCMe)₄] (Cotton *et al.*, 1984), 2.609 (9) Å in [UCl₄(Me₂NCH₂CH₂NMe₂)₂] (Zalkin *et al.*, 1986), and 2.869 (3) and 2.638 (4) Å in UCl₄ (Taylor & Wilson, 1973).

The U—O bond lengths of the title complex range from 2.315 (2)–2.391 (2) Å, with an average value of 2.36 (3) Å. The two most closely related uranium(IV) complexes show a similar range of U—O bond lengths, *e.g.* 2.36 (4)–2.27 (4) Å in [UCl₂(dms₆)₆]²⁺ (Bombieri & Bagnall, 1975) and 2.30 (1)–2.40 (1) Å in [UCl(dmf)₇]³⁺ (Kepert *et al.*, 1983). The S—O bond lengths of the coordinated DMSO ligands are lengthened to an average value of 1.540 (5) Å compared to the value in free DMSO of 1.492 (1) Å (Calligaris & Carugo, 1996).

Experimental

UCl₄ (100 mg, 0.263 mmol) was dissolved in dimethyl sulfoxide (10 ml) to give a homogeneous forest-green solution, which was carefully layered with diethyl ether (10 ml) and allowed to stand for 2 d. A few well formed deep-green crystals were separated and coated with mineral oil. In the absence of mineral oil, isolated crystals rapidly became opaque due to desolvation, as evidenced by elemental analysis, which correctly analyzed for UCl₄·5DMSO. Analysis calculated for C₁₀H₃₀Cl₄O₅S₅U: C 15.67, H 3.94%; found: C 15.56, H 4.16%.

Crystal data

[UCl(C₂H₆OS)₇]Cl₃
M_r = 926.73
 Monoclinic, *P*₂₁/*n*
a = 9.6350 (5) Å
b = 22.0785 (11) Å
c = 15.5217 (8) Å
 β = 91.818 (1)°
V = 3300.2 (3) Å³
Z = 4

D_x = 1.865 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 8192 reflections
 θ = 1.6–26.4°
 μ = 5.72 mm⁻¹
T = 203 (2) K
 Irregular, emerald green
 0.12 × 0.10 × 0.04 mm

Data collection

Bruker *P4*/CCD diffractometer
 ω and φ scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
*T*_{min} = 0.59, *T*_{max} = 0.69
 14 577 measured reflections
 6416 independent reflections

5686 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.023
 θ _{max} = 26.4°
h = -11 → 11
k = -27 → 25
l = -19 → 17

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.023
wR(*F*²) = 0.056
S = 0.99
 6416 reflections
 298 parameters

H-atom parameters not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0325P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.05 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.91 \text{ e } \text{Å}^{-3}$

H-atom positions were idealized, and allowed to ride on the parent atoms. All H-atom isotropic displacement parameters were set at 0.08 Å².

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Table 1

Selected geometric parameters (Å, °).

U1—O4	2.315 (2)	U1—O6	2.381 (2)
U1—O7	2.336 (2)	U1—O2	2.390 (2)
U1—O3	2.352 (2)	U1—O1	2.391 (2)
U1—O5	2.378 (2)	U1—Cl1	2.7207 (9)
O4—U1—O7	100.89 (8)	O6—U1—O2	75.18 (8)
O4—U1—O3	82.03 (8)	O4—U1—O1	146.91 (8)
O7—U1—O3	141.80 (8)	O7—U1—O1	78.64 (9)
O4—U1—O5	72.52 (8)	O3—U1—O1	118.90 (9)
O7—U1—O5	73.48 (8)	O5—U1—O1	75.77 (8)
O3—U1—O5	140.93 (8)	O6—U1—O1	138.33 (8)
O4—U1—O6	70.30 (8)	O2—U1—O1	69.37 (8)
O7—U1—O6	74.31 (8)	O4—U1—Cl1	88.57 (6)
O3—U1—O6	70.96 (8)	O7—U1—Cl1	144.29 (6)
O5—U1—O6	124.08 (8)	O3—U1—Cl1	73.28 (6)
O4—U1—O2	143.62 (8)	O5—U1—Cl1	76.86 (6)
O7—U1—O2	80.15 (8)	O6—U1—Cl1	140.42 (6)
O3—U1—O2	76.12 (8)	O2—U1—Cl1	111.92 (6)
O5—U1—O2	139.62 (7)	O1—U1—Cl1	75.13 (7)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1197). Services for accessing these data are described at the back of the journal.

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