Di-µ-chlorido-bis[chloridobis(dimethyl sulfoxide)dioxidouranium(VI)]

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In the crystal structure of the title compound, $[U_2Cl_4O_4(C_2H_6OS)_4]$, the compound has a centrosymmetric dimeric structure bridged by two chloride anions. Each U^{VI} atom is seven-coordinate in a pentagonal-bipyramidal geometry. In the equatorial plane of the uranyl unit there are two O atoms from non-adjacent dimethyl sulfoxides and three chloride ions (of which two chlorides are bridging). The compound is of interest as an anhydrous starting material of the uranyl(VI) ion.

Related literature

For related structures, see: Berthet *et al.* (2000); Charpin *et al.* (1987); Rebizant *et al.* (1987); Wilkerson *et al.* (1999). For the synthesis, see: Calderazzo *et al.* (1997); Berthet *et al.* (2000).
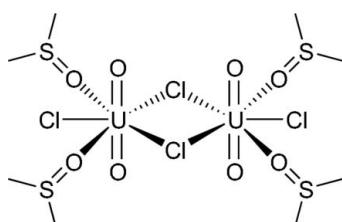
Experimental

Crystal data

$[U_2Cl_4O_4(C_2H_6OS)_4]$	a = 9.172 (3) Å
M_r = 994.37	b = 12.833 (4) Å
Monoclinic, $P2_1/c$	c = 10.691 (2) Å
β = 97.72 (2)°	μ = 13.76 mm^{-1}
V = 1247.0 (6) Å^3	T = 173 (2) K
Z = 2	$0.33 \times 0.21 \times 0.15$ mm
Mo $K\alpha$ radiation	

Data collection

Rigaku R-AXIS RAPID IP diffractometer	10244 measured reflections
Absorption correction: multi-scan (Higashi, 1999)	2849 independent reflections
T_{min} = 0.051, T_{max} = 0.128	2330 reflections with $I > 2\sigma(I)$
	R_{int} = 0.084

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043	120 parameters
$wR(F^2)$ = 0.111	H-atom parameters constrained
S = 1.10	$\Delta\rho_{max}$ = 2.54 e Å^{-3}
2849 reflections	$\Delta\rho_{min}$ = −2.25 e Å^{-3}

Table 1
Selected interatomic distances (Å).

U1—O1	1.746 (7)	U1—Cl2	2.686 (2)
U1—O2	1.757 (6)	U1—Cl1	2.844 (2)
U1—O3	2.349 (6)	U1—Cl1^i	2.909 (2)
U1—O4	2.360 (6)		

Symmetry code: (i) $-x + 2, -y + 1, -z + 1$.

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2000-2006); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2000-2006); program(s) used to solve structure: *SIR92* (Altomare *et al.* 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2386).

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‡ This author's last name has been changed from 'Mizuoka'.

supplementary materials

Di-μ-chlorido-bis[chloridobis(dimethyl sulfoxide)dioxidouranium(VI)]

K. Takao and Y. Ikeda

Comment

The title compound (**I**) was unexpectedly obtained from a hydrochloric acid aqueous solution containing U^{4+} and dimethyl sulfoxide (DMSO). It is reasonable to consider that **I** was formed by aerobic oxidation of U^{4+} to UO_2^{2+}.

The title compound **I** has a dimeric structure which is bridged by two μ-Cl^- between $UO_2Cl(DMSO)_2$ fragments as shown in Fig. 1. There is an inversion center in the molecular structure of **I**. Each U atom is seven-coordinated in a pentagonal-bipyramidal geometry. Two O atoms are at the axial positions [mean $U=O_{yl}$ = 1.75 (1) Å] (Table 1). In the equatorial plane of each U, there are three Cl^- ions; two of them act as μ-Cl^- to bridge the U atoms in **I** [mean $U–Cl_{bridge}$ = 2.88 (3) Å], and the remaining Cl^- is placed at the position independent of the bridge formation [$U–Cl_{non-bridge}$ = 2.686 (2) Å]. The DMSO molecules in the equatorial plane coordinates to U through its O, and are non-adjacent [mean $U–O_{DMSO}$ = 2.35 (1) Å]. Deviations of Cl^- and O of DMSO from the mean equatorial plane are within 0.15 Å. Interatomic distances between U(1)⋯U(1)[i] and μ-Cl(1)⋯μ-Cl(1)[i] [symmetry code: (i) -*x* + 2, -*y* + 1, -*z* + 1] are 4.7669 (3) and 3.221 (3) Å, respectively, which indicate no interatomic interaction in each pair. These structural features of **I** are similar to that of $[UO_2Cl(THF)_2]_2(\mu\text{-}Cl)_2$ (THF = tetrahydrofuran) reported by Charpin *et al.* (1987).

Previously, some anhydrous uranyl(VI) salts, $UO_2Br_2(THF)_3$, $UO_2Cl_2(THF)_3$, $[UO_2Cl(THF)_2]_2(\mu\text{-}Cl)_2$, and $UO_2(CF_3SO_3)_2L_3$ (*L* = THF, pyridine), were reported (Rebizant *et al.* 1987, Wilkerson *et al.* 1999, Charpin *et al.* 1987, Berthet *et al.* 2000, respectively). In syntheses of water-sensitive uranyl(VI) compounds, *e.g.*, alkoxides and amides, anhydrous starting materials must be used. On the other hand, THF is not very stable, and may be decomposed by its polymerization in presence of a strong acid, *e.g.* CF_3SO_3H (Calderazzo *et al.* 1997 and Berthet *et al.* 2000). Compound **I** also has simple composition, *i.e.*, consisting only of UO_2^{2+}, Cl^-, and DMSO. The use of DMSO insead of THF expands the number of choices of the anhydrous uranyl(VI) salts as the starting material.

Experimental

Uranium(VI) trioxide was dissolved in 5 *M* hydrochloric acid solution. With heating and vigrous stirring, 2 molar amount of silver powder was added in the HCl aq. After 30 min, the mixture was cooled to room temperature. The insoluble residue of AgCl was removed by filtration. Small portion (*ca* 1 ml) of this filtrate was separated in a test tube. In this sample, some drops of dimethyl sulfoxide was added. The mixture was allowed to the air. After several days, yellow crystals of the title compound deposited.

supplementary materials

Refinement

H atoms were placed in calculated positions with C—H = 0.98 Å and torsion angles were refined to fit the electron density, with $U_{iso}(H) = 1.2U_{eq}(C)$. The highest peak in the final difference Fourier map is 0.91 Å apart from the U atom.

Figures
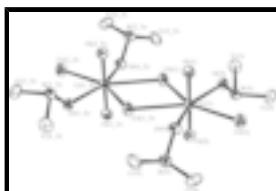
Fig. 1. Molecular structure of **I** drawn by thermal ellipsoids in 50% probability level. Asymmetric unit was expanded by the symmetry operation; (i) -*x* + 2, -*y* + 1, -*z* + 1. Hydrogen atoms are omitted for clarity.
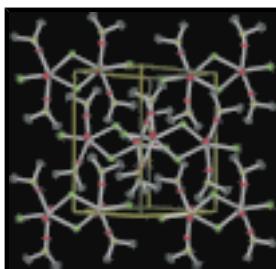

Fig. 2. Packing view of **I** drawn by thermal ellipsoids in 50% probability level. Hydrogen atoms are omitted for clarity.

Di-µ-chlorido-bis[chloridobis(dimethyl sulfoxide)dioxidouranium(VI)]

Crystal data
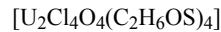
[U$_2$Cl$_4$O$_4$(C$_2$H$_6$OS)$_4$]	$F_{000} = 904$
$M_r = 994.37$	$D_x = 2.648$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71075$ Å
Hall symbol: -P 2ybc	Cell parameters from 10519 reflections
$a = 9.172$ (3) Å	$\theta = 3.1–27.5°$
$b = 12.833$ (4) Å	$\mu = 13.76$ mm^{-1}
$c = 10.691$ (2) Å	$T = 173$ (2) K
$\beta = 97.72$ (2)°	Block, yellow
$V = 1247.0$ (6) Å^3	$0.33 \times 0.21 \times 0.15$ mm
$Z = 2$	

Data collection

Rigaku R-AXIS RAPID IP diffractometer	2849 independent reflections
Radiation source: fine-focus sealed tube	2330 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.084$
Detector resolution: 10.00 pixels mm^{-1}	$\theta_{max} = 27.5°$
$T = 173(2)$ K	$\theta_{min} = 3.2°$

ω scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan (Higashi, 1999)	$k = -16 \rightarrow 15$
$T_{min} = 0.051$, $T_{max} = 0.128$	$l = -13 \rightarrow 13$
10244 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.043$	$w = 1/[\sigma^2(F_o{}^2) + (0.0595P)^2]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.111$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.10$	$\Delta\rho_{max} = 2.54$ e Å^{-3}
2849 reflections	$\Delta\rho_{min} = -2.25$ e Å^{-3}
120 parameters	Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0012 (2)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
U1	0.78418 (3)	0.51860 (2)	0.35047 (3)	0.02280 (14)
Cl1	0.9986 (2)	0.37721 (17)	0.4687 (2)	0.0309 (5)
Cl2	0.5528 (3)	0.5489 (2)	0.1718 (2)	0.0381 (5)
S1	0.7780 (2)	0.28472 (17)	0.1748 (2)	0.0279 (5)
S2	0.8069 (3)	0.78684 (18)	0.3045 (2)	0.0319 (5)
O1	0.6738 (8)	0.4945 (5)	0.4683 (6)	0.0310 (14)
O2	0.8996 (8)	0.5398 (5)	0.2345 (6)	0.0327 (15)
O3	0.7203 (7)	0.3496 (5)	0.2783 (5)	0.0280 (13)
O4	0.7311 (7)	0.6977 (5)	0.3661 (5)	0.0296 (14)
C1	0.7963 (11)	0.1587 (7)	0.2424 (9)	0.037 (2)
H1A	0.8810	0.1575	0.3089	0.044*

H1B	0.8112	0.1077	0.1771	0.044*
H1C	0.7068	0.1412	0.2788	0.044*
C2	0.6207 (11)	0.2632 (8)	0.0621 (8)	0.038 (2)
H2A	0.5958	0.3275	0.0145	0.045*
H2B	0.5377	0.2424	0.1055	0.045*
H2C	0.6416	0.2078	0.0039	0.045*
C3	0.8216 (13)	0.8880 (8)	0.4207 (9)	0.047 (3)
H3A	0.8973	0.8694	0.4907	0.057*
H3B	0.7269	0.8965	0.4523	0.057*
H3C	0.8487	0.9534	0.3826	0.057*
C4	0.6660 (13)	0.8391 (8)	0.1913 (8)	0.044 (3)
H4A	0.6462	0.7909	0.1199	0.053*
H4B	0.6980	0.9064	0.1612	0.053*
H4C	0.5762	0.8488	0.2303	0.053*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.0247 (2)	0.0179 (2)	0.0251 (2)	0.00006 (13)	0.00058 (12)	0.00017 (11)
Cl1	0.0314 (12)	0.0197 (11)	0.0385 (11)	0.0033 (9)	−0.0067 (8)	−0.0050 (8)
Cl2	0.0366 (13)	0.0324 (13)	0.0412 (13)	0.0003 (10)	−0.0095 (9)	0.0021 (10)
S1	0.0264 (12)	0.0235 (12)	0.0338 (11)	−0.0005 (9)	0.0040 (8)	−0.0015 (8)
S2	0.0318 (13)	0.0245 (12)	0.0395 (12)	0.0020 (9)	0.0052 (9)	0.0044 (9)
O1	0.036 (4)	0.025 (3)	0.032 (3)	−0.001 (3)	0.004 (3)	−0.003 (2)
O2	0.036 (4)	0.033 (4)	0.029 (3)	−0.003 (3)	0.004 (2)	0.000 (3)
O3	0.032 (4)	0.023 (3)	0.027 (3)	0.000 (3)	0.000 (2)	−0.003 (2)
O4	0.038 (4)	0.014 (3)	0.036 (3)	0.002 (3)	0.004 (2)	0.002 (2)
C1	0.038 (6)	0.020 (5)	0.051 (6)	0.010 (4)	0.001 (4)	−0.002 (4)
C2	0.043 (6)	0.037 (6)	0.030 (5)	0.008 (5)	−0.007 (4)	−0.002 (4)
C3	0.051 (7)	0.027 (6)	0.061 (7)	−0.013 (5)	−0.001 (5)	−0.001 (5)
C4	0.055 (7)	0.041 (6)	0.036 (5)	0.011 (5)	0.001 (4)	0.018 (4)

Geometric parameters (Å, °)

U1—O1	1.746 (7)	S2—C4	1.779 (9)
U1—O2	1.757 (6)	S2—C3	1.789 (10)
U1—O3	2.349 (6)	C1—H1A	0.9800
U1—O4	2.360 (6)	C1—H1B	0.9800
U1—Cl2	2.686 (2)	C1—H1C	0.9800
U1—Cl1	2.844 (2)	C2—H2A	0.9800
U1—Cl1^i	2.909 (2)	C2—H2B	0.9800
Cl1—U1^i	2.909 (2)	C2—H2C	0.9800
U1—U1^i	4.7669 (16)	C3—H3A	0.9800
Cl1—Cl1^i	3.221 (3)	C3—H3B	0.9800
S1—O3	1.535 (6)	C3—H3C	0.9800
S1—C1	1.770 (9)	C4—H4A	0.9800
S1—C2	1.773 (9)	C4—H4B	0.9800
S2—O4	1.533 (6)	C4—H4C	0.9800

O1—U1—O2	178.0 (3)	C4—S2—C3	100.3 (5)
O1—U1—O3	86.0 (2)	S1—O3—U1	130.0 (4)
O2—U1—O3	93.4 (2)	S2—O4—U1	125.9 (4)
O1—U1—O4	88.6 (3)	S1—C1—H1A	109.5
O2—U1—O4	92.8 (3)	S1—C1—H1B	109.5
O3—U1—O4	151.3 (2)	H1A—C1—H1B	109.5
O1—U1—Cl2	93.4 (2)	S1—C1—H1C	109.5
O2—U1—Cl2	88.2 (2)	H1A—C1—H1C	109.5
O3—U1—Cl2	76.21 (15)	H1B—C1—H1C	109.5
O4—U1—Cl2	76.03 (16)	S1—C2—H2A	109.5
O1—U1—Cl1	90.0 (2)	S1—C2—H2B	109.5
O2—U1—Cl1	88.1 (2)	H2A—C2—H2B	109.5
O3—U1—Cl1	71.59 (15)	S1—C2—H2C	109.5
O4—U1—Cl1	136.62 (15)	H2A—C2—H2C	109.5
Cl2—U1—Cl1	147.29 (7)	H2B—C2—H2C	109.5
O1—U1—Cl1^i	90.8 (2)	S2—C3—H3A	109.5
O2—U1—Cl1^i	88.5 (2)	S2—C3—H3B	109.5
O3—U1—Cl1^i	139.54 (15)	H3A—C3—H3B	109.5
O4—U1—Cl1^i	68.58 (15)	S2—C3—H3C	109.5
Cl2—U1—Cl1^i	144.24 (7)	H3A—C3—H3C	109.5
Cl1—U1—Cl1^i	68.09 (7)	H3B—C3—H3C	109.5
U1—Cl1—U1^i	111.91 (7)	S2—C4—H4A	109.5
O3—S1—C1	102.9 (4)	S2—C4—H4B	109.5
O3—S1—C2	104.3 (4)	H4A—C4—H4B	109.5
C1—S1—C2	99.2 (5)	S2—C4—H4C	109.5
O4—S2—C4	104.1 (5)	H4A—C4—H4C	109.5
O4—S2—C3	103.9 (4)	H4B—C4—H4C	109.5
O1—U1—Cl1—U1^i	−90.9 (2)	Cl2—U1—O3—S1	92.7 (4)
O2—U1—Cl1—U1^i	89.2 (2)	Cl1—U1—O3—S1	−81.5 (4)
O3—U1—Cl1—U1^i	−176.64 (17)	Cl1^i—U1—O3—S1	−86.3 (4)
O4—U1—Cl1—U1^i	−2.9 (3)	C4—S2—O4—U1	113.6 (5)
Cl2—U1—Cl1—U1^i	172.88 (11)	C3—S2—O4—U1	−141.8 (5)
Cl1^i—U1—Cl1—U1^i	0.0	O1—U1—O4—S2	169.6 (5)
C1—S1—O3—U1	138.5 (5)	O2—U1—O4—S2	−9.0 (5)
C2—S1—O3—U1	−118.4 (5)	O3—U1—O4—S2	−111.3 (5)
O1—U1—O3—S1	−172.8 (5)	Cl2—U1—O4—S2	−96.5 (4)
O2—U1—O3—S1	5.3 (5)	Cl1—U1—O4—S2	81.1 (4)
O4—U1—O3—S1	107.4 (5)	Cl1^i—U1—O4—S2	78.3 (4)

Symmetry codes: (i) $-x+2, -y+1, -z+1$.

Fig. 1

Fig. 2