Preparation, Characterization, and Crystal Structure of *cis*-Dichloro-[*meso*-bis(*trans*-2-hydroxycyclohexyl) sulphide-*OOS*]dioxouranium(VI)

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trans-Bis(2-hydroxycyclohexyl) sulphide, prepared by a simplified synthesis, and its product with uranyl chloride have been characterized. The crystal structure of the complex containing the ligand in the *meso*-form has been determined from three-dimensional *X*-ray diffraction data. Crystals are triclinic, space group $P\bar{1}$, with $a = 11.274(2)$, $b = 10.173(2)$, $c = 9.367(2)$ Å, $\alpha = 111.41(5)$, $\beta = 97.46(5)$, and $\gamma = 111.21(5)°$, with $Z = 2$. The structure was solved by the heavy-atom method from diffractometer data, and refined by least-squares to a final R of 6.2%. The co-ordination polyhedron around uranium is distorted pentagonal bipyramidal. The neutral ligand is terdentate with the hydroxy-oxygens and sulphur directly bonded to uranium.

It is well known that the uranyl ion is a 'hard' Lewis acid.[1] Thus the formation of co-ordinate bonds of the type $>S\rightarrow UO_2$ with the typically 'soft' sulphur atom is not to be expected in principle, and no example of a thioether sulphur atom co-ordinated to uranyl ion has been reported. Many attempts to isolate such complexes, even polydentate ones, were unsuccessful, and even when sulphur-donor sites are present in potentially chelating molecules co-ordination usually occurs only through nitrogen and oxygen.[2] However, we now report the preparation and characterization of a uranyl complex with bis(2-hydroxycyclohexyl) sulphide, in which sulphur is directly co-ordinated to uranium.

EXPERIMENTAL

Materials.—Reagent-grade uranyl chloride trihydrate, sodium sulphide, cyclohexene oxide, and solvents were used without further purification.

Preparation of the Ligand.—The ligand was obtained by reaction (70 °C, 1 h) of an excess of disodium sulphide with cyclohexene oxide in alcoholic solution. The product was separated by extraction with benzene and purified on a chromatographic column (SiO_2/Et_2O) by separating the fast-running colourless fraction from a small slightly yellow one 'fixed' at the bottom.

Evaporation of the eluate gave white crystals, m.p. 70 °C (Found: C, 63.05; H, 9.80; S, 14.10. Calc. for $C_{12}H_{22}O_2S$: C, 62.60; H, 9.56; S, 13.91%).

Preparation of the Complex.—To a solution of $UO_2Cl_2\cdot 3H_2O$ in ethyl acetate, an excess of the ligand in the same solvent was added at room temperature. The brilliant yellow anhydrous crystals which formed overnight were washed with small portions of ethyl acetate and dried *in vacuo*. Crystals have relatively high solubility in many solvents, are non-hygroscopic, m.p. (decomp.) 177—194° C (Found: C, 25.1; H, 4.15; Cl, 12.3; U, 41.5. $C_{12}H_{22}SCl_2O_4U$ requires C, 25.2; H, 3.85; Cl, 12.43; U, 41.68%). Uranium was determined gravimetrically.[3]

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[1] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

[2] S. Degetto, unpublished results.

[3] G. Marangoni, S. Degetto, and U. Croatto, *Talanta*, 1973, **20**, 1217.

Physical Measurements.—I.r. spectra (4 000—400 cm^{-1}) were recorded on a Perkin-Elmer 621 i.r. spectrophotometer in Nujol mulls and KBr discs. The far-i.r. spectrum (400—50 cm^{-1}) was taken as a Nujol mull between polyethylene plates with a Beckman i.r. 11 instrument. The electronic absorption spectrum was taken as KBr pellets by use of a Perkin-Elmer 356 spectrophotometer. ^{1}H n.m.r. spectra for deuterioacetone and CCl_4 solutions were recorded by use of a Varian T 60 spectrometer. Some results are summarized in Table 1.

Intensity Data.—Precise unit-cell parameters were obtained by a least-squares refinement of the 2θ values of 20 reflections measured on a diffractometer.

TABLE 1

Some physical data for the ligand and for the complex

	M.p./°C	^{1}H n.m.r.^{a} τ/p.p.m.	Band maxima/nm (KBr pellets, 400—500 nm)	I.r./cm^{-1}
(*a*) Ligand	70	between 5 and 6.5 (2 H); 6.7 (br, 2 H); 7.5 (br, 2 H); 7.9br, 8.2br, 8.6br (16 H) ^{b,c}		3 360s, br ν(OH)
(*b*) Complex	177—194	between 5 and 6s (2 H); 6.3 (br, 2 H); 7.1 (br, 2 H); 7.9br, 8.2br, 8.6br (16 H) ^{b}	410, 420, 434, 447, 456, 463, 472, 478sh, 488	3 200s br ν(OH); 948s, ν_{as}(OUO); 264s, 251s, 223s (?)

^{a} Tetramethylsilane as reference. ^{b} Deuterioacetone solution. ^{c} CCl_4 solution.

TABLE 2

Fractional co-ordinates and anisotropic * temperature factors (× 10^4), whites timated standard deviations in parentheses

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	3 090(1)	1 720(1)	1 780(1)	490(7)	248(6)	411(7)	206(5)	210(5)	195(5)
Cl(1)	4 140(8)	2 919(8)	4 952(8)	968(60)	354(40)	406(42)	256(40)	281(40)	200(34)
Cl(2)	1 008(7)	−281(9)	2 193(10)	519(47)	639(51)	936(60)	229(41)	343(44)	537(47)
S	3 923(7)	2 153(7)	−930(8)	536(45)	269(37)	459(43)	151(34)	148(35)	224(33)
O(1)	3 845(17)	430(21)	1 414(21)	644(122)	677(124)	627(121)	457(106)	455(102)	465(104)
O(2)	2 342(21)	2 986(27)	1 960(26)	1 002(164)	1 275(183)	1 097(172)	936(154)	926(147)	971(157)
O(3)	1 462(18)	−4(21)	−949(23)	556(122)	565(121)	681(137)	243(102)	208(104)	328(106)
O(4)	5 372(16)	3 828(18)	2 489(18)	594(115)	408(101)	312(97)	172(89)	193(87)	157(83)
C(1)	6 128(27)	4 330(28)	1 462(31)	603(197)	289(149)	550(179)	218(142)	297(156)	221(141)
C(2)	7 595(28)	5 136(31)	2 276(32)	561(196)	448(168)	479(174)	147(150)	103(150)	216(143)
C(3)	8 367(27)	5 512(33)	1 125(35)	543(189)	536(190)	596(199)	155(155)	122(157)	302(170)
C(4)	7 992(30)	4 035(37)	−396(38)	618(223)	744(228)	737(228)	270(183)	242(179)	441(200)
C(5)	6 489(29)	3 236(30)	−1 230(32)	643(206)	385(163)	471(176)	116(150)	200(154)	137(139)
C(6)	5 678(27)	2 856(27)	−94(29)	690(188)	294(148)	416(161)	281(140)	255(142)	181(132)
C(7)	3 183(27)	15(26)	−2 240(28)	646(204)	212(138)	303(154)	120(135)	63(133)	90(118)
C(8)	3 525(30)	−467(30)	−3 800(29)	870(223)	419(172)	241(151)	196(159)	218(148)	135(131)
C(9)	2 736(35)	−2 295(32)	−4 780(33)	1 055(281)	357(177)	436(182)	170(178)	247(179)	162(146)
C(10)	1 255(34)	−2 847(34)	−5 055(37)	834(258)	450(188)	607(220)	59(180)	86(184)	204(164)
C(11)	910(32)	−2 326(31)	−3 471(35)	840(234)	348(168)	560(200)	108(163)	203(172)	146(149)
C(12)	1 724(26)	−520(30)	−2 521(31)	485(189)	477(176)	417(174)	155(146)	46(139)	217(142)

* In the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

Crystal Data—$C_{12}H_{22}Cl_2O_4SU$, $M = 571$, Triclinic, $a = 11.274(2)$, $b = 10.173(2)$, $c = 9.367(2)$ Å, $\alpha = 111.41(5)$, $\beta = 97.46(5)$, $\gamma = 111.21(5)°$, $U = 889$ Å^3, $D_c = 2.13$ g cm^{-3}, $Z = 2$, $F(000) = 536$. Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 118.4 cm^{-1}.

Intensities were measured by the ω scan method on a Philips PW 1100 four-circle diffractometer, by use of graphite-monochromatized Mo-K_α radiation, with a scan width 0.8°, scan speed 6° min^{-1}, and two 4 s background counts. Intensities of 1 655 reflections with $I \geqslant 0$ for $3° \leqslant \theta \leqslant 20°$ were measured, corrected for Lorentz effects, and placed on an approximately absolute scale by Wilson's method.* No absorption correction was made. Of 1 617 structure factors recorded, 1 528 had $I \geqslant 3\sigma(I)$.

Determination of the Structure.—The structure was determined by the heavy-atom method. The hydrogen atoms of the cyclohexane rings were introduced in calculated positions assuming C–H 1.05 Å. Atomic scattering factors were taken from ref. 4 for non-hydrogen atoms, and from ref. 5 for hydrogen atoms. For uranium a correction was applied for the real and imaginary part of the anomalous dispersion.[6] The refinement of the parameters was carried out by full-matrix least-squares calculations. The function minimized was $\Sigma(k|F_o| - |F_c|)^2$ and unit weights were assigned to all reflections used. Anisotropy was introduced for all non-hydrogen atoms. Hydrogen atoms were introduced with isotropic temperature factors related to the temperature factors of the atoms to which they are bonded. Parameters were refined until every shift became $<0.1\sigma$. The final R, calculated on the observed reflections, was 0.062.

A final difference-Fourier map showed no relevant residual electron density, and the hydrogen atoms of the hydroxy-groups were not located.

Calculations were performed on a CDC 6600 computer using the 'X-Ray' program system.[7]

Final positional and anisotropic thermal parameters

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* High scan speed and relatively low-angle limit were used in order to prevent decomposition of the crystals during irradiation.

[4] D. T. Cromer and I. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[5] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[7] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, '*X*-Ray system of crystallographic programs, Report of July 1970, University of Maryland.

obtained from the least-squares refinements are given in Table 2, and bond lengths and angles in Tables 3 and 4.

Table 3

Interatomic distances (Å), with estimated standard deviations in parentheses

(*a*) Co-ordination polyhedron

U–Cl(1)	2.67(1)	U–O(2)	1.75(3)
U–Cl(2)	2.67(1)	U–O(3)	2.48(2)
U–S	2.94(1)	U–O(4)	2.49(2)
U–O(1)	1.77(2)		

(*b*) Organic ligand

S–C(6)	1.79(3)	O(3)–C(12)	1.48(4)
S–C(7)	1.84(2)	O(4)–C(1)	1.47(4)
C(1)–C(2)	1.49(4)	C(7)–C(8)	1.51(4)
C(2)–C(3)	1.54(5)	C(8)–C(9)	1.56(4)
C(3)–C(4)	1.51(4)	C(9)–C(10)	1.51(5)
C(4)–C(5)	1.53(4)	C(10)–C(11)	1.54(5)
C(5)–C(6)	1.55(4)	C(11)–C(12)	1.54(3)
C(6)–C(1)	1.51(3)	C(12)–C(7)	1.49(4)

Table 4

Bond angles (°), with estimated standard deviations in parentheses

(*a*) Co-ordination polyhedron *

O(1)–U–O(2)	175(1)	Cl(2)–U–O(3)	75.1(5)
Cl(1)–U–Cl(2)	84.6(2)	S–U–O(3)	62.5(5)
Cl(1)–U–O(4)	73.7(4)	S–U–O(4)	64.2(4)

(*b*) Organic ligand

U–O(4)–C(1)	131(1)	U–O(3)–C(12)	129(1)
U–S–C(6)	98(1)	U–S–C(7)	93(1)
O(4)–C(1)–C(2)	111(2)	O(3)–C(12)–C(7)	109(2)
O(4)–C(1)–C(6)	106(2)	O(3)–C(12)–C(11)	109(2)
C(1)–C(2)–C(3)	110(2)	C(7)–C(8)–C(9)	108(2)
C(2)–C(3)–C(4)	111(2)	C(8)–C(9)–C(10)	112(3)
C(3)–C(4)–C(5)	110(3)	C(9)–C(10)–C(11)	112(3)
C(4)–C(5)–C(6)	112(3)	C(10)–C(11)–C(12)	108(3)
C(5)–C(6)–C(1)	110(2)	C(11)–C(12)–C(7)	113(3)
C(6)–C(1)–C(2)	114(3)	C(12)–C(7)–C(8)	112(2)
C(5)–C(6)–S	113(2)	C(8)–C(7)–S	116(2)
C(1)–C(6)–S	107(2)	C(12)–C(7)–S	104(2)
C(6)–S–C(7)	109(2)		

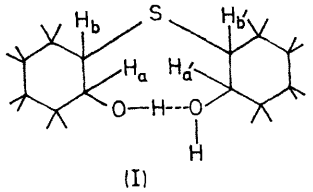
* All other angles in the co-ordination polyhedron are *ca.* 90°.

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21381 (2 pp., 1 microfiche).*

DISCUSSION

The preparation of the ligand can result, in theory, in the formation of numerous stereoisomers with ring substituents in equatorial and/or axial positions. However, under the experimental conditions described, only *trans*-equatorial isomers were obtained.

A first indication of this is given from the m.p. (70 °C), which is very close to that reported[8] for the *trans* (*meso* and racemic) mixture (72 °C) obtained by reaction of (±)-*trans*-2-chlorocyclohexanol with Na_2S. The m.p. of the *cis*-stereoisomeric mixture, resulting from reaction of (±)-*cis*-2-chlorocyclohexanol, is 104 °C.[8] The ^1H n.m.r. spectrum of the ligand mixture in CCl_4 displays between τ 5 and 6.5 two hydroxy-peaks of equal intensity, exchangeable with D_2O, each one corresponding to one proton, whose position is concentration, temperature, and solvent dependent. These peaks are not due to different (axial and equatorial) positions of the substituents, but to the formation of intramolecular ring-forming hydrogen bridges as in (I).



(I)

This is supported by the following ^1H n.m.r. results for solutions of the ligand. (i) Addition of a trace of acid gives a single line, concentration dependent, and further addition of anhydrous sodium carbonate re-establishes the two peaks. (ii) By dilution, no change in the separation and intensity of the two peaks and only a relatively small shift at higher field are observed. (iii) On increasing the temperature, the two hydroxy-peaks collapse with no change in the form and position of the resonances at τ 6.7 and 7.5, due to the protons on the carbon atoms α to the substituents, *i.e.* H_a, $H_{a'}$, and H_b,$H_{b'}$.

Also, in the solid state hydrogen bonds are present, as shown by the stretching frequency at 3 360 cm^{-1}, characteristic of associated alcoholic groups.

Molecular models of the various stereoisomers show no constraint in the formation of intramolecular hydrogen bridges, except when the substituents are both axial in at least one of the cyclohexyl rings. *X*-Ray analysis has established that crystals of the complex are formed, at least in part, by the isomer in which the ligand displays the *meso-trans* configuration, with all substituents equatorial. The ^1H n.m.r. spectrum of a homogeneous sample of the complex in deuterioacetone shows only one resonance for the hydroxy-protons, thus indicating that all the hydroxy-groups are equatorial.

Furthermore, the ^1H n.m.r. spectra of the starting ligand and of the ligand displaced from the complex are practically identical, particularly as far as the peaks of the H_a, $H_{a'}$ and H_b, $H_{b'}$ protons are concerned.

It is reasonable to conclude that the ligand obtained is a mixture of *meso*- and racemic stereoisomers in the *trans*-equatorial conformation, and does not contain the *cis*-forms with equatorial hydroxy-groups, for which significant differences should be expected for the H_a and $H_{a'}$ proton signals.

The existence of different crystalline forms which decompose at different temperatures in the 177—194 °C range could indicate that the mixture also contains complexes with the racemic form of the ligand, whose geometry does not preclude co-ordination to uranium.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

[8] M. Mousseron, *Compt. rend.*, 1942, **215**, 357; 1943, **216**, 812, 813; *Bull. Soc. chim. France*, 1948, **84**, 88.

The molecular structure of the complex is shown in Figure 1 together with the atom numbering scheme used. Figure 2 shows the projection along [010]. The uranium atom is seven-co-ordinate, with the uranyl group perpendicular to the equatorial plane. The organic ligand is terdentate, being co-ordinated to uranium through the two oxygen and the sulphur atoms.

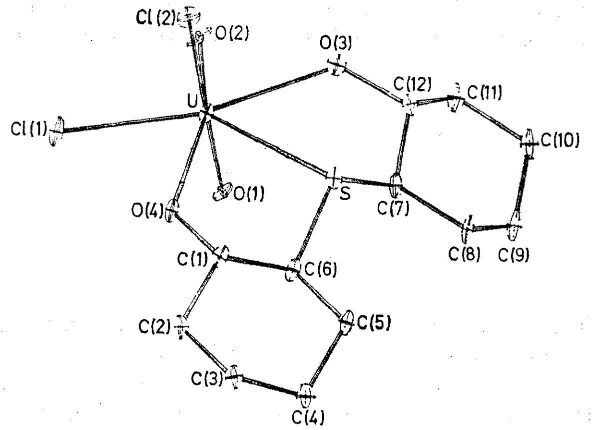

FIGURE 1 The complex, showing the atom numbering scheme used, drawn by the program ORTEP (Report ORNL 3794, Oak Ridge National Laboratory, Tennessee, 1965)

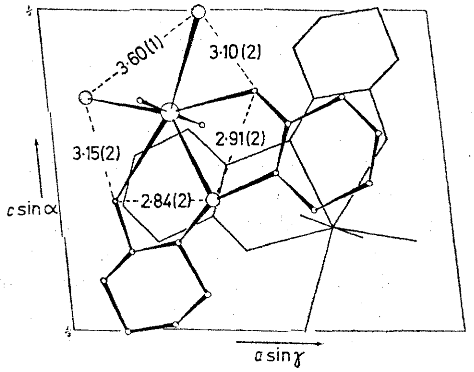

FIGURE 2 Projection of the unit cell contents down *b*

The uranyl U–O distances are normal. The two independent U–Cl distances [2.67(1) Å] are consistent with the sum of the crystal radii (2.68 Å) [9] and with the values found in other uranyl compounds,[10-12] but they are significantly greater than those found in compounds of U^{IV}.[13,14]

The U–O(ligand) distances are chemically equivalent and are comparable with the values usually found for U–O(alcohol) bonds.[15,16]

An interesting feature of the ^1H n.m.r. spectra is the comparable shift ($\simeq$0.4 p.p.m.) observed on co-ordination for both peaks relative to the protons of the carbon atoms in positions α to the oxygen and sulphur atoms respectively, indicating a comparable bonding interaction between uranium and the oxygen and sulphur atoms.

The U–S distance [2.94(1) Å] represents the first determination of a U^{VI}–S(thioether) bond distance. It is *ca.* 0.1 Å longer than U–S bonds in dithio-acetate or -carbamate uranyl complexes.[17,18] The difference of *ca.* 0.4 Å between the U–S(thioether) and the U–O(ether) bond distance [2.55(1) Å] [19] compares well with the difference in covalent radii of oxygen and sulphur.

Because of the almost symmetrical disposition assumed by the ligand the entire molecule can be considered to approximate to C_s symmetry. The equation of the least-squares plane through U, Cl(1), Cl(2), S, O(3), and O(4), is, in orthogonal Å space *: $-0.736I + 0.652J - 0.178K = -1.199$ with the deviations (Å) from the plane: U 0.05, Cl(1) 0.01, Cl(2) −0.06, S −0.05, O(3) 0.05, O(4) 0.00.

The best planes through the cyclohexane rings, which are in the characteristic chair conformation, make an angle of 18° to each other. Furthermore the C(1)—(6) ring (mean plane) is tilted at 27° and the C(7)—(12) ring (mean plane) at 42° with respect to the equatorial plane. Torsion angles in the rings and all other distances and angles in the molecule are as expected.

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* Defined as three orthogonal vectors, *I*, *J*, and *K*, 1 Å in magnitude with *I* parallel to *a*, *K* perpendicular to *a* in the plane of *a* and *c*, and *J* perpendicular to the plane of *a* and *c*.

[9] R. D. Shannon and C. T. Prewitt, *Acta Cryst.*, 1970, **B26**, 104.

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