FIESER, L. F. & FIESER, M. (1959). *Steroids.* New York: Reinhold.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B26, 274–285.

GIGLIO, E. & QUAGLIATA, C. (1975). *Acta Cryst.* B31, 743–746.

HALL, S. R., MASLEN, E. N. & COOPER, A. (1974). *Acta Cryst.* B30, 1441–1447.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

JOHNSON, P. L. & SCHAEFER, J. P. (1972). *Acta Cryst.* B28, 3083–3088.

KLYNE, W. & PRELOG, V. (1960). *Experientia*, 16, 521–523.

MUETTERTIES, E. L. (1974). *Tetrahedron*, 30, 1595–1604.

NORTON, D. A. & HANER, B. (1965). *Acta Cryst.* 19, 477–478.

SCHAEFER, J. P. & REED, L. L. (1972). *Acta Cryst.* B28, 1743–1748.

WOLF, A. A. (1976). *Physiol. Chem. Phys.* 8, 495–518.

WOLF, A. A. & HALPERN, E. H. (1976). *Physiol. Chem. Phys.* 8, 31–36, 135–142.

The Structure of Tetrachlorotetrakis(diphenyl sulphoxide)thorium(IV)

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Abstract

[Th($C_{12}H_{10}OS)_4Cl_4$], $C_{48}H_{40}Cl_4O_4S_4$Th, crystallizes in the orthorhombic system, space group *Pbcn*, with $a = 17.909$ (2), $b = 13.453$ (1), $c = 19.636$ (2) Å, $Z = 4$. The structure was refined to $R = 0.041$ for 1877 counter reflexions. The Th atom is eight coordinate with dodecahedal geometry, the Cl atoms occupying the dodecahedral *B* sites and the sulphoxide O atoms the *A* sites.

Introduction

Since the original analysis of eight-coordinate geometry was given by Hoard & Silverton (1963), many structures of eight-coordinate complexes have been published. However, few examples containing two different ligands, say $4X$ and $4Y$, giving complexes of the type MX_4Y_4 have been investigated. Calculations (Kepert, 1978) have suggested that the energy equivalence between the dodecahedron and square antiprism may be upset in this case in favour of the dodecahedron where the ligands may be sorted into the two different coordination sites. Complexes of the actinide metals provide examples in which effects such as π bonding, which may also enhance dodecahedral stability (Orgel, 1960), should be small and hence provide a good test of theoretical predictions. Accordingly we have investigated the structure of tetrachlorotetrakis(diphenyl sulphoxide)thorium(IV) to provide further structural information on complexes of this type.

Experimental

The complex was prepared by the method of Alvey, Bagnall, Brown & Edwards (1973) and irregular crystals were obtained from nitromethane. Preliminary photography showed orthorhombic symmetry with systematic absences corresponding to space group *Pbcn*. In addition, reflections with $h + k = 2n + 1$ were systematically weak, consistent with the heavy atom occupying the $4(c)$ special position. Accurate cell parameters were obtained by least squares from the four-circle coordinates of 12 reflections. Owing to their irregular shape, the crystals were ground to spheres for data collection, a specimen of radius 0.17 mm being used. Data were collected on a Hilger & Watts four-circle diffractometer with $2\theta/\omega$ scans and Mo $K\alpha$ radiation. Each reflection was scanned through 0.60° in steps of 0.01° at 1 s per step, with stationary background counts of 15 s taken at each scan limit. 3416 reflections were measured to a 2θ limit of 48°, of which 1877 had intensities $> 3\sigma(F^2)$. Lorentz and polarization corrections were applied and spherical absorption corrections made. E.s.d.'s calculated as $\sigma^2(F^2) = S + (B1 + B2)T + pS^2$ where S, $B1$ and $B2$ are respectively the scan counts and two background counts, T is the correction factor for the difference between scan and background count times and p was taken as 0.05.

Crystal data

Tetrachlorotetrakis(diphenyl sulphoxide)thorium(IV), $C_{48}H_{40}Cl_4O_4S_4$Th, $M_r = 1182$, $a = 17.909$ (2), $b =$

13·453 (1), $c = 19·636$ (2) Å, $U = 4730·9$ (7) Å^3, $D_m = 1·63$ (1), $D_c = 1·63$ Mg m^{-3}, $Z = 4$, space group $Pbcn$, μ(Mo $K\alpha$) = 3·972 mm^{-1}, λ(Mo $K\alpha$) = 0·7107 Å.

Structure solution and refinement

The structure was solved by heavy-atom methods. The initial electron density map, phased by Th alone, showed the expected false symmetry due to use of data with $h + k = 2n$ only, but a subsequent map phased by the addition of S and Cl allowed all non-hydrogen atoms to be assigned. Scattering factors for Th were taken from Cromer & Mann (1968) and for all other atoms from *International Tables for X-ray Crystallography* (1962). Refinement was by full-matrix least squares; the function minimized was $\sum w|F_o - F_c|^2$ with weights $4F_o^2/\sigma^2(F^2)$. Initial isotropic refinement converged to $R = 0·077$. H atoms were then included in their calculated positions but not refined, and dispersion corrections (Cromer, 1965) applied to Th. Further refinement with all non-hydrogen atoms anisotropic converged to $R = 0·041$ ($R_w = 0·049$) at which time all shifts were <25% of e.s.d.'s. Final atomic coordinates are listed in Table 1.*

Description of the structure

A perspective view of the molecule is given in Fig. 1 which also shows the numbering scheme. Interatomic distances and angles are given in Figs. 2 and 3. E.s.d.'s

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34815 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
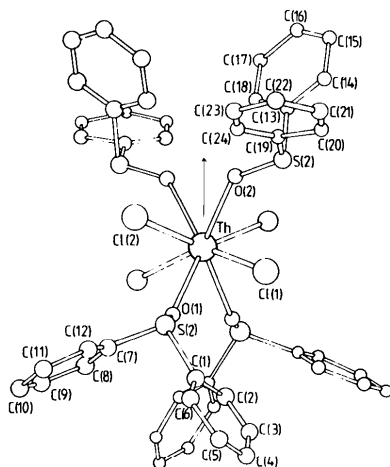

Fig. 1. Perspective view of the molecule.

Table 1. *Atomic coordinates and e.s.d.'s*

The H atoms are numbered as the C atom to which they are bonded.

	x	y	z
Th	0·0	0·12002 (5)	0·25
Cl(1)	0·1273 (2)	0·0628 (3)	0·1816 (2)
Cl(2)	0·0772 (3)	0·1789 (3)	0·3647 (2)
S(1)	0·0229 (2)	−0·0547 (3)	0·3892 (2)
S(2)	0·1459 (2)	0·3069 (3)	0·2185 (2)
O(1)	0·0329 (6)	−0·0307 (7)	0·3142 (5)
O(2)	0·0661 (5)	0·2719 (7)	0·2149 (5)
C(1)	−0·0305 (9)	−0·1681 (11)	0·3898 (9)
C(2)	−0·0590 (10)	−0·2015 (12)	0·3292 (10)
C(3)	−0·0995 (11)	−0·2887 (15)	0·3287 (11)
C(4)	−0·1121 (13)	−0·3433 (14)	0·3876 (15)
C(5)	−0·0831 (10)	−0·3082 (15)	0·4508 (12)
C(6)	−0·0388 (9)	−0·2175 (13)	0·4531 (10)
C(7)	0·1124 (8)	−0·1020 (9)	0·4135 (8)
C(8)	0·1626 (9)	−0·1377 (11)	0·3669 (9)
C(9)	0·2308 (9)	−0·1763 (11)	0·3886 (10)
C(10)	0·2450 (11)	−0·1863 (14)	0·4593 (11)
C(11)	0·1929 (12)	−0·1510 (13)	0·5069 (11)
C(12)	0·1249 (10)	−0·1092 (13)	0·4868 (8)
C(13)	0·1402 (9)	0·4229 (11)	0·2646 (7)
C(14)	0·2038 (9)	0·4863 (12)	0·2659 (7)
C(15)	0·1996 (11)	0·5739 (13)	0·3039 (9)
C(16)	0·1361 (13)	0·5935 (12)	0·3407 (9)
C(17)	0·0745 (11)	0·5291 (15)	0·3399 (9)
C(18)	0·0771 (10)	0·4403 (14)	0·3023 (8)
C(19)	0·1628 (8)	0·3533 (10)	0·1340 (8)
C(20)	0·2379 (9)	0·3694 (14)	0·1177 (10)
C(21)	0·2555 (12)	0·4062 (14)	0·0519 (10)
C(22)	0·1948 (14)	0·4278 (14)	0·0081 (11)
C(23)	0·1212 (13)	0·4058 (14)	0·0246 (9)
C(24)	0·1054 (9)	0·3663 (12)	0·0913 (8)
H(2)	−0·060	−0·190	0·297
H(3)	−0·137	−0·298	0·296
H(4)	−0·136	−0·398	0·396
H(5)	−0·082	−0·348	0·486
H(6)	−0·017	−0·203	0·486
H(8)	0·155	−0·126	0·322
H(9)	0·265	−0·215	0·389
H(10)	0·281	−0·209	0·460
H(11)	0·193	−0·153	0·548
H(12)	0·100	−0·110	0·526
H(14)	0·244	0·435	0·236
H(15)	0·236	0·593	0·319
H(16)	0·121	0·672	0·368
H(17)	0·026	0·541	0·362
H(18)	0·050	0·402	0·313
H(20)	0·281	0·334	0·136
H(21)	0·321	0·403	0·038
H(22)	0·204	0·463	−0·018
H(23)	0·086	0·404	0·016
H(24)	0·075	0·355	0·090

in distances are 0·004 Å for distances involving Th and 0·02 Å for distances between light atoms. E.s.d.'s in angles are 0·8 and 1·5° respectively for angles around Th and around light atoms. The coordination polyhedron (Fig. 4) is a slightly distorted dodecahedron with the sulphoxide ligands in the A sites and the Cl atoms in the B sites.

The Th—Cl distances are 2·757 and 2·759 Å. There are no similar structures with which these can be
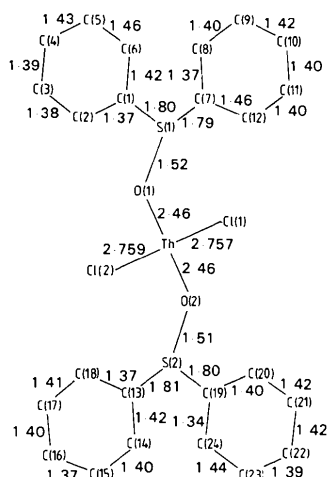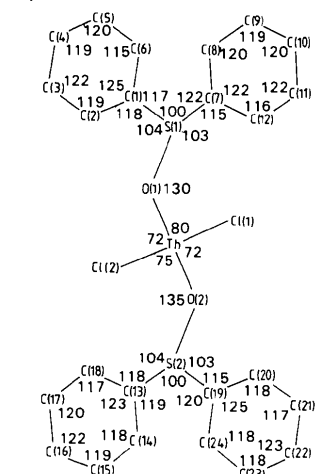
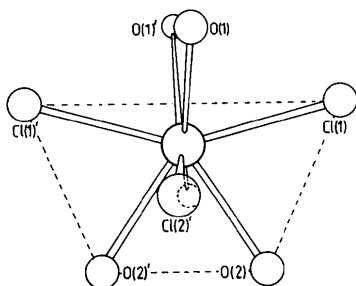Fig. 2. Interatomic distances (Å).

Fig. 3. Interatomic angles (°).

Fig. 4. The coordination polyhedron.

Table 2. *Least-squares planes*

Plane Cl(1), Cl(1)′, O(2), O(2)′

$$-0.507X + 0.000Y - 0.862Z - 4.229 = 0$$

Distances from plane: Cl(1), 0.00 (1); Cl(1)′, 0.00 (1);

O(2), −0.01 (1); O(2)′, 0.01 (1) Å.

Plane Cl(2), Cl(2)′, O(1), O(1)′

$$0.856X + 0.000Y - 0.512Z - 2.541 = 0$$

Distances from plane: Cl(2), 0.02 (1); Cl(2)′, −0.02 (1);

O(2), −0.15 (1); O(2)′, 0.15 (1) Å.

ideal 90°, although the second of these shows minor deviations from planarity (Table 2). The shape parameters are close to those predicted for the most favourable polyhedron (Hoard & Silverton, 1963); θ_A = 34.5 (9), 33.8 (9)°, predicted 35.2°; θ_B = 73.8 (9), 73.3 (9)°, predicted 73.5°. The ratio of the metal–ligand distances, $M-A:M-B$, is 0.892 in contrast to the predicted 1.03; thus the siting of the Cl atoms in the B sites does not conform to prediction. Indeed, theory would predict that in a dodecahedral structure Cl would occupy the A sites and O the B sites, an arrangement which would also place the bulky sulphoxide ligands further apart. There is no obvious reason why the arrangement adopted is preferred to that predicted.

The S—O distance (1.52 Å) is longer than that found in the free ligand, 1.47 Å (Abrahams, 1957), as predicted from electronic considerations (Bennett, Cotton & Weaver, 1967), and is identical to that in $UCl_4.3Me_2SO$ (Bombieri & Bagnall, 1975). C—C distances are all close to the expected value as are all angles within the aromatic rings; all rings have a high degree of planarity. Dihedral angles between the rings are 96.3 and 102.2° compared to 75.8° in diphenyl sulphoxide. There are no abnormal intermolecular interactions.

References

Abrahams, S. C. (1957). *Acta Cryst.* **10**, 417–422.

Alvey, P. J., Bagnall, K. W., Brown, D. & Edwards, J. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2308–2314.

Bennett, M. J., Cotton, F. A. & Weaver, D. L. (1967). *Acta Cryst.* **23**, 581–586.

Bombieri, G. & Bagnall, K. W. (1975). *Chem. Commun.* pp. 188–189.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Hoard, J. L. & Silverton, J. V. (1963). *Inorg. Chem.* **2**, 235–243.

International Tables for X-ray Crystallography (1962). Vol. III, p. 203. Birmingham: Kynoch Press.

Kepert, D. L. (1978). *Prog. Inorg. Chem.* **24**, 179–249.

Mucker, K., Smith, G. S., Johnson, Q. & Elson, R. E. (1969). *Acta Cryst.* **B25**, 2362–2365.

Orgel, L. E. (1960). *J. Inorg. Nucl. Chem.* **14**, 136–138.

Singer, N., Studd, B. F. & Swallow, A. G. (1970). *Chem. Commun.* pp. 342–343.

compared; however, in $ThCl_4$ (Mucker, Smith, Johnson & Elson, 1969), where all Cl atoms are bridging, the structure is again dodecahedral. The independent Th—Cl distances are 2.903 (A sites) and 2.718 Å (B sites), which are similar to the distance observed here. The Th—O distance (2.46 Å) is identical to that in the dimethyl sulphoxide complex Th(quinolino-lato)$_4$. $(Me_2SO)_2$ (Singer, Studd & Swallow, 1970).

The two trapezia which make up the polyhedron have an interplanar angle of 89.3 (7)°, close to the