

Fig. 1. The structure of the  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  anion. The thermal ellipsoids are scaled to enclose 30% probability.

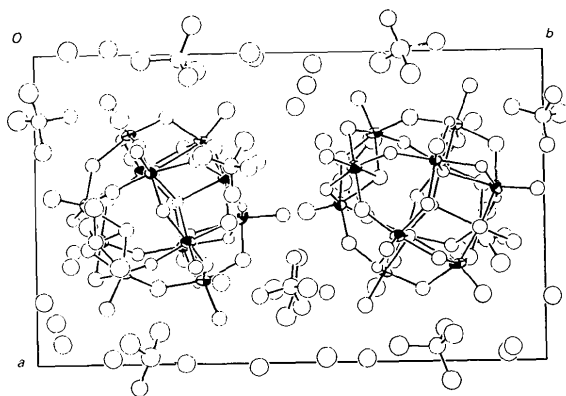


Fig. 2. The crystal structure projected along the  $c^*$  axis.

The crystal structure along the  $c^*$  axis is represented in Fig. 2. There is a three-dimensional intermolecular network. Only  $O_p$  atoms, one of the three types of peripheral O atoms in the polyanion, are free from any strong interactions within 3.0 Å. There are no direct anion-anion interactions.

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### Structure of *cis*-[3,4-Bis(trifluoromethyl)-2,5-dithiahexane]dichloroplatinum(II), *cis*-[Pt{CH<sub>3</sub>SCH(CF<sub>3</sub>)CH(CF<sub>3</sub>)SCH<sub>3</sub>}Cl<sub>2</sub>]

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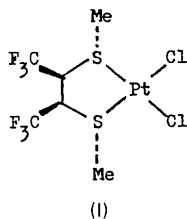
**Abstract.**  $M_r = 524.2$ , tetragonal,  $P4_2/nbc$  (origin at  $\bar{1}$ ),  $a = 14.081(2)$ ,  $c = 27.121(2)$  Å,  $U = 5377$  Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 2.590$  g cm<sup>-3</sup>; Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 112.9$  cm<sup>-1</sup>,  $F(000) = 3872$ ,  $T = 293$  K;  $R = 0.018$  for 1869 unique reflections with

$I \geq 3\sigma(I)$ . The sulphur methyl substituents are mutually *syn* and lie on the opposite side of the chelate ring from the trifluoromethyl groups. The molecular configuration in the solid corresponds to that assigned to the predominant isomer in solution by <sup>19</sup>F NMR.

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**Introduction.** Four isomers of the title compound (I) can be detected in solution at ambient temperature. A maximum of six isomers can exist on the assumption that conformational interchange is slow for the sulphur substituents but rapid for the chelate ring (Cross, Rycroft, Sharp & Torrens, 1980). Crystals grown from acetonitrile are either needles or cube-like—corresponding to the ( $\pm$ ) and *meso* diastereomers of the thioether. The structure analysis establishes that the cube-like habit is associated with the *meso* ligand and confirms the spectroscopic assignments of configuration proposed by Cross *et al.* (1980).



**Experimental.** Yellow crystal of cube-like habit, 0.18 × 0.21 × 0.17 mm, exhibiting {100}, {010}, and {001}, Enraf–Nonius CAD-4F diffractometer, Mo X-rays, graphite monochromator; cell dimensions by least-squares fit to the setting angles of 25 automatically-centred reflections; intensities of 7613 reflections with  $2 \leq \theta(\text{Mo } K\alpha) \leq 30^\circ$  in the  $+h, +k, +l$  octant measured,  $\theta/2\theta$  scans of  $0.75^\circ$  in  $\theta$ ; correction for Lp and absorption effects (Gaussian quadrature,  $F^2$  transmission factors 0.13–0.24), merging of equivalent intensities ( $R_{\text{int}} = 0.024$  for 3693 duplicates), 3920 independent structure amplitudes; 1869 with  $I \geq 3\sigma(I)$  used subsequently, virtually all of these having  $\theta(\text{Mo } K\alpha) < 25^\circ$ . Patterson and difference syntheses, refinement by full-matrix least squares on  $F$ ;  $w^{-1} = \sigma^2(F) + 0.0004F^2$ ; final adjustment of 187 parameters (scale, isotropic extinction parameter; Pt, Cl, S, F, and C anisotropic, H isotropic) gave  $wR = 0.019$ ,  $S = 1.1$ , mean  $\Delta/\sigma = 0.02$ , maximum = 0.26 for H parameters and 0.10 for the remainder; final value of the extinction parameter  $6.8(3) \times 10^{-3}$ ; final  $\Delta\rho$  values  $-0.71$  to  $0.70 \text{ e } \text{\AA}^{-3}$ ; scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); *GX* crystallographic program package (Gilmore, Malinsson, Muir & White, 1981).

**Discussion.** Atomic coordinates are in Table 1.\* The crystals are built of well-separated molecules (Fig. 1) in which the Pt atom displays near-ideal *cis*-square-planar

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38855 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

coordination, the Pt, Cl, and S atoms lying within  $\pm 0.017 \text{ \AA}$  of their common plane.

The molecule has a chelate ring with absolute configuration  $\delta$  [the S(1)–C(3)–C(5)–S(2) torsion angle is  $+48.8(3)^\circ$ ]. The other four chiral centres, S(1), C(3), C(5) and S(2), then have absolute configurations *S, S, R, R* respectively and the thioether is therefore of the *meso* form. The chelate ring adopts a conformation intermediate between envelope and symmetrically puckered: ring torsion angles are  $16.9(2)$  and  $5.2(2)^\circ$  across Pt–S(1) and Pt–S(2), and  $-41.0(3)$  and  $-32.4(4)^\circ$  across S(1)–C(3) and S(2)–C(5). The C(4) and C(6) trifluoromethyl groups lie on the opposite side of the chelate ring from the methyl substituents and are

Table 1. Atomic fractional coordinates and isotropic thermal parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{eq}}^*/U_{\text{iso}}$
Pt	0.03822 (1)	-0.01512 (1)	0.09197 (1)	0.0356 (1)
Cl(1)	0.13556 (8)	-0.14834 (8)	0.08978 (5)	0.0505 (9)
Cl(2)	0.14781 (9)	0.07296 (9)	0.04767 (5)	0.0531 (9)
S(1)	-0.05253 (7)	0.11460 (7)	0.09568 (5)	0.0383 (7)
S(2)	-0.06905 (8)	-0.09828 (8)	0.13530 (5)	0.0471 (9)
F(1)	-0.1558 (3)	0.1271 (3)	0.2292 (1)	0.087 (3)
F(2)	-0.0529 (3)	0.2066 (3)	0.1887 (1)	0.093 (4)
F(3)	-0.0237 (2)	0.0626 (3)	0.2084 (1)	0.082 (3)
F(4)	-0.1894 (2)	-0.0616 (3)	0.2260 (1)	0.079 (3)
F(5)	-0.3052 (2)	0.0100 (3)	0.1916 (1)	0.072 (3)
F(6)	-0.2723 (3)	-0.1331 (2)	0.1718 (2)	0.083 (3)
C(1)	-0.1291 (4)	0.1135 (4)	0.0421 (2)	0.050 (4)
C(2)	-0.1198 (4)	-0.1808 (4)	0.0916 (4)	0.076 (8)
C(3)	-0.1368 (3)	0.0885 (3)	0.1458 (2)	0.039 (3)
C(4)	-0.0918 (4)	0.1218 (4)	0.1938 (2)	0.059 (4)
C(5)	-0.1699 (3)	-0.0150 (3)	0.1424 (2)	0.039 (3)
C(6)	-0.2347 (4)	-0.0496 (4)	0.1833 (2)	0.056 (4)
H(1A)	-0.168 (3)	0.165 (3)	0.048 (2)	0.04 (1)
H(1B)	-0.158 (4)	0.054 (4)	0.040 (2)	0.07 (2)
H(1C)	-0.086 (4)	0.120 (4)	0.017 (2)	0.06 (2)
H(2A)	-0.063 (5)	-0.219 (5)	0.086 (2)	0.11 (2)
H(2B)	-0.162 (5)	-0.218 (5)	0.106 (3)	0.10 (3)
H(2C)	-0.151 (6)	-0.154 (6)	0.066 (4)	0.15 (4)
H(3)	-0.185 (3)	0.123 (3)	0.141 (2)	0.05 (1)
H(4)	-0.201 (3)	-0.020 (3)	0.116 (2)	0.04 (2)

\*  $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$  for non-hydrogen atoms.

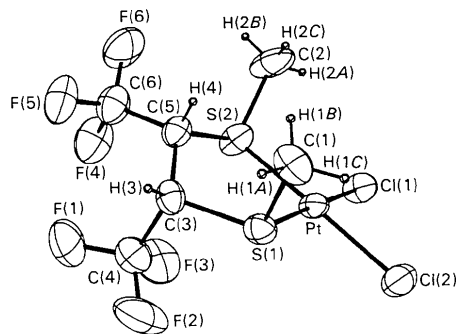


Fig. 1. View of the *cis*-[Pt{CH<sub>3</sub>SCH(CF<sub>3</sub>)CH(CF<sub>3</sub>)SCH<sub>3</sub>}Cl<sub>2</sub>] molecule showing the atom numbering and 50% vibration ellipsoids. Hydrogen atoms are represented by spheres of arbitrary size.

Table 2. Bond lengths (Å) and interbond angles (°)

Pt—Cl(1)	2.324 (2)	Pt—Cl(2)	2.316 (2)
Pt—S(1)	2.231 (1)	Pt—S(2)	2.244 (2)
S(1)—C(1)	1.809 (7)	S(1)—C(3)	1.841 (5)
S(2)—C(2)	1.807 (9)	S(2)—C(5)	1.852 (5)
F(1)—C(4)	1.318 (7)	F(2)—C(4)	1.321 (8)
F(3)—C(4)	1.331 (8)	F(4)—C(6)	1.332 (7)
F(5)—C(6)	1.320 (7)	F(6)—C(6)	1.328 (7)
C(3)—C(4)	1.522 (8)	C(3)—C(5)	1.533 (7)
C(5)—C(6)	1.516 (8)		
Cl(1)—Pt—Cl(2)	91.5 (1)	Cl(1)—Pt—S(1)	178.4 (1)
Cl(1)—Pt—S(2)	89.4 (1)	Cl(2)—Pt—S(1)	88.1 (1)
Cl(2)—Pt—S(2)	179.1 (1)	S(1)—Pt—S(2)	91.0 (1)
Pt—S(1)—C(1)	107.3 (3)	Pt—S(1)—C(3)	103.8 (2)
C(1)—S(1)—C(3)	101.9 (3)	Pt—S(2)—C(2)	104.9 (3)
Pt—S(2)—C(5)	103.9 (2)	C(2)—S(2)—C(5)	99.9 (3)
S(1)—C(3)—C(4)	107.6 (4)	S(1)—C(3)—C(5)	110.0 (4)
C(4)—C(3)—C(5)	118.1 (5)	F(1)—C(4)—F(2)	107.9 (5)
F(1)—C(4)—F(3)	108.1 (5)	F(1)—C(4)—C(3)	110.8 (5)
F(2)—C(4)—F(3)	107.4 (5)	F(2)—C(4)—C(3)	111.3 (5)
F(3)—C(4)—C(3)	111.2 (5)	S(2)—C(5)—C(3)	112.1 (4)
S(2)—C(5)—C(6)	109.5 (4)	C(3)—C(5)—C(6)	116.4 (5)
F(4)—C(6)—F(5)	107.0 (5)	F(4)—C(6)—F(6)	106.4 (5)
F(4)—C(6)—C(5)	112.9 (5)	F(5)—C(6)—F(6)	107.7 (5)
F(5)—C(6)—C(5)	111.9 (5)	F(6)—C(6)—C(5)	110.6 (5)

respectively pseudo-axial and pseudo-equatorial, the corresponding Pt—S—C—CF<sub>3</sub> torsion angles being 88.8 (4) and -163.1 (4)°. The conformation in the crystal corresponds to that proposed by Cross *et al.* (1980) for the most abundant isomer in solution; they also suggest that it is the least sterically crowded.

The Pt—S distances [2.231 (1) and 2.244 (2) Å] and the Pt—Cl distances [2.324 (2) and 2.316 (2) Å] (Table 2) are respectively slightly shorter and slightly longer on average than corresponding distances in *cis*-[Pt{CF<sub>3</sub>SCH<sub>2</sub>CH(CH<sub>3</sub>)SCF<sub>3</sub>}Cl<sub>2</sub>] [Pt—S 2.239 (3) and

2.260 (4) Å; Pt—Cl 2.290 (4) and 2.295 (3) Å] (Manojlović-Muir, Muir & Solomun, 1977). Evidently replacement of electron-withdrawing CF<sub>3</sub> substituents on S by electron-releasing CH<sub>3</sub> causes only a minor alteration in the  $\sigma$ -electron framework of these complexes, with a stronger Pt—S and weaker Pt—Cl bonding. This contrasts with the effect of a similar substituent replacement at donor phosphorus in platinum(II) complexes (Macleod, Manojlović-Muir, Millington, Muir, Sharp & Walker, 1975): increased electron release at P weakens both the *trans*-Pt—Cl and the Pt—P bonding substantially, a result which has been interpreted in terms of significant Pt—P back-donation (Manojlović-Muir, 1978).

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## Structure of Carbonyldichloro(cyclopropyl)bis(methyldiphenylphosphine)iridium(III), [IrCl<sub>2</sub>(C<sub>3</sub>H<sub>5</sub>)(CO){P(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>]

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**Abstract.**  $M_r = 732.6$ , rhombohedral,  $R\bar{3}$ ,  $a = 17.863$  (5) Å,  $\alpha = 108.97$  (2)°,  $V = 4468$  (7) Å<sup>3</sup>,  $Z = 6$ ,  $D_x = 1.63$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 47.7$  cm<sup>-1</sup>,  $F(000) = 2151$  electrons (with anomalous

dispersion),  $T = 295$  K,  $R = 0.060$  for 2866 averaged reflections. The Ir atom is six-coordinate with the chloro ligands having a *cis* configuration and the phosphine ligands having a *trans* configuration. The cyclopropyl ligand is  $\sigma$  bonded to the Ir atom and has a mean C—C bond length of 1.56 (2) Å.

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