The Crystal and Molecular Structure of *Cis*-Dichloro-[1,2-bis(methylthio)1,1-difluoro-ethane] platinum(II)

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Although many complexes of fluorinated 1,2-bis(alkylthio)ethanes are known [1], the molecular structure has only been determined for [$PtCl_2(CF_3SCH(CH_3)CH_2SCF_3)$] [2]. This lack of information has made it difficult to assess the importance of the electron-withdrawing effects of fluorine atoms. The fluorinated moiety is likely to reduce the availability of the sulphur lone pairs for σ–bonding to the metal, enhancing π back-bonding from the metal to sulphur.

We felt that the determination of the molecular structure of an asymmetrical complex such as [$PtCl_2(CH_3SCF_2CH_2SCH_3)$], could be relevant to the understanding of the influence of strongly electronegative groups on the metal–sulphur bonds. The molecular structure and labeling scheme for [$PtCl_2(CH_3SCF_2CH_2SCH_3)$] are shown in Fig. 1.**

The crystals contain [$PtCl_2(CH_3SCF_2CH_2SCH_3)$] molecules which exhibit the expected *cis*-square-planar co-ordination at the platinum atom. The methyl substituents of the sulphur atoms are mutually *syn*. The same configuration has been found in dithioether or diselenoether complexes of platinum(II) [2], palladium(II) [5] and rhenium(I) [6]. The *anti* structure has been established for a macrobicyclic ligand [7] and for bis(thioether) complexes of copper(I) [5] and chromium(0) [8]. Valency angles around the platinum atom are all within 2° of the ideal values of 90 and 180°. The platinum–chloride bond lengths are equal (2.299(3) Å and 2.306(3) Å) and lie at the lower end of the range found for terminal Pt(II)–Cl distances (2.26–2.45 Å) [9] indicating that the *trans*-influence of the ligand is relatively weak.

The Pt–S distances differ by 0.03 Å (2.240(3) Å and 2.270(3) Å), the shorter bond being adjacent to the S–CF_2 group. The difference in bond lengths for [$PtCl_2(CF_3SCH(CH_3)CH_2SCF_3)$] is 0.021 Å. The slightly larger difference reported here probably reflects the influence of the fluorinated moiety, whereas that with trifluoromethyl substituents involves the inductive effect of the methyl group, further complicated by the participation of the sulphur and chlorine donor atoms in strong intermolecular interactions. In any case, the assessment of the influence of the electron-withdrawing fluorinated groups on the metal–ligand bonding is rendered difficult, but in the compound reported here it may be responsible for a contraction of the platinum–sulphur bond by 0.03–0.06 Å.

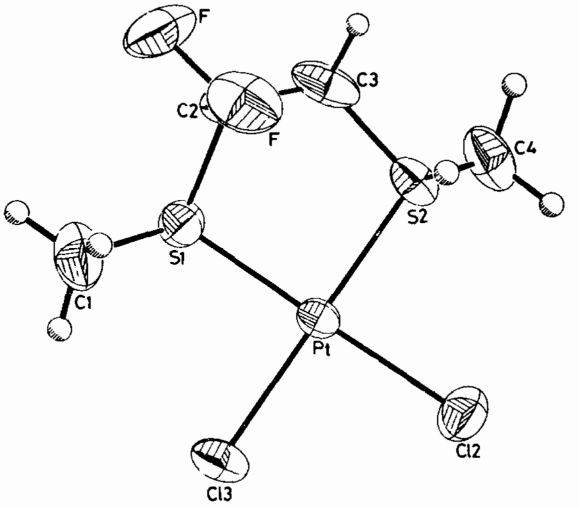

Fig. 1. Molecular structure of the title compound. Relevant bond lengths and angles are: Pt–S1, 2.240(3); Pt–S2, 2.270(3), Pt–Cl2, 2.306(3); Pt–Cl3, 2.299(3) Å. S1–Pt–S2, 90.2(1); Cl2–Pt–Cl3, 91.1(1); Pt–S2–C4, 106.6(4), S2–C3–C2, 115.2(7)°.

The two methyl groups adopt similar conformations relative to the chelate ring. The corresponding torsion angles about the S–C bonds are all within 6°. The conformations are such that the C–H bonds involving the atoms H3 and H6 point inwards and almost to each other.

Both sulphur atoms adopt *quasi*-tetrahedral coordinations. Corresponding interbond angles at sulphur agree to within 4°, and all are less than the tetrahedral angle. The four sulphur–carbon bond lengths agree to within experimental error, the mean value of 1.797 Å being typical for a bond of unit order.

Crystal Data

[$PtCl_2(CH_3SCF_2(CH_2SCH_3)$]. Monoclinic, space group $P2_1/n$; $Z = 4$; $a = 8.953(6)$, $b = 13.628(8)$, $c = 9.105(4)$ Å, $\beta = 114.95°$; $F(000) = 923.81$; μ(Mo-Kα)

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**The atomic coordinates have been deposited with the Cambridge Crystallographic Data Center and with the Editor, from whom copies can be obtained on request.

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$= 13.84$ cm^{-1}. A total of 9889 independent reflexions were measured by the ω-scan technique on a Nicolet R3M Diffractometer ($2\theta_{max} = 60°$). No absorption correction was applied. The structure was solved by direct method (Shelxtl, Rev. 3.0), and refined by full-matrix least squares to an R value of 0.032 for 8500 reflections with $I > 3\sigma(I)$, with all non H atoms anisotropic. H atoms fixed at C–H = 0.095 Å with a common B_{iso}.

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