Platinum(II) Complexes of Chelating Polyfluoroalkyldithioethanes.† *X*-Ray Structure of One Isomer of 1,2-Bis(trifluoromethylthio)propane-(dichloro)platinum

By RONALD J. CROSS, LJUBICA MANOJLOVIĆ-MUIR, KENNETH W. MUIR, DAVID S. RYCROFT, DAVID W. A. SHARP,* TIHOMIR SOLOMUN, and HUGO TORRENS MIGUEL

(*Department of Chemistry, University of Glasgow, Glasgow* G12 8QQ)

Summary Platinum(II) chloride complexes of $\mathrm{MeSCF_2CH_2SMe}$, $\mathrm{CF_3SC_2H_4SCF_3}$, and $\mathrm{CF_3SCHMeCH_2SCF_3}$ have been prepared as mixtures of isomers in solution: the crystal structure of one form of $[\mathrm{PtCl_2(CF_3SCHMeCH_2SCF_3)}]$ has been determined.

ALTHOUGH many bis(alkylthio)ethanes containing fluorine in either the sulphur-substituent or the bridge have been prepared and characterised,[1] nothing is known of the properties of such compounds as ligands. The strongly electronegative groups may reduce the availability of the sulphur lone-pairs for co-ordination but could also facilitate back donation from platinum to sulphur; both effects would lessen the *trans* influence of the sulphur atom. The $\mathrm{CF_3S}$ grouping is well known to form bridges[2] between metal atoms suggesting that sulphur atoms are able to co-ordinate to metals even when linked to strongly electronegative groupings.

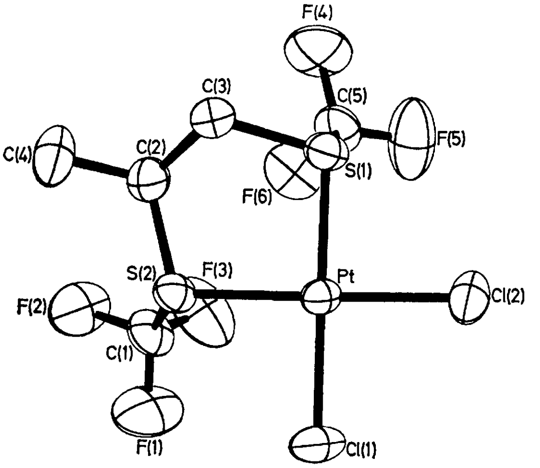
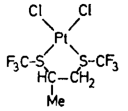


FIGURE 1. Perspective view of *X*-ray structure of one isomer of $[\mathrm{PtCl_2(CF_3SCHMeCH_2SCF_3)}]$ (III). Bond lengths (Å) are: Pt–Cl(1) 2·295(4), Pt–Cl(2) 2·293(4), Pt–S(1) 2·240(4), Pt–S(2) 2·259(3), mean S–C 1·84(1), mean C–C 1·53(1), mean C–F 1·30(1). Internal torsion angles around bonds in chelate ring are: Pt–S(1) 11(1), S(1)–C(3) −38(1), C(3)–C(2) 48(1), C(2)–S(2) −34(1), S(2)–Pt 10(1)°.

Treatment of aqueous ethanolic solutions of $\mathrm{K_2PtCl_4}$ with the dithioethanes $\mathrm{MeSCF_2CH_2SMe}$, $\mathrm{CF_3SC_2H_4SCF_3}$, or $\mathrm{CF_3SCHMeCH_2SCF_3}$ gives the neutral complexes $[\mathrm{PtCl_2(MeSCF_2CH_2SMe)}]$(I), $[\mathrm{PtCl_2(CF_3SC_2H_4SCF_3)}]$ (II), or $[\mathrm{PtCl_2(CF_3SCHMeCH_2SCF_3)}]$ (III) as yellow crystalline solids. *X*-Ray structure determination of (III)‡ (Figure 1) reveals almost exactly square-planar platinum co-ordination with Pt–S distances slightly shorter than corresponding values in *cis*-$[\mathrm{PtCl_2\{S(C_6H_4Cl)_2\}_2}]$[3] [2·278(7) and 2·292(6) Å] and *cis*-$[\mathrm{PtCl_2}$(L-methionine)][4] (2·26 Å). The Pt–Cl bond length in all three compounds agree well. Thus the $\mathrm{CF_3}$-substituents do not greatly affect the nature of the platinum–ligand bonds. This contrasts with the situation in *cis*-$[\mathrm{PtCl_2\{(CF_3)_2PCH_2CH_2PPh_2\}}]$ where the $\mathrm{CF_3}$-substituted phosphorus atom forms an unusually short bond to platinum and has an extremely weak *trans*-influence.[5]

Bond angles at sulphur (97—106°) indicate that these atoms retain quasi-tetrahedral hybridisation. The $\mathrm{CF_3}$-groups are mutually *syn*; the methyl group attached to C(2) is *pseudo*-equatorial relative to the almost symmetrically puckered chelate ring. The crystal structure contains equal numbers of enantiomeric molecules. In those in which the chelate ring configuration is δ [S(1)C(3)C(2)S(2) torsion angle + 48(1)°] the absolute configurations at S(1), S(2), and C(2) are respectively (*R*), (*S*), and (*S*).



(III)

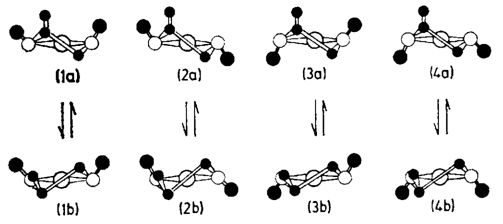


FIGURE 2. Possible isomers of (III).

^{1}H N.m.r. studies[6] of the symmetrical sulphide complexes $[\mathrm{(RSC_2H_4SR)MX_2}]$ (M = Pd or Pt) showed the presence of *syn* and *anti* isomers in solution, these being inter-converted by lone-pair inversion at sulphur. The ^{19}F n.m.r. spectrum of (III) in acetone at ambient temperature shows the presence of 4 isomers in the approximate ratios 1 : 1 : 2 : 8, and over a fairly wide temperature range (173—323 K) there is no rapid interconversion of the isomers. For rigid chelate rings, 8 isomers would be expected for (III) (Figure 2). Thus we conclude that the barrier to ring fluxion is low, and the four isomers observed are assigned to the four pairs of diastereoisomers shown. Isomer (**4b**) corresponds to the form identified in the solid.

Two isomers of (III) show F–F coupling. We associate this with those isomers with *syn* $\mathrm{CF_3}$ groups (**1** and **4** in

---

† No reprints available.

‡ Monoclinic, space group $P2_1/n$ with four molecules in a cell of dimensions a = 7·557(2), b = 12·942(2), c = 12·340(2) Å, β = 91·42(2)°. Least-squares refinement of 145 structural parameters currently gives R 0·064 for 2301 diffractometric data.

Figure 2). In the solid the shortest intramolecular F · · · F separation between fluorine atoms attached to different carbons is only 2·83 Å (the van der Waals radius of F is 1·35 Å). It seems probable that this coupling is a through-space effect connected with the close approach of the F atoms. The most abundant isomer of (III) shows this coupling, consistent with its assignment to configuration (**4**) (Figure 2), on the assumption that the isomer present in the solid will be the predominant one in solution.

The complexes (I) and (II) in acetone solution at ambient temperature each consist of two isomers as shown by their ^{19}F n.m.r. spectra. Long range F–F coupling can be observed in one of the isomers of $[PtCl_2(CF_3SC_2H_4SCF_3)]$ (II) from the ^{13}C satellites of the CF_3 groups (the CF_3 groups are formally equivalent); the *syn* isomer would be expected to have closely adjacent CF_3 groups as found for (III).

Thus the spectroscopic and structural evidence on disulphide complexes of these types, particularly those with novel asymmetrical ligands, strongly supports the operation of easy ring fluxion in solution. The isomers obtained arise from configurational rather than conformational effects. The same is probably true for related diselenide complexes,[7] though an alternative view has been expressed.[8]

We thank Johnson, Matthey and Co. Ltd. for the loan of K_2PtCl_4 and the British Council and S.R.C. for financial support.

(*Received, 9th February* 1976; *Com.* 137.)

[1] G. Haran and D. W. A. Sharp, *J.C.S. Perkin I*, 1972, 34.

[2] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 813 and references therein; K. R. Dixon, K. C. Moss, and M. A. R. Smith, *ibid.*, 1974, 971.

[3] W. A. Spofford, E. L. Amma, and C. V. Senoff, *Inorg. Chem.*, 1971, **10**, 2309.

[4] H. C. Freeman and M. L. Golomb, *Chem. Comm.*, 1970, 1523.

[5] I. D. MacLeod, Lj. Manojlović-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, and R. Walker, *J. Organometallic Chem.*, 1975, **97**, C7.

[6] E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Comm.*, 1966, 58; R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J.C.S. Dalton*, 1972, 992.

[7] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Chem. Comm.*, 1974, 207; *J.C.S. Dalton*, in the press.

[8] G. Hunter and R. C. Massey, *J.C.S. Chem. Comm.*, 1973, 797.