*Inorganica Chimica Acta*, 22 (1977) 69–74

# The Crystal and Molecular Structure of *cis*-Dichloro[1,2-bis(trifluoromethylthio)-propane] platinum(II)

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Received August 4, 1976

*The crystal structure of* cis-$PtCl_2(F_3CSCHMeCH_2SCF_3)$ *has been determined by X-ray methods. The compound crystallises in the monoclinic system, space group* $P2_1/n$, *with four molecules in a unit cell of dimensions* $a = 7.557(2)$, $b = 12.942(2)$, $c = 12.340(2)$ Å, $\beta = 91.42(2)°$. *The structure has been refined by full-matrix least-squares to R 0.054 (on* $|F_0|$*) for 2301 diffractometric intensity data. The crystals contain discrete monomeric molecules in which the platinum atom displays the expected* cis-*square-planar co-ordination. Selected bond lengths are: Pt–S 2.239(3) and 2.260(3), and Pt–Cl 2.290(4) and 2.295(3) Å. The metal–ligand bonding does not appear to be strongly influenced by the electron-withdrawing properties of the trifluoromethyl substituents of the sulphur atoms. The chelate ring has a symmetrically-puckered* gauche *conformation. The methyl substituent is* pseudo-*equatorial and the trifluoromethyl groups are mutually* syn. *Pairs of centrosymmetrically-related molecules are arranged so that there are short S···Cl and Pt···Pt contacts of* ca. *3.4 Å.*

## Introduction

It is by now well established that the presence of electron-withdrawing substituents on a ligand donor atom tends to shorten, and hence presumably to strengthen, transition-metal–ligand bonds. Churchill has shown, for example, that the metal–carbon bonds are shorter in fluoroalkyl complexes than in alkyl complexes of similar formulation and has discussed at some length the electronic factors which may be responsible for this phenomenon [1]. The controversy over the extent of backdonation in transition-metal–phosphine complexes has led to much interest in the relationship between M–P bond lengths and the electron-withdrawing ability of the substituents of the phosphorus atom. At present one of the strongest arguments in favour of the significant M→P back-donation is based upon the shortening of the Cr–P bond length in $X_3PCr(CO)_5$ complexes by 0.11 Å when X is changed from $C_6H_5$ to $C_6H_5O$ [2, 3].

We have recently shown that the metal–ligand bonding in *cis*-$M^{II}Cl_2[Ph_2PCH_2CH_2P(CF_3)_2]$ complexes, where M = Pd or Pt, is sensitive to the electron-withdrawing properties of the substituents on phosphorus [4]. The M–P bond lengths differ by *ca.* 0.07 Å, the shorter bond being adjacent to the trifluoromethyl groups. The M–Cl distances indicate that the *trans*-influence of the $P(CF_3)_2$ group is much weaker than that of the $PPh_2$ group. In this context it is worth noting that trifluoromethyl comes highest in Tolman's ranking of substituent electron-withdrawing ability [5].

The recent synthesis of the complex *cis*-$PtCl_2\cdot(F_3CSCHMeCH_2SCF_3)$ has given us the opportunity to investigate the effect of trifluoromethyl substituents on the *trans*-influence and bonding to platinum of a thioether ligand [6]. A further motive for the structure analysis was provided by the $^{19}F$ n.m.r. spectrum of the complex in acetone at ambient temperature. This spectrum is consistent with the presence in solution of four diastereoisomeric forms of the complex. Over the temperature range 173–323 °K rapid interconversion of isomers does not appear to occur. Two of the isomers display long range F–F coupling which may be associated with a *syn* arrangement of the trifluoromethyl groups [6]. We felt that the determination of the molecular structure of the complex in the solid-state might contribute to the interpretation of these results.

## Experimental

### *Crystal Data*

$PtCl_2(F_3CSCHMeCH_2SCF_3)$, $M = 510.2$, monoclinic, $a = 7.557(2)$, $b = 12.942(2)$, $c = 12.340(2)$ Å, $\beta = 91.42(2)°$, $U = 1206.5$ Å$^3$, $Z = 4$, $D_c = 2.808$ g cm$^{-3}$, F(000) = 936, Mo-K$_\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu$(Mo-K$_\alpha$) = 125.7 cm$^{-1}$, space group $C^5_{2h}$ (No. 14)–$P2_1/n$ with equivalent positions $\pm(x, y, z)$; $\pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$.

### *Measurements*

The crystals are needles elongated along *a*. The dimensions of the specimen used in the analysis were 0.66 × 0.14 × 0.16 mm. The space group and approximate cell dimensions were determined from Weissenberg and rotation photographs. Final values

TABLE I. Final Fractional Co-ordinates and Thermal Parameters

| Atom | $x$[a] | $y$ | $z$ | $U_{iso}$ or $U_{11}$[b] | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Pt | 09767(6) | 09798(3) | 07246(3) | 401(3) | 334(2) | 380(2) | −33(2) | 65(2) | −34(2) |
| S(1) | −0400(4) | 0337(2) | 2163(2) | 55(2) | 40(2) | 42(2) | −2(1) | 8(1) | 4(1) |
| S(2) | −1189(4) | 2167(2) | 0477(2) | 55(2) | 35(1) | 43(2) | 0(1) | 4(1) | 1(1) |
| Cl(1) | 2361(5) | 1594(3) | −0779(3) | 69(2) | 65(2) | 49(2) | −10(2) | 21(2) | 2(2) |
| Cl(2) | 3134(4) | −0246(3) | 0978(3) | 48(2) | 54(2) | 79(2) | 11(2) | 2(2) | −4(2) |
| F(1) | 0582(17) | 3776(7) | −0075(10) | 128(10) | 58(6) | 126(9) | −28(6) | 41(7) | 7(6) |
| F(2) | −1388(16) | 4107(6) | 1021(10) | 124(9) | 40(5) | 136(9) | 2(5) | 50(7) | −8(5) |
| F(3) | 1017(17) | 3406(7) | 1584(10) | 140(10) | 59(6) | 129(9) | −30(6) | −60(8) | 5(6) |
| F(4) | −0438(17) | 0836(8) | 4188(6) | 133(8) | 122(9) | 40(5) | −1(7) | 18(5) | −2(5) |
| F(5) | 2087(15) | 0503(10) | 3583(9) | 106(8) | 127(9) | 99(8) | 54(8) | −48(7) | −31(7) |
| F(6) | 0874(13) | 1939(7) | 3266(7) | 106(7) | 68(6) | 66(5) | −11(5) | −17(5) | −15(5) |
| C(1) | −0182(21) | 3418(10) | 0776(13) | 71(10) | 34(7) | 74(10) | 5(7) | 1(8) | 5(7) |
| C(2) | −2550(17) | 2070(10) | 1701(11) | 48(7) | 47(7) | 65(8) | 6(6) | 7(6) | 1(7) |
| C(3) | −2561(17) | 0969(11) | 2084(11) | 44(7) | 63(8) | 57(7) | 1(7) | 12(6) | 8(7) |
| C(4) | −4430(19) | 2454(12) | 1455(13) | 51(9) | 66(9) | 87(11) | 7(7) | −1(8) | −5(8) |
| C(5) | 0610(21) | 0959(12) | 3367(10) | 77(10) | 67(10) | 38(7) | 12(9) | −1(6) | −2(7) |
| H(1) | −309 | 093 | 282 | 7(4) | | | | | |
| H(2) | −333 | 055 | 156 | 11(6) | | | | | |
| H(3) | −201 | 251 | 230 | 9(5) | | | | | |
| H(4) | −499 | 201 | 088 | 11(6) | | | | | |
| H(5) | −516 | 239 | 213 | 7(4) | | | | | |
| H(6) | −443 | 319 | 122 | 15(7) | | | | | |

[a] Fractional co-ordinates have been multiplied by $10^5$ for Pt, by $10^3$ for H, and by $10^4$ for other atoms. [b] The form of the anisotropic temperature factor is $\exp(-2\pi^2 \times 10^{-n} \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}h_ih_ja_i^*a_j^*)$, where $n = 4$ for Pt and 3 for other atoms; $U_{iso}$ values for hydrogen atoms are multiplied by $10^2$.

of the unit cell dimensions and the intensities of all unique reflexions with $\theta(\text{Mo-K}_\alpha) \leqslant 30°$ were measured using standard techniques [7] on a Hilger and Watts Y290 diffractometer. Each reflexion was scanned symmetrically over 35 steps of 0.02° in $\theta/\omega$. At each step counting continued for 2.5 s. The background was measured at each extreme of the scan for 15 s, with crystal and counter stationary. The intensities of three standard reflexions, which were periodically remeasured during the experiment, displayed only random fluctuations of less than 5% of the corresponding mean values.

Structure amplitudes and their standard deviations were derived as described previously, the empirical factor $q$ being taken as 0.04 [7]. Corrections were made for absorption using a Gaussian integration method. The transmission factors on $F_0^2$ ranged between 0.14 and 0.23. A total of 2301 unique reflexions with $I \geqslant 3\sigma(I)$ were used in the subsequent analysis.

## *Structure Analysis*

The platinum atom was located from the three-dimensional Patterson function and the other atoms, except for hydrogen, from subsequent difference syntheses.

The structure was refined by full-matrix least-squares minimisation of $\Sigma\{(|F_0| - |F_c|)/\sigma(F_0)\}^2$. Atomic scattering factors, apart from that for hydrogen [8], and also the anomalous dispersion corrections for Pt, Cl, and S atoms were taken from International Tables [9]. Adjustments of the positional and isotropic vibrational parameters of the non-hydrogen atoms led to R = 0.08. When anisotropic temperature factors were introduced R fell to 0.064. The positions of the hydrogen atoms were then calculated so as to be consistent with the stereochemistry of adjacent carbon and sulphur atoms; they were compatible with appropriate peaks in a low-angle difference synthesis. Allowance was then made for the scattering of the hydrogen atoms; the calculated positional parameters were kept fixed but the isotropic thermal parameters were allowed to vary. Values of R and R′ were thus reduced to 0.058 and 0.065. The absorption correction was then applied and the refinement converged with R 0.054 and R′ 0.060. In the final cycle of refinement no parameter of a non-hydrogen atom shifted by more than 0.02σ. The final difference synthesis was featureless, apart from extreme function values of + 3.0 and − 4.8 eÅ$^{-3}$ close to the position of the platinum atom. The adequacy of the weighting scheme was

TABLE II. Interatomic Distances (Å) and Angles (°)

(a) Bond Lengths

| | |
|---|---|
| Pt–S(1) | 2.239(3) |
| Pt–S(2) | 2.260(3) |
| Pt–Cl(1) | 2.295(3) |
| Pt–Cl(2) | 2.290(4) |
| S(1)–C(3) | 1.83(1) |
| S(1)–C(5) | 1.84(1) |
| S(2)–C(1) | 1.82(1) |
| S(2)–C(2) | 1.85(1) |
| C(2)–C(3) | 1.50(2) |
| C(2)–C(4) | 1.53(2) |
| C(1)–F(1) | 1.30(2) |
| C(1)–F(2) | 1.32(2) |
| C(1)–F(3) | 1.33(2) |
| C(5)–F(4) | 1.31(2) |
| C(5)–F(5) | 1.28(2) |
| C(5)–F(6) | 1.29(2) |

(b) Interbond Angles

| | |
|---|---|
| S(1)–Pt–S(2) | 90.6(1) |
| S(1)–Pt–Cl(1) | 178.2(1) |
| S(1)–Pt–Cl(2) | 88.7(1) |
| S(2)–Pt–Cl(1) | 89.9(1) |
| S(2)–Pt–Cl(2) | 179.0(1) |
| Cl(1)–Pt–Cl(2) | 90.8(1) |
| Pt–S(1)–C(3) | 102.9(4) |
| Pt–S(1)–C(5) | 106.6(5) |
| C(3)–S(1)–C(5) | 101.5(7) |
| Pt–S(2)–C(1) | 106.2(5) |
| Pt–S(2)–C(2) | 105.0(4) |
| C(1)–S(2)–C(2) | 97.6(7) |
| S(2)–C(2)–C(3) | 109.2(9) |
| S(2)–C(2)–C(4) | 110.4(10) |
| C(3)–C(2)–C(4) | 111.0(11) |
| S(1)–C(3)–C(2) | 115.5(9) |
| S(2)–C(1)–F(1) | 110.2(10) |
| S(2)–C(1)–F(2) | 111.1(11) |
| S(2)–C(1)–F(3) | 114.5(10) |
| F(1)–C(1)–F(2) | 105.6(12) |
| F(1)–C(1)–F(3) | 107.6(13) |
| F(2)–C(1)–F(3) | 107.4(12) |
| S(1)–C(5)–F(4) | 108.9(11) |
| S(1)–C(5)–F(5) | 108.0(11) |
| S(1)–C(5)–F(6) | 114.4(10) |
| F(4)–C(5)–F(5) | 108.8(12) |
| F(4)–C(5)–F(6) | 107.0(12) |
| F(5)–C(5)–F(6) | 109.6(14) |

(c) Intramolecular Non-Bonded Distances

| | |
|---|---|
| F(3)···F(6) | 2.817(14) |
| S(1)···Cl(2) | 3.167(5) |
| S(2)···Cl(1) | 3.218(5) |
| S(1)···S(2) | 3.199(4) |
| Cl(1)···Cl(2) | 3.264(5) |

(d) Intermolecular Contacts Less than the Sum of the van der Waals Radii

| | |
|---|---|
| S(1)···Cl(1$^{\mathrm{I}}$) | 3.352(5) |
| S(2)···Cl(2$^{\mathrm{I}}$) | 3.382(5) |
| Pt···Pt$^{\mathrm{I}}$ | 3.417(1) |
| Cl(1)···C(2$^{\mathrm{II}}$) | 3.560(14) |
| Cl(1)···C(3$^{\mathrm{I}}$) | 3.693(14) |
| Cl(1)···C(4$^{\mathrm{III}}$) | 3.793(15) |

Roman numerals refer to the folllwing transformations of the fractional co-ordinates in Table I:

| | | | |
|---|---|---|---|
| I | $\bar{x}$ | $\bar{y}$, | $\bar{z}$; |
| II | ½+$x$, | ½–$y$, | –½+$z$; |
| III | 1 +$x$, | $y$, | $z$. |

(e) Torsion Angles

| | |
|---|---|
| PtS(1)C(5)F(4) | 163(0.9) |
| PtS(1)C(5)F(5) | –79(1.1) |
| PtS(1)C(5)F(6) | 43(1.2) |
| C(3)S(1)C(5)F(4) | 55(1.1) |
| C(3)S(1)C(5)F(5) | 173(1.0) |
| C(3)S(1)C(5)F(6) | –64(1.2) |
| PtS(2)C(1)F(1) | 85(1.1) |
| PtS(2)C(1)F(2) | –158(0.9) |
| PtS(2)C(1)F(3) | –37(1.2) |
| C(2)S(2)C(1)F(1) | –167(1.1) |
| C(2)S(2)C(1)F(2) | –50(1.1) |
| C(2)S(2)C(1)F(3) | 72(1.2) |
| PtS(1)C(3)C(2) | –37(1.0) |
| C(5)S(1)C(3)C(2) | 73(1.1) |
| S(1)C(3)C(2)S(2) | 47(1 2) |
| S(1)C(3)C(2)C(4) | 169(0.9) |
| C(3)C(2)S(2)Pt | –33(1.0) |
| C(3)C(2)S(2)C(1) | –142(1.0) |
| C(4)C(2)S(2)Pt | –156(0.9) |
| C(4)C(2)S(2)C(1) | 95(1.0) |
| C(2)S(2)PtS(1) | 10(0.5) |
| C(1)S(2)PtS(1) | 112(0.5) |
| S(2)PtS(1)C(3) | 11(0.5) |
| S(2)PtS(1)C(5) | –96(0.5) |

verified by establishing that mean values of $||F_0| - |F_c||/\sigma(F_0)$ showed little variation with either $|F_0|$ or $\sin\theta/\lambda$. The standard deviation of an observation of unit weight was 2.0. Extinction corrections were not applied.

The final atomic parameters and a selection of functions derived from them are presented in Tables I–III. A perspective view of the molecule is displayed in Figure 1. Final observed and calculated structure amplitudes may be obtained by application to the Editor.

The programs used in this work were the HILGER data processing program of P. R. Mallinson, K. W. Muir and D. N. J. White, the Hilger and Watts software system for the Y290 diffractometer, and J. M. Stewart's X-RAY72 system.

TABLE III. Equations[a] of, and Atomic Displacements (Å × $10^3$) from, Weighted Least-squares Planes.

Plane 1, defined by Pt, S(1), S(2), Cl(1) and Cl(2):
$-0.499X - 0.637\,Y - 0.587\,Z = -1.689$;
Pt −2(1), S(1) 28(3), S(2) 12(3), Cl(1) 35(4), Cl(2) 16(4).

Plane 2, defined by Pt, S(1), S(2), C(2), C(3):
$-0.488\,X - 0.633\,Y - 0.600\,Z = -1.689$;
Pt 0(1), S(1) −9(3), S(2) 6(3), C(1) −1608(15),
C(2) −300(13), C(3) 328(13), C(4) 257(15),
C(5) −1765(15).

[a] In terms of orthogonal co-ordinates *X, Y, Z* along *a*, *b* and *c**.

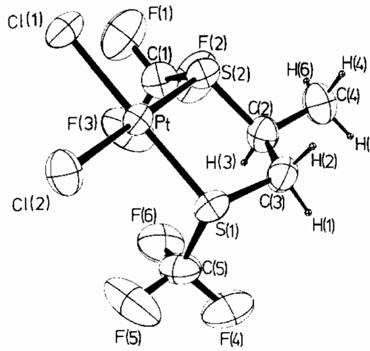

Fig. 1. A perspective view of the molecule.

## Discussion

The crystals contain $PtCl_2(F_3CSCHMeCH_2SCF_3)$ molecules which exhibit the expected *cis*-square-planar co-ordination at the platinum atom (Figure 1). The methyl group is *pseudo*-equatorial with respect to the chelate ring and the trifluoromethyl substituents of the sulphur atoms are mutually *syn*. Comparisons with other bis(thioether) chelate complexes of platinum(II) cannot be made since there is no structural information available. However, in bis(thioether) and bis(selenoether) chelate complexes of palladium(II) the terminal substituents of the group VIA donor atoms are usually found to be *syn* [10, 11]. The only exception involves an unusual macrobicyclic ligand where the *anti* configuration may well be a consequence of the constrained geometry of the ligand [12].

The crystal packing is predominantly of the van der Waals type (Table IId), but it also involves strong interactions between pairs of centrosymmetrically-related molecules (Figure 2). The constituent molecules of each pair are arranged so that the platinum co-ordination planes are antiparallel and the metal–ligand bonds are eclipsed. The resulting Pt···Pt separation of 3.42 Å is too long to be indicative of normal covalent bonding; the lengths of Pt–Pt single bonds in platinum(II) complexes are typically 2.77–2.87 Å [13, 14]. The Pt···Pt contact is also longer than the corresponding distance in Magnus' Green Salt (3.25 Å) [15] and related compounds. However, it agrees well with the value of 3.39 Å found in *cis*-dichloro(ethylenediamine)platinum(II), crystals of which contain infinite stacks of molecules arranged so that adjacent metal co-ordination planes are antiparallel [16]. In *cis*-$PtCl_2(F_3CSCHMeCH_2SCF_3)$ the formation of infinite stacks of molecules appears to be prevented by the *syn* trifluoromethyl groups, which leave only one side of the metal co-ordination plane open for close approach to a neighbouring molecule. The eclipsing of the metal–ligand bonds leads to intermolecular Cl···S separations of 3.35 and 3.38 Å which are slightly shorter than the Pt···Pt contact. This is brought about by a small but significant pyramidal distortion of the platinum co-ordination. The displacement of the platinum atom from the weighted $PtS_2Cl_2$ plane is −0.002(1) Å, whereas the displacements of the atoms S(1), S(2), Cl(1), and Cl(2) are respectively 0.028(3), 0.012(3), 0.035(4), and 0.016(4) Å (a positive displacement is in the direction of the centrosymmetrically-related molecule). This contrasts with the situation in complexes containing covalent Pt–Pt bonds, such as bis(ethylene-1,2-dithiolato)platinum (II) dimer, for example [13], where the metal atoms are displaced by *ca.* 0.1 Å from their co-ordination planes towards rather than away from each other. Accordingly, we consider that the pairing of centrosymmetrically-related *cis*-$PtCl_2(F_3CSCHMeCH_2SCF_3)$ molecules is best explained by electrostatic interactions between electron-deficient sulphur atoms and negatively charged chloro ligands and that there is little, if any, direct bonding between the platinum atoms. This view is in conformity with a semi-empirical M.O. calculation on Magnus' Green Salt which indicated that the covalent Pt–Pt bond order is about 0.04 [17].

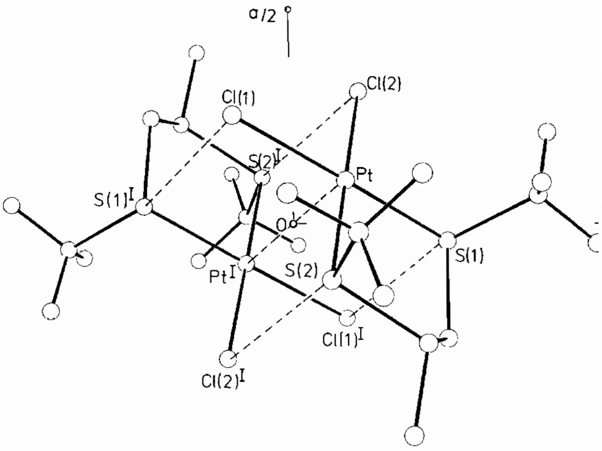

Fig. 2. The crystal packing.

Despite the pyramidal distortion of its co-ordination, valency angles subtended at the platinum atom are all within 2° of the ideal values of 90 or 180°. The Pt–Cl bond lengths are equal. Their mean of 2.293(3) Å lies at the lower end of the range of terminal $Pt^{II}$–Cl distances (2.26–2.45 Å) [18], indicating that in this compound the *trans*-influence of the thioether ligands is relatively weak. The Pt–S distances of 2.239(3) and 2.260(3) Å differ slightly, the longer bond being adjacent to the chelate-ring methyl substituent. Assessment of the influence of the electron-withdrawing trifluoromethyl groups on the metal–ligand bonding is rendered difficult by the lack of structural data on related compounds. The problem is further complicated by the participation of the sulphur and chlorine donor atoms in strong intermolecular interactions. Perhaps the most directly comparable structure is that of *cis*-$PtCl_2[S(p\text{-}C_6H_4Cl)_2]_2$ where the mean Pt–S and Pt–Cl distances are 2.285(7) and 2.300(5) Å [19]. Shorter, but less accurately determined Pt–S distances of 2.25 Å *trans* to amine in chloro(glycyl-*L*-methionine)platinum(II) and of 2.26 Å *trans* to chlorine in dichloro(*L*-methionine)platinum(II) have also been reported [20]. In the latter compound the Pt–Cl (*trans* to S) bond length is 2.32 Å. The only other Pt–S (thioether) distance which has been determined is that for the bridging bonds in $\mu$-$(SEt_2)_2(PtBr_2)_2$; the mean value of 2.22(1) Å is remarkably short, for reasons which at present are uncertain [21]. We can suggest only tentatively that, by comparison with *cis*-$PtCl_2[S(p\text{-}C_6H_4Cl)_2]_2$, the trifluoromethyl groups in *cis*-$PtCl_2(F_3CSCHMeCH_2SCF_3)$ have little effect on the *trans*-influence of the thioether ligand, but that they may be responsible for a contraction of the Pt–S bonds by 0.03–0.05 Å.

The two trifluoromethyl groups adopt similar conformations relative to the chelate ring, so that corresponding torsion angles about the S–C bonds agree to within 8°. The conformations are such that the C–F bonds involving the atoms F(3) and F(6) point inwards and almost towards each other. The resulting F(3)···F(6) non-bonded contact of 2.82 Å, though greater than the van der Waals diameter of fluorine (2.70 Å), nevertheless suggests that the isomer present in the solid may be one of those which display F–F coupling in acetone solution. Interestingly, the S–C–F angles involving F(3) and F(6) are both some 5° larger than the other S–C–F angles, which average 109.6(7)°. However, there are no significant differences between the C–F bond lengths or between F–C–F bond angles, the respective means being 1.305(7) Å and 107.7(6)°.*

Both sulphur atoms adopt similar *quasi*-tetrahedral co-ordinations. Corresponding interbond angles at sulphur agree to within 4°, and all are less than the tetrahedral angle (109.5°). The four S–C bond lengths agree to within experimental error, the mean value of 1.835(7) Å being typical for a bond of unit order.

The chelate ring has a symmetrically-puckered *gauche* conformation. This is apparent from the internal torsion angles: the CCSPt angles differ by only 4° and the CSPtS angles by 1°. It is also evident from the displacements of the atoms from the weighted $PtS_2C_2$ mean plane (Table III); the platinum and sulphur atoms lie within 0.01 Å of the plane whereas the atoms C(2) and C(3) are displaced by nearly equal amounts (0.30 and 0.33 Å) in opposite directions.

Molecules of *cis*-$PtCl_2(F_3CSCHMeCH_2SCF_3)$ contain four chiral centres, namely the asymmetric atoms S(1), S(2), and C(2), and the chelate ring, so that in principle eight enantiomeric pairs of diastereoisomers may exist. The crystalline form which we have studied is, of course, racemic. In those molecules in which the chelate ring configuration is $\delta$ [S(1)C(3)C(2)S(2) torsion angle +47°, as in Figure 1], the absolute configurations at the atoms S(1), S(2), and C(2) are respectively (*R*), (*S*), and (*S*).

## Acknowledgments

We thank Professor D. W. A. Sharp, Dr. R. J. Cross and Mr H. T. Miguel for suggesting the problem and for a gift of crystals, the University of Glasgow for a studentship (to T.S.), and Dr. P. R. Mallinson for assistance with the computing.

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*Limits of error on means are standard deviations and are the larger of the estimates: $(\sum_i \sigma_i^{-2})^{-1/2}$ and $[\sum_i (x_i - \bar{x})^2/n(n-1)]^{1/2}$, where the $n$ individual bond lengths, or angles, $x_i$ have standard deviations $\sigma_i$ and mean $\bar{x}$.

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