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Structure of *cis*-Tetrachloro(3-trifluoromethyl-2,5-dithiahexane)platinum(IV)

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Abstract. $[PtCl_4(C_5H_9F_3S_2)]$, $M_r = 527{\cdot}2$, monoclinic, $P2_1/n$, $a = 7{\cdot}431\,(4)$, $b = 15{\cdot}154\,(9)$, $c = 11{\cdot}721\,(7)$ Å, $\beta = 99{\cdot}29\,(1)^\circ$, $U = 1302{\cdot}6\,(13)$ Å^3, $Z = 4$, $D_x = 2{\cdot}688$ g cm^{-3}, D_m not measured, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 120{\cdot}2$ cm^{-1}, $F(000) = 976$, $T = 293$ K, $R = 0{\cdot}020$ for 1648 unique reflections with $I \geq 3\sigma(I)$. The Pt atom displays distorted octahedral coordination with Pt—Cl = 2·314 (2)–2·338 (2) Å and Pt—S = 2·317 (2) and 2·320 (2) Å. The CF_3 substituent is pseudoequatorial with respect to the PtS_2C_2 chelate ring and the *S*-methyl substituents are mutually *anti*.

Introduction. The title complex was prepared by chlorine oxidation of the corresponding $[PtCl_2L]$ complex, where L = racemic $MeSCH_2CH(CF_3)SMe$. In its acetone-d^6 solutions four isomers with relative abundances 52:40:4:4 can be observed by ^{19}F NMR at ambient temperatures. The isomers can be identified by comparison with analogous platinum(II) complexes (Cross, Rycroft, Sharp & Torrens, 1980; Torrens, 1977; Hunter, 1982). They correspond to four enantiomeric pairs of diastereomers arising from the presence of a chiral C and two chiral S atoms. The PtS_2C_2 chelate ring constitutes a fourth chiral centre but interconversion in solution between its δ and λ forms is too fast for detection on the NMR timescale. This crystal-structure analysis reveals that the solid form of the title compound corresponds to the isomer identified as the second most abundant in solution.

Experimental. Crystals grown from acetone solution by solvent evaporation at 277 K; yellow needle; forms displayed and distances (cm) of faces from centroid {011} 0·003 and {10$\bar{1}$} 0·009; Enraf–Nonius CAD-4F diffractometer, Mo $K\alpha$ X-rays, graphite monochromator; cell dimensions by least-squares fit to the setting angles of 23 automatically centred reflections with $10 < \theta < 13^\circ$; intensities of 3589 reflections with $2 \leq \theta \leq 25^\circ$ and $0 \leq h \leq 8$, $-18 \leq k \leq 7$, $-13 \leq l \leq 13$ measured from continuous $\theta/2\theta$ scans of 0·90° in θ; two intensity standards measured every two hours; corrections for Lp and absorption (Gaussian quadrature, 96 grid points, transmission factors on F^2 0·45–0·72), no correction for decomposition or extinction required; $R_{\rm int}$ 0·022 for 1057 independent reflections measured at least twice; 2287 independent structure amplitudes; 1648 with $I \geq 3\sigma(I)$ used subsequently; structure solved by Patterson and difference syntheses; full-matrix least-squares refinement on F; $w^{-1} = \sigma^2(F) + 2{\cdot}25 \times 10^{-4}F^2$; final adjustment of 172 parameters (isotropic U for H atoms; anisotropic U_{ij} for the others) gave $wR = 0{\cdot}019$, $S = 1{\cdot}2$; maximum $\Delta/\sigma = 0{\cdot}018$; final $|\Delta\rho|$ values $< 0{\cdot}63$ e Å^{-3}; neutral-atom scattering factors and complex anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); *GX* crystallographic program package (Mallinson & Muir, 1985). Final atomic coordinates are presented in Table 1.[*]

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[*] Lists of structure amplitudes, anisotropic displacement parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42884 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic fractional coordinates with e.s.d.'s in parentheses and equivalent isotropic displacement parameters* (Å²)

U_{eq} is the mean latent root of the anisotropic displacement tensor.

	x	y	z	U_{eq}
Pt	0·13296 (3)	0·16764 (1)	0·16203 (1)	0·033
Cl(2)	0·16645 (21)	0·01591 (10)	0·15697 (11)	0·059
Cl(2)	0·41674 (18)	0·18712 (11)	0·27850 (10)	0·052
Cl(3)	0·26198 (18)	0·17923 (10)	−0·00437 (10)	0·049
Cl(4)	−0·00526 (20)	0·15705 (10)	0·32513 (10)	0·055
S(1)	0·09459 (17)	0·31840 (9)	0·18037 (10)	0·038
S(2)	−0·14691 (16)	0·16032 (8)	0·04167 (9)	0·035
F(1)	−0·0962 (5)	0·4881 (2)	0·1291 (3)	0·070
F(2)	−0·3608 (5)	0·4412 (2)	0·0578 (3)	0·067
F(3)	−0·2493 (6)	0·4108 (2)	0·2318 (3)	0·076
C(1)	0·2493 (10)	0·3756 (5)	0·1027 (7)	0·064
C(2)	−0·2836 (10)	0·0767 (4)	0·0939 (6)	0·052
C(3)	−0·1249 (6)	0·3373 (3)	0·0863 (4)	0·036
C(4)	−0·2077 (8)	0·4199 (4)	0·1274 (5)	0·045
C(5)	−0·2503 (7)	0·2591 (3)	0·0913 (4)	0·038

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

Pt—Cl(1)	2·314 (2)	Pt—Cl(2)	2·338 (2)
Pt—Cl(3)	2·315 (2)	Pt—Cl(4)	2·317 (2)
Pt—S(1)	2·317 (2)	Pt—S(2)	2·320 (2)
S(1)—C(1)	1·799 (7)	S(1)—C(3)	1·838 (5)
S(2)—C(2)	1·793 (7)	S(2)—C(5)	1·821 (6)
F(1)—C(4)	1·323 (7)	F(2)—C(4)	1·329 (6)
F(3)—C(4)	1·317 (7)	C(3)—C(4)	1·509 (7)
C(3)—C(5)	1·514 (7)		
Cl(1)—Pt—Cl(2)	92·9 (1)	Cl(1)—Pt—Cl(3)	89·6 (1)
Cl(1)—Pt—Cl(4)	90·9 (1)	Cl(1)—Pt—S(1)	175·9 (1)
Cl(1)—Pt—S(2)	91·5 (1)	Cl(2)—Pt—Cl(3)	91·4 (1)
Cl(2)—Pt—Cl(4)	90·3 (1)	Cl(2)—Pt—S(1)	86·2 (1)
Cl(2)—Pt—S(2)	175·3 (1)	Cl(3)—Pt—Cl(4)	178·2 (1)
Cl(3)—Pt—S(1)	94·4 (1)	Cl(3)—Pt—S(2)	86·8 (1)
Cl(4)—Pt—S(1)	85·1 (1)	Cl(4)—Pt—S(2)	91·4 (1)
S(1)—Pt—S(2)	89·5 (1)	Pt—S(1)—C(1)	109·2 (3)
Pt—S(1)—C(3)	102·0 (2)	C(1)—S(1)—C(3)	101·5 (4)
Pt—S(2)—C(2)	109·1 (3)	Pt—S(2)—C(5)	98·6 (2)
C(2)—S(2)—C(5)	100·4 (3)	S(1)—C(3)—C(4)	107·8 (4)
S(1)—C(3)—C(5)	110·3 (4)	C(4)—C(3)—C(5)	110·6 (5)
F(1)—C(4)—F(2)	106·9 (5)	F(1)—C(4)—F(3)	108·0 (5)
F(1)—C(4)—C(3)	111·5 (5)	F(2)—C(4)—F(3)	106·9 (5)
F(2)—C(4)—C(3)	111·0 (5)	F(3)—C(4)—C(3)	112·3 (5)
S(2)—C(5)—C(3)	109·7 (4)		

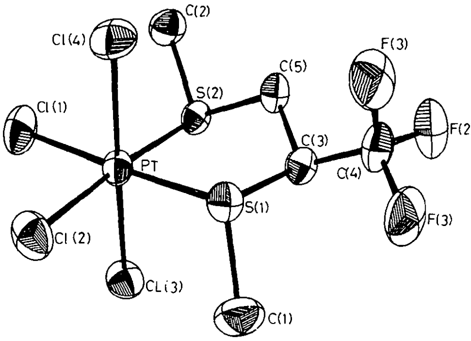

Fig. 1. A perspective view of the complex showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Discussion. The crystal structure is built of discrete *cis*-[$PtCl_4\{CH_3SCH_2CH(CF_3)SCH_3\}$] molecules. The Pt atom shows slightly distorted octahedral coordination: bond angles at Pt (Table 2) are all within 5° of 90 or 180°. The Pt–Cl distances agree with values for other Pt^{IV}–Cl bonds subject to low *trans* influence (Hartley, 1973) and also agree to within 0·03 Å with the values of 2·303 (4) and 2·308 (4) Å found in the analogous Pt^{II} complex *cis*-[$PtCl_2\{CH_3SCH_2CH(CF_3)SCH_3\}$] (Hunter, Muir & Sharp, 1985). This contrasts with the behaviour of the Pt—S bond lengths, the values found here being *ca* 0·08 Å longer than corresponding values in the analogous Pt^{II} complex. In the only other Pt^{IV}–thioether complex which has been structurally characterized, [$(PtMe_3Cl)_2(\overline{SCH_2SCH_2SCH_2})$] (Abel, Booth, Orrell, Pring & Cameron, 1981) the Pt^{IV}—S bond lengths of 2·458 (5) and 2·473 (6) Å are 0·15 Å longer than the values found here. This lengthening most probably reflects the high *trans* influence of alkyl compared with chloride (Manojlović-Muir & Muir, 1974).

The molecule depicted in Fig. 1 and defined by the coordinates in Table 1 has a chelate ring with absolute configuration λ [torsion angle S(1)—C(3)—C(5)—S(2) = −60·7 (4)°]. The other three chiral centres S(1), S(2) and C(3) then display absolute configuration *S*.

The PtS_2C_2 chelate ring displays an envelope conformation with C(5) at the flap: thus the internal torsion angle across Pt—S(1) is near zero [−1·8 (2)°] whereas the angles across S(1)—C(3) and C(3)—C(5) [34·7 (4) and −60·7 (4)°] differ in sign but agree in magnitude to within 11° with those across Pt—S(2) and S(2)—C(5) [−23·9 (2) and 52·9 (4)°]. The pseudo-equatorial position of the CF_3 substituent is established by the Pt—S(1)—C(3)—C(4) torsion angle of 155·5 (4)°. The *S*-methyl substituents are mutually *anti*, lying on opposite sides of the PtS_2 plane from one another. A similar arrangement is also found in the octahedral species *cis*-[$Cr(CO)_4\{EtSCH_2CH_2SEt\}$] (Baker & Larsen, 1976). In contrast, square-planar *R*SCH_2CH_2S*R* complexes usually display *syn* conformations (*e.g.* Hunter, Muir & Sharp, 1984).

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Structures of One-Dimensional Pd^{II}–Pd^{IV} Mixed-Valence Complexes, $[Pd^{II}L][Pd^{IV}Cl_2L]Y_4$ ($Y = ClO_4$ and PF_6), and Their Parent Pd^{II} and Pd^{IV} Complexes, $[Pd^{II}L](ClO_4)_2$ and $[Pd^{IV}Cl_2L](NO_3)_2.HNO_3.H_2O$, with 1,4,8,11-Tetraazacyclotetradecane (L)

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Abstract. Molecular and crystal structures of the title compounds, $[Pd^{II}L](ClO_4)_2$ (1), $[Pd^{IV}Cl_2L](NO_3)_2.HNO_3.H_2O$ (2), $[Pd^{II}L][Pd^{IV}Cl_2L](ClO_4)_4$ (3), and $[Pd^{II}L][Pd^{IV}Cl_2L](PF_6)_4$ (4), have been determined by single-crystal X-ray diffraction at room temperature, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å. Crystal data are: for (1), $C_{10}H_{24}Cl_2N_4O_8Pd$, $M_r = 505{\cdot}65$, orthorhombic, *Pbnm*, $a = 13{\cdot}337\,(2)$, $b = 14{\cdot}492\,(3)$, $c = 9{\cdot}746\,(2)$ Å, $U = 1883{\cdot}8\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}78$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 1{\cdot}30$ mm^{-1}, $F(000) = 1024$, $R = 0{\cdot}054$, $wR = 0{\cdot}066$ for 1824 observed reflections; for (2), $C_{10}H_{27}Cl_2N_7O_{10}Pd$, $M_r = 582{\cdot}69$, triclinic, $P\bar{1}$, $a = 9{\cdot}549\,(1)$, $b = 16{\cdot}034\,(1)$, $c = 7{\cdot}863\,(1)$ Å, $\alpha = 86{\cdot}59\,(1)$, $\beta = 111{\cdot}51\,(1)$, $\gamma = 103{\cdot}27\,(1)°$, $U = 1089{\cdot}6\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}78$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 1{\cdot}15$ mm^{-1}, $F(000) = 592$, $R = 0{\cdot}023$, $wR = 0{\cdot}035$ for 5730; for (3), $C_{20}H_{48}Cl_6N_8O_{16}Pd_2$, $M_r = 1082{\cdot}20$, monoclinic, $C2/c$, $a = 17{\cdot}649\,(12)$, $b = 9{\cdot}738\,(8)$, $c = 11{\cdot}067\,(8)$ Å, $\beta = 91{\cdot}33\,(6)°$, $U = 1901\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}89$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 1{\cdot}43$ mm^{-1}, $F(000) = 1092$, $R = 0{\cdot}041$, $wR = 0{\cdot}061$ for 1708; for (4), $C_{20}H_{48}Cl_2F_{24}N_8P_4Pd_2$, $M_r = 1264{\cdot}25$, monoclinic, $P2_1/m$, $a = 9{\cdot}978\,(5)$, $b = 11{\cdot}638\,(4)$, $c = 9{\cdot}917\,(3)$ Å, $\beta = 117{\cdot}17\,(2)°$, $U = 1024{\cdot}6\,(7)$ Å^3, $Z = 1$, $D_x = 2{\cdot}05$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 1{\cdot}30$ mm^{-1}, $F(000) = 626$, $R = 0{\cdot}055$, $wR = 0{\cdot}080$ for 2299. The coordination geometry of (1) is of the square-planar type with an average Pd–N distance of $2{\cdot}051\,(7)$ Å, whereas (2) is a six-coordinate complex of the *trans*-$PdCl_2N_4$ type with mean Pd–N and Pd–Cl lengths of $2{\cdot}062\,(4)$ and $2{\cdot}303\,(1)$ Å, respectively. In (3) and (4), the four-coordinate Pd^{II} and six-coordinate Pd^{IV}, both of which have a 2+ charge, are stacked alternately in the direction of the needle axis, constructing linear chains of $\cdots Cl{-}Pd^{IV}{-}Cl\cdots Pd^{II}\cdots$ segments. Neighboring Pd^{II} and Pd^{IV} units are connected by hydrogen bonds, $NH\cdots X\cdots HN$ ($X = O$ for 3 and $X = F$ for 4). In both (3) and (4), the bridging Cl atoms are statistically disordered and all Pd sites comprise $\frac{1}{2}Pd^{II} + \frac{1}{2}Pd^{IV}$. Average coordination bond distances in the chain structures are: Pd–N = $2{\cdot}055\,(5)$ Å for (3) and $2{\cdot}049\,(8)$ Å for (4); Pd^{IV}–Cl = $2{\cdot}319\,(3)$ Å for (3) and $2{\cdot}309\,(3)$ Å for (4); $Pd^{II}\cdots Cl = 3{\cdot}219\,(3)$ Å for (3) and $3{\cdot}514\,(3)$ Å for (4). In all the complexes, the macrocyclic ligand L adopts the same, most stable, chelate ring conformation, the two six- and two five-membered rings being in chair and *gauche* forms, respectively. Structural changes upon the formation of the one-dimensional linear chain structure are discussed.

Introduction. Recently much interest has been attracted to one-dimensional M^{II}–M^{IV} mixed-valence complexes of Pt, Pd and Ni from the viewpoint of the chemistry and physics of low-dimensional compounds (Miller & Epstein, 1976; Yamashita, Nonaka, Kida, Hamaue & Aoki, 1981; Aoki, Hamaue, Kida, Yamashita, Takemura, Furuta & Kawamori, 1982; Clark, Kurmoo, Galas & Hursthouse, 1981). They show lustrous deep color with strong dichroism and semiconducting behavior (Matsumoto, Yamashita & Kida, 1978*a*; Hamaue, Aoki, Yamashita & Kida, 1981). In the crystal structures, the four-coordinate M^{II} and six-coordinate M^{IV} units are stacked alternately, constructing linear chains.