centrosymmetry where none existed, and dissuaded elimination of symmetry when preliminary results indicated its presence.

From among over 1300 data collections processed by our laboratory in the past eight years, about 60 have been consigned to our 'morgue' for unsolved structures: those that defied our every attempt to extract a chemically sensible product. An examination of the space groups of these moribund structures revealed that more than 3/4 were in ambiguous space groups, with greater than half occurring in the systems mentioned above. In the past several months, we have found that the application of the procedures outlined above allowed us to solve suc-

cessfully about 20 of these structures. Not one of these re-examinations revealed that the *absence* of symmetry was the cause of the original difficulty.

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The Structure of a Platinum Polyfluorophenylthiolate, *trans*-[Pt(SC$_6$F$_5$)$_2$(SEt$_2$)$_2$]

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Abstract. *trans*-Bis(diethyl sulfide)bis(pentafluorobenzenethiolato)platinum(II), [Pt(C$_6$F$_5$S)$_2$(C$_4$H$_{10}$S)$_2$], $M_r = 773.71$, monoclinic, $P2_1/n$, $a = 10.775\,(3)$, $b = 12.842\,(7)$, $c = 10.052\,(3)$ Å, $\beta = 113.65\,(2)°$, $V = 1274$ Å^3, $Z = 2$, $D_c = 1.99$, $D_x = 2.02$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 59.58$ cm^{-1}, $F(000) = 743.86$, room temperature, final $R = 0.0315$ for 2212 unique observed reflexions. The Pt atom lies on an inversion centre, and shows *trans* square planar geometry. Not only are the SC$_6$F$_5$ groups planar but so are the non-H atoms of the S(C$_2$H$_5$)$_2$ moieties. The SC$_6$F$_5$ moieties have bond distances Pt—S 2.323 (1) and S—C 1.760 (7) Å; the S(C$_2$H$_5$)$_2$ has Pt—S 2.302 (1) and S—C 1.805 (6) and 1.808 (5) Å.

Introduction. There is some considerable interest in homodonor (sulfur) compounds of the platinum metals in view of their relevance to biological systems and catalytic processes and their usefulness in chemical synthesis (Hagen, Stephan & Holm, 1982; Roesky, 1986; Ueyama, Sugawara, Sasaki, Nakamura, Yamashita, Wakatsuk, Yamazaki & Yasuoka, 1988). In a number of cases unusual structures are stabilized (Catala, Cruz-Garritz, Hills,

Hughes, Richards, Terreros & Torrens, 1987; Catala, Cruz-Garritz, Hills, Hughes, Richards, Sosa & Torrens, 1987).

Experimental. The title compound was formed in 81% yield from the reaction of Pb(SC$_6$F$_5$)$_2$ with [PtCl$_2$(SEt$_2$)$_2$] in acetone solution and subsequent addition of water (after filtering off of PbCl$_2$). The yellow crystals were recrystallized from acetone. X-ray reflexion data from a small (approx. 0.15 × 0.20 × 0.25 mm) block-shaped crystal were collected on a Nicolet *R*3*M* 4-circle automatic diffractometer operating in the ω-scan mode and using Mo $K\alpha$ radiation (graphite monochromator). The unit-cell parameters were determined by least squares from the setting angles of 25 well centred reflexions in the range $5 < 2\theta < 23°$. Density by flotation in a mixture of iodobenzene and toluene. An empirical absorption correction was applied from azimuthal scans on seven reflexions (252 measurements) and gave maximum and minimum transmission factors of 0.379 and 0.287 respectively. Reflexion data in the range $6.5 < 2\theta < 55°$ and having $0 < h < 14$, $0 < k < 17$, and $-14 < l < 14$ were collected. Two check reflexions were monitored every 100 reflexions and showed

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($\text{Å}^2 \times 10^3$)

	x	y	z	U*
Pt(1)	0	0	0	35 (<1)
S(1)	915·0 (1·4)	−378·5 (1·1)	2467·3 (1·4)	51 (1)
S(2)	−1844·0 (1·4)	−1018·7 (1·1)	−271·3 (1·4)	47 (1)
C(1)	−795 (6)	−1183 (4)	3621 (6)	52 (2)
C(2)	−1859 (6)	−1148 (5)	4060 (6)	65 (3)
C(3)	−2560 (6)	−253 (5)	3922 (6)	65 (3)
C(4)	−2237 (7)	586 (6)	3361 (6)	64 (3)
C(5)	−1172 (6)	565 (5)	2960 (6)	55 (3)
C(6)	−428 (6)	−333 (4)	3040 (5)	45 (2)
F(1)	−118 (4)	−2073 (3)	3784 (4)	82 (2)
F(2)	−2157 (5)	−2000 (3)	4649 (5)	106 (3)
F(3)	−3590 (3)	−222 (3)	4367 (4)	92 (2)
F(4)	−2920 (4)	1479 (3)	3259 (5)	109 (2)
F(5)	−867 (4)	1437 (3)	2432 (4)	88 (2)
C(7)	−1759 (6)	−2130 (4)	−1331 (6)	· 68 (3)
C(8)	−531 (6)	−2773 (5)	−469 (7)	79 (4)
C(9)	−3374 (6)	−415 (5)	−1548 (6)	65 (3)
C(10)	−3665 (7)	557 (6)	−910 (9)	102 (4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

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

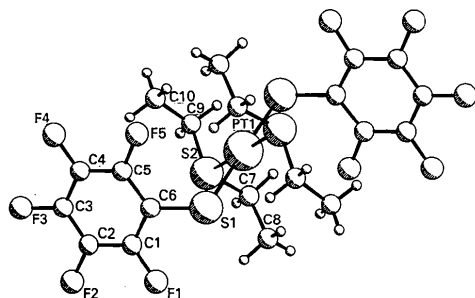|			
Pt(1)—S(1)	2·323 (1)	Pt(1)—S(2)	2·302 (1)
S(1)—C(6)	1·760 (7)	S(2)—C(7)	1·805 (6)
S(2)—C(9)	1·808 (5)	C(1)—C(2)	1·384 (10)
C(1)—C(6)	1·368 (8)	C(1)—F(1)	1·331 (7)
C(2)—C(3)	1·353 (9)	C(2)—F(2)	1·342 (8)
C(3)—C(4)	1·325 (10)	C(3)—F(3)	1·353 (8)
C(4)—C(5)	1·361 (11)	C(4)—F(4)	1·345 (9)
C(5)—C(6)	1·388 (9)	C(5)—F(5)	1·336 (8)
C(7)—C(8)	1·505 (8)	C(9)—C(10)	1·492 (10)
S(1)—Pt(1)—S(2)	89·1(< 1)	S(1)—Pt(1)—S(2a)	90·9(< 1)
Pt(1)—S(1)—C(6)	106·8 (2)	Pt(1)—S(2)—C(7)	105·9 (2)
Pt(1)—S(2)—C(9)	109·8 (2)	C(7)—S(2)—C(9)	99·7 (3)
C(2)—C(1)—C(6)	121·9 (6)	C(2)—C(1)—F(1)	118·1 (6)
C(6)—C(1)—F(1)	120·0 (6)	C(1)—C(2)—C(3)	119·7 (6)
C(1)—C(2)—F(2)	119·3 (6)	C(3)—C(2)—F(2)	121·0 (7)
C(2)—C(3)—C(4)	120·2 (7)	C(2)—C(3)—F(3)	119·3 (6)
C(4)—C(3)—F(3)	120·5 (6)	C(3)—C(4)—C(5)	120·4 (7)
C(3)—C(4)—F(4)	119·7 (7)	C(5)—C(4)—F(4)	119·7 (7)
C(4)—C(5)—C(6)	122·4 (7)	C(4)—C(5)—F(5)	118·1 (6)
C(6)—C(5)—F(5)	119·5 (6)	S(1)—C(6)—C(1)	122·0 (5)
S(1)—C(6)—C(5)	122·7 (5)	C(1)—C(6)—C(5)	115·4 (6)
S(2)—C(7)—C(8)	109·6 (4)	S(2)—C(9)—C(10)	110·0 (4)

Fig. 1. Molecular structure and numbering scheme.

no evidence of decay. 3280 measurements were made of 2913 unique reflexions, of which 2212 were accepted as observed [$|F| > 3\sigma(F)$]. R_{int} was 0·0118. The structure was solved by Patterson and difference Fourier methods and refined by cascade blocked diagonal least squares [function minimized $\Sigma w(F_o - F_c)^2$] with weights $w = 1/[\sigma^2(F)]$, to a final R of 0·0315 ($wR = 0·0243$) (161 refined parameters). Eight of the ten independent hydrogens were located from a low-angle difference Fourier synthesis. All H atoms were constrained to ride each on its neighbouring heavy atom with calculated bond lengths and angles. The (isotropic) hydrogen thermal parameters were each fixed at 1·2 times U_{eq} for the adjacent heavy atom. An extinction correction of the form $F^* = F_c/[1 + 0·002 \times F^2/\sin(2\theta)]^{0·25}$ was applied, with $x = 0·00099$. The shifts on the final cycle of refinement were all less than 0·004 of the corresponding e.s.d.'s; the final difference Fourier map showed maximum and minimum densities of 0·7 and −0·8 e Å^{-3} and showed no peak which could be interpreted as an atom. Analysis of variance against $\sin\theta$ and against $|F|$ showed no unusual features; neither did the normal probabil-

ity plot. Atomic scattering factors, linear absorption coefficients, and f' and f'' values were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The *SHELXTL* suite of crystallographic programs (Sheldrick, 1983) was used throughout on a NOVA3 computer.

The atomic parameters are listed in Table 1 and principal bond lengths and angles are in Table 2.* The structure is illustrated in Fig. 1.

Discussion. The Pt lies on the crystallographic inversion centre; so the molecule must have the *trans* configuration. The whole molecule may be described in terms of three nearly orthogonal planes. Firstly the coordination plane of the Pt and the four S atoms. The benzene rings (necessarily parallel to each other) are inclined at 78·0° to this plane. Thirdly and perhaps surprisingly, the five non-H atoms of each SEt_2 group [*i.e.* S(2) and C(7) to C(10)] are closely coplanar (r.m.s. deviation 0·003 Å). These planes are inclined 94·5° to the Pt—S plane and 89·1° to the benzene ones.

The bond angles at the Pt atom are within 1° of the ideal values for square-planar coordination; those at the S atom are within 4° of the tetrahedral angle.

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Structure Cristalline et Electronique du Diiodure du Bis[(hydroxyiminométhyl-2 méthyl-1 pyridyl)-3 oxy]-1,3 Propane

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Abstract. $C_{17}H_{22}N_4O_4^{2+}.2I^-.H_2O$, $M_r = 618\cdot2$, monoclinic, $P2_1/n$, $a = 6\cdot772$ (3), $b = 13\cdot205$ (2), $c = 25\cdot805$ (4) Å, $\beta = 95\cdot83$ (3)°, $V = 2296$ Å^3, $Z = 4$, $D_x = 1\cdot789$ Mg m^{-3}, λ(Mo $K\alpha$) = $0\cdot7107$ Å, graphite monochromator, $\mu = 28\cdot1$ cm^{-1}, $F(000) = 1208$, $T = 298$ K, $R = 0\cdot058$ for the 2114 observed reflections. The title compound is a powerful activator of acetylcholinesterase. The positively charged organic cation envelops one I^- anion. CNDO calculations show the perturbation of the molecular orbitals by one of the I^- anions. Crystal cohesion depends both on hydrogen bonds and electrostatic interactions.

Introduction. Les organophosphorés inhibent l'acétylcholinestérase (AChE) irréversiblement en phosphorylant l'hydroxyle de la serine du site actif enzymatique. Les oximes nucléophiles, dérivés de sels d'aldoximes de pyridinium, sont susceptibles de déplacer le groupement phosphate, rétablissant l'activité enzymatique et sont, pour cette raison, utilisés comme agents thérapeutiques (Schoene, 1976).

De nouveaux réactivateurs de l'AChE ont été synthétisés. Ce sont des sels de bis[(hydroxyiminométhyl)-2 méthyl-1] pyridinium où les deux entités chargées sont reliées par une chaîne alkyldioxy. Ce sont actuellement les réactivateurs les plus puissants contre le tabun et le paraoxon; le dérivé possédant une chaîne propyldioxy est aussi un bon réactivateur de l'AChE inhibée par le sarin (Demerseman, Kiffer, Debussche, Lion, Royer & Sentenac-Roumanou, 1988).

Nous présentons ici la structure cristalline et l'étude théorique de ce dernier composé, dont la formule peut être représentée par le schéma suivant; m_1 et m_2 représentent les deux parties, en principe identiques, de cette molécule, π_1 et π_2, les deux cycles pyridinium.
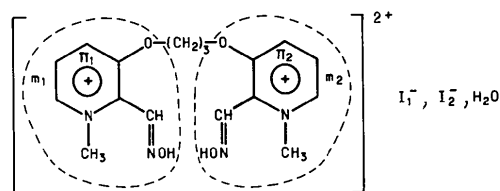
Partie expérimentale. Des cristaux ont été obtenus par diffusion de méthanol dans une solution aqueuse du composé; dimensions du cristal: $0,2 \times 0,4 \times 0,8$ mm; 25 réflexions avec θ compris entre 13 et 19° ont été utilisées pour le réglage du cristal; largeur de balayage $\Delta\omega = (2,0 + 0,35\mathrm{tg}\theta)$°, largeur de fente du détecteur de $(1,4 + 1,1\mathrm{tg}\theta)$°; mesure des intensités diffractées avec un diffractomètre Enraf–Nonius CAD-4 pour $\sin\theta/\lambda < 0,54$ Å^{-1} ($h < 7$, $k < 15$, $l < 29$) avec un balayage ω–2θ; correction d'absorption expérimentale; pas de décroissance des intensités de référence $0\bar{2}3$, $\bar{2}64$ et $\bar{4}00$; 2114 réflexions indépendantes avec $I > 2,5\sigma(I)$ ont été obtenues; la structure a été résolue grâce au programme *MITHRIL* (Gilmore, 1984); les atomes d'hydrogène ont été placés en position théorique sauf ceux de la molécule