

Table 3. Torsion angles ($^{\circ}$) involving the piperidine ring

	Molecule A	Molecule B
N(1)–C(2)–C(3)–C(4)	–55.2 (5)	–55.5 (8)
C(2)–C(3)–C(4)–C(5)	54.1 (5)	53.7 (8)
C(3)–C(4)–C(5)–C(6)	–53.9 (5)	–54.9 (8)
C(4)–C(5)–C(6)–N(1)	56.0 (4)	57.1 (7)
C(5)–C(6)–N(1)–C(2)	–60.8 (4)	–61.6 (7)
C(6)–N(1)–C(2)–C(3)	56.0 (4)	61.1 (7)

exception (other than the present work) being that of $\text{Cu}(\text{S}_2\text{CNMePh})_2$, where the dimer formation is prevented by the steric hindrance of the phenyl rings.

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Acta Cryst. (1988). **C44**, 1381–1383

[Di(azathien)-1-yl- S^1, N^4]bis(triethylphosphine)platinum(II) Hexafluorophosphate

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(Received 5 November 1987; accepted 22 April 1988)

Abstract. $[\text{Pt}(\text{HN}_2\text{S}_2)(\text{C}_6\text{H}_{15}\text{P})_2][\text{PF}_6]$, $M_r = 669.51$, monoclinic, $P2_1/n$, $a = 8.716$ (3), $b = 20.335$ (10), $c = 13.590$ (5) Å, $\beta = 99.47$ (3) $^{\circ}$, $V = 2376$ Å 3 , $Z = 4$, $D_x = 1.88$ Mg m $^{-3}$, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 15.22$ mm $^{-1}$, $F(000) = 1304$, room temperature, $R = 0.042$ for 2176 observed reflections with $|F_o| > 3\sigma(|F_o|)$. The structure of $[\text{Pt}(\text{PEt}_3)(\text{S}_2\text{N}_2\text{H})][\text{PF}_6]$ consists of channels of cations and anions. The cation has normal square-planar geometry with Pt–P distances of 2.320 (3) and 2.270 (3), Pt–S 2.282 (3), Pt–N 2.022 (9) Å. The S–Pt–N and P–Pt–P angles are 83.5 (2) and 97.5 (1) $^{\circ}$, respectively. The PtS_2N_2 ring contains two short [1.570 (9), 1.536 (10) Å] and one long [1.659 (10) Å] S–N bonds. The interplanar separations between adjacent cations are 4.06 (2) and 4.22 (2) Å.

Introduction. Several metal–sulfur–nitrogen compounds containing phosphine ligands have been reported (Kelly & Woollins, 1986; Jones, Kelly, Williams & Woollins, 1988). One particularly interesting feature of complexes of the type $[\text{Pt}(\text{PR}_3)_2(\text{S}_2\text{N}_2\text{H})]X$ ($X = \text{PF}_6$, BF_4 , Cl) is that in the solid state the cations and anions pack into channels. The dependence of the interplanar

separation between adjacent cations in $[\text{Pt}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{N}_2\text{H})]X$, (2), on the nature of the anion has been investigated (Jones *et al.*, 1988) but the effect of the nature of the phosphine is poorly understood. Here we report on the structure of $[\text{Pt}(\text{PEt}_3)_2(\text{S}_2\text{N}_2\text{H})][\text{PF}_6]$, (1), in comparison with (2).

Experimental. Single crystals of (1), suitable for X-ray crystallography, were grown at room temperature from dichloromethane/hexane and had m.p. 549 K. Crystal size 0.10 × 0.12 × 0.22 mm. Refined unit-cell parameters obtained from setting angles of 12 reflections with $8.7 \leq \theta \leq 23.9^{\circ}$. Nicolet R3m diffractometer. 2441 independent reflections ($\theta \leq 50^{\circ}$) measured, Cu $K\alpha$ radiation (graphite monochromator), ω scan. 2176 [$|F_o| > 3\sigma(|F_o|)$] considered observed, index range $h - 8/8$, $k 0/20$, $l 0/13$; two check reflections measured every 50 reflections, net count constant; Lorentz and polarization corrections, analytical absorption correction (face indexed crystal), max. and min. transmission factors 0.37 and 0.16. Structure solved by heavy-atom method; non-hydrogen atoms refined anisotropically; PF_6 anion refined as a rigid body; N(1) hydrogen atom refined isotropically; positions of

remaining H atoms calculated (C—H 0.96 Å); H atoms assigned isotropic thermal parameters, $U(H) = 1.2 \times U_{eq}(C)$, and allowed to ride on parent C atoms; methyl groups refined as rigid bodies. An empirical extinction correction was applied [$g = 0.0011(1)$]. Refinement using F magnitudes by block-cascade full-matrix least squares; $R = 0.042$, $wR = 0.045$ [$w^{-1} = \sigma^2(F) + 0.00062F^2$]. $S = 1.508$. $(\Delta/\sigma)_{max} = 0.100$; residual electron density in difference map within -0.75 and 1.19 e \AA^{-3} ; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

Discussion. The structure of (1) with the atom numbering is shown in Fig. 1. Table 1* lists the fractional atomic coordinates of the non-hydrogen atoms and Table 2 the bond lengths and angles. The structure consists of [Pt(PEt₃)₂(S₂N₂H)]⁺ cations and PF₆⁻ anions. Within the cations the Pt—P distances [Pt—P(1) 2.320 (3), Pt—P(2) 2.270 (3) Å] are typical for Pt^{II} complexes and similar to those in [Pt-(PMe₂Ph)₂(S₂N₂H)][PF₆], (3) [2.305 (2), 2.262 (2) Å, respectively], and [Pt(PEt₃)₂(S₂N₂H)][Me₃SnCl₃], (4) [2.306 (4), 2.263 (3) Å] (Jones *et al.*, 1988). The metal—ligand distances in (1) [Pt—S(2) 2.282 (3), Pt—N(1) 2.022 (9) Å] are close to those in (3) and (4) [2.282 (2) and 2.038 (7); 2.281 (4) and 2.091 (9) Å, respectively]. Within the PtS₂N₂ metallacycle the S—N distances in (1) are within statistical significance the same as those in (3) and (4). The cations in (1) stack in a similar fashion to those in (2) with the PtS₂N₂H rings partially overlaying each other (Fig. 2). In the case of

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44979 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

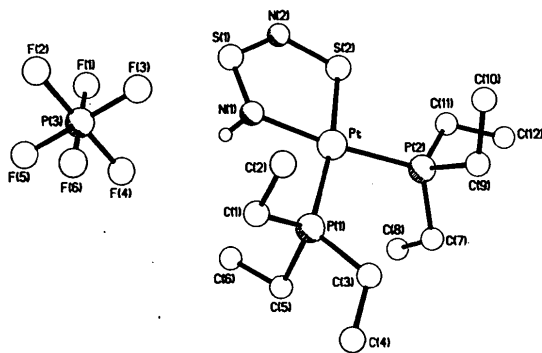


Fig. 1. Ball-and-stick representation of the structure of (1) showing the atomic numbering scheme.

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

	x	y	z	U_{eq} *
Pt	-2532 (1)	885 (1)	1028 (1)	53 (1)
S(1)	-2254 (5)	24 (2)	-868 (2)	102 (1)
S(2)	-2750 (4)	-232 (1)	1061 (2)	90 (1)
P(1)	-2385 (3)	2007 (1)	750 (2)	58 (1)
P(2)	-2775 (3)	936 (1)	2664 (2)	60 (1)
N(1)	-2236 (12)	730 (4)	-398 (6)	78 (3)
N(2)	-2508 (14)	-479 (4)	-67 (7)	102 (3)
C(1)	-1155 (16)	2212 (6)	-148 (12)	149 (3)
C(2)	556 (16)	1991 (8)	211 (19)	269 (3)
C(3)	-1874 (21)	2563 (2)	1749 (10)	133 (3)
C(4)	-1895 (17)	3314 (2)	1528 (11)	115 (3)
C(5)	-4431 (14)	2364 (5)	347 (9)	153 (3)
C(6)	-5162 (14)	1959 (5)	-591 (9)	135 (3)
C(7)	-4244 (5)	1485 (5)	3001 (8)	84 (3)
C(8)	-5934 (6)	1327 (7)	2484 (9)	111 (3)
C(9)	-1023 (11)	1195 (5)	3478 (8)	75 (3)
C(10)	418 (14)	754 (7)	3415 (12)	138 (3)
C(11)	-3256 (16)	138 (5)	3140 (3)	86 (3)
C(12)	-3443 (19)	136 (7)	4260 (4)	137 (3)
P(3)	-1901 (2)	1301 (1)	-3177 (1)	84 (1)
F(1)	-2707 (3)	615 (1)	-3276 (2)	151 (3)
F(2)	-729 (3)	1061 (1)	-3851 (2)	133 (3)
F(3)	-781 (3)	1057 (1)	-2236 (1)	160 (3)
F(4)	-3070 (3)	1540 (1)	-2503 (2)	149 (3)
F(5)	-3022 (3)	1543 (1)	-4118 (2)	175 (3)
F(6)	-1093 (3)	1985 (1)	-3079 (2)	220 (3)

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

Table 2. Bond lengths (Å) and angles ($^\circ$)

Pt—S(2)	2.282 (3)	Pt—P(1)	2.320 (3)
Pt—P(2)	2.270 (3)	Pt—N(1)	2.022 (9)
S(1)—N(1)	1.570 (9)	S(1)—N(2)	1.536 (10)
S(2)—N(2)	1.659 (10)	P(1)—C(1)	1.801 (16)
P(1)—C(3)	1.766 (10)	P(1)—C(5)	1.920 (12)
P(2)—C(7)	1.814 (9)	P(2)—C(9)	1.811 (10)
P(2)—C(11)	1.821 (11)	C(1)—C(2)	1.557 (19)
C(3)—C(4)	1.557 (6)	C(5)—C(6)	1.562 (16)
C(7)—C(8)	1.557 (9)	C(9)—C(10)	1.557 (17)
C(11)—C(12)	1.558 (9)	P(3)—F(1)	1.557 (3)
P(3)—F(2)	1.557 (3)	P(3)—F(3)	1.557 (2)
P(3)—F(4)	1.557 (3)	P(3)—F(5)	1.556 (2)
P(3)—F(6)	1.555 (2)		
S(2)—Pt—P(1)	171.9 (1)	S(2)—Pt—P(2)	90.3 (1)
P(1)—Pt—P(2)	97.5 (1)	S(2)—Pt—N(1)	83.5 (2)
P(1)—Pt—N(1)	88.8 (2)	P(2)—Pt—N(1)	173.3 (2)
N(1)—S(1)—N(2)	108.3 (5)	Pt—S(2)—N(2)	105.0 (3)
Pt—P(1)—C(1)	113.1 (4)	Pt—P(1)—C(3)	121.2 (3)
C(1)—P(1)—C(3)	105.7 (7)	Pt—P(1)—C(5)	110.1 (4)
C(1)—P(1)—C(5)	110.4 (6)	C(3)—P(1)—C(5)	94.8 (6)
Pt—P(2)—C(7)	117.3 (3)	Pt—P(2)—C(9)	114.0 (4)
C(7)—P(2)—C(9)	103.1 (4)	Pt—P(2)—C(11)	111.8 (2)
C(7)—P(2)—C(11)	104.2 (5)	C(9)—P(2)—C(11)	105.2 (5)
Pt—N(1)—S(1)	122.6 (5)	S(1)—N(2)—S(2)	120.5 (6)
P(1)—C(1)—C(2)	111.5 (12)	P(1)—C(3)—C(4)	119.1 (9)
P(1)—C(5)—C(6)	105.6 (8)	P(2)—C(7)—C(8)	114.4 (8)
P(2)—C(9)—C(10)	113.9 (8)	P(2)—C(11)—C(12)	114.7 (7)
F(1)—P(3)—F(2)	89.9 (2)	F(1)—P(3)—F(3)	89.9 (1)
F(2)—P(3)—F(3)	90.0 (1)	F(1)—P(3)—F(4)	90.0 (2)
F(2)—P(3)—F(4)	180.0 (4)	F(3)—P(3)—F(4)	89.9 (1)
F(1)—P(3)—F(5)	90.0 (1)	F(2)—P(3)—F(5)	90.0 (1)
F(3)—P(3)—F(5)	180.0 (4)	F(4)—P(3)—F(5)	90.1 (1)
F(1)—P(3)—F(6)	180.0 (2)	F(2)—P(3)—F(6)	90.0 (2)
F(3)—P(3)—F(6)	90.0 (1)	F(4)—P(3)—F(6)	90.1 (2)
F(5)—P(3)—F(6)	90.1 (1)		