

*Acta Cryst.* (1975). B31, 305**Tetrakis-(2-thienyldifluorophosphine)nickel**

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**Abstract.** Ni[PF<sub>2</sub>(C<sub>4</sub>H<sub>3</sub>S)]<sub>4</sub>, NiP<sub>4</sub>F<sub>8</sub>S<sub>4</sub>C<sub>16</sub>H<sub>12</sub>, tetragonal,  $P\bar{4}2_1c$ ,  $a = 10.120$  (2),  $c = 12.427$  (2) Å,  $M = 667.03$ ,  $Z = 2$ ,  $D_x = 1.74$  g cm<sup>-3</sup>. Tetrahedral coordination is observed at nickel with a very short Ni-P bond length of 2.093 (3) Å. There is no interaction between the sulphur atoms of the thiophene rings and the central nickel atom. The mean P-F bond length of 1.579 (5) Å is similar to that of 1.569 (1) Å observed in PF<sub>3</sub>.

**Introduction.** Cell dimensions were determined from measurements of 15 high- $2\theta$ -angle reflexions with Mo  $K\alpha_1$  radiation ( $\lambda = 0.70926$  Å). The intensities, from an approximately spherical crystal (dimension 0.015 cm) sealed in a Lindemann glass capillary, were collected on a Syntex  $P2_1$  four-circle diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. Measurements were carried out in the  $\theta$ - $2\theta$  mode at scan speeds varying linearly between 2.02° min<sup>-1</sup> (150 c.p.s. and below) and 29.30° min<sup>-1</sup> (3500 c.p.s. and above). Scan and background times were equal. Three standard reflexions did not display any significant variations. Of the 1338 reflexions recorded, 287 (21.4%) were rejected because the net count was less than 1.96 $\sigma$  based on the counting statistics. Lorentz and polarization, but no absorption [ $\mu(\text{Mo } K\alpha) = 13.9$  cm<sup>-1</sup>] corrections were applied. When equivalent reflexions had been averaged (internal consistency  $R$  index = 0.024), 573 unique reflexions were obtained.

The observed systematic absences  $hhl$  ( $l$  odd) and  $h00$  ( $h$  odd) uniquely designated  $P\bar{4}2_1c$  as the space group. A difference synthesis based on the nickel atoms alone, which for  $Z = 2$  must occupy twofold special positions  $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , yielded the locations of the phosphorus and sulphur atoms. The remaining non-hydrogen atoms were located from subsequent difference syntheses; positional parameters and anisotropic temperature-factor components were refined by full-matrix least-squares calculations. At this stage  $R_G = [\sum w\Delta^2 / \sum wF_o^2]^{1/2}$  had converged to 0.066 with a corresponding  $R_w = \sum w^{1/2}\Delta / \sum w^{1/2}F_o$  of 0.059. A difference synthesis then clearly revealed the positions of the three hydrogen atoms. However, an attempt to allow their positional parameters and isotropic temperature factors to refine freely was abandoned after it led to unreasonable C-H lengths. The hydrogen atom positions were, therefore, introduced as fixed parameters in the final cycles, with an overall isotropic temperature factor which subsequently refined to 0.024 (16) Å<sup>2</sup>. The terminal value of  $R_G$  was 0.057 with  $R_w = 0.053$  and

$R = 0.050$ .\* The weights adopted were those obtained from the counting statistics where a standard deviation  $\sigma(I) = t[N_s + N_b]^{1/2}$  was assigned to each net intensity  $I$ ,  $t$  being the scan rate,  $N_s$  the gross count and  $N_b$  the total background count. Complex neutral-atom scattering factors (Cromer, 1965; Cromer & Waber, 1965) were employed. The final atom coordinates are listed in Table 1 and their anisotropic temperature-factor components in Table 2. The full covariance matrix was implemented in the estimation of the bond lengths and selected bond angles presented in Tables 3 and 4.

Table 1. *Atom positional parameters* ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
Ni	0	0	0
P	537 (3)	1562 (3)	-1013 (2)
S	1966 (4)	4193 (4)	-1375 (3)
F(1)	-579 (6)	2112 (6)	-1773 (5)
F(2)	1548 (8)	1235 (6)	-1949 (5)
C(2)	1224 (10)	3073 (10)	-538 (8)
C(3)	1261 (11)	3471 (11)	525 (9)
C(4)	1900 (14)	4722 (13)	591 (10)
C(5)	2298 (14)	5195 (14)	-308 (11)

Table 2. *Anisotropic temperature factors* (Å<sup>2</sup>  $\times 10^3$ )

The anisotropic temperature factor takes the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Ni	42 (1)	42 (1)	38 (1)	0	0	0
P	53 (1)	44 (1)	41 (1)	-1 (1)	2 (1)	-4 (1)
S	120 (3)	67 (2)	81 (2)	13 (2)	10 (2)	-31 (2)
F(1)	85 (5)	84 (5)	70 (4)	21 (4)	-35 (4)	-16 (4)
F(2)	121 (6)	65 (4)	76 (4)	-11 (4)	49 (5)	-6 (4)
C(2)	41 (6)	50 (6)	70 (6)	8 (6)	3 (5)	1 (5)
C(3)	63 (7)	48 (6)	64 (6)	-12 (6)	-5 (6)	-2 (5)
C(4)	96 (10)	71 (10)	74 (8)	-19 (7)	-13 (8)	13 (8)
C(5)	96 (10)	59 (9)	115 (10)	9 (8)	-14 (9)	-13 (8)

Table 3. *Bond lengths* (Å)

Ni—P	2.093 (3)	P—C(2)	1.781 (11)
P—F(1)	1.574 (6)	P—F(2)	1.584 (6)
S—C(2)	1.711 (10)	S—C(5)	1.703 (14)
C(2)—C(3)	1.382 (13)	C(4)—C(4)	1.280 (16)
C(3)—C(4)	1.424 (17)		

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30676 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Bond angles ( $^{\circ}$ )

P' and P'' have the following equivalent positions relative to P: P'(-x, -y, z), P''(y, -x, -z).

P—Ni—P'	106.1 (2)	P—Ni—P''	111.2 (2)
Ni—P—F(1)	116.2 (3)	Ni—P—F(2)	116.9 (3)
No—P—C(2)	123.4 (4)	F(1)—P—F(2)	95.6 (4)
F(1)—P—C(2)	100.1 (4)	F(2)—P—C(2)	99.8 (4)
P—C(2)—S	122.6 (6)	P—C(2)—C(3)	125.3 (8)
C(2)—S—C(5)	90.4 (6)	C(3)—C(2)—S	112.1 (9)
C(4)—C(3)—C(2)	109.0 (11)	C(5)—C(4)—C(3)	115.1 (12)
S—C(5)—C(4)	113.3 (11)		

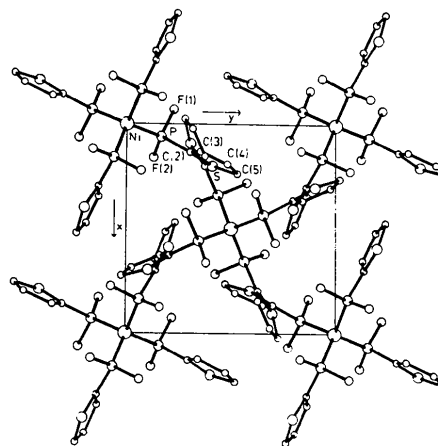


Fig. 1. Projection of the structure perpendicular to [001] with atom numbering.

**Discussion.** 2-Thienyldifluorophosphine reacts with nickel carbonyl to yield white crystals (m.p. 135–136 $^{\circ}$ ) of the tetra-substituted derivative (I), tetrakis-(2-thienyldifluorophosphine)nickel (Röschentaler & Schmutzler, 1974). By analogy with the results of two electron-diffraction studies of Ni(PF<sub>3</sub>)<sub>4</sub> (Almenningen, Andersen & Astrup, 1970; Marriott, Salthouse, Ware & Freeman, 1970) a shortening of the Ni–P bond length, in comparison with that found in other (non-fluoro)-phosphine complexes of nickel, is to be expected in (I). In fluorophosphine complexes, in particular those containing the zero-valent metal,  $\pi$  back-donation of the nickel *d*-electrons into the empty 3*d* phosphorus orbitals should be favoured because the energy of these orbitals will be reduced by the highly electronegative fluorine atoms. A crystal-structure analysis of (I) has been carried out in view of this and because the possibility exists that the sulphur atom of the thiophene ring could behave as a donor ligand to nickel.

The results confirm that tetrahedral coordination is observed at nickel [P–Ni–P 106.1 (2) and 111.2 (2) $^{\circ}$ ] (Fig. 1) with the sulphur atom displaying no donor activity towards the nickel atom (Ni...S 4.99 Å). The Ni–P bond length of 2.093 (3) Å is similar to those of 2.099 (3) and 2.116 (10) Å observed in the two studies of Ni(PF<sub>3</sub>)<sub>4</sub>. These values are of the order of 0.2 Å shorter than those observed in other (non-fluoro)-phosphine complexes of nickel (Sheldrick & Stelzer, 1973) as is to be expected in accordance with the above reasoning. It is interesting to note, however, that a much smaller degree of bond shortening is observed (Sheldrick & Stelzer, 1973) in NiBr<sub>2</sub>(PFBu<sub>2</sub>)<sub>2</sub> [Ni–P 2.232 (3) Å]. Contributing factors in this case may be the presence of divalent nickel, of only one fluorine on the phosphorus or of a different hybridization in this square-planar complex as opposed to the tetrahedral complexes.  $\sigma$ -donation from the highest filled orbital of PF<sub>3</sub> might be expected to shorten,  $\pi$ -acceptance into the first virtual orbital of PF<sub>3</sub> to lengthen the P–F bond distance in (I). In fact, in common with Ni(PF<sub>3</sub>)<sub>4</sub>, these factors would appear to be almost balanced, with the mean P–F bond length of 1.579 (5) Å not significantly different from that of 1.569 (1) Å observed in PF<sub>3</sub> (Morino, Kuchitsu & Moritani, 1969). The P–C bond length of 1.781 (11), however, is significantly shorter than those of 1.828 (3) and 1.841 (3) Å found in the trivalent phosphorus compounds, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P and

(CH<sub>3</sub>)<sub>3</sub>P respectively (Daly, 1964; Lide & Mann, 1958). In addition, the Ni–P–C bond angle of 123.4 (4) $^{\circ}$  shows a much greater distortion from the perfect tetrahedral value than those of 116.2 (3) and 116.9 (3) $^{\circ}$  obtained for the two Ni–P–F angles.

With the exception of the curiously short C(4)–C(5) length of 1.280 (16) Å and the subsequent associated distortion of the ring angles at C(2) and C(3), there are no significant differences between the dimensions of the thiophene ring in (I) and those obtained in a microwave study of the free molecule (Bak, Christensen, Rastrup-Anderson & Tannenbaum, 1956).

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