The reliability of the dimensions of this compound is disappointingly low; indeed the data reported here are the third attempt with the sample. Previously the crystals had required absorption corrections and the refinements had converged at $R = 0\cdot07$, with a needle-shaped fragment cut from a larger crystal and $R = 0\cdot09$ with a less-regular fragment. Although R is $0\cdot04$ in this third attempt, the resolution of the structure is not much improved.

It seems therefore that there is some other factor inherent in the crystal structure which is causing the poor resolution. The two most likely possibilities are either some static disorder, or large molecular librations. The molecule possesses an approximate C_2 axis (Fig. 1a) which passes through the Fe atom and bisects the C(22)–C(23) bond. Operation around this axis would exchange O(1) with H(211) and H(212) with the π electrons on C(24) but otherwise would interchange similar atoms. The space actually occupied by C(24)–O(1) and C(21)–H(211) with C(21)–H(212) is approximately equivalent so an attempt was made to refine the structure with the two possible orientations present simultaneously. Both orientations were refined as rigid bodies (André, Fourme & Renaud, 1972) with each given a single occupation factor. The value of each occupation factor was refined and the sum of them both was kept equal to one. The refinement converged with one occupation factor at one and the other zero. The difference Fourier series at this stage had no unusual features, so that significant static disorder is unlikely.

The temperature factors of C(13), C(14), C(21) and C(22) are unusually large, and this suggests a libration of the C(11)–C(15) ring pivoting somewhere close to C(11) and involving the atoms on either side [i.e. C(13), C(14) in the ring and C(21), C(22) attached to it]. A van der Waals plot (Watkin, 1972) shows that the molecules are not as closely packed as is usual although there are no gross interstices. This absence of strong intermolecular attractions fits in with the observed significant vapour pressure of the crystal and is not inconsistent with large molecular librations. These librations therefore are the most reasonable explanation for the poor resolution of the structure.

References

ANDRÉ, D., FOURME, R. & RENAUD, M. (1972). *Acta Cryst.* A**28**, 458–463.

BARR, T. H., BOULTON, E. S., LENTZNER, H. L. & WATTS, W. E. (1969). *Tetrahedron*, **25**, 5245–5253.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JONES, N. D., MARSH, R. E. & RICHARDS, J. H. (1965). *Acta Cryst.* **19**, 330–336.

SHELDRICK, G. M. (1976). *X-ray System Report.* Univ. of Cambridge, England.

SHUL'PIN, G. B. & RYBINSKAYA, M. I. (1974). *Russ. Chem. Rev.* **43**, 716–732.

WATKIN, D. J. (1972). *Acta Cryst.* A**28**, 33–35.

WATTS, W. E. (1967). *Organomet. Chem. Rev.* **2**, 231–254.

Two Modifications of Bis[(2-thienyl)methyldithiophosphinato]nickel(II)

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Abstract. $Ni(C_5H_6PS_3)_2$, $C_{10}H_{12}NiP_2S_6$, monoclinic, $P2_1/c$, $Z = 2$, $M_r = 445\cdot25$. Modification A: $a = 8\cdot499$ (4), $b = 6\cdot513$ (4), $c = 16\cdot413$ (7) Å, $\beta = 108\cdot91$ (4)°, $D_m = 1\cdot70$, $D_x = 1\cdot72$ Mg m^{-3}, μ(Mo $K\alpha$) $= 2\cdot04$ mm^{-1}. Modification B: $a = 7\cdot964$ (4), $b = 11\cdot640$ (10), $c = 9\cdot439$ (3) Å, $\beta = 106\cdot52$ (3)°, $D_m = 1\cdot67$, $D_x = 1\cdot76$ Mg m^{-3}, μ(Mo $K\alpha$) $= 1\cdot99$ mm^{-1}. The crystal structures of modifications A and B were refined to $R = 0\cdot04$. Both molecules are centrosymmetric with Ni at $\bar{1}$; thus the thienyl and methyl groups are *trans* with respect to the plane of the four-coordinated Ni atoms. The thienyl rings show a twofold disorder with the predominating orientation opposite in both structures.

Introduction. The crystal structures of several $Ni(S_2PR^1R^2)_2$ complexes with identical substituents R have been reported: CH_3 (Jones, Ansell & Katz, 1969), C_2H_5 (Shetty & Fernando, 1969), C_6H_5 (Porta, Sgamellotti & Vinciguerra, 1968), CH_3O (Kastalsky & McConnell, 1969), and C_2H_5O (McConnell & Kastalsky, 1967). In all these structures there is a planar

NiS_4 arrangement with the Ni atom at a crystallographic centre of symmetry. The compound under study is the first dithiophosphinato complex of Ni^{II} with different substituents R^1 and R^2. Thus, cis and trans isomers are possible. To determine the configurations of modifications A and B, their crystal structures were studied.

The preparation of the title compound has been reported by Diemert & Kuchen (1977); crystals were received from these authors. The compound crystallizes as deep-purple needles (modification A) together with a few (<0·1%) rhombic prisms (modification B) of identical colour. For both modifications the systematic absences were unique for space group $P2_1/c$. The lattice parameters were determined from optimized diffractometer angles. The intensities of all symmetry-independent reflections with $7 \le 2\theta \le 55°$ were measured on a paper-tape-driven diffractometer (Siemens AED) with β-filtered Mo $K\alpha$ radiation, a variable $\theta/2\theta$ scan and the five-value-measurement technique. After elimination of a few reflections with inconsistent intensities $[|I(\text{right}) + I(\text{left}) - I(\text{total})| > 3\sigma_I]$ the sets of data contained 1980 (A) and 1936 (B) reflections, all classified as observed. The phase problem was solved by the Patterson method. The thienyl rings show orientational disorder around the P—C bond, more or less superposing C(3) with C(4), and C(2) with S(3). For the latter two positions the scattering factors of S were used and the population factors were refined to

0·556 (5) and 0·810 (4) in A, and 0·465 (5) and 0·869 (4) in B. The sums of these values, 1·366 in A and 1·334 in B, agree well with the expected relative number of electrons, $(16 + 6)/16 = 1·375$. Thus the atoms designated S(3) and C(2) in this paper are S_xC_{1-x} and $S_{1-x}C_x$ with average x values of 0·70 in A and 0·82 in B. All H atoms except those at the disordered C(2) could be located and were included with isotropic temperature factors in the refinement (110 variables) converging at $R = 0·039$, $R_w = 0·042$ (A) and $R = 0·041$, $R_w = 0·048$ (B) for all reflections. Scattering factors were taken from Cromer & Mann (1968), except those for H (Stewart, Davidson & Simpson, 1965). The scattering factors of Ni were corrected for anomalous dispersion. The weights were derived from counter statistics by $1/w = \sigma_F^2$. All calculations were performed with XRAY 72 on a Cyber 72/76 computer. Tables 1 and 2 contain the final positional parameters.*

Discussion. Both molecules have a trans configuration with the Ni atom at a crystallographic centre of

Table 1. *Positional parameters* $(\times 10^4)$*, with e.s.d.'s in parentheses, of modifications A and B*

	Modification A			Modification B		
	x	y	z	x	y	z
Ni	0	0	0	0	0	0
S(1)	2335 (1)	1838 (1)	500 (0)	−2553 (1)	−683 (1)	192 (1)
S(2)	−708 (1)	1097 (1)	1126 (0)	856 (1)	206 (1)	2454 (1)
S(3)	4184 (1)	3873 (2)	3088 (1)	−2105 (1)	2162 (1)	3051 (1)
P	1409 (1)	2744 (1)	1429 (0)	−1575 (1)	−331 (1)	2361 (1)
C(1)	2724 (3)	2197 (4)	2496 (2)	−2738 (4)	761 (2)	3012 (3)
C(2)	2652 (3)	33 (3)	2913 (1)	−4293 (4)	566 (3)	3539 (3)
C(3)	4061 (4)	433 (6)	3778 (2)	−4734 (7)	1732 (4)	3922 (6)
C(4)	4844 (4)	2236 (6)	3894 (2)	−3747 (5)	2583 (3)	3731 (4)
C(5)	1077 (5)	5463 (5)	1408 (2)	−1628 (5)	−1555 (3)	3494 (4)

Table 2. *Hydrogen-atom positional parameters* $(\times 10^3)$ *and isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

The H atoms are bonded to the C atoms with the identical first digit of the labelling.

	Modification A				Modification B			
	x	y	z	B	x	y	z	B
H(3)	421 (4)	−40 (5)	413 (2)	6 (1)	−518 (5)	180 (4)	415 (5)	3 (1)
H(4)	556 (5)	267 (6)	436 (3)	7 (1)	−400 (4)	333 (4)	392 (4)	5 (1)
H(51)	216 (5)	615 (6)	152 (3)	7 (1)	−73 (8)	−140 (5)	424 (7)	13 (2)
H(52)	48 (5)	582 (6)	85 (3)	8 (1)	−150 (6)	−241 (4)	291 (5)	9 (1)
H(53)	72 (5)	593 (6)	182 (3)	9 (1)	−261 (6)	176 (3)	337 (4)	6 (1)

symmetry. Fig. 1 shows bond lengths between non-hydrogen atoms; the corresponding bond angles are listed in Table 3. Distances and angles involving the H atoms are in the expected range and are not reported. In both molecules the Ni atom is coordinated by four S atoms in an almost perfect square. The average bond length and the average bond angle are Ni—S 2·236 Å and S(1)—Ni—S(2) 88·30°. The geometry of the Ni coordination is in agreement with that of the complexes

Table 3. Bond angles (°) in Ni(C₅H₆PS₃)₂

The e.s.d.'s are 0·03–0·05° in the four-membered ring and 0·1–0·4° otherwise.

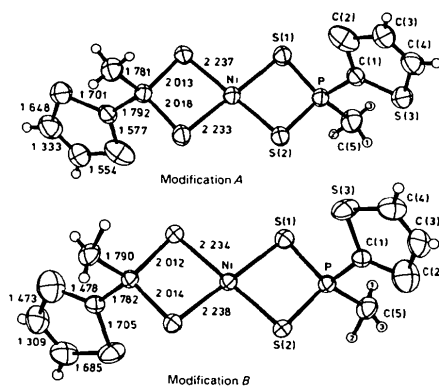|	Modification A	Modification B
S(1)—Ni—S(2)	88·29	88·31
Ni—S(2)—P	85·23	85·13
S(2)—P—S(1)	101·14	101·36
P—S(1)—Ni	85·21	84·97
S(1)—P—C(1)	114·2	114·0
S(1)—P—C(5)	111·8	112·2
S(2)—P—C(1)	111·3	110·6
S(2)—P—C(5)	113·5	114·0
C(1)—P—C(5)	105·1	105·0
P—C(1)—S(3)	122·9	120·7
P—C(1)—C(2)	120·3	125·0
S(3)—C(1)—C(2)	116·7	114·3
C(1)—C(2)—C(3)	96·9	102·8
C(2)—C(3)—C(4)	118·6	118·0
C(3)—C(4)—S(3)	115·5	113·2
C(4)—S(3)—C(1)	92·2	91·7

Fig. 1. Molecules of Ni(C₅H₆PS₃)₂, modifications A and B, in comparable, arbitrary crystallographic orientations with thermal ellipsoids at 50% probability (ORTEP II; Johnson, 1976) and bond lengths in Å. The e.s.d.'s are: Ni—S, S—P 0·001; P—C 0·002–0·004; C—S, C—C 0·003–0·007 Å. Because of the disorder the thermal ellipsoids of the thienyl rings are enlarged. The H atoms of the methyl group are identified by the last digit of their labelling and are shown with radii of 0·1 Å².

cited above. The four-membered chelate rings have an average S—P length of 2·014 Å. The P atoms are about 0·1 Å out of the NiS₄ plane, thus reducing the distance between Ni and the thienyl ring and increasing the Ni—C(methyl) distance. The tetrahedral configuration around the P atoms is distorted, with angles between 101·2 and 114·2°. The static disorder of the thienyl ring around P—C(1) affects the positional and thermal parameters of C(2), C(3), C(4) and S(3), and falsifies the standard geometry of a thienyl ring. The bond lengths and angles given have at best to be interpreted as the average of a 70:30 (A) and 18:82 (B) superposition of two rings rotated by π. Static or dynamic disorder of thiophene rings has been observed in several structures, e.g. tri(3-thienyl)phosphine (Hazell, Hazell & Pawley, 1977) and 5,5'-bis[dimethyl(2-thienyl)-silyl]-2,2'-bithienyl (Lipka & von Schnering, 1977).

The four-membered rings are planar within 0·03 (A) and 0·04 Å (B); the atoms of the thienyl ring deviate less than 0·008 (A) and 0·001 Å (B) from coplanarity. The essential difference in the molecular geometry of (A) and (B) is the predominating orientation of the thienyl rings given by the dihedral angle C(5)—P—C(1)—S(3), which is 32·5 in A and −144·2° in B. The packing of the molecules is different in the two modifications. In A there is a short intermolecular distance from Ni to a methyl group [Ni···C(5) 3·7 Å], whereas in B a thienyl ring has Ni···S(3) 3·9 and Ni···C(4) 4·0 Å.

References

CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–324.

DIEMERT, K. & KUCHEN, W. (1977). Phosphorus Sulfur, 3, 131–136.

HAZELL, A. C., HAZELL, R. G. & PAWLEY, G. S. (1977). Acta Cryst. B33, 1105–1108.

JOHNSON, C. K. (1976). ORTEP II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

JONES, P. E., ANSELL, G. B. & KATZ, L. (1969). Acta Cryst. B25, 1939–1943.

KASTALSKY, V. & MCCONNELL, J. F. (1969). Acta Cryst. B25, 909–915.

LIPKA, A. & VON SCHNERING, H. G. (1977). Chem. Ber. 110, 1377–1381.

MCCONNELL, J. F. & KASTALSKY, V. (1967). Acta Cryst. 22, 853–859.

PORTA, P., SGAMELLOTTI, A. & VINCIGUERRA, N. (1968). Inorg. Chem. 7, 2625–2629.

SHETTY, P. S. & FERNANDO, Q. (1969). Acta Cryst. B25, 1294–1298.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.