

**(2,2'-Bipyridyl)bis(O,O'-dimethyl dithiophosphato)nickel(II)**

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**Abstract.**  $(C_{10}H_8N_2) \cdot [(CH_3O)_2PS_2]_2Ni$ ,  $M_r = 529.22$ , monoclinic,  $C2/c$  (systematic absences  $hkl$   $h + k \neq 2n$ ,  $h0l$   $l \neq 2n$ ,  $0k0$   $k \neq 2n$ ),  $a = 12.131$  (6),  $b = 15.102$  (9),  $c = 13.972$  (8) Å,  $\beta = 121.06$  (4)°,  $Z = 4$ ,  $D_c = 1.581$ ,  $D_m = 1.547$  g cm<sup>-3</sup>,  $\mu = 8.9$  cm<sup>-1</sup> [ $\lambda(\text{Mo } K\alpha) = 0.71073$  Å]. The structure was refined to a final  $R$  value of 0.030 for 1587 reflexions. The bidentate ligand, 2,2'-bipyridyl, forms a *cis* adduct. The three chelate rings are approximately at right angles to each other.

**Introduction.** The structures of the adducts formed with heterocyclic ligands containing N donor atoms and planar Ni<sup>II</sup> chelates of dialkyl dithiophosphates have been reported (Ooi & Fernando, 1967; Shetty & Fernando, 1970), and were based on photographic data. The standard deviations of the bond distances in the heterocyclic ligands were large and therefore no attempt was made to evaluate the effect of the Ni atom on the coordinated N heterocycle. The structure of the *cis* adduct that was formed with 2,2'-bipyridyl and bis(O,O'-dimethyl dithiophosphato)nickel(II), Ni(dmp)<sub>2</sub>, was reported (Ooi, Carter & Fernando, 1968), but the refinement of the structure was not completed. New data for this adduct were collected on an automated diffractometer and the atomic parameters refined. The results show the effect of the Ni atom on the structural parameters of the coordinated 2,2'-bipyridyl.

Green needle-shaped crystals in the monoclinic space group  $Cc$  or  $C2/c$  were obtained from an ethanol solution of 2,2'-bipyridyl and Ni(dmp)<sub>2</sub>. The structure was solved with the data collected on a Buerger diffractometer (Ooi, Carter & Fernando, 1968).

New data were collected with a crystal that measured  $0.08 \times 0.10 \times 0.45$  mm mounted along the  $c$  axis. A Syntex four-circle computer-controlled diffractometer with a graphite monochromator and pulse-height analyzer was used for the collection of diffraction intensities. The cell constants were determined by a least-squares treatment of 13 reflections. The  $\theta$ - $2\theta$  scan technique was employed at a constant scan rate of  $1.0^\circ$  min<sup>-1</sup> (in  $2\theta$ ). The scan range varied from  $2.0^\circ$  at  $2\theta = 3^\circ$  to  $2.3^\circ$  at  $2\theta = 50^\circ$ . One-half of the total scan time

was spent counting background at each end of the scan range. 2165 reflections with  $2\theta < 50^\circ$  were collected. There were no significant variations in the intensities of three check reflections that were monitored after every 100 reflections. Standard deviations were assigned in the usual manner (Corfield, Doedens & Ibers, 1967) and a value of 0.02 was assigned to  $p$ , the empirical parameter. The net counts were corrected for Lorentz and polarization effects. Only those reflexions (1587) for which the net counts exceeded three times the corresponding e.s.d.'s were used in the structure refinement. Isotropic refinement of the structure was carried out to an  $R_1$  index,  $(\sum |F_o - |F_c||) / \sum F_o$ , of 0.076; anisotropic refinement gave  $R_1 = 0.052$ . At this stage a difference Fourier map revealed the positions of all the H atoms. Subsequent anisotropic refinement of the nonhydrogen atoms reduced  $R_1$  to 0.030 and  $R_2$ ,  $[\sum w(F_o - |F_c|)^2] / \sum wF_o^2$ , to 0.032. The refinement was based on  $F_o$ , and the quantity minimized was  $\sum w(F_o - |F_c|)^2$ . The

Table 1. Atomic positions ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
Ni	5000 (0)	219 (0)	2500 (0)
S(1)	2795 (1)	116 (1)	2252 (1)
S(2)	4076 (1)	-933 (1)	1018 (1)
P	2644 (1)	-897 (1)	1304 (1)
O(1)	1300 (3)	-967 (2)	182 (2)
O(2)	2547 (3)	-1760 (2)	1904 (2)
N	4529 (3)	1272 (2)	1416 (2)
C(1)	4743 (3)	2076 (2)	1889 (3)
C(2)	4492 (4)	2840 (3)	1265 (3)
C(3)	4012 (4)	2776 (3)	130 (3)
C(4)	3801 (4)	1964 (3)	-348 (3)
C(5)	4072 (4)	1227 (3)	314 (3)
C(6)	976 (6)	-373 (5)	-726 (5)
C(7)	2643 (8)	-2623 (4)	1536 (6)
H(C2)	4664 (41)	3340 (29)	1594 (35)
H(C3)	3833 (44)	3291 (31)	-311 (40)
H(C4)	3478 (42)	1887 (29)	-1208 (38)
H(C5)	3932 (36)	650 (26)	19 (32)
H1(C6)	1505 (55)	-391 (36)	-980 (45)
H2(C6)	1256 (69)	82 (48)	-129 (59)
H3(C6)	117 (63)	-355 (43)	-1208 (54)
H1(C7)	3515 (63)	-2654 (43)	1638 (54)
H2(C7)	1954 (65)	-2686 (44)	810 (57)
H3(C7)	2639 (54)	-3027 (40)	2013 (47)

scattering factors used were those of Hanson, Herman, Lea & Skillman (1964). Corrections were made for the anomalous dispersion of Ni and S atoms. The values used were  $\Delta f' = 0.4$  and  $\Delta f'' = 1.2$  for Ni and  $\Delta f' = 0.1$  and  $\Delta f'' = 0.2$  for S.

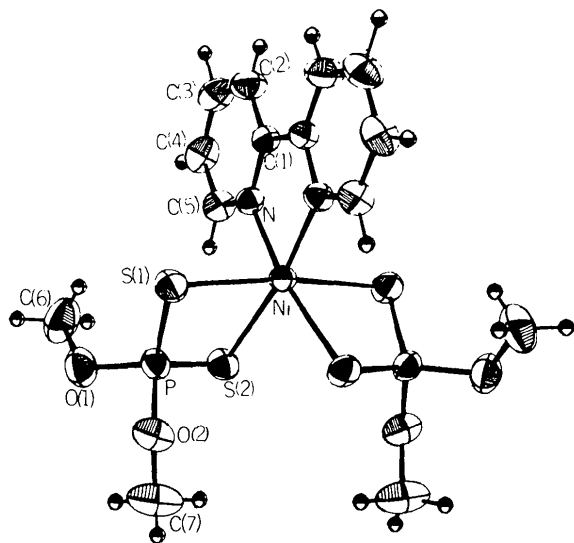


Fig. 1. The molecular configuration of (2,2'-bipyridyl)bis(O,O'-dimethyl dithiophosphato)nickel(II).

Table 2. Bond distances (Å) and bond angles (°) involving non-hydrogen atoms

Ni-S(1)	2.519 (2)	S(1)-Ni-S(2)	81.46 (10)
Ni-S(2)	2.485 (2)	S(1)-Ni-S'(1)	172.89 (12)
Ni-N	2.063 (3)	S(1)-Ni-N	94.28 (16)
S(1)-P	1.970 (2)	S(1)-Ni-N'	91.20 (11)
S(2)-P	1.973 (2)	S(2)-Ni-N	95.35 (16)
P-O(1)	1.577 (3)	S(2)-Ni-N'	170.51 (16)
P-O(2)	1.587 (3)	S(2)-Ni-S'(1)	93.54 (12)
N-C(1)	1.342 (4)	S(2)-Ni-S'(2)	91.12 (11)
C(1)-C(2)	1.382 (5)	N-Ni-N'	79.12 (13)
C(2)-C(3)	1.382 (6)	Ni-S(1)-P	82.16 (10)
C(3)-C(4)	1.356 (6)	Ni-S(2)-P	83.02 (11)
C(4)-C(5)	1.375 (6)	S(1)-P-S(2)	111.82 (11)
C(5)-N	1.343 (5)	S(1)-P-O(1)	114.18 (15)
O(2)-C(7)	1.427 (7)	S(1)-P-O(2)	106.76 (16)
O(1)-C(6)	1.433 (7)	S(2)-P-O(1)	111.35 (15)
C(1)-C'(1)	1.485 (5)	S(2)-P-O(2)	113.44 (16)
		P-O(1)-C(6)	120.57 (32)
		P-O(2)-C(7)	121.14 (42)
		Ni-N-C(1)	115.24 (27)
		N-C(1)-C'(1)	115.19 (29)
		N-C(1)-C(2)	121.40 (33)
		C(1)-C(2)-C(3)	119.44 (39)
		C(1)-N-C(5)	118.09 (29)
		C(2)-C(3)-C(4)	119.28 (40)
		C(2)-C(1)-C'(1)	123.41 (37)
		C(3)-C(4)-C(5)	118.76 (38)
		C(4)-C(5)-N	123.03 (34)
		C(5)-N-Ni	125.65 (29)

**Discussion.** The final positional parameters are given in Table 1. The unique bond lengths and bond angles together with their standard deviations (in parentheses) are given in Table 2.\* Fig. 1 shows the ORTEP drawing of the molecule. As expected, the N atoms of the bidentate ligand, 2,2'-bipyridyl, occupy *cis* positions in the hexacoordinated Ni complex. There is a small but significant difference in the Ni-S distances. In the equatorial plane of the coordination polyhedron, the Ni-S(2) bond (2.485 Å) is shorter than the Ni-S(1) bond (2.519 Å) since S(2) lies opposite a N atom and S(1) lies opposite a S atom. The Ni-N distances in the hexacoordinated adducts of dialkyl dithiophosphates with N heterocycles lie between 2.11 Å for the bipyridine adduct (Ooi & Fernando, 1967) and 2.08 Å for the 1,10-phenanthroline adduct (Shetty & Fernando, 1970). The Ni-N distance (2.063 Å) in the 2,2'-bipyridyl adduct is slightly shorter. The rest of the distances in the dialkyl dithiophosphate moiety are normal.

The 2,2'-bipyridyl molecule is planar and the two N atoms are in a *trans* configuration in the solid state (Merritt & Schroeder, 1956). A certain amount of distortion in each of the heterocyclic rings is caused by the presence of two short C-N bonds in each ring. The ring distortion is also evident in the chelated 2,2'-bipyridyl which has assumed a *cis* configuration since the heterocyclic rings are free to rotate about the C(1)-C'(1) single bond. The 2,2'-bipyridyl and the chelate ring formed with the two N donor atoms and the Ni atom are coplanar. In the coordinated bipyridyl ligand the two C-N bonds are shorter than the C-C bonds. One of these C-C bonds however, C(3)-C(4), is significantly shorter than the other three C-C bonds.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32774 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

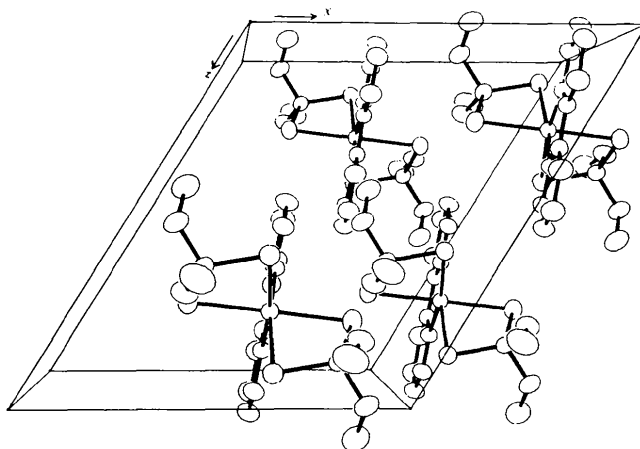


Fig. 2. Molecular packing in the unit cell.

A similar trend has been found in the 2,2'-bipyridyl that is coordinated to Mn in the complex trinitrato-2,2'-bipyridylmanganese(III) (Einstein, Johnson & Sutton, 1972).

The packing of the molecules in the unit cell is shown in Fig. 2. There are no intermolecular distances less than 3.5 Å.

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## 1-{1-[3-(2- $\alpha,\alpha,\alpha$ -Trifluoromethyl-10-phenothiazinyl)propyl]-4-piperidinyl}-2-benzimidazolinone

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**Abstract.** C<sub>28</sub>H<sub>27</sub>N<sub>4</sub>OF<sub>3</sub>S, FW 524.6, monoclinic, C2/c,  $a = 24.497$  (6),  $b = 5.802$  (1),  $c = 36.573$  (9) Å,  $\beta = 102.73$  (4)°,  $Z = 8$ ,  $t = 25^\circ\text{C}$ . The molecules form centrosymmetric dimers linked through the amide groups.

**Introduction.** The title compound is a neuroleptic phenothiazine derivative. The space group was determined from photographs. The final cell dimensions and intensities were measured on a Hilger & Watts computer-controlled four-circle diffractometer. The instrumental settings are given in Table 1.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Full-matrix least-squares

refinement was performed with the *SDP 75* program system (Okaya & Frenz, 1975) and gave a final  $R$  of 0.10 for all observed reflexions. The scattering factors were those of *International Tables for X-ray Crystallography* (1974). The final coordinates are listed in Table 2. Fig. 1 gives bond lengths and angles and the atomic numbering.\*

**Discussion.** The phenothiazine group is folded along the S—N(1) line, the angle between the planes of the benzene rings being 149°. The conformation of the molecule is defined by the torsion angles given in Table 3.

Folding of the side chain involves van der Waals interactions between the benzimidazolinone group and the F substituents: C(27)—F(1) 3.56, C(27)—F(2) 3.77 Å.

The angle between the least-squares mean plane of

Table 1. *Instrumental settings for the data collection*

Source: Mo  $K\alpha$ ;  $\lambda = 0.7107$  Å;  $\omega$ - $2\theta$  step scan  
 $\theta_{\max} = 58^\circ$   
 Confidence level: 3.0  
 Total number of independent reflexions: 3527  
 Total observed: 2221

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32762 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.