

## The Crystal and Molecular Structure of Bis(diethyldithiophosphinato)nickel(II)

BY P. S. SHETTY AND QUINTUS FERNANDO

*Department of Chemistry, University of Arizona, Tucson, Arizona, U.S.A.*

(Received 27 June 1968)

The crystal structure of bis(diethyldithiophosphinato)nickel(II),  $\text{Ni}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$ , has been determined from three-dimensional X-ray diffraction data. The crystals are monoclinic in the space group  $C2/m$  with two molecules in a unit cell of dimensions  $a = 8.25$ ,  $b = 12.80$ ,  $c = 8.17 \text{ \AA}$ ,  $\beta = 104^\circ 10'$ . The structure consists of discrete molecular units of nickel(II) chelates containing four-membered chelate rings. The coordination around the nickel atom is planar and the stereochemistry of the phosphorus atoms is approximately tetrahedral.

Two isomeric forms of bis(diethyldithiophosphinato)nickel(II),  $\text{Ni}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$ , have been synthesized (Malatesta & Pizzotti, 1945, 1946; Malatesta, 1947), and have been reported to be two stereoisomers in which the spatial arrangement of the atoms around the phosphorus atoms in the two compounds are different. Although two forms of the nickel(II) chelate were isolated by the reported method, one form (the  $\alpha$ -form) was shown to be bis(diethyldithiophosphinato)nickel(II) and the second form (the  $\beta$ -form) was shown to be a mixture of bis(diethyldithiophosphinato)nickel(II) and bis(*O*-ethylethyldithiophosphinato)nickel(II),  $\text{Ni}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)(\text{C}_2\text{H}_5)]_2$ . These conclusions were arrived at primarily on the basis of chemical and spectroscopic evidence (Shetty, Jose, & Fernando, 1968). We have undertaken three-dimensional X-ray structure determinations of the two nickel(II) chelates in order to verify the structures we have postulated. The results of the structure determination of bis(diethyldithiophosphinato)nickel(II),  $\text{Ni}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$ , are reported here.

### Experimental

Bis(diethyldithiophosphinato)nickel(II) was prepared as follows (Malatesta & Pizzotti, 1945, 1946; Malatesta, 1947): ethyl bromide was treated with phosphorus pentasulphide suspended in ether and refluxed for 12 hours. The product was decomposed by the addition of water and the aqueous layer was neutralized, clarified with animal charcoal, acidified with dilute hydrochloric acid and extracted with diethyl ether. The ether extract was dried over sodium sulfate and an ammonium salt was precipitated by passing ammonia through the dried ether extract. The salt was separated, dissolved in water and an excess  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  was added. The resulting solution was extracted with benzene and the crude bis(diethyldithiophosphinato)nickel(II) which was obtained on evaporation of the benzene was purified by repeated fractional crystallization from ethanol. Single crystals of the compound which were grown from an ethanol-acetone mixture were tabular and appeared to be either blue or purple in reflected as well as in transmitted light (m.p.  $142^\circ$ ).

Cell constants calculated from oscillation and Weissenberg photographs taken around all three axes with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) are as follows:

$\text{Ni}(\text{S}_2\text{PC}_4\text{H}_{10})_2$ ; Formula weight = 364.9.

$a = 8.25 \pm 0.02$ ,  $b = 12.80 \pm 0.02$ ,  $c = 8.17 \pm 0.02 \text{ \AA}$ ,  $\beta = 104^\circ 10' \pm 30'$ ;  $V = 836.5 \text{ \AA}^3$ ; observed density =  $1.45 \text{ g.cm}^{-3}$  (by flotation in an aqueous zinc chloride solution), calculated density =  $1.448 \text{ g.cm}^{-3}$  for  $Z = 2$ ;  $F(000) = 380$ ; systematic absence of reflections  $hkl$  when  $h + k = 2n + 1$  is characteristic of the space groups  $C2$ ,  $Cm$  or  $C2/m$ .

Three small crystals were used in obtaining the photographs for intensity measurements. The  $c$  axis data were taken with a crystal mounted along the needle axis. The  $a$  and  $b$  axis data were taken with two crystals that were cut from a larger crystal. The cross-sectional areas of all three crystals were approximately equal ( $0.3 \times 0.2 \text{ mm}$ ). The intensity data were determined visually on equi-inclination Weissenberg photographs, obtained using the multiple-film technique and Cu  $K\alpha$  radiation. A total of 680 non-zero independent reflections ( $0kl$ ,  $h0l - h7l$ , and  $hk0 - hk4$ ) were measured visually by comparison with a calibrated density scale. The reflections on the various levels were placed on a common scale by the use of inter-layer scale factors which were calculated for the common reflections. The intensities were corrected for Lorentz and polarization factors in the usual manner. The atomic scattering factors used were those adopted in *International Tables for X-ray Crystallography* (1962). Dispersion corrections of  $-3.1$  electron were added to the scattering factor of Ni; the imaginary part of the dispersion correction was neglected.

### Structure analysis and refinement

A choice had to be made from among the three space groups  $C2$ ,  $Cm$ , and  $C2/m$ . The space group  $C2/m$  was chosen for the following reasons; bis(diethyldithiophosphinato)nickel(II) was expected to have a centrosymmetric structure analogous to the structures which have been reported for bis(dimethyldithiophosphinato)nickel(II) (Jones, Ansell & Katz, 1968), bis(benzo-

*O*-ethylthiophosphonato)nickel(II) (Hartung, 1967) and bis(*O,O'*-diethylthiophosphato)nickel(II) (Fernando & Green, 1967). The  $N(z)$  test (Howells, Phillips & Rogers, 1950) for the  $h0l$ ,  $0kl$  and  $hk0$  data (Fig. 1) showed centric intensity distributions in all projections.

In the space group  $C2/m$ , the nickel atom, which is the center of symmetry of the molecule, could be placed at (0,0,0) and the sulfur and phosphorus atoms in the  $a$ - $c$  plane. A two-dimensional Patterson synthesis from the  $h0l$  data showed the prominent nickel-sulfur and nickel-phosphorus vectors from which the approximate positions of the phosphorus and sulfur atoms were obtained. These positions were refined by successive Fourier and difference Fourier syntheses with isotropic temperature factors of  $4.0 \text{ \AA}^2$  for all atoms, until the conventional  $R$  value was 0.32. The carbon atoms in the trial structure were located from Fourier syntheses with the  $0kl$  data. Approximate fractional coordinates for all the atoms except hydrogen were then obtained from the three sets of data ( $h0l$ ,  $0kl$ , and  $hk0$ ) and the structure was refined by a full-matrix least-squares

technique with all the 680 observed reflections and individual atom isotropic temperature factors, until the  $R$  value was 0.14. At this stage the shifts in the atomic coordinates were within their standard deviations.

The linear absorption coefficient for the crystal is  $91.8 \text{ cm}^{-1}$ . Application of absorption corrections on the assumption that the crystal was approximately cylindrical (Bond, 1959), for the  $0kl$  and  $h0l-h7l$  data did not improve the  $R$  value significantly and therefore all the data were not corrected for absorption effects.

The structure was further refined by the least-squares technique with anisotropic temperature factors for all atoms. After three cycles of refinement the conventional  $R$  value was 0.106. The weighting scheme used was  $w = 1/(A + BF_o + CF_o^2)$  (Cruickshank, 1961) where  $A = 40$ ,  $B = 0.25$  and  $C = 0.005$ . The quantity minimized was  $\sqrt{\sum w(F_o - F_c)^2}$  and the maximum shift in the positional parameters as a fraction of the estimated standard deviations in the final refinement cycle was 0.08 for the carbon atom C(2). No attempt was made to locate the hydrogen atoms in this structure.

### Description of the structure

The fractional coordinates and estimated standard deviations of the atoms in the asymmetric unit are listed in Table 1, and the anisotropic temperature factors with their standard deviations in Table 2. The nickel atom lies at a center of symmetry and is coordinated to four sulfur atoms which lie in the  $a$ - $c$  plane. Therefore, the atoms Ni, S(1), S(2), P, S(1'), S(2') and P' all lie in the  $a$ - $c$  plane; atoms C(1) and C(2) are 1.41 and 2.77  $\text{\AA}$ , respectively, from this plane. The atoms P, C(1), C(2), C(1') and C(2') all lie on a plane perpendicular to the  $x$ - $z$  plane. The atoms, S(1) and S(2) are 1.53 and 1.54  $\text{\AA}$  from this plane.

Table 1. Positional parameters for the atoms in the asymmetric unit with their standard deviations

Atomic parameters have been multiplied by  $10^4$

	$x/a$	$y/b$	$z/c$
Ni	0	0	0
S(1)	259 (5)	0	2768 (5)
S(2)	-2757 (5)	0	-313 (5)
P	-2257 (5)	0	2205 (5)
C(1)	-3135 (15)	1115 (10)	3120 (16)
C(2)	-2531 (19)	2159 (11)	2532 (22)

The bond distances and bond angles with their estimated standard deviations (Cruickshank, 1949) are collected in Tables 3 and 4 and Fig. 2. The relative positions of the two molecules in the unit cell are shown in Fig. 3. The shortest van der Waals distance found was 3.77  $\text{\AA}$  between two sulfur atoms in different molecules. The average Ni-S distance is 2.22  $\text{\AA}$  which is the expected value for low-spin nickel(II) chelates containing four-membered chelate rings (Gaspari, Nardelli & Villa, 1967). The average P-S distance of 2.00  $\text{\AA}$  is almost identical with the P-S distance of  $2.01 \pm 0.01 \text{ \AA}$

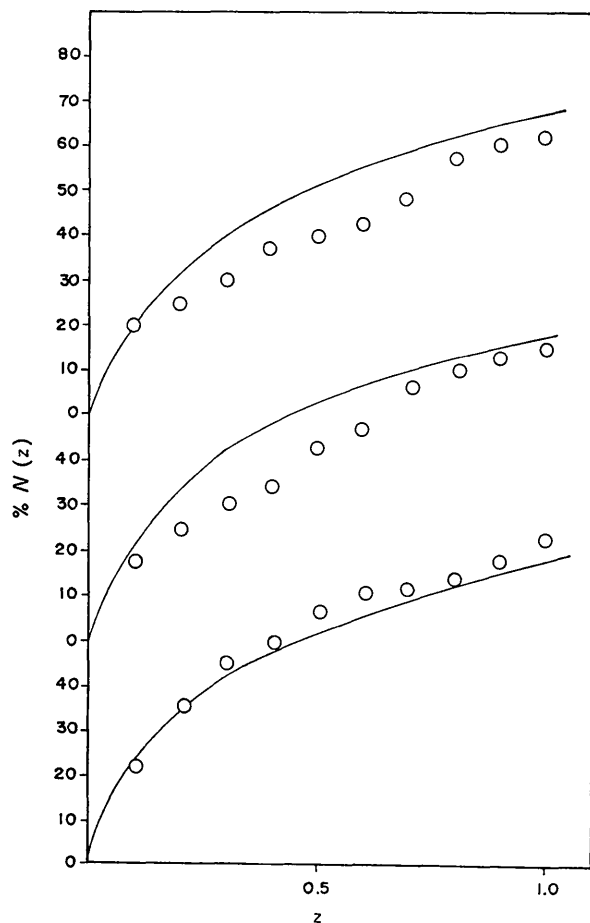


Fig. 1.  $N(z)$  Test for zones of reflections  $hk0$ ,  $0kl$  and  $h0l$  (from top to bottom in the Figure). The circles represent the experimental values and the solid lines are curves for  $\bar{I}$ .

Table 2. *Anisotropic thermal parameters with their standard deviations*

The general anisotropic temperature factor has the form

$$\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$$

	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Ni	855 (52)	358 (24)	1120 (56)	0	-46 (41)	0
S(1)	996 (56)	541 (29)	1124 (57)	0	-31 (46)	0
S(2)	955 (60)	744 (36)	1228 (64)	0	-119 (48)	0
C(1)	1449 (190)	503 (77)	1960 (219)	203 (102)	322 (168)	-182 (116)
C(2)	2559 (334)	499 (93)	3492 (393)	153 (139)	1103 (306)	150 (162)
P	983 (58)	340 (25)	1138 (59)	0	-7 (46)	0

found in bis(dimethyldithiophosphinato)nickel(II) (Jones, Ansell, & Katz, 1968). The P-C and the C-C distances are normal. The bond angles in the chelate ring assume the expected values and the two sulfur atoms and two carbon atoms around each phosphorus atom are in an approximately tetrahedral configuration

Table 3. *Interatomic distances and the standard deviations (e.s.d.'s in Å)*

Lattice errors have been taken into account in the calculation of e.s.d.'s.

Ni-S(1)	2.22	(0.01)
Ni-S(2)	2.23	(0.01)
P-S(1)	2.01	(0.01)
P-S(2)	2.00	(0.01)
P-C(1)	1.84	(0.01)
C(1)-C(2)	1.54	(0.02)

Table 4. *Bond angles and their standard deviations (degrees)*

S(1)-Ni-S(2)	87.6	(0.2)
Ni-S(1)-P	86.0	(0.3)
Ni-S(2)-P	86.2	(0.3)
S(2)-P-S(1)	100.2	(0.3)
S(1)-P-C(1)	113.2	(0.4)
S(2)-P-C(1')	114.6	(0.4)
C(1)-P-C(1')	101.7	(0.8)
P-C(1)-C(2)	110.8	(0.9)

The least-squares refinement cycles were calculated with *ORFLS* (Busing, Martin & Levy, 1962) and the estimated standard deviations in the bond distances and bond angles with *ORFFE* (Busing, Martin & Levy, 1964). The plots shown in Figs. 2 and 3 were obtained with *ORTEP* (Johnson, 1966).

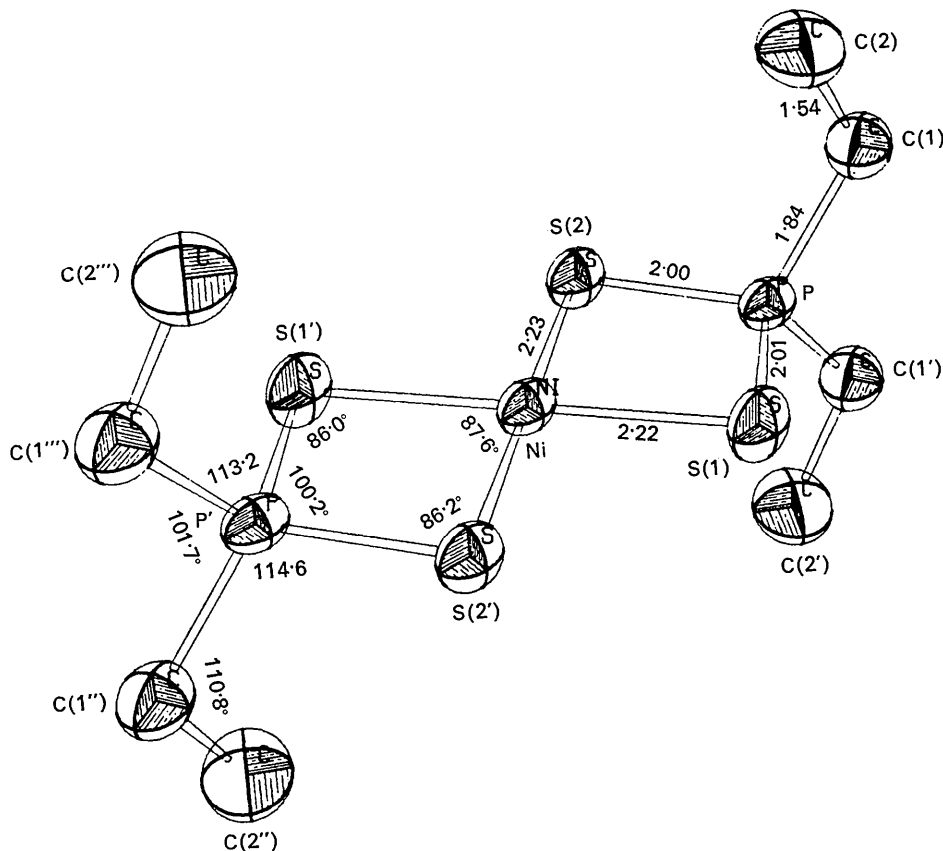
Fig. 2. Bond lengths and bond angles in  $\text{Ni}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$ .

Table 5. Observed and calculated structure factors

H				K				L				FC				FC			
H	K	L	FC	H	K	L	FC	H	K	L	FC	H	K	L	FC	H	K	L	FC
0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0	0	1
0	0	1	71.7	0	0	1	68.0	0	0	1	68.0	0	0	1	68.0	0	0	1	68.0
0	0	2	143.4	0	0	2	136.0	0	0	2	136.0	0	0	2	136.0	0	0	2	136.0
0	0	3	215.1	0	0	3	204.0	0	0	3	204.0	0	0	3	204.0	0	0	3	204.0
0	0	4	286.8	0	0	4	272.0	0	0	4	272.0	0	0	4	272.0	0	0	4	272.0
0	0	5	358.5	0	0	5	340.0	0	0	5	340.0	0	0	5	340.0	0	0	5	340.0
0	0	6	430.2	0	0	6	408.0	0	0	6	408.0	0	0	6	408.0	0	0	6	408.0
0	0	7	501.9	0	0	7	476.0	0	0	7	476.0	0	0	7	476.0	0	0	7	476.0
0	0	8	573.6	0	0	8	544.0	0	0	8	544.0	0	0	8	544.0	0	0	8	544.0
0	0	9	645.3	0	0	9	616.0	0	0	9	616.0	0	0	9	616.0	0	0	9	616.0
0	0	10	717.0	0	0	10	688.0	0	0	10	688.0	0	0	10	688.0	0	0	10	688.0
0	1	0	71.7	0	1	0	68.0	0	1	0	68.0	0	1	0	68.0	0	1	0	68.0
0	1	1	143.4	0	1	1	136.0	0	1	1	136.0	0	1	1	136.0	0	1	1	136.0
0	1	2	215.1	0	1	2	204.0	0	1	2	204.0	0	1	2	204.0	0	1	2	204.0
0	1	3	286.8	0	1	3	272.0	0	1	3	272.0	0	1	3	272.0	0	1	3	272.0
0	1	4	358.5	0	1	4	340.0	0	1	4	340.0	0	1	4	340.0	0	1	4	340.0
0	1	5	430.2	0	1	5	408.0	0	1	5	408.0	0	1	5	408.0	0	1	5	408.0
0	1	6	501.9	0	1	6	476.0	0	1	6	476.0	0	1	6	476.0	0	1	6	476.0
0	1	7	573.6	0	1	7	544.0	0	1	7	544.0	0	1	7	544.0	0	1	7	544.0
0	1	8	645.3	0	1	8	616.0	0	1	8	616.0	0	1	8	616.0	0	1	8	616.0
0	1	9	717.0	0	1	9	688.0	0	1	9	688.0	0	1	9	688.0	0	1	9	688.0
0	1	10	788.7	0	1	10	760.0	0	1	10	760.0	0	1	10	760.0	0	1	10	760.0
1	0	0	71.7	1	0	0	68.0	1	0	0	68.0	1	0	0	68.0	1	0	0	68.0
1	0	1	143.4	1	0	1	136.0	1	0	1	136.0	1	0	1	136.0	1	0	1	136.0
1	0	2	215.1	1	0	2	204.0	1	0	2	204.0	1	0	2	204.0	1	0	2	204.0
1	0	3	286.8	1	0	3	272.0	1	0	3	272.0	1	0	3	272.0	1	0	3	272.0
1	0	4	358.5	1	0	4	340.0	1	0	4	340.0	1	0	4	340.0	1	0	4	340.0
1	0	5	430.2	1	0	5	408.0	1	0	5	408.0	1	0	5	408.0	1	0	5	408.0
1	0	6	501.9	1	0	6	476.0	1	0	6	476.0	1	0	6	476.0	1	0	6	476.0
1	0	7	573.6	1	0	7	544.0	1	0	7	544.0	1	0	7	544.0	1	0	7	544.0
1	0	8	645.3	1	0	8	616.0	1	0	8	616.0	1	0	8	616.0	1	0	8	616.0
1	0	9	717.0	1	0	9	688.0	1	0	9	688.0	1	0	9	688.0	1	0	9	688.0
1	0	10	788.7	1	0	10	760.0	1	0	10	760.0	1	0	10	760.0	1	0	10	760.0
1	1	0	71.7	1	1	0	68.0	1	1	0	68.0	1	1	0	68.0	1	1	0	68.0
1	1	1	143.4	1	1	1	136.0	1	1	1	136.0	1	1	1	136.0	1	1	1	136.0
1	1	2	215.1	1	1	2	204.0	1	1	2	204.0	1	1	2	204.0	1	1	2	204.0
1	1	3	286.8	1	1	3	272.0	1	1	3	272.0	1	1	3	272.0	1	1	3	272.0
1	1	4	358.5	1	1	4	340.0	1	1	4	340.0	1	1	4	340.0	1	1	4	340.0
1	1	5	430.2	1	1	5	408.0	1	1	5	408.0	1	1	5	408.0	1	1	5	408.0
1	1	6	501.9	1	1	6	476.0	1	1	6	476.0	1	1	6	476.0	1	1	6	476.0
1	1	7	573.6	1	1	7	544.0	1	1	7	544.0	1	1	7	544.0	1	1	7	544.0
1	1	8	645.3	1	1	8	616.0	1	1	8	616.0	1	1	8	616.0	1	1	8	616.0
1	1	9	717.0	1	1	9	688.0	1	1	9	688.0	1	1	9	688.0	1	1	9	688.0
1	1	10	788.7	1	1	10	760.0	1	1	10	760.0	1	1	10	760.0	1	1	10	760.0

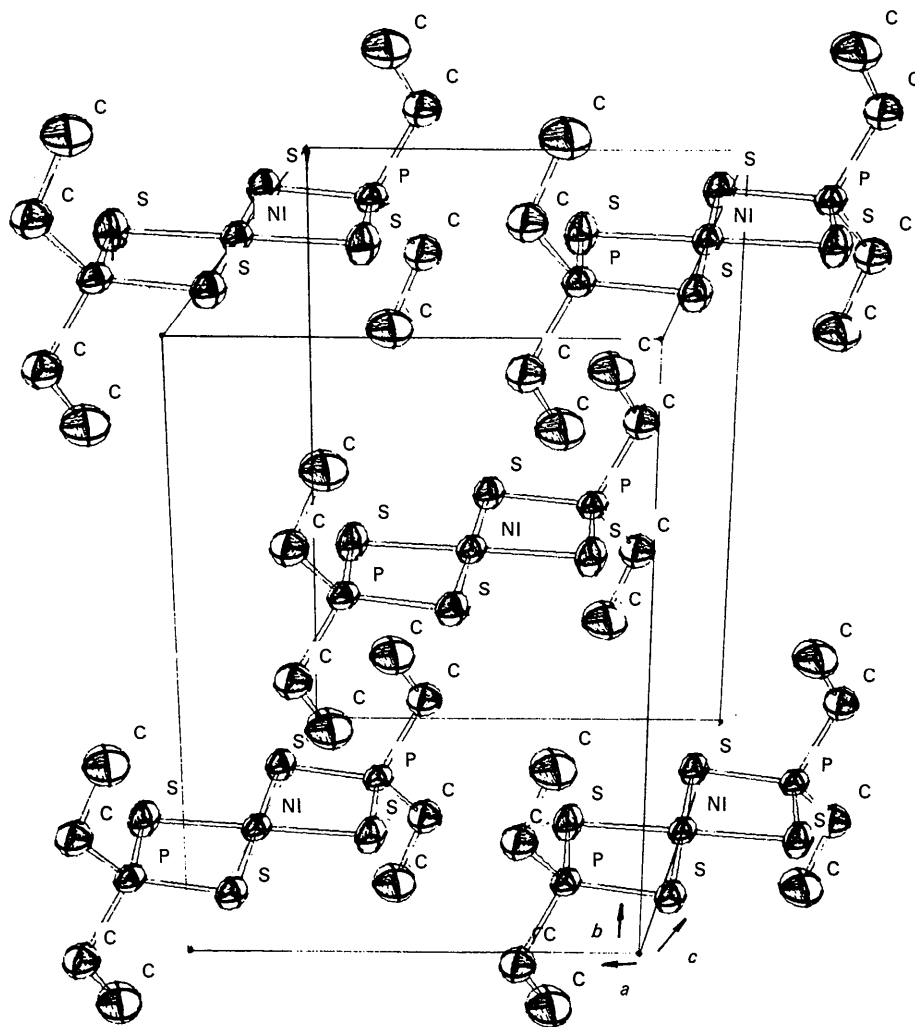


Fig. 3. Relative positions of the two molecules in the unit cell.

This work was supported by the National Science Foundation. We thank the University of Arizona Computer Center for services provided.

#### References

- BOND, W. L. (1959). *Acta Cryst.* **12**, 375.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least Squares Program*. U.S. Atomic Energy Commission Publication ORNL-TM-305.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE, A Fortran Crystallographic Function and Error Program*. U.S. Atomic Energy Commission Publication ORNL-TM-306.
- CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
- CRUICKSHANK, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Ed. R. PEPIŃSKY, J. M. ROBERTSON & J. C. SPEAKMAN, p. 45. Oxford: Pergamon Press.
- FERNANDO, Q. & GREEN, C. D. (1967). *J. Inorg. Nucl. Chem.* **29**, 647.
- GASPARRI, G. F., NARDELLI, M. & VILLA, A. (1967). *Acta Cryst.* **23**, 384.
- HARTUNG, H. (1967). *Z. Chem.* **7**(6), 241.
- HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
- International Tables for X-Ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1966). *ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structures*. U.S. Atomic Energy Commission Publication ORNL-3794.
- JONES, P. E., ANSELL, G. B. & KATZ, L. (1968). *Chem. Comm.* p. 78.
- MALATESTA, L. (1947). *Gazz. chim. ital.* **77**, 509.
- MALATESTA, L. & PIZZOTTI, R. (1945). *Chim. e Industr.* **27**, 6.
- MALATESTA, L. & PIZZOTTI, R. (1946). *Gazz. chim. ital.* **76**, 167.
- SHETTY, P. S., JOSE, P. & FERNANDO, Q. (1968). *Chem. Comm.* p. 788.