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The Crystal and Molecular Structure of Bis(dimethyldithiophosphato)nickel(II), Ni[(CH₃O)₂PS₂]₂

BY V. KASTALSKY AND J. F. MCCONNELL

School of Physics, University of New South Wales, Sydney, Australia

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Crystals of bis(dimethyldithiophosphato)nickel(II) are orthorhombic, space group *Pbca*, with $Z=4$. Unit-cell dimensions are $a=10.290\pm 0.002$, $b=8.640\pm 0.002$, $c=16.356\pm 0.004$ Å. The structure has been determined from a three-dimensional Patterson synthesis and a series of three-dimensional ρ and $A\rho$ syntheses, and refined by the method of full-matrix least squares. The molecular structure has been found to be similar to the ethyl compound, Ni[(C₂H₅O)₂PS₂]₂, but has been more accurately determined by use of scaled two-axis Weissenberg data and refined to a value of $R=0.075$. The molecule is centrosymmetric about the nickel atom, and the nickel and four sulphur atoms are in square-planar configuration. The Ni-S bond lengths of 2.22 and 2.23 Å agree very well with those found in the ethyl compound and other square-planar nickel(II) complexes.

Introduction

The structure of bis(diethyldithiophosphato)nickel(II) has been reported (McConnell & Kastalsky, 1967). The present structure of the corresponding methyl compound has been determined with a much greater accuracy ($R=0.075$ against 0.115), by means of three-dimensional data obtained about two axes. In the report on the ethyl compound, reservations were expressed with regard to the significance of the thermal ellipsoids obtained, in view of the fact that data had been obtained about one axis only, and were also considered less accurate than in the present case for other reasons. It is interesting to report that the molecular structure of the methyl compound is very similar, with thermal ellipsoids of the same general shape and orientation, thus tending to confirm the original tentative conclusions.

Both compounds are diamagnetic, deep purple in colour and highly soluble in both polar and non-polar solvents. This combination of properties was considered sufficiently unusual to warrant the structure determination of these two compounds in order to verify the theoretical predictions of a square-planar configuration of nickel and sulphur, with Ni-S distances of 2.1–2.3 Å (Lopez-Castro & Truter, 1963).

Experimental

Crystal data

Bis(dimethyldithiophosphato)nickel(II), Ni[(CH₃O)₂PS₂]₂.

Colour: deep purple, almost opaque.

Solubility: highly soluble in most organic solvents, both polar and non-polar; soluble also in water and very slightly in paraffin oil.

Unit-cell dimensions at 20°C:

$$\begin{aligned} a &= 10.290 \pm 0.002 \text{ \AA} , \\ b &= 8.640 \pm 0.002 \text{ \AA} , \\ c &= 16.356 \pm 0.004 \text{ \AA} . \end{aligned}$$

The errors quoted are three times the estimated standard deviation. Space group extinctions from Weissenberg photographs are:

$$\begin{aligned} 0kl: k &= 2n + 1 , \\ h0l: l &= 2n + 1 , \\ hk0: h &= 2n + 1 , \end{aligned}$$

indicating the orthorhombic space group *Pbca*.

Because of the high solubility of the substance, its density was estimated by measuring the dimensions and mass of a well developed crystal. Although the value determined in this way, 1.96 g.cm⁻³, was clearly of poor accuracy, it was sufficient to determine the number of molecules per unit cell as 4. The calculated density, using *Z* = 4, was 1.68 g.cm⁻³.

With four molecules in space group *Pbca*, the nickel atom must be in a special position at a centre of symmetry; the molecule is centrosymmetric with one half of each molecule occupying one of the eight general positions of the space group.

Accurate unit-cell dimensions were determined from *OkI* and *h0I* Weissenberg photographs obtained with crystals coated with silicon powder* as a calibrating substance.

The cell parameters and their standard deviations were obtained using a least-squares program written for the IBM 360/50 computer at the University of New South Wales.

Standards used:

$$\begin{aligned} \lambda(\text{Cu } K\alpha_1) &= 1.54051 \text{ \AA} , \\ \lambda(\text{Cu } K\alpha_2) &= 1.54433 \text{ \AA} . \end{aligned}$$

For Si line 444:

$$\theta(\text{Cu } K\alpha_2) = 80.100^\circ .$$

For Si line 642:

$$\theta(\text{Cu } K\beta_1) = 73.576^\circ .$$

Crystals used for the collection of intensity data were obtained by slow evaporation of an acetone solution at a few degrees below 0°C. They had a plate-like habit, and in nearly all cases had one dimension an order of magnitude smaller than the other two. Two crystals were selected.

Crystal I was a slab, approximately 0.17 × 0.17 × 0.05 mm, and crystal II was dissolved from a larger crystal to an approximately spherical shape of diameter 0.17 mm.

Using a Unicam Weissenberg camera and the multiple-film technique, 13 layers of *c* axis data, *hk0* through *hk12*, using crystal II, and 9 layers, *OkI* through

8kl, of *a* axis data, using crystal I were taken with Cu *Kα* radiation, and measured visually with the aid of a calibration strip. Intensities were corrected for Lorentz and polarization factors and for absorption.

For Cu *Kα* radiation, the linear absorption coefficient, μ , is 89.6 cm⁻¹. For the absorption correction to the *c* axis data it was considered to be sufficiently accurate to use the corrections given in *International Tables for X-ray Crystallography* (1952) for a spherical crystal with $\mu R = 0.76$. The *a* axis data were corrected using a program (*CDRABS*) written by G. Cox of the Australian Atomic Energy Commission for an IBM 7040 computer.

All photographs were taken at 20°C, and the number of reflexions measured (including unobserved) was 1338 about the *a* axis and 1248 about the *c* axis. 817 common reflexions were used for scaling and this resulted in a set of 1627 independent reflexions, including 354 unobserved. No corrections were made for extinction. During the determination of intensities the film factor of Morimoto & Uyeda (1963) of 2.93 for Ilford 'Industrial G' film was used, since a careful assessment of the attenuation ratios for the *hk0* and *OkI* photographs showed no deviation from this value.

The data were scaled by obtaining the best overall fit to the reflexions common to both axes, using as references the *2kl* and *hk1* sets of reflexions. Of the 817 common reflexions, 285 were rejected, some because of obvious unreliability and others because of poor agreement after rough scaling.

Weighting scheme

The structure factors obtained from reliable common reflexions were then divided into thirteen ranges. These were in steps of 5 electrons below 50, 50–60, 60–80 and greater than 80. For each range, calculations were

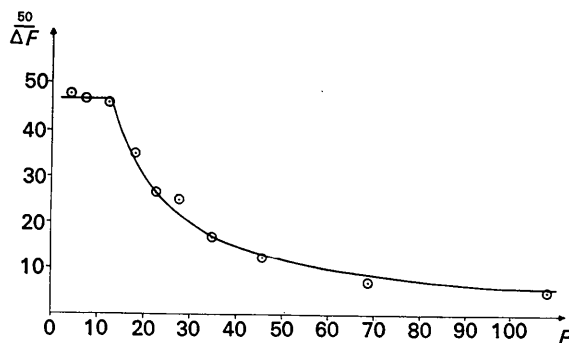


Fig. 1. Weighting curve.

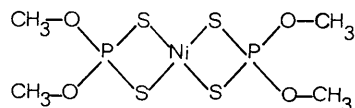


Fig. 2. Structural configuration for Ni[(CH₃O)₂PS₂]₂.

* Standardized Si powder was obtained from Dr W. Parrish, Philips Laboratories, Irvington-on-Hudson, New York, U.S.A.

made of the average value of the structure factor, \bar{F} , and of ΔF , where ΔF is the average value of the difference between scaled structure factors of different sets.

A plot $50/\Delta F$ against \bar{F} is shown in Fig. 1, together with the line which was taken as an approximation to the experimental curve for purposes of calculation. This gives for every $|F|$ an estimated standard deviation of

$$\sigma = \frac{\Delta F}{2} = \begin{cases} 0.52 & \text{for } |F| \leq 12.5 \\ \frac{|F|}{24} & \text{for } |F| > 12.5. \end{cases}$$

The above results were used to calculate the individual weight, w , from the relationship

$$w = 1/\sigma^2.$$

This weighting scheme, arrived at experimentally, is essentially the same as that used by Hughes (1941), and also proposed by Monahan, Schiffer & Schiffer (1967) with the essential feature of a constant percentage-error for reflexions above a certain magnitude. However, Jeffery (1967) has pointed out that this is true only for the case of negligible absorption. In the present case it was obtained experimentally after the absorption correction.

Preliminary structure determination

Initially, data of the type $0kl-8kl$, roughly scaled against the $hk0$ layer, were used for a three-dimensional unsharpened Patterson synthesis, which provided information about positions of the sulphur and phosphorus atoms with regard to the nickel atom at the origin. At this stage a series of pairs of ϱ and $\Delta\varrho$ syntheses using the same selected data proved to be quite successful in establishing the approximate positions of the oxygen and carbon atoms. The authors have found that the use of such pairs of ϱ and $\Delta\varrho$ syntheses, together with the Patterson map, is of considerable help

in the elimination of spurious features so common in the early stages of structure analysis. In this way the approximate configuration of atoms was found to be consistent with that shown in Fig. 2. The residual at this stage was 0.316 using an overall isotropic temperature factor of $B=4.5 \text{ \AA}^2$. This part of the computation was performed on UTECOM, a DEUCE computer.

Refinement of the structure

The refinement was carried out on the IBM 360/50 computer of the University of New South Wales, using the complete set of scaled data about the 'a' and 'c' axes. As described earlier, these data, $0kl$ to $8kl$ and $hk0$ to $hk12$, had been reduced, corrected for absorption and scaled, common reflexions had been averaged and all the data in a combined set individually weighted. At this stage, refinement was commenced by a full-matrix least-squares procedure, in which the function minimized was $\sum w(|F_o| - |F_c|)^2$. The programs by Busing, Martin & Levy were adapted for the 360/50 computer by Craig (1967). The scattering factors used were taken from *International Tables for X-ray Crystallography* (1962), but anomalous dispersion corrections were taken from the publication by Cromer (1965).

Atoms were assigned individual isotropic temperature factors and several cycles of refinement reduced the residual to 0.161. Unobserved reflexions had been removed from the refinement. At this stage anisotropic temperature factors were introduced and this reduced the residual to 0.102 in one cycle. Such a result indicated the possibility that the data were sufficiently good to locate hydrogen atoms, and it was decided, as a preliminary, to proceed with the refinement on high angle data only ($\sin \theta/\lambda > 0.3$) and to include unobserved reflexions in the refinement. Refinement on high angle data minimizes the effect of hydrogen atoms which, at such an advanced stage, may be regarded as a significant systematic error. Following Cruickshank & Pilling (1961) the common weight for unobserved reflexions had been adjusted in such a way

Table 1. *Positional and thermal parameters for the atoms in the asymmetric unit*

The B_{ij} 's are the coefficients in $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

All parameters have been multiplied by 10^4 .

| | $x(\sigma_x)$ | $y(\sigma_y)$ | $z(\sigma_z)$ | $B_{11}(\sigma_{B_{11}})$ | $B_{22}(\sigma_{B_{22}})$ | $B_{33}(\sigma_{B_{33}})$ | $B_{12}(\sigma_{B_{12}})$ | $B_{13}(\sigma_{B_{13}})$ | $B_{23}(\sigma_{B_{23}})$ |
|------|---------------|---------------|---------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| Ni | 0 | 0 | 0 | 125 (2) | 151 (2) | 36 (1) | 23 (1) | 1 (1) | 4 (1) |
| S(1) | 201 (2) | 111 (2) | -1349 (1) | 175 (2) | 204 (3) | 39 (1) | 45 (2) | 6 (1) | 4 (1) |
| S(2) | -826 (2) | 2379 (2) | -35 (1) | 185 (2) | 175 (3) | 46 (1) | 50 (2) | 4 (1) | 2 (1) |
| P | -635 (2) | 2169 (2) | -1234 (1) | 121 (2) | 169 (2) | 44 (1) | 9 (1) | -2 (1) | 17 (1) |
| O(1) | -1924 (5) | 2358 (5) | -1732 (3) | 134 (5) | 198 (7) | 59 (2) | -3 (5) | -17 (3) | 26 (3) |
| O(2) | 102 (4) | 3533 (6) | -1656 (3) | 145 (5) | 220 (8) | 61 (2) | -26 (5) | -1 (3) | 34 (3) |
| C(1) | -3030 (7) | 1372 (8) | -1551 (5) | 131 (8) | 214 (12) | 81 (4) | -14 (8) | -7 (4) | 2 (5) |
| C(2) | 1428 (7) | 3952 (11) | -1443 (5) | 137 (9) | 267 (14) | 88 (5) | -25 (9) | 7 (5) | 6 (7) |
| H(1) | -3073 | 1448 | -960 | | | | | | |
| H(2) | -3927 | 1778 | -1888 | | | | | | |
| H(3) | -2711 | 496 | -1815 | | | | | | |
| H(4) | 1293 | 4186 | -905 | | | | | | |
| H(5) | 1299 | 4925 | -1842 | | | | | | |
| H(6) | 1952 | 3078 | -1576 | | | | | | |

The isotropic temperature factor used for all hydrogen atoms is $B=8.5 \text{ \AA}^2$.

Table 2. Observed and calculated structure factors (10 × absolute scale)

| h | k | l | F _o | F _c | U |
|-----|---|---|----------------|----------------|---|
| 1 | 0 | 0 | 100 | 100 | 0 |
| 2 | 0 | 0 | 400 | 400 | 0 |
| 3 | 0 | 0 | 900 | 900 | 0 |
| 4 | 0 | 0 | 1600 | 1600 | 0 |
| 5 | 0 | 0 | 2500 | 2500 | 0 |
| 6 | 0 | 0 | 3600 | 3600 | 0 |
| 7 | 0 | 0 | 4900 | 4900 | 0 |
| 8 | 0 | 0 | 6400 | 6400 | 0 |
| 9 | 0 | 0 | 8100 | 8100 | 0 |
| 10 | 0 | 0 | 10000 | 10000 | 0 |
| 11 | 0 | 0 | 12100 | 12100 | 0 |
| 12 | 0 | 0 | 14400 | 14400 | 0 |
| 13 | 0 | 0 | 16900 | 16900 | 0 |
| 14 | 0 | 0 | 19600 | 19600 | 0 |
| 15 | 0 | 0 | 22500 | 22500 | 0 |
| 16 | 0 | 0 | 25600 | 25600 | 0 |
| 17 | 0 | 0 | 28900 | 28900 | 0 |
| 18 | 0 | 0 | 32400 | 32400 | 0 |
| 19 | 0 | 0 | 36100 | 36100 | 0 |
| 20 | 0 | 0 | 40000 | 40000 | 0 |
| 21 | 0 | 0 | 44100 | 44100 | 0 |
| 22 | 0 | 0 | 48400 | 48400 | 0 |
| 23 | 0 | 0 | 52900 | 52900 | 0 |
| 24 | 0 | 0 | 57600 | 57600 | 0 |
| 25 | 0 | 0 | 62500 | 62500 | 0 |
| 26 | 0 | 0 | 67600 | 67600 | 0 |
| 27 | 0 | 0 | 72900 | 72900 | 0 |
| 28 | 0 | 0 | 78400 | 78400 | 0 |
| 29 | 0 | 0 | 84100 | 84100 | 0 |
| 30 | 0 | 0 | 90000 | 90000 | 0 |
| 31 | 0 | 0 | 96100 | 96100 | 0 |
| 32 | 0 | 0 | 102400 | 102400 | 0 |
| 33 | 0 | 0 | 108900 | 108900 | 0 |
| 34 | 0 | 0 | 115600 | 115600 | 0 |
| 35 | 0 | 0 | 122500 | 122500 | 0 |
| 36 | 0 | 0 | 129600 | 129600 | 0 |
| 37 | 0 | 0 | 136900 | 136900 | 0 |
| 38 | 0 | 0 | 144400 | 144400 | 0 |
| 39 | 0 | 0 | 152100 | 152100 | 0 |
| 40 | 0 | 0 | 160000 | 160000 | 0 |
| 41 | 0 | 0 | 168100 | 168100 | 0 |
| 42 | 0 | 0 | 176400 | 176400 | 0 |
| 43 | 0 | 0 | 184900 | 184900 | 0 |
| 44 | 0 | 0 | 193600 | 193600 | 0 |
| 45 | 0 | 0 | 202500 | 202500 | 0 |
| 46 | 0 | 0 | 211600 | 211600 | 0 |
| 47 | 0 | 0 | 220900 | 220900 | 0 |
| 48 | 0 | 0 | 230400 | 230400 | 0 |
| 49 | 0 | 0 | 240100 | 240100 | 0 |
| 50 | 0 | 0 | 250000 | 250000 | 0 |
| 51 | 0 | 0 | 260100 | 260100 | 0 |
| 52 | 0 | 0 | 270400 | 270400 | 0 |
| 53 | 0 | 0 | 280900 | 280900 | 0 |
| 54 | 0 | 0 | 291600 | 291600 | 0 |
| 55 | 0 | 0 | 302500 | 302500 | 0 |
| 56 | 0 | 0 | 313600 | 313600 | 0 |
| 57 | 0 | 0 | 324900 | 324900 | 0 |
| 58 | 0 | 0 | 336400 | 336400 | 0 |
| 59 | 0 | 0 | 348100 | 348100 | 0 |
| 60 | 0 | 0 | 360000 | 360000 | 0 |
| 61 | 0 | 0 | 372100 | 372100 | 0 |
| 62 | 0 | 0 | 384400 | 384400 | 0 |
| 63 | 0 | 0 | 396900 | 396900 | 0 |
| 64 | 0 | 0 | 409600 | 409600 | 0 |
| 65 | 0 | 0 | 422500 | 422500 | 0 |
| 66 | 0 | 0 | 435600 | 435600 | 0 |
| 67 | 0 | 0 | 448900 | 448900 | 0 |
| 68 | 0 | 0 | 462400 | 462400 | 0 |
| 69 | 0 | 0 | 476100 | 476100 | 0 |
| 70 | 0 | 0 | 490000 | 490000 | 0 |
| 71 | 0 | 0 | 504100 | 504100 | 0 |
| 72 | 0 | 0 | 518400 | 518400 | 0 |
| 73 | 0 | 0 | 532900 | 532900 | 0 |
| 74 | 0 | 0 | 547600 | 547600 | 0 |
| 75 | 0 | 0 | 562500 | 562500 | 0 |
| 76 | 0 | 0 | 577600 | 577600 | 0 |
| 77 | 0 | 0 | 592900 | 592900 | 0 |
| 78 | 0 | 0 | 608400 | 608400 | 0 |
| 79 | 0 | 0 | 624100 | 624100 | 0 |
| 80 | 0 | 0 | 640000 | 640000 | 0 |
| 81 | 0 | 0 | 656100 | 656100 | 0 |
| 82 | 0 | 0 | 672400 | 672400 | 0 |
| 83 | 0 | 0 | 688900 | 688900 | 0 |
| 84 | 0 | 0 | 705600 | 705600 | 0 |
| 85 | 0 | 0 | 722500 | 722500 | 0 |
| 86 | 0 | 0 | 739600 | 739600 | 0 |
| 87 | 0 | 0 | 756900 | 756900 | 0 |
| 88 | 0 | 0 | 774400 | 774400 | 0 |
| 89 | 0 | 0 | 792100 | 792100 | 0 |
| 90 | 0 | 0 | 810000 | 810000 | 0 |
| 91 | 0 | 0 | 828100 | 828100 | 0 |
| 92 | 0 | 0 | 846400 | 846400 | 0 |
| 93 | 0 | 0 | 864900 | 864900 | 0 |
| 94 | 0 | 0 | 883600 | 883600 | 0 |
| 95 | 0 | 0 | 902500 | 902500 | 0 |
| 96 | 0 | 0 | 921600 | 921600 | 0 |
| 97 | 0 | 0 | 940900 | 940900 | 0 |
| 98 | 0 | 0 | 960400 | 960400 | 0 |
| 99 | 0 | 0 | 980100 | 980100 | 0 |
| 100 | 0 | 0 | 1000000 | 1000000 | 0 |
| 101 | 0 | 0 | 1019100 | 1019100 | 0 |
| 102 | 0 | 0 | 1038400 | 1038400 | 0 |
| 103 | 0 | 0 | 1057900 | 1057900 | 0 |
| 104 | 0 | 0 | 1077600 | 1077600 | 0 |
| 105 | 0 | 0 | 1097500 | 1097500 | 0 |
| 106 | 0 | 0 | 1117600 | 1117600 | 0 |
| 107 | 0 | 0 | 1137900 | 1137900 | 0 |
| 108 | 0 | 0 | 1158400 | 1158400 | 0 |
| 109 | 0 | 0 | 1179100 | 1179100 | 0 |
| 110 | 0 | 0 | 1199900 | 1199900 | 0 |
| 111 | 0 | 0 | 1220900 | 1220900 | 0 |
| 112 | 0 | 0 | 1242000 | 1242000 | 0 |
| 113 | 0 | 0 | 1263200 | 1263200 | 0 |
| 114 | 0 | 0 | 1284500 | 1284500 | 0 |
| 115 | 0 | 0 | 1305900 | 1305900 | 0 |
| 116 | 0 | 0 | 1327400 | 1327400 | 0 |
| 117 | 0 | 0 | 1349000 | 1349000 | 0 |
| 118 | 0 | 0 | 1370700 | 1370700 | 0 |
| 119 | 0 | 0 | 1392500 | 1392500 | 0 |
| 120 | 0 | 0 | 1414400 | 1414400 | 0 |
| 121 | 0 | 0 | 1436400 | 1436400 | 0 |
| 122 | 0 | 0 | 1458500 | 1458500 | 0 |
| 123 | 0 | 0 | 1480700 | 1480700 | 0 |
| 124 | 0 | 0 | 1503000 | 1503000 | 0 |
| 125 | 0 | 0 | 1525400 | 1525400 | 0 |
| 126 | 0 | 0 | 1547900 | 1547900 | 0 |
| 127 | 0 | 0 | 1570500 | 1570500 | 0 |
| 128 | 0 | 0 | 1593100 | 1593100 | 0 |
| 129 | 0 | 0 | 1615800 | 1615800 | 0 |
| 130 | 0 | 0 | 1638500 | 1638500 | 0 |
| 131 | 0 | 0 | 1661300 | 1661300 | 0 |
| 132 | 0 | 0 | 1684100 | 1684100 | 0 |
| 133 | 0 | 0 | 1707000 | 1707000 | 0 |
| 134 | 0 | 0 | 1730000 | 1730000 | 0 |
| 135 | 0 | 0 | 1753000 | 1753000 | 0 |
| 136 | 0 | 0 | 1776000 | 1776000 | 0 |
| 137 | 0 | 0 | 1799000 | 1799000 | 0 |
| 138 | 0 | 0 | 1822000 | 1822000 | 0 |
| 139 | 0 | 0 | 1845000 | 1845000 | 0 |
| 140 | 0 | 0 | 1868000 | 1868000 | 0 |
| 141 | 0 | 0 | 1891000 | 1891000 | 0 |
| 142 | 0 | 0 | 1914000 | 1914000 | 0 |
| 143 | 0 | 0 | 1937000 | 1937000 | 0 |
| 144 | 0 | 0 | 1960000 | 1960000 | 0 |
| 145 | 0 | 0 | 1983000 | 1983000 | 0 |
| 146 | 0 | 0 | 2006000 | 2006000 | 0 |
| 147 | 0 | 0 | 2029000 | 2029000 | 0 |
| 148 | 0 | 0 | 2052000 | 2052000 | 0 |
| 149 | 0 | 0 | 2075000 | 2075000 | 0 |
| 150 | 0 | 0 | 2098000 | 2098000 | 0 |
| 151 | 0 | 0 | 2121000 | 2121000 | 0 |
| 152 | 0 | 0 | 2144000 | 2144000 | 0 |
| 153 | 0 | 0 | 2167000 | 2167000 | 0 |
| 154 | 0 | 0 | 2190000 | 2190000 | 0 |
| 155 | 0 | 0 | 2213000 | 2213000 | 0 |
| 156 | 0 | 0 | 2236000 | 2236000 | 0 |
| 157 | 0 | 0 | 2259000 | 2259000 | 0 |
| 158 | 0 | 0 | 2282000 | 2282000 | 0 |
| 159 | 0 | 0 | 2305000 | 2305000 | 0 |
| 160 | 0 | 0 | 2328000 | 2328000 | 0 |
| 161 | 0 | 0 | 2351000 | 2351000 | 0 |
| 162 | 0 | 0 | 2374000 | 2374000 | 0 |
| 163 | 0 | 0 | 2397000 | 2397000 | 0 |
| 164 | 0 | 0 | 2420000 | 2420000 | 0 |
| 165 | 0 | 0 | 2443000 | 2443000 | 0 |
| 166 | 0 | 0 | 2466000 | 2466000 | 0 |
| 167 | 0 | 0 | 2489000 | 2489000 | 0 |
| 168 | 0 | 0 | 2512000 | 2512000 | 0 |
| 169 | 0 | 0 | 2535000 | 2535000 | 0 |
| 170 | 0 | 0 | 2558000 | 2558000 | 0 |
| 171 | 0 | 0 | 2581000 | 2581000 | 0 |
| 172 | 0 | 0 | 2604000 | 2604000 | 0 |
| 173 | 0 | 0 | 2627000 | 2627000 | 0 |
| 174 | 0 | 0 | 2650000 | 2650000 | 0 |
| 175 | 0 | 0 | 2673000 | 2673000 | 0 |
| 176 | 0 | 0 | 2696000 | 2696000 | 0 |
| 177 | 0 | 0 | 2719000 | 2719000 | 0 |
| 178 | 0 | 0 | 2742000 | 2742000 | 0 |
| 179 | 0 | 0 | 2765000 | 2765000 | 0 |
| 180 | 0 | 0 | 2788000 | 2788000 | 0 |
| 181 | 0 | 0 | 2811000 | 2811000 | 0 |
| 182 | 0 | 0 | 2834000 | 2834000 | 0 |
| 183 | 0 | 0 | 2857000 | 2857000 | 0 |
| 184 | 0 | 0 | 2880000 | 2880000 | 0 |
| 185 | 0 | 0 | 2903000 | 2903000 | 0 |
| 186 | 0 | 0 | 2926000 | 2926000 | 0 |
| 187 | 0 | 0 | 2949000 | 2949000 | 0 |
| 188 | 0 | 0 | 2972000 | 2972000 | 0 |
| 189 | 0 | 0 | 2995000 | 2995000 | 0 |
| 190 | 0 | 0 | 3018000 | 3018000 | 0 |
| 191 | 0 | 0 | 3041000 | 3041000 | 0 |
| 192 | 0 | 0 | 3064000 | 3064000 | 0 |
| 193 | 0 | 0 | 3087000 | 3087000 | 0 |
| 194 | 0 | 0 | 3110000 | 3110000 | 0 |
| 195 | 0 | 0 | 3133000 | 3133000 | 0 |
| 196 | 0 | 0 | 3156000 | 3156000 | 0 |
| 197 | 0 | 0 | 3179000 | 3179000 | 0 |
| 198 | 0 | 0 | 3202000 | 3202000 | 0 |
| 199 | 0 | 0 | 3225000 | 3225000 | 0 |
| 200 | 0 | 0 | 3248000 | 3248000 | 0 |
| 201 | 0 | 0 | 3271000 | 3271000 | 0 |
| 202 | 0 | 0 | 3294000 | 3294000 | 0 |
| 203 | 0 | 0 | 3317000 | 3317000 | 0 |
| 204 | 0 | 0 | 3340000 | 3340000 | 0 |
| 205 | 0 | 0 | 3363000 | 3363000 | 0 |
| 206 | 0 | 0 | 3386000 | 3386000 | 0 |
| 207 | 0 | 0 | 3409000 | 3409000 | 0 |
| 208 | 0 | 0 | 3432000 | 3432000 | 0 |
| 209 | 0 | 0 | 3455000 | 3455000 | 0 |
| 210 | 0 | 0 | 3478000 | 3478000 | 0 |
| 211 | 0 | 0 | 3501000 | 3501000 | 0 |
| 212 | 0 | 0 | 3524000 | 3524000 | 0 |
| 213 | 0 | 0 | 3547000 | 3547000 | 0 |
| 214 | 0 | 0 | 3570000 | 3570000 | 0 |
| 215 | 0 | 0 | 3593000 | 3593000 | 0 |
| 216 | 0 | 0 | 3616000 | 3616000 | 0 |
| 217 | 0 | 0 | 3639000 | 3639000 | 0 |
| 218 | 0 | 0 | 3662000 | 3662000 | 0 |
| 219 | 0 | 0 | 3685000 | 3685000 | 0 |
| 220 | 0 | 0 | 3708000 | 3708000 | 0 |
| 221 | 0 | 0 | 3731000 | 3731000 | 0 |
| 222 | 0 | 0 | 3754000 | 3754000 | 0 |
| 223 | 0 | 0 | 3777000 | 3777000 | 0 |
| 224 | 0 | 0 | 3800000 | 3800000 | 0 |
| 225 | 0 | 0 | 3823000 | 3823000 | 0 |
| 226 | 0 | 0 | 3846000 | 3846000 | 0 |
| 227 | 0 | 0 | 3869000 | 3869000 | 0 |
| 228 | 0 | 0 | 3892000 | 3892000 | |

both cases was found to be 'highly significant' (*i.e.* 0.005 confidence level or better).

During the collection of the 'c' axis data, it became evident that the crystal had suffered some radiation damage. Later, during the refinement process, it was noted that the isotropic temperature parameters seemed unduly high. This led to speculation as to whether an artificial temperature factor had been created by the damage. In order to check this, the two layers originally taken first, *hk0* and *hk10*, were repeated. About 700 hours of irradiation separated the two sets of exposures. Wilson plots gave essentially the same slope for both sets, indicating the absence of any artificial temperature factor. It appears, therefore, that damage to the crystal was confined to an increase in mosaic spread.

Discussion of the structure

The final difference synthesis produced a generally flat topography with background fluctuations rarely exceeding $\pm 0.3 \text{ e.}\text{\AA}^{-3}$. A few peaks of about $\pm 0.6 \text{ e.}\text{\AA}^{-3}$ occur near the heavy part of the molecule. $\Delta\rho$ is approximately zero at all atom sites with the exceptions of Ni and S(2), where it is about $0.7 \text{ e.}\text{\AA}^{-3}$. These latter peaks are probably caused by small systematic errors in scale factors and absorption corrections. However, considering the fact that all reflexions, including unobserved and those removed from the refinement, were

used for this computation, these results can be regarded as satisfactory.

Bond lengths and angles are listed in Table 3, and are also shown on the schematic diagram of the molecule in Fig. 3. The packing of the molecules is shown in Fig. 4, which is a view down the *b* axis, and the shorter intermolecular distances are indicated. To avoid confusion, most of the hydrogen atoms have been omitted. It can be seen that nickel has a coordination number 4, and the sulphur atoms are in square-planar configuration. The Ni-S distances (2.225 Å and 2.219 Å) agree very well with those in the ethyl compound (McConnell & Kastalsky, 1967) and with other square-planar nickel(II) complexes.

The phosphorus atom is very close to the S(1)-Ni-S(2) plane, the calculated distance from this plane being 0.10 Å. The O(1)-P-O(2) plane is practically at right angles to the previous one, the calculated angle being 89.6° . This plane passes through the origin within the limits of observational error (calculated distance from Ni atom 0.007 Å). The bond distribution around P is, therefore, approximately tetrahedral. C(2) can be considered to be in the O(1)-P-O(2) plane (deviation distance calculated to be 0.01 Å), but C(1) lies slightly out of the plane (0.08 Å).

The above conclusions are practically identical with those reached in the ethyl compound. In that report, however, the results of an analysis of thermal motion

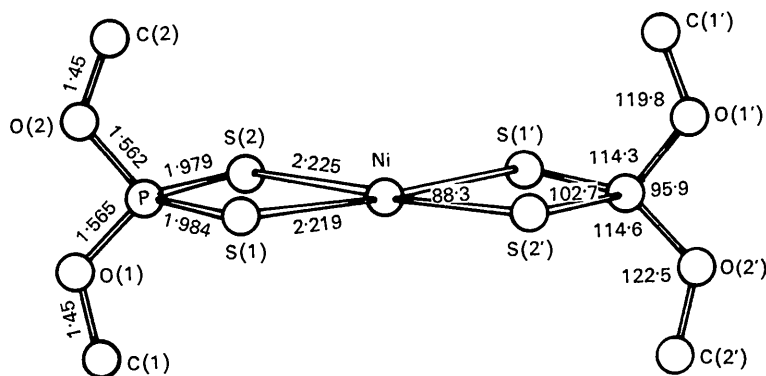


Fig. 3. Bond lengths (Å) and bond angles ($^\circ$).

Table 3. Interatomic distances and bond angles, and their standard errors

| | | | |
|-----------|-------------------------------|--|----------------------|
| Ni—S(1) | $2.219 \pm 0.002 \text{ \AA}$ | S(1)—Ni—S(2) | $88.3 \pm 0.1^\circ$ |
| Ni—S(2) | 2.225 ± 0.002 | S(1)—P—S(2) | 102.7 ± 0.1 |
| S(1)—P | 1.984 ± 0.002 | S(1)—P—O(1) | 114.3 ± 0.2 |
| S(2)—P | 1.979 ± 0.002 | S(2)—P—O(2) | 114.6 ± 0.2 |
| P—O(1) | 1.565 ± 0.005 | O(1)—P—O(2) | 95.9 ± 0.2 |
| P—O(2) | 1.562 ± 0.005 | P—O(1)—C(1) | 119.8 ± 0.4 |
| O(1)—C(1) | 1.45 ± 0.01 | P—O(2)—C(2) | 122.5 ± 0.5 |
| O(2)—C(2) | 1.45 ± 0.01 | All H—C—O angles are between 86° and 111° . | |
| C(1)—H(1) | 1.0 | All H—C—H angles are between 108° and 122° . | |
| C(1)—H(2) | 1.1 | | |
| C(1)—H(3) | 0.9 | | |
| C(2)—H(4) | 0.9 | | |
| C(2)—H(5) | 1.1 | | |
| C(2)—H(6) | 1.0 | | |

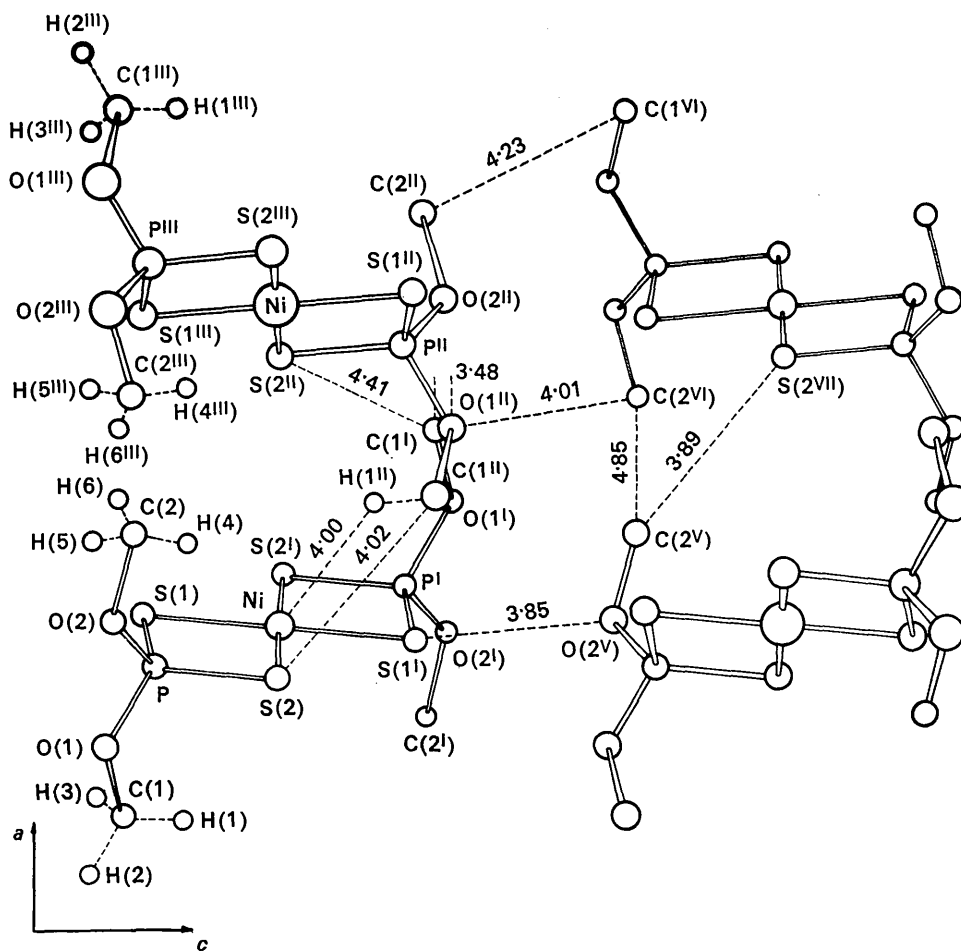


Fig. 4. (010) projection, showing intermolecular distances and the relative positions of the four molecules in the unit cell. The observed cleavage plane parallel to (001) is clearly visible in this projection.

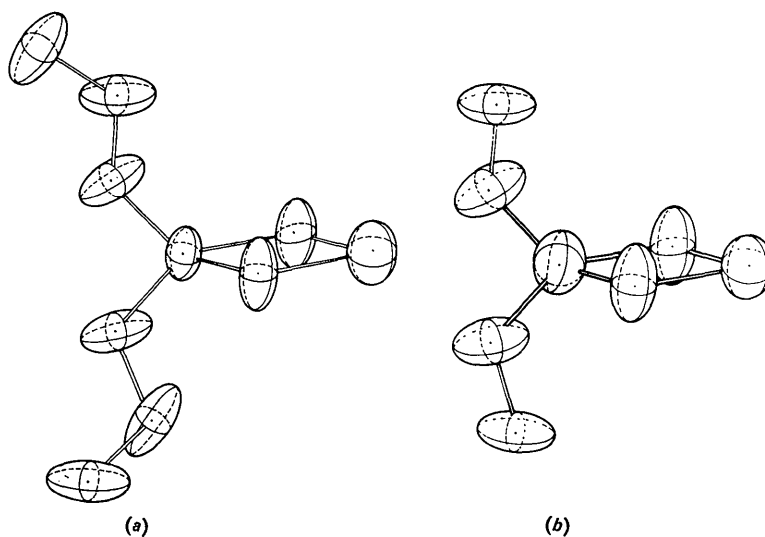


Fig. 5. Vibrational ellipsoids, (a) for Ni[(C₂H₅O)₂PS₂]₂. (b) for Ni[(CH₃O)₂PS₂]₂.

Table 4. *The magnitudes (R) and directions (φ) of r.m.s. components of thermal displacement along principal axes* R_i ($i=1,2,3$) in Å.The angles $\varphi_a, \varphi_b, \varphi_c$ represent the angles in degrees made by R_i with the crystallographic axes a, b, c respectively.

| | Axis i | R_i | φ_a | φ_b | φ_c |
|------|----------|--------|-------------|-------------|-------------|
| Ni | 1 | 0.22 Å | 103° | 61° | 148° |
| | 2 | 0.23 | 120 | 46 | 58 |
| | 3 | 0.27 | 147 | 123 | 95 |
| S(1) | 1 | 0.23 | 84 | 88 | 174 |
| | 2 | 0.25 | 124 | 34 | 91 |
| | 3 | 0.33 | 146 | 124 | 96 |
| S(2) | 1 | 0.23 | 63 | 153 | 94 |
| | 2 | 0.25 | 92 | 95 | 6 |
| | 3 | 0.33 | 153 | 117 | 95 |
| P | 1 | 0.22 | 104 | 51 | 138 |
| | 2 | 0.26 | 18 | 91 | 108 |
| | 3 | 0.27 | 102 | 141 | 126 |
| O(1) | 1 | 0.23 | 119 | 55 | 132 |
| | 2 | 0.27 | 38 | 52 | 92 |
| | 3 | 0.32 | 67 | 123 | 138 |
| O(2) | 1 | 0.24 | 70 | 46 | 129 |
| | 2 | 0.28 | 26 | 93 | 64 |
| | 3 | 0.33 | 74 | 136 | 130 |
| C(1) | 1 | 0.26 | 156 | 113 | 96 |
| | 2 | 0.29 | 112 | 24 | 98 |
| | 3 | 0.33 | 81 | 95 | 170 |
| C(2) | 1 | 0.26 | 158 | 110 | 82 |
| | 2 | 0.32 | 111 | 23 | 97 |
| | 3 | 0.35 | 95 | 100 | 169 |

were treated with caution because of the presence of a number of systematic errors. Corrections had not been applied for absorption or dispersion, and data had been collected about one axis only, giving rise to the possibility of interaction between scaling and temperature factors. Refinement had proceeded only to $R=0.115$, and it was felt that although the thermal vibration parameters appeared quite credible, too much reliance could not be placed upon them.

In the present structure, the above systematic errors have been minimized, and it is interesting to note the similarity between the thermal ellipsoids in the two compounds (Fig. 5). For ease of comparison, the ellipsoids have been drawn with approximately the same magnitudes; those for the methyl compound [Fig. 5(b)] are, in fact, larger by a factor of about 30%. The thermal ellipsoids in both cases were calculated using the

ORFFE program of Busing, Martin & Levy (1964). In both cases it can be seen that the directions of maximum vibration coincide with those of least constraint. Of the heavier atoms Ni, S and P the sulphur atoms have the largest amplitude normal to the Ni-S(1)-P-S(2) plane, while the P atom, particularly in the methyl compound, tends to vibrate much more isotropically because of its tetrahedral constraint. It appears, therefore, that despite the known inaccuracies, the thermal parameters of the ethyl compound were quite meaningful.

The magnitudes and directions of the root mean square components of thermal displacement with respect to the crystallographic axes are presented in Table 4 for the case of the methyl compound.

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