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

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#### Abstract

The structure of bis(dimethyldithiophosphinato)nickel(II), $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{CH}_{3}\right)_{2}\right]_{2}$, has been determined from three-dimensional X-ray data collected by counter methods. The probable space group is $P 2_{1} / c$; cell dimensions are $a=9 \cdot 261(6), b=12 \cdot 004(8), c=11 \cdot 016(6) \AA, \beta=91 \cdot 14(6)^{\circ}$. The observed density is $1.676 \mathrm{~g} . \mathrm{cm}^{-3}$, which agrees well with the density calculated for four molecules in the unit cell, $1.677 \mathrm{~g} . \mathrm{cm}^{-3}$. A three-dimensional least-squares refinement based on 1001 observed reflections led to a final $R$ value based on $F$ of $7.8 \%$ (weighted $R=6.3 \%$ ). There are two kinds of molecules in the unit cell, each with its nickel atom at a center of symmetry; thus, the $\mathrm{NiS}_{4}$ groups are planar. The phosphorus atoms, however, are somewhat out of these planes. Though the two sets of molecules are independent they are structurally very similar. Ni-S bonds range from $2.229(5)$ to $2 \cdot 242(5) \AA, \mathrm{P}-\mathrm{S}$ bonds from $1.991(7)$ to $2 \cdot 018(7) \AA$, and P-C bonds from $1 \cdot 80(2)$ to $1.83(2) \AA$.


## Introduction

In a recent study of the crystal structure of bis(diethyldithiophosphato)nickel(II), $\mathrm{Ni}\left[\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{O}\right)_{2} \mathrm{PS}_{2}\right]_{2}$, McConnell \& Kastalsky (1967) remarked on the comparative rarity of four-membered rings like Ni-S-P-S. With their work and the work of Franzini (1963) and of Fernando (Fernando \& Green, 1967; Ooi \& Fernando, 1967) this feature in known structures has become less rare. In the present case of $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{CH}_{3}\right)_{2}\right]_{2}$ it is again easy to postulate several possible structure models of quite different types. Our study was undertaken in part to determine whether the $\mathrm{Ni}-\mathrm{S}-\mathrm{P}-\mathrm{S}$ four-membered ring was a feature of this structure also and to establish the molecular geometry for possible subsequent spectroscopic analysis.

## Experimental

The compound was prepared according to the procedure of Kuchen \& Metten (1962). A tabular single crystal, grown from chloroform solution, was observed under the microscope to have $2 / m$ symmetry. It was mounted along the twofold axis on the tip of a glass capillary with epoxy cement and shaped to an approximate cube ( $0.015 \times 0.015 \times 0.019 \mathrm{~cm}$ ) with solventmoistened fine emery paper.

Photographic investigation of the crystal with a Buerger precession camera indicated Laue symmetry $2 / m$ with systematic absences occuring in the $h 0 l$ reflections for $l=2 n+1$ and in the $0 k 0$ reflections for $k=2 n+1$. The probable space group is thus $P 2_{1} / c$. It was also observed that reflections for which $h, k$, and $l$ were neither all odd nor all even were relatively weak.

[^0]Unit-cell dimensions were determined from measurements of high order reflections along each reciprocal axis with unfiltered Mo radiation on a General Electric XRD-5 diffractometer equipped with a single crystal orienter. These dimensions are $a=9 \cdot 261 \pm$ $0.006, b=12.004 \pm 0.008, c=11.016 \pm 0.006 \AA$, and $\beta=91 \cdot 14 \pm 0.06^{\circ}$. The measurements were made at room temperature, about $22^{\circ} \mathrm{C}$, and the standard errors quoted were estimated from the observed deviations of individual values from their mean. Intensities were measured at room temperature on the manually operated single-crystal orienter by use of Zr -filtered Mo radiation with pulse height discrimination, a scintillation counter, and a $2^{\circ}$ take-off angle. A total of 1457 reflections were measured by the moving crystalmoving counter technique using a $2.66^{\circ}$ scan of $2 \theta$. Of this total, 456 reffections were considered unobserved in that no peak was observed on the recorder with the highest available sensitivity. Background was measured by offsetting $\varphi$ and repeating the scan, though in retrospect this method appears less satisfactory than offsetting $\theta$. All reflections were measured in pairs related by the twofold symmetry, averaged, and corrected in the usual manner for Lorentz and polarization factors. Absorption corrections were not applied. From the linear absorption coefficient for the crystal, $24.66 \mathrm{~cm}^{-1}$, maximum errors in the raw intensities resulting from neglect of absorption corrections were estimated to be $7 \%$.

## Structure determination

For four formula units in the cell, the calculated density is $1.677 \mathrm{~g} . \mathrm{cm}^{-3}$; the observed density, measured by flotation in a bromoform-benzene mixture, is $1.676 \pm$ $0.005{\mathrm{~g} . \mathrm{cm}^{-3}}$. Since the general position is fourfold, there is no immediate crystallographic requirement on the molecular symmetry. The fact that intensities for
reflections for which $h, k$, and $l$ were neither all odd nor all even were in general relatively weak suggested that the Ni atoms might be arranged in a face-centered way. Ni atoms in two sets of twofold positions or in the general position with $x \simeq \frac{1}{4}, y \simeq 0, z \simeq \frac{1}{4}$ could produce the observed intensity effect.

By the use of the special positions and refining scale factor, nickel atoms alone gave $R=72 \%$. By the use of general positions, a refinement on $F$ of scale factor and atomic positions gave $R=56 \%$, whereas placing nickel atoms randomly in the unit cell gave $R$ about $80 \%$. (In all of the above cases, isotropic temperature factors were used and held fixed at $0 \cdot 8$.) From the above results, it was assumed that the nickel atoms should be placed in the general position.

A three-dimensional Patterson map was calculated and the orientation of a planar $\mathrm{NiS}_{4} \mathrm{P}_{2}$ group was established from important peaks close to the origin. A least-squares refinement of positions, however, only reduced $R$ to $46 \%$. It finally became clear that despite the better initial $R$ value with nickel atoms in the general position, this position was not correct. A construction of a model, assuming a tetrahedral environment for phosphorus, also revealed that the packing was unsatisfactory.

Further study of the Patterson map indicated that a second $\mathrm{NiS}_{4}$ group could be located in a plane approximately perpendicular to that of the original $\mathrm{NiS}_{4} \mathrm{P}_{2}$. Such an arrangement required the Ni atoms to be in special positions, and each molecule would then be required to be centrosymmetric. After refining scale factor, isotropic temperature factors, and atomic positions $R$ dropped to $30 \%$. The remaining phosphorus and methyl groups were then located on a difference map and the unweighted $R$, after isotropic refinement, dropped to $12 \cdot 6 \%$. Anisotropic refinement, with temperature factors of the form $\exp \left[-\left(\beta_{11} h^{2}+\beta_{22} k^{2}+\beta_{33}{ }^{2}+\right.\right.$ $\left.\beta_{12} h k+\beta_{13} h l+\beta_{23} k l\right)$ ], reduced $R$ to $10 \cdot 1 \%$. About seven-ty-five reflections whose observed and calculated structure factors did not agree within $15 \%$ were then remeasured on the goniostat; several were found to be in error. With the corrected data, the unweighted $R$ was $7 \cdot 3 \%$, while the weighted $R$ was $8.1 \%$.

The weighting scheme $\sqrt{ } w=\left|F^{*}\right| /\left|F_{0}\right|$ for $\left|F_{0}\right| \geq\left|F^{*}\right|$, $V w=1$ for $\left|F^{* *}\right|<\left|F_{0}\right|<\left|F^{*}\right|$, and $V w=\left|F_{0}\right| /\left|F^{* *}\right|$ for $\left|F_{o}\right| \leq\left|F^{* *}\right|$, where $\left|F^{*}\right|$ and $\left|F^{* *}\right|$ were taken as $75 \%$ and $25 \%$ of the maximum $\left|F_{o}\right|$ respectively, was then introduced. The unweighted $R$ increased to $7 \cdot 9 \%$, but the weighted $R$ decreased to $6 \cdot 3 \%$. Correction of the scattering factor curves of $\mathrm{Ni}^{2+}, \mathrm{S}^{0}$, and $\mathrm{P}^{0}$ for anomalous dispersion (Cromer, 1965) followed by leastsquares refinement until no parameter change was greater than one-tenth of its standard error produced negligible changes and resulted in the final values of $7 \cdot 8 \%$ for unweighted $R$ and $6.3 \%$ for weighted $R \dagger$. A difference Fourier synthesis calculated at this time gave

[^1]no indication of errors in atomic positions nor of hydrogen atoms and the refinement was not continued further. All least-squares refinements were based on $F$. The standard deviation of an observation of unit weight was $0 \cdot 61$. Extinction corrections were not made, but the intensity fit for the most intense reflections was still fairly good. The scattering factor curves used were obtained from International Tables for X-ray Crystal$\operatorname{lography}$ (1962) for sulfur, phosphorus, and carbon and from Thomas \& Umeda (1957) for nickel. The fullmatrix least-squares refinement was carried out on an IBM 360-65 computer using the Busing, Martin, \& Levy program ORFLS (1962). The Patterson, Fourier and difference Fourier maps were calculated with a Fourier program supplied by S. Trotter, University of British Columbia, Vancouver, B.C.
Final atomic positions, anisotropic temperature factors, and observed and calculated structure factors are listed in Tables 1,2, and 3.

Table 1. Final positional parameters and their standard deviations* for $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{CH}_{3}\right)_{2}\right]_{2}$
All parameters (except for Ni ) are times $10^{4}$.

| Molecule 1. |  |  |  |
| :---: | :---: | :---: | :---: |
|  | $x$ | $y$ | $z$ |
| Ni | 0 | 0 | 0 |
| S(1) | 9303 (5) | 9723 (4) | 1910 (4) |
| S(2) | 7919 (5) | 917 (4) | 9675 (4) |
| P | 7549 (5) | 611 (4) | 1418 (4) |
| C(1) | 7389 (25) | 1860 (15) | 2363 (20) |
| C(2) | 5905 (17) | 9805 (17) | 1674 (16) |
| Molecule 2 |  |  |  |
| Ni | $\frac{1}{2}$ | 0 | $\frac{1}{2}$ |
| S(1) | 2814 (5) | 9595 (4) | 4231 (5) |
| S(2) | 4337 (5) | 1791 (4) | 4989 (5) |
| P | 2519 (5) | 1237 (4) | 4148 (5) |
| C(1) | 2357 (26) | 1745 (15) | 2613 (19) |
| C(2) | 887 (19) | 1701 (17) | 4849 (16) |

[^2]

Fig. 1. Molecular configuration of $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{CH}_{3}\right)_{2}\right]_{2}$.

## Discussion

The presence of square-planar coordination for Ni and four membered $\mathrm{Ni}-\mathrm{S}-\mathrm{P}-\mathrm{S}$ rings was confirmed for the structure of $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{CH}_{3}\right)_{2}\right]_{2}$ (Fig. 1). In their common aspects, this structure agrees quite well with those of $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{2} \mathrm{H}_{5}\right)_{2}\right]_{2}$ and $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{2} \mathrm{H}_{5}\right)_{2}\right] .2 \mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}$. The molecules in all of these cases are centrosymmetric so that the $\mathrm{NiS}_{4}$ groups are necessarily planar. However, there is no requirement that the phosphorus atoms lie in these planes, and in the present case it appears that they do not, at least for one of the two molecules. If one considers the planes determined by the nickel and sulfur atoms in $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{CH}_{3}\right)_{2}\right]_{2}$, for one of the molecules phosphorus is out of the plane by about $0.05 \AA$ and for the other molecule the phosphorus is out of the plane by $0.19 \AA$. A more conservative test for nonplanarity is based on the best planes calculated with the phosphorus atoms included. Then the maximum deviation from the best plane is $0.02 \AA$ for one molecule, but for the other molecule this maximum deviation is $0.08 \AA$. Since the estimated standard error in these distances is less than $0.02 \AA$, it appears that in at


Fig.2. Stereoscopic illustration of the $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{CH}_{3}\right)_{2}\right]_{2}$ unit cell. The origin is in the lower right rear corner of the cell, the $z$ axis is vertical, the $x$ axis is horizontal, and the $y$ axis points towards the viewer.
least one pair of molecules the $\mathrm{NiS}_{4} \mathrm{P}_{2}$ groups are not strictly planar.

Bond lengths and angles were calculated with the ORFFE program of Busing, Martin, \& Levy (1964) and are listed in Table 4. The Ni-S distances (2-239, 2-242, 2.229 and $2.235 \AA$ ) are very close to those found in $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{O}\right)_{2}\right]_{2}$ by McConnell \& Kastalsky ( $2 \cdot 230 \pm$ 0.004 and $2.236 \pm 0.004 \AA$ ). However, in the bispyridine adduct of $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{2} \mathrm{H}_{5}\right)_{2}\right]_{2}$, the nickel is hexacoordinated, and the $\mathrm{Ni}-\mathrm{S}$ distances are lengthened to $2.49 \pm 0.01$ and $2.50 \pm 0.01 \AA$ (Ooi \& Fernando, 1967). This is consistent with the hypothesis of Ooi \& Fernando that the chelate rings may be weakened by molecules that complete the coordination sphere of the metal ion.

Although the two sets of molecules are independent, they are in fact very similar. The maximum deviation from their mean for all $\mathrm{Ni}-\mathrm{S}$ bond distances is less than $0.007 \AA$, which is about equal to the maximum standard error found in these values. For the S-P bond distances this maximum deviation is less than $0.013 \AA$, which is about twice the standard error, and for the P-C distances the maximum deviation is $0.016 \AA$, which is less than the largest standard error. All corresponding bond angles for the two molecules agree with their mean within twice their standard errors.

A stereoscopic illustration of the unit cell and its contents, which was drawn using Jonhson's ORTEP (1965), is shown in Fig. 2.

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Table 2. Final thermal parameters and their standard deviations* for $\mathrm{Ni}^{[ }\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{CH}_{3}\right)_{2}\right]_{2}$
All parameters are times $10^{4}$.

|  | Molecule 1 |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
| Ni | 75 (4) | 55 (2) | 63 (3) | -10 (3) | 5 (3) | 2 (3) |
| S(1) | 121 (6) | 76 (5) | 72 (4) | 16 (5) | 11 (4) | 13 (4) |
| S(2) | 108 (7) | 96 (5) | 76 (4) | 17 (5) | 6 (5) | 28 (4) |
| P | 93 (5) | 62 (4) | 69 (4) | 13 (5) | 12 (5) | -2 (4) |
| C(1) | 184 (32) | 77 (16) | 113 (22) | 15 (2) | 27 (3) | 7 (20) |
| C(2) | 92 (21) | 103 (21) | 121 (19) | 15 (29) | 45 (18) | -31(20) |
| Molecule 2 |  |  |  |  |  |  |
| Ni | 75 (4) | 44 (2) | 71 (3) | 4 (3) | 11 (3) | -2 (3) |
| S(1) | 96 (6) | 43 (3) | 149 (7) | 7 (4) | -10 (6) | 7 (4) |
| S(2) | 113 (6) | 57 (4) | 115 (6) | 11 (5) | -9 (6) | -9 (5) |
| P | 79 (6) | 57 (4) | 73 (5) | 2 (4) | 3 (6) | -3 (4) |
| C(1) | 188 (33) | 91 (17) | 81 (20) | -20 (26) | -4 (24) | 28 (20) |
| C(2) | 128 (26) | 113 (20) | 63 (17) | 37 (23) | 34 (20) | -13 (17) |

[^3]Table 3．Observed and calculated structure factors
The columns are $k, l,\left|F_{o}\right|$ ，and $\left|F_{c}\right|$ ．







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 Nunnro $\begin{array}{ccc}0 & 20 & 24 \\ -0 & 16 & 15 \\ -0 & 3 \\ -2 & 20 & 10 \\ 0 & 12 & 16 \\ 0 & 16 & 15 \\ H= & 14 & \\ 0 & & \\ 0 & 14 & 11 \\ 0 & 11 & 10\end{array}$

Table 4. Interatomic bond distances, bond angles and their standard deviations for $\mathrm{Ni}\left[\mathrm{S}_{2} \mathrm{P}\left(\mathrm{CH}_{3}\right)_{2}\right]_{2}$

| Bonds |  | Angles |  |  |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Ni}-\mathrm{S}(1)$ | $2 \cdot 239$ (4) | $\mathrm{S}(1)-\mathrm{Ni}-\mathrm{S}(2)$ | (outside of ring) | 92.3 (2) |
| $\mathrm{Ni}-\mathrm{S}(2)$ | 2.242 (5) | $\mathrm{S}(1)-\mathrm{Ni}-\mathrm{S}(2)$ | (inside of ring) | 87.7 (2) |
| S(1)-P | $2 \cdot 014$ (6) | $\mathrm{Ni}-\mathrm{S}(1)-\mathrm{P}$ |  | 85.1 (2) |
| S(2)-P | 1.994 (6) | Ni -S(2)-P |  | 85.5 (2) |
| P--C(1) | 1.832 (20) | $\mathrm{S}(1)-\mathrm{P}-\mathrm{S}(2)$ |  | 101.6 (3) |
| $\mathrm{P}-\mathrm{C}(2)$ | 1.824 (18) | $\mathrm{S}(1)-\mathrm{P}-\mathrm{C}(1)$ |  | $110 \cdot 5$ (7) |
|  |  | $\mathrm{S}(1)-\mathrm{P}-\mathrm{C}(2)$ |  | $110 \cdot 4$ (6) |
|  |  | $\mathrm{S}(2)-\mathrm{P}-\mathrm{C}(1)$ |  | 114.4 (7) |
|  |  | $\mathrm{S}(2)-\mathrm{P}-\mathrm{C}(2)$ |  | $114 \cdot 1$ (6) |
|  |  | $\mathrm{C}(1)-\mathrm{P}-\mathrm{C}(2)$ |  | $105 \cdot 7$ (9) |
| Molecule 2 |  |  |  |  |
| $\mathrm{Ni}-\mathrm{S}(1)$ | $2 \cdot 229$ (5) | $\mathrm{S}(1)-\mathrm{Ni}-\mathrm{S}(2)$ | (outside of ring) | 92.3 (2) |
| $\mathrm{Ni}-\mathrm{S}(2)$ | $2 \cdot 235$ (5) | $\mathrm{S}(1)-\mathrm{Ni}-\mathrm{S}(2)$ | (inside of ring) | $87 \cdot 7$ (2) |
| S(1)-P | 1.991 (7) | $\mathrm{Ni}-\mathrm{S}(1)-\mathrm{P}$ |  | $85 \cdot 8$ (2) |
| S(2)-P | 2.018 (7) | $\mathrm{Ni}-\mathrm{S}(2)-\mathrm{P}$ |  | 85.0 (2) |
| $\mathrm{P}-\mathrm{C}(1)$ | 1.803 (20) | $\mathrm{S}(1)-\mathrm{P}-\mathrm{S}(2)$ |  | $101 \cdot 0$ (3) |
| $\mathrm{P}-\mathrm{C}(2)$ | 1.799 (17) | $\mathrm{S}(1)-\mathrm{P}-\mathrm{C}(1)$ |  | $113 \cdot 0$ (7) |
|  |  | $\mathrm{S}(1)-\mathrm{P}-\mathrm{C}(2)$ |  | $113 \cdot 6$ (7) |
|  |  | $\mathrm{S}(2)-\mathrm{P}-\mathrm{C}(1)$ |  | $111 \cdot 8$ (7) |
|  |  | $\mathrm{S}(2)-\mathrm{P}-\mathrm{C}(2)$ |  | 113.7 (7) |
|  |  | $\mathrm{C}(1)-\mathrm{P}-\mathrm{C}(2)$ |  | $104 \cdot 1$ (9) |

* Standard errors, as calculated by $O R F F E$, are given in parentheses.


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# Détermination et Etude de la Structure Cristalline de la Jouravskite $\mathrm{Ca}_{3} \mathrm{Mn}^{\mathrm{IV}}\left(\mathrm{SO}_{4}\right)\left(\mathrm{CO}_{3}\right)(\mathbf{O H})_{6} .12 \mathrm{H}_{2} \mathrm{O}$ 

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The crystal structure of jouravskite, $\mathrm{Ca}_{3} \mathrm{Mn}^{\mathrm{IV}}\left(\mathrm{SO}_{4}\right)\left(\mathrm{CO}_{3}\right)(\mathrm{OH})_{6} .12 \mathrm{H}_{2} \mathrm{O}$, has been determined by threedimensional methods, using minimum function, Fourier synthesis and least-squares refinement. The final reliability index $R$ is $0 \cdot 16$ with 736 reflexions. The structure is made up of manganese octahedra bonded to eight-cornered calcium polyhedra. Between these polyhedra lie the $\mathrm{SO}_{4}$ and $\mathrm{CO}_{3}$ anions, each of which is surrounded by twelve $\mathrm{H}_{2} \mathrm{O}$ molecules, belonging to the Ca polyhedra.

## Introduction

Gaudefroy \& Permingeat (1965) ont découvert la jouravskite dans des échantillons de minerai de man-
ganèse provenant du gisement marocain de Tachgagalt et en ont effectué la description minéralogique complète.

Ce minéral se présente généralement en grains de quelques dixièmes de millimètre, étroitement associé


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    $\dagger$ Present address: U.S. Naval Ordnance Test Station, China Lake, California, U.S.A.

[^1]:    $\dagger R=\left(\Sigma| | F_{o}|-k| F_{c}| |\right) / \Sigma\left|F_{o}\right| ;$
    weighted $R=\sqrt{\Sigma w\left(\left|F_{0}\right|-\right.} \overline{\left.k\left|F_{c}\right|\right)^{2} /} \sqrt{\Sigma w} \overline{F_{0}{ }^{2}}$.

[^2]:    * Standard deviations, as calculated by $O R F L S$, are given in parentheses.

[^3]:    * Standard deviations, as calculated by $O R F L S$, are given in parentheses.

