The Crystal Structure of Bis(dimethyl dithiophosphinato)nickel(II)

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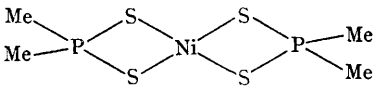
THE detailed structure determination of bis-(dimethyl dithiophosphinato)nickel(II), $Ni(S_2PMe_2)_2$, is the first of a series suggested by Dr. D. S. Klett to aid in the interpretation of infrared spectra of this and related compounds. Single crystals of the material were prepared by the method of Kuchen and Metten[1] and provided by Dr. Klett.

The crystals are monoclinic with $a = 9{\cdot}26$, $b = 12{\cdot}00$, $c = 11{\cdot}02$ Å, $\beta = 91{\cdot}1°$. The space group is $P2_1/c$, and there are four molecules per unit cell. The structure determination was based on 1000 independent reflections measured by the moving-crystal moving-counter method on a General Electric single crystal orienter with Zr-filtered Mo-radiation, pulse height selection, and a scintillation counter.

Examination of the raw intensity data revealed a pattern of strong and weak reflections which suggested a face-centred arrangement of the nickel atoms. Packing considerations based on the expected molecular size favoured placing the centres of the molecules (the nickel atoms) on two sets of two-fold positions rather than on the sites of the general, four-fold, position. Such a choice requires that the molecules be centrosymmetric, but means that one pair is independent of the

other pair. From a three-dimensional Patterson synthesis indications of two square planar NiS_4 groupings were found, one roughly parallel to the (010) plane and the other almost at right angles to it. The nickel positions of 000, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, and



FIGURE

the deduced sulphur positions provided the start for finding the phosphorus and carbon atoms by application of electron density maps, chemical considerations, and full-matrix least-squares refinement. At present, isotropic refinement has led to an unweighted reliability index, *R*, of 12·6%. The thermal parameters, B, are 2·5 and 2·3 Å^2 for nickel; 3·3—3·7 Å^2 for sulphur; 2·7 and 2·8 Å^2 for phosphorus, and 4·2—5·0 Å^2 for carbon.

[1] W. Kuchen and J. Metten, Ger. Pat. 1137732/1962.

Although the two sets of molecules are independent, they appear to be almost identical. The Figure indicates the molecular configuration. For both molecules the nickel and four sulphur atoms are in a nearly square planar arrangement, and the two sulphur atoms and two carbon atoms around each phosphorus atom are in a distorted tetrahedral configuration. The average bond lengths, with the estimated standard deviation for a single value in parentheses, are: Ni–S, 2·24 Å (0·01); S–P, 2·01 Å (0·01); P–C, 1·84 Å (0·04). Bond angles at this stage are: Ni–S–P, 85° (1); S–Ni–S inside the ring, 88° (1); S–P–S, 101° (1); C–P–C, 105° (2). Values for the angles S–P–C range from 109—116° (2). The anisotropic refinement is being continued.

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