The Crystal and Molecular Structure of the Five-co-ordinated Nickel Complex 2,9-Dimethyl-1,10-phenanthrolinebis-(*O,O'*-dimethyldithiophosphato)nickel(II)

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Summary The structure of the five-co-ordinate intermediate formed by the displacement of a co-ordinated sulphur atom in the four-co-ordinate chelate, bis-(*O,O'*-dimethyldithiophosphato)nickel(II) by the ligand 2,9-dimethyl-1,10-phenanthroline, has been determined.

BIDENTATE chelating agents react with low-spin four-co-ordinate nickel complexes and usually form *cis*-adducts which are high-spin six-co-ordinate nickel complexes. A series of adducts of bis-(*O,O'*-dimethyldithiophosphato)-nickel(II) with a variety of heterocyclic nitrogen bases has been prepared and their spectra and magnetic properties have been investigated.[1] The structure of one of the adducts with the bidentate chelating agent, 2,2'-bipyridyl, has been determined by a single-crystal X-ray analysis and was found to be the expected *cis*-adduct.[1,2] The structure of the adduct formed with 2,9-dimethyl-1,10-phenanthroline is reported below.

Green, needle-shaped crystals of the adduct were grown by the slow evaporation of an ethanol solution containing 2,9-dimethyl-1,10-phenanthroline and bis-(*O,O'*-dimethyldithiophosphato)nickel(II). Crystal data: monoclinic; space group $P2_1/c$; $a = 7{\cdot}86$, $b = 15{\cdot}51$; $c = 21{\cdot}79$ Å, $\beta = 92{\cdot}50°$; $Z = 4$; $F(000) = 1200$; $U = 2483$ Å^3, $\lambda = 1{\cdot}5418$ Å.

Data were collected on a Buerger automated diffractometer with Cu-K_α radiation. The structure was solved by the heavy-atom method and refined by full-matrix least squares with anisotropic temperature factors to an R value of 10·6% over 2680 observed non-zero reflections (0kl—6kl).

The structure consists of discrete molecules of 2,9-dimethyl-1,10-phenanthrolinebis-(*O,O'*dimethyldithiophosphato)nickel(II) in which each nickel atom is co-ordinated to three out of the four sulphur atoms which are potential donors in the two dithiophosphate ligands, and the two nitrogen donor atoms in 1,10-phenanthroline. The co-ordination polyhedron, shown in the Figure, is a distorted square pyramid. The two Ni–N bond distances are almost identical (2·00 Å) and are slightly shorter than the Ni–N distances (2·07 Å) that were found in the six-co-ordinate adduct, 2,2'-bipyridylbis-(*O,O'*-dimethyldithiophosphato)-nickel(II).[1] The three Ni–S distances are unequal and are greater than the Ni–S distance found in low-spin four-co-ordinate nickel complexes. The bond distances have a standard deviation of 0·01 Å. The four atoms, Ni, S(2), S(3), and N(1) lie approximately in one plane; the nickel atom being 0·18 Å above the best plane through these four atoms. The atom S(1) lies 0·9 Å below this plane. The angles in the co-ordination polyhedron are: N(2)–Ni–S(1) = 130·2°; N(2)–Ni–N(1) = 82·5°; N(2)–Ni–S(2) = 93·0°; N(2)–Ni–S(3) = 100·2°; S(1)–Ni–N(1) = 146·2°; S(2)–Ni–S(3) = 165·8°; N(1)–Ni–S(3) = 97·1°; N(1)–Ni–S(2) = 89·4;° S(2)–Ni–S(1) = 81·7°; S(1)–Ni–S(3) = 85·9°. The standard deviation of these angles is 0·5°.

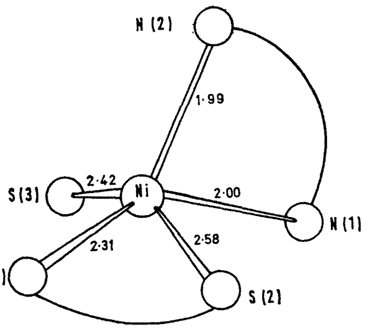

FIGURE. *Co-ordination around the nickel atom.*

The compound is paramagnetic (μ_{eff} = 3·03 B.M.)[1]: this is surprising in view of the three weakly electronegative sulphur atoms that are co-ordinated to the nickel atom. The structure of this compound is of interest since it represents the first instance in which a five-co-ordinate reaction intermediate of the type ML_3X_2 has been isolated.

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[1] D. E. Carter, Ph.D., Dissertation, "Structure and Properties of Certain Planar Metal Chelates and Their Adducts," University of Arizona, 1969.

[2] S. Ooi, D. E. Carter, and Q. Fernando, Abstract in Proceedings of the 11th International Conference on Coordination Chemistry, Haifa, 1968.