The Structure of a New High-spin Five-co-ordinated Nickel(II) Complex

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RECENTLY there has been great interest in five-co-ordination in 3*d*-transition-metals. So far, only one structure of a high-spin five-co-ordinated nickel(II) complex has been described by *X*-ray diffraction.[1]

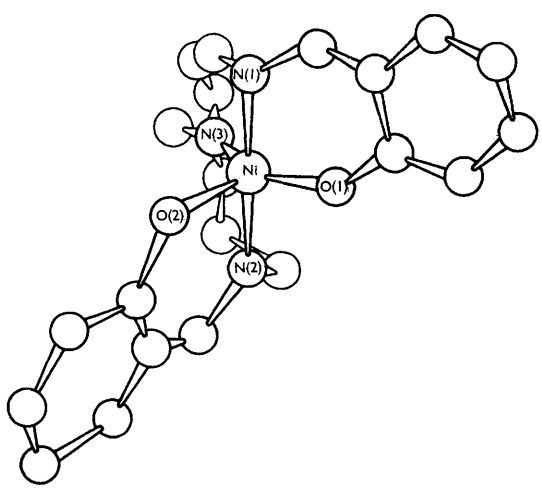
We report here the results of an *X*-ray investigation on the structure of the nickel(II) complex with the potentially five-dentate ligand bis(salicylidene-γ-iminopropyl)methylamine (SalMeDPT) {*o*-(OH)-$C_6H_4CH{=}N{-}[CH_2]_3NMe$}.

The magnetic susceptibility of the non-methylated derivative has been reported by Calvin,[2] who studied extensively the oxygen carrier properties of the cobalt(II) analogue. Preparation and physicochemical properties of the nickel(II), copper(II), and zinc(II) derivatives are reported elsewhere.[3]

Crystal data for the complex are: $a = 6{\cdot}87$, $b = 13{\cdot}91$, $c = 19{\cdot}83$ Å, $\beta = 91°54'$, space group $P2_1/c$, $Z = 4$, $d_c = 1{\cdot}437$ g/cm^3.

The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by several cycles of block diagonal least-squares. The present value of the *R*-factor is 11·8% over 1544 independent observed reflections.

The structure consists of discrete molecules of NiSalMeDPT (see Figure) in which the metal atom is five-co-ordinated by the three nitrogens and the two oxygens. The arrangement of the ligands about the nickel atom is mainly determined by the geometry of the ligand molecule.



The co-ordination configuration can be more easily described in terms of a distorted trigonal

bipyramid, with O(1), O(2), and N(3) in the equatorial plane and N(1) and N(2) in the axial positions. The N(1)–Ni–N(2) axis is almost perpendicular to the equatorial plane. The angles in the plane are: O(1)–Ni–O(2) = 142°, O(2)–Ni–N(3) = 105°, N(3)–Ni–O(1) = 113°.

Current bond distances in the polyhedron are: Ni–O(1) = 1·96, Ni–O(2) = 1·94, Ni–N(1) = 2·01, Ni–N(2) = 1·98, Ni–N(3) = 2·07 Å. The angle between the mean planes through the salicylaldimines is 101°.

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[2] H. Calvin and C. H. Berkelew, *J. Amer. Chem. Soc.*, 1946, **68**, 2267.
[3] L. Sacconi and I. Bertini, to be published.