Five-co-ordinated Structure of the Cobalt(II) Chloride Complex with *N*-Methylated Diethylenetriamine

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A SERIES of complex compounds of divalent 3*d*-metals, with the general formula M(denMe)X$_2$ [M = Mn, Fe, Co, Ni, Cu, Zn; denMe = bis(2-dimethylaminoethyl)methylamine, Me$_2$N[CH$_2$]$_2$-NMe·[CH$_2$]$_2$NMe$_2$; X = Cl, Br, I, NCS] have been prepared in this Institute. All these are high-spin complexes.

On the basis of molecular weights and spectral and magnetic results, a five-co-ordinated structure has been proposed for all the complexes.

We have investigated the structure of the cobalt(II) compound, with X = Cl, by means of *X*-ray diffraction, Cu-$K\alpha$ radiation being used.

Crystal data for this complex are: $a = 8{\cdot}38$, $b = 29{\cdot}19$, $c = 12{\cdot}01$ Å, $\beta = 102°06'$, $V = 2872{\cdot}9$ Å^3, $d_c = 1{\cdot}409$ g./cm.^{3}, space group $P2_1/c$, $Z = 8$. There are two molecules in the asymmetric unit.

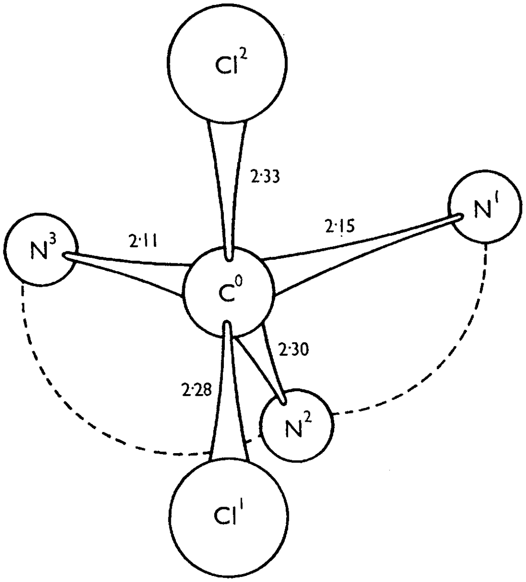
The three-dimensional *X*-ray analysis was undertaken on the basis of 1572 independent, observed reflections, which were measured photometrically on integrated Weissenberg films.

The structure determination was carried out by means of one Patterson and four three-dimensional Fourier syntheses, followed by three cycles of block diagonal least-squares. At the present stage of refinement, the *R* factor is 14·5%.

The structure consists of discrete molecules of Co(denMe)Cl$_2$ in which the cobalt atoms are five-co-ordinated in an environment of two chlorine and the three nitrogen atoms of the ligand. Bond lengths about the cobalt atom are shown in the Figure. The angles are: Cl^1–Co–Cl^2 = 104°, Cl^1–Co–N^1 = 107°, Cl^1–Co–N^2 = 93°, Cl^1–Co–N^3 = 113°, Cl^2–Co–N^1 = 95°, Cl^2–Co–N^2 = 162°, Cl^2–Co–N^3 = 94°, N^1–Co–N^2 = 78°, N^2–Co–N^3 = 80°, N^1–Co–N^3 = 135°.

Bond lengths and angles are average between the corresponding values in the two crystallographic independent molecules. In fact, at the present stage of refinement, there are no significant differences between the co-ordination polyhedra of the two molecules. It should be noted that the central Co–N distance is longer than the other two, probably due to steric effects.

The Co–Cl distances (av. 2·31 Å) compare very well with the sum (2·31 Å) of the Pauling covalent radii of the cobalt (octahedral) and of the chlorine. The shortest intermolecular Co–Cl distance is 5·14 Å. The arrangement of the ligands about the cobalt atom cannot be easily described in terms of square pyramidal or trigonal bipyramidal geometries, even allowing for distortion. Steric repulsions appear to play an important role in determining the distribution of the ligands about the cobalt.



FIGURE

Sketch of the molecular structure of Co(denMe)Cl$_2$, viewed down the lines bisecting the Cl^1–Co–Cl^2 angle. The CH$_2$–CH$_2$ chains are schematically represented by dotted lines.

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[1] M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, in the press.

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