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The Molecular Structure (X-ray Analysis) of a Paramagnetic Five-co-ordinate Cobalt(III) Compound, $[Co(C_{28}H_{22}Cl_2N_4)Cl]$

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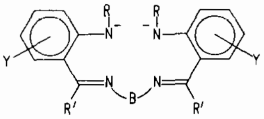
We have previously reported[1] that the cobalt(III) compounds $[CoN_4X]$ (where N_4 represents the quadridentate dianionic ligands I, and X is a halogen) are paramagnetic, with almost complete population of an S = 1 excited state



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at room temperature. The data appeared to suggest a five co-ordinate structure for the paramagnetic species; and this is now confirmed by an X-ray structural analysis of one compound in the series.

Usable, although imperfect, crystals were obtained for the compound [Co(I)Cl] (in which I has the substituents R = H, R′ = Ph, Y = 5-Cl and B = $-(CH_2)_2-$) by reacting the cobalt(II) compound with $CHCl_3$ in CH_2Cl_2. A solvate was obtained with approximately equal amounts of both chlorocarbon species.

Crystal data

$C_{28}H_{22}Cl_3CoN_4$, n $CHCl_3$, m CH_2Cl_2 ($n = m = 0.5$), $M = 682.1$, Monoclinic, $a = 6.92(2)$, $b = 16.19(5)$, $c = 26.69(8)$ Å, $\beta = 95.3(3)^\circ$, D_m (flotation) $= 1.50$ g cm^{-3}, Z = 4, $D_c = 1.52$ g cm^{-3}. Space group $P2_1/c$ [C^5_{2h}, No. 14].

Layers $\{0 \rightarrow 8, k, l\}$ were collected on a Stoë Stadi-2 two-circle diffractometer with stationary counter and moving crystal, giving 1305 independent reflections ($I > 3\sigma$).

The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares to a current R of 0.094. Within the cobalt molecular species, anisotropic vibration parameters have been allowed for the Co and Cl atoms, but isotropic parameters for the C and N atoms. The current model for the disordered solvent is one of total occupancy of the site by either $CHCl_3$ or CH_2Cl_2 (equal abundance). These have been defined as idealised groups and given isotropic thermal parameters.

The cobalt(III) molecular species has the expected five-co-ordinate square pyramidal structure. The four nitrogen donors of the ligand are coplanar (r.m.s. deviation = 0.01 Å); the cobalt is 0.19 Å out of this plane towards the apical chlorine; but an unexpected feature of the structure is a long Co–Cl bond of 2.509(7) Å.

The latter is ~ 0.25 Å longer than a normal Co–Cl bond, and approaches the 2.575(3) Å recently reported[2] for *trans*-$[Co(en)_2Cl(NO)]$. A strong *trans*-influence of the nitrosyl can be postulated to account for the bond lengthening in the nitrosyl, but not in our paramagnetic species. Perhaps it is a result of occupation of the 'd_{z^2}' orbital by one of the unpaired electrons, but it is difficult to see how this alone could lead to bond-lengthening greater than that in square-pyramidal high spin nickel(II) species, where[3] Ni–Cl $\approx$ 2.33 Å. The present structure is approaching the four-co-planar one reported for another paramagnetic cobalt(III) compound[4] – potassium bis(3-n-propylbiuretato)cobaltate(III).

The cobalt–nitrogen bond-lengths are within the range, but near the lower limits, observed for low-spin (diamagnetic) octahedral or five-co-ordinate cobalt(III) species[5]. Those to the iminato nitrogens ($R-NH^-$) are shorter {1.86(2) and 1.85(2) Å} than those to the azomethine nitrogens {1.91(2) and 1.93(2) Å}.

Bond lengths and angles within the quadridentate ligand are normal.

Acknowledgements

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