The Crystal and Molecular Structure of the Five-co-ordinated Complex of Cobalt(II) Isothiocyanate with the Ligand Bis-*NN*-2-diethylaminoethyl-2-methylthioethylamine

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THE tripod-like ligand bis-*NN*-(2-diethylaminoethyl)-2-methylthioethylamine, $(Et_2N{\cdot}CH_2{\cdot}CH_2)_2N(CH_2{\cdot}CH_2{\cdot}SMe)$ (bdme), which is potentially tetradentate with four donor atoms, 3 nitrogen and 1 sulphur, forms high-spin five-co-ordinate complexes of formula [MX bdme BPh_4 (M = Co^{II}, Ni^{II}; X = halogen, or NCS)]. These behave as 1 : 1 electrolytes.

The same ligand reacted with cobalt or nickel thiocyanate in butanol to yield products of formulae $M(NCS)_2$. These two high-spin complexes are shown by their *X*-ray powder photographs to be isomorphic. Their reflectance and absorption spectra in dichloroethane indicate five-co-ordination. The compounds are monomeric and practically undissociated in that solvent, and their i.r. spectra show that both NCS groups co-ordinate through the nitrogen. Hence, it was assumed that the ligand bdme is tridentate

and that the metal atom is co-ordinated to five nitrogen atoms.[1]

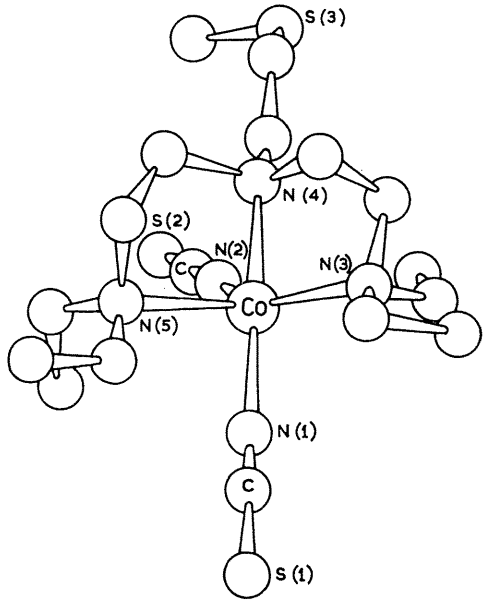

FIGURE. *A perspective view of the molecular configuration of* $Co(NCS)_2$ bdme.

The structure of the cobalt complex has now been investigated by three-dimensional *X*-ray analysis.

Crystal data: space group $P2_1/c$; $a = 7{\cdot}615 \pm 0{\cdot}002$, $b = 13{\cdot}927 \pm 0{\cdot}004$, $c = 25{\cdot}442 \pm 0{\cdot}010$ Å, $\beta = 97° 59' \pm 3'$; D_m (by flotation = 1·26 g. cm.$^{-3}$; $D_c = 1{\cdot}25$ g. cm.$^{-3}$, for $Co(NCS)_2$bdme,$\frac{1}{2}$BuOH.

Multiple-film equi-inclination Weissemberg data were collected using Fe–K_α radiation and the intensities of 1332 reflections were measured. The structure was solved by the heavy atom method and refined by full-matrix least-squares, with anisotropic temperature factors, to R 6·9% (observed reflections only).

The structure consists of discrete molecules of $Co(NCS)_2$-bdme (Figure) in which the five-co-ordinate cobalt(II) atom is bonded to five nitrogen donor-atoms, three from the ligand molecule and two from isothiocyanate groups, a distorted trigonal bipyramid with N(1) and N(4) in the axial positions. The sulphur atom of the ligand molecule is not bonded to the metal (Co · · · S 5·82 Å).

Bond lengths and angles in the polyhedron are: Co–N(1) 1·99, Co–N(2) 1·97, Co–N(3) 2·16, Co–N(4) 2·25, Co–N(5) 2·15 Å, N(1)–Co–N(2) 99·4°, N(1)–Co–N(3) 92·0°, N(1)–Co–N(4) 169·7°, N(1)–Co–N(5) 97·9°, N(2)–Co–N(3) 127·5°, N(2)–Co–N(4) 90·7°, N(2)–Co–N(5) 105·6°, N(3)–Co–N(4) 80·3°, N(3)–Co–N(5) 123·4°, N(4)–Co–N(5) 81·0°; mean estimated standard deviations 0·01 Å and 0·5°. The metal atom is displaced by 0·22 Å from the equatorial plane, toward N(1). The solvent molecules are disordered and occupy large voids in the structure.

Recently, the structure of the compound $Ni(NCS)_2$-bddae (bddae = bis-*NN*-2-diethylaminoethyl)-2-diphenylarsinoethylamine), has been determined.[2] The environment of the metal atom is the same in that complex and in $Co(NCS)_2(N_3S)$, but the co-ordination geometry in $Ni(NCS)_2$-(N_3As) closely approaches square pyramidal.

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[1] L. Sacconi and R. Morassi, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 449.
[2] M. Di Vaira and L. Sacconi, *Chem. Comm.*, 1969, 10.