Structural Evidence for Ground-state Steric Effects in Chloropentakis(methylamine)cobalt(III) Nitrate

By Bruce M. Foxman
(*Research School of Chemistry, The Australian National University, P.O. Box 4, Canberra, A.C.T. 2600, Australia*)

Summary Severe steric interactions in $[Co(NH_2Me)_5Cl](NO_3)_2$ cause large angle deformations in Co–N–C (*ca.* 11—15°) and N–Co–N or –Cl (up to *ca.* 7°) angles.

Considerable evidence has accumulated recently to support the proposal that the base hydrolysis of $Co(NH_3)_5X^{2+}$ ions (X = Cl, Br, I, or NO_3) takes place by a dissociative (S_N1CB) mechanism.[1] For such a dissociative process, steric crowding in cobalt(III) complexes of this type should lead to an acceleration in the rate of base hydrolysis by relief of steric strain as the reactant proceeds through the activated complex to the relatively stabilized five-coordinate intermediate. This hypothesis has recently been examined[2] for the hydrolysis of a series of amine complexes of the type $(RNH_2)_5CoCl^{2+}$. The supposedly sterically hindered species containing five primary amine ligands showed very large increases ($>10^5$) in the rate of base hydrolysis relative to the corresponding ammonia complex. Evaluation of minimized non-bonded interactions for the methylamine complex (using rigid models) indicated that severe steric interactions were present which would undoubtedly lead to deformation and hence reduced stability in the reactant ground state. Additional evidence for these ground-state steric effects was sought in an *X*-ray crystal structure analysis of the methylamine complex.

Crystals of chloropentakis(methylamine)cobalt(III) dinitrate $[Co(NH_2Me)_5Cl](NO_3)_2$ are triclinic, space group $B\bar{1}$ (general positions: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2} + x, y, \frac{1}{2} + z$; $\frac{1}{2} - x, \bar{y}, \frac{1}{2} - z$), $a = 8·151(4)$, $b = 14·067(7)$, $c = 14·163(7)$ Å, $\alpha = 106·78(10)°$, $\beta = 93·45(10)°$, $\gamma = 89·56(10)°$, $Z = 4$. The 2068 independent reflexions, for which $I/\sigma(I) \geqslant 3·0$, were measured on a PICKER FACS-I automatic diffractometer crystal monochromated Cu-K_α radiation). Least-squares refinement, using absorption-corrected data, of positional and anisotropic thermal parameters for all non-hydrogen atoms has converged to a conventional *R*-factor of 0·061. E.s.d.s of the bond lengths at the present stage of refinement are: Co–Cl, 0·002; Co–N, 0·005; N–C, 0·009 Å.

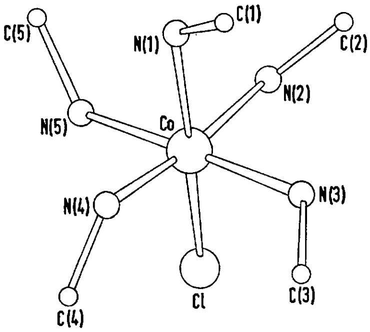

Figure. *The geometry of the complex cation in* $[Co(NH_2Me)_5Cl](NO_3)_2$. *Angles showing largest deformations:* Co–N(1)–C(1), 120·3; Co–N(2)–C(2), 122·1; Co–N(3)–C(3), 120·9; Co–N(4)–C(4), 122·9; Co–N(5)–C(5), 124·2; N(1)–Co–N(3), 96·6; N(1)–Co–N(4), 85·8; N(3)–Co–N(4), 93·7, N(4)–Co–Cl, 95·1; N(5)–Co–Cl, 84·8°. *Estimated standard deviations:* Co–N–C, 0·4; N–Co–N, 0·2; N–Co–Cl, 0·15°.

The cobalt atom is in a distorted octahedral environment (see Figure). The most striking feature of the structure is that, while all bond lengths are near normal (Co–N range, 1·983—2·005; N–C range 1·479—1·516; Co–Cl, 2·285 Å), there are large distortions in Co–N–C angles. Thus, Co–N–C angles lie in the range 120—124°; there are distortions of as much as 15° from 'expected' tetrahedral values. Also, the valence angles about the cobalt atom are substantially distorted by as much as 6·6° from 'expected' octahedral values. It is unlikely that the distortions are caused by crystal packing forces, as all intermolecular contacts appear to be normal. Further, the geometry of the nitrate anions is quite normal (N–O range, 1·23—1·25 Å; O–N–O range 118—121°). Hence the large angle deformations must be a consequence of severe non-bonded interactions. A similar distortion appears to occur at the bound carbon atom in $Rh(NH_3)_5Et^{2+}$ (Rh–C–C, 121·2°).[3]

Strain-energy minimization calculations[4] indicate that non-bonded interactions and valence angle deformations, as well as contributions from torsional and bond-stretching effects, predominate in the determination of distortions from regular geometry in sterically hindered complexes. After hydrogen atoms have been located for the methylamine complex, a more detailed calculation[4] of the ground-state strain energy will be carried out.

(*Received, 8th February* 1972; *Com.* 211.)

[1] M. L. Tobe, *Accounts Chem. Res.*, 1970, **3**, 377, and references therein.

[2] D. A. Buckingham, B. M. Foxman, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 1790.

[3] A. C. Skapski and P. G. H. Troughton, *Chem. Comm.*, 1969, **666**.

[4] M. R. Snow, *J. Amer. Chem. Soc.*, 1970, **85**, 3610; D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *ibid.*, p. 3617.