Five-co-ordinate, Square-pyramidal, High-spin Nickel(II) Compounds with a Linear Tetra-amine Ligand

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Summary The first proven example of a square-pyramidal five-co-ordinate halogenotetra-aminenickel(II) cation is reported.

THE tetra-amine ligand *NN'*-di-(3-aminopropyl)piperazine (abbreviated as 3,22,3-tet—*cf.* ref. 1) forms compounds of relatively low stability with first row transition-metal ions so that metal "hydroxides" usually are precipitated from aqueous mixtures.[2] However, compounds of the types $M(3,22,3\text{-tet})X_2$ (where X = Cl, Br, I, NCS, NO_3, BF_4, ClO_4, and PF_6; and M = Fe, CO, Ni, Cu, Zn) and $M(3,22,3\text{-tet})X^1X^2$ (where X^1 = Cl, Br, and NCS; and X^2 = ClO_4, BF_4, and PF_6) can be obtained from nonaqueous solvents (alcohols, dimethylformamide, Me_2SO, tetrahydrofuran, *etc.*); and many of them contain square-pyramidal five-co-ordinate cations of the type $[MN_4X]^+$. Their structures have been correlated initially by X-ray powder photography, visible and i.r. spectra, and magnetic measurements; and one compound [Ni(3,22,3-tet)Cl]Cl then was chosen as a representative species for a three-dimensional X-ray structural analysis.

Crystals were obtained from NN-dimethylformamide as blue-green monoclinic prisms with unit-cell parameters $a = 7{\cdot}85$, $b = 14{\cdot}47$, $c = 14{\cdot}14$ Å, $\beta = 110{\cdot}0^\circ$ and $Z = 4$, corresponding to a calculated density of 1·49 g.cm.$^{-3}$. The experimental density, measured by flotation, was 1·46 g.cm.$^{-3}$. Systematic absences of $\{h0l\}$, $l = 2n + 1$ and $\{0k0\}$ $k = 2n + 1$ gave the space group unambiguously as $P2_1/c$. From a crystal mounted in a Lindeman glass capillary, photographic data were collected by Weissenberg and precession methods (1126 independent reflections). The structure was solved by conventional Patterson and Fourier techniques, and has been refined by least-squares methods to $R = 0{\cdot}111$, anisotropic thermal motion being allowed for the nickel and two chlorine atoms, and isotropic thermal motion for all remaining non-hydrogen atoms.

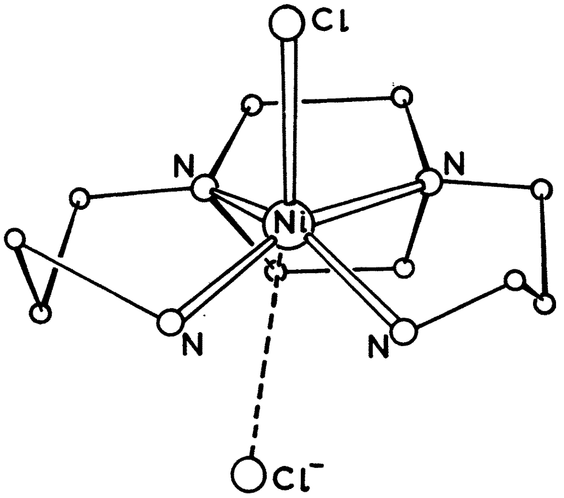

FIGURE 1. *The geometry of* [Ni(3,22,3-tet)Cl]Cl.

The analysis shows the cation to have a five-co-ordinate square-pyramidal geometry as in Figure 1. The four N donor atoms are coplanar, with Ni–N bond distances of 2·07 and 2·11 Å (mean values for primary and tertiary nitrogens, respectively) and an Ni–Cl bond distance of 2·33 Å. The nickel atom is 0·34 Å out of the plane of the nitrogen atoms in the direction of the bonded chlorine. The other chlorine atom (chloride ion) lies close to the sixth co-ordination site of an octahedron at 3·4 Å from the nickel, but it is closer to the primary nitrogen atoms (3·22 and 3·30 Å) to which it appears to be hydrogen-bonded.

The five-co-ordinate geometry in this nickel(II) compound is undoubtedly largely of steric origin. The quadridentate tetra-amine is non-facultative (see ref. 1) and must dispose its four nitrogen atoms in essentially the same plane. If, in addition, two chloride ions were to bond to the metal in *trans*-octahedral sites, each would experience a significant repulsion from the hydrogen atoms of the piperazine ring (those marked with an asterisk in Figure 2). By contrast, the total steric effect in the five-co-ordinate species is much less, since the positioning of the nickel atom out of the tetra-amine plane allows the piperazine ring to twist away from the bonded anion. A necessary result of this twist is that one pair of piperazine hydrogen atoms now blocks the sixth co-ordination site. The adjustments of geometry in this case are represented by the broken lines in Figure 2.

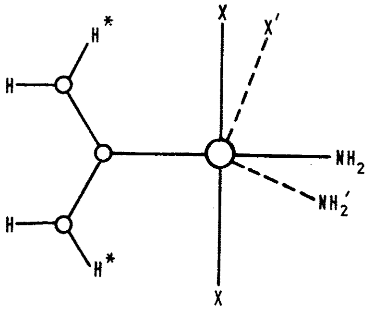

FIGURE 2. *A projection perpendicular to the piperazine planes showing the geometry of one half of the molecule and the steric effects of the piperazine hydrogen atoms. The full lines refer to the projection of the octahedron, and the broken lines to the adjustments which occur in the five-co-ordinate geometry.*

The magnitudes of the steric repulsions in such a complex, and their effect on stereochemistry, will depend, of course, on the size of the anion, and this is reflected in the compounds isolated with different anions. For isothiocyanate (-NCS), with a smaller effective radius than chloride, both the six-co-ordinate [Ni(3,22,3-tet)(NCS)$_2$] and five-co-ordinate [Ni(3,22,3-tet)NCS]SCN isomers have been obtained and, for the larger bromide ion, both the five-co-ordinate [Ni(3,22,3-tet)Br]Br and four-co-ordinate [Ni(3,22,3-tet)]Br$_2$ isomers.

This ligand is the precursor of a class of linear tetra-amines (for example, those derived from the seven- and eight-membered heterocyclic ring systems hexahydro-1,4-diazepine and octahydro-1,5-diazocine) which can be expected to give high-spin five-co-ordinate square-pyramidal nickel(II) cations, in contrast to the trigonal bipyramidal geometry of the halogenotetra-aminenickel(II) cations obtained from the "tripod" ligands.[3]

We thank the S.R.C. for a Studentship (to J.G.G.).

(*Received, May* 21*st*, 1969; *Com.* 720.)

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[1] B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc.* (*A*), 1966, 1331.

[2] W. Wind and D. E. Goldberg, *J. Inorg. Nuclear Chem.*, 1969, **31**, 575.

[3] P. Dapporto and L. Sacconi, *Chem. Comm.*, 1969, 329; L. Sacconi in "Transition-Metal Chemistry," vol 4, ed. R. Carlin, 1968, p. 199, and references therein.