A Novel Square Pyramidal High-spin Nickel(II) Complex involving the Quinquedentate NNN'-Tris[2-(2'-pyridyl)ethyl]ethylenediamine

By W. MAZUREK and A. T. PHILLIP*

(Australian Defence Scientific Service, Defence Standards Laboratories, P.O. Box 50, Ascot Vale, Victoria, 3032, Australia)

and B. F. HOSKINS and F. D. WHILLANS

(Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia)

Summary   The complex cation in the compound [Ni(tpen)]-$(ClO_4)_2$,$MeNO_2$, where tpen denotes the quinquedentate ligand NNN'-tris[2-(2'-pyridyl)ethyl]ethylenediamine, has been found (from its electronic spectrum and in its crystal structure) to be five covalent with all five nitrogen atoms of the chelate molecule bonded to the nickel atom in a somewhat distorted square pyramidal configuration.

THE quinquedentate chelate NNN'-tris-[2-(2'-pyridyl)-ethyl]ethylenediamine[(I) tpen] forms a dark blue complex with nickel perchlorate which has the composition [Ni-(tpen)]$(ClO_4)_2$. The complex behaves as a 1:2 electrolyte in nitromethane solution; the molar conductance is 184 cm.[2] ohm[-1] mole[-1] at 301° K. The magnetic moment of the nickel atom is 3·14 B.M. at 287° K which indicates a high-spin configuration. These data strongly suggest that the complex ion has a stereochemistry based on a five-co-ordinated nickel atom. Molecular models show that the five potential nitrogen-donor atoms of the quinquedentate

(I)
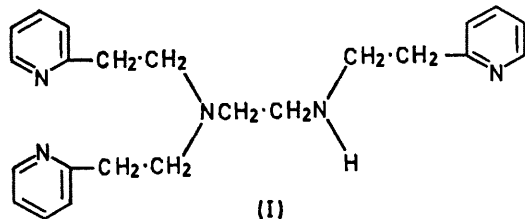
ligand (I), are all capable of simultaneous co-ordination to the nickel atom from the apices of either a trigonal bipyramid or a square pyramid without strain of the natural valence angles. Therefore, it is not possible to predict the stereochemistry of the nickel atom on steric grounds alone. However, the square pyramidal geometry was strongly favoured because the electronic absorption spectrum of the complex in nitromethane solution agreed very well with the transition energies calculated by Ciampolini[1] for the high-spin nickel(II) ion situated in a square pyramidal field of five dipoles each of strength 4·85 D; these data are summarised in the Table. Further, a structure based on the square

high-spin penta-co-ordinated nickel(II) ion is bonded to five nitrogen atoms of a quinquedentate ligand in a square pyramidal environment.

The ligand was synthesised by a modification of the method reported by Profft and Lojack.[2] The crystals used in the structure determination were grown from nitromethane solution of the complex and had the composition [Ni(tpen)]$(ClO_4)_2$,$MeNO_2$.

Crystal data: $C_{24}H_{32}O_{10}N_6Cl_2Ni$, $M = 694$, monoclinic, $a = 12·840 \pm 0·005$, $b = 13·865 \pm 0·005$, $c = 18·850 \pm 0·005$ Å, $\beta = 116·76 \pm 0·03°$, $U = 2997$ Å^3, $D_m = 1·52 \pm 0·02$ (by flotation), $Z = 4$, $D_c = 1·539$ g.cm.$^{-3}$, space group $P2_1/c$ (C_{2h}^5, No. 14), Cu-K_α radiation, Siemens automatic diffractometer, $\mu = 31·06$ cm.$^{-1}$, absorption corrections were applied. Complete data were recorded to a maximum Bragg angle of 45° and for the case of the $h0l$, $h1l$, and $h2l$ reflections the maximum Bragg angle was 70°. This gave 2704 "significant" reflections.
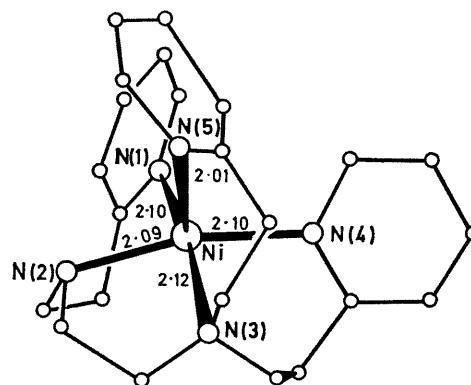
The co-ordinates of the nickel atom were obtained from

TABLE

Observed and calculated transition energies

Spin-allowed transitions	Frequencies (cm.$^{-1}$)		
	Observed (ϵ molar)		Calculated[1]
$^3E \leftarrow {}^3B_1$	7385	(12·5)	7200
$^3A_2 \leftarrow {}^3B_1$	11,870	(6·9)	10,800
$^3B_2 \leftarrow {}^3B_1$	13,630	(5·9)	12,300
$^3E \leftarrow {}^3B_1$	17,510	(47·8)	17,300

pyramidal configuration has been found by a crystal structure determination using X-ray diffraction methods. This we believe is the first report of a structure where a

FIGURE.   The complex ion [Ni(tpen)]$^{2+}$ viewed down the b axis of [Ni(tpen)]$(ClO_4)_2$,$MeNO_2$.   The atoms N(1), N(2), N(3), and N(4) constitute the basal plane and N(5) the apical atom of the distorted square pyramidal environment about the nickel atom.   Nickel to nitrogen bond lengths are shown.   Bond angles around the co-ordination sphere of the nickel atom are: N(1)–Ni–N(5) 101, N(2)–Ni–N(5) 98, N(3)–Ni–N(5) 96, N(4)–Ni–N(5) 102, N(1)–Ni–N(2) 86, N(2)–Ni–N(3) 86, N(3)–Ni–N(4) 91, N(4)–Ni–N(1) 91, N(1)–Ni–N(3) 162, N(2)–Ni–N(4) 160°.

a three-dimensional Patterson synthesis and the remainder of the non-hydrogen atoms were located in subsequent three-dimensional electron-density distributions and difference syntheses. The structure is being refined by a least-squares procedure where individual anisotropic temperature factors are being applied. Although there is strong evidence of preferred orientations of the perchlorate anions their oxygen atoms are vibrating markedly and could be disorded. This probably accounts for the relatively high R-factor which is, based on the significant terms only, 0·09.

The crystal consists of complex cations of composition [Ni(tpen)]$^{2+}$, perchlorate anions, and discrete nitromethane molecules. Each nickel atom is covalently bonded to all five nitrogen atoms of the ligand which are situated at the corners of a somewhat distorted square pyramid (see Figure). The four atoms comprising the basal plane [N(1), N(2), N(3), and N(4)] are co-planar and the nickel atom and the apical atom [N(5)] lie along a line which is approximately 2° to the normal of the basal plane; the nickel atom is, however, 0·32 Å [estimated standard deviation (e.s.d.) 0·005 Å] above the basal plane towards the apical nitrogen atom.

The nickel to nitrogen bond distances seem to fall into two distinct groups because the nickel to basal-nitrogen atom bond lengths which range from 2·09 to 2·12 Å (average e.s.d. 0·010 Å) do not differ significantly from each other but differ significantly from the nickel to apical-nitrogen atom bond length of 2·01 Å (e.s.d. 0·010 Å).

Three of the recently reported penta-co-ordinated nickel(II) complexes have been high-spin and square pyramidal. These are monochloro-NN'-di-(3-amino-propyl)-piperazinenickel(II) chloride,[3] bis-(N-β-diethyl-aminoethyl-5-chlorosalicylaldimato)nickel(II),[4] and di-iso-thiocyanato-[NN-bis-(2-diethylaminoethyl)-2-diphenylars-inoethylamine]nickel(II).[5] In these compounds the nickel atoms are above the basal plane by 0·34, 0·36, and 0·35 Å respectively and show the same behaviour as our compound.

[1] M. Ciampolini, *Inorg. Chem.*, 1966, **5**, 35.
[2] E. Profft and S. Lojack, *Rev. Roumaine Chim.*, 1962, **7**, 405.
[3] N. A. Bailey, J. G. Gibson, and E. D. McKenzie, *Chem. Comm.*, 1969, 741.
[4] P. L. Orioli, M. DiVaira, and L. Sacconi, *J. Amer. Chem. Soc.*, 1965, **87**, 2059; 1966, **88**, 4383.
[5] M. DiVaira and L. Sacconi, *Chem. Comm.*, 1969, 10.