Crystal and Molecular Structure of Five-co-ordinate *NNN'*-Tris[2-(2'-pyridyl)ethyl]ethane-1,2-diaminenickel(II) Perchlorate–Nitromethane

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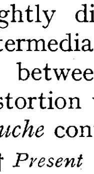
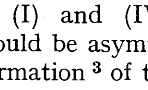
The structure of the title compound has been determined from single-crystal three-dimensional *X*-ray diffractometric data. The structure was solved by Patterson and Fourier methods, and refined by least-squares techniques to *R* 0·082 for 2704 independent reflections. The nickel atom in the complex cation, surrounded by five nitrogen atoms of the ligand in a square pyramidal arrangement, lies 0·33 Å above the plane of the four basal nitrogen atoms. The Ni–N(apical pyridyl) distance [2·011(6) Å] is significantly shorter than the mean (2·091 Å) for the four Ni–N(basal nitrogen) distances. The nitromethane is present as a molecule of crystallisation. The unit cell is monoclinic with $Z = 4$, $a = 12{\cdot}840 \pm 0{\cdot}005$, $b = 13{\cdot}865 \pm 0{\cdot}005$, $c = 18{\cdot}850 \pm 0{\cdot}005$ Å, $\beta = 116{\cdot}76 \pm 0{\cdot}03°$, space group $P2_1/c$.

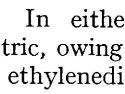
MAZUREK and Phillip[1] isolated a new quinquedentate ligand, *NNN'*-tris[2-(2'-pyridyl)ethyl]ethane-1,2-diamine (tepen), $R_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NHR$ (R = 2'-pyridylethyl). This ligand reacts with nickel ions in alcoholic solutions to give a precipitate of $[Ni(tepen)](ClO_4)_2$ which forms large deep blue crystals of $[Ni(tepen)](ClO_4)_2,MeNO_2$ when recrystallised from nitromethane. Conductimetric, magnetic, i.r. and u.v.–vis. spectral investigations suggested that the complex cation was a monomeric square-pyramidal complex with all the nitrogen atoms of tepen bonded to the nickel ion.[1] However, molecular models indicated that five nitrogen-donor atoms were all capable of simultaneous co-ordination to the nickel atom from the apices of either a trigonal bipyramid (I) or a square pyramid [(II)—(IV)] without any substantial strain of the natural valency angles. A definite prediction of the geometry about the nickel atom was not therefore possible; we considered that it might be slightly distorted, causing the complex to have an intermediate-type geometry,[2] either between (I) and (II) or between (I) and (IV). In either situation the distortion would be asymmetric, owing to the expected *gauche* conformation[3] of the ethylenediamine moiety.



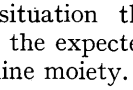
(I)



(II)



(III)



(IV)

This structure determination by *X*-ray diffraction methods was undertaken in order to examine the geometry of the donor atoms about the nickel atom and to provide further structural data on five-co-ordinate nickel(II) complexes with five similar donor atoms.

EXPERIMENTAL

Crystal Data.—$C_{24}H_{32}Cl_2O_{10}N_6Ni$, $M = 694$, Monoclinic, $a = 12{\cdot}840 \pm 0{\cdot}005$, $b = 13{\cdot}865 \pm 0{\cdot}005$, $c = 18{\cdot}850 \pm 0{\cdot}005$ Å, $\beta = 116{\cdot}76 \pm 0{\cdot}03°$, $U = 2997$ Å^3, $D_m = 1{\cdot}52 \pm 0{\cdot}02$, $Z = 4$, $D_c = 1{\cdot}539$ g cm^{-3}, $F(000) = 4 \times 360$. Space group $P2_1/c$ (C^5_{2h}, No. 14). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) = 31·06 cm^{-1}, $c_z = 1{\cdot}3 \times 10^{-6}$. Siemens automatic diffractometer; absorption and secondary extinction corrections were applied.

All crystals were parallelepipeds with well-developed $\pm(\bar{1}02)$, $\pm(110)$, and $\pm(1\bar{1}0)$ morphological crystal faces; the angles of each of the six faces, all parallelograms, were within 1° of 80 and 100°. The chosen crystal (1·5 × 0·30 × 0·35 mm) was cut parallel to the $(\bar{1}02)$ face with a thin blade so that the needle length was reduced to 0·27 mm.

Collection and Processing of Diffraction Data.—A least-squares procedure was used to obtain the best set of accurate cell parameters. Complete data were recorded to a maximum Bragg angle of 45° and those of the *h0l*, *h1l*, and *h2l* classes of reflections were recorded to a maximum of 70°. The diffractometer settings used are as follows: five value intensity measurements per reflection (I_1 and I_5 half-scans and I_3 a full-scan of the intensity profile in 0·02° integrated steps each of 0·6 s, I_2 and I_4 background counts each for the same time as a full scan); scan range in θ determined from 0·50 + 0·10 tan θ for the half-scan at lower θ and 0·45 + 0·10 tan θ for the half-scan at higher θ; this scan range allowed adequately for any small diffractometer–crystal misalignment. Check reflection measurement

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[1] A. T. Phillip, W. Mazurek, and A. T. Casey, *Austral. J. Chem.*, 1971, **24**, 501; W. Mazurek, A. T. Phillip, B. F. Hoskins, and F. D. Whillans, *Chem. Comm.*, 1970, 184.

[2] B. F. Hoskins and F. D. Whillans, *Co-ordination Chem. Rev.*, 1973, **9**, 365.

[3] R. D. Gillard and H. M. Irving, *Chem. Rev.*, 1965, **65**, 603.

indicated a reasonably stable crystal alignment and negligible nitromethane loss during data collection.

Those reflections with $I < 2\sigma(I)$ were not processed. Lorentz, polarisation, and absorption corrections were applied and data were placed on an absolute scale; corrections according to the method of Zachariasen [4] were applied. Equivalent reflections were combined during a sorting of the data, to give 2704 unique reflections, which were used in the structure determination and refinement. Two reflections, 147 and 442, were lost during the data collection.

Structure Determination and Refinement.—The approximate position of the nickel atom was determined from a three-dimensional Patterson synthesis. The positions of all other non-hydrogen atoms were located from cycles of electron-density distributions. In these calculations the chlorine positions were initially given a scattering-factor curve of a freely rotating perchlorate ion [5] until difference syntheses indicated that each perchlorate ion could be described more adequately as individual chlorine and oxygen atoms.

A least-squares refinement, in which $\Sigma w(|F_o| - |F_c|)^2$ was minimised, was applied using ORFLS,[6] where the weight, w, assigned to each reflection was $w = [\sigma^2(|F_o|) + A|F_o|^2 + B\sum_j f_j^2]^{-1}$, where $\sum_j f_j^2$ is the sum over all atoms in the unit cell of the square of the scattering factor at a Bragg angle (θ) of zero and where $|F_o|$ and $\sigma^2(|F_o|)$ are on the absolute scale.[7] Initial values of 0·005 and 0·0001 respectively were arbitrarily assigned to the empirical coefficients A and B, later changed to 0·0028 and 0·0003 in order to maintain mean values of $w(|F_o| - |F_c|)^2$ approximately constant over ranges of $|F_o|$ and $\sin \theta$.

As the minimum value of $\Sigma w(|F_o| - |F_c|)^2$ achieved with isotropic thermal parameters was much higher than expected for data of good quality (R was 0·15), individual anisotropic temperature factors for all atoms, except those of the eight perchlorate oxygen atoms [O(3)—(10)], were introduced. It was found that until these atoms (with high isotropic temperature factors) were treated anisotropically no marked drop in the value of $\Sigma w(|F_o| - |F_c|)^2$ could be achieved, but after this was done R was reduced to 0·09. As the perchlorate oxygen atom [O(10)] tended to have shifts in its thermal parameters which caused its temperature-factor expression to become non-positive definite (*i.e.* physically unrealistic) and because the Cl(2)–O(10) bond length was approximately parallel to the b axis, it was decided to maintain its b_{12} and b_{23} thermal parameters at an arbitrary value of zero.

As only 157 parameters could be varied in each cycle of the refinement, three cycles of full-matrix least-squares [6] were required to refine all the parameters at least once. In each step of the refinement the positional parameters were initially refined, followed by cycles in which the three positional and six thermal parameters of atoms in close proximity were refined.[8] Refinement was continued until all positional and thermal parameters had shifts which were $< 0{\cdot}2\sigma$.

Scattering-factor curves chosen were those for neutral chlorine, nitrogen, carbon, and oxygen atoms, and for divalent nickel cation; [9] that for nickel was corrected for the rather large anomalous dispersion with Cu-K_α radiation.[9]

Final calculated structure factors, observed structure amplitudes, and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21210 (8 pp., 1 microfiche).†

The rather high R factor of 0·082 and weighted R' of 0·124 [$R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$] are attributed to the inadequate five-atom model provided for the disordered perchlorate ions; two peaks of $+2{\cdot}2$ eÅ^{-3}, due to this disorder, and observed in the final difference synthesis at 0·06, 0·12, 0·15 and 0·36, 0·25, 0·00 could not be reduced in size satisfactorily.

TABLE 1

Final atomic (fractional) co-ordinates * ($\times 10^4$)

	x/a	y/b	z/c
Ni	6938(1)	3024(1)	4280(1)
N(1)	7039(5)	1760(4)	4923(3)
N(2)	5162(5)	3020(5)	3956(4)
N(3)	6513(6)	4021(5)	3335(3)
N(4)	8503(4)	2720(4)	4271(3)
N(5)	7409(5)	4027(4)	5140(3)
C(1)	7803(6)	1617(6)	5670(4)
C(2)	7871(9)	753(8)	6093(6)
C(3)	7086(11)	46(8)	5684(9)
C(4)	6240(11)	208(7)	4887(9)
C(5)	6251(6)	1075(6)	4522(5)
C(6)	5414(8)	1290(8)	3684(5)
C(7)	4575(7)	2107(8)	3594(6)
C(8)	4656(8)	3881(8)	3433(6)
C(9)	5228(8)	3939(8)	2863(5)
C(10)	7084(8)	3818(7)	2807(4)
C(11)	7373(7)	2734(6)	2836(4)
C(12)	8502(6)	2538(5)	3570(4)
C(13)	9499(7)	2226(6)	3538(5)
C(14)	10528(7)	2107(7)	4242(6)
C(15)	10531(6)	2329(6)	4954(5)
C(16)	9504(6)	2633(5)	4949(4)
C(17)	6850(10)	5041(6)	3639(5)
C(18)	7996(9)	5088(6)	4345(5)
C(19)	7955(8)	4864(6)	5123(5)
C(20)	8276(10)	5521(7)	5715(6)
C(21)	8107(10)	5344(7)	6386(5)
C(22)	7525(9)	4511(6)	6404(5)
C(23)	7193(6)	3860(6)	5776(4)
N(6)	8314(6)	−10(5)	3742(4)
O(1)	8464(7)	212(8)	4394(4)
O(2)	7416(6)	192(7)	3157(4)
C(24)	9333(10)	−422(10)	3669(6)
Cl(1)	4429(2)	2316(2)	771(1)
O(3)	5257(6)	2989(5)	788(5)
O(4)	3395(9)	2704(12)	618(11)
O(5)	4898(10)	1871(8)	1515(6)
O(6)	4336(10)	1512(8)	260(6)
Cl(2)	1130(2)	1750(2)	2252(1)
O(7)	31(8)	2180(10)	1908(6)
O(8)	1712(9)	2025(16)	3047(6)
O(9)	1781(10)	2075(12)	1866(7)
O(10)	1054(25)	915(8)	2278(22)

* Numbers in parentheses here and in succeeding Tables are estimated standard deviations in the least significant digits.

Final positional parameters for nonhydrogen atoms are listed in Table 1, bond lengths in Table 2, bond angles in Table 3, and relevant mean planes in Table 4.

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[4] W. H. Zachariasen, *Acta Cryst.*, 1963, **16**, 1139.

[5] B. Dawson, personal communication.

[6] W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, Report ORNL TM 305, Oak Ridge, Tennessee, 1962.

[7] D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Cryst.*, 1969, **B25**, 374; R. C. G. Killean, *ibid.*, p. 977.

[8] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1362.

[9] 'International Tables for *X*-Ray Crystallography,' vol. III, 1962, pp. 202—207 and 214.

Table 2

Intramolecular covalent bond lengths (Å)

Ni–N(1)	2·100(6)	C(10)–C(11)	1·543(13)
Ni–N(2)	2·079(6)	C(11)–C(12)	1·512(10)
Ni–N(3)	2·124(6)	C(12)–N(4)	1·344(8)
Ni–N(4)	2·061(5)	C(12)–C(13)	1·378(10)
Ni–N(5)	2·011(6)	C(13)–C(14)	1·399(12)
N(1)–C(5)	1·345(9)	C(14)–C(15)	1·376(12)
N(1)–C(1)	1·320(9)	C(15)–C(16)	1·379(10)
C(1)–C(2)	1·419(12)	C(16)–N(4)	1·349(8)
C(2)–C(3)	1·368(16)	N(3)–C(17)	1·514(12)
C(3)–C(4)	1·420(17)	C(17)–C(18)	1·476(14)
C(4)–C(5)	1·389(14)	C(18)–C(19)	1·524(12)
C(5)–C(6)	1·488(13)	C(19)–N(5)	1·364(10)
C(6)–C(7)	1·519(15)	C(19)–C(20)	1·353(12)
C(7)–N(2)	1·474(12)	C(20)–C(21)	1·398(14)
N(2)–C(8)	1·497(12)	C(21)–C(22)	1·383(14)
C(8)–C(9)	1·554(13)	C(22)–C(23)	1·395(12)
C(9)–N(3)	1·484(11)	C(23)–N(5)	1·367(9)
N(3)–C(10)	1·506(10)		
N(6)–O(1)	1·196(9)	N(6)–C(24)	1·489(13)
N(6)–O(2)	1·217(9)		
Cl(1)–O(3)	1·405(7)	Cl(2)–O(7)	1·394(9)
Cl(1)–O(4)	1·338(10)	Cl(2)–O(8)	1·393(11)
Cl(1)–O(5)	1·396(9)	Cl(2)–O(9)	1·407(11)
Cl(1)–O(6)	1·443(10)	Cl(2)–O(10)	1·165(12)

Table 3

Bond angles (°)

N(1)–Ni–N(2)	86·7(2)	N(2)–Ni–N(4)	160·4(2)
N(1)–Ni–N(3)	162·4(2)	N(2)–Ni–N(5)	97·5(2)
N(1)–Ni–N(4)	91·6(2)	N(3)–Ni–N(4)	90·5(2)
N(1)–Ni–N(5)	101·2(2)	N(3)–Ni–N(5)	95·5(2)
N(2)–Ni–N(3)	85·5(3)	N(4)–Ni–N(5)	102·0(2)
Ni–N(1)–C(1)	124·4(5)	C(10)–C(11)–C(12)	108·9(6)
Ni–N(1)–C(5)	115·5(5)	C(11)–C(12)–N(4)	116·3(6)
C(1)–N(1)–C(5)	120·2(7)	C(11)–C(12)–C(13)	122·8(6)
N(1)–C(1)–C(2)	123·7(8)	C(13)–C(12)–N(4)	120·8(6)
C(1)–C(2)–C(3)	116·4(10)	C(12)–C(13)–C(14)	119·6(7)
C(2)–C(3)–C(4)	120·1(9)	C(13)–C(14)–C(15)	119·1(7)
C(3)–C(4)–C(5)	119·1(9)	C(14)–C(15)–C(16)	118·6(7)
C(4)–C(5)–N(1)	120·4(9)	C(15)–C(16)–N(4)	122·3(6)
C(4)–C(5)–C(6)	122·5(9)	C(16)–N(4)–Ni	121·8(4)
N(1)–C(5)–C(6)	117·1(7)	C(16)–N(4)–C(12)	119·6(6)
C(5)–C(6)–C(7)	113·9(7)	C(12)–N(4)–Ni	118·5(4)
C(6)–C(7)–N(2)	113·6(6)	N(3)–C(17)–C(18)	112·4(7)
C(7)–N(2)–Ni	113·8(5)	C(17)–C(18)–C(19)	114·0(8)
C(7)–N(2)–C(8)	113·5(7)	C(18)–C(19)–C(20)	121·8(8)
Ni–N(2)–C(8)	106·6(5)	C(18)–C(19)–N(5)	115·9(7)
N(2)–C(8)–C(9)	107·3(7)	C(20)–C(19)–N(5)	121·5(8)
C(8)–C(9)–N(3)	109·5(6)	C(19)–C(20)–C(21)	121·0(9)
C(9)–N(3)–Ni	104·5(5)	C(20)–C(21)–C(22)	118·3(8)
C(9)–N(3)–C(10)	109·3(6)	C(21)–C(22)–C(23)	118·8(8)
C(9)–N(3)–C(17)	110·5(7)	C(22)–C(23)–N(5)	122·0(8)
Ni–N(3)–C(10)	114·5(5)	C(23)–N(5)–Ni	118·9(5)
Ni–N(3)–C(17)	111·7(4)	C(23)–N(5)–C(19)	118·3(6)
C(10)–N(3)–C(17)	106·5(7)	Ni–N(5)–C(19)	122·8(5)
N(3)–C(10)–C(11)	109·8(6)		
Ni–N(1)–C(3)	176·6(4)	Ni–N(5)–C(21)	177·2(4)
Ni–N(4)–C(14)	173·8(3)		
O(1)–N(6)–O(2)	121·5(8)	O(2)–N(6)–C(24)	121·2(8)
O(1)–N(6)–C(24)	116·8(8)		
O(3)–Cl(1)–O(4)	114·0(8)	O(4)–Cl(1)–O(5)	109·4(9)
O(3)–Cl(1)–O(5)	106·9(6)	O(4)–Cl(1)–O(6)	113·0(9)
O(3)–Cl(1)–O(6)	111·1(5)	O(5)–Cl(1)–O(6)	101·5(7)
O(7)–Cl(2)–O(8)	108·9(8)	O(8)–Cl(2)–O(9)	108·2(9)
O(7)–Cl(2)–O(9)	109·6(7)	O(8)–Cl(2)–O(10)	104·0(20)
O(7)–Cl(2)–O(10)	111·0(15)	O(9)–Cl(2)–O(10)	114·9(19)

Table 4

Equations of planes in the form $lX + mY + nZ + d = 0$ where X, Y, and Z are orthogonal co-ordinates in Å related to fractional co-ordinates of Table 1 by $X = x + z\cos\beta$, $Y = y$, and $Z = z\sin\beta$. Deviations (10^{-3} Å) of atoms from the planes are given in square brackets. χ^2 Was obtained by minimising $\sum_{i=1}^{N}(D_i/\sigma_i)^2$ where D_i is the perpendicular distance of atom i from the plane

Plane (1): N(1)—(4)

$$0{\cdot}0293X - 0{\cdot}6527Y - 0{\cdot}7570Z + 7{\cdot}7056 = 0$$

[N(1) −18, N(2) 27, N(3) −21, N(4) 15, Ni −330; χ^2 48·2]

Plane (2): N(1), C(1)—(5)

$$0{\cdot}8688X - 0{\cdot}3862Y - 0{\cdot}3098Z - 0{\cdot}7088 = 0$$

[N(1) 5, C(1) −7, C(2) −1, C(3) 17, C(4) −11, C(5) −3, Ni 25; χ^2 3·5]

Plane (3): N(4), C(12)—(16)

$$0{\cdot}3035X + 0{\cdot}9502Y - 0{\cdot}0707Z - 5{\cdot}2996 = 0$$

[N(4) −10, C(16) 9, C(15) 7, C(14) −19, C(13) 3, C(12) 13, Ni −224; χ^2 12·9]

Plane (4): N(5), C(19)—(23)

$$-0{\cdot}7555X + 0{\cdot}4589Y - 0{\cdot}4675Z + 5{\cdot}3700 = 0$$

[N(5) −5, C(23) 6, C(22) 8, C(21) −25, C(20) 22, C(19) 1, Ni −61; χ^2 9·5]

Plane (5): N(6), O(1), O(2), C(24)

$$0{\cdot}4164X + 0{\cdot}9065Y - 0{\cdot}0703Z - 2{\cdot}7019 = 0$$

[N(6) −35, O(1) 17, O(2) 15, C(24) 27; χ^2 30·3]

Plane (6): Ni, N(2), N(3)

$$0{\cdot}1732X - 0{\cdot}7568Y - 0{\cdot}6303Z + 6{\cdot}7990 = 0$$

[C(8) −384, C(9) 370]

Plane (7): N(1), N(3), N(5), Ni

$$-0{\cdot}9850X + 0{\cdot}0888Y - 0{\cdot}1481Z + 5{\cdot}8859 = 0$$

[N(1) 87, N(3) 100, N(5) 26, Ni −6; χ^2 419]

Plane (8): N(2), N(4), N(5), Ni

$$0{\cdot}1591X + 0{\cdot}7227Y - 0{\cdot}6725Z + 0{\cdot}9733 = 0$$

[N(2) 42, N(4) 25, N(5) 10, Ni −2; χ^2 65·3]

RESULTS AND DISCUSSION

Intermolecular Structure.—The crystals consist of complex [Ni(tepen)]$^{2+}$ cations, perchlorate ions, and nitromethane molecules (Figure 1). The complex cation of the asymmetric unit has twelve unique contacts <3·4 Å with perchlorate oxygen atoms, and four unique contacts <3·4 Å with nitromethane atoms; the shortest of these contacts is [N(2) · · · O(6$^{\text{I}}$) 3·15 Å [with O(6$^{\text{I}}$) at $x, \frac{1}{2} - y, \frac{1}{2} + z$].

All the contacts involving the nitromethane molecule indicate that it is a molecule of crystallisation. It is approximately parallel to the pyridyl ring containing the atom N(4) [hereafter referred to as the N(4)-pyridyl ring]; both the dihedral angle of 6·9° [planes (3) and (5), Table 4] and the distances of 3·49 Å for the shortest contacts [O(1) · · · N(4) and O(2) · · · C(12)] between these two groups suggest that this is no more than a weak van der Waals interaction. However, the nitromethane molecule appears to be significantly non-coplanar; while it is difficult to account satisfactorily for the large distance (0·055 Å) of the central atom [N(6)] from the plane of the other three atoms, since polarisation bonding seems to be precluded,[10] it must be noted that the three terminal atoms of the nitromethane molecule are drawn towards the N(4)-pyridyl ring. The bond parameters of the nitromethane molecule were not observed to be significantly different from those reported for nitromethane itself.[11]

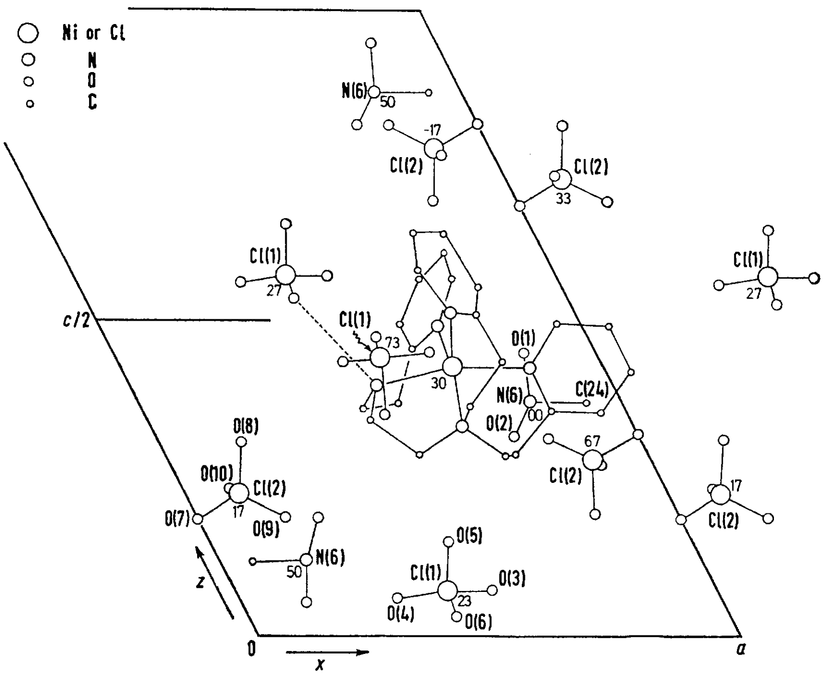

FIGURE 1 The arrangement of perchlorate ions and nitromethane molecules surrounding one of the complex $[Ni(tepen)]^{2+}$ ions in a view along the *b* axis; the fractional co-ordinate *y*/*b* ($\times 10^2$) of the central atom of each species is given

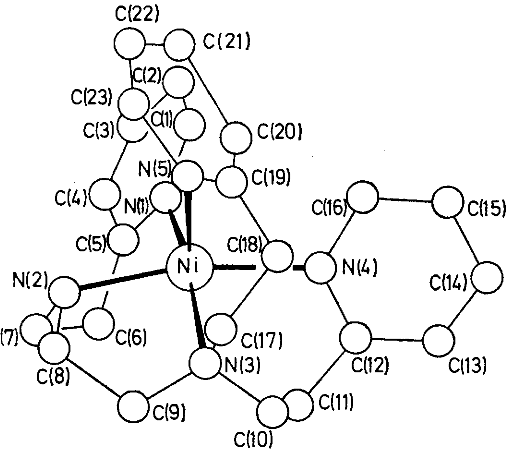

FIGURE 2 The complex $[Ni(tepen)]^{2+}$ ion viewed along the *b* axis

Nickel Environment.—The nickel atom is surrounded by five nitrogen atoms in a square pyramidal arrangement [see the geometric arrangement (II) and Figure 2]. While the four atoms comprising the basal plane [N(1)—(4)] are approximately coplanar [plane (1), Table 4], they have significant deviations (0·015—0·027 Å; 2·5—4·0 σ) from it; however, the deviations are negligible when compared with those of *ca.* 1 Å needed to produce a trigonal bipyramidal arrangement of donor atoms. The nickel atom lies 0·33 Å above this basal plane towards the apical atom [N(5)]; in other square-pyramidal high-spin nickel(II) complexes the nickel atom has been observed [12,13] to lie 0·30—0·36 Å above the basal plane.

The nickel–nitrogen bond distances involving the basal nitrogen atoms are 2·061(5)—2·124(6) Å, significantly longer than that [2·011(6) Å] involving the apical nitrogen atom. The mean (2·091 Å) for the basal bond lengths in $[Ni(tepen)]^{2+}$ compares favourably with that (2·10 Å) obtained for three square-pyramidal high-spin nickel complexes with basal nitrogen donor atoms.[12] While there seem to be no genuine high-spin square-pyramidal examples of apical nitrogen bond lengths to compare with the value of 2·011 Å observed in $[Ni(tepen)]^{2+}$, values of 1·98—2·06 Å (mean 2·02 Å) have been observed [14] for nickel to apical-nitrogen bonds in high-spin intermediate-type [2] five-co-ordinate complexes. This comparison and the observation that the N(5)-

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pyridylethyl substituent can easily bridge from the basal to the apical co-ordinating position [compare ' inner ' bond angle, Ni–N(5)–C(19) 122·8(5)°, with ' outer ' bond angle, Ni–N(5)–C(23) 118·9(5)°] suggest that the difference between the basal and the apical bond lengths may be due to some electronic cause. A study of the metal–donor-atom bond lengths in a high-spin square-pyramidal nickel complex with five identical ligands {*e.g.* $[Ni(OAsMe_3)_5]^{2+}$ ref. 13(*a*) and $[Ni(OPMe_3)_5]^{2+}$ ref. 15} would help in explaining the observed difference.

Stereochemistry of $[M(tepen)]^{n+}$ *Complexes*.—A square-pyramidal geometry in high-spin d^8 complexes is stabilised with respect to a trigonal bipyramidal geometry by the crystal-field stabilisation energy, CFSE. This stabilisation increases from 17 to 37% as the apical to basal bond angle decreases from 105 to 90° respectively.[16] In the $[Ni(tepen)]^{2+}$ ion these bond angles ranged from 95·5 to 102·0° (mean 99°).

It seems appropriate here to consider the possibility of cationic $[M(tepen)]^{2+}$ complexes which possess an intermediate [2] geometry. It is considered that this geometry is possible for complex ions in which the CFSE does not favour a C_{4v} symmetry relative to a D_{3h} symmetry as much as it does for high-spin nickel(II) complexes, and for complexes where greater intraligand repulsion is experienced by the use of smaller metal ions. A structure determination of the copper(II) analogue would be of interest: Cu^{II} fits both requirements, and while its e.s.r. spectrum suggests a square-pyramidal geometry, the electronic-absorption spectrum suggests a trigonal bipyramidal geometry.[1]

The Ligand.—The N(1)-pyridyl ring of the ligand has dihedral angles of 59·2 and 32·4° with the basal plane [N(1)—(4)] and the ' vertical ' plane [plane (7), Table 4] N(1), N(3), N(5), and Ni, so that its attached ethylene group [C(6), C(7)] lies below the basal plane (Figure 2). Likewise, the N(4)-pyridyl ring has dihedral angles of 56·1 and 38·5° with the basal plane and the ' vertical ' plane [plane (8)] N(2), N(4), N(5), and Ni, so that its attached ethylene group [C(10), C(11)] also lies below the basal plane. The N(5)-pyridyl ring has a dihedral angle of 88·1° with the basal plane, and dihedral angles of 31·3 and 58·3° with the ' vertical ' planes (7) and (8) respectively; its ethylene group [C(17), C(18)] is displaced towards the N(4)-pyridyl ring. There are only three non-bonding contacts <4 Å between the carbon atoms of different pyridyl rings in the same chelate [C(1) · · · C(16) 3·36, C(1) · · · C(23) 3·23, and C(16) · · · C(19) 3·77 Å].

As expected, the ethylenediamine moiety has a *gauche*-conformation.[3] The C(8) and C(9) atoms are found to have deviations of 0·38 and 0·37 Å respectively from the plane comprising the Ni, N(2), and N(3) atoms [plane (6), Table 4]. The sum of these two deviations is larger than the values (0·56—0·73 Å) for nickel(II) complexes with substituted or unsubstituted ethylenediamine ligands,[3] suggesting that the nitrogen atoms of the ethylenediamine moiety have been pushed together in order to relieve strain in other parts of the ligand.

The mean values and ranges of the bond lengths and bond angles involving the three chemically similar, but stereochemically different, 2-pyridylethyl substituents of the tepen ligand are given in Figure 3; the differences in some of these bond parameters are attributed to the different environments of these substituents. For the pyridyl rings the C–C and C–N bond lengths vary from **1·353** to **1·420** [mean **1·388(13)** *] and **1·320** to **1·367** [mean **1·348(9)** Å *] respectively; the mean values for these bond lengths do not differ significantly from those (**1·394** and **1·340** Å) for pyridine.[17]

The C–C and C–N bond distances in the remainder of the chelate vary from **1·476** to **1·554** Å [mean **1·517(13)** Å] and **1·474** to **1·514** [mean **1·495(12)** Å], in good agreement with values quoted [11] for respective single-bond distances.

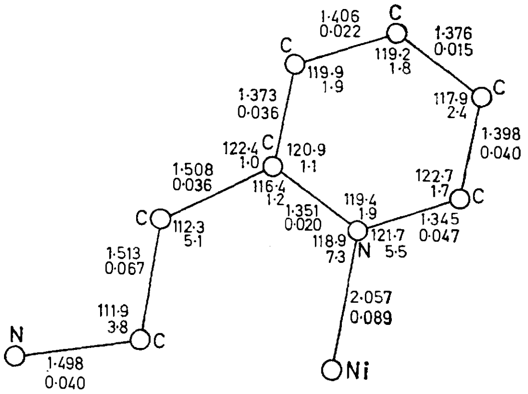

FIGURE 3 The mean values and ranges of the bond distances (Å) and bond angles (°) of the three (2-pyridyl)ethyl moieties of the complex $[Ni(tepen)]^{2+}$ ion. ' Inner ' and ' outer ' Ni–N–C bond angles vary from 115·5 to 122·8 and from 118·9 to 124·4° respectively

Evaluation of Accuracy.—A comparison of the constituent bond lengths and angles of the three pyridyl rings in the chelate with the mean bond lengths and angles found for several pyridyl rings observed in other structural determinations suggests that the positional σ values of $[Ni(tepen)]^{2+}$ may have been underestimated by *ca.* 20%.

Assuming that all the perchlorate oxygen atoms are equivalent, an analysis of the bond lengths and angles of the two perchlorate ions suggests that their positional σ values may have been underestimated by a factor of *ca.* 3.

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* The estimated standard deviation quoted is the mean of the individual σ.

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