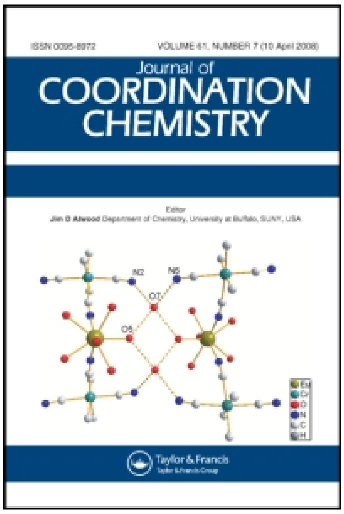

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THE CRYSTAL STRUCTURE OF TRIETHYLENETETRAMINENICKEL(II) PERCHLORATE[1]

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The crystal structure of Ni(trien)$(ClO_4)_2$ (trien = triethylenetetramine, $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$) has eight formula units in an orthorhombic unit cell of dimensions: $a = 14.67$, $b = 14.95$, and $c = 13.85$ Å, with a space group of $Pna2_1$–C^9_{2v}. The structure was solved by Patterson and Fourier methods using film data and refined by least squares to a conventional R factor of 0.136 for the 1583 observed reflections. The coordination around each nickel atom is planar with four nitrogens in a trapezoidal arrangement. The perchlorate groups do not occupy the fifth and sixth coordination positions, but link, through hydrogen bonds, the essentially identical ligand complexes that comprise the asymmetric unit. The complex is the *meso* isomer with the central ring in the eclipsed *cis* form. Although the normal *gauche* conformation is not present in the central ring formed by the secondary nitrogens, the *gauche* conformation is present in the chelates formed between the secondary and primary nitrogens.

INTRODUCTION

Triethylenetetramine (trien) can be arranged about a metal ion in a number of topological ways. Thus for the cobalt(III) complex, Co(trien)Cl_2^+, an α and β form of the *cis* complex exists as well as the *trans* complex.[3,4] Additional conformational and optical isomers lead to a total of nine possible

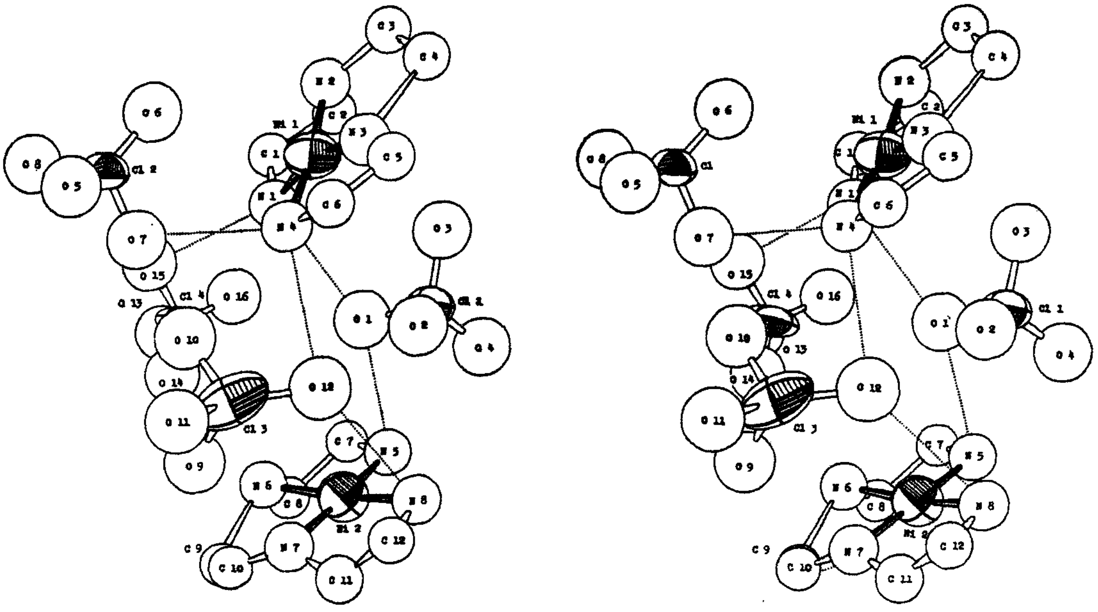

FIGURE 1 A stereoscopic drawing (program ORTEP written by Carroll K. Johnson at Oak Ridge National Laboratory) of the asymmetric unit of Ni(trien) $(ClO_4)_2$ showing the thermal vibration of the nickel and chlorine atoms (corresponding to 75 percent probability elipsoids) and the hydrogen bonding arrangement linking two Ni(trien)$^{2+}$ complexes. The *b* axis is vertical and the *a* axis is horizontal.

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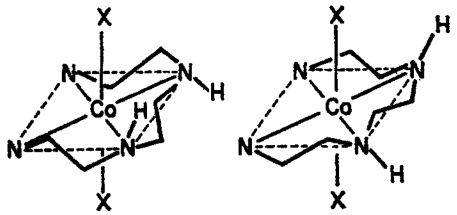
isomers of $Co(trien)Cl_2^+$ of which five have been reported. The *trans* isomers are optically active and therefore must have *gauche* ring conformations (structure *a*) as opposed to an eclipsed central ring (structure *b*) which would be the *meso* isomer, but has not been found.



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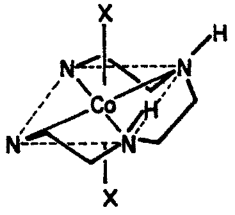

(*b*)

The trien complex of nickel(II) is blue in aqueous solutions of low electrolyte concentration. It has been argued from spectral evidence that $Nitrien(H_2O)_2^{2+}$ is a *cis*-octahedral complex.[5] A yellow form of nickel-trien coexists in aqueous solutions and the proportion of the yellow species increases with added electrolyte and increased temperature. The rate of interconversion of the blue and yellow forms in solution is extremely rapid, being much faster than the rate of nickel-nitrogen bonded dissociation.[6] Crystalline salts of the yellow (or yellowish-red) complex show that this form of the complex is desolvated. In the present work crystals of Ni (trien) $(ClO_4)_2$ were prepared[7] for x-ray single-crystal analysis. The main points of interest in this structural determination were the coordination number of nickel, the geometry of the nickel-nitrogen bonds and the conformations of the chelate rings. One reason why the arrangement of the nitrogens and chelate rings is of interest is that 2,3,2-tet ($NH_2CH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2NH_2$) with a 5,6,5-membered chelate ring system forms a much more stable nickel complex than the 5,5,5-membered chelate ring system of nickel-trien.[8] In chelates without linked consecutive rings the normal effect of increasing the chelate ring size from 5 to 6 is to decrease the stability constant of the complex. Thus, log K_1 for the nickel complex of ethylenediamine is 7.60 and for 1,3-diaminopropane it is 6.39.[9,10]

The structural analysis of $Nitrien(ClO_4)_2$ shows that the perchlorate oxygens are not coordinated to the nickel and in fact are not in the axial positions. Although the trien molecule is wrapped around the nickel to give a square-planar type complex there is some distortion and the central ring is in an eclipsed conformation. It should be emphasized here that the objective of this analysis was to find the overall structural features, rather than the accurate determination of atomic positions.

EXPERIMENTAL

The $Ni(trien)(ClO_4)_2$ was prepared from the reaction of $Ni_2(trien)_3(ClO_4)_2$ with $Ni(ClO_4)_2$ following the procedure of Curtis and House.[6] However, good crystals could not be obtained by trituration with isopropanol as recommended for the preparation. A gummy product resulted which on the addition of isopropanol quickly turned into a fine powdery product. Large crystals were obtained by recrystallization from absolute ethanol. Rust colored crystals of $Ni(trien)(ClO_4)_2$ were formed when the recrystallization was permitted from warm solutions (35–40°). The crystals were washed with absolute ethanol and ether and were dried under vacuum in a desiccator. Blue crystals were obtained by the same procedure when the recrystallization was performed in cold (–7°) absolute ethanol. The blue crystals contain ethanol and correspond to the formula $Ni(trien)(ClO_4)_2(C_2H_5OH)_2$. The blue crystals lose ethanol easily and when dried under vacuum they slowly convert to a yellow form.

Anal. calcd. for $Ni(trien)_2(ClO_4)_2$: C, 17.89; H, 4.50; N, 13.90; Cl, 17.55. Found for the rust colored crystals for which the present structure was done: C, 18.09; H, 4.35; N, 13.70; Cl, 17.30.

Magnetic susceptibility measurements using a Faraday balance showed the rust colored crystals to be diamagnetic while the blue crystals and aqueous solutions were paramagnetic. The $Ni(trien)(ClO_4)_2$ formed large prisms, elongated along the *a* axis, occurring generally as twins or aggregates. Buerger precession photographs showed the reciprocal lattice symmetry *mmm* and extinctions of $(0kl)$ when $k + l$ is odd as well as $(h0l)$ when h is odd. This led to the orthorhombic unit cell of dimensions $a = 14.67$, $b = 14.95$, and $c = 13.85$ Å, having space group symmetry either $Pnam - D^{7}_{2h}$ or $Pna2_1 - C^{9}_{2v}$. Assumption of eight formula units of Ni(trien)$(ClO_4)_2$ in the unit cell gives a calculated density of 1.69 gm–cm.$^{-3}$ in agreement with the density as measured by floatation of 1.71 gm–cm.$^{-3}$

An attempt was made to distinguish between the two possible space groups by a statistical test based on the relative magnitude of structure amplitudes,[11] but the results were inconclusive. A single crystal of dimensions .77 × .52 × .30 mm. was used for the entire data collection. An equi-inclination Weissenburg camera with nickel-filtered CuKα radiation was used to photograph layers $h0l$ through $h7l$, and layers $0kl$ through $10kl$. To improve scaling, layers hkk through $hkk + 3$ were also recorded. Exposures of 25 hr and 3 hr were made of each layer with three films in the camera for both occasions.

The relative intensities were estimated visually with respect to a calibrated sequence of intensities. The measurements from the 23 reciprocal lattice planes were corrected for Lorentz, polarization and absorption effects,[12] and scaled together by a method similar to that of Hamilton, Rollett and Sparks.[13] The scaling procedure reduced the data to 1583 independent, non-zero reflections. The mean standard deviation of reflections observed on more than one film expressed as the ratio of mean structure amplitude was 0.098. All computations were performed on a CDC 6500 digital computer.

Structure Determination and Refinement

Inspection of the three Harker sections and three Harker lines, on an unsharpened Patterson synthesis, corresponding to the space group Pnam showed that of these, only the plane at $z = \frac{1}{2}$ was heavily populated. This corresponds to the single Harker plane of the non-centric space group $Pna2_1$. Furthermore, the two Harker lines generated by the latter also contained high density regions. Hence the non-centric space group, requiring two formula units per asymmetric unit, was tentatively accepted. This assumption later was shown to be correct.

From a Wilson plot an approximate absolute scale and overall temperature factor ($B = 3.3$ Å^2) was found which permitted the calculations of a much improved point sharpened Patterson. Because the asymmetric unit contains six heavy atoms, two nickels and four chlorines, it was not possible to simply locate the nickel-nickel interactions in the Patterson map and deduce positions from these. The overlap of peaks was appreciable, and a comparison of the number of outstanding peaks observed in the map with the number predicted, indicated that every large peak was of high multiplicity, a result which was confirmed from a knowledge of the absolute scale. Nevertheless, the Harker plane and the Harker lines plus trial and error fitting produced a set of six heavy atom coordinates which were consistent with the large peaks in the Patterson map. At this stage it was not possible to distinguish between nickel and chlorine atoms.

Structure factors were calculated based on six equal heavy atoms placed at the six positions determined from the Patterson, and the computed signs from the centric array of heavy atoms employed to calculate a difference electron density map. Two of the atomic positions used in the phasing appeared as strong positive peaks, the other four near background. The nickel atoms were assigned to these two positions, and chlorine atoms to the remaining four. Differentiation between the two types of heavy atoms did not, however, break the centric nature of the solution.

A difference electron map based on the two nickel and four chlorine atoms produced reasonable peaks at almost all of the positions later shown to be occupied by atoms. Each peak was accompanied by a centrosymmetrically related ghost.The nitrogen atoms were identified by their roughly square planar arrangement about the nickel atoms. The carbon atoms, now greatly restricted in their possible positions, were fixed with relative ease by altering difference Fourier maps with two cycles of least squares refinement. As more light atoms were added to the phase calculations, the ghost problem gradually disappeared.

The perchlorate groups were, to a great extent, all disordered. Each lay on, or straddled in pairs, pseudo mirror planes. Every perchlorate group was, therefore, reflected back upon itself producing eight rather than four oxygen peaks around each chlorine, four real and four imaginary. Because of the disorder, six of these eight peaks around each chlorine were appreciably smeared out. Four of the sixteen oxygens, one from each perchlorate group, could be identified with relative certainty because of the disparity in peak height between two mirror related atoms. These four unique oxygens later refined rather quickly and had low temperature factors. The remaining twelve had to be extracted one or two at a time by alternating Fourier and least squares cycles, and by applying the constraint of tetrahedral symmetry. All of these twelve oxygens refined poorly and had unusually high isotropic temperature factors. Because of the large number of parameters, no attempt was made to assign anisotropic temperature factors to the oxygen atoms.

Least squares refinement was performed with a program written by Lary W. Finger.[14] Because of storage requirements, the temperature factors and positional parameters were refined as two separate blocks. By doing three cycles of refinement on each

TABLE I

Fractional atomic positional parameters and isotropic thermal parameters[a–d]

Atom	*x*	*y*	*z*	*B*
Ni(1)	.1251 (2)	.0832 (2)	.0000	—[c]
Ni(2)	.4451 (2)	.1357 (2)	.5012 (3)	—[c]
Cl(1)	.3931 (3)	.0590 (3)	.0038 (5)	—[c]
Cl(2)	−.0462 (3)	−.1096 (3)	.0040 (3)	—[c]
Cl(3)	.7465 (8)	.1828 (7)	.2503 (5)	—[c]
Cl(4)	.7476 (8)	.1755 (7)	.7661 (5)	—[c]
N(1)	.1654 (10)	.0065 (11)	.1021 (12)	2.7 (5)
N(2)	.0741 (8)	.1558 (8)	.0905 (9)	1.6 (4)
N(3)	.0941 (11)	.1669 (12)	.8986 (12)	3.1 (5)
N(4)	.1563 (11)	.0063 (11)	.8961 (13)	3.2 (6)
N(5)	.5257 (10)	.1580 (9)	.6080 (10)	3.3 (5)
N(6)	.3638 (11)	.0925 (10)	.5933 (11)	2.5 (4)
N(7)	.3460 (14)	.1272 (14)	.4006 (15)	4.8 (6)
N(8)	.5220 (14)	.1731 (14)	.3931 (13)	3.7 (6)
C(1)	.1271 (19)	.0489 (20)	.1938 (18)	3.0 (5)
C(2)	.0526 (16)	.1079 (17)	.1789 (16)	3.7 (6)
C(3)	−.0099 (16)	.2087 (15)	.0485 (15)	3.7 (7)
C(4)	.0263 (20)	.2397 (21)	.9444 (20)	7.5 (1.0)
C(5)	.0657 (21)	.1158 (25)	.8177 (25)	4.5 (8)
C(6)	.1524 (17)	.0580 (18)	.8017 (18)	3.7 (7)
C(7)	.4645 (25)	.1311 (26)	.6976 (26)	8.4 (10)
C(8)	.4405 (26)	.0482 (27)	.6787 (28)	8.8 (12)
C(9)	.2876 (20)	.0502 (19)	.5517 (19)	5.3 (7)
C(10)	.2898 (17)	.0283 (16)	.4378 (16)	5.7 (7)
C(11)	.4004 (15)	.0847 (14)	.3145 (14)	3.4 (6)
C(12)	.4859 (15)	.1557 (14)	.3024 (14)	3.7 (6)
O(1)	.1484 (10)	.4740 (10)	.5268 (10)	5.6 (5)
O(2)	.3305 (10)	.1300 (10)	.9602 (10)	8.5 (8)
O(3)	.4756 (20)	.0603 (23)	.9351 (13)	11.9 (1.1)
O(4)	.4429 (18)	.0506 (20)	.1018 (20)	14.3 (1.5)
O(5)	−.1254 (11)	−.1679 (12)	−.0296 (12)	8.1 (7)
O(6)	−.0609 (15)	−.0190 (16)	−.0313 (16)	11.2 (1.0)
O(7)	.0379 (18)	−.1360 (20)	−.0601 (19)	12.3 (1.2)
O(8)	−.0092 (13)	−.1257 (19)	.0917 (14)	10.4 (9)
O(9)	.8317 (18)	.1562 (20)	.2069 (19)	11.4 (9)
O(10)	.7276 (19)	.2489 (22)	.3120 (22)	10.0 (8)
O(11)	.7275 (18)	.2175 (18)	.1547 (18)	14.2 (1.7)
O(12)	.6952 (10)	.0997 (10)	.2742 (10)	4.9 (5)
O(13)	.6690 (18)	.1803 (18)	.8496 (18)	11.6 (1.0)
O(14)	.7072 (17)	.2615 (21)	.7182 (21)	9.6 (8)
O(15)	.7010 (14)	.1146 (15)	.6910 (15)	9.6 (8)
O(16)	.8550 (14)	.1618 (16)	.7549 (16)	8.4 (6)

[a] See Figure 2 for numbering scheme.

[b] Of form exp $(-B\lambda^{-2}\sin^2\theta)$ where B is in A^2.

[c] Treated anisotropically. See Table II.

[d] Numbers in parentheses are estimated standard deviations in the last significant figure.

TABLE II

Nickel and chlorine anisotropic temperature factors in the form $\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	.0059 (2)	.0037 (2)	.0047 (2)	.0001 (2)	.0005 (4)	.0001 (3)
Ni(2)	.0053 (2)	.0050 (2)	.0050 (2)	−.0003 (2)	−.0005 (4)	.0003 (3)
Cl(1)	.0037 (3)	.0022 (2)	.0043 (3)	−.0001 (2)	−.0001 (6)	.0001 (5)
Cl(2)	.0050 (4)	.0028 (2)	.0063 (4)	−.0006 (2)	−.0005 (7)	.0009 (6)
Cl(3)	.0056 (6)	.0022 (3)	.0092 (7)	.0001 (4)	.0028 (6)	.0017 (4)
Cl(4)	.0087 (9)	.0042 (5)	.0078 (7)	.0027 (5)	.0008 (7)	−.0010 (5)

group, using unitary weights, then returning to the initial set and performing a second three cycles on each group, convergence was obtained on all parameters. The two nickel and four chlorine atoms were refined with anisotropic temperature parameters while all light atoms were given isotropic temperature factors. The function minimized in the refinement was

$$\frac{\Sigma w^* (\text{delta})^2}{\Sigma w^* (|F_{\text{obs}}|)^2} \text{ where delta} = (|F_{\text{obs}}| - |F_{\text{calc}}|).$$

The final residual was $R = 0.134$ for the observed reflections where

$$R \text{ is } \frac{\Sigma|\text{delta}|}{\Sigma|F_{\text{obs}}|}.$$

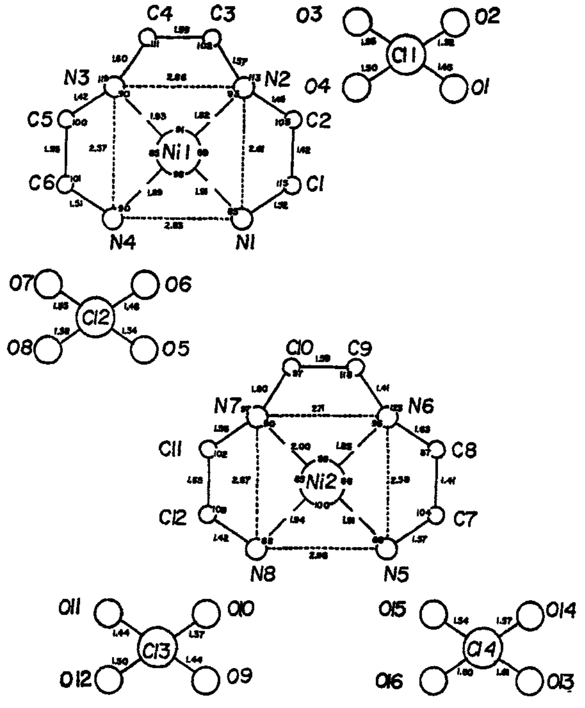

FIGURE 2 Schematic diagram of the asymmetric unit of Ni(trien)$(ClO_4)_2$ with calculated bond lengths and angles. Bonds between carbon and nitrogen atoms have average estimated standard deviations of .05 Å, chlorine to oxygen bonds, .04 Å, and nickel to nitrogen bonds .02 Å. All angles have estimated standard deviations of approximately 5 degrees.

The final coordinates and the estimated errors for each parameter are shown in Table I. The relatively high residual is due to several sources of error. The quality of the data was limited by the visual estimation technique and the difficulty in properly characterizing the disordered groups were contributing factors. The high estimated errors for several of the carbon atom coordinates (Table I) are reflected in the obviously poor accuracy of some of the bond distances shown in Figure 2.

DISCUSSION

The packing arrangement within the unit cell is shown in Figure 3. Each nickel–ligand complex is surrounded by a shell of perchlorate groups at less than five Angstroms. The plane normals of each complex form an angle of 80° ± 3° with the z–axis, and are at an angle of 82° ± 3° to each other. No two nickel atoms approach closer than 7 Å to each other. Two of the independent chlorines lie on an n glide plane separated by roughly a half along z (.5059 $\bar{c}$). One of the nickel atoms was used to fix the arbitrary origin along the z-axis, the other nickel atom then lies in the plane $z = \frac{1}{2}$, within the limits of accuracy of the structure determination.

The asymmetric unit consists of two nickel-ligand complexes plus four perchlorate groups. Each complex contains an approximate mirror plane parallel with the x–y plane at $z = 0$ and $z = \frac{1}{2}$. The two complexes that comprise the asymmetric unit are essentially the same. A least squares fit between the rotated coordinates of one complex with those of the other revealed no two atoms separated by more than three standard deviations of their positions.

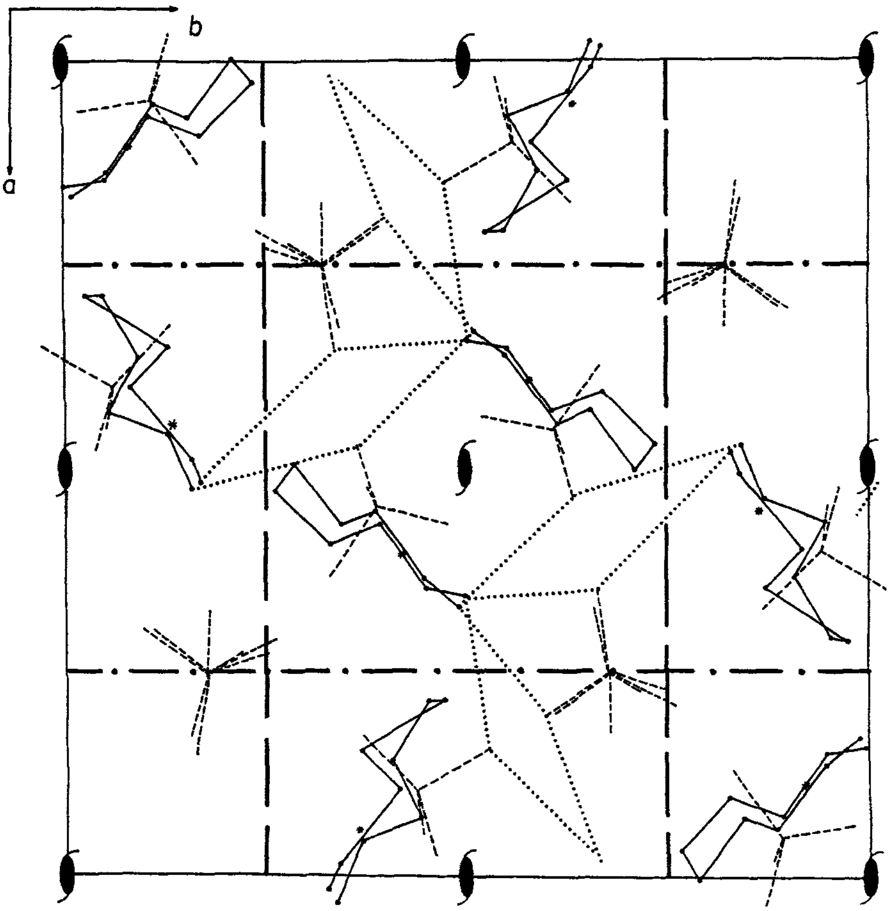

FIGURE 3 Projection onto the *ab* plane of the contents of one unit cell of Ni(trien)(ClO_4)$_2$. Solid lines represent bonds within the trien chelate, dashed lines the chlorine oxygen bonds, and dotted lines, hydrogen bonds.

The nitrogen atoms of each ligand form an approximately square planar array about each nickel atom, the deformation towards a trapezoidal arrangement reflecting the difficulty in stretching the ligand. The primary nitrogens are 0.21 ± .04 Å farther apart than the secondary nitrogens. The four nitrogen atoms and one nickel atom of each complex in the asymmetric unit were fitted to an unweighted least squares plane[15] (Table III). The plane is determined primarily by the more inaccurate nitrogen atoms, hence the distance of the nickel atom from the plane does not appear to be significant.

The carbon atoms bridging the secondary nitrogens are in the eclipsed form. The carbon atoms forming the opposing closed sides of the ligand are in the gauche configuration. The nickel

TABLE III

Distances (in Å) of the nitrogen and nickel atoms from their least square planes.[a]

Equation of the least square planes, where X, Y, and Z are the coordinates in Å along the orthogonal crystallographic *a*, *b*, and *c* axes, respectively.

Through Ni(1) $13.19X + 6.54Y - .09Z - 2.14 = 0$
Ni(2) $-4.64X + 1.40Y + 1.92Z - .84 = 0$

Plane Containing Ni(1)		*Plane Containing Ni*(2)	
Atom	Dist to LS plane	Atom	Dist to. LS plane
Ni(1)	.060	Ni(2)	−.040
N (1)	.081	N (5)	.104
N (2)	−.146	N (6)	−.092
N (3)	−.118	N (7)	.108
N (4)	−.112	N (8)	−.079

[a] The least squares planes are not weighted.

atoms are coordinated only with the nitrogen atoms, there is no possibility that any of the perchlorate groups occupy the fifth or sixth coordination positions. There appears to be no direct interaction between the nickel and perchlorate groups.

For each perchlorate group, the unique oxygen atom which refined readily provides the direct interaction with the ligand. Each of these oxygens appears to form a double hydrogen bond which completes a bridge between the primary nitrogens of two ligand complexes. Both the axial and equatorial hydrogens are involved in one of these bifuricated hydrogen bonds (Table IV). Therefore any given complex is linked to others through four hydrogen bridges (Figures 1 and 3). From the appearance of the perchlorate groups in difference Fourier maps, the bond between the chlorine and the single hydrogen bonded oxygen seems to form an axis about which the group rotates to produce the observed disorder.

TABLE IV

Hydrogen bonds in the Ni(trien)$(ClO_4)_2$ crystal

N(1)—H . . . . O(1)	2.96Å
N(1)—H . . . . O(15)	2.94
N(5)—H . . . . O(1)	2.87
N(5)—H . . . . O(15)	2.86
N(4)—H . . . . O(12)	3.18
N(4)—H . . . . O(7)	2.83
N(8)—H . . . . O(12)	3.20
N(8)—H . . . . O(7)	3.05

Comparison with Structures of Other Metal-Trien Complexes

A number of metal–polyamine structures have been reported recently including a cobalt(III) trien and a copper(II) trien complex, both of which differ from nickel-trien in coordination number and in the manner in which trien is wrapped around the metal.

In the structure of *cis*-β-[Co(trien)$ClOH_2$]$(ClO_4)_2$ four nitrogen atoms occupy three equatorial and one apical position of an octahedron.[16, 17] This structure agrees with that predicted from stereochemical studies and corresponds to the hydrolysis product of the *cis*-β-[Co(trien)Cl_2]$^+$ ion as opposed to the *trans* isomer in structure (a).

The crystal structure of [Cu (trien) SCN]NCS shows the copper to be five-coordinated.[18] The copper is located about 0.4 Å above the plane of the four nitrogen atoms of trien and the fifth, apical, position is occupied by the sulfur atom of a thiocyanate group. All three ethylenediamine rings have the *gauche* conformation. As is the case with nickel-trien, the geometry of the four nitrogen atoms is close to a trapezoid. In the copper-trien structure the nitrogens bridged by carbon atoms are all 2.71–2.72 Å apart and the terminal nitrogens are 3.05 Å apart. This compares to a distance of 2.63 Å between the bridged nitrogen atoms in the plane of the cobalt complex and 2.57 to 2.67 Å for the nitrogens in the puckered rings of nickel-trien is 2.66 to 2.71 in the stretched central chelate ring and the terminal nitrogens are separated by a distance of 2.83–2.96 Å.

The Co—N distances average 1.93 Å, the Cu—N average 2.02 Å and the Ni—N distances average 1.91 Å.

In the three trien complexes the hydrogen helps to hold the cations and anions together. In Co(trien)$ClOH_2(ClO_4)_2$. the hydrogen bonds to $ClO^-{}_4$ are through the coordinated H_2O molecule, while in Nitrien^{2+} the amine hydrogen atoms appear to be hydrogen bonded to $ClO^-{}_4$. In [Cu(trien)SCN]$^+$ hydrogen bonding occurs between the amine hydrogens and both the N and S of the uncoordinated thiocyanate.

The structure of both the blue and yellow crystals of bis(*meso*-stilbenediamine)nickel)II) dichloroacetate have been determined.[19] The yellow crystals contain nickel in two environments; nickel is octahedrally coordinated to four nitrogens and two water molecules and it also occurs in a planar form with only nitrogen coordination. The crystals have a magnetic moment indicative of mixed paramagnetic and diamagnetic nickel ions. The nickel in the planar environment has Ni—N bond distances of 1.89–1.90 Å which are very similar to that found for the "tighter" nickel-trien structure in the present work. The stilbenediamine complex in the octahedral environment has Ni—N bond distances of 2.03 to 2.07 Å.

In various octahedral nickel ethylenediamine complexes[20–23] the Ni—N bond distances vary from 2.09 to 2.17 Å and the N—Ni—N bond angles vary from 82 to 88°. In all structures the ethylenediamine molecules are in the *gauche* form.

CONCLUSIONS

The metal atom in Ni-trien$(ClO_4)_2$ is four coordinate with a high degree of coplanarity with the nitrogen atoms. The perchlorate ions are located in such a manner that they cannot contribute at all to the nickel coordination above and below the plane of the Nitrien^{2+} group. Direct addition of two solvent molecules to the yellow complex would give a *trans*-octahedral blue complex and in solution there is a very rapid interconversion of the yellow and blue forms. In order for the blue complex to be *cis*-octahedral there must be a rapid rearrangement of the trien nitrogens around nickel (without nickel-nitrogen bond cleavage) during or after the addition of solvent molecules. The distortion of the yellow form of the complex may be important in the ease of rearrangement.

In the crystal structure the trien molecule appears to be stretched in an attempt to achieve a square-planar coordination and the actual arrangement is a trapezoidal distortion. In addition the central chelate ring is in an eclipsed rather than in the normal *gauche* form.

The effect of relieving the stretch of the ligand by use of a homologue of trien with three carbons between the secondary nitrogens is dramatic. The 2,3,2-tet complex (which is a mixture of blue and yellow forms) has a stability constant 100 times greater than that of nickel-trien.[8] In terms of the stabilities of the yellow forms of the two ligands the effect is even greater. The stability constant for [Ni(2,3,2-tet)(yellow)]$^{2+}$ is more than 10^3 times greater than the stability constant for [Nitrien(yellow)]$^{2+}$ in aqueous solution.[24] This is in agreement with the structural evidence that trien has difficulty in spanning the square-planar coordinate sites.

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REFERENCES AND NOTES

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