

4.6  $\text{ohm}^{-1}$  in *N,N*-dimethylformamide. Acid hydrolysis in aqueous HCl gave  $\text{dbi}^+\text{Cl}^-$  in 89% yield and Htmhd (isolated as the Cu(II) complex) in 77% yield. The ir spectrum in the  $1500\text{--}1800\text{-cm}^{-1}$  region shows absorption bands at 1519 (mw), 1525 (mw), 1558 (m), 1565 (m), 1590 (m), and  $1595\text{ cm}^{-1}$  (m). There is no significant absorption between 1600 and  $1800\text{ cm}^{-1}$ . The uv spectrum ( $10^{-5}\text{ M}$  in methanol solution) shows a double peak at 266 and 274  $\text{m}\mu$  ( $\epsilon$  19,900) and a shoulder at 224  $\text{m}\mu$  on an absorption band whose maximum lies at  $\lambda < 200\text{ m}\mu$ ; it is essentially a superposition of the spectra of the  $\text{dbi}^+$  ion and Htmpd. The presence of the 265- $\text{m}\mu$  band (characteristic of the  $\text{dbi}^+$  cation) in the spectrum of *dbi-tmpd*, contrasted with its absence in the spectrum of *dbi-dppd*, suggests that the former is largely dissociated in methanol at  $10^{-5}\text{ M}$  concentration, whereas the latter suffers very little dissociation in ethanol at the same concentration.

Linear, nonchelate complexes of iodine(I) by nitrogen bases such as pyridine have been recognized

for some time.<sup>14</sup> *Dbi-dppd* and *dbi-tmpd* are, however, the first reported examples of chelate complexation of a halogen atom. We speculate, on the basis of the simple electron-pair repulsion theory of molecular structure, that the local bonding geometry about the iodine atom is essentially square planar.

We were unable to isolate the corresponding compounds of the diphenyliodonium cation, possibly because the lack of rigid planarity of this cation reduces the activation energy for decomposition by nucleophilic attack by the anion on a carbon atom bonded to the iodine. Perhaps the recently reported and even more rigidly planar 4,5-phenanthryleneiodonium cation<sup>15</sup> will permit the isolation of a greater variety of complexed iodonium compounds.

(14) J. A. Creighton, I. Haque, and J. L. Wood, *Chem. Commun.*, 229 (1966); S. G. W. Ginn and J. L. Wood, *Trans. Faraday Soc.*, 62, 777 (1966).

(15) See Beringer, *et al.*, ref 3.

## Crystal and Molecular Structure of the Macrocyclic Complex, 11,13-Dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) Perchlorate

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**Abstract:** The structure of 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) perchlorate,  $[\text{NiAT}]\text{ClO}_4$ , has been determined by three-dimensional single-crystal X-ray methods. The orthorhombic unit cell dimensions are:  $a = 12.385 \pm 0.015$ ,  $b = 14.744 \pm 0.015$ , and  $c = 8.713 \pm 0.010\text{ \AA}$ , space group *Pbcn*,  $d_{\text{obsd}} = 1.56\text{ g/cm}^3$ ,  $d_{\text{calcd}} = 1.534\text{ g/cm}^3$ ,  $Z = 4$ . Intensity data were collected on a Philips PAILED automated diffractometer with monochromatic Mo  $K\alpha$  radiation. The structure was solved by Patterson and Fourier techniques, and refined by the full-matrix least-squares method to a conventional *R* factor of 0.072 for the 659 independent nonzero reflections. The  $[\text{NiAT}]^+$  cation and  $\text{ClO}_4^-$  anion lie on crystallographic twofold axes. The square planar coordination of the Ni atom has a slight tetrahedral distortion. The Ni-N(trigonal) and Ni-N(tetrahedral) bond distances are  $1.83 \pm 0.01$  and  $1.88 \pm 0.01\text{ \AA}$ , respectively. Bond angles in the 13-membered macrocyclic ligand show that there is some strain associated with the square planar coordination of this relatively small macrocycle. Calculations suggest that square planar coordination of a 12-membered macrocycle is possible; the estimated bonding parameters for such a complex are little different from those of the  $[\text{NiAT}]^+$  cation. The molecular packing of  $[\text{NiAT}]\text{ClO}_4$  alternates cations and anions in all three crystallographic directions.

The condensation of triethylenetetraamine (trien) with  $\beta$ -diketones in the presence of nickel(II) yields uninegative tetradentate macrocyclic complexes with 13 atoms in the macrocycle.<sup>1,2</sup> The macrocycles produced, being uninegative with a delocalized ring, are analogs to the corrin ring in vitamin B<sub>12</sub>.

The structure determination of 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) perchlorate (abbreviated  $[\text{NiAT}]\text{ClO}_4$ ; shown schematically below) was undertaken in order to provide information

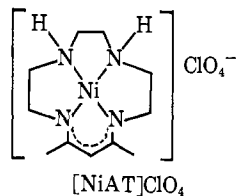
about the bonding of the macrocycle. Square planar coordination about the Ni ion was proposed on the basis of magnetic and spectral data.<sup>1,2</sup> Since most known square planar macrocyclic complexes contain 14 or more atoms in the macrocycle, it was of primary interest to find out how readily the relatively small AT macrocycle accommodates itself to square planar coordination. In particular, it was desired to see if there were signs of strain that would indicate that macrocycles with smaller ring sizes could not hold a metal ion in the macrocyclic plane.

A further goal of the work was to determine the isomeric form in which the complex exists; *i.e.*, there are two possible isomers for square planar coordination of the AT ligand. One has a twofold rotation axis with

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(1) S. C. Cummings and R. E. Sievers, *Inorg. Chem.*, 9, 1131 (1970).

(2) W. H. Elfring, Jr., and N. J. Rose, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14-18, 1970.



the protons on the imine nitrogens trans to each other, while the other has the protons on the imine nitrogens cis, on the same side of the macrocyclic ring.

## Experimental Section

Crystals of [NiAT]ClO<sub>4</sub> were kindly supplied by Dr. S. C. Cummings. The orange needles were examined under a polarizing microscope and several suitable crystals were mounted on glass fibers with their needle axes parallel to the fiber. Two of these were used for the preliminary photographic study and determination of cell dimensions, and one, 0.10 × 0.14 × 1.0 mm, parallel to *a*, *b*, and *c*, respectively, was ultimately used for the collection of intensity data.

Oscillation and Weissenberg photographs revealed that the crystals are orthorhombic, and the absences uniquely define space group *Pbcn* (*D*<sub>2h</sub><sup>14</sup>; no. 60) (*Ok*l absent for *k* odd, *h*0l absent for *l* odd, and *hk*0 absent for *h* + *k* odd). Cell dimensions were determined with a General Electric X-ray spectrometer equipped with a single-crystal orienter and scintillation detector with pulse-height analyzer. The radiation was nickel-filtered Cu Kα ( $\lambda_{K\alpha} = 1.5418$  Å,  $\lambda_{K\alpha_1} = 1.5405$  Å); the take-off angle was 1°. The crystal was oriented about the *c*\* axis. Slow  $\theta$ - $2\theta$  scans of the *h*00, 0*k*0, and 00*l* reflections out to  $2\theta \approx 90^\circ$  yielded the following cell dimensions: *a* = 12.385 ± 0.015, *b* = 14.744 ± 0.015, *c* = 8.713 ± 0.010 Å. The deviations given are our estimates of the possible errors, and are somewhat larger than the standard deviations computed from the variance of the measurements. The measured density (by flotation in CCl<sub>4</sub>-hexane) is 1.56 g/cm<sup>3</sup>; the density calculated for four formula units in the cell is 1.534 g/cm<sup>3</sup>.

Intensity data were collected on a Philips automated diffractometer, PAILRED. Graphite-monochromatized Mo Kα radiation was used in conjunction with a scintillation counter detector. The take-off angle was 6°. The counter aperture was 1.5°. Data collection proceeded as follows: the background was counted for 100 sec on one side of the reflection, an  $\omega$  scan was made at the rate of 0.5°/min, and background was counted for 100 sec on the other side of the reflection. The following scan ranges were chosen: for  $\gamma \geq 20^\circ$ , 2° for *hk*0-*hk*4 and 2.2° for *hk*5-*hk*10; for  $\gamma \leq 20^\circ$ , 2° for *hk*0-*hk*2, 2.4° for *hk*3-*hk*4, 3.0° for *hk*5-*hk*6, 3.4° for *hk*7, 4.0° for *hk*8, and 5.0° for *hk*9-*hk*10.

A standard reflection was measured on each layer every few hours, and a standard on the zero layer (350) was measured before and after the collection of each succeeding layer. On one very hot, humid day during the collection of the third layer, the standard dropped by 15% over a short period of time and then increased slightly, to ~90% of its original value. Reflections collected during and after this time were brought to the level of the initially collected reflections by applying a correction factor based on the 350 reflection. Except for this one large variation, the variations in the standard reflections did not exceed ± 3% from the mean and showed no distinct trend with time. We chose to make no other correction for crystal decomposition-instrumental instability since the time interval between standards was fairly long, and experience without diffractometer suggests that the variations in intensity of a standard occur fairly rapidly.

The net intensity  $I_{net}$  and standard deviation  $\sigma_{I_{net}}$  are given by eq 1 and 2, where *I* is the raw counts, *T<sub>s</sub>* and *T<sub>b</sub>* are the scanning time

$$I_{net} = I - T_s/T_b(B_1 + B_2) \quad (1)$$

$$\sigma_{I_{net}} = [I + (T_s/T_b)^2(B_1 + B_2) + (pI_{net})^2]^{1/2} \quad (2)$$

and the total time spent counting the background, respectively, *B*<sub>1</sub> and *B*<sub>2</sub> are the background counts on either side of the reflection, and *p* is an adjustable parameter, initially taken as 0.08.

The data were examined, and in those cases where a badly asymmetric background indicated the reflection was not centered in the scan, the reflection was remeasured after centering.

The intensities were converted to structure factors by the application of Lorentz polarization factors. Allowance was made for

polarization due to the crystal monochromator. An absorption correction was not made; for  $\mu = 14.07$  cm<sup>-1</sup>, the transmission factors were estimated to vary from 0.87 to 0.75.

Data from two equivalent octants, *hkl* and  $\bar{h}\bar{k}l$ , were obtained by the automatic scanning method used by the PAILRED. An average  $F_o^2$  and  $\sigma_{F_o^2}$  were computed for the equivalent reflections. These reflections were combined with the reflections for which no equivalents were available. Reflections for which  $F_o^2 \leq 3\sigma_{F_o^2}$  were rejected as unobserved. A total of 1767 independent reflections was obtained with  $\sin \theta/\lambda \leq 0.66$ , of which 659 were classified as observed. The large number of unobserved reflections is due to two factors: the  $\sin \theta/\lambda$  cutoff was somewhat larger than necessary (few reflections were observed beyond  $\sin \theta/\lambda = 0.55$ ), and nearly all reflections with (*h* + *k*) odd were very weak because of the positioning of the molecules on the twofold axes.

**Structure Determination and Refinement.** The atomic scattering factors for neutral Ni, Cl, O, N, and C were taken from Cromer and Waber;<sup>3</sup> those for hydrogen were from the compilation of Ibers.<sup>4</sup> The real and imaginary parts of the anomalous scattering of nickel were obtained from the compilation of Templeton.<sup>5</sup> Major computer programs included local versions of Zalkin's FORDAP for the Fourier syntheses, Busing and Levy's ORFLS for the full-matrix least-squares refinement, and Busing, Martin, and Levy's ORFFE for function and error analysis.

Since there are only four formula units of [NiAT]ClO<sub>4</sub> in the unit cell, the Ni and Cl atoms must be located at special positions in space group *Pbcn*. The 4(*c*) positions on the twofold axes were deemed most probable, as the other special positions in *Pbcn* require a center of inversion and were considered unlikely in view of the proposed structure of the compound.<sup>1</sup> A three-dimensional unsharpened Patterson synthesis confirmed that the Ni and Cl atoms lay in the 4(*c*) positions and yielded the *y* coordinates of these atoms. Refinement of the *y* coordinates, one scale factor, and the overall temperature factor yielded *R* = 0.50, *R<sub>w</sub>* = 0.48, after two cycles. The function minimized was  $\sum w(F_o - F_c)^2$ , where  $w = 1/\sigma_{F_o^2}$  and *F<sub>o</sub>* and *F<sub>c</sub>* are the observed and calculated structure factors, respectively. The conventional *R* factor, *R*, is defined as  $\sum(F_o - F_c)/\sum F_o$ , while the weighted *R* factor, *R<sub>w</sub>*, is defined as  $[\sum w(F_o - F_c)^2/\sum w F_o^2]^{1/2}$ .

A difference Fourier synthesis phased by the Ni and Cl atoms was calculated. The positions of the remaining nonhydrogen atoms were determined from this map, albeit with some difficulty in view of the pronounced elongation of the peaks in the *c* direction, due to the fact that the Ni and Cl atoms define pseudomirror planes perpendicular to this axis. Two cycles of refinement of the scale factors for all nonhydrogen atoms gave *R* = 0.11, *R<sub>w</sub>* = 0.14.

Another difference Fourier synthesis revealed that the nickel, chlorine, and two oxygen atoms were vibrating anisotropically.

Treatment of these atoms as anisotropic yielded *R* = 0.80, *R<sub>w</sub>* = 0.103. This Fourier synthesis also exhibited peaks close to where the hydrogen atoms should be located on the trien backbone (the peaks appeared at distances of 0.8-1.4 Å from the carbon and nitrogen atoms); there was also a peak 1.2 Å from the  $\gamma$ -carbon atom of the acac residue, but no distinct peaks around the methyl carbon atom. The positions of all of the hydrogen atoms (except those on the methyl carbon atom, which were neglected in further refinements) were calculated, assuming *d*<sub>C-H</sub> = *d*<sub>N-H</sub> = 1.0 Å, sp<sup>3</sup> hybridization for the  $\gamma$ -carbon atom of the acac residue, and sp<sup>3</sup> hybridization for the remaining carbon and nitrogen atoms. These positions were introduced into the least-squares calculations as fixed parameters. Each hydrogen atom was assigned an isotropic temperature factor of 6.0 Å<sup>2</sup>. Two cycles of least-squares refinement (50 variables) now resulted in convergence at *R* = 0.072, *R<sub>w</sub>* = 0.087.

Hamilton's test<sup>6</sup> shows that the introduction of anisotropic temperature factors for Ni, Cl, O(1), and O(2), and the inclusion of the hydrogen atoms, are both significant beyond the 99.5% level.

A weighting analysis at this point revealed no change of the average value of  $\sum w(F_o - F_c)^2$  over various ranges of *F<sub>o</sub>* and  $\sin \theta/\lambda$ , and so no changes were made in the adjustable parameter *p* (eq 2).

No parameter change exceeded 0.1 standard deviation in the last cycle of refinement. The error in an observation of unit weight

(3) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(4) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(5) Reference 4, p 215.

(6) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

**Table I.** Atomic Parameters and Isotropic Temperature Factors for [NiAT]ClO<sub>4</sub>

Atom	x	y	z	B, Å <sup>2</sup>
Ni	0.0	0.17818 (13)	0.25	3.60 (7) <sup>a</sup>
N(1)	0.0907 (8)	0.0980 (7)	0.3461 (11)	4.3 (2)
N(2)	0.0718 (8)	0.2714 (7)	0.3553 (11)	4.6 (2)
C(1)	0.0	-0.0340 (13)	0.25	5.4 (5)
C(2)	0.0796 (9)	0.0079 (9)	0.3389 (14)	4.5 (3)
C(3)	0.1615 (12)	-0.0524 (10)	0.4211 (16)	6.2 (3)
C(4)	0.1729 (11)	0.1380 (9)	0.4371 (14)	5.0 (3)
C(5)	0.1831 (10)	0.2391 (9)	0.3827 (15)	5.5 (3)
C(6)	0.0584 (9)	0.3585 (9)	0.2759 (15)	4.9 (3)
H(1)	0.0	-0.101	0.25	6.0
H(2)	0.153	0.135	0.548	6.0
H(3)	0.242	0.105	0.421	6.0
H(4)	0.219	0.277	0.464	6.0
H(5)	0.226	0.243	0.286	6.0
H(6)	0.037	0.277	0.458	6.0
H(7)	0.108	0.362	0.185	6.0
H(8)	0.073	0.410	0.346	6.0
Cl	0.5	0.1413 (4)	0.25	6.4 (1) <sup>a</sup>
O(1)	0.4237 (15)	0.0922 (11)	0.1682 (19)	13.7 (6) <sup>a</sup>
O(2)	0.4464 (11)	0.1995 (13)	0.3485 (22)	13.2 (6) <sup>a</sup>

<sup>a</sup> Obtained before refinement in the anisotropic approximation.

**Table II.** Anisotropic Temperature Factors<sup>a</sup>

Atom	β <sub>11</sub>	β <sub>22</sub>	β <sub>33</sub>	β <sub>12</sub>	β <sub>13</sub>	β <sub>23</sub>
Ni	0.00628 (15)	0.00326 (9)	0.0155 (3)	0.0	-0.0003 (3)	0.0
Cl	0.0132 (5)	0.0063 (3)	0.0160 (7)	0.0	-0.0005 (9)	0.0
O(1)	0.0340 (14)	0.0125 (12)	0.037 (3)	-0.0088 (13)	-0.0092 (22)	-0.0018 (15)
O(2)	0.0157 (14)	0.0216 (18)	0.053 (4)	0.0046 (12)	-0.0021 (18)	-0.0162 (22)

<sup>a</sup> The anisotropic temperature factor is defined as  $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$ .

was 2.03. The observed and calculated structure factors are given elsewhere.<sup>7</sup> The positional parameters and temperature factors, together with the estimated standard deviations, are given in Tables I and II.

A final difference Fourier synthesis based on all of the observed data showed that the largest peaks were a few peaks 0.6 e/Å<sup>3</sup> high. There were also a few holes 0.6 e/Å<sup>3</sup> deep. These features were concentrated in the vicinity of the nickel atom and the perchlorate group. In particular, the perchlorate group is either somewhat disordered or else is undergoing great thermal motion, as indicated by isotropic temperature factors of ~14 Å<sup>2</sup> for the oxygen atoms. Treatment of the oxygen atoms as anisotropically vibrating is not a truly satisfactory solution for either of these possibilities, and it is not surprising that the difference Fourier map shows small peaks and holes around the perchlorate group.

Structure factors were calculated for all of the unobserved reflections. There were only rare instances in which the calculated intensity exceeded the observed intensity by more than 2σ.

## Discussion of the Structure

Figure 1a shows a projection of the [NiAT]<sup>+</sup> cation onto the average Ni-N(1)-N(2)-N(1')-N(2)' plane. Bond distances and angles, along with their standard deviations, are given in this figure. The dimensions of the perchlorate group are given in Figure 1b. Table III gives the root-mean-square displacements along the principal axes of the thermal ellipsoids of Ni, Cl, O(1), and O(2).

**The Nickel(II) Coordination.** The macrocycle is coordinated to the nickel ion with the donor atoms in approximately square planar locations. There is a

(7) Tables of the structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-4134. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

slight tetrahedral distortion, as alternate nitrogen atoms lie 0.11 Å above and below the best plane through Ni, N(1), N(2), N(1)', and N(2)' (the nickel atom lies exactly in this plane). This type of distortion is often observed in structures of macrocyclic complexes, and is apparently not a function of macrocycle size—the extent of distortion is about the same in [NiAT]<sup>+</sup> (13-membered) as in Curtis compounds (14-membered),<sup>8,9</sup> corrin complexes (15-membered),<sup>10,11</sup> and porphyrin complexes (16-membered).<sup>12-14</sup> In fact, such a tetrahedral distortion is even observed for the four nitrogen atoms of the trien ligand in [Cu(trien)SCN]NCS, where macrocycle formation is not involved.<sup>15</sup> The distortion probably serves to relieve internal strain in the ligand.<sup>8,16</sup> Other minor distortions from square planarity include differences in the Ni-N and N···N distances and in the N-Ni-N angles (see Figure 1).

The Ni-N(1)(trigonal) bond length of 1.83 ± 0.01 Å is slightly, but significantly, shorter than the Ni-N(2)-(tetrahedral) length of 1.88 ± 0.01 Å. The difference may be due to the smaller radius of trigonally sp<sup>2</sup>-hy-

**Table III.** Sizes and Orientations of the Thermal Ellipsoids<sup>a</sup>

Atom	R	$\bar{u}_R$	θ <sub>x</sub>	θ <sub>y</sub>	θ <sub>z</sub>
Ni	1	0.191 (3)	90 (0)	0 (0)	90 (0)
	2	0.221 (3)	171 (9)	90 (0)	99 (9)
	3	0.245 (3)	99 (9)	90 (0)	9 (9)
Cl	1	0.248 (6)	86 (7)	90 (0)	4 (7)
	2	0.264 (6)	90 (0)	180 (0)	90 (0)
	3	0.321 (6)	4 (7)	90 (0)	94 (7)
O(1)	1	0.28 (2)	63 (3)	43 (6)	60 (7)
	2	0.39 (2)	91 (5)	123 (7)	33 (7)
	3	0.56 (2)	27 (3)	113 (4)	104 (4)
O(2)	1	0.31 (2)	47 (14)	124 (6)	118 (10)
	2	0.36 (2)	135 (14)	110 (9)	129 (9)
	3	0.58 (2)	79 (3)	41 (3)	129 (4)

<sup>a</sup> Principal axes R of the anisotropic temperature factors. The root-mean-square displacements ( $\bar{u}_R$ ) along the principal axes are given in ångströms. θ<sub>x</sub>, θ<sub>y</sub>, and θ<sub>z</sub> are the direction angles (in degrees) with respect to the crystallographic x, y, and z axes.

bridized nitrogen as compared to tetrahedrally sp<sup>3</sup>-hybridized nitrogen.

**The AT Ligand.** The overall conformation of the trien residue is very similar to the conformation of trien in [Cu(trien)SCN]NCS,<sup>15</sup> where trien forms the base of

(8) B. T. Kilbourn, R. R. Ryan, and J. D. Dunitz, *J. Chem. Soc. A*, 2407 (1969).

(9) P. R. Ireland and W. T. Robinson, *ibid.*, 663 (1970).

(10) D. C. Hodgkin, *Proc. Roy. Soc., Ser. A*, 288, 294 (1965).

(11) J. D. Dunitz and E. F. Meyer, *ibid., Ser. A*, 288, 324 (1965).

(12) E. B. Fleischer, *J. Amer. Chem. Soc.*, 85, 1353 (1963).

(13) E. B. Fleischer, *ibid.*, 85, 146 (1963).

(14) E. B. Fleischer, C. K. Miller, and L. E. Webb, *ibid.*, 86, 2342 (1964).

(15) R. G. Mirongiu, E. C. Lingafelter, and P. Paoletti, *Inorg. Chem.*, 8, 2763 (1969).

(16) T. A. Hamor, W. S. Caughey, and L. J. Hoard, *J. Amer. Chem. Soc.*, 87, 2305 (1965).

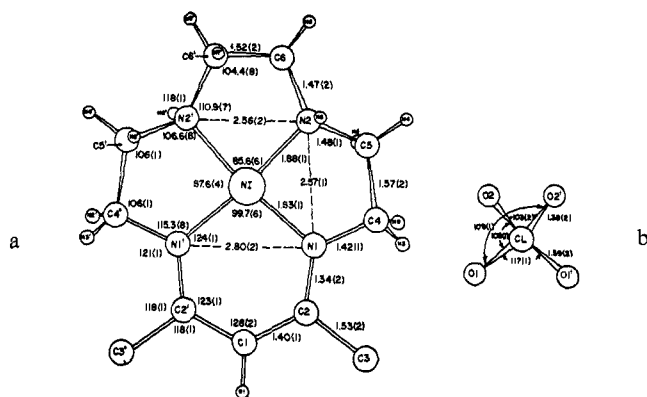


Figure 1. (a) Projection of the  $[\text{NiAT}]^+$  cation onto the average  $\text{NiN}_4$  plane, and the bond distances, angles, and standard deviations. The primed atoms are related to the unprimed atoms by the twofold axis passing through Ni and C(1). H(1) is behind C(6). (b) Dimensions in the  $\text{ClO}_4^-$  anion.

a square pyramid. The N(1)-C(4)-C(5)-N(2) ring has a *k* configuration<sup>17</sup> and an unsymmetrical gauche form, with C(4) and C(5) 0.11 and 0.68 Å below the N(1)-Ni-N(2) plane. The (2)-C(6)-C(6')-N(2)' ring has a *k'* configuration and a symmetrical gauche form, with C(6) 0.36 Å below the N(2)-Ni-N(2)' plane and C(6)' 0.36 Å above this plane.

The ethylenediamine ring conformations can also be described in terms of the dihedral angle made by the intersection of the NCC planes in each ring.<sup>18</sup> These angles are 40.0° in the N(1)-C(4)-C(5)-N(2) ring and 50.9° in the N(2)-C(6)-C(6')-N(2)' ring.

The acetylacetonate residue is essentially planar, with an average deviation of 0.01 Å from the best plane through C(3), C(2), C(1), C(2)', and C(3)'. The Ni atom lies in this plane, while the N(1) and N(1)' atoms deviate by -0.006 and +0.006 Å, respectively. The C-C distances and C-C-C angles in the acac residue are similar to those found in acetylacetonate complexes,<sup>19</sup> while the C(2)-N(1) distance of  $1.34 \pm 0.02$  Å compares with values of 1.29–1.34 Å found for the corresponding bond in bis(acetylacetonate)ethylenediamine compounds.<sup>20–22</sup>

**Molecular Packing.** The molecular packing is shown in Figure 2. There is a possible weak hydrogen bond between N(2) and O(2)'', where O(2)'' is related to O(2) by the transformation  $(x - 1/2, 1/2 - y, 1 - z)$ . The N(2)···O(2)'' and H(6)···O(2)'' distances are  $3.04 \pm 0.02$  and 2.50 Å, respectively; the N(2)-H(6)-O(2)' angle is 171°. However, the fact that there is large thermal motion or disorder of the perchlorate oxygen atoms means that hydrogen bonding cannot be very important here. The infrared spectrum shows no evidence of hydrogen bonding between the N(2)-H(6) group and the perchlorate ion.<sup>23</sup>

There are no unusually short intermolecular contacts. The shortest intermolecular contacts involving

(17) E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

(18) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 843 (1968).

(19) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

(20) G. R. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 223 (1968).

(21) G. R. Clark, D. Hall, and T. N. Waters, *ibid.*, 823 (1969).

(22) D. Bruins and D. L. Weaver, *Inorg. Chem.*, **9**, 130 (1970).

(23) S. C. Cummings, private communication, Oct 1970.

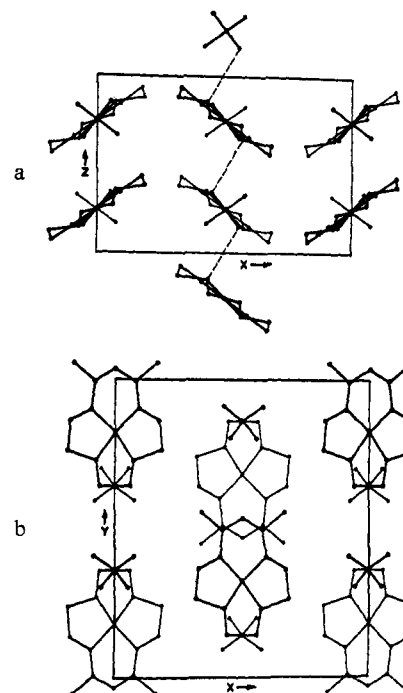


Figure 2. Molecular packing in  $[\text{NiAT}]\text{ClO}_4$ . For clarity, the hydrogen atoms are not shown. The heavily drawn structures represent molecules in the top half of the unit cell, closest to the viewer: (a) projection onto (010); the possible hydrogen bonding scheme is illustrated by dashed lines for the column of ions in the middle foreground; (b) projection onto (001).

the nickel atom are 3.95 Å from Ni to C(3)'' at  $(x, -y, z - 1/2)$  and 3.99 Å from Ni to O(2)'' at  $(1/2 - x, 1/2 - y, z - 1/2)$ . The shortest C···C, N···O (other than the possible hydrogen bond mentioned above), and C···O distances are as follows: 3.44 Å between C(2) and C(2)'' at  $(-x, -y, 1 - z)$ ; 3.39 Å between N(2) and O(1)'' at  $(1/2 - x, 1/2 - y, 1/2 + z)$ ; and 3.32 Å between C(5) and O(2).

**Strain in the Macrocyclic and Implications for the Square Planar Coordination of Smaller Macrocyclics.** The structure determination of  $[\text{NiAT}]\text{ClO}_4$  is the first which provides details on the square planar coordination of a 13-membered macrocycle. Since there are no known examples of square planar coordination by a 12-membered macrocycle, and instances of such coordination by 13-membered macrocycles are rare,<sup>24</sup> it is of interest to compare the  $[\text{NiAT}]\text{ClO}_4$  structure with other macrocyclic complex structures and examine the 13-membered macrocycle for evidence of strain.

Detailed structural information is available for square planar Ni complexes with 14-, 15-, and 16-membered macrocycles.<sup>8,11,16,25–27</sup> Table IV gives a comparison of two of the most pertinent structural parameters, the average Ni-N bond length and the average N-N "bite."<sup>28</sup> These quantities tend to decrease in value as

(24) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968), and references cited therein.

(25) S. W. Hawkinson and E. B. Fleischer, *Inorg. Chem.*, **8**, 2402 (1969).

(26) M. F. Bailey and I. E. Maxwell, *Chem. Commun.*, 908 (1966), cited in ref 24.

(27) I. E. Maxwell and M. F. Bailey, *ibid.*, 883 (1966), cited in ref 24.

(28) We have chosen to take averages in order to derive an approximate measure of the size of the "hole" in the ligand into which the metal must fit. Averaging obliterates differences in some of the parameters (e.g., differences between the bites of five- and six-membered rings), but nevertheless is of value in describing the general characteristics of a given class of macrocycles.

Table IV. Some Dimensions of Square Planar Nickel Macrocyclic Complexes

Compd no.	Atoms in mac	Ligand type	No. of examples	Ni-N dist	N-N bite	Ref
1	16	Porphyrin	1	1.96	2.77	16
2 <sup>a</sup>	16	TAAB <sup>b</sup>	1	1.90	2.69	25
3 <sup>c</sup>	15	Corrin	1	1.87	2.63	11
4	14	Curtis	1	1.91	2.70	8
5 <sup>c</sup>	14	Curtis	2	1.88	2.67	26, 27
6	13	AT	1	1.86	2.63	This work

<sup>a</sup> Structure disordered. <sup>b</sup> TAAB is tetrabenzob[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine. <sup>c</sup> Preliminary structures.

Table V. Nickel-Nitrogen and Nitrogen-Nitrogen Distances in Some Square Planar Nickel Chelates

Compound <sup>a</sup>	Donors <sup>b</sup>	Av Ni-N bond length, Å	N-N distances, Å			Ref
			Five-membered ring bite	Six-membered ring bite	Adjacent unchelated N-N dist	
Ni(stien) <sub>2</sub> <sup>2+</sup>	N <sub>4</sub>	1.89	2.60		2.77	29
Ni(EBG) <sub>2</sub> <sup>2+</sup>	N <sub>4</sub>	1.865	2.57	2.68	2.62	30
Ni(Gly) <sub>2</sub>	N <sub>4</sub>	1.874	2.46		2.80	31
Ni(opd) <sub>2</sub>	N <sub>4</sub>	1.832	2.49		2.68	32
Ni(Mesim) <sub>2</sub>	N <sub>2</sub> O <sub>2</sub>	1.922				33
Ni(PrMesim) <sub>2</sub>	N <sub>2</sub> O <sub>2</sub>	1.920				34
Ni(Hysim) <sub>2</sub>	N <sub>2</sub> O <sub>2</sub>	1.855				35
Ni(trien) <sub>2</sub> <sup>2+</sup>	N <sub>4</sub>	1.91	2.63		2.89	42
[NiAT] <sup>+</sup>	N <sub>4</sub>	1.85	2.56	2.80		This work

<sup>a</sup> Abbreviations: stien = *meso*-stilbenediamine, EBG = ethylenebis(biguanidine), gly = glyoxime, opd = *o*-phenylenediamine, Mesim = *N*-methylsalicylaldimine, PrMesim = *N*-propyl-3-methylsalicylaldimine, Hysim = *N*-hydroxysalicylaldimine. <sup>b</sup> The number and type of donor atoms are shown: thus, N<sub>4</sub> means four nitrogen donor atoms.

the number of atoms in the macrocycle decrease, although the trend is not regular because of the superposition of other factors, such as changes in the nitrogen radius due to different hybridization.

The question arises, what are the optimum values for the Ni-N bond length and the N-N bite, *i.e.*, what values represent an unstrained configuration of four nitrogen atoms arranged in a square plane about a nickel atom? This question cannot be answered unequivocally, due to the lack of structural determinations of nickel complexes with four monodentate, sterically unrestrained nitrogen donors. It might be expected that examination of complexes with bi- or tetradentate (nonmacrocyclic) ligands would provide reasonable estimates of the normal Ni-N bond length and N-N distance. Table V presents some of the relevant data taken from the literature.<sup>29-35</sup>

At this point we note that the Ni-N distance is 1.96 Å in the Ni-porphyrin complex studied by Hamor, Caughey, and Hoard.<sup>15</sup> This value is somewhat greater than those listed in Table V, and thus may not be the most desirable bonding situation for Ni. However, the radius of the hole in uncomplexed porphyrin molecules is ~2.05 Å,<sup>36-38</sup> and Hoard, *et al.*,<sup>39</sup> have

estimated that the optimum value (*i.e.*, the value imposing the least strain on the porphyrin skeleton) is 2.01 Å. The value of 1.96 Å for the Ni-N bond length thus appears to be a compromise between the steric requirements of the porphyrin ligand and those of the nickel atom. Collins and Hoard<sup>40</sup> reached similar conclusions about the Ni complex while examining bond strain in porphine complexes.

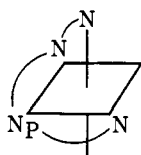
We turn now to the question of whether appreciable strain exists in the [NiAT]<sup>+</sup> complex. There are three parameters which relate directly to possible "strangulation" of the nickel ion by the macrocycle, and which might be expected to be strain indicators. There are: the Ni-N bond length, the N-N "bites," and the extracyclic angles at the nitrogen atoms. Table V shows that the Ni-N bond length and the N-N bites in the five-membered rings compare fairly closely with the values found in the nonmacrocyclic complexes. The bite in the six-membered, acetylacetonate-like ring (2.80 Å) lies very nearly in the center of the range observed for O-O bites in acetylacetonate complexes<sup>41</sup> and is similar to the value observed<sup>29</sup> for the six-membered ring bite in Ni(EBG)<sub>2</sub><sup>2+</sup> (2.68 Å) as well as to the distance between nitrogen atoms not joined by a chelate ring<sup>29-32</sup> (2.62-2.80 Å). There consequently appears to be no unusual shortening in the Ni-N or N-N distances that would reflect any appreciable strain in the 13-membered macrocycle or compression of the donor atoms to positions closer to the nickel than normally expected.

- (29) S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, **3**, 468 (1964).  
 (30) B. L. Holian and R. E. Marsh, *Acta Crystallogr., Sect. B*, **26**, 1049 (1970).  
 (31) M. Calleri, G. Ferraris, and D. Viterbo, *ibid.*, **22**, 468 (1967).  
 (32) G. S. Hall and R. H. Soderberg, *Inorg. Chem.*, **7**, 2300 (1968).  
 (33) M. R. Fox and E. C. Lingafelter, *Acta Crystallogr.*, **22**, 943 (1967).  
 (34) R. L. Braun and E. C. Lingafelter, *ibid.*, **21**, 546 (1966).  
 (35) R. C. Srivastava, E. C. Lingafelter, and P. C. Jain, *ibid.*, **22**, 922 (1967).  
 (36) L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, **43**, 3100 (1965).  
 (37) S. J. Silvers and A. Tulinsky, *J. Amer. Chem. Soc.*, **89**, 333 (1967).  
 (38) M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **86**, 1938 (1964).

- (39) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. L. Caughey, *ibid.*, **87**, 2312 (1965).  
 (40) D. M. Collins and J. L. Hoard, *ibid.*, **92**, 3761 (1970).  
 (41) E. C. Lingafelter and R. L. Braun, *ibid.*, **88**, 2951 (1966).

Of special interest is the recently published structure<sup>42</sup> of Ni(trien)(ClO<sub>4</sub>)<sub>2</sub>, as this compound is directly analogous to [NiAT]ClO<sub>4</sub>. The average bond distance, 1.91 Å, from Ni to the nitrogen atoms (which are all tetrahedral in the Ni(trien)<sup>2+</sup> cation) is slightly larger than our value of 1.88 Å for Ni-N(tetrahedral). The N-N distances of the five-membered rings are somewhat shorter in [NiAT]<sup>+</sup> than in Ni(trien)<sup>2+</sup> (2.56 vs. 2.63 Å), and joining of the primary nitrogen atoms by acetylacetonate ring results in slight shortening of this N-N distance (from 2.89 Å in Ni(trien)<sup>2+</sup> to 2.80 Å in [NiAT]<sup>+</sup>). Thus, the overall picture that obtains from this comparison is that macrocycle formation has resulted in shortening some of the relevant distances, and hence possibly in minor strain.

The extracyclic angle at the tetrahedral nitrogen atom in [NiAT]<sup>+</sup> is 118 ± 1°, or about nine standard deviations greater than the ideal tetrahedral angle of 109.5°. Widening of this angle can be visualized as due to the Ni atom "pushing open" the hole in the macrocycle. This angle is apparently easily distorted, as evidenced by comparison with [Cu(trien)(SCN)]<sup>+</sup> (115° av), the Curtis compound 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-dienickel(II) perchlorate (115°),<sup>8</sup> and various β-triethylenetetramine complexes, where the angle at the "planar secondary nitrogen atom" (N<sub>p</sub> below) is expanded beyond the tetrahedral value.<sup>43</sup> The average value of the corresponding angle in Ni(trien)<sup>2+</sup> is 113 ± 6°.



In summary, the strain energy of [NiAT]<sup>+</sup> would seem not to be very large. This conclusion is supported by

(42) A. McPherson, M. G. Rossmann, D. W. Margerum, and M. R. James, *J. Coord. Chem.*, **1**, 39 (1971).

(43) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and H. C. Freeman, *Inorg. Chem.*, **9**, 1921 (1970).

the ease of formation of [NiAT]<sup>+</sup> and its stability in various solvents,<sup>1</sup> as well as the stability toward X-radiation observed in the present work.

Finally, the question of the feasibility of square planar coordination by a tetradentate, 12-membered macrocycle will be considered. We estimate the size of the hole in a 12-membered macrocycle by taking the N-N bite as 2.57 Å, in accordance with the value for [NiAT]<sup>+</sup>, and assuming the four nitrogen atoms to be at the corner of a square. The distance thus calculated from the center of the macrocycle to the nitrogen atoms is 1.815 Å. In other words, if a metal atom were located in the center of the macrocycle, the metal-nitrogen bond distance would be 1.815 Å. This value is not very different from the ones observed for Ni-N (trigonal, sp<sup>2</sup>) distances in [NiAT]<sup>+</sup> (1.83 Å) and in the nickel-*o*-phenylenediamine complex (1.832 Å average), but is probably significantly shorter than an unstrained Ni-N (tetrahedral, sp<sup>3</sup>) distance (e.g., 1.89 Å in Ni(stien)<sub>2</sub><sup>2+</sup>).<sup>29</sup> In conclusion, we feel that the 13-membered macrocycle is not the limiting ring size for square planar coordination. Square planar coordination of nickel to an unsaturated 12-membered macrocycle appears possible, as does planar coordination of saturated macrocycles (e.g., cyclen<sup>44</sup>) to metal ions smaller than nickel, and perhaps even with nickel if bond strain is outweighed by other stabilizing factors.

**Acknowledgments.** We thank Dr. Sue Cummings for giving us the crystals, Dr. Donald Sands for generously making available the X-ray equipment at the University of Kentucky, and Dr. Peter W. R. Corfield for helpful discussions of the solution of the structure. M. F. R. was a Visiting Research Associate at ARL under an Air Force Ohio State University Research Foundation contract during this research.

(44) Cyclen is 1,4,7,10-tetraazacyclododecane. A study of some cyclen complexes<sup>46</sup> showed that in those particular cases, cyclen was coordinated to four vertices of an octahedron in a folded configuration. However, there are several possible isomers of cyclen some of which are better suited for planar coordination and some for coordination in a folded configuration. No studies have been carried out on this aspect of cyclen coordination.

(45) J. P. Collman and P. W. Schneider, *Inorg. Chem.*, **5**, 1390 (1966)