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Crystal and Molecular Structure of the Five-Coordinate Macrocyclic Iron(II) Complex, Chloro(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)iron(II) Iodide

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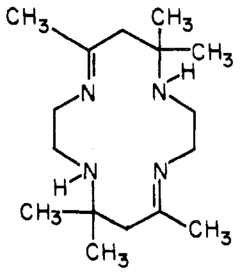
The crystal structure of a high-spin five-coordinate iron(II) complex, $[Fe(C_{16}H_{32}N_4)Cl]I$, of the macrocyclic ligand 5,7,7,-12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene has been determined by three-dimensional X-ray diffraction techniques. The complex crystallizes with the monoclinic space group $C2$ (C_2^3, No. 5) with the cell dimensions a = 17.479 (6), b = 6.729 (2), c = 9.628 (3) Å, β = 108.08 (3)°, and z = 2. The intensities were collected on a Picker FACS-I automated diffractometer (Mo Kα radiation, λ 0.71069 Å) and the structure solved by the heavy-atom Patterson method. Full-matrix least-squares refinement of the positional and thermal parameters for all the nonhydrogen atoms converged to a conventional discrepancy index of 0.079 for 1192 independent reflections. The structure consists of five-coordinate iron(II) bound to the four nitrogen atoms of a folded form of the macrocyclic ligand and a chloride ion occupying the axial site. The iron(II) coordination moiety has crystallographic twofold symmetry with the symmetry axis along the iron–chlorine bond. The iron–nitrogen distances, 2.134 (9) and 2.166 (8) Å, as well as the iron–chlorine distance, 2.306 (4) Å, are normal for high-spin iron(II). The unusual coordination geometry about the iron(II) arises because the steric constraints of the cyclic ligand do not permit the iron to fit into the plane of the four nitrogen atoms and the ligand is not flexible enough to permit sufficient folding to accommodate a sixth ligand cis to the chloride. The iodide anion is disordered about a twofold axis and lies in either end of an alongated dumbbell-shaped cavity generated by the packing arrangement of the complex cation.

Introduction

The new synthetic macrocyclic ligand complexes of iron provide a convenient medium for studying the fundamental chemistry of iron(II) in strong planar ligand fields and for comparing their properties with the naturally occurring iron complexes of heme proteins. Although a considerable amount of structural effort has been devoted to metalloporphyrins,[1,2] to date there have been no single-crystal X-ray structures of high-spin iron(II) complexes of porphyrins or other macrocyclic ligands reported which might be structurally similar to the five-coordinate deoxy forms of hemoglobin and myoglobin.

Iron(II) complexes of the macrocyclic ligand 5,7,7,12,14,-14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, I,



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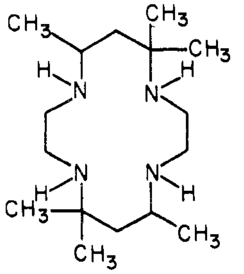

II

have reactivity patterns similar to iron heme proteins. Like iron(II) porphyrins, iron(II) complexes of I form spin-paired six-coordinate complexes in the presence of ligands of moderately strong field strengths such as nitrogen donor atoms but form high-spin five-coordinate complexes in the presence of weak-field ligands such as halides.[3,4] This behavior is undoubtedly due to the larger ionic radius of high-spin (as opposed to low-spin) iron(II)[5] which does not permit it to fit in the plane of the four nitrogen atoms. This is presumed to be the case for the title compound, the five-coordinate chloroiron(II) complex of I, $[Fe(C_{16}H_{32}N_4)Cl]^+$. The chloride ion has insufficient ligand field strength to force spin pairing of the iron(II) and the iron(II) is then forced out of the plane of the constricting array of nitrogen donor atoms. This interpretation is supported indirectly by the formation of high-spin six-coordinate iron(II) complexes, such as $[Fe(C_{16}H_{36}N_4)Cl_2]$, with the fully saturated ligand II.[6] This ligand is more flexible, has a larger core radius than I, and is able to accommodate the high-spin iron(II) ion in the plane of macrocyclic donor atoms.

The crystal structure of the title compound was undertaken to examine the details of the metal–ligand bonding, to explore the cause of this unusual coordination number of iron(II), and to compare the results with that predicted for five-coordinate high-spin iron(II) heme complexes.[1]

Experimental Section

Preparation of $[Fe(C_{16}H_{32}N_4)Cl]I$. The preparation of the five-coordinate complex $[Fe(C_{16}H_{32}N_4)Cl]I$ utilized a procedure similar to that reported for the preparation of the perchlorate salt $[Fe(C_{16}H_{32}N_4)Cl](ClO_4)$.[3] One equivalent of the hydriodide salt of the ligand $C_{16}H_{32}N_4 \cdot 2HI$ (prepared according to the method of Curtis[7]) was added to an anhydrous acetonitrile solution containing 1 equiv of anhydrous $FeCl_2$. Two equivalents of triethylamine was then added to neutralize the acid form of the salt which permitted insertion of the iron(II) into the core of the macrocyclic ligand. The white product, which precipitated on chilling, was filtered under a blanket of nitrogen. The crystals used in this study were obtained by recrystallization of the crude product in an acetone–acetonitrile solution under nitrogen. Although solutions of this complex are extremely reactive toward molecular oxygen, yielding rust and the acid salt of the ligand, the crystals are quite stable over a period of many months.

Collection and Reduction of Intensity Data. A small crystal, 0.1 × 0.1 × 0.075 mm, was examined by zero- and upper-layer precession photographs (Cu Kα radiation) and found to be monoclinic. The systematic absences observed were hkl ($h + k \neq 2n$), $h0l$ ($h \neq 2n$), and $0k0$ ($k \neq 2n$) and indicated $C2$ or $C2/m$ as the most probable space group. The cell constants were obtained by least-squares refinement of the 2θ, χ, and ϕ angles of 12 accurately centered general reflections on a Picker FACS-1 diffractometer with Mo Kα radiation. They were found to be a = 17.479 (6), b = 6.729 (2), c = 9.628 (3) Å, and β = 108.08 (3)°. The measured density, 1.56 (2) g/cm³, com-

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[1] J. L. Hoard, *Science*, 174, 1295 (1971), and references cited therein.

[2] E. B. Fleischer, *Accounts Chem. Res.*, 3, 105 (1970), and references cited therein.

[3] V. L. Goedken, P. H. Merrill, and D. H. Busch, *J. Amer. Chem. Soc.*, 94, 3397 (1972).

[4] V. L. Goedken, P. M. Merrell, D. H. Busch, and I. Stone, *J. Amer. Chem. Soc.*, 92, 7590 (1970).

[5] Normal low-spin d^6 Fe^{II}–N bond distances are about 1.97 Å, while high-spin Fe^{II}–N bonds are about 2.15 Å long.[1]

[6] J. Dabrowiak, P. Merrell, and D. H. Busch, *Inorg. Chem.*, 11, 1979 (1972).

[7] N. F. Curtis, *Chem. Commun.*, 525 (1966).

pares favorably with the calculated density, 1.538 g/cm^3 for $Z = 2$.

Intensity measurements were taken from the above crystal which was mounted with the b crystal axis nominally collinear with the goniometer ϕ axis. Data were collected using Mo Kα radiation by the θ–2θ technique with a takeoff angle of 2.0°. A basic scan range of 1.6° at $2\theta = 0.0°$ was increased as a function of 2θ to compensate for α_1–α_2 splitting. The scan speed was 1°/min. Stationary-counter, stationary-crystal background counts of 20 sec were measured at each end of the scan. Attenuators were inserted automatically when the intensity of the reflections exceeded 10,000 counts/sec during the scan. The intensities of three standard reflections were chosen from widely separated regions of reciprocal space and were measured after every 100 reflections. The deviations of the check reflections were random during the data collection and varied no more than 2% from the average value.

The data were reduced in the conventional manner. The formula used for the Lp correction under the condition of monochromatized radiation was that given by Azaroff,[8] where θ_M and θ_S are respectively the Bragg angles for the monochromator and specimen.

$$\frac{1}{Lp} = \frac{(1 + \cos^2 2\theta_M) \sin 2\theta_S}{\cos^2 2\theta_S + \cos^2 2\theta_M} \qquad (1)$$

Standard deviations in the reflection intensities were estimated using the formula

$$\sigma(I) = [S + T_S{}^2 B_1 B_2 / T_B{}^2 (B_1 + B_2) + (pS)^2]^{1/2} \qquad (2)$$

where S, B_1, and B_2 are the accumulated scan and background counts, T_S and T_B are the scan and individual background counting times, and p is a factor, here taken as 0.02, to account for machine fluctuations and other sources of error which would be expected to result in variations proportional to the diffracted intensity.[9] The variances in the F's were calculated using the approximation

$$\sigma^2(F) = \sigma^2(I)/4F^2(Lp)^2 \qquad (3)$$

Intensities were measured for 1511 unique reflections of which 1169 had F^2's greater than 2σ and were used in the final refinement of the structure. The small size and regular dimensions of the data crystal minimized the effects of absorption even though $\mu_\lambda = 23$. The consequences of absorption on this structure were judged to be minimal and no corrections were made. The minimum and maximum transmission coefficients for the longest and shortest dimensions of the crystal were 0.69 and 0.79, respectively.

Solution and Refinement of the Structure. The structure was solved using conventional Fourier and least-squares techniques.[10] Scattering factors of neutral atoms were taken from standard sources.[11] Structure factor calculations used the $\Delta f'$ and $\Delta f''$ values of Cromer in estimating the real and imaginary parts of anomolous scattering by the iodine, iron, and chlorine atoms.[12,13] The density and cell volume require two molecules per unit cell. The cation possesses at most twofold symmetry thus indicating $C2$ as the most probable space group and also suggests that both the cation and anion lie on special positions. However, the analysis of the Patterson map indicated that *both* heavy atoms, iron and iodide, were displaced slightly (about 0.5 Å) from the twofold axes, 0.0, y, 0.0 and 0.5, y, 0.5. Disorder of the type in which both the complex cation and the anion were disordered about twofold axes appeared unlikely. It was assumed therefore that the iron atom was on the twofold axis, 0.0, 0.25, 0.0, and that the iodide was displaced from the twofold axis at 0.441, 0.066, 0.433. The chloride ion was assumed to be coordinated to the iron(II) and was also placed on the twofold axis at 0.0, 0.60, 0.0 which gave a normal iron–chloride distance of 2.3 Å. Least-squares refinement of positional parameters and isotropic thermal parameters and the scale factor with the 660 most significant data yielded the discrepancy factor $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o| = 0.30$. A difference Fourier utilizing these phases revealed the position of the carbon and nitrogen atoms of the ligand. Refinement of the positional and thermal parameters of these atoms with anisotropic thermal parameters for the heavy atoms and isotropic thermal parameters for the light atoms yielded $R_1 = 7.90\%$. A difference Fourier map calculated using these phases revealed substantial anisotropic thermal motion of the methyl groups. In the next cycles of refinement, all data with $F^2 > 2\sigma$, 1169, were included. Refinement with anisotropic thermal parameters for the methyl carbon atoms, as well as for the heavy atoms, and with a weighting scheme based on eq 3 converged to a discrepancy index of $R_1 = 8.36$, $R_2 = 7.95\%$ where $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. At this point, the y coordinates were inverted to test for the correct absolute configuration. Rerefinement to convergence yielded $R_1 = 8.28$, $R_2 = 7.85\%$. Application of Hamiltons' significance test to R_2 indicates that the original structure model could be rejected at the 99.5% probability level.[14,15]

The positions for all hydrogen atoms, except for those of the methyl groups, were calculated assuming tetrahedral geometry and C–H and N–H bond distances of 1.0 Å. These atoms were included but their parameters were not refined in the final least-squares cycles. Two cycles of full-matrix least-squares refinement then yielded $R_1 = 7.94$, $R_2 = 7.46\%$; the largest parameter shift was 0.25σ.

The final difference Fourier indicated that most of the electron density was well accounted for. The highest peak was about 1.5 e/Å^3 and was located on the twofold axis between the half iodine atoms. All other peaks were less than 0.7 e/Å^3. None of the methyl hydrogen atoms were observed in the difference Fourier maps.

Table I lists the final atomic coordinates and thermal parameters and the rms thermal amplitudes for the anisotropically refined atoms. Bond distances and angles with errors estimated from the elements of the inverted matrix of the last least-squares cycle appear in Table II. A table of calculated and observed structure factor amplitudes is available.[16]

Description and Discussion of the Structure

The cation consists of five-coordinate high-spin iron(II) bound to a chloride ion and to the four nitrogen atoms of a somewhat folded form of the macrocyclic ligand. The Fe–Cl bond is collinear with a crystallographic twofold axis. A view of the cation down the Fe–Cl bond and the atomic number scheme of the ligand is shown in Figure 1. The iron coordination is probably best described as distorted trigonal bipyramidal, with N(2) and N(2') occupying the apical positions (Figure 2). However, in terms of the ligand field environment, where the crystal field strength varies as a high power of the internuclear distance, $Dq \propto 1/r^6$,[17] the iron experiences a ligand field more readily interpretable as a square-pyramidal geometry where the ligand field contribution from each of the four nitrogen atoms is equivalent and that from the chloride ion is less. This interpretation is supported both by the Mossbauer[4] and the ligand field spectra[3] which indicate a strong tetragonal rather than a trigonal ligand field.

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[8] L. V. Azaroff, *Acta Crystallogr.*, 8, 701 (1955).

[9] W. Busing and H. A. Levy, *J. Chem. Phys.*, 26, 563 (1957); P. W. R. Corfield, R. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

[10] Two other crystalline modifications of this cation were isolated as perchlorate salts, $[Fe(C_{16}H_3N_4)Cl]ClO_4$, and examined crystallographically. Both modifications were very closely related to the iodide structure reported here. Modification A crystallized in the space group $C2$ with $a = 17.431$ (5), $b = 6.779$ (2), $c = 19.900$ (7) Å, $\beta = 110.19$ (3)°, and $Z = 4$. There were two independent cations present and each was located on independent twofold axes, 0.0, 0.25, 0.0 and 0.5, 0.264, 0.5, with the iron–chlorine bonds coincident with the twofold crystallographic axes. The structural refinement was halted when it became apparent that the perchlorate anion was severely disordered. Modification B crystallized in the space group $C2$ with $a = 17.38$ (1), $b = 6.821$ (4), $c = 9.965$ (8) Å, $\beta = 109.82$ (6)°, and $Z = 2$. The cell volume of the "B" modification was half that of the "A" modification indicating that both the cation and anions should lie on special positions. However, Patterson and difference Fourier maps indicated that the perchlorate anion was located about 0.5 Å *off the twofold axis*. Refinement was discontinued when it became obvious that the perchlorate anion possessed rotational disorder in addition to the translational disorder about the twofold axis.

[11] The scattering factors for Fe, C, N, Cl, and I were taken from D. Cromer, A. C. Larson, and J. T. Waber, *Acta Crystallogr.*, 17, 1044 (1964); that for hydrogen was taken from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

[12] D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

[13] All calculations were performed on an IBM 7094 computer using the following programs: Sly-Shoemaker Fourier "ERFR2," Dewar's SORFLS and SORFEE, which are modified versions of the Busing and Levy least-squares "ORFLS" and the Busing and Levy function and error program "ORFFE."

[14] W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

[15] T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Crystallogr.*, 20, 836 (1966).

[16] See paragraph at end of paper regarding supplementary material.

[17] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.

Table I

Final Atomic Positions and Isotropic Thermal Parameters for (Fe($C_{16}H_{32}N_4$)Cl]I

	x	y	z	B, Å^2	rms displacement, Å
I	0.4444 (2)	0.0660	0.4496 (2)		
Fe	0.0	0.2548 (4)	0.0		
Cl	0.0	0.5976 (7)	0.0		
N(1)	0.0990 (5)	0.0907 (16)	−0.0267 (9)	4.2 (2)	0.232 (5)
N(2)	0.0474 (5)	0.1987 (14)	0.2326 (9)	3.7 (2)	0.220 (5)
C(1)	0.0925 (7)	0.0863 (24)	−0.1838 (13)	5.2 (2)	0.258 (7)
C(2)	−0.0059 (7)	0.0501 (22)	0.2688 (12)	4.7 (2)	0.242 (7)
C(3)	0.1347 (7)	0.1680 (22)	0.2949 (13)	5.2 (3)	0.255 (7)
C(4)	0.1590 (7)	−0.0126 (22)	0.2220 (14)	5.5 (3)	0.262 (8)
C(5)	0.1511 (7)	−0.0216 (22)	0.0694 (14)	5.4 (3)	0.262 (8)
C(6)	0.2969 (9)	0.3301 (28)	−0.0218 (23)		
C(7)	0.1728 (8)	0.3530 (23)	0.2689 (14)		
C(8)	0.1538 (10)	0.1274 (30)	0.4643 (14)		

Final Anisotropic Thermal Parameters[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	120 (2)	195 (5)	180 (3)	0 (2)	93 (2)	5 (3)
Fe	20 (1)	134 (6)	51 (2)	0	7 (1)	0
Cl	55 (2)	138 (11)	138 (6)	0	5 (3)	0
C(6)	81 (9)	351 (55)	489 (50)	−114 (19)	143 (19)	−182 (46)
C(7)	57 (7)	335 (47)	131 (18)	−53 (14)	−21 (9)	27 (24)
C(8)	115 (12)	542 (81)	111 (19)	−63 (26)	−30 (12)	120 (33)

Hydrogen Atom Positions

	x	y	z
H(1)	−0.0115	−0.0912	−0.2431
H(2)	−0.0036	0.0495	−0.3801
H(3)	0.1300	−0.0220	−0.2039
H(4)	0.1116	0.2210	−0.2151
H(5)	0.1243	−0.1275	0.2393
H(6)	0.2174	−0.0384	0.2773
H(7)	0.0361	0.3273	0.2812

Root-Mean-Square Amplitudes of Vibration (Å) along the Principal Axes of the Ellipsoids

	Major	Intermed	Minor
Fe	0.175 (4)	0.173 (3)	0.147 (3)
Cl	0.310 (6)	0.229 (6)	0.178 (8)
I	0.414 (3)	0.224 (3)	0.211 (3)
C(6)	0.502 (24)	0.286 (23)	0.163 (27)
C(7)	0.378 (19)	0.246 (19)	0.188 (18)
C(8)	0.488 (25)	0.320 (23)	0.171 (21)

[a] Anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})] \times 10^4$.

Table II. Bond Distances and Bond Angles for [Fe($C_{16}H_{32}N_4$)Cl]I

Distances			
Fe–Cl	2.306 (4)	C(3)–C(4)	1.53 (2)
Fe–N(1)	2.13 (1)	C(3)–C(7)	1.48 (2)
Fe–N(2)	2.17 (1)	C(3)–C(8)	1.58 (2)
N(1)–C(1)	1.48 (1)	C(4)–C(5)	1.43 (2)
C(1)–C(2)	1.50 (2)	C(5)–C(6)	1.51 (2)
C(2)–N(2)	1.48 (1)	C(5)–N(1)	1.32 (1)
N(2)–C(3)	1.46 (1)		

Angles			
N(1)–Fe–N(1)	117.7 (6)	N(2)–C(3)–C(7)	106.4 (11)
N(2)–Fe–N(2)	159.9 (5)	N(2)–C(3)–C(8)	108.3 (11)
N(1)–Fe–Cl	121.2 (3)	N(2)–C(3)–C(4)	109.3 (10)
N(2)–Fe–Cl	100.0 (3)	C(7)–C(3)–C(8)	110.8 (13)
N(1)–Fe–N(2)	81.3 (3)	C(7)–C(3)–C(4)	112.4 (10)
N(2)–Fe–N(1)	88.3 (3)	C(8)–C(3)–C(4)	109.5 (13)
Fe–N(1)–C(1)	109.0 (7)	C(3)–C(4)–C(5)	123.5 (12)
N(1)–C(1)–C(2)	107.7 (9)	C(5)–N(1)–Fe	128.5 (8)
C(1)–C(2)–N(2)	111.4 (10)	C(4)–C(5)–N(1)	121.4 (12)
C(2)–N(2)–Fe	107.1 (6)	C(4)–C(5)–C(6)	117.5 (13)
Fe–N(2)–C(3)	117.7 (7)	N(1)–C(5)–C(6)	121.0 (12)

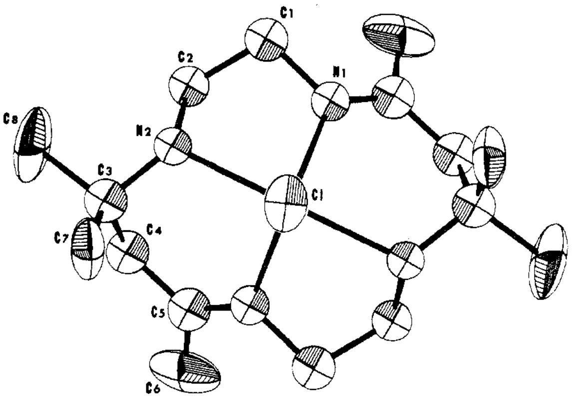

Figure 1. Macrocyclic complex cation and labeling scheme as viewed down the twofold axis (y axis) of the crystal system.

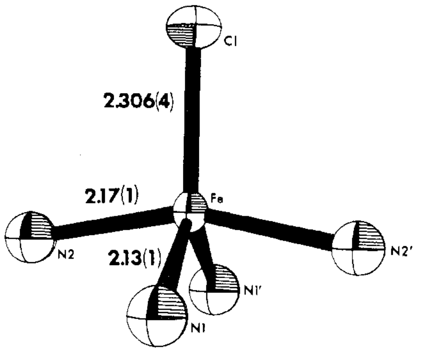

Figure 2. Side view of the coordination sphere which partially illustrates the deformation of the four nitrogens from planarity.

The five-coordinate structure found in this complex represents an unusual example where the constricting environment of the macrocyclic ligand forces the metal out of the plane of the four nitrogen atoms and allows only one ligand to occupy an axial site. This structural feature has an analogy with the high-spin five-coordinate deoxyhemoglobin[18] and chloroiron(III) porphyrins[19,20] where similar arguments have been put forth to account for their five-coordinate nature and also to account for the metal atom lying out of the plane of the four nitrogen atoms.[1]

The basic geometry of our five-coordinate complex, [Fe($C_{16}H_{32}N_4$)Cl]$^+$, as determined in the solid state is also maintained in solution, since the solid-state and solution d-d electronic spectra, which are sensitive to changes in coordination number, electronic spin configuration, and tetragonal distortions, are almost identical.[3] This behavior contrasts with that of the octahedral six-coordinate complexes of Co(II) and Ni(II) containing folded forms of this ligand which have been isolated with bidentate oxalate.[21,22] Both of these complexes revert to low-spin electronic configurations in solution, thus indicating that the metal ion is once again experiencing the strong ligand field of the planar form of the ligand.

The structures of several related macrocyclic complexes have been reported.[23-26] The fully saturated ligand II is much more flexible than I and can fold readily when biden-

[18] M. F. Perutz, *Nature (London)*, 228, 726, 734 (1970).

[19] D. F. Koenig, *Acta Crystallogr.*, 18, 663 (1965).

[20] J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, 89, 1992 (1967).

[21] V. L. Goedken and D. H. Busch, submitted for publication.

[22] N. F. Curtis, *J. Chem. Soc.*, 4109 (1963).

[23] P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc. A*, 1956 (1970).

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

[25] M. F. Bailey and I. E. Maxwell, *Chem. Commun.*, 908 (1966).

[26] I. E. Maxwell and M. F. Bailey, *Chem. Commun.*, 883 (1966).

tate ligands such as acetate are introduced into the coordination sphere. The N-Ni-N angles between trans nitrogen atoms of the folded macrocyclic ligand are 175.2 (4) and 103.3 (3)°.[23] The corresponding angles in our structure are substantially less, 159.9 (5) and 117.7 (6)°, and merely reflect the added rigidity associated with the incorporation of the two double bonds in positions 4 and 11 of the macrocyclic ligand.

The abnormally short C(4)-C(5) single-bond distance, 1.44 (2) Å, and wide C(3)-C(4)-C(5) bond angle, 122 (1)°, have already been observed in structural investigations of planar ligand nickel(II) complexes of related ligands, but not to the degree found here. These anomalous values have been interpreted by Kilbourn, *et al.*,[24] as arising from the severe bonding strain in the six-membered metal ligand rings which contain a C=N double bond. The larger C(3)-C(4)-C(5) bond angle in our structure is due to the increased angular strain resulting from the partial folding of the ligand.

The Fe-N distances found for our structure, 2.134 (9) and 2.166 (8) Å, are quite close to the 2.19 Å predicted by Hoard[1] for high-spin iron(II)-nitrogen distances in deoxyhemoglobin. They are also in the range of metal-nitrogen distances found for high-spin cobalt(II) and nickel(II) complexes.[27,28] The structures of very few high-spin iron(II) complexes with nitrogen donor ligands which may be used for comparison have been reported. The Fe-N distances of the $[Fe(py)_6]^{2+}$ cation vary from 2.22 (3) to 2.29 (3) Å[29] and the average Fe-N distance in the eight-coordinate complex tetrakis(1,8-naphthyridine)iron(II) perchlorate is 2.29 (Å).[30] In both of these complexes, steric interactions of the ligands as well as the higher coordination numbers would result in long Fe-N distances. The most valid structure which may be used for comparison is that of the five-coordinate tris(2-dimethylaminoethyl)amine iron(II) bromide cation which has Fe-N distances of 2.21 and 2.15 (Å).[31] The iron-nitrogen distances of these high spin complexes are significantly longer (about 0.2 Å) than observed for iron(II)-nitrogen distances in a number of spin-paired iron(II) complexes where distances as short as 1.91 Å have been observed.[32,33]

The iron-nitrogen and iron-chloride distances in this five-coordinate complex are about 0.1 Å longer than the iron(III)-nitrogen distances, 2.049 (9) Å, and the iron(III)-chloride distance, 2.192 (12) Å, of high-spin chlorotetraphenylporphineiron(III). The shorter iron(III)-ligand distances in the porphyrin compound merely reflect the smaller radius of iron(III) compared to that of iron(II).

The somewhat less than ideal R value for this structure and the magnitude of the estimated standard deviations in bond lengths and angles are, to a large part, the effect of the disordered iodide anion on the positional parameters of other atoms in the structure. Figure 3 illustrates a partial packing diagram as viewed down the y axis. The packing of the large cations creates an elongated cavity with there being an equal probability of the iodide ion occupying either end of the cavity. The large apparent thermal vibrations of the methyl groups, especially those of C(8) which point toward the cavity, are the result of only one end of the cavity being occupied. Consequently, the coordinates of any atoms or groups of atoms (*e.g.*, the methyl group of C(8) or the methylene groups of C(1) and C(2) which have hydrogen atoms within van der Waals distances of the iodide) can be expected to be a function of the occupancy of that end of the cavity. The best way to accommodate this disorder is by allowing apparent anisotropic thermal motion to account for the electron density which provides a satisfactory approximation for the conformational information desired from this structure.

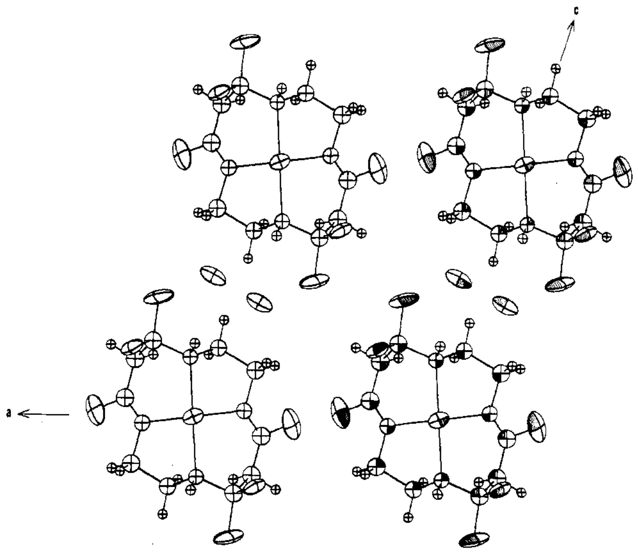

Figure 3. Partial packing diagram illustrating the placement of the iodide ions within the elongated cavity generated by the cation arrangement.

The large cavity size is indicated by the fact that the corresponding perchlorate salt $[Fe(C_{16}H_{32}N_4)Cl]ClO_4$ is isomorphous with the iodide salt[10] even though the perchlorate anion is significantly larger than iodide and also accounts for the unusually large thermal excursions, up to 0.414 (2) Å, of the iodide anion. Comparison of the closest intramolecular contacts with the iodide ion at its refined position with those closest contacts calculated by assuming the iodide anion was located on the twofold axis at the same y coordinate did not reveal any overall substantiative differences. The only exception was N(1) and its hydrogen atom which would both be closer to the iodide ion by 0.1 Å if the iodide were located on the twofold axis.

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Supplementary Material Available. A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2894.

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