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THE CRYSTAL AND MOLECULAR STRUCTURE OF AN OCTACOORDINATED IRON(II) COMPOUND—TETRAKIS(1,8-NAPHTHYRIDINE)Fe(II) PERCHLORATE

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**THE CRYSTAL AND MOLECULAR STRUCTURE OF AN
OCTACOORDINATED IRON(II) COMPOUND—
TETRAKIS(1,8-NAPHTHYRIDINE)Fe(II)
PERCHLORATE†**

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Recently, Hendricker and Bodner reported the synthesis of a series of first-row transition metal complexes of the type $M(L)_4(ClO_4)_2$, where M is a metal of the 3d transition series and $L = 1,8$ -naphthyridine. Preliminary space group determination indicates that all the perchlorates of the 3d-transition series from $M = Mn^{2+}$ to $M = Zn^{2+}$ are isomorphous. Single crystals suitable for X-ray diffraction studies were grown from methanol solutions of the perchlorate salts. Red, prismatic, crystals of the Fe(II) salt were found to be triclinic with the following cell dimensions: $a = 9.163(3)$, $b = 9.315(3)$, $c = 20.116(8)$ Å, $\alpha = 99.66(8)$, $\beta = 77.37(8)$ and $\gamma = 91.70(8)^\circ$; $Z = 2$ molecules/unit cell. $V(obs) = 1651.62(\text{Å})^3$ $D(exp) = 1.57$; $D(calc) = 1.56$ gms/cc. It was assumed that the space group is $P\bar{1}$, which was verified by structure solution and refinement. The intensity data were collected with MoK_α radiation ($\lambda = 0.71069$ Å) using a manually-operated Picker four-circle goniometer. In all 1969 non-zero, independent, reflections were obtained for which the value of $|F^2| > 3\sigma$. The structure was solved by standard Patterson methods using an unsharpened 3-dimensional function. The coordination polyhedron is a distorted dodecahedron, the distortions of which are the result of the rather rigid constraints introduced by a planar, inflexible ligand having a small "bite" and by ligand-ligand repulsions. The disposition of the nitrogen ligands around Fe(II) can be described as follows: one nitrogen of each naphthyridine ligand occupies the A positions of the dodecahedron while the second is constrained to occupy the B positions. The Fe—N bond of the latter set is shorter than the Fe—N bonds formed by the A set of nitrogen ligands. One Fe—N bond is longer (2.756 Å) than the rest which range from 2.184 to 2.465 Å. The average length for the eight Fe—N bonds is 2.35 Å, which is in close agreement with similar Fe—N bonds studied elsewhere. The naphthyridine fragments are planar and in the four ligands the worst deviation of any atom from planarity is 0.02 Å. The perchlorate anions have considerable freedom of libration. Their bond lengths were corrected for errors due to torsional motion and the average value of the corrected Cl—O bonds is 1.450 Å. The final value of the discrepancy indices are $R_1 = 0.069$ and $R_2 = 0.071$.

INTRODUCTION

Hendricker and Bodner have reported the synthesis of a series of compounds of the type $M(L)_4(ClO_4)_2$, where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Cd(II) and L is 1,8-naphthyridine.^{2,3} The electronic spectrum of the crystalline iron(II) complex, milled with nujol, gave a single strong absorption band centered approximately at $21,000\text{ cm}^{-1}$ (in addition to typical ligand bands). However, in acetonitrile solution, the spectrum changes yielding a single broad band centered at 9000 cm^{-1} . This solution spectrum is very similar to that of the tris(2,7-dimethyl-1,8-naphthyridine)Fe(II) perchlorate in which the iron atom is known to be octahedrally coordinated.² Thus, it

† Work performed in part under the auspices of the U.S. Atomic Energy Commission.

was suspected that the solid tetrakis-complexes were eight-coordinate. However, it is possible for a bidentate ligand to behave as a monodentate ligand. For example, in dithiocarbamates of the type $(dtc)_3M(NO)$ with $M = Ru, Mo$, one of the dtc ligands is monodentate in the ruthenium complex⁴ while in the molybdenum derivative all of them are bidentate.⁵ Similarly the complex bis(1,8-naphthyridine) dichlorocopper has been found to contain two monodentate 1,8-naphthyridine ligands.⁶ Thus, it is conceivable that the 1,8-naphthyridine complexes could have coordination numbers ranging from four to eight. In order to settle this question the solution of their crystal structures was undertaken.

In a recent communication the preliminary results of a determination of the crystal structure of tetrakis(1,8-naphthyridine)Fe(II) perchlorate was

presented.⁷ The refinement of the structure has since been completed and the details are given below.

EXPERIMENTAL SECTION

The techniques used in the preparation of the complex were reported by Hendricker and Bodner.² Bright-red, prismatic, crystals suitable for data collection were prepared by recrystallization from methanol and supplied to us by Hendricker and Bodner.

A crystal of approximate dimensions $0.2 \times 0.07 \times 0.6$ mm was mounted along the long needle axis (*b*-axis). Weissenberg and precession photographs taken with nickel-filtered copper radiation ($\text{CuK}\alpha$, $\lambda = 1.5418$) revealed that the lattice was triclinic. Accurate unit cell dimensions were determined on a manually operated Picker 4-circle diffractometer using a small take-off angle (1.5°) and a narrow slit. The cell dimensions were found to be $a = 9.163 \pm 0.003$ Å, $b = 9.315 \pm 0.003$ Å, $c = 20.116 \pm 0.008$ Å, $\alpha = 99.68 \pm 0.08^\circ$, $\beta = 77.37 \pm 0.08^\circ$, $\gamma = 91.70 \pm 0.08^\circ$, $V = 1651.62$ (Å)³, $F.W. = 775.35$. The calculated density with $Z = 2$ is 1.560 g/cm³ in good agreement with the observed density of 1.57 g/cm³ determined by flotation in a benzene-carbon tetrachloride solution. The space group was assumed to be $\text{P}\bar{1}$, which was later confirmed by the structure analysis.

Intensities were measured by the θ - 2θ scan technique at a scan speed of 2° per minute and a 2.5° take-off angle. In scanning the peak account was taken of the variation in mosaic spread and the white radiation that remains when using zirconium-filtered molybdenum radiation ($\lambda = 0.71069$ Å). Stationary background counts of 10 sec duration were made at both ends of the 2θ scan and multiplied by the appropriate time factor so that the background counting times and scan times were equal. No attenuation of the primary beam was found to be necessary and the (0,0,5) reflection was chosen as a standard of intensity which was measured every 30 reflections. No deterioration of the crystal was observed. All reflections within a region of reciprocal space for which $2\theta \leq 40^\circ$ were scanned. Of the 7,525 unique reflections possible 1969 were observed with intensity values above threshold.

The integrated intensities were corrected for background and Lorentz and polarization effects

but not for absorption. The errors introduced by absorption were considered to be unimportant because of the small linear absorption coefficient ($\mu = 5.7$ cm⁻¹).^{8a}

Structure Determination and Refinement

The positions of the iron and chlorine atoms in the asymmetric unit were obtained by direct interpretation of a partially sharpened three-dimensional Patterson synthesis. The sharpening function was $2 \sin 2\theta / (1 + \cos^2 2\theta)$. A Fourier map was then computed based on the phases of 504 reflections which were calculated from the iron atom parameters only. This Fourier confirmed the positions of the chlorine atoms and in addition revealed the positions of two oxygen atoms attached to Cl(1) and all ten atoms of the naphthyridine ring containing atoms N(1) and N(2). The positions of the remaining thirty-six non-hydrogen atoms in the asymmetric unit were located in two successive Fourier syntheses. At this stage of the calculations an overall scale and temperature factor obtained by Wilson's method were used.⁹

Initially, the positional parameters and individual isotropic thermal parameters for all 51 atoms in the asymmetric unit were refined simultaneously by the full-matrix least squares method. The function minimized in the least-squares refinement was

$$\sum w(|F_0| - |F_c|)^2$$

The residual

$$R = \frac{\sum ||F_0| - |F_c||}{\sum F_0}$$

was reduced from 0.21 to 0.12 in four cycles. At this point anisotropic thermal parameters were introduced for the iron, carbon and nitrogen atoms and refinement continued by the block-diagonal method. Three additional cycles of refinement reduced the residual to 0.10. The perchlorate groups exhibited rather large isotropic temperature factors and low peak heights in the Fourier maps. Thus, the possibility that they were disordered had to be considered. A difference synthesis clearly showed that the motion of the perchlorate groups was not isotropic but could be described as a rocking motion or oscillation of the groups about an axis roughly parallel to the *b* axis. Since our programs could not duplicate this motion, the individual perchlorate atoms were given anisotropic thermal parameters which closely paralleled the observed motion. Attempts were also made to represent the perchlorate groups by a suitable disordered model

by placing fractional atoms at the maxima in the difference Fourier. As with similar efforts by other workers,¹⁰ these models did not refine as well as the anisotropic refinement of single atoms. At this stage, the ideal positions of the naphthyridine hydrogen atoms were computed and included in the structure factor calculations (with an isotropic temperature factor of 6.0 Å²) but not in the least-squares refinement. In three more cycles of refinement the shifts in parameters became negligibly small, the largest shift being only ½ its e.s.d. and the average of all shifts being 0.05 of their e.s.d.'s. The final value of *R* was 0.069 and the weighted *R* = 0.071.

The weighting scheme used in the above calculations was

$$w = \left[1 + \left(\frac{|F_0| - p_2}{p_1} \right)^2 \right]^{-1}$$

where *w* is the weight assigned to a reflection of structure amplitude $|F_0|$, $p_1 = 30$ and $p_2 = 50$. This function gives maximum weight to reflections of medium intensity.

Neutral atom scattering factor curves used for all calculations were taken from the compilations in the *International Tables*.^{8b} The scattering curve for iron was modified for the real part of the dispersion correction.^{8c} The computations were carried out either at the CDC 6600 computer of BNL, using local programs or at Ohio University's IBM/360 Model 44 computer, using programs of Ahmed *et al.*¹¹ The final positional and thermal parameters and their e.s.d.'s for the non-hydrogen atoms are given in Table I. The B's except those for the H atoms which were fixed at 6.0 Å², are given from

the last cycle of isotropic refinement. The e.s.d.'s were calculated from the diagonal elements of the inverse matrix of the normal equations in the least-squares refinement. The assumed hydrogen atom parameters are listed in Table I. Bond lengths and bond angles, not corrected for thermal motions, and their e.s.d.'s are shown in Figure 2 for the cation, and are given in Table VII for the anions.

Description and Discussion of Structure

The structure of the tetrakis(1,8-naphthyridine) iron(II) cation is shown in Figure 1. The eight nitrogen atoms of the naphthyridine rings form a distorted dodecahedron around the metal atom. The iron-nitrogen bond distances are given in Table II and the angles subtended by the four

TABLE II
Iron-nitrogen bond distances

Distance	Value (Å)	Distance	Value (Å)
Fe-N (1)	2.284 (11)	Fe-N (2)	2.335 (10)
Fe-N (3)	2.188 (10)	Fe-N (4)	2.378 (11)
Fe-N (6)	2.213 (10)	Fe-N (5)	2.465 (11)
Fe-N (7)	2.184 (11)	Fe-N (8)	2.756 (11)

membered rings in Table III. As stated previously⁷ one nitrogen of each naphthyridine ligand occupies the B positions of the dodecahedron¹² while the other is constrained to occupy the A positions. The nitrogen atoms in the B positions form the shorter

TABLE III
Interatomic angles subtended by the four-membered Fe-N-C-N rings

Angle	Degree	Angle	Degree
Ring I			
N(1)-C(1)-N(2)	112.3 (1.0)	N(1)-Fe-N(2)	58.9 (0.4)
C(1)-N(1)-Fe	95.4 (0.7)	C(1)-N(2)-Fe	93.4 (0.7)
Ring II			
N(3)-C(9)-N(4)	109.1 (1.0)	N(3)-Fe-N(4)	57.2 (0.4)
C(9)-N(3)-Fe	101.2 (0.7)	C(9)-N(4)-Fe	92.3 (0.7)
Ring III			
N(5)-C(17)-N(6)	112.4 (1.0)	N(5)-Fe-N(6)	56.8 (0.4)
C(17)-N(5)-Fe	90.6 (0.7)	C(17)-N(6)-Fe	100.1 (0.7)
Ring IV			
N(7)-C(25)-N(8)	112.4 (1.1)	N(7)-Fe-N(8)	53.0 (0.4)
C(25)-N(7)-Fe	110.2 (0.8)	C(25)-N(8)-Fe	84.1 (0.7)

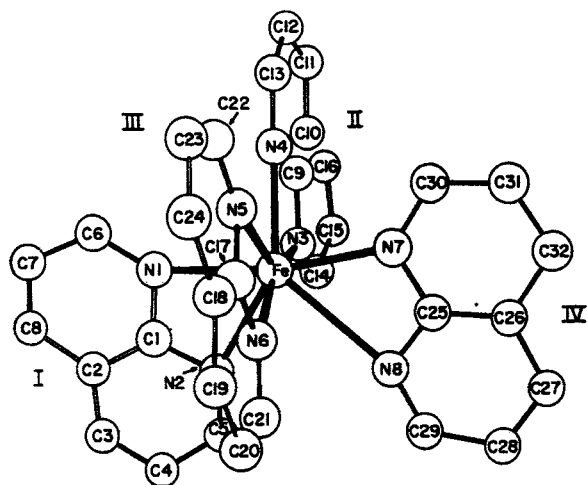


FIGURE 1 The shape of the cation and the numbering system employed in the structural analysis.

bonds. The distortion arises from the unequal bond lengths as discussed in more detail below. That the arrangement of the nitrogen atoms about the central metal is dodecahedral is shown by consideration of the various shape parameters of the coordination polyhedron^{12,13} (see Figures 3 and 4). A dodecahedron can be described as composed of two interpenetrating bisphenoids with $\bar{4}2m$ symmetry. One of the bisphenoids is elongated while the other is flattened with a corresponding decrease and increase in their vertical angles, respectively. The two bisphenoids are clearly evident in Figures 1 and 3. The approximate $\bar{4}$ axis passes midway between the line joining N(8) and N(2), through the iron atom, and midway between N(4) and N(5). The two two-fold axes are perpendicular to $\bar{4}$ and between the midpoints of N(1)-N(3), N(6)-N(7) and N(1)-N(6), N(3)-N(7), respectively. The angles

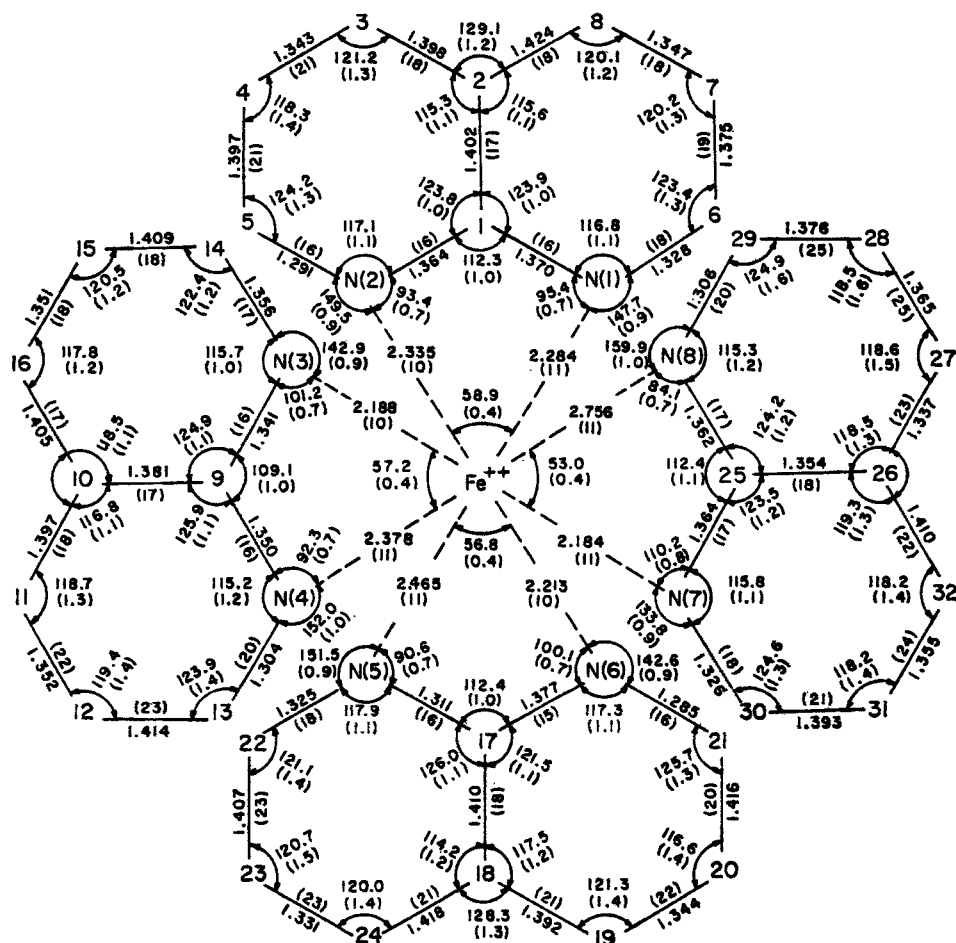


FIGURE 2 Bond lengths and angles within the cation. This is a summary provided for the convenience of the reader in following our arguments.

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between the $\bar{4}$ axis and the M—A type bonds, θ_A , average 41.1° and between the $\bar{4}$ axis and the M—B type bonds, θ_B , 82.3° . The corresponding angles for the hard sphere model would be 36.9° and 69.5° , respectively, if all the bonds were equal,

TABLE IV
Some angles of interest

Bisphenoid angles	
Angle	Degree
N(2)—Fe—N(8)	80.4
N(4)—Fe—N(5)	84.1
N(1)—Fe—N(7)	167.6
N(3)—Fe—N(6)	161.9
Dihedral angles between naphthyridine rings	
Angle	Degree
Rings I—II	94.9
Rings II—IV	87.2
Rings I—III	90.3
Rings III—IV	82.8

whereas for the most favorable polyhedron, calculated to minimize ligand repulsive energies, these values are 37.1° and 71.2° , respectively.¹² The dihedral angles between the naphthyridine rings, which should ideally be 90° for dodecahedral coordination, are as follows: between rings I and II, 94.9° ; between II and IV, 87.2° ; between III and IV,

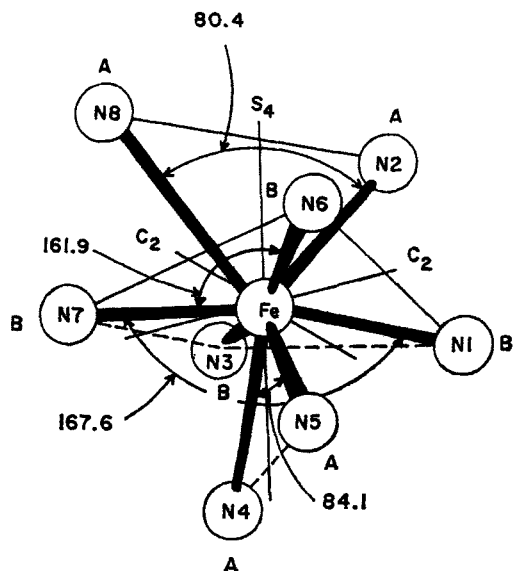


FIGURE 3 Shape parameters for the dodecahedron.

82.8° and between I and III, 90.3° . These shape parameters fall well within the ranges observed for other dodecahedral complexes.¹⁴

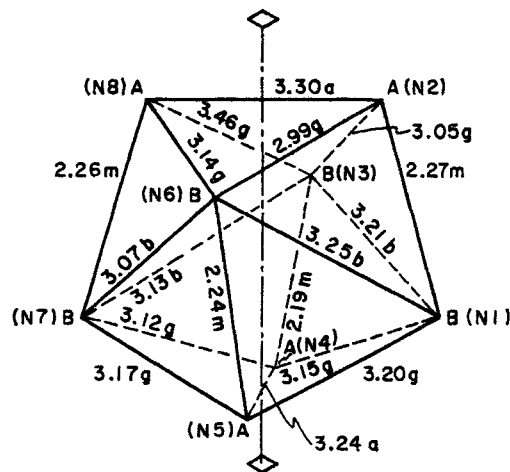


FIGURE 4 Shape parameters for the dodecahedron.

Stereochemistry of the Ligands

The bond distances and angles for the naphthyridine rings are given in Figure 2 and their averages in Figure 5. The rings are planar as shown by the equations of their mean planes given in Table V. The mean planes were calculated by the method of Blow¹⁵ with x' along the a -axis, y' in the ab plane and z' along c^* . None of the atoms is more than 0.02 \AA away from its mean plane. The ring bond

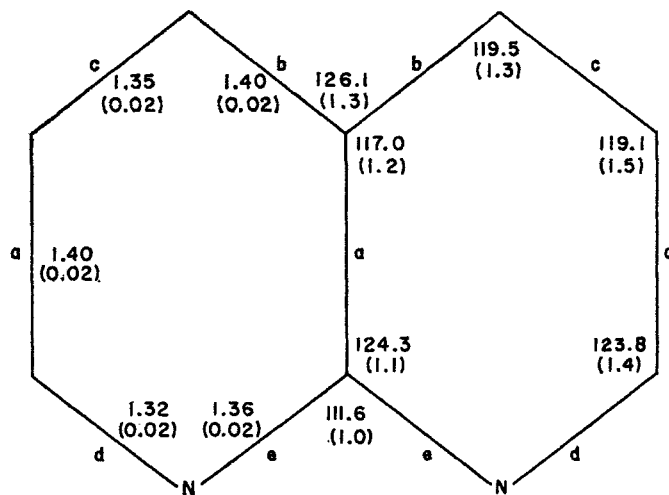


FIGURE 5 Average values of the bond lengths and angles within the ligands. The types of bond have been labelled using the convention of Pauling (see Ref. 18).

distances are in good agreement with those observed in 1,5- and 2,6-naphthyridine,^{16,17} and the relative values of a,b,c,d and e type bonds are in conformity with those predicted by Pauling¹⁸ for naphthalene. However, there are significant differences in the bond angles. The average N-C-N angle we observe

TABLE V

Mean plane equations for the naphthyridine rings

Ring	Equation	χ^2
I	$0.3392X' - 0.8995Y' - 0.2753Z' + 0.9962 = 0$	12.3
II	$0.8992X' + 0.4374Y' - 0.0096Z' - 1.2665 = 0$	12.3
III	$0.9199X' + 0.3813Y' - 0.0915Z' - 1.0744 = 0$	10.6
IV	$0.4687X' - 0.8559Y' - 0.2186Z' + 0.3367 = 0$	4.8

in the 1,8-naphthyridine ligands, 111.6° , is considerably smaller than the roughly 120° angles observed in the other naphthyridines.^{16,17} This decrease is probably the result of the parallel lone pair orbitals of the nitrogens attempting to achieve maximum overlap with the metal bonding orbitals. The external ring angles, bb, increase correspondingly to decrease ring strain. The internal ring angles (Figure 5) ab and ac compensate for this distortion by a corresponding decrease and increase, respectively, in their values so as to maintain a planar configuration.

TABLE VI

Mean bond lengths for the chemically equivalent bonds in the naphthyridine rings

Bond	Type	Number	Range (Å)	Mean (Å)
C—C	a	12	1.354–1.416	1.395
C—C	b	8	1.377–1.424	1.403
C—C	c	8	1.331–1.365	1.349
C—N	d	8	1.285–1.356	1.315
C—N	e	8	1.311–1.377	1.355

The average standard deviation in the bond lengths is 0.0018 Å.

The large isotropic thermal parameters of the oxygen atoms associated with both perchlorate groups are indicative of some sort of disorder, particularly for the group associated with Cl(2). Therefore, as mentioned previously, the oxygen and chlorine atoms were refined anisotropically and the final set of positional and thermal parameters derived by this procedure are given in Table I. As can be appreciated from Figures 6

and 7 both perchlorate groups are executing a librational motion; however, the displacement of the oxygens from their mean position is at least twice as large for group 2 than for group 1. The estimated amplitudes of the librational motion, as computed by the method of Schomaker and Trueblood,¹⁹ are quite large. (For details see Table VII.)

The refined fractional coordinates give Cl—O lengths which range between 1.367 and 1.405 Å for group 1 and 1.334 to 1.373 Å for group 2. In the case of ordered perchlorate groups studied by X-ray diffraction Cl—O bond lengths of 1.464(7) were found for nitronium perchlorate,²⁰ while for bis(o-phenylene-bis(2-imidazole))-di-perchlorate²¹ the value is 1.430 Å. Given the degree of libration in our crystals it is not surprising that the perchlorate groups give Cl—O bonds far removed from the values found in ordered structures. In an attempt to overcome these difficulties, we corrected the Cl—O bond lengths¹⁹ and found that the values for group 1 now range from 1.425 to 1.462 Å, while those for group 2 have been lengthened to values between 1.432 and 1.510 Å (see Table VII).

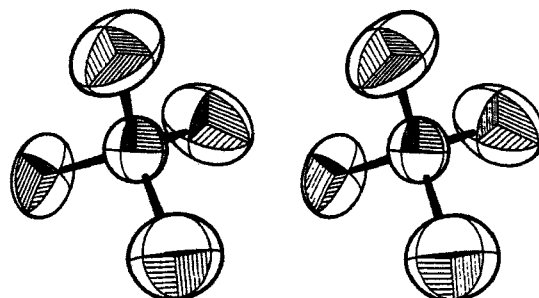


FIGURE 6 The ellipsoids of thermal motion for perchlorate group 1. The view distance was 24 inches. (See caption of Figure 7.) This is a stereo pair.

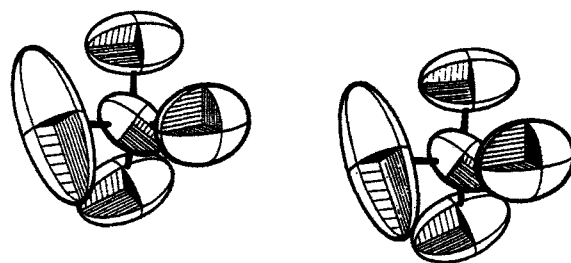


FIGURE 7 The ellipsoids of thermal motion for perchlorate group 2. The view distance was 100 inches. This is a stereo pair.

TABLE VII

Bond lengths and angles of the perchlorate groups

Bond	Uncorrected length	Corrected length ^a
Cl(1)—O(11)	1.405(11)	1.462
—O(12)	1.381(13)	1.433
—O(13)	1.396(12)	1.456
—O(14)	1.367(12)	1.425
Av =	1.387(12)	1.444
Cl(2)—O(21)	1.355(18)	1.462
—O(22)	1.373(14)	1.496
—O(23)	1.344(14)	1.432
—O(24)	1.334(20)	1.510
Av =	1.352(17)	1.475

Angle	Degree	Angle	Degree
O(11)—Cl(1)—O(12)	107.8 (7)	O(21)—Cl(2)—O(22)	107.5 (10)
O(11)—Cl(1)—O(13)	110.5 (7)	O(21)—Cl(2)—O(23)	118.3 (10)
O(11)—Cl(1)—O(14)	109.8 (8)	O(21)—Cl(2)—O(24)	107.6 (12)
O(12)—Cl(1)—O(13)	109.5 (8)	O(22)—Cl(2)—O(23)	110.5 (10)
O(12)—Cl(1)—O(14)	110.1 (8)	O(22)—Cl(2)—O(24)	101.3 (12)
O(13)—Cl(1)—O(14)	109.7 (8)	O(23)—Cl(2)—O(24)	110.2 (12)

^a Correction was performed using Schomaker and Trueblood's program TLS-6. For perchlorate group 1 the principal axes of L(ω) were 12.97, 12.74 and 8.52 degrees. For the second perchlorate group they were 24.32, 17.71 and 3.63 degrees. See Ref. 19.

Similar results have been obtained by McCullough *et al.*²² for perchlorate salts.

Packing

The packing within the unit cell is quite simple (see Figure 8). Since the rings form a paddle wheel

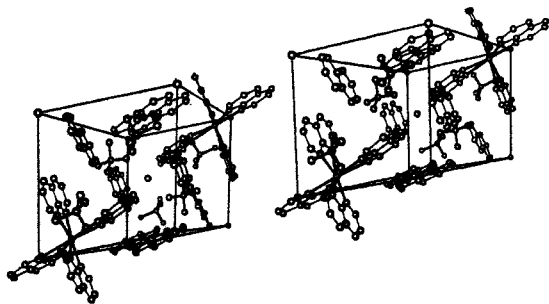


FIGURE 8 The packing of the cations and anions in the lattice. This is a stereo pair.

arrangement about the iron atom, the length and width of the cation are roughly identical and equal to 9.5 Å. The iron atoms are located at approximately .05, 0.1, 1/4 and -.05, -0.1, 3/4. Thus,

there are two cations per unit cell length roughly centered along the *c*-axis. The ring systems are not parallel to any of the basal planes but are centered relative to them. The perchlorate groups lie about the centers of symmetry at $\frac{1}{2}00$ and $\frac{1}{2}0\frac{1}{2}$. Thus, they lie between the cations alternately on either side of the *ab* planes at $Z = 0$ and $Z = \frac{1}{2}$. In the *a* and *b* directions the cations are separated by van der Waals radii.

DISCUSSION

The tetrakis(1,8-naphthyridine)Fe(II) cation represents the first example of an authenticated cationic dodecahedron. Numerous examples of anionic dodecahedral coordination in transition metal complexes are known.¹⁴ Another unusual feature of the iron(II) complex is that it is one of the few authenticated examples of eight coordination in which the transition metal has more than a half-filled *d*-shell. Two others are the eight-coordinate cobalt(II)tetra-(perfluoroacetato) and tetranitrato anions.^{23, 24} A detailed comparison of the similarities between the cobalt complexes and the iron(II)

cation have already been presented.² The most striking feature in these compounds is the short interatomic distances from the metal to N or O in the B positions and the longer interatomic distances to these atoms in the A positions of the dodecahedron. These wide variations in bond lengths arise from two major effects. The atoms in the B positions lie closer to the d_{xy} metal orbital and may partake in $d\pi-p\pi$ bonding. The second factor of importance in determining the bond distances is ligand-ligand repulsion. The requirement of fitting together four bulky, quite rigid, planar rings around the small Fe(II) ion results in considerable ligand-ligand repulsion. This is shown by the way in which the iron-nitrogen distances distribute themselves in pairs. Reference to Table II shows that the metal-nitrogen distances to the two nitrogens in the same ring are distributed in the following way. Each ring has a short and a long Fe-N bond. The ring with the shortest iron-nitrogen distance also contains the longest iron-nitrogen distance. The pattern of long-short iron-nitrogen bonds does not follow a simple sequence for the entire cation. Thus, while the average iron-nitrogen bond distance (omitting the longest Fe-N bond) in the tetrakis(1,8-naphthyridine)Fe(II) cation is in good agreement with the value of 2.27 Å found for the hexa(pyridine)Fe(II) cation,²⁵ the distribution reflects the two factors described above.

It has been suggested^{23, 24} that in many cases the tetrahedral appearance of the electronic spectra of complexes with dodecahedral symmetry can be explained by showing that an approximate tetrahedral symmetry of the ligand field exists when one assumes that the "center of gravity" of the electronic charge from the bidentate ligand is situated mid-way between its two donor atoms. However, in the present case such a "center of gravity" tetrahedron gives four angles which are close to $98^\circ \pm 3^\circ$ and two which are close to $135^\circ \pm 3^\circ$. Therefore, the distortions from true tetrahedral symmetry might be too severe for it to be a meaningful alternative to the proposed (distorted) dodecahedral symmetry. Finally, it may be stated that this series of transition-metal tetrakis(1,8-naphthyridine) complexes, being isomorphous,³ affords the opportunity of assessing the effect of increasing electron occupancy of the metal d-orbitals upon the geometry and bonding in the complex. Thus,

we have initiated crystal structure studies on other members of this series.

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