

Synthesis and Structural Characterization of Iron(II) Complexes of a New Completely Conjugated Macrocyclic Ligand Derived from 2,6-Diacetylpyridine and Hydrazine

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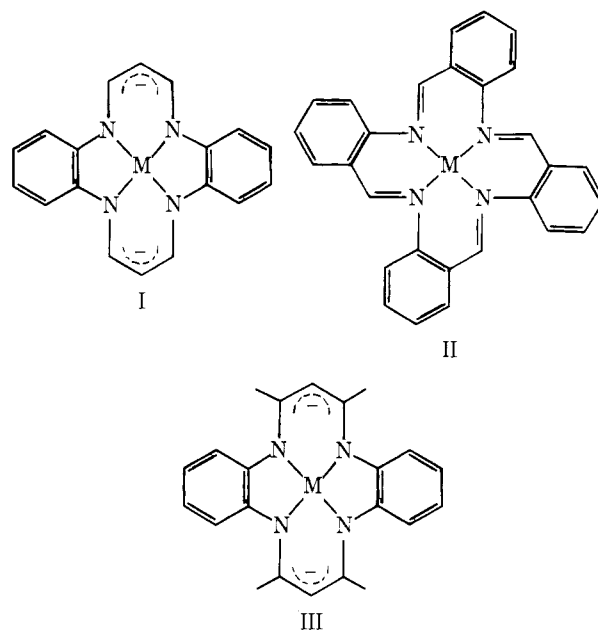
Abstract: Completely conjugated 14-membered ring hexaaza ligand complexes have been synthesized by the template condensation of 2,6-diacetylpyridine with hydrazine on iron(II). Low-spin six-coordinate complexes of this ligand are obtained with axial ligands such as halides, pseudo-halide anions, acetonitrile, nitrite, and carbon monoxide. Although the macrocyclic ligand formally contains α -diimine linkages, the electronic spectra of these complexes differ substantially from low spin iron(II) complexes with isolated α -diimine chromophores and suggest that delocalization extends beyond the α -diimine moieties. The normally planar macrocyclic ligand can be forced into a folded conformation with strong bidentate chelating ligands such as 1,10-phenanthroline or α,α' -dipyridyl. The accompanying spectral changes are characteristic of complexes containing tris- α -diimine chromophores and indicate that folding of the macrocyclic ligand is accompanied by a diminution of delocalization. A crystal structure of the bisacetonitrile complex, $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$, space group $P2_1/c$ with $a = 9.772(2) \text{ \AA}$, $b = 8.379(3) \text{ \AA}$, $c = 16.525(4) \text{ \AA}$, $\beta = 91^\circ 58'$, and $Z = 2$, has been refined to R factors, $R_1 = 8.90$, $R_2 = 7.1\%$ for 2508 data with $F^2 \geq 2\sigma$ collected by θ - 2θ scans on a Picker FACS-1 automated diffractometer. The macrocyclic ligand is flat, and the iron(II)-nitrogen distances of 1.899 (5) and 1.892 (7) \AA are shorter than normal and indicate some metal ion constriction by the ligand. The inner 14-membered ring of the macrocyclic ligand has an alternating double bond structure more typical of a conjugated than an aromatic type of delocalization. The imine C=N distances of 1.297 (9) and 1.326 (9) \AA are slightly longer than normal for isolated imine linkages.

The importance of studying the class of metal complexes containing macrocyclic ligands has become widely recognized in recent years. The early investigations of these complexes dealt primarily with saturated or partially unsaturated ligands.¹⁻³ These invaluable studies clearly delineated the fundamental characteristics of macrocyclic ligand complexes through the evaluation of their general stabilities, ligand field properties, and reactivities. More recently, a number of highly unsaturated to completely conjugated macrocyclic ligand complexes have been prepared and investigated.⁴⁻⁹ The completely conjugated macrocyclic complexes studied have included neutral,⁴ monoanionic,¹⁰ and dianionic⁷⁻⁹ ligands primarily of 14-membered rings, but 13-, 15-, and 16-membered rings have also been investigated. Most of this work has been devoted to complexes of nickel(II), cobalt(II), and copper(II), and only recently have studies devoted exclusively to the macrocyclic complexes of iron(II) been reported.¹¹⁻¹⁵

The effects of extensively conjugated ligands on metal complex character may be even more profound than those bestowed by simple saturated macrocyclic ligands. Ligands having highly delocalized electron systems have more intimate interactions between metal and ligand orbitals. Another consequence of highly conjugated macrocyclic ligands is a reduction in the "core" size as each double bond is introduced into the ligand. Such constrictive effects would be expected to be more important in 14-membered rings than in larger rings.

Some metal-directed template condensations lead directly to completely conjugated metal complexes. Examples are the metal-directed condensations of propargyl aldehyde with *o*-phenylenediamine, I,⁶ the tetramerization of *o*-aminobenzaldehyde, II,⁴ and the condensation of *o*-phenylenediamine with 2,4-pentanedione, III.⁷ Another route to highly unsaturated macrocyclic complexes utilizes the higher unstable oxidation states of the coordinated metals to promote an internal redox process, oxidative dehydrogenation, in which additional double bonds are introduced into the coordinated ligands.¹⁵⁻¹⁷

Iron(II) has not been used extensively as a directing

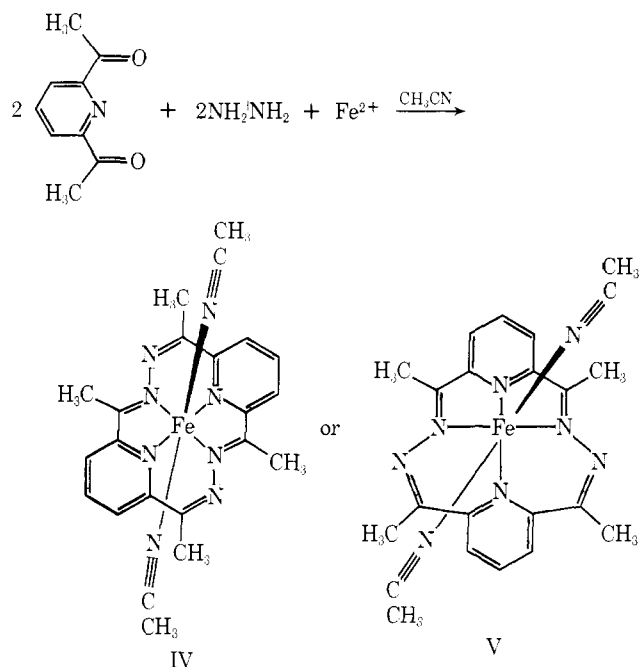


metal in macrocyclic ligand synthesis. This arises from the low affinity of iron(II) toward simple amines and the tendency toward formation of highly insoluble hydroxo and oxo species. In spite of these difficulties, Rose and coworkers¹⁴ have succeeded in obtaining, in small yields, stable iron(II) complexes derived from 2,3-butanedione and 1,3-diaminopropane. Busch and coworkers have isolated iron(II) complexes of the 16-membered macrocyclic ligand, TAAB, II, also in low yields, from the tetramerization of *o*-aminobenzaldehyde.¹⁸

The exceptional stability of α -diimine complexes of iron(II) can be used to surmount some of the synthetic difficulties mentioned above. If the starting fragment contains dangling functional groups which can be linked together, macrocyclic formation with iron(II) should become as facile as nickel(II) and copper(II) Schiff base condensations with aliphatic amines. The synthesis of clathrochelates of iron(II)

from dimethylglyoxime and boron trifluoride¹⁹⁻²¹ and the variety of iron(II) complexes formed from the condensation of 2,3-butanedihydrazone with aldehydes are good examples of the use of this concept.²²

The condensation reactions of 2,6-diacetylpyridine have previously been employed in the synthesis of multidentate Schiff base ligands. Tetra-,²³ penta-,²⁴ and hexadentate²⁵ macrocyclic ligands have been prepared by condensing them with various amines. This paper reports the direct formation of the fully conjugated hexaaza macrocyclic complex of iron(II) from the template condensation of 2,6-diacetylpyridine with hydrazine. By employing iron(II) as the directing metal, the bifunctionality of hydrazine can be utilized to link two molecules of 2,6-diacetylpyridine together while a second hydrazine molecule condenses with the remaining two carbonyl functions to complete the 14-membered ring formation. There are two possible isomers from



the reaction, IV and V.²⁶ Each isomer can be represented with two α -diimine chromophores within the conjugated system. The inner 14-membered ring is a potentially aromatic 14 π -electron system whereas the entire 20-atom π -system would be antiaromatic.

The present study is concerned with the preparation and characterization of the iron complexes of this ligand, the determination of the extent of delocalization present in the system, and the examination of the stability and reactivity of its iron(II) complexes.²⁷ The reactions, electronic parameters, and magnetic properties will be compared with other similar macrocyclic iron(II) complexes.

Experimental Section

Materials. Anhydrous hydrazine and 2,6-diacetylpyridine were purchased from the Aldrich Chemical Co. Trifluoroethanol was purchased from Halocarbon Products Inc. Acetonitrile, reagent analytical grade, was purchased from J. T. Baker Chemical Co. The 2,6-diacetylpyridine was recrystallized from ethanol before use. Acetonitrile and trifluoroethanol were dried with molecular sieves and distilled prior to use.

Syntheses. $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$. A solution of 1.6 g (10 mmol) of 2,6-diacetylpyridine in 15 ml of acetonitrile was added to a solution of 20 mmol of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 30 ml of acetonitrile. To this red solution, 0.3 g (10 mmol) of anhydrous hydrazine in 10 ml of acetonitrile was added dropwise over a period of 20 min. Less than the stoichiometric amounts of 2,6-diacetylpyridine and hydrazine are required to prevent the formation of the

octahedral complex of bis-2,6-diacetylpyridinedihydrazone. Excess hydrazine must be avoided because the macrocyclic ligand complexes are destroyed by any base. An intense blue-green precipitate slowly formed during the next hour. The solution was filtered and the precipitate was recrystallized from trifluoroethanol. The product was then filtered, washed with ethanol and dried *in vacuo*. *Anal.* Calcd for $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$: C, 40.13; H, 3.65; N, 17.03; Cl, 10.83. Found: C, 39.78; H, 3.76; N, 16.98; Cl, 10.14.

$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$. A solution of 20 mmol of $\text{Fe}(\text{PF}_6)_2$ in 40 ml of acetonitrile was prepared by the addition of a large excess (tenfold) of NH_4PF_6 to a solution of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. The solution was allowed to stand several hours and then the NH_4ClO_4 precipitate was filtered from the solution. To this solution, 2,6-diacetylpyridine and hydrazine were added as in the preparation of the perchlorate salt. The precipitate was filtered, washed with a minimum amount of acetonitrile, and then recrystallized from acetonitrile. The compound was dried *in vacuo* and stored under nitrogen. Both analytical data and ir spectra indicate that a small amount of perchlorate was still present in the compound (which is not unexpected since the perchlorate and hexafluorophosphate salts are isomorphous).

$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(2,2'\text{-dipy})(\text{PF}_6)_2$. A methyl alcohol solution containing 0.2 g of 2,2'-dipyridyl was added to a solution of 0.8 g of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ dissolved in a minimum amount of acetonitrile. The blue-green solution immediately turned deep red on the addition of the dipyridyl solution. Ethyl ether was added dropwise until the solution became slightly turbid. The red crystalline precipitate which formed on chilling the solution for 1 hr was filtered, washed with methanol, and dried *in vacuo*. *Anal.* Calcd for $\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{PF}_6)_2$: C, 40.97; H, 3.17; N, 13.66. Found: C, 40.95; H, 3.07; N, 13.60.

$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{NO}_2)_2] \cdot \frac{1}{2}\text{CF}_3\text{CH}_2\text{OH}$. A solution of 0.1 g of NaNO_2 in 5 ml of CH_3OH was added to a solution of 0.5 g of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ dissolved in 10 ml of $\text{CF}_3\text{CH}_2\text{OH}$. Diethyl ether was added dropwise to induce precipitation. After chilling for 1 hr in a refrigerator, the solution was filtered, washed with water then ethanol, and dried *in vacuo*. *Anal.* Calcd for $\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{NO}_2)_2 \cdot \frac{1}{2}\text{CF}_3\text{CH}_2\text{OH}$: C, 44.20; H, 3.78; N, 21.71; Fe, 10.83. Found: C, 44.46; H, 4.14; N, 21.74; Fe, 9.80.

$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})(\text{CO})](\text{PF}_6)_2$. Carbon monoxide gas was bubbled through a solution of 0.5 g of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ in trifluoroethanol in a serum-capped bottle vented with a syringe needle until the solution turned red (about 10 min). A solution of 0.3 g of NH_4PF_6 in 10 ml of methanol was added with a syringe. The purple precipitate which formed was filtered, washed with water to remove any NH_4ClO_4 , and dried *in vacuo*. *Anal.* Calcd for $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})(\text{CO})](\text{PF}_6)_2$: C, 34.39; H, 2.87; N, 13.37; Fe, 7.62. Found: C, 34.45; H, 2.94; N, 13.77; Fe, 7.19.

$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)\text{Cl}(\text{CO})\text{PF}_6$. One-tenth gram of LiCl dissolved in 2 ml of methanol was added to the red solution obtained by bubbling carbon monoxide gas through 0.5 g of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ dissolved in 15 ml of $\text{CF}_3\text{CH}_2\text{OH}$. A solution of 0.1 g of NH_4PF_6 in 2 ml of methanol was added to isolate the compound as the hexafluorophosphate salt. The dark violet crystals which precipitated were contaminated with white NH_4ClO_4 . The product was filtered, washed with water to remove the NH_4ClO_4 , and dried *in vacuo*. *Anal.* Calcd for $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)\text{Cl}(\text{CO})\text{PF}_6$: C, 39.16; H, 3.09; N, 14.42; Cl, 6.09. Found: C, 38.25; H, 3.19; N, 13.73; Cl, 6.00.

$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)\text{Br}_2]$. A degassed solution of 0.2 g of LiBr in 5 ml of methanol was added to a solution of 0.8 g of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ in acetonitrile under a nitrogen atmosphere. The dark brown precipitate which formed immediately was filtered, washed with acetonitrile, and dried *in vacuo*. *Anal.* Calcd for $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)\text{Br}_2]$: C, 40.48; H, 3.37; N, 15.74; Br, 29.95. Found: C, 40.72; H, 3.35; N, 15.58; Br, 29.82.

$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)\text{Cl}_2]$. A solution of 0.2 g of LiCl in methanol was added to a solution of 0.8 g of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ in acetonitrile. The dark brown precipitate which formed was filtered, washed, and dried *in vacuo*. *Anal.* Calcd for $\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)\text{Cl}_2$: C, 48.60; H, 4.05; N, 18.88; Cl, 15.95. Found: C, 46.79; H, 4.01; N, 18.40; Cl, 15.87.

$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{NCS})_2]$. A solution of 0.2 g of NaSCN in methanol

nol was added gradually, under nitrogen, to a solution of 0.8 g of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ in trifluoroethanol. Precipitation of the very finely divided product occurs immediately on the addition of the NaSCN . The deep brown precipitate was filtered from the solution, washed first with trifluoroethanol then methanol, and then dried *in vacuo*. *Anal.* Calcd for $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{NCS})_2]$: C, 48.99; H, 3.67; N, 22.86. Found: C, 48.00; H, 3.60; N, 22.80.

$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{N}_3)_2]$. A solution of 0.3 g of NaN_3 in 5 ml of methanol was added to a solution of 2.0 g of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ in acetonitrile under a nitrogen atmosphere. The dark brown precipitate which formed was filtered, washed with acetonitrile, and dried *in vacuo*. *Anal.* Calcd for $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{N}_3)_2]$: C, 47.18; H, 3.93; N, 36.69. Found: C, 47.31; H, 3.89; N, 36.52.

Physical Measurements. All temperatures and pressures reported are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Magnetic susceptibilities were determined at 20° at two magnetic field strengths by the Faraday method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. Diamagnetic corrections were calculated from tables of Pascal's constants.

Infrared spectra were recorded on Beckman IR 10 using Nujol and hexachlorobutadiene mulls and were calibrated with polystyrene film.

Electronic absorption spectra of solutions of the complexes were recorded on a Cary Model 14 spectrophotometer. Absorption spectra of selected solid samples were obtained by preparing Nujol or hexachlorobutadiene mulls on filter paper with finely ground samples. Filter paper soaked with the appropriate mulling agent was placed in the reference beam to compensate for the light scattering of the filter paper.

Crystal Examination and Data Collection

Crystals used for the X-ray analysis were obtained by the slow diffusion of hydrazine into an acetonitrile solution of 2,6-diacetylpyridine and ferrous perchlorate hexahydrate. Preliminary precession X-ray photographs of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ exhibited monoclinic symmetry with systematically absent reflections uniquely demanded by the monoclinic space group $P2_1/c-C_{2h}^5$. Lattice constants and their estimated standard deviations for $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$, obtained by least-squares refinement of $+$ and -2θ values obtained from 25 accurately centered reflections on a Picker FACS-1 automated diffractometer at 22° are: $a = 9.772$ (2), $b = 8.379$ (3), $c = 16.525$ (4) Å; $\beta = 91^\circ 58'$; $\rho_{\text{calcd}} = 1.617$, $\rho_{\text{obsd}} = 1.61$ g/cm³ for which $Z = 2$.

A hexagonal prismatic crystal of uniform dimensions 0.30 × 0.27 × 0.30 mm, mounted with the a^* axis nominally colinear with the goniometer ϕ axis was used for the data collection. Least-squares refinement of 2θ , χ , and ϕ angles from 12 accurately centered reflections from widely separated regions of reciprocal space were used to calculate the matrix from which the diffractometer setting angles for all data reflections were generated. Graphite monochromatized Mo $K\alpha$ radiation (λ 0.71069 Å) with a takeoff angle of 3.0° was used for the data collection. The intensities of 3119 reflections were measured up to $2\theta = 60^\circ$ using $\theta-2\theta$ scans with a scan rate of 2.0°/min. The scan width, 2.5° at $2\theta = 0.0^\circ$, was increased as a function of θ to compensate for $\alpha_1-\alpha_2$ splitting. Stationary crystal-stationary counter background counts of 20 sec each were collected at the high and low angle limits of the scan window for each reflection. Three check reflections were measured every 100 reflections to check on crystal alignment and condition. The variation in the intensities of the check reflections was random and varied no more than 2% of the average value during the data collection. The data were reduced in the conventional manner with corrections for Lorentz and polarization effects. The formula used for the L_p correction under the condition of monochromatized radiation was that given by Azaroff.²⁸ Estimated standard deviations in the reflection intensities and the derived F^2 's based primarily on counting statistics were calculated using the following equation.

$$\sigma(I) = \left[S + \frac{T_s^2(B_1 B_2)}{T_B^2(B_1 + B_2)} + (pS)^2 \right]^{1/2} \quad (1)$$

S , B_1 , and B_2 are the accumulated counts for the scan and the two backgrounds, T_s and T_B are the scan and individual back-

ground counting times, and p is a factor,²⁹ here taken to be 0.02 to account for machine fluctuations and other factors which would be expected to cause variations proportional to the reflected intensity. The F^2 's and F 's were calculated in the usual way from the intensities and the F 's were calculated using the approximation

$$\sigma(F) = \sigma(I)/2F(L_p)^{1/2} \quad (2)$$

A total of 2508 independent reflections having F^2 's $\geq 2\sigma$ were used in the final stages of the refinement.

The effects of absorption ($\mu\lambda$ 8.37) were judged to be minimal and were not compensated for. The transmission coefficients for the minimum and maximum diagonal crystal dimensions were 0.78 and 0.72, respectively, which does not substantially effect the F 's derived from the intensities.

Structural Determination and Refinement

The structure was solved by standard heavy-atom methods and refined by full-matrix least-squares techniques.³⁰ Scattering factors of neutral atoms were taken from standard sources.³¹ Corrections for anomalous dispersion were applied to iron and chlorine atoms from the values of $\Delta f'$ and $\Delta f''$ tabulated by Cromer.³² The Patterson map indicated that the iron atom should be placed at the origin and the chlorine atom at $x = 0.524$, $y = 0.281$, and $z = 0.128$. One cycle of least-squares refinement varying the scale factor and thermal and positional parameters yielded a conventional R factor of 40%. A difference Fourier based on the phases obtained from the heavy atoms revealed the remaining nonhydrogen atoms. Refinement of the scale factor and positional and thermal parameters with anisotropic thermal parameters for the chlorine and iron atoms yielded $R = 16\%$ with 985 most significant data. Careful inspection of a difference Fourier at this point revealed severe disorder of the macrocyclic complex itself, as well as appreciable anisotropic thermal motion of the perchlorate oxygen atoms. The disorder of the macrocyclic complex cation appeared to be that obtained by rotation of the cation by 180° through the pseudo-twofold axis passing through the nitrogen atoms of the pyridine rings and the iron atom (Figure 4). An attempt to refine the disordered atoms individually failed due to the high correlations between atoms of the disordered portion and those of the major fraction of the molecule. The nitrogen atoms of the minor fraction of the hydrazine linkages were separated sufficiently from other atoms to be refined individually and indicated that the ratio of the dominant to minor fraction of the cation was 0.70 to 0.30. The refinement was continued by using several tandem least-squares cycles in which the positional and thermal parameters of the major fraction of the molecule were varied in the first cycle and by varying the parameters of the minor disordered fraction in the second cycle using the weighting scheme based on eq 1. The iron and chlorine atoms, as well as the oxygen atoms, were refined using anisotropic thermal parameters at this point. At convergence, $R_1 = 8.3\%$ and $R_2 = 6.4\%$ for all 2508 data with $F^2 \geq 2\sigma$.³⁴ However, some of the interatomic distances and angles calculated for the macrocyclic ligand were chemically unreasonable. This degree of refinement was deemed insufficient for our purposes, so a better model was sought.

At this point, it appeared best to treat the disordered fraction of the molecule as a rigid body whose geometry was identical with that of the major orientation, but whose orientation was related by a pseudo-twofold rotation axis. This was done by assuming a twofold axis through the iron and two pyridine residues and calculating the position of the atoms of the major orientation when rotated by 180° through the axis. This was the starting orientation of the minor "rigid body." Refinement was then continued in two-cycle stages by varying the individual atoms of the major portion and the minor portion as a rigid body in each cycle. After each two cycles of least-squares refinement, the geometry of the minor disordered fraction was recalculated from the major portion. At near convergence, a difference Fourier was obtained and examined for hydrogen atoms. Enough were observed to determine the positions for nine hydrogen atoms assuming idealized geometry. All the hydrogen atoms of the major portion fraction of the molecule were then included as fixed contributions in the final cycles of least-squares refinement. At convergence, $R_1 = 8.90$ and $R_2 = 7.10\%$ (the data to parameter ratio was 1 to 20). Although the R value is slightly higher than when the individual disordered atoms were varied in

Table I. Fractional Coordinates and Thermal Parameters for $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$

Atom	X	Y	Z	B, Å ²		
		Major Portion				
Fe	0	0	0			
Cl	0.5189 (2)	0.2809 (2)	0.2131 (1)			
O(1)	0.5369 (7)	0.1750 (9)	0.1929 (4)			
O(2)	0.4151 (6)	0.2170 (8)	0.0722 (4)			
O(3)	0.6447 (5)	0.2725 (9)	0.0876 (3)			
O(4)	0.4872 (7)	0.4280 (7)	0.1557 (5)			
N(1)	0.0352 (6)	0.1978 (8)	0.0518 (4)	2.78 (13)		
C(1)	0.1637 (9)	0.4596 (10)	0.0453 (5)	4.06 (19)		
C(2)	0.1170 (7)	0.2974 (9)	0.0142 (4)	2.66 (14)		
C(3)	0.1538 (7)	0.2345 (9)	-0.0649 (4)	2.43 (14)		
N(2)	0.1064 (6)	0.0878 (7)	-0.0830 (3)	2.19 (11)		
C(4)	0.2420 (9)	0.3207 (11)	-0.1123 (5)	4.40 (20)		
C(5)	0.2698 (10)	0.2458 (12)	-0.1850 (6)	4.53 (22)		
C(6)	0.2274 (8)	0.0953 (11)	-0.2033 (5)	3.68 (18)		
C(7)	0.1364 (7)	0.0087 (10)	-0.1513 (4)	2.73 (13)		
C(8)	0.0852 (8)	-0.1546 (10)	-0.1666 (5)	3.14 (16)		
N(3)	0.0084 (7)	-0.2499 (9)	-0.1262 (4)	3.30 (13)		
C(9)	0.1256 (9)	-0.2322 (12)	-0.2455 (6)	4.98 (22)		
N(4)	-0.1662 (4)	0.0832 (5)	-0.0517 (2)	2.77 (9)		
C(10)	-0.2695 (5)	0.1237 (7)	-0.0776 (3)	2.84 (10)		
C(11)	-0.4083 (7)	0.1649 (9)	-0.1113 (4)	5.05 (15)		
		Disordered Portion				
DN(1)	0.0078 (14)	-0.1506 (18)	-0.0847 (9)	2.40 (27)		
DN(3)	0.0512 (14)	0.3030 (18)	0.0875 (9)	2.76 (28)		
DC(1)	0.0983	-0.2061	-0.2236	4.09		
DC(2)	0.0825	-0.1044	-0.1470	2.97		
DC(3)	0.1428	0.0531	-0.1374	2.81		
DN(2)	0.1169	0.1279	-0.0069	2.98		
DC(4)	0.2104	0.1106	-0.2049	4.44		
DC(5)	0.2610	0.2620	-0.1892	4.03		
DC(6)	0.2324	0.3448	-0.1189	3.65		
DC(7)	0.1579	0.2771	-0.0503	3.39		
DC(8)	0.1232	0.3538	0.0275	3.65		
DC(9)	0.1754	0.5198	0.0400	5.37		
DC(11)	0.5962	0.2705	0.3987	5.05		
		Anisotropic Thermal Parameters ($\times 10^3$) ^a				
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	3.30 (10)	10.43 (17)	2.09 (4)	0.34 (15)	0.28 (5)	0.30 (9)
Cl	8.64 (19)	17.71 (32)	4.63 (8)	0.01 (21)	1.14 (9)	-0.37 (13)
O(1)	23.6 (11)	36.0 (18)	6.9 (4)	3.0 (12)	1.7 (5)	4.8 (7)
O(2)	15.5 (8)	29.6 (15)	9.3 (4)	-1.2 (10)	-4.6 (5)	-1.6 (7)
O(3)	12.3 (7)	63.8 (23)	6.0 (3)	8.6 (11)	3.0 (4)	-2.6 (7)
O(4)	21.4 (11)	21.9 (12)	13.8 (5)	-0.5 (9)	3.2 (6)	-5.5 (7)

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

the tandem cycles, the distances and angles appeared much more reasonable with chemically equivalent atoms agreeing very well. The final difference Fourier had a noise level of approximately 0.3 e/Å³ with the highest peak of 0.5 e/Å³. Table I lists the atomic coordinates in the asymmetric unit and Table II lists the inter atomic distances and angles. A listing of the observed and calculated structure factor amplitudes is available.³⁵

Results and Discussion

Product Identification and Characterization. The reaction of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Fe}(\text{PF}_6)_2 \cdot 6\text{H}_2\text{O}$ with 2,6-diacetonitrile and hydrazine as described in the experimental section yields an intensely blue-green colored product of the formulation $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$. The same compound is obtained in a smaller yield from the reaction of 2,6-diacetylpyridinedihydrazone with iron(II) perchlorate and 2,6-diacetylpyridine, but the reaction times must be increased by a factor of 10. The nmr spectrum of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ in deuterioacetonitrile consists of four absorptions. The methyl peaks occur at 2.90 and 3.23 ppm and the pyridine protons at 8.33 ppm. The acetonitrile protons are found at 2.00 ppm, the same position as for free acetonitrile, and it must be assumed that the axial acetonitrile molecules exchange with the solvent in the time required to dissolve the sample and run the spectrum.

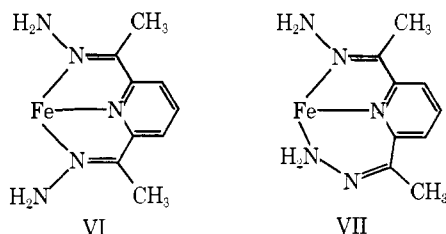
However, the acetonitrile remains coordinated when the compound is dissolved in trifluoroethanol, and the protons from it are observed at 1.83 ppm. The exchange rate is slow on the nmr time scale. The addition of a tenfold molar excess of deuterioacetonitrile to the complex in trifluoroethanol results in nearly complete exchange of acetonitrile with deuterioacetonitrile in about 12 min. The ir spectrum contains no absorptions attributable to either N-H stretching modes or any absorptions in the 1600–1700-cm⁻¹ range that are characteristic of either carbonyl or isolated imine groups, but does contain some absorptions between 1500 and 1600 cm⁻¹ arising from the overlap of pyridine ring vibrations with those expected from imine bond formation. It was concluded that condensation had occurred to give the desired macrocyclic complex.

The two structures, IV and V are both compatible with the above data. Although the 5–6–5–6 chelate ring arrangement of IV presents less angular strain and would appear to be the more likely structure, the 5–5–6–6 arrangement of V has been observed in other macrocyclic complexes. The coordination of 2,6-diacetylpyridinedihydrazone itself to iron(II) was found to form two five-membered chelate rings as illustrated in VI³⁶ rather than the 5–6 chelate arrangement of VII, even though the 5–6 configuration might be

Table II. Interatomic Distances (Å) and Angles (deg)

—Bond lengths—		—Selected interatomic angles—	
Fe—N(1)	1.892 (7)	N(1)—Fe—N(2)	83.8 (3)
Fe—N(2)	1.899 (5)	N(2)—Fe—N(1')	96.2 (3)
Fe—N(4)	1.938 (4)	N(1)—Fe—N(4)	88.8 (2)
Cl—O(1)	1.460 (2)	N(2)—Fe—N(4)	90.8 (2)
Cl—O(2)	1.401 (2)	N(3')—N(1)—C(2)	115.3 (7)
Cl—O(3)	1.382 (2)	N(3')—N(1)—Fe	128.4 (6)
Cl—O(4)	1.383 (2)	C(2)—N(1)—Fe	116.3 (5)
N(1)—C(2)	1.326 (9)	N(1)—C(2)—C(1)	125.8 (7)
N(1)—N(3')	1.386 (9)	N(1)—C(2)—C(3)	111.3 (7)
C(2)—C(1)	1.518 (11)	C(1)—C(2)—C(3)	122.9 (7)
C(2)—C(3)	1.466 (9)	C(2)—C(3)—N(2)	115.7 (6)
C(3)—N(2)	1.344 (8)	C(2)—C(3)—C(4)	119.5 (7)
C(3)—C(4)	1.387 (11)	N(2)—C(3)—C(4)	124.5 (7)
C(4)—C(5)	1.391 (12)	C(3)—N(2)—C(7)	123.5 (6)
C(5)—C(6)	1.358 (12)	C(3)—N(2)—Fe	112.7 (5)
C(6)—C(7)	1.452 (10)	C(7)—N(2)—Fe	123.6 (5)
C(7)—N(2)	1.349 (8)	C(3)—C(4)—C(5)	121.4 (8)
C(7)—C(8)	1.476 (11)	C(4)—C(5)—C(6)	122.9 (9)
C(8)—N(3)	1.297 (9)	C(5)—C(6)—C(7)	113.4 (8)
C(8)—C(9)	1.521 (11)	C(6)—C(7)—N(2)	113.8 (7)
N(4)—C(10)	1.136 (6)	C(6)—C(7)—C(8)	124.9 (7)
C(10)—C(11)	1.489 (8)	N(2)—C(7)—C(8)	121.1 (6)
		C(7)—C(8)—N(3)	133.0 (7)
		C(7)—C(8)—C(9)	116.6 (7)
		N(3)—C(8)—C(9)	110.5 (7)
		C(8)—N(3)—N(1')	117.6 (7)
		Fe—N(4)—C(10)	174.1 (4)
		N(4)—C(10)—C(11)	175.9 (6)

expected to produce less angular strain. In view of the stability of VI and its possible role in macrocyclic formation, structure V could not be ruled out *a priori*. It has been observed that complexes which have the 5-5-6-6 chelate ar-



rangement isomerize to the more favorable 5-6-5-6 if the potential for such a rearrangement exists. This occurs when the macrocyclic ligand has hydrazine linkages where the chelate ring size can be altered from 5 to 6 by switching donor atoms of the bifunctional hydrazine.²² Since we were unable to force any isomerization of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2]^{2+}$, it was assumed, and subsequently found that the structure possessed C_i symmetry.

The perchlorate and hexafluorophosphate salts of the bisacetonitrile complexes served as the starting materials for the complexes reported in Table III. The hexafluorophosphate salt was moderately soluble only in acetonitrile while the perchlorate salt was soluble in trifluoroethanol but insoluble or only sparingly soluble in all other solvents. Even though the perchlorate salts were stable toward violent decomposition in our hands, they do contain an unfortunate combination of oxidant, reductant, and transition metal catalyst and must be viewed as extremely treacherous. They were prepared only in small amounts for conversion to other derivatives and to provide crystals for the X-ray structural analysis.

The $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2]^{2+}$ species is stable when dissolved in acetonitrile and shows no tendency whatsoever to react with molecular oxygen over extended periods of time either in acetonitrile or in the solid state. The electron-

Table III. Carbon Monoxide Stretching Frequency of a Number of Iron(II) Complexes with Strong Field Tetradentate Ligands

Compound	CO (cm ⁻¹)	Ref
$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})(\text{CO})](\text{PF}_6)_2$	2040	<i>a</i>
$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{Cl})(\text{CO})](\text{PF}_6)_2$	2037	<i>a</i>
$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{Br})(\text{CO})](\text{PF}_6)_2$	2030	<i>a</i>
$[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{I})(\text{CO})](\text{PF}_6)_2$	2020	<i>a</i>
$[\text{Fe}(\text{TIM})(\text{CH}_3\text{CN})(\text{CO})](\text{PF}_6)_2$	2031	<i>b</i>
$[\text{Fe}(\text{DPGH})(\text{C}_6\text{H}_5\text{N})(\text{CO})]$	1996	<i>c</i>
$[\text{Fe}(\text{DPGH})(p\text{-CH}_3\text{py})(\text{CO})]$	1995	<i>c</i>
$[\text{Fe}(\text{DPGH})(\text{Clpy})(\text{CO})]$	2000	<i>c</i>
$[\text{Fe}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{NH}_2\text{NH}_2)(\text{CO})]$	1940	<i>d</i>
$[\text{Fe}(\text{C}_{16}\text{H}_{32}\text{N}_4)(\text{CH}_3\text{CN})(\text{CO})](\text{ClO}_4)_2$	1950	<i>e</i>
$[\text{Fe}(\text{tetren})(\text{Cl})(\text{CO})](\text{ClO}_4)_2$	1940	<i>f</i>
$[\text{Fe}(\text{hemoglobin})(\text{CO})]$	1951.9	<i>g</i>

^a This work. ^b Reference 14. ^c L. Vaska and T. Yamanji, *J. Amer. Chem. Soc.*, **93**, 6673 (1971). ^d Reference 7b. ^e V. Goedken and M. Suh, unreported results, $\text{C}_{16}\text{H}_{32}\text{N}_4 = 5,7,7,12,12,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. ^f L. R. Melby, *Inorg. Chem.*, **9**, 2186 (1970). ^g J. Alben and W. Caughey, *Biochemistry*, **7**, 175 (1968).

ic spectra of solutions of the perchlorate salt, $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$, dissolved in trifluoroethanol are identical with the spectra in acetonitrile solutions of the hexafluorophosphate derivative. This indicates very little dissociation of the coordinated acetonitrile (as also indicated by the nmr studies) and the low coordinating power of trifluoroethanol. The adducts with phenanthroline or α,α -dipyridyl are soluble in acetonitrile and also display no reactivity toward oxygen.

Solutions of the halogeno complexes are sensitive to molecular oxygen and the macrocyclic complexes are destroyed within minutes when exposed to the atmosphere. In view of the ease with which hydrazine linkages are normally oxidized, it is not surprising that all attempts to isolate iron(III) complexes failed.

The macrocyclic ligand in these iron complexes is somewhat atypical of most other macrocyclic ligands which have been studied, especially with regards to its fragility in solutions containing ligands which can act as nucleophiles. Although the complexes of this ligand can be worked with in slightly acidic media, they are destroyed rapidly (within minutes) by bases such as pyridine, imidazole, hydrazine, and cyanide and slowly by thiocyanate, azide, and halides. Consequently, we were unable to prepare or study extensively as large an array of complexes of this ligand with various axial substituents as intended.

The instability of the complexes of this macrocyclic ligand compared to other macrocyclic complexes has two probable causes. The first is that the tendency toward addition of nucleophiles to the imine functions should be enhanced when the α -diimine is constructed from the electron withdrawing hydrazine and 2,6-diacetylpyridine moieties. The second factor arises from the isolation of the imine function located in the six-membered chelate rings from the metal ion. It should be noted that most metal complexes containing imine functions stabilize the imine by the direct coordination of the metal ion to the nitrogen of the imine function. It has previously been observed that the imine linkages in a number of nickel(II) complexes are subject to nucleophilic attack.³⁷ The increased susceptibility to nucleophiles of our hexaaza macrocyclic ligand probably accounts for our inability to isolate analogous nickel complexes of this ligand.

The cobalt(II) analog, $[\text{Co}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$, of the iron(II) bisacetonitrile complex was obtained under similar conditions. The electronic and vibrational spectra are strikingly similar to the analogous iron(II) com-

pounds. The magnetic moment, 1.83 BM, is diagnostic of low spin cobalt(II). The compound is very unstable; acetonitrile solutions of the complex decompose on contact with air and even deaerated acetonitrile solutions of the complex decompose within a few hours.

Magnetic Properties. All of the iron complexes prepared in this study of this ligand are spin paired and diamagnetic. In this respect, they differ from less conjugated macrocyclic ligands which were found to be high spin and either five^{14,15} or six coordinate¹⁶ with weak field ligands such as halides occupying axial sites. The bishalogeno complexes of iron(II) containing the α -diimine ligands phenanthroline or α, α' -dipyridine are high spin even though these diimine ligands normally force the iron(II) into the spin paired configuration.³⁸ The low spin configuration observed with our macrocyclic complexes presumably results from the extraordinary high ligand field produced from constrictive effects of the macrocyclic ligand.

Carbon Monoxide Complexes. A number of carbon monoxide complexes have been obtained by bubbling carbon monoxide through solutions containing $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{X}_2)]^{2+}$, X = halide or acetonitrile species. Solutions of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2]^{2+}$ in acetonitrile exhibit no tendency to bind carbon monoxide at 2 atm of pressure. However, when carbon monoxide is passed through a solution of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})_2]^{2+}$ in trifluoroethanol solution (which does not compete effectively with acetonitrile as a ligand), the color of the solution changes from deep blue-green to the burgundy color of the carbon monoxide complex, $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})(\text{CO})]^{2+}$, which can then be isolated by the addition of hexafluorophosphate anion. Analogous complexes are obtained when the bishalogeno complexes are substituted for the acetonitrile complex in either acetonitrile or trifluoroethanol solution.

The carbon monoxide stretching frequencies for these complexes are in the range 2040–2020 cm^{-1} and are listed in Table III³⁹ together with other monocarbon monoxide complexes of iron(II) of widely varying ligand systems which have been reported in recent years. The carbon monoxide stretching frequencies are very close to those reported by Rose and coworkers for the $[\text{Fe}(\text{TIM})(\text{CH}_3\text{CN})(\text{CO})](\text{PF}_6)_2$ compound in which the macrocyclic TIM ligand contains two "pure" α -diimine moieties.¹⁴ They are much higher than those observed in similar environments with a planar arrangement of four nitrogen donor atoms. For example, those complexes which do not contain α -diimine moieties have carbon monoxide stretching frequencies about 50 cm^{-1} lower. Carbon monoxide complexes of hemoglobin and the iron(II) complexes of the pentamine, tetren, the dianionic macrocyclic complex formed from the condensation of *o*-phenylenediamine with acetylacetone, and the diene of the Curtis macrocyclic ligand, $\text{C}_{16}\text{H}_{32}\text{N}_4$, all absorb at much lower frequencies.

The CO stretching frequencies of monocarbon monoxide complexes are not markedly sensitive to the axial ligands. Our infrared measurements, as well as most of those reported in Table III, were restricted to the solid state due to limitations of solubility. The differences of CO stretching frequency on going from acetonitrile to the various other halides are not sufficient to draw reliable conclusions, since differences of this magnitude can be attributed to varying lattice forces in the different compounds. The very strong binding of CO produces a strong trans effect; weaker ligands trans to CO will be held loosely and have little effect on the CO stretching frequency, as illustrated in Table III.

The carbon monoxide stretching frequencies are observed to be much more dependent on the nature of the planar ligands. Those complexes which have α -diimine functions, *i.e.*, TIM, DPGH, and $\text{C}_{18}\text{H}_{18}\text{N}_6$, have CO stretching frequen-

cies which are nearly 50 cm^{-1} higher than the other complexes. The weaker binding of carbon monoxide of those complexes containing α -diimine chelates can be attributed to the strong competition between the antibonding π -orbitals of the imine functions and those of the carbon monoxide for the back-bonding filled metal d_{xz} and d_{yz} orbitals.

Another indication of the weak binding of carbon monoxide in our complexes is the ease with which it is lost in solution. Dissolution of $[\text{Fe}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{CH}_3\text{CN})(\text{CO})](\text{PF}_6)_2$ in acetonitrile is followed by the complete dissociation of carbon monoxide and the formulation of the bisacetonitrile complex within 10 min. Those complexes which have halide ions trans to the carbon monoxide are somewhat more stable toward loss of carbon monoxide. The partial transfer of negative charge by the halide ion to the iron(II) may produce enough radial expansion of the d_{xz} and d_{yz} orbitals to increase the stability of carbon monoxide binding.

Although the compounds listed in Table III contain a diverse array of nitrogen donor ligands, a number of closely related iron(II) complexes of phthalocyanine, dimethylglyoxime, and *N,N'*-ethylenebis(salicylideneimine) do not coordinate with carbon monoxide at atmospheric pressure. The last example does not show any evidence for coordination of carbon monoxide even at 100 atm of pressure.⁴⁰

Electronic Spectra. The electronic spectra of low spin iron(II) complexes of ligands containing α -diimine functions have as one of their most diagnostic features a strong charge transfer absorption near 540 nm with an extinction coefficient around 3000 per diimine chromophore.^{41–44} For convenience, we will classify α -diimine ligands into two types in the discussion to follow. The first category contains those well-known amines such as 1,10-phenanthroline and α, α' -dipyridyl where the α -diimine moiety is an integral part of an aromatic ring system. The second category contains ligands having "pure" α -diimine functions not imbedded in an aromatic ring or involved in other extensively conjugated systems. Ligands such as dimethylglyoxime, glyoxalbis(methylimine), and 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene will be considered to belong to the latter category. Despite appreciable differences in the extent of delocalization in these two types of amine ligands, the properties of their iron(II) complexes are strikingly similar. Both classes of α -diimines behave as strong field ligands producing spin paired iron(II) and iron(III) complexes. The electronic spectra of both types of α -diimine complexes are similar.

The spectra of the iron(II) complexes of IV with either acetonitrile or nitrito ligands in the axial positions differ markedly from the examples cited above (Table IV, Figure 1). The spectra of the two compounds are similar and each is characterized by a number of absorptions throughout the visible region of the spectrum which might be indicative of low lying states of an extensively delocalized system. The bands at 14,190 and 12,990 cm^{-1} occur at lower energy than normally observed for α -diimines. The extinction coefficients (1700) are also much lower than for iron(II) diimine complexes. The much more intense band which is normally present with iron(II) complexes of α -diimine ligands in the vicinity of 540 nm is absent.

Our initial speculation that the completely conjugated flat ligand might resist bending or folding by strong bidentate ligands was unfounded. A 1:1 adduct readily formed when either 1,10-phenanthroline or α, α' -dipyridyl were added to solutions of the complex. These two diamines can coordinate only to the cis positions of the coordination sphere, and the interaction of the hydrogen atoms of these diamines must induce folding of the macrocyclic ligand, such that two cis positions are also occupied by the macrocyclic ligand as illustrated schematically in V. Any appre-

Table IV. Electronic Spectra of the New Complexes

Compound	Solvent	Absorption (cm ⁻¹)
[FeL(CH ₃ CN) ₂](PF ₆) ₂	Acetonitrile	12,990 (1876), 14,190 (1517), 21,750 (sh 503), 24,200 (sh, 1472), 26,700 (2034), 27,900 (2011), 28,600 (sh, 2202), 34,500 (34,380)
[FeL(phenan)](PF ₆) ₂	CF ₃ CH ₂ OH	20,040 (10,532), 21,505 (sh, 8565), 28,170 (2850), 34,010 (16,933)
[FeL(NO ₂) ₂] · 1/2 CF ₃ CH ₂ OH	CF ₃ CH ₂ OH	13,245 (2949), 23,585 (sh, 2,683), 25,250 (3448), 26,600 (sh, 3,224), 32,260 (sh, 17,290), 35,336 (38,300), 44,640 (30,968)
[FeL(2,2'-dipy)](PF ₆) ₂	CF ₃ CH ₂ OH	20,000 (8763), 21,740 (sh, 6131), 23,260 (sh 3682), 29,850 (sh, 3695), 34,250 (24,760), 43,100 (27,470)
FeLCl ₂	CF ₃ CH ₂ OH	15,880 (482), 17,950 (sh, 609), 18,950 (667), 20,400 (sh, 571), 21,450 (599), 23,350 (sh, 1,040), 26,450 (sh, 2575) 33,700 (10,680), 40,700 (8440)
[FeLBr ₂]	CF ₃ CH ₂ OH	19,050 (1198), 22,200 (sh, 1580), 26,300 (3860), 34,500 (23,150)
[FeLCO(CH ₃ CN)](ClO ₄) ₂	CF ₃ CH ₂ OH	16,170 (sh, 376), 20,130 (192), 33,000 (sh, 19,950), 34,500 (sh, 25,000), 35,200 (27,500), 43,700 (27,700)
[FeLCOCl]ClO ₄	CF ₃ CH ₂ OH	18,200 (1327), 24,650 (sh, 1288), 26,100 (sh, 1745), 27,500 (sh, 1944), 34,250 (sh, 22,700), 34,850 (23,000), 40,000 (sh, 18,720), 43,300 (23,950)
[CoL(CH ₃ CN) ₂](PF ₆) ₂	CH ₃ CN	15,270 (sh, 1475), 16,560 (1811), 23,950 (sh, 1602), 25,160 (sh, 2131), 28,900 (sh, 4208), 33,670 (32,259), 34,360 (sh, 30,656), 41,320 (23,301)

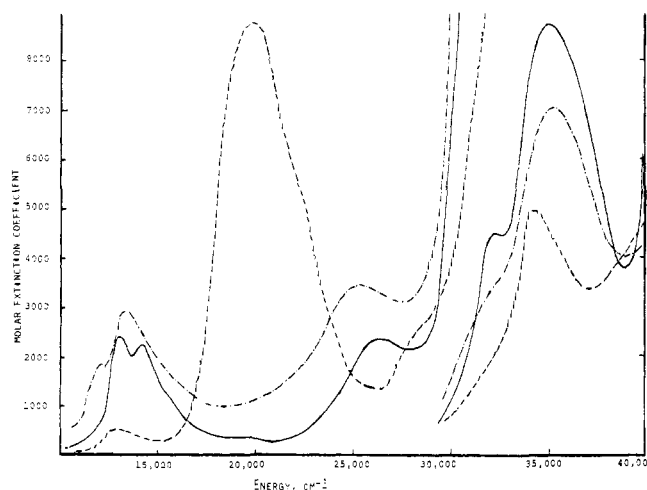
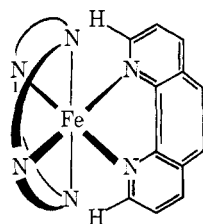


Figure 1. Electronic spectra of the hexaaza macrocyclic complexes of iron(II) illustrating the differences in the planar and bent form of the ligand: —, [Fe(C₁₈H₁₈N₆)(CH₃CN)₂](PF₆)₂; - · - · -, [Fe(C₁₈H₁₈N₆)(NO₂)₂]; - - - -, [Fe(C₁₈H₁₈N₆(bipy))₂](PF₆)₂.



ciable ligand deformation from planarity should affect those electronic transitions arising from delocalized systems whose conjugation would be decreased by bending.

The electronic spectra of the folded complexes depart markedly from those of the starting compounds. All of the absorptions found in the spectra of the planar species disappear and a strong, broad absorption typical of pure α -diimines with ϵ_{\max} 10,000 appears at 540 nm. This strongly suggests that the low energy transitions in the planar form of the macrocyclic ligand arise from a conjugated system more extensive than a simple α -diimine. This delocalization probably extends across the hydrazine linkages, since molecular models indicate that folding is most likely to occur

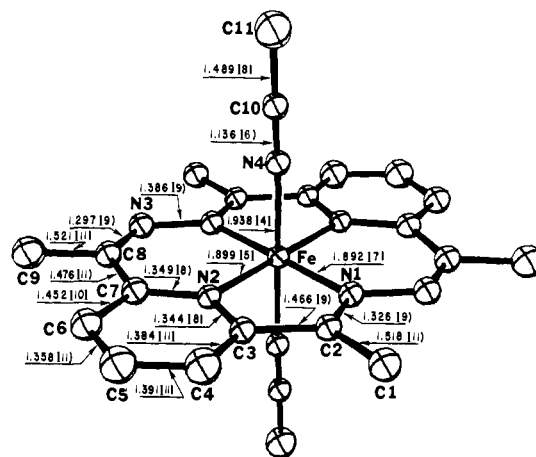


Figure 2. Molecular structure, labeling scheme, and interatomic distances of the macrocyclic complex, [Fe(C₁₈H₁₈N₆)(CH₃CN)₂](ClO₄)₂.

at the hydrazine nitrogen atoms. A single-crystal X-ray structural determination of [Fe(C₁₈H₁₈N₆)(CH₃CN)₂](ClO₄)₂ was undertaken to evaluate the effect of bond delocalization present in this complex.

Description of the Structure

The structure consists of a six coordinate iron(II) ion girded by four nitrogen atoms of the planar macrocyclic ligand with two molecules of acetonitrile occupying the axial sites of the complex (Figure 2). The complex has *C*_i symmetry since the iron is located on a crystallographic inversion center. The perchlorate ion is located in a general position as observed in the packing diagram, Figure 3.⁴⁵ The macrocyclic ligand is essentially planar with only small deviations of the atoms from the least-squares plane defined by the 14 atoms of the macrocycle. The largest deviations of the ring atoms from the plane are -0.03 and -0.04 Å for atoms N(2) and C(2); the methyl groups C(9) and C(1) deviate slightly more, 0.04 and 0.09 Å, respectively.

The accuracy of this structural determination is limited primarily by the severe disorder present in both the macrocyclic ligand and in the ill-behaved perchlorate anions. The disorder can be visualized as resulting from the failure of

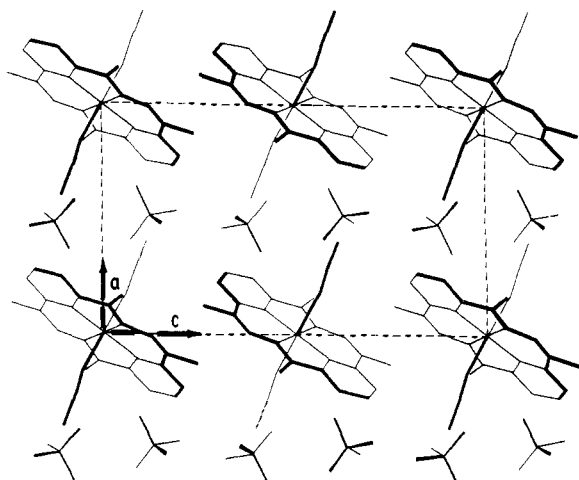


Figure 3. Diagram projected down the *b* axis illustrating the packing of the cations and ions in the unit cell.

the lattice to distinguish between the possibility of one orientation (bold faced outline, Figure 4) and that obtained by reflecting the cation through one of the pseudo-mirror planes. Disorder of a very similar nature has been observed in the structures of two nickel complexes of the macrocyclic ligand tetrabenzob[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine.⁴⁶ In each case, the ratio of the major to minor disordered fraction was close to the 0.7 and 0.3 observed in our structure. Despite the limitations on the accuracy of this structure, most of the bond distances of chemically equivalent atoms agree reasonably well and also agree with accepted values of more highly refined structures. For example, the C–C single bond distances of the methyl to carbon atoms of the macrocyclic ring, C(9)–C(8) and C(1)–C(2) of 1.521 (11) and 1.518 (11) Å, are well within the range of values normally found for methyl carbon atoms to other carbon atoms in similar environments. The departure of the C(6)–C(7) bond length of the pyridine ring from the accepted value of 1.40 Å may be attributable to a somewhat less than satisfactory handling of the disorder problem.

The macrocyclic complex contains six fused rings of three different types. There are two pyridine rings, two five-membered chelate rings, and two six-membered chelate rings. Some cumulative strain is to be expected in these angles from the following considerations; the average values of the angles in flat five- and six-membered rings must be 108 and 120°, respectively. Yet the sum of the angles subtended at the iron atom by two contiguous, partially fused chelate rings can be only 180°. Averaged values of the angle subtended at the carbon and nitrogen atoms, 124.75 and 111.4°, in the respective six- and five-membered chelate rings display only part of this strain because it is not uniformly distributed. The observed ranges observed for these angles are from 117.6 to 133.0° and from 111.3 to 116.3° in the respective six- and five-membered chelate rings.⁴⁷

However, the strain energies associated with bond deformations are small. The fact that the condensation of the macrocyclic complex occurs readily at room temperature in the absence of forcing conditions implies a low activation barrier for complex formation and a low strain energy for the product.

A number of bond distances warrant special discussion. First, the iron(II)–nitrogen distances of the macrocyclic ligand are quite short, 1.899 (4) and 1.892 (7) Å. They are about 0.1 Å shorter than the iron(II)–nitrogen distances observed in porphyrin complexes⁴⁸ and 0.1 Å shorter than predicted on the basis of the normal covalent radii for iron(II) and nitrogen.⁴⁹

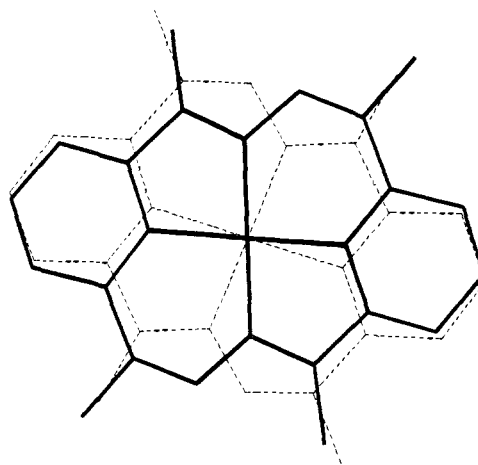


Figure 4. Diagram illustrating the disorder in the cation as viewed down the axial ligands.

The short iron–nitrogen distances may be attributable to two independent but nondifferentiable effects. The first may result from a constriction of the iron by the macrocyclic ligand. The metal–nitrogen distances are considerably shorter than that observed in a number of other macrocyclic complexes of saturated or partially unsaturated ligands. Since double bonds are about 0.15 Å shorter than single bonds, a completely conjugated 14-membered ring ligand with the equivalent of seven double bonds would be expected to result in substantially shortened metal–ligand bond distances. However, a second effect, the extensive back-bonding of iron to the antibonding α -diimine orbitals, also produces abnormally short iron(II)–nitrogen distances. This effect is considerably more marked with ligands having pure α -diimine functions than with those which are incorporated into an aromatic system such as phenanthroline and α,α' -dipyridine. Two structures of iron(II) containing α -diimine groups have recently been reported. One contains coordinated *o*-benzoquinonediimine and has iron–nitrogen distances of 1.912 and 1.905 Å (which are shorter than the iron–carbon distances to the cyanide ions in the same species).⁵⁰ The other structure is that of bis(dimethylglyoximate)diimidazoleiron(II) which has iron–nitrogen distances of 1.918 (6) and 1.893 (6) Å.⁵¹ It must be concluded that the short iron(II)–nitrogen bonds are primarily the result of strong back-bonding between the iron(II) and the ligand and not due to constriction of the metal radius by the macrocyclic ligand.

When the complexed α -diimine is incorporated into aromatic rings such as phenanthroline, the iron–nitrogen distances are significantly longer, 1.97 Å.⁵² This is attributable to the fact that the C=N bonds (C–N distance = 1.37 Å) display little imine character and the metal ion stabilization of the α -diimine structure is less than the resonance stabilization of aromatic systems.

Examination of the interatomic distances of the macrocyclic ligand indicate that with the exception of the pyridine ring, the structure shows essentially alternating double and single bond character. The two imine C–N distances, 1.297 (9) and 1.326 (9) Å, are somewhat longer than those found in complexes having isolated imine linkages where the C–N distances are about 1.27 Å.⁵³ It should be noted that the imine of the five-membered ring is longer than in the six-membered chelate ring, probably due to the strong back-bonding of iron to the coordinated imine. The C–N distance of this five-membered ring, 1.326 (9) Å, is about midway between that of isolated imines and the C–N distance of pyridine, 1.35 Å, and indicates significant delocalization.

The N–N linkages are chemically equivalent, as well as crystallographically equivalent due to the center of symmetry. However, the hydrazine atoms of the disordered portion were sufficiently separated from the other atoms to be refined independently. The two values for the N–N distance, 1.386 (9) for the major portion and 1.40 (2) for the disordered portion, are slightly shorter than those observed for hydrazine linkages of similar systems. The bond distances of C(7)–C(8) and C(2)–C(3), 1.476 (11) and 1.466 (9) Å, indicate primarily single bond character, slightly shortened as a result of conjugation with the imine linkages and the aromatic pyridine rings.

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Supplementary Material Available. A listing of 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, 24× 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 \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-7693.

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