The Crystal and Molecular Structure of an Octaaza[14]annulene Complex of Iron(II). A Molecular Oxygen Carrier

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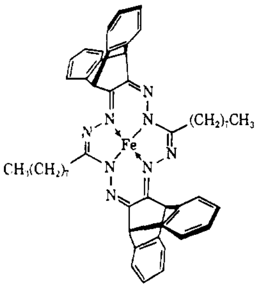
Abstract: The four-coordinate iron(II) complex of the substituted octaaza[14]annulene reported by Baldwin and Huff (*J. Am. Chem. Soc.*, **95**, 5757 (1973)) to be a molecular oxygen carrier has been characterized by a complete X-ray structural determination. The complex crystallizes with two molecules in space group C_{2h}^5-$P2_1/c$ of the monoclinic system in a cell of dimensions, a = 11.976 (8) Å, b = 8.147 (5) Å, c = 22.567 (14) Å, and β = 98.83(4)°. A crystallographic center of inversion is imposed on each molecule. The structure has been refined anisotropically to a final R index (on F) of 0.085 for the 2651 measured intensities having $F_o^2 > 3\sigma(F_o^2)$. The coordination about the iron atom is approximately square-planar with two unequal Fe–N bond lengths of 1.846 (4) and 1.826 (4) Å. The bond lengths within the macrocyclic ligand are nearly identical with those observed in other octaaza[14]annulene complexes, although the ligand is distinctly nonplanar in this complex. We believe the short Fe–N bond lengths in the complex result in part from the constrictive effect of the macrocycle.

In 1973 Baldwin and Huff reported the synthesis of the first iron complex to mimic hemoglobin by reversibly binding dioxygen in solution.[1] Previous work[2,3] indicated that Fe(II) complexes were irreversibly oxidized by molecular oxygen because of the rapid bimolecular reaction:

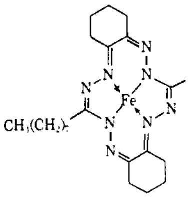
$$\mathrm{Fe(II)} + \mathrm{O_2} \rightleftharpoons \mathrm{Fe^{II}O_2} + \mathrm{Fe(II)} \rightarrow \mathrm{Fe^{II}\text{-}O\text{-}O\text{-}Fe^{II}} \rightarrow 2\mathrm{Fe(III)}$$

Baldwin and Huff reasoned that the dimerization reaction could be impeded if the iron atom were protected by the presence of bulky groups about the periphery of the complex. Therefore the complex, I, was synthesized in which the iron atom is effectively sequestered in a 5 Å deep hydrophobic pocket formed by the 9,10-dihydroanthryl and *n*-octyl groups.

Baldwin and Huff demonstrated that the complex I reversibly binds dioxygen at low temperatures, but that the less hindered complex, II, is irreversibly oxidized. In II the effective depth of the hydrophobic pocket was estimated to be 2.2 Å. Subsequent work on related systems has demonstrated that steric hindrance and a hydrophobic pocket are important,[4] but not obligatory features[5] of such compounds. Indeed it has recently been shown that simple unhindered iron porphyrins, such as ferrous tetraphenylporphyrin, will also bind dioxygen reversibly at low temperatures.[5]



I



II

In addition to its ability to bind dioxygen, compound I has been shown[6] to have an effective magnetic moment of 2.8 μ_B at 28° and thus to contain iron in the unusual S = 1 spin state. In view of the appreciable current interest in iron macrocycles and molecular oxygen carriers of iron we have undertaken a full crystallographic description of the environment of the iron atom.

Experimental Section

Crystals of the complex, I, were grown from dimethylformamide–acetonitrile solutions. Preliminary precession photographs ($0kl$, $\bar{1}kl$, $h0l$, $h1l$) taken with Mo Kα radiation show systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) characteristic of the space group C_{2h}^5-$P2_1/c$. The crystal selected for data collection was a parallelepiped truncated by a large (001) face. The major, bounding faces were of the forms {010}, {$\bar{1}$02}, and {101}. The distances between the faces of these forms were 0.51, 0.33, and 0.77 mm. The crystal was mounted with the [101] direction approximately along the spindle axis.

The lattice parameters, obtained as previously described[7,8] by hand-centering of 12 reflections with Mo Kα_1 radiation (λ 0.70930 Å) in the range 30 < 2θ < 35°, are a = 11.976 (8) Å, b = 8.147 (5) Å, c = 22.567 (14) Å, and β = 98.83 (4)° (t = 22°). The calculated density, based on two molecules of the complex per unit cell, is 1.26 g/cm³.

Data were collected in shells of 2θ by the θ–2θ scan method using Mo Kα radiation. The scan range in 2θ was from 1° below the Mo Kα_1 peak to 1° above the Mo Kα_2 peak. The takeoff angle was 2.2° and the receiving counter was positioned 33 cm from the crystal preceded by an aperture 5.0 mm high and 5.0 mm wide. The pulse-height analyzer was set to admit about 90% of the Mo Kα peak. Initially background counts of 10 sec were taken at each end of the scan range. Past a 2θ of 20° this was increased to 20 sec, and finally it was increased to 40 sec for 2θ greater than 45°. A scan rate of 2° in 2θ per min was used. Attenuators were automatically inserted if the intensity of the diffracted beam exceeded approximately 7000 counts/sec during a scan. The attenuators were of Cu foil and gave attenuator factors of about 2.3. Data were collected in the range 2° < 2θ < 48°. Data collection was terminated when less than 5% of the measured reflections were statistically observable. During the course of data collection six standard reflections from diverse regions of reciprocal space were measured every 100 reflections. The deviations of these standards from their averages were all within counting statistics.

The data were processed as previously described using a value of 0.05 for p.[7] Of the 4810 reflections measured, 3617 have $F_o^2 > 3\sigma(F_o^2)$ and of these 2651 are unique and were used in subsequent refinements. Data were collected with h < 1 and k > −1, so 372 pairs of Friedel or symmetry equivalent reflections were measured. These reflections deviate by 2.3% from their average values. Sample calculations[9] for an absorption correction were made using a

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Table II. Atomic Parameters for $FeC_{50}H_{54}N_8$[b]

Atom	x	y	z	B (Å^2) or β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0	0	0	384 (8)	1566 (2)	167 (3)	100 (11)	−70 (3)	−134 (7)
N(1)	−0.1099 (3)	0.1502 (5)	0.0118 (2)	40 (3)	155 (8)	16 (1)	9 (4)	−5 (1)	−12 (2)
N(2)	0.0279 (3)	0.2357 (6)	0.0892 (2)	47 (3)	155 (8)	15 (1)	12 (4)	−2 (1)	−12 (2)
N(3)	0.0815 (3)	0.1043 (5)	0.0641 (2)	42 (3)	150 (8)	15 (1)	9 (4)	−4 (1)	−10 (2)
N(4)	0.2196 (3)	−0.1631 (5)	0.0167 (2)	39 (3)	149 (8)	17 (1)	7 (4)	−4 (1)	−8 (2)
C(1)	−0.0740 (4)	0.2540 (7)	0.0597 (2)	44 (4)	136 (9)	17 (1)	2 (5)	1 (2)	−9 (3)
C(2)	−0.1457 (4)	0.3896 (7)	0.0775 (2)	46 (4)	181 (11)	17 (1)	15 (5)	−2 (2)	−15 (3)
C(3)	−0.1527 (6)	0.5371 (8)	0.0371 (3)	97 (6)	204 (13)	19 (1)	34 (7)	4 (2)	2 (3)
C(4)	−0.2198 (6)	0.6784 (8)	0.0573 (3)	107 (6)	172 (12)	24 (2)	35 (7)	0 (2)	−3 (3)
C(5)	−0.1645 (7)	0.7649 (10)	0.1120 (4)	141 (8)	222 (15)	29 (2)	22 (9)	6 (3)	1 (4)
C(6)	−0.2285 (9)	0.9115 (12)	0.1311 (4)	186 (11)	242 (18)	40 (3)	34 (12)	22 (4)	−25 (6)
C(7)	−0.1600 (15)	1.0160 (18)	0.1838 (7)	312 (24)	482 (40)	52 (4)	−51 (22)	49 (8)	−26 (10)
C(8)	−0.1657 (15)	0.9763 (20)	0.2376 (7)	240 (22)	681 (49)	54 (4)	−83 (24)	−9 (8)	41 (12)
C(9)	−0.1116 (10)	1.0939 (15)	0.2894 (5)	214 (14)	430 (28)	44 (3)	−57 (17)	−25 (5)	−19 (8)
C(10)	0.1856 (4)	0.0675 (7)	0.0861 (2)	39 (4)	140 (9)	13 (1)	−5 (4)	−4 (2)	−3 (2)
C(11)	0.2493 (4)	−0.0604 (7)	0.0610 (2)	42 (4)	139 (8)	14 (1)	6 (4)	−4 (16)	−1 (3)
C(12)	0.3731 (4)	−0.0625 (7)	0.0917 (2)	38 (4)	162 (9)	16 (1)	11 (5)	−6 (2)	−7 (3)
C(13)	0.4161 (3)	0.1108 (3)	0.0859 (2)	3.1 (1)					
C(14)	0.5072 (3)	0.1573 (4)	0.0581 (2)	3.7 (1)					
C(15)	0.5337 (3)	0.3227 (4)	0.0535 (2)	4.3 (1)					
C(16)	0.4690 (3)	0.4415 (3)	0.0768 (2)	4.5 (1)					
C(17)	0.3779 (3)	0.3950 (3)	0.1046 (2)	3.8 (1)					
C(18)	0.3515 (3)	0.2296 (4)	0.1091 (2)	3.2 (1)					
C(19)	0.2561 (4)	0.1604 (7)	0.1379 (2)	44 (4)	156 (10)	14 (1)	7 (5)	−4 (2)	−11 (3)
C(20)	0.3066 (3)	0.0307 (4)	0.1827 (2)	3.6 (1)					
C(21)	0.2982 (3)	0.0259 (5)	0.2435 (2)	4.7 (1)					
C(22)	0.3544 (4)	−0.0955 (6)	0.2799 (1)	5.6 (1)					
C(23)	0.4191 (4)	−0.2121 (5)	0.2555 (2)	6.0 (2)					
C(24)	0.4275 (3)	−0.2073 (4)	0.1946 (2)	4.6 (1)					
C(25)	0.3713 (3)	−0.0859 (5)	0.1582 (1)	3.5 (1)					

Group[c]	x_c	y_c	z_c	δ	ϵ	η
Ring 1	0.4426 (2)	0.2761 (3)	0.0813 (1)	0.1927 (20)	−2.9361 (22)	2.5187 (24)
Ring 2	0.3628 (2)	−0.0907 (3)	0.2191 (1)	−2.5057 (27)	−3.1216 (20)	−1.6453 (26)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ The anisotropic thermal parameters have all been multiplied by 10^4, except those for the metal atom, which have been multiplied by 10^5. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures. [c] The various group parameters have been defined previously. See S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

linear absorption coefficient of 3.87 cm^{-1}. The transmission factors calculated ranged from 0.824 to 0.895, and an absorption correction was applied.

Solution and Refinement of the Structure. Normalized structure factors ($|E|$'s) scaled such that $\langle E^2 \rangle = 1.0$ were calculated from the measured structure amplitudes. The statistical distribution of the $|E|$'s closely resembled that expected for a centrosymmetric structure.

Using the quantities $|E^2 - 1|$ a sharpened, origin-removed Patterson map was calculated. From this map the positions of the iron atom and of all of the carbon and nitrogen atoms of the macrocycle, except for atoms C(2)-C(9) of the octyl chain, were obtained. A subsequent difference Fourier synthesis phased on these atomic positions revealed the positions of the remaining seven atoms, C(2)-C(9).

The structure was refined as follows. The two aromatic rings of the 9,10-dihydroanthryl group were idealized and refined as rigid groups. Three cycles of least-squares refinement of the 18 independent atoms and the two groups, using isotropic thermal parameters and a random half of the data, reduced R and R_w to 0.17 and 0.21. The structure was refined by full-matrix least-squares techniques. The quantity minimized is $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. The agreement indices are defined as

$$R = \sum||F_o| - |F_c||/\sum|F_o|$$

and

$$R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$$

Values of the atomic scattering factors and anomalous terms[10] were taken from the usual sources. The 24 H atoms of the benzene rings, bridgehead carbon atoms (C(12), C(19)), and the methylene positions of the octyl chain were idealized (C–H = 0.95 Å, B(H) $= B$(C) + 1.0 Å^2) and added as fixed contributions in subsequent refinements. One cycle of isotropic refinement and one of anisotropic refinement using all the data reduced R and R_w to 0.13 and 0.18, respectively. Two cycles of anisotropic, full-matrix least-squares refinement of the 18 nongroup atoms and isotropic treatment of the two groups (individual, isotropic thermal parameters for the group atoms) converged with R and R_w equal to 0.085 and 0.117, respectively. Refinement was terminated at this point since the last cycle led to insignificant shifts in the atomic parameters of all atoms.

An analysis of $|F_o|$ and $|F_c|$ as a function of setting angles, $|F_o|$, and Miller indices shows no unusual trends. The standard deviation of an observation of unit weight is 3.74 electrons. A final difference Fourier map revealed the position of the methyl hydrogen atoms on C(9). Other peaks on the map (0.99–0.50 e/Å^3) were associated with the benzene rings which had been treated as groups.

A structure factor calculation for the 785 unique reflections having $F_o^2 < 3\sigma(F_o^2)$, which were omitted from the refinement, showed no reflections having $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. These reflections were omitted from Table I[11] where the values of $10|F_o|$ and $10|F_c|$ are given.

The final atomic parameters and their errors are listed in Table II. The calculated atomic parameters for the hydrogen atoms are given in Table III.[11] Table IV presents the root-mean-square amplitudes of thermal vibration.[11]

Description and Discussion of the Structure

The crystal structure consists of discrete molecules of $FeC_{50}H_{54}N_8$. The contents of one unit cell are shown in Figure 1. The numbering scheme used in this paper to describe the centrosymmetric molecule is shown in Figure 2. The intermolecular contacts are normal, the shortest being 2.44 Å between HC(14) atoms on adjacent molecules. The

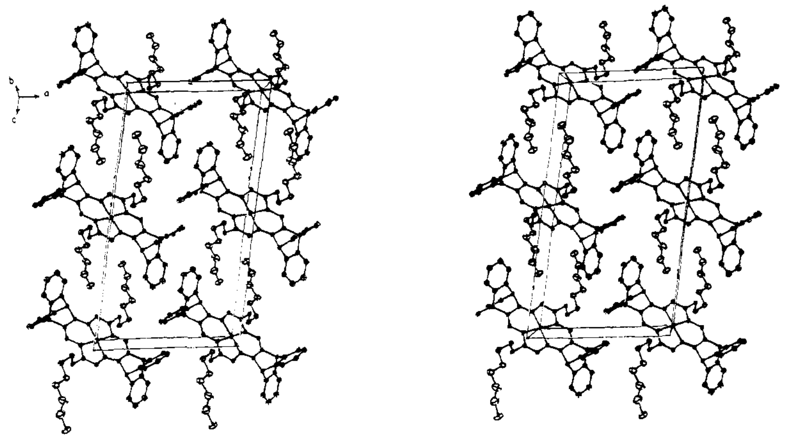

Figure 1. Stereoscopic view of the molecular packing in one unit cell. The four molecules at the front corners of the cell have been omitted for clarity.

Table V. Bond Distances (Å) and Angles (deg) in $FeC_{50}H_{54}N_8$

Fe–N(1)	1.846 (4)	Fe–N(1)–C(1)	112.0 (3)
Fe–N(3)	1.826 (4)	Fe–N(1)–N(4)*	129.3 (3)
N(1)-N(4)*[a]	1.376 (5)	Fe–N(3)–C(10)	124.0 (4)
N(2)–N(3)	1.411 (6)	Fe–N(3)–N(2)	116.8 (4)
C(1)–N(1)	1.387 (7)	N (1)–Fe–N(3)	83.3 (2)
C(1)–N(2)	1.306 (6)	N(1)–C(1)–N(2)	118.8 (4)
C(1)–C(2)	1.492 (7)	N(1)–C(1)–C(2)	122.6 (4)
C(10)–N(3)	1.304 (6)	N(1)*–N(4)–C(11)	115.8 (4)
C(10)–C(11)	1.456 (8)	C(1)–N(1)–N(4)*	118.5 (4)
C(10)–C(19)	1.532 (6)	C(1)–N(2)–N(3)	109.2 (4)
C(11)–C(12)	1.537 (6)	C(1)–C(2)–C(3)	114.2 (5)
C(11)–N(4)	1.311 (6)	C(2)–C(3)–C(4)	114.1 (5)
C(12)–C(13)	1.516 (6)	C(3)–C(4)–C(5)	114.9 (6)
C(12)–C(25)	1.516 (6)	C(4)–C(5)–C(6)	115.4 (7)
C(19)–C(18)	1.507 (6)	C(5)–C(6)–C(7)	114.2 (10)
C(19)–C(20)	1.522 (6)	C(6)–C(7)–C(8)	118.9 (14)
C(2)–C(3)	1.503 (9)	C(7)–C(8)–C(9)	118.6 (14)
C(3)–C(4)	1.514 (9)	N(2)–C(1)–C(2)	118.6 (4)
C(4)–C(5)	1.486 (10)	N(2)–N(3)–C(10)	119.2 (4)
C(5)–C(6)	1.517 (11)	N(3)–C(10)–C(19)	124.0 (5)
C(6)–C(7)	1.585 (18)	N(3)–C(10)–C(11)	122.9 (4)
C(7)–C(8)	1.27 (2)	N(4)–C(11)–C(10)	131.0 (4)
C(8)–C(9)	1.572 (19)	N(4)–C(11)–C(12)	117.8 (4)
		C(10)–C(11)–C(12)	111.0 (4)
		C(10)–C(19)–C(18)	102.8 (4)
		C(10)–C(19)–C(20)	106.2 (4)
		C(11)–C(10)–C(19)	112.9 (4)
		C(11)–C(12)–C(13)	105.5 (4)
		C(11)–C(12)–C(25)	106.8 (4)
		C(13)–C(12)–C(25)	105.1 (4)
		C(18)–C(19)–C(20)	107.2 (3)

[a] Atoms superscripted with an asterisk are the centrosymmetric equivalents of the nonsuperscripted atoms.

conformation of an individual molecule is such that the octyl chains are extended away from, rather than folded over, the iron atom.

The coordination about the iron atom is approximately square-planar, with two unequal Fe–N bond lengths of 1.846 (4) and 1.826 (4) Å (Table V). The N(1)–Fe–N(3) bond angle is 83.8°. The macrocycle itself is distinctly nonplanar, as is shown in Figure 2 and in Table VI. The N(3), C(10), C(11), N(4), N(1) portion of the macrocyclic ring (plane 2) is puckered with respect to the coordination plane and makes a dihedral angle of 3° with that plane. This results in a significant canting of the dihydroanthryl groups with respect to the plane of the macrocycle. As a result, the carbon atoms at the periphery of the anthryl rings are unequally disposed 3.7 Å (C(15), C(16)) and 2.8 Å (C(22), C(23)) to either side of the plane of the macrocycle. The canting of the centrosymmetrically related rings is illustrated in Figure 2 and in Figure 3, where a view of the inside of the hydrophobic pocket is presented. The maximum depth of the pocket, as measured from the hydrogen atom positions, is 4.56 Å. The octyl chains appear to be relatively unimportant in forming the hydrophobic pocket. The bond lengths and bond angles associated with the dibenzobicyclo[2.2.2]octane moiety are unremarkable and compare well with those observed in triptycene[12,13] and 9,10-dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarbonitrile.[14]

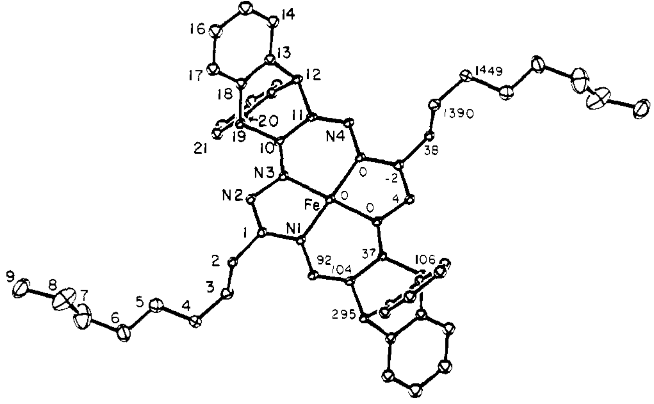

Figure 2. Drawing to indicate the numbering sequence used in this paper for the 30, independent, non-hydrogen atoms in the centrosymmetric molecule. The carbon atoms are indicated by a number only. The right hand side of the diagram shows (small type) the perpendicular displacement of an atom from the plane of the macrocycle (see Table VI).

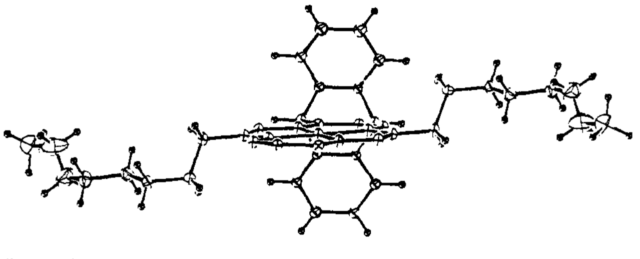

Figure 3. A view of the $FeC_{50}H_{54}N_8$ molecule, which shows the depth of the hydrophobic pocket formed by the 9,10-dihydroanthracene rings. The ring toward the viewer has been omitted for clarity, and the hydrogen atoms in the molecule have been drawn artifically small.

There appears to be some positional disorder in the *n*-octyl chain, involving carbon atoms C(7) and C(8). These atoms have slightly larger than normal thermal parameters.

The bond lengths and bond angles in the ligand may be compared with those found in a nickel complex of a related octaaza[14]annulene, the structure of which was recently

Table VI. Deviations (Å) ($\times 10^3$) and Equations of Weighted Least-Squares Planes

Atom	Plane 1	2	3	4	5	6	7	8	9
Fe	0	65	0 (2)						
N(1)	0 (0)		0 (4)						
N(2)	4		2 (5)						
N(3)	0 (0)	12 (4)	−1 (4)						
N(4)	92	10 (4)							
N(1)*	0 (0)	−10 (4)							
N(3)*	0 (0)								
C(1)	−2		−2 (6)						0 (0)
C(2)	38								0 (0)
C(3)	1390								0 (0)
C(4)	1449								
C(10)	37	−20 (5)				13 (5)			
C(11)	104	4 (5)				−14 (5)			
C(12)	295			−68	18	8 (5)	−13 (5)	−11 (5)	
C(13)				0 (0)			12 (3)		
C(14)				0 (0)					
C(15)	3764			0 (0)					
C(16)	3672			0 (0)					
C(17)				0 (0)					
C(18)				0 (0)			−11 (3)		
C(19)	106	5	102	2	80	−8 (5)	13 (5)	11 (5)	
C(20)					0 (0)			−11 (4)	
C(21)					0 (0)				
C(22)	−2878				0 (0)				
C(23)	−2756				0 (0)				
C(24)					0 (0)				
C(25)					0 (0)			11 (4)	
HC(15)	4560								
HC(16)	4405								
HC(22)	−3566								
HC(23)	−3360								

Coefficients of the Plane Equation $Ax + By + Cz = D$[b]

Plane	*A*	*B*	*C*	*D*	Plane	*A*	*B*	*C*	*D*
1	5.451	5.204	−15.411	0.000	6	4.216	5.426	−15.884	−0.232
2	4.880	5.309	−15.679	−0.065	7	5.636	−0.646	17.966	3.805
3	5.444	5.202	−15.423	0.000	8	9.496	4.622	2.215	3.468
4	5.691	−0.415	17.943	3.863	9	8.622	3.215	10.239	0.790
5	9.347	4.835	1.680	3.321					

Angles between Normals to Planes

Plane A	Plane B	Angle (deg)	Plane A	Plane B	Angle (deg)
1	2	3.0	4	6	116.4
1	3	0.0	4	7	1.6
1	4	111.2	5	6	57.3
1	5	52.2	5	8	2.2
1	6	6.5	6	7	117.7
1	9	77.0	6	8	59.3
4	5	59.1			

[a] The entries for which an error is *not* indicated are for atoms which were not included in the calculation of the plane. [b] The plane is in crystal coordinates as defined by W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

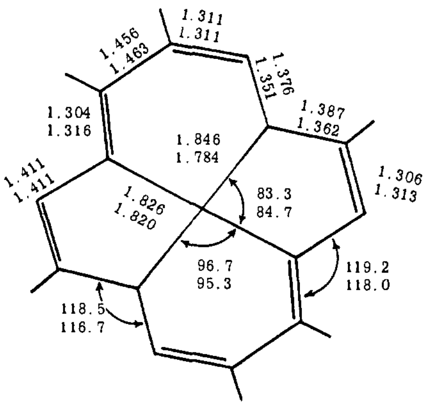

Figure 4. Drawing of the octaaza[14]annulene ring, comparing the bond distances and angles found in the iron complex with those observed by Goedken and Peng[15] in a similar nickel complex (lower entries).

reported by Goedken and Peng.[15] Figure 4 presents the important bond lengths and bond angles found in the two complexes. It is evident that all of the bond lengths within the framework of the two macrocycles are identical in the two structures, except for those about N(1). The N(1)-C(1) and N(1)-N(4) bond lengths in the iron complex are 0.02 Å longer than those in the nickel complex. This lengthening is accompanied by a puckering of the macrocycle about N(1). The distortion of the macrocycle about N(1) appears to be necessary if the ligand is to accommodate an Fe-N(1) bond length of 1.846 (4) Å.

As noted by Goedken and Peng[15] a distinct pattern of alternating double and single bonds is found in the ligand confirming the structural assignments of Baldwin et al.[16] It is interesting that in this iron complex the shorter of the two metal-nitrogen bonds involves N(3) rather than N(1), even though the latter nitrogen atom is formally negatively charged.[15]

The Fe-N bond lengths found in this octaaza[14]annulene complex, 1.826 (4) and 1.846 (4) Å, are the shortest observed to date in any iron(II) macrocycle. The complex has a magnetic moment of 2.8 μ_B at 28° and thus contains iron in the unusual $S = 1$ spin state. The Fe–N bond length found in the complex may be compared with an Fe–N bond length of 1.971 Å found in ferrous tetraphenylporphyrin,[17,18] ($S = 1$, $\bar{\mu} = 4.4\ \mu_B$ at 25°)[18] and with an estimated Fe–N bond length of 1.87 Å[19] for ferrous phthalocyanine ($\mu = 3.96$ at 25°).[20] These data suggest that a relationship exists between the observed magnetic moments and the Fe–N bond lengths in four-coordinate ferrous macrocycles.

The Fe–N bond lengths in this macrocyclic complex are also shorter than the Fe–N bond lengths observed in *low-spin*, octahedral ferrous complexes,[21-28] 1.893–2.166 Å, and are significantly shorter than the *low-spin* Fe–N bond length of 2.01 (2) Å which would be predicted on the basis of effective ionic radii considerations.[29,30]

Goedken et al.[28] have recently suggested that the short equatorial Fe–N bond lengths found in a number of ferrous macrocyclic complexes result from strong back-bonding by iron into the antibonding orbitals of the macrocycles. The constrictive effect of the ligand was held to be of secondary importance. The examples cited by Goedken et al. involved macrocycles containing α-diimine groups and it was suggested that the Fe–N bonds in such systems were particularly strong. In the present complex, I, no such α-diimine linkages are present.

The fact that the macrocycle is puckered in the iron derivative and planar in the nickel complex strongly suggests that the ideal metal–nitrogen bond lengths are somewhat *shorter* than those observed in the iron complex. If the puckering is indicative of strain then it appears, at least in the present case, that stereochemical arguments cannot be discounted as an explanation of the short metal–ligand bond lengths. Hoard[31] has used similar arguments in his discussion of the stereochemistry of metalloporphyrin complexes.

The observation that the iron atom fits within the octaaza[14]annulene ring, despite an effective ionic radius which is 0.1–0.2 Å larger than the hole in the macrocycle, is a good demonstration of the anisotropic nature of transition metal atomic radii. The anisotropy of metal radii is also evident in the structures of a number of metalloporphyrins. The five-coordinate porphyrin complexes of Co(II), Mn(II), and Fe(II)[17,25,30-35] show displacements of the metal atoms which are clearly less than would be predicted from the effective ionic radii of the metals involved. Furthermore, in the six-coordinate complexes of these metals, the metal atoms are centered within the macrocycles, but have elongated axial bonds. Scheidt[33] has pointed out that in the Co(II) complexes the average cobalt–ligand bond length is nonetheless nearly equal to that expected for a Co(II) complex with O_h symmetry. The short equatorial bonds appear to be compensated for by elongated axial bonds. The structures of the four- and five-coordinate complexes may be best explained by describing them as extreme examples of tetragonal distortion. Strong metal–ligand back-bonding need not be invoked.

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Supplementary Material Available. Table I of structure amplitudes, Table III, the parameters for the hydrogen atoms, and Table IV, the root-mean-square amplitudes of vibration, 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 Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-7049.

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