radicals with shorter uv (1500–2000 Å) obtained from a xenon microwave discharge unit did not alter its esr spectrum.

Acknowledgment. The authors wish to thank Drs. E. Hedaya and L. Skattebøl for their stimulating discussions and kind supply of 2- and 4-iodopyridines.

Crystal and Molecular Structure of Bis(dimethylglyoximato)diimidazoleiron(II)–Dimethanol

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Abstract: The crystal and molecular structure of bis(dimethylglyoximato)diimidazoleiron(II)–dimethanol ($Im_2Fe(DMG)_2 \cdot 2CH_3OH$) has been determined from the intensities of 1061 unique observed reflections collected by counter techniques. The complex crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions a = 8.217 (3), b = 10.534 (3), c = 13.260 (5) Å, and β = 94.85 (3)°; d_{measd} = 1.42 (3) g/cm^3, d_{calcd} = 1.41 g/cm^3 for Z = 2. The structure was solved by the heavy atom method and refined by full-matrix least-squares methods to a conventional R = 0.052 and weighted R = 0.058. The complex is centrosymmetric and the iron atom is bound to six nitrogen atoms in a tetragonally distorted octahedral configuration. The O···O contact between the two dimethylglyoxime ligands is 2.588 (8) Å. There is a hydrogen bond between each pair of oxygen atoms and the two O–H distances are 1.0 (1) and 1.5 (1) Å. The O–H···O angle is 159 (4)°. The two N–O distances are significantly different (1.408 (7) and 1.365 (7) Å) resulting from the asymmetry of the hydrogen bond with the longer N–O distance being associated with the shorter O–H bond length. The equatorial Fe–N distances are 1.893 (6) and 1.918 (6) Å and the axial Fe–N bond length is 1.985 (5) Å. In the absence of steric interference between the imidazole hydrogens and the DMG ligands, the axial Fe–N bond distance can be taken as the one to be expected for Fe(II) bound to an axial imidazole.

One of the most interesting and yet unsolved problems of biochemistry is the question of the reversible uptake of molecular oxygen and the cooperative effect observed for this process in hemoglobin. There is little known about the special structural factors in oxygen-carrying complexes since investigations are hampered by the high molecular weight protein portion. There is therefore great interest in low molecular weight metal complexes whose structures resemble those of iron porphyrins. Such model compounds are required to possess unsaturated equatorial ligands containing nitrogen donor atoms and biologically important axial ligands. One such complex is bis(dimethylglyoximato)diimidazoleiron(II) ($Im_2Fe(DMG)_2$).

Although we fully realize that dimethylglyoxime is not a porphyrin ring,[2a] we feel that important structural information can be obtained from such a complex, particularly with regard to the iron–imidazole configuration. In this paper we report the results of the structural determination of the title compound.[2b]

Experimental Section

The crystals were prepared in a special vessel constructed from two 500-ml erlenmeyer flasks connected by a sintered glass frit of medium porosity. During the entire experiment both of the compartments were kept under purified nitrogen. In the first compartment 0.50 g (0.0014 mol) of ferrous perchlorate hexahydrate, 0.33 g (0.0028 mol) of dimethylglyoxime, and 0.19 g (0.0028 mol) of imidazole were placed in 150 ml of dimethylformamide. The second compartment contained 10.9 g (0.0042 mol of tetrabutylammonium hydroxide) of a 10% by weight solution of tetrabutylammonium hydroxide in methanol in 450 ml of methanol. The two compartments were closed under nitrogen and the pressure was adjusted to allow a slow diffusion from the second compartment into the first compartment. After 1 week analytically pure deep red crystals suitable for X-ray diffraction studies were obtained from the first compartment. *Anal.* Calcd for $Im_2Fe(DMG)_2 \cdot 2CH_3OH$: C, 39.52; H, 6.21; N, 23.03. Found:[3] C, 40.37; H, 6.26; N, 23.10.

The space group and approximate unit cell dimensions were determined from preliminary precession and Weissenberg photographs using Ni-filtered Cu Kα radiation. The observed extinctions, $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, suggested the centrosymmetric space group $P2_1/c$ (C_{2h}^5, no. 14).

A small crystal (0.22 × 0.25 × 0.18 mm) in the form of a parallelepiped was chosen and mounted with its a^* axis coincident with the ϕ axis of a G.E. Quarter Circle Orienter incorporated into a G.E. XRD-6 diffractometer system. The air-sensitive crystal was coated with spray varnish to prevent decomposition. All measurements were made at 25° at a take-off angle of 3° with Zr-filtered Mo Kα radiation (λ = 0.7107 Å). A least-squares refinement[4] of accurately measured angular settings for 23 reflections gave the following unit cell parameters: a = 8.217 (7), b = 10.534 (3), c = 13.260

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[2] (a) Cobaloxime, for example, successfully mimics the chemistry of vitamin B_{12}: G. N. Schrauzer, *Accounts Chem. Res.*, 1, 97 (1968). (b) The structure of bis(cyclohexane-1,2-dioximato)diimidazoleiron(II) dihydrate was reported by Prout [C. K. Prout and T. J. Wiseman, *J. Chem. Soc. A*, 497 (1964)], but because of disorder in the cyclohexyl rings the important structural parameters are not accurately known.

[3] Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. 11377.

[4] In addition to the PICKLIST setting program, the main programs used in this work were local modifications of the Busing–Levy ORFLS least-squares program, the Zalkin FORDAP Fourier program, the Busing–Martin–Levy ORFFE function and error program, and the Johnson ORTEP plotting program. Various other local programs were also used. All computing was performed on the Temple University CDC 6400 computer.

(5) Å; $\beta = 94.85(3)°$ and $V = 1143.7$ Å^3. The experimental density of 1.42 (3) g/cm^3 obtained by flotation in carbon tetrachloride–hexane agrees well with the calculated density of 1.41 g/cm^3 for two molecules per unit cell.

The intensities were measured on a manually operated G.E. XRD-6 diffractometer by a scintillation counter with the pulse height selector set to receive 90% of the Mo Kα line. A coupled θ–2θ scanning technique was employed with a scan speed of 2°/min and a scan range of 2° centered on the calculated 2θ value. Background measurements for 20 sec were made both at the beginning and end of the scan range.

A total of 1426 independent reflections was collected ($2\theta_{\max} = 45°$). The intensities of four reflections [(300), (020), (002), (011)] chosen as standards were monitored every 4 hr to check crystal and instrument stability. The alignment of the crystal was checked twice a day. Deviations of the intensities of the standard reflections from their mean values never exceeded 3%.

After the data had been corrected for background, Lorentz and polarization factors were applied to the observed intensities to obtain a set of $|F_o|^2$ values, where $|F_o|$ is the observed structure factor amplitude. No absorption correction was applied because of the uniformity of the crystal and the small linear absorption coefficient (μ 7.84 cm^{-1}), and because of the observation that at $\chi = 90°$ the intensities of several $h00$ reflections varied by less than 1% as a function of ϕ. The resulting $|F_o|^2$ were then brought to an approximately absolute scale through a modification of Wilson's procedure.

Solution and Refinement

Since the molecule is required to possess a crystallographic center of symmetry, the iron atoms were placed at the 2a special position of the unit cell and a difference Fourier map based on phases obtained from the iron atoms revealed the positions of all nonhydrogen atoms with the exception of the solvent of crystallization.

The complete trial structure was refined by a least-squares method. The function minimized was $\Sigma w \cdot (|F_o| - |F_c|)^2$ where the weights were taken as $4F_o^2/\sigma^2(F_o)^2$ and the standard deviations were estimated according to the formula[5]

$$\sigma(F_o^2) = (1/Lp)(C + B + (0.02P)^2)^{1/2}$$

in which Lp is the Lorentz–polarization factor, C is the count accumulated during the scan, B is the total background count, and P is the net count for the reflection. The neutral O, N, C, and H scattering factors were obtained from Ibers' tabulation.[6] The neutral Fe scattering factors were obtained from Cromer and Waber[7] and the anomalous parts of the Fe scattering factors were obtained from Cromer's tabulation[8] and included in the calculated structure factors. Only those reflections with $F_o^2 > 2\sigma(F_o^2)$ were included in the refinement and in the calculation of the discrepancy indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

Three cycles of least-squares refinement in which individual positional and isotropic thermal parameters were varied converged to $R = 0.204$ and $R' = 0.239$. A difference Fourier map calculated at this stage showed several peaks of relatively high electron density and these were assumed to be associated with the solvent molecule. One of the peaks had electron density comparable to a carbon atom in this structure (3.0 e/Å^3) while the other peaks were considerably lower. This indicated to us that the methanol molecule is disordered. After testing several configurations we concluded that the best model involves an ordered carbon atom and three oxygen positions each with an occupancy of 0.33. Three cycles of refinement based on this model converged to $R = 0.091$ and $R' = 0.100$.

Table I. Positional and Thermal Parameters for $Im_2Fe(DMG)_2 \cdot 2CH_3OH$

Atom	X	Y	Z	B, Å^2
Fe[a]	0.0 (0)	0.0 (0)	0.0 (0)	2.33 (5)[b]
O_1	−0.1837 (6)	0.2365 (4)	−0.0356 (4)	3.6 (2)[b]
O_2	−0.1129 (5)	−0.2552 (4)	−0.0456 (3)	3.1 (2)[b]
N_1	−0.1816 (8)	0.1031 (5)	−0.0428 (4)	2.6 (3)[b]
N_2	−0.1504 (7)	−0.1289 (6)	−0.0504 (4)	2.6 (3)[b]
N_3	−0.0769 (6)	−0.0135 (6)	0.1376 (3)	2.5 (2)[b]
N_4	−0.1292 (8)	−0.0906 (5)	0.2873 (5)	3.2 (3)[b]
C_1	−0.3118 (10)	0.0476 (6)	−0.0874 (6)	2.9 (4)[b]
C_2	−0.2950 (10)	−0.0910 (7)	−0.0898 (6)	2.9 (3)[b]
C_3	−0.4643 (9)	0.1189 (7)	−0.1316 (6)	4.3 (4)[b]
C_4	−0.4257 (9)	−0.1821 (7)	−0.1344 (7)	4.6 (4)[b]
C_5	−0.1354 (9)	0.0825 (7)	0.1956 (6)	3.0 (4)[b]
C_6	−0.1670 (10)	0.0371 (6)	0.2880 (6)	3.2 (4)[b]
C_7	−0.0753 (9)	−0.1149 (7)	0.1959 (6)	3.0 (3)[b]
H_1	−0.0700	0.2650	0.0000	6 (3)
H_2	−0.1234	0.1656	0.1647	2 (2)
H_3	−0.2169	0.1026	0.3449	4 (2)
H_4	−0.1162	−0.1647	0.3446	3 (2)
H_5	−0.0408	−0.1976	0.1697	1 (2)
C_8	0.2736	0.0033	0.3911	9.2 (6)[b]
O_3	0.3391	0.0826	0.4652	6.4 (5)
O_4	0.4377	0.0323	0.3831	8.8 (6)
O_5	0.2948	0.1264	0.3981	10.0 (8)

[a] Estimated standard deviations in the least significant figure(s) in this and all subsequent tables are given in parentheses. [b] These thermal parameters are the isotropic equivalents of the anisotropic parameters in Table II.

At this point it was noticed by examination of the structure factor table that several reflections showed large discrepancies between $|F_o|$ and $|F_c|$. These reflections were found to be affected by streaking and thus omitted from subsequent calculation.

The difference Fourier map obtained after additional least-squares refinement in which all of the atoms of the complex and the methanol carbon were refined anisotropically revealed several peaks of electron density 0.6 e/Å^3. The positions of these peaks agreed well with the anticipated positions of the imidazole hydrogen atoms and the hydrogen atom bridging the two oxygen atoms of the DMG ligands. They were assigned isotropic thermal parameters and included in the final three cycles of refinement which converged to $R = 0.058$ and $R' = 0.052$ for 1061 reflections above 2σ. The final difference Fourier map exhibited no peaks higher than 0.2 e/Å^3. The esd of an observation of unit weight was 1.54, and the largest parameter shifts in the final cycle of refinement were less than 0.11 of their estimated standard deviation.

A table of the final values of $|F_c|$ and $|F_o|$ is available.[9] Final positional coordinates and thermal parameters are given in Tables I and II, respectively. Root mean square amplitudes of vibration along the principle ellipsoid axes are shown in Table III. The important

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(5) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, Appendix H.

(6) J. A. Ibers, "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, 1962, Table 3.3.1.

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

(8) D. T. Cromer, *ibid.*, 18, 104 (1965).

(9) The calculated value of $F(000)$ is 500. A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table II. Thermal Parameters for Atoms Varied Anisotropically^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.0110 (2)	0.0049 (1)	0.00257 (7)	0.0002 (2)	−0.0002 (2)	0.0001 (1)
O_1	0.0174 (11)	0.0044 (5)	0.0058 (4)	0.0010 (6)	−0.0004 (5)	0.0000 (3)
O_2	0.0167 (10)	0.0045 (5)	0.0039 (3)	−0.0005 (6)	0.0000 (5)	−0.0006 (3)
N_1	0.0138 (13)	0.0046 (6)	0.0030 (5)	0.0002 (7)	0.0006 (6)	0.0000 (4)
N_2	0.0133 (13)	0.0052 (7)	0.0029 (4)	−0.0011 (7)	0.0009 (6)	−0.0002 (4)
N_3	0.0129 (10)	0.0045 (5)	0.0026 (3)	−0.0001 (8)	0.0001 (4)	0.0010 (5)
N_4	0.0154 (13)	0.0065 (7)	0.0035 (4)	−0.0002 (8)	0.0001 (6)	0.0003 (5)
C_1	0.0137 (17)	0.0060 (8)	0.0032 (5)	−0.0000 (9)	0.0001 (8)	0.0000 (5)
C_2	0.0113 (17)	0.0072 (8)	0.0032 (5)	0.0005 (10)	−0.0004 (7)	0.0007 (5)
C_3	0.0142 (17)	0.0104 (10)	0.0060 (7)	0.0052 (11)	−0.0035 (8)	−0.0000 (6)
C_4	0.0115 (15)	0.0101 (10)	0.0082 (7)	−0.0031 (10)	−0.0039 (8)	−0.0028 (7)
C_5	0.0142 (17)	0.0057 (8)	0.0040 (6)	−0.0002 (9)	0.0014 (7)	0.0004 (5)
C_6	0.0157 (16)	0.0072 (9)	0.0034 (5)	−0.0003 (9)	0.0014 (7)	−0.0005 (5)
C_7	0.0143 (16)	0.0063 (9)	0.0033 (5)	0.0077 (10)	0.0007 (7)	−0.0006 (6)
C_8	0.0326 (27)	0.0151 (13)	0.0169 (10)	−0.0034 (23)	−0.0010 (13)	−0.0029 (15)

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

Table III. Root Mean Square Amplitudes of Vibration along Principle Ellipsoid Axes (Å)

Atom	Min	Intermediate	Max
Fe	0.148 (2)	0.166 (2)	0.197 (2)
O_1	0.156 (10)	0.220 (9)	0.254 (8)
O_2	0.154 (10)	0.190 (9)	0.240 (8)
N_1	0.160 (12)	0.163 (13)	0.216 (11)
N_2	0.158 (13)	0.167 (12)	0.216 (11)
N_3	0.131 (16)	0.178 (12)	0.211 (8)
N_4	0.174 (12)	0.193 (11)	0.230 (10)
C_1	0.168 (15)	0.185 (13)	0.217 (13)
C_2	0.158 (17)	0.203 (14)	0.205 (12)
C_3	0.144 (17)	0.235 (13)	0.296 (13)
C_4	0.127 (19)	0.252 (12)	0.306 (12)
C_5	0.172 (15)	0.193 (14)	0.222 (14)
C_6	0.167 (14)	0.203 (14)	0.232 (12)
C_7	0.164 (17)	0.194 (15)	0.221 (13)
C_8	0.266 (19)	0.342 (17)	0.401 (13)

Table IV. Significant Intramolecular Distances (Å) and Angles (Degrees) for $Im_2Fe(DMG)_2 \cdot 2CH_3OH$

Atoms	Distance	Atoms	Angle
$Fe{-}N_1{}^a$	1.893 (6)	N_2FeN_1	80.4 (6)
$Fe{-}N_2$	1.918 (6)	FeN_1C_1	118.1 (5)
$Fe{-}N_3$	1.985 (5)	$N_1C_1C_2$	112.1 (8)
$N_1{-}O_1$	1.408 (7)	$C_1C_2N_2$	112.1 (8)
$N_2{-}O_2$	1.365 (7)	C_2N_2Fe	117.1 (5)
$N_1{-}C_1$	1.315 (9)	$N_2C_2C_4$	123.0 (7)
$N_2{-}C_2$	1.319 (9)	$C_4C_2C_1$	124.8 (8)
$C_1{-}C_2$	1.467 (9)	$N_1C_1C_3$	124.2 (7)
$C_1{-}C_3$	1.533 (10)	$C_2C_1C_3$	123.6 (8)
$C_2{-}C_4$	1.523 (10)	FeN_2O_2	122.5 (5)
$O_1{-}O_{2i}$	2.588 (8)	FeN_1O_1	124.5 (5)
$O_1{-}H_1$	1.0 (1)	N_3FeN_2	91.3 (2)
$O_{2i}{-}H_1$	1.5 (1)	N_3FeN_1	90.7 (3)
$N_3{-}C_5$	1.382 (9)	$N_3C_5C_6$	110.2 (7)
$C_5{-}C_6$	1.359 (10)	$C_5C_6N_4$	106.0 (7)
$C_6{-}N_4$	1.381 (8)	$N_4C_7O_5$	68.0 (6)
$N_4{-}C_7$	1.349 (9)	$C_7N_3C_5$	104.6 (6)
$C_7{-}N_3$	1.319 (9)	C_7N_3Fe	127.5 (5)
$C_3{-}C_4$	3.187 (12)	$N_2O_2H_{1i}$	106 (4)
$C_5{-}H_2$	1.0 (1)	$O_2H_{1i}O_{1i}$	159 (4)
$C_6{-}H_3$	1.1 (1)	$N_3C_5H_2$	112 (4)
$N_4{-}H_4$	1.1 (1)	$H_2C_5C_6$	137 (4)
$C_7{-}H_5$	1.0 (1)	$C_5C_6H_4$	126 (4)
$H_5{-}O_2$	2.9 (1)	$C_6N_4H_4$	135 (4)
$H_2{-}O_1$	2.8 (1)	$H_4N_4C_7$	118 (4)
$C_8{-}O_3$	1.365 (22)	$N_4C_7H_5$	128 (4)
$C_8{-}O_4$	1.395 (23)	$H_5C_7N_3$	120 (4)
$C_8{-}O_5$	1.311 (29)	$N_1O_1H_1$	107 (4)
$O_4{-}O_5$	1.562 (34)	$N_{2i}FeN_1$	99.6 (2)
$O_3{-}O_4$	1.507 (28)	$O_1N_1C_1$	117.3 (6)
$O_5{-}O_3$	1.040 (31)	$C_2N_2O_2$	120.4 (6)
$Fe{-}C_8$	5.476 (12)	FeN_3C_5	127.7 (5)
		$C_6N_4C_7$	106.4 (7)
		$N_4C_7N_3$	112.6 (7)
		$C_5C_6H_4$	119 (4)
		$H_4C_6N_4$	134 (4)

Table V. Analysis of the Agreement between Observed and Calculated Structure Factor Amplitudes[9]

Range of sin θ/λ	No. of reflections within range	R	R'
0.000–0.228	94	0.057	0.062
0.228–0.304	128	0.046	0.042
0.304–0.380	214	0.051	0.042
0.380–0.456	282	0.064	0.053
0.456–0.532	308	0.078	0.067
All	1061	0.058	0.052

bond lengths and bond angles are depicted in Figures 1 and 2 and in Table IV. Table V shows an analysis of the agreement between observed and calculated structure factor amplitudes. A perspective view of the molecule is shown in Figure 3.

Description of the Structure and Discussion

The $Im_2Fe(DMG)_2 \cdot 2CH_3OH$ molecule is required to be centrosymmetric with the iron atom occupying the center of symmetry. Each iron atom is bound to six nitrogen donor atoms in a tetragonally distorted octahedral configuration. As expected, both the DMG and the imidazole ligands are planar. The bond distances and bond angles within the imidazole ring are very similar to those observed in other metal complexes containing this ligand.[10] The two C–N bond lengths in the DMG ligand are not significantly different and their average value is 1.317 Å. The C–Me distances average 1.528 Å, in good agreement with a C–C single bond value.[11] The C_1–C_2 distance of 1.467 (9) Å is significantly shorter than the C–Me distances and this is expected for a five-membered ring system in which some electron delocalization occurs.

An electron density map through the $Fe(DMG)_2$ plane is depicted in Figure 4. The positions of the two bridging hydrogen atoms are quite apparent and each is clearly located closer to one of the oxygen atoms. The two O–H distances are 1.0 (1) and 1.5 (1) Å and the

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(10) H. C. Freeman, *Advan. Protein Chem.*, **22**, 290 (1967).

(11) A. Almenningen and O. Bastiansen, *Acta Chem. Scand.*, **9**, 815 (1955).

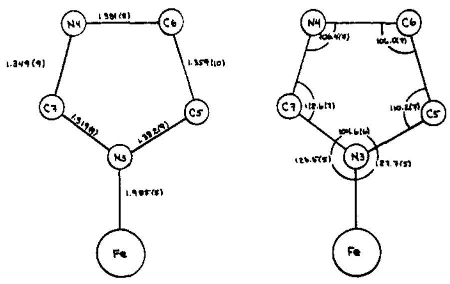

Figure 1. Bond lengths and angles for the imidazole moiety.

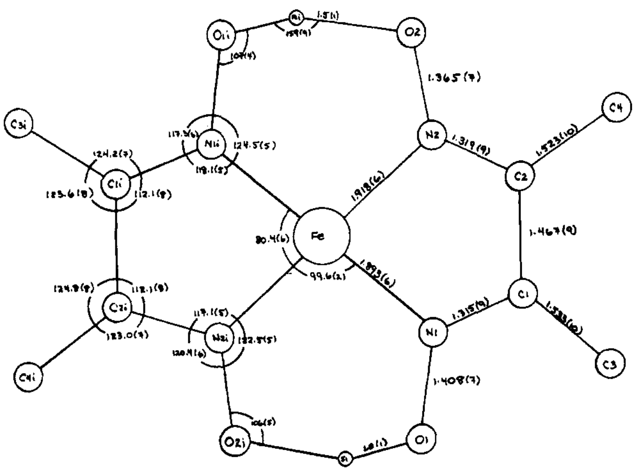

Figure 2. Bond lengths and angles for the DMG plane.

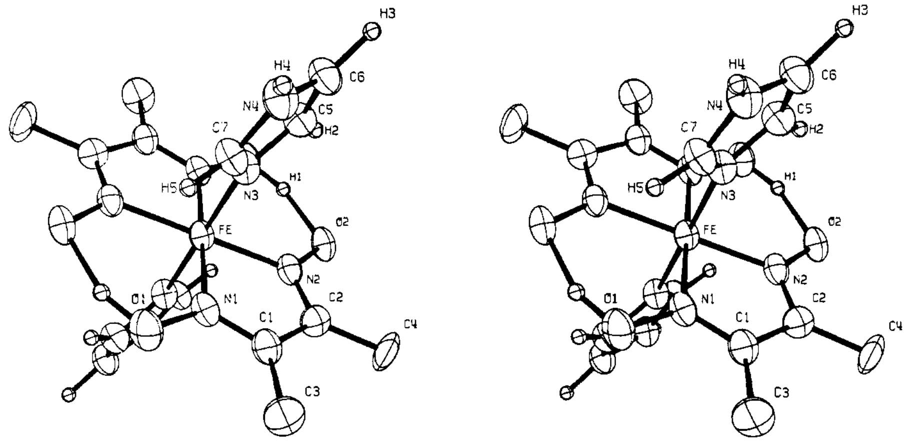

Figure 3. A perspective view of the $Im_2Fe(DMG)_2$ molecule.

O-H-O angle is 159 (4)°. Thus, the O-H···O bridge can be thought of as having one O-H covalent bond and one O···H hydrogen bond in contrast to a symmetrical configuration in which both bonds can be considered as hydrogen bonds. The two O-H distances are in good agreement with those observed in the structure of $(glycine)_2HNO_3$.[12] In support of the above conclusion we note that the two independent N-O distances are significantly different, being 1.408 (7) and 1.365 (7) Å for N_1–O_1 and N_2–O_2, respectively. The long N-O distance is associated with the oxygen atom which is covalently bound to the hydrogen atom. The use of the N-O distances as criteria for the configuration of the hydrogen bridge is quite useful especially in those cases where the hydrogen atom can not be located with certainty. Thus, the hydrogen bridge in $Ni(DMG)_2$ is probably symmetric since the two N-O distances are the same.[13] On the other hand, in $Cu(DMG)_2$ where the hydrogen was found to be closer to one of the oxygen atoms, the two N-O distances are significantly different, being 1.385 (5) and 1.331 (5) Å.[14]

The disordered methanol molecule was best accounted for, as previously mentioned, by a model in which the carbon atom is ordered and each of the three oxygen positions is occupied one-third of the time. This model results in an average C-O distance of 1.36 (3) Å. Although this distance is somewhat shorter than the expected value of 1.427 (7) Å,[15] we feel that this model adequately describes the disorder. Since no correlation between the parameters of the solvent molecule and those of the complex was found, this point was not investigated further.

Of particular interest in this structure is the configuration of the coordination sphere. As mentioned previously, the six nitrogen donor atoms impose a tetragonally distorted octahedral configuration on the iron atom. The in-plane Fe-N distances (average 1.905 Å) are significantly shorter than the axial Fe-N bond length of 1.985 (5) Å, and this undoubtedly results from the hydrogen bonds which hold the two DMG ligands tightly together. The axial Fe-N bond is normal to the plane of the molecule, but the imidazole ring is tilted with respect to this plane by 4°. (The dihedral angle between the plane of the imidazole and the DMG plane is 86.0 (5)°.) The orientation of the ring is such that the C_5 hydrogen is situated above O_1 at a distance of 2.8 (1) Å where 2.8 Å is the van der Waals' radius[16] while the C_7 hydrogen lies above the O_2–O_{1i} midpoint 2.9 (1) Å from O_2. Thus, in the absence of steric interference between the DMG ligands and the above hydrogen atoms the axial Fe-N distance can be taken as the one to be expected for Fe(II) bound to an axial imidazole.[2]

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A very useful comparison can now be made between this structure and the structure of bis(imidazole)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III) chloride (Im_2FeTPP^+) recently reported by Hoard.[17] We first note that the in-plane Fe–N distances in the DMG complex are considerably shorter than the value of 1.989 Å observed in Im_2FeTPP^+ and this lends strong support to Hoard's conclusion that the equatorial Fe–N bond lengths in porphyrin complexes are governed by the "resistance of the porphyrin skeleton to undue radial contraction."

Of the two axial Fe–N distances in Im_2FeTPP^+ [1.991 (5) and 1.957 (4) Å] the shorter distance is of interest since in the absence of steric interference between the imidazole hydrogens and the porphyrin ring, this distance can be taken as the one to be expected for Fe(III) bound to an axial imidazole. It is reasonable to suggest that the contraction of the Fe–imidazole bond length by approximately 0.03 Å is directly related to the oxidation state of the iron and as expected the shorter distance is observed for the higher oxidation state.

These results suggest to us that structural studies on DMG complexes of Fe(II) can be very useful in investigating structural problems of iron–porphyrin complexes. One such problem which has drawn considerable attention in the last several years is determining the spatial configuration of the iron atom and the imidazole moiety with respect to the plane of the porphyrin ring. Of particular interest in this respect are complexes in which one of the imidazole rings is replaced by ligands such as CO, NO, N_3^-, and CN^-. These complexes are currently under investigation in our laboratories.

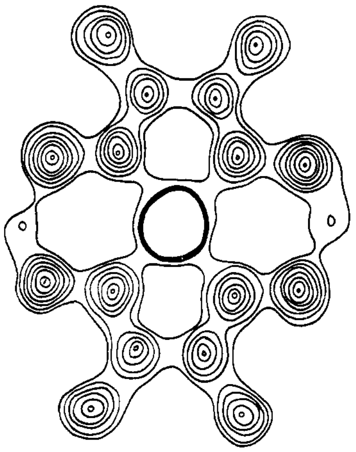

Figure 4. Electron density map through the DMG plane. The lowest contour on the map represents an electron density of 0.2 e/Å and succeeding contours are in increments of 0.5 e/Å. Electron densities greater than 5.0 e/Å are not depicted.

Acknowledgments. We wish to thank Messrs. S. Lipton, B. Spivack, and J. Reed for assistance and the Temple University Chemistry Department for financial support. We also wish to thank the Temple University Computer Center and the Research Corporation for its Equipment Grant.

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Nuclear Magnetic Resonance Spectra of Bis(pyridinato)iron(III)–Protoporphyrin IX Complexes

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Received October 30, 1970

Abstract: The ^1H nuclear magnetic resonance spectra of a series of bis(pyridinato)iron(III)-protoporphyrin IX complexes are described. There is a linear relationship between the paramagnetic chemical shifts of the porphyrin protons and the basicity of the coordinated pyridine which is most marked for the peripheral methyl protons. The pseudocontact contribution to the shifts has been estimated and is considered to be appreciable at the meso hydrogens. The main mechanism for spin delocalization at the pyrrole ring carbons is deduced to be charge transfer from a ligand π orbital to the iron. The temperature dependence of the shifts provides evidence for a low-spin–high-spin equilibrium.

The nuclear magnetic resonance (nmr) spectroscopy of paramagnetic metal complexes has proved[3] most useful in revealing details of electronic and molecular structure. In particular it has been possible to derive unequivocal information on electron delocalization. We have previously investigated[4] electron delocalization in diamagnetic complexes but in a number of cases the interpretation of the results was complicated by possible contributions from electric field and ring current effects. Therefore we sought a series of complexes in which one of the ligands was easily varied and most important that the scalar contribution to the paramagnetic shift was large compared to the dipolar term. Since preliminary investigations of bispyridine

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