Article

Synthesis of Binuclear Bismacrocyclic Iron(II) Complex by the Aerobic Oxidation of Iron(II) Complex of 1,4,8,11-Tetraazacyclotetradecane

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The aerobic oxidation of the Fe(II) complex of 1,4,8,11-tetraazacyclotetradecane, $[Fe(cyclam)(CH_3CN)_2](ClO_4)_2$, in MeCN in the presence of a few drops of $HClO_4$ leads to low spin Fe(III) species $[Fe(cyclam)(CH_3CN)_2](ClO_4)_3$. The Fe(III) cyclam complex is further oxidized in the air in the presence of a trace of water to produce the deep green binuclear bismacrocyclic Fe(II) complex $[Fe_2(C_{20}H_{36}N_8)(CH_3CN)_4](ClO_4)_4 \cdot 2CH_3CN$. The Fe(II) ions of the complex are six-coordinated and the bismacrocyclic ligand is extensively unsaturated. $[Fe_2(C_{20}H_{36}N_8)(CH_3CN)_4](ClO_4)_4 \cdot 2CH_3CN$ crystallizes in the monoclinic space group $P2_1/n$ with $a=13.099$ (1) Å, $b=10.930$ (1) Å, $c=17.859$ (1) Å, $\beta=95.315$ (7)°, and $Z=2$. The structure was solved by heavy atom methods and refined anisotropically to R values of $R=0.0633$ and $R_w=0.0702$ for 1819 observed reflections with $F>4\sigma(F)$ measured with Mo Kα radiation on a CAD-4 diffractometer. The two macrocyclic units are coupled through the bridgehead carbons of β-diimine moieties by a double bond. The double bonds in each macrocycle unit are localized. The average bond distances of $Fe(II)-N_{imine}$, $Fe(II)-N_{amine}$, and $Fe(II)-N_{MeCN}$ are 1.890 (5), 2.001 (5), and 1.925 (6) Å, respectively. The complex is diamagnetic, containing two low spin Fe(II) ions in the molecule. The complex shows extremely intense charge transfer band in the near infrared at 868 nm with $\varepsilon=25,000$ $M^{-1}cm^{-1}$. The complex shows a one-electron oxidation wave at $+0.83$ volts and two one-electron reduction waves at -0.43 and -0.72 volts vs. Ag/AgCl reference electrode. The complex reacts with carbon monoxide in $MeNO_2$ to form carbonyl adducts, whose ν_{CO} value (2010 cm^{-1}) indicates the π-accepting property of the present bismacrocyclic ligand.

Introduction

Metal-catalyzed aerobic oxidation is an interesting subject.[1-12] Some porphyrin and macrocyclic complexes have been reported to catalyze the aerobic oxidation of organic compounds.[1-8] In addition, some macrocyclic complexes themselves are oxidized by dioxygen to yield the complexes of unsaturated or oxygenated macrocyclic ligand, depending on the metal ion and the type of macrocyclic ligand.[13-30] For example, the aerobic oxidation reactions described in Eq. (1)-(4) occurs with Fe(II) and Co(II) macrocyclic complexes.[15,16,19,20]

$$(1)$$

(AN = MeCN)

$$(2)$$

$$(3)$$

$$(4)$$
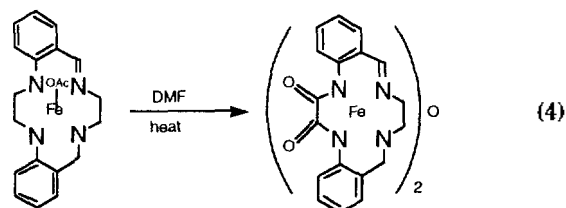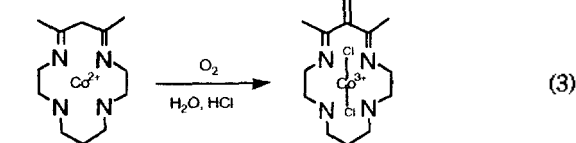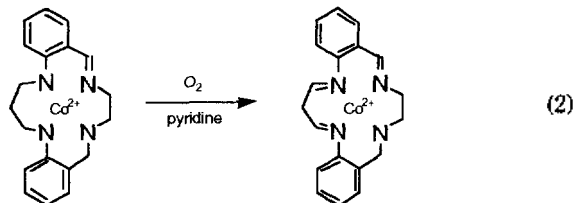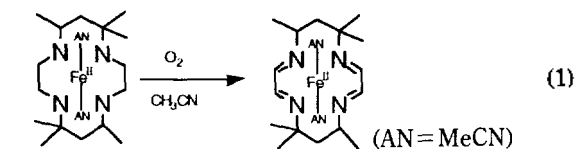
Previously, we reported that the aerobic oxidation of Fe(II) cyclam complex produced an intense green Fe(II) complex.[22] We postulated that the green complex was the highly unsaturated monomacrocyclic Fe(II) complex **A**. However, we have recently reexamined the green complex and found that the complex is a binuclear bismacrocyclic Fe(II) complex **2** (Eq. 5) instead of **A**.[23] Here, we report the formation, properties, and the structure of the binuclear bismacrocyclic Fe(II) complex.[23-25]

A

$$(5)$$

1   **2**

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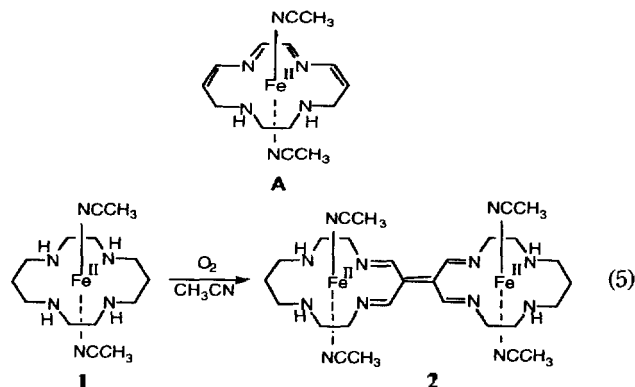
Experimental Section

Reagents. All chemicals and solvents, except acetonitrile, used in the syntheses were of reagent grade and were used without purification. Acetonitrile was purified according to the literature method.[26]

Measurements. Infrared spectra were recorded with a Perkin-Elmer 782 infrared spectrophotometer. Conductance measurements were performed by using YSI model 32 conductometer. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker AC80 FT NMR spectrometer. Electronic absorption spectra were obtained on a Shimadzu 260 UV/vis spectrophotometer. Elemental analyses were performed by Galbraith Laboratories Inc. Knoxville. TN. Cyclic voltammetry was carried out with BAS 100A Electrochemical Analyzer. The electrochemical data were obtained in MeCN with 0.1 M (n-Bu)$_4$NClO$_4$ as supporting electrolyte. The working electrode was a platinum disc, the auxiliary electrode was a coiled platinum wire, and the reference electrode was a Ag/AgCl. Magnetic susceptibility was measured with Faraday type magnetometer and calibrated with Gd$_2$O$_3$.

Synthesis. Safety Note. *Caution!*. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

The Fe(II) cyclam complex [Fe(cyclam)(CH$_3$CN)$_2$](ClO$_4$)$_2$ was prepared according to the method previously reported.[22]

[Fe^{III}(cyclam)(CH$_3$CN)$_2$](ClO$_4$)$_3$. [Fe(cyclam)(CH$_3$CN)$_2$]-(ClO$_4$)$_2$ (1 g) was dissolved in MeCN (20 mL) and a few drops of HClO$_4$ were added. The solution was stirred rapidly in the air for several minutes until yellow precipitates formed, which were filtered, washed with MeCN, and dried *in vacuo*. Yield: ~90%. Anal. Calcd for FeC$_{14}$H$_{30}$N$_6$Cl$_3$O$_{12}$: C, 26.41; H, 4.75; N, 13.20. Found: C, 26.45; H, 4.70; N, 13.19.

[Fe$_2^{II}$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](ClO$_4$)$_4$·2CH$_3$CN. To the MeCN suspension (20 mL) of Fe(III) complex (1 g) were added a few drops of H$_2$O and the solution was stirred in the air at room temperature for several days. The color of the solution turned to deep violet and the deep green crystals precipitated from the solution. The green crystals were filtered and washed with a 1:1 mixture of MeCN and ethyl ether. The single crystals used for the X-ray diffraction studies were obtained from the crude product. Yield = ~70%. Anal. Calcd for [Fe$_2$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](ClO$_4$)$_4$·2CH$_3$CN: C, 33.59; H, 4.76; N, 17.14. Found: C, 32.36; H, 4.21; N, 17.96.

[Fe$_2^{II}$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](PF$_6$)$_4$. The crude product [Fe$_2$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](ClO$_4$)$_4$·2CH$_3$CN often contained rusts which interfered measurements of NMR spectrum and cyclic voltammogram, and was purified according to the following method. To the MeCN suspension (15 mL) of the perchlorate complex (1 g) was added excess NH$_4$PF$_6$ (1.3 g). The complex went into the solution and NH$_4$ClO$_4$ precipitated, which was filtered off. Water was added dropwise to the green solution to induce crystallization. The crystals were filtered, washed with a 1:1 mixture of MeCN and water, and dried *in vacuo*. The PF$_6^-$ salt was dissolved in a minimum amount of MeCN, and the solution was centrifuged to remove the rust. The solution was filtered and then ethyl ether was added dropwise to the solution until the solution became turbid. The solution was allowed to stand

Table 1. Crystal Data and Data Collection for [Fe$_2$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](ClO$_4$)$_4$·2CH$_3$CN

|	
formula	Fe$_2$C$_{28}$H$_{48}$N$_{12}$Cl$_4$O$_{16}$·(CH$_3$CN)$_2$
f_w	1144.39
space group	$P2_1/n$
a, Å	13.099 (1)
b, Å	10.930 (1)
c, Å	17.859 (1)
β, deg	95.315 (7)
V, Å^3	2545.8 (5)
Z	2
d_{calcd}, gcm^{-3}	1.50
crystal size, mm	0.21×0.27×0.39
μ, cm^{-1}	7.90
scan method	$\omega/2\theta$
data collected	h, k, ±1, 1<2θ<23
no. total observation	2306
no. unique data>4σ(F)	1819
no. parameters refined	310
abs. corr. factor range	0.9545-0.9995
largest shift/esd	0.03
gof	0.372
$R=(\Sigma F_o-F_c)/\Sigma F_o$	0.0633
$R_w=(\Sigma F_o-F_cw^{1/2})/\Sigma F_ow^{1/2}$	0.0702

$w=1.000/(\sigma^2(F)+0.003599\,F^2)$

in a refrigerator until crystals formed. The green PF$_6^-$ crystals were filtered, washed with a 1:1 mixture of MeCN and ethyl ether, and dried *in vacuo*. Anal. Calcd for [Fe$_2$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](PF$_6$)$_4$: C, 27.03; H, 3.89; N, 13.51. Found: C, 26.93; H, 3.52; N, 13.98.

[Fe$_2$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_2$(CO)$_2$](PF$_6$)$_4$. Complex [Fe$_2$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](ClO$_4$)$_4$·2CH$_3$CN was dissolved in a minimum amount of MeNO$_2$, and CO gas was bubbled through the solution until the color of the solution turned to purple. Ethyl ether was added to the solution to precipitate out the carbonyl adducts. The purple precipitates were filtered, washed with 1:1 mixture of MeNO$_2$ and ethyl ether, and then dried with stream of CO gas. The complexes were kept in the bottle filled with CO gas.

X-ray Structure Determination. The crystallographic data collection and refinement details for the structure determination of [Fe$_2$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](ClO$_4$)$_4$·2CH$_3$CN are summarized in Table 1. The intensity data were measured on a CAD-4 Enraf Diffractometer (Mo Kα radiation, monochromated, θ-2θ scans). Absorption corrections were made. The structures were solved by the heavy-atom method. All non-hydrogen atoms were refined anisotropically. All calculations were done by using the program SHELX 76.[27]

Results and Discussion

Synthesis. Fe(II) cyclam complex [Fe(cyclam)](ClO$_4$)$_2$ is oxidized by air, which is a mild oxidant, in MeCN solutions containing a small amount of HClO$_4$ and yields Fe(III) cyclam complex [Fe(cyclam)(CH$_3$CN$_2$](ClO$_4$)$_3$. The magnetic moment (μ_{eff}) of Fe(III) cyclam complex is 2.66 BM, indicating that the Fe(III) ion of the complex is a low spin d.[5] The value

Binuclear Bismacrocyclic Iron(II) Complex

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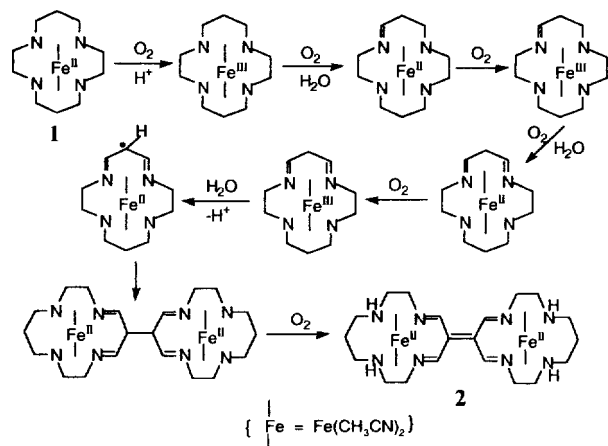
Scheme 1.

of molar conductance (Λ_M) is 300 $\Omega^{-1}cm^{-1}M^{-1}$ in MeCN, which corresponds to a 1:3 electrolyte.[28] Electronic spectrum of the complex (in MeCN) shows maximum absorptions at 372 nm ($\varepsilon=340$ $M^{-1}cm^{-1}$) and 417 sh ($\varepsilon=204$ $M^{-1}cm^{-1}$).

Further aerobic oxidation of Fe(III) cyclam complex [Fe-(cyclam)(CH$_3$CN$_2$](ClO$_4$)$_3$ in MeCN in the presence of traces of water results in binuclear bismacrocyclic Fe(II) complex [Fe$_2$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](ClO$_4$)$_4$·2CH$_3$CN. The proposed reaction path is shown in Scheme 1. The air oxidation of Fe(II) cyclam complex giving Fe(III) species is apparently accelerated by the trace of acid added. The Fe(III) complex is unstable in the presence of a few drops of added water, and the facile electron transfer occurs between the Fe(III) metal center and the coordinated macrocyclic ligand to result in the Fe(II) species having the ligand unsaturation. It was reported that Co(III) or Ni(III) macrocyclic complexs proceeded the base-induced reduction, giving Co(II) or Ni(II) complexes with increased ligand unsaturation.[18,29] The repeated cycle of air-oxidation of Fe(II) species to Fe(III) species followed by the intramolecular electron transfer in the Fe(III) species eventually produces the Fe(II) dimeric complex 2. The major driving force of the intra-molecular electron transfer must be the ligand field stabilization energy of the low spin d^6 Fe(II) ion versus that of low spin d^5 Fe(III) ion.

The crude product of [Fe$_2$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](ClO$_4$)$_4$·2CH$_3$CN is not very soluble in most of the solvents and often contains rusts which interfere the measurements of magnetic susceptibility, NMR spectrum, and cyclic voltammetry. Therefore, the complex has to be purified according to the procedure described in the Experimental Section, changing ClO$_4^-$ anion to PF$_6^-$.

X-ray Structure. A single crystal X-ray structural data of [Fe$_{20}$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](ClO$_4$)$_4$·2CH$_3$CN are summarized in Table 2 and 3. ORTEP plot with the atomic numbering scheme and the packing diagram are presented in Figure 1 and 2, respectively. The complex contains two Fe(II) ions in the two macrocyclic units which are coupled through the bridgehead carbons of the β-diimine moieties by the double bond. The complex has an inversion center at the center of this double bond (C8-C8'). Each Fe(II) ion is coordinated with the four nitrogen donors of the macrocyclic ligand and with two acetonitrile molecules. Each macrocyclic ligand unit contains two imine nitrogens and two amine nitrogens. The

Table 2. Positional and Equivalent Isotropic Thermal Parameters for [Fe$_2$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](ClO$_4$)$_4$·2CH$_3$CN

Atom	x	y	z	U_{eq}[a]
Fe	0.2395 (1)	0.2221 (1)	0.4985 (1)	0.037 (1)
Cl(1)	0.4754 (3)	0.3443 (3)	0.7380 (2)	0.087 (3)
Cl(2)	0.2256 (3)	0.7024 (3)	0.4864 (3)	0.108 (4)
N(1)	0.2219 (6)	0.3390 (7)	0.5774 (4)	0.049 (5)
N(2)	0.2589 (5)	0.1095 (7)	0.4188 (4)	0.046 (5)
N(3)	0.2642 (6)	0.3640 (7)	0.4310 (4)	0.051 (5)
N(4)	0.1007 (5)	0.2367 (6)	0.4617 (4)	0.041 (4)
N(5)	0.2095 (5)	0.0885 (6)	0.5607 (3)	0.036 (4)
N(6)	0.03849 (6)	0.2006 (7)	0.5404 (4)	0.050 (5)
C(1)	0.2135 (8)	0.4146 (10)	0.6202 (6)	0.060 (8)
C(2)	0.2038 (11)	0.5123 (12)	0.6781 (7)	0.096 (11)
C(3)	0.2653 (7)	0.0393 (10)	0.3736 (6)	0.053 (7)
C(4)	0.2763 (8)	−0.0539 (12)	0.3131 (7)	0.095 (11)
C(5)	0.1753 (7)	0.3775 (8)	0.3753 (5)	0.055 (6)
C(6)	0.0790 (7)	0.3520 (8)	0.4184 (5)	0.053 (6)
C(7)	0.0271 (7)	0.1586 (8)	0.4628 (5)	0.043 (6)
C(8)	0.0409 (6)	0.0449 (8)	0.5044 (5)	0.039 (5)
C(9)	0.1293 (6)	0.0193 (7)	0.5568 (5)	0.039 (5)
C(10)	0.2973 (7)	0.0545 (9)	0.6166 (5)	0.055 (7)
C(11)	0.3947 (7)	0.0749 (9)	0.5761 (6)	0.057 (7)
C(12)	0.4668 (8)	0.2273 (11)	0.4911 (7)	0.078 (10)
C(13)	0.4539 (8)	0.3557 (10)	0.4566 (7)	0.071 (8)
C(14)	0.3602 (8)	0.3688 (10)	0.3962 (7)	0.074 (8)
O(1)	0.4530 (7)	0.4032 (9)	0.6692 (5)	0.118 (8)
O(2)	0.3934 (14)	0.3506 (19)	0.7795 (7)	0.241 (26)
O(3)	0.5556 (12)	0.3871 (13)	0.7799 (8)	0.230 (17)
O(4)	0.4895 (11)	0.2201 (11)	0.7264 (8)	0.172 (15)
O(5)	0.1433 (9)	0.6329 (11)	0.4976 (9)	0.173 (15)
O(6a)[b]	0.3023 (15)	0.6152 (18)	0.4947 (19)	0.137 (40)
O(6b)[b]	0.2867 (24)	0.6606 (23)	0.4341 (21)	0.173 (39)
O(7)	0.2636 (25)	0.7564 (26)	0.5601 (16)	0.339 (39)
O(8a)[b]	0.2272 (38)	0.8122 (15)	0.4670 (21)	0.220 (66)
O(8b)[b]	0.1689 (66)	0.7811 (77)	0.4415 (49)	0.528 (99)
N(S)	0.4801 (14)	0.1267 (19)	0.2815 (11)	0.184 (7)
C(1S)	0.4969 (14)	0.2054 (21)	0.2421 (12)	0.146 (7)
C(2S)	0.5154 (17)	0.3006 (24)	0.1905 (14)	0.182 (9)

[a] Equivalent isotropic U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Disordered atom.

Table 3. Selected Bond Distances (Å) and Angles (°) for [Fe$_2$(C$_{20}$H$_{36}$N$_8$)(CH$_3$CN)$_4$](ClO$_4$)$_4$·2CH$_3$CN

Fe-N(1)	1.932 (8)	N(4)-C(7)	1.289 (11)
Fe-N(2)	1.917 (8)	C(7)-C(8)	1.451 (12)
Fe-N(3)	2.008 (8)	C(8)-C(9)	1.448 (11)
Fe-N(4)	1.882 (7)	C(9)-N(5)	1.290 (11)
Fe-N(5)	1.898 (7)	N(5)-C(10)	1.498 (11)
Fe-N(6)	1.995 (7)	C(10)-C(11)	1.540 (14)
N(1)-C(1)	1.137 (13)	C(11)-N(6)	1.515 (12)
C(1)-C(2)	1.502 (17)	N(6)-C(12)	1.479 (14)
N(2)-C(3)	1.122 (13)	C(12)-C(13)	1.536 (16)
C(3)-C(4)	1.502 (17)	C(13)-C(14)	1.563 (15)
N(3)-C(5)	1.468 (12)	C(14)-N(3)	1.454 (14)

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C(5)-C(6)	1.562 (14)	C(8)-C(8)'	1.451 (12)	
C(6)-N(4)	1.492 (11)			
N(2)-Fe-N(1)	178.4 (3)	C(7)-N(4)-C(6)	117.4 (7)	
N(3)-Fe-N(1)	87.9 (3)	C(9)-N(5)-Fe	129.1 (5)	
N(3)-Fe-N(2)	90.6 (3)	C(10)-N(5)-Fe	113.1 (5)	
N(4)-Fe-N(1)	91.3 (3)	C(10)-N(5)-C(9)	117.5 (7)	
N(4)-Fe-N(2)	89.1 (3)	C(11)-N(6)-Fe	107.8 (5)	
N(4)-Fe-N(3)	86.0 (3)	C(12)-N(6)-Fe	118.3 (6)	
N(5)-Fe-N(1)	92.1 (3)	C(12)-N(6)-C(11)	113.1 (7)	
N(5)-Fe-N(2)	89.4 (3)	C(2)-C(1)-N(1)	178.7 (11)	
N(5)-Fe-N(3)	177.3 (3)	C(4)-C(3)-N(2)	178.7 (11)	
N(5)-Fe-N(4)	91.4 (3)	C(6)-C(5)-N(3)	105.9 (7)	
N(6)-Fe-N(1)	88.8 (3)	C(5)-C(6)-N(4)	106.4 (7)	
N(6)-Fe-N(2)	90.9 (3)	C(8)-C(7)-N(4)	121.1 (8)	
N(6)-Fe-N(3)	96.6 (3)	C(9)-C(8)-N(7)	123.4 (7)	
N(6)-Fe-N(4)	177.5 (3)	C(8)-C(9)-N(5)	121.3 (7)	
N(6)-Fe-N(5)	86.1 (3)	C(11)-C(10)-N(5)	105.9 (7)	
C(1)-N(1)-Fe	174.7 (8)	C(10)-C(11)-N(6)	106.7 (7)	
C(3)-N(2)-Fe	175.5 (8)	C(13)-C(12)-N(6)	111.1 (9)	
C(5)-N(3)-Fe	108.8 (8)	C(14)-C(13)-C(12)	114.2 (9)	
C(14)-N(3)-Fe	118.6 (6)	C(13)-C(14)-N(3)	110.9 (9)	
C(14)-N(3)-C(5)	111.7 (8)	C(7)-C(8)-C(8)'	117.9 (7)	
C(6)-N(4)-Fe	112.6 (5)	C(9)-C(8)-C(8)'	118.6 (8)	
C(7)-N(4)-Fe	129.7 (6)			

Figure 2. A packing diagram of [Fe₂(C₂₀H₃₆N₈)(CH₃CN)₄](ClO₄)₄·2CH₃CN.

Figure 1. ORTEP drawing of cation of [Fe₂(C₂₀H₃₆N₈)(CH₃CN)₄]-(ClO₄)₄·2CH₃CN. The atoms are represented by 50% probable thermal ellipsoid.
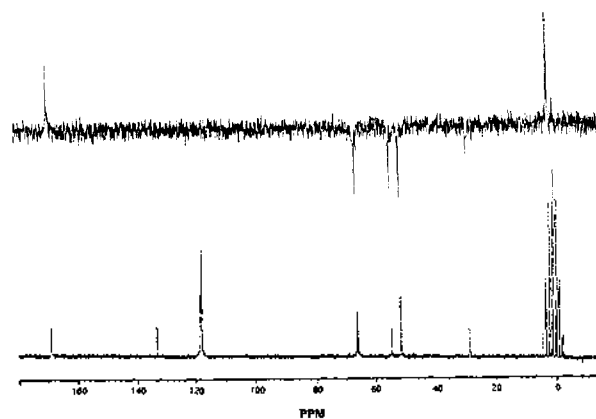
Figure 3. ^{13}C DEPT NMR spectrum of [Fe₂(C₂₀H₃₆N₈)(CH₃CN)₄]-(PF₆)₄ measured in d³-MeCN.

average Fe(II)-imine nitrogen bond distance is 1.890 (5) Å which is significantly shorter than the Fe(II)-amine nitrogen bond distance of 2.001 (5) Å. The bite distance and bite angle involving imine nitrogens [N4-N5, 2.70 (1) Å; N4-Fe-N5, 91.4 (3)°] are much smaller than those involving amine nitrogens [N6-N3, 2.99 (1) Å; N3-Fe-N6, 96.6 (3)°]. The average bond distance between Fe(II) ion and the coordinated acetonitriles is 1.925 (6) Å. The bond distance between C8 and C8' is 1.451 (16) Å, which is longer than the one expected for a double bond. However, the NMR spectra clearly identifies it as a double bond. The lengthening of C8-C8' bond is probably due to the van der Waals repulsion of the azomethine hydrogens. The C7-N4 and C9-N5 bond lengths are 1.289 (11) Å and 1.290 (11) Å respectively, indicating the localized C=N bond. Six atoms array C7, C8, C9, C7', C8', and C9' forms a least square plane with a mean deviation from planarity being 0.008 Å. The bond lengths of C8-C7, C8-C9,
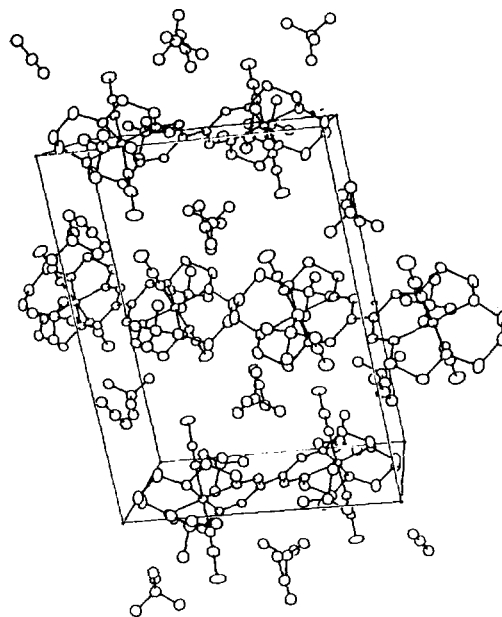
and C8-C8' are 1.451 (12), 1.448 (11), and 1.451 (16) Å, which indicate the delocalization of $p\pi$ electrons through the two macrocyclic rings. N3, N4, N5, N6, and Ni atoms form essentially a plane with the deviations from the least squares plane of less than 0.001 Å.

Properties. Binuclear bismacrocyclic Fe(II) perchlorate complex [Fe₂(C₂₀H₃₆N₈)(CH₃CN)₄](ClO₄)₄·2CH₃CN is reasonably stable in the air both in solid state and in MeCN solutions. The complex contains two Fe(II) ions in six-coordinate low spin states. The magnetic moment of the complex is $\mu_{eff}=0.57$ BM. Infrared spectrum shows ν_{NH} at 3225 cm⁻¹, ν_{CN} of coordinated acetonitrile at 2285 cm⁻¹ and that of uncoordinated acetonitrile at 2248 cm⁻¹, $\nu_{C=N}$ at 1610 cm⁻¹, and $\nu_{C=C}$ at 1550 cm⁻¹. The ^{13}C-DEPT NMR spectrum (Figure 3) of PF₆⁻ salts shows azomethine carbons at δ 168.9, olefinic carbons at δ 133.5, coordinated acetonitrile carbons at δ 118.4, and carbon peaks of saturated hydrocarbon moieties at δ 66.4, 54.6, 51.7, and 29.2 ppm. ¹H-NMR spectrum shows protons of the azomethine carbons at δ 9.75 ppm, and
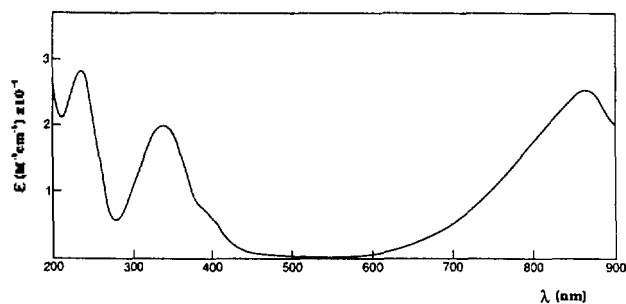
Binuclear Bismacrocyclic Iron(II) Complex

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Figure 4. UV/vis absorption spectrum of $[Fe_2(C_{20}H_{36}N_8)(CH_3CN)_4]$-$(PF_6)_4$ in MeCN solution.
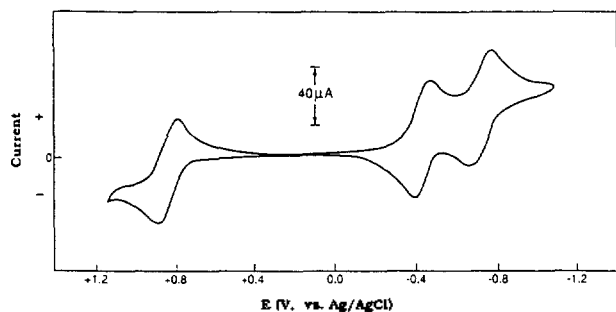
Figure 5. Cyclic voltammogram of $[Fe_2(C_{20}H_{36}N_8)(CH_3CN)_4](PF_6)_4$ (1.39×10^{-3} M) measured in MeCN containing 0.1 M n-Bu$_4$N ClO$_4$ (scan rate 20 mV/sec). Potential in volts vs. Ag/AgCl.

the methylene protons at δ 2.20-4.80 ppm. The value of the molar conductance for the MeCN solutions of the PF$_6$ salt is 457 Ω $^{-1}$cm^{2}M^{-1}, indicating that the complex is a 1:4 type electrolyte.[28] Electronic absorption spectrum for the MeCN solution (Figure 4) shows remarkably intense charge transfer bands at 868 nm (ε = 25,000 M^{-1}cm^{-1}), 343 nm (ε = 20,000 M^{-1}cm^{-1}), and 237 nm (ε = 28,000 M^{-1}cm^{-1}). It is noteworthy that the complex absorbs at much longer wavelengths with about ten times larger extinction coefficient than the low spin Fe(II) complex of completely conjugated ligand system **B**, which absorbs at 770 nm (ε = 1880) and 705 (ε = 1520).[30]

B
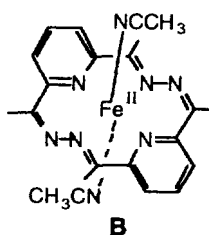
Cyclic voltammetry (Figure 5) indicates a one-electron oxidation wave at +0.83 volts and two one-electron reduction waves at −0.43 and −0.72 volts vs. Ag/AgCl reference electrode. This shows more difficult oxidation and significantly easier reduction of the Fe(II) dimer complex **2** than the parent Fe(II) cyclam complex (Fe^{II}/Fe^{III}, +0.54 volts; Fe^{II}/Fe^{I}, < −2.0 volts).[31] It has been observed for other macrocyclic complexes that the oxidation of the metal ion becomes more difficult and the reduction becomes easier as the degree of unsaturation of the macrocyclic ligand increases.[31]

The complex does not coordinate CO in competing solvent MeCN, but it binds CO in noncoordinating solvent MeNO$_2$

to form carbonyl adduct $[Fe_2(C_{20}H_{36}N_8)(CH_3CN)_2(CO)_2](PF_6)_4$. It has been observed that the affinity of Fe(II) macrocyclic complex $[Fe(L)(CH_3CN_2)]^{2+}$ for CO in MeCN solution decreases as the π-conjugation of the macrocyclic ligand increases, which reflects the π-accepting property of the π-conjugated ligand.[32] The v_{CO} value of the carbonyl complex is 2010 cm^{-1}, which is substantially low compared with v_{CO} values of other Fe(II) complexes with saturated macrocyclic ligands.[32] This indicates that the present bismacrocycle is a good π-accepting ligand.

It is interesting to obtain free ligand from the present Fe(II) complex and synthesize other bimetallic complexes. However, the attempts to obtain the free ligand were failed. As H$_2$S gas was bubbled through the MeCN solution of the complex, the Fe(II) ions were precipitated out from the complex as FeS but the free ligand was decomposed in the solution simultaneously. It is also interesting to oxidize the complex further and introduce more double bonds in the ligand because a part of the ligand is completely saturated and contains secondary nitrogens. For this purpose, the secondary nitrogens of the complex were deprotonated with KOH in a Me$_2$SO solution and then the solution was bubbled with the dry oxygen. However, the reaction just yielded the rusts instead of Fe(II) complexes containing more double bonds in the ligand.

Conclusion

The Fe(II) cyclam complex is oxidized by air to produce the extensively unsaturated bismacrocyclic Fe(II) complex. The oxidative dehydrogenations of Fe(II) complexes with macrocyclic ligands, such as Me$_6$[14]4,11-dieneN$_4$ and Me$_6$[14]aneN$_4$, generally yielded the monomeric Fe(II) complex with α-diimine linkages.[13,19] However, this study shows that extensive oxidative dehydrogenation as well as the ligand coupling occurs for the completely saturated and unsubstituted Fe(II) macrocyclic ligand system. Considering that [Ni (cyclam)]$^{2+}$ and [Ru(cyclam)Cl$_2$]$^+$ are stable in the air and the Co(II) cyclam complex is oxidized to μ-peroxo Co(III) complex,[33,34] we presume that Fe(II) ion is an efficient metal ion for promoting the aerobic oxidation of the coordinated ligand.

Supplementary Material Available. Listings of complete bond lengths and angles and anisotropic thermal parameters (Table S1 and S2; 2 pages); Ordering information is given on any current masthead page.

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Kinetic Studies on the Reaction of Iron(III) with D-penicillamine in Acidic Solution[1]

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Anaerobic oxidation of D-penicillamine by Fe(III) in acidic solution has been studied kinetically by the use of stopped-flow system. The reaction is biphasic with a rapid complexation of 1 : 1 complex, Fepen⁺ (pen = D-penicillamine dianion) which is then internally reduced to Fe(II) and disulfide. Rates of both the complexation and the redox process are pH dependent and also are affected by the presence of chloride ion. Different from the reaction of Cu(II) with D-penicillamine, partially oxidized mixed-valence complex is not formed even transiently in this reaction.

Introduction

D-penicillanine [HS(CH₃)₂CCH(NH₂)COOH, H₂pen], one of the sulfur-containing amino acids, has been used as a medi-

cinal chelating agent and the oral administration of the D-penicillamine to patients with Wilson's disease promotes the urinary excretion of excess copper ions.[3] Beacuse of the physiological relevance, considerable emphasis has been placed