Inorg. Chem. **2001,** *40,* 4036−4039

Structural, Magnetic and Catalytic Properties of a Self-Recognized μ-Oxo-Bridged Diiron(III) Bis(benzimidazole) Complex

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Received December 6, 2000

The inherent nonplanarity and C_2 symmetry of the dimethyl-substituted bis(benzimidazole) ligand (Me_2BBZ) results in two distinct atropisomers that, when separated, have been suggested to have potential for chiral recognition and catalysis. Here is reported the synthesis and characterization of a diiron μ-oxo-bridged bis(benzimidazole) complex, **1**, that provides indirect support for this hypothesis. Dimerization of a racemic solution of iron−Me_2BBZ monomers via the μ-oxo bridge yields (+,+) and (−,−) diastereomers whose complementary association can be attributed to the inherent sidedness of the metal−Me_2BBZ interaction surface, and to the differences in the torsional angles of the phenyl(benzimidazole) units (34°) and the Schiff base linkages (54°). These results highlight the steric differences between the phenyl(benzimidazole) and Schiff-base portions of the ligand, features that could be important in the chiral recognition of ligands and in differentiating substrate trajectories as required for asymmetric catalysis. For completeness, studies of **1** in the catalytic epoxidation of styrene are also reported.

Introduction

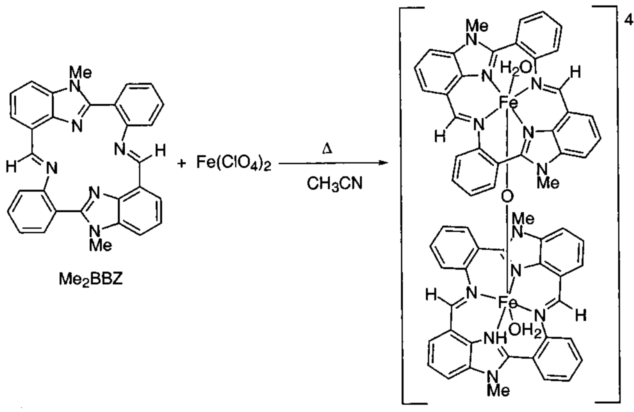
The dimethyl-substituted bis(benzimidazole) ligand (Me_2BBZ) is a new class of porphyrin analogue with an identical ring size and a similar set of donor atoms.[1,2] The lower symmetry (C_2) and inherent nonplanarity of Me_2BBZ's, however, leads to a distinct handedness and sidedness that is not present in porphyrins (Scheme 1). Because of these features, pentacoordinate metallo−bis(benzimidazole)s exhibit a single interaction surface whose chirality is dependent the atropisomeric hand of the complex. This has led to the suggestion that isolated metallo−bis(benzimidazole) atropisomers could be suitable for chiral recognition and catalysis.[1,2] Here we describe the synthesis and characterization of a diiron μ-oxo-bridged Me_2BBZ complex, $[Fe(Me_2BBZ)OFe(Me_2BBZ)](ClO_4)_4(H_2O)_3(CH_3CN)_3$ (**1**), that provides indirect support for this hypothesis.

Experimental Section

General Considerations. Unless otherwise noted, all materials were obtained commercially and used without further purification. Silica gel (Scientific Adsorbents Inc. 32-63 U, 40 μm) was used for column chromatography.

Preparation of $[Fe(Me_2BBZ)OFe(Me_2BBZ)](ClO_4)_4(H_2O)_3(CH_3CN)_3$ (1). *CAUTION*: Perchlorate salts are potentially explosive and should be handled with care! The dimethyl-substituted bis(benzimidazole) ligand (0.341 g, 0.728 mmol) was mixed with $Fe(ClO_4)_2\cdot xH_2O$ (0.186 g, 0.728 mmol) in CH_3CN and allowed to reflux for 20 h. Removal of the solvent by rotary evaporation yielded a crude product that was purified by column chromatography (CH_2Cl_2:hexane:MeOH = 3:1:1) to give a red solid (0.41 g, 70% yield). Anal. Calcd for $[Fe(Me_2BBZ)OFe(Me_2BBZ)](ClO_4)_4(H_2O)_3(CH_3CN)_3$, $C_{66}H_{59}N_{15}O_{20}Cl_4Fe_2$: C, 48.46; H, 3.60; N, 12.84; Cl, 8.67: Found: C, 48.95; H, 3.34; N, 12.25; Cl, 8.96. UV−vis [λ (ϵ, M^{-1} cm^{-1}) in CH_3CN]: 244 (3.73×10^5), 331 (3.74×10^5). IR (KBr, cm^{-1}): 3418 s, br, 1667 s, 1559 s, 1477 vs, 1432 m, 1400 m, 1380 m, 1311 w, 1229 m, 1089 vs, br, 929 w, 890 s, 851 s, 811 w, 777 w, 751 s, 712 w, 624 s.

Scheme 1



1

Crystallographic Procedures. Single-crystal X-ray data on compound **1** were collected at 173 K on a Nonius Kappa CCD diffractometer (Table 1). Examination of the diffraction pattern indicated a primitive monoclinic crystal system. A quadrant of reciprocal space was measured using ω scans with a frame width of 0.5°. Data integration was done with Denzo,[3] and scaling and merging of the data was done with Scalepack.[3]

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10.1021/ic0013781 CCC: $20.00

Table 1. Crystallographic Data for **1**

formula	$C_{132}H_{124}Cl_8Fe_4N_{30}O_{43}$
fw	3325.65
temp, K	173
λ	0.71073 Å
cryst syst	monoclinic
space group	$P2_1$
a, Å	15.4832(4)
b, Å	30.1771(7)
c, Å	16.2334(4)
β, deg	97.208(1)
Z, formula unit	2
V, Å^3	7525
d_{calcd}, g/mL	1.47
μ_{calcd}, mm^{-1}	0.610
no. of data collected	72054
no. of unique data (all)	24518
no. of variable params	1201
R1,[a] wR2[b] (2σ)	0.082, 0.221
R1,[a] wR2[b] (all data)	0.106, 0.241
GOF on F^2 (all data)	1.065

[a] $R1 = \sum||F_o| - |F_o||/\sum|F_o|$. [b] $wR2(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

The positions of the Fe atoms were located by the direct methods procedure in SHELXS-86[4] in $P2_1$. The remaining atoms were found by a combination of DIRDIF[5] and Fourier methods in SHELXL-93.[6] The asymmetric unit consists of two Fe dimer molecules, eight perchlorate ions, six acetonitrile molecules, and six water molecules. The labeling scheme names the corresponding atoms of each half of a dimer molecule with the same numbers, but different letters (e.g., one dimer contains N(1A), N(2A) etc. in one half and N(1B), N(2B), etc. in the other half). The halves of the other dimer are labeled as C and D. The two dimers differ slightly. For one of the two dimers, both ferric ions are hexacoordinate with weakly associated water molecules (2.31−2.39 Å) serving as the axial ligands trans to the bridging oxo group. In the second dimer, one of the ferric ions is hexacoordinate with a weakly bound water, while the other is pentacoordinate with no second axial ligand.

The hydrogen atoms for the Me_2BBZ ligands and one of the acetonitrile solvent molecules were included in the model at calculated positions. No hydrogen atoms were included for the remaining solvent molecules and the terminal oxygen atoms of the dimer. Both dimers, all of the perchlorate groups, and three of the acetonitrile molecules were refined anisotropically. All of the solvent water molecules were kept isotropic. Additional details regarding the crystallographic data and analysis are available as Supporting Information.

General Epoxidation Procedure. A solution of styrene (10 μL, 96 μmol), NMO (100 mg, 0.854 mmol), and complex **1** (1.37 mg, 0.837 μmol) in 3 mL of CH_3CN was cooled to −15 °C. Solid *m*-CPBA (150 mg, 0.869 mmol) was added in three roughly equal portions over a 2 min period. The reaction mixture was stirred for 60 min at −15 °C, and then 5 mL of 1 N NaOH was added. The resulting solution was extracted twice with CH_2Cl_2 (2 × 2.5 mL). The combined organic phases were washed with brine and dried over Na_2SO_4. The organic phase was passed through a small bed of silica to remove residual iron contaminants, and then the resulting solution was diluted to 10 mL.

Results and Discussion

The inherent sidedness of metallo−bis(benzimidazole) complexes was first noted in previous studies of a series of mononuclear metal−Me_2BBZ complexes.[1] Here the two sides can be distinguished by a horizontal plane passing through the four liganding nitrogen atoms (the N4 plane) with the phenyl groups of the Me_2BBZ ligand lying on one side of this plane (defined to be above), and the benzimidazole groups lying on the opposite side (defined to be below). Importantly, in all pentacoordinate metal−Me_2BBZ complexes characterized to date, the metal and its axial ligand lie above this plane. Hence, steric interactions of bound axial ligands or substrates in pentacoordinate metal−Me_2BBZ complexes will be dominated by interactions with the phenyl rings of the Me_2BBZ macrocycle.

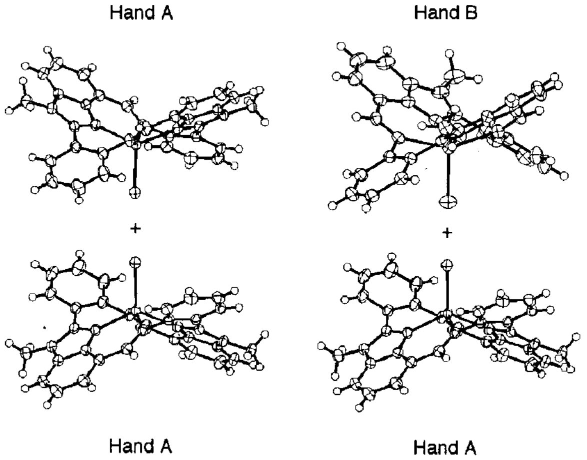

Figure 1. Mode of interaction of two mononuclear Fe−Me_2BBZ complexes:[1] (a, left) between two atropisomers of the same hand and (b, right) between two atropisomers with different hands.

A major consequence of the sidedness and C_2 symmetry of bis(benzimidazole) macrocycles is the generation of two distinct atropisomers upon metal incorporation. This feature is important because the chirality of the interaction surface depends on the atropisomeric hand of the complex. Thus isolated metallo−bis(benzimidazole) atropisomers should interact differently with substrate enantiomers.

One aspect of this chiral recognition could be in self-discrimination. For example, dimerization of racemic mixtures of mononuclear Fe−Me_2BBZ complexes could, in principle, result in three distinct diastereomers, (+,+), (+,−), and (−,−). If the interaction surface of the Fe−Me_2BBZ complex can be used in discrimination, however, then dimerization should result in either a mixture of (+,+) and (−,−) diastereomers corresponding to self-recognition (Figure 1a) or in (+,−) and (−,+) diastereomers corresponding to opposite-hand recognition (Figure 1b). One way to evaluate the ability of metallo−bis(benzimidazole)s to serve as chiral agents, then, would be to prepare and structurally characterize a dimeric metallo−bis(benzimidazole) complex. This would help to confirm that self-discrimination can be achieved and, more importantly, would help to elucidate the features that promote this discrimination.

Hence our interest when it was determined that aerobic stirring of the mononuclear iron(II)−Me_2BBZ complex, $[Fe(Me_2BBZ)Cl]^+$ (**2**),[1] results in formation of a new complex (**1**) with distinct spectral properties (Scheme 1). In particular, **1** exhibits a strong 890 cm^{-1} IR band not observed in any other mononuclear metal−Me_2BBZ complex, including **2**.[1,2] As similar bands had been observed and assigned to asymmetric vibrations of the linear Fe−O−Fe unit in μ-oxo-bridged iron porphyrins,[7−10] it appeared likely that **1** was a μ-oxo-bridged iron−Me_2BBZ dimer.

To confirm this assignment, crystals of **1** suitable for X-ray analysis were obtained by slow diffusion of pentane into an

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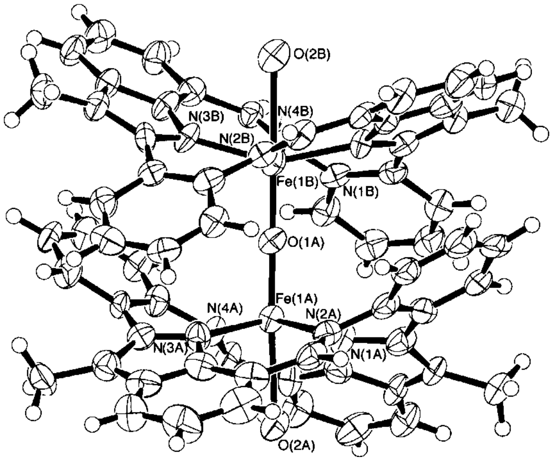

Figure 2. Structure of the μ-oxo-bridged diiron bis(benzimidazole) complex, **1** (both halves have the same hand; the ClO_4^- anions and solvent molecules are omitted for clarity), with 50% probability displacement ellipsoids for the non-H atoms. Selected bond lengths (Å) and angles (deg) for one of the two crystallographic molecules: Fe(1A)−O(1A) 1.755(5), Fe(1B)−O(1A) 1.772(5), Fe(1A)−O(2A) 2.389(6), Fe(1B)−O(2B) 2.385(6), Fe(1A)−N(1A) 2.002(6), Fe(1A)−N(2A) 2.139(6), Fe(1A)−N(3A) 2.024(6), Fe(1A)−N(4A) 2.142(6), Fe(1B)−N(1B) 2.009(6), Fe(1B)−N(2B) 2.137(6), Fe(1B)−N(3B) 2.010(6), Fe(1B)−N(4B) 2.140(6), Fe(1A)−O(1A)−Fe(1B) 176.8(3).

acetonitrile solution over 5 days at −7 °C. The structure determination from these crystals (Table 1) confirms that **1** is a μ-oxo-bridged diferric complex with the basic formulation $[Fe(Me_2BBZ)OFe(Me_2BBZ)](ClO_4)_4(H_2O)_{1-2}$ (Figure 2). On the basis of the structure, self-recognition is favored with dimers of both atropisomers, (+,+) and (−,−), present in the crystal. Examination of the structure reveals that the origin of this self-complementation arises from differences in the torsional angles of the phenyl(benzimidazole) units, and the Schiff base linkages. Perhaps due to the greater steric constraints, the torsional angles within the phenyl(benzimidazole) units are smaller (34°) than those for Schiff base linkages (52°). Overlap of the groups with similar twist angles is favored, resulting in the observed self-recognition of monomeric Fe−Me_2BBZ units that is observed. As these steric features would also influence the differential binding of chiral substrates, these results provide indirect support for the potential of the metal−Me_2BBZ complexes in chiral recognition and catalysis.

Electron paramagnetic resonance (EPR) and bulk magnetic susceptibility measurements were performed to confirm the oxidation state assignments and to elucidate the nature of the magnetic coupling mediated by the linear Fe−O−Fe bond. The χ versus T plot is consistent with antiferromagnetic coupling. At low temperature, however, the temperature dependence of the magnetization follows the Curie law, suggesting the presence of a small amount of uncoupled species. Current evidence suggests that these species are high-spin iron(III) and frozen molecular oxygen. The EPR spectrum taken at 4 K exhibits a small signal at $g \sim 7$ indicative of rhombic ferric ion, while the χ versus T plot contains a slight blip at 50 K that coincides with the phase transition for molecular oxygen. Unfortunately, we were unable to develop a convenient model to account for the oxygen impurity and, as such, fit the data to a combination of only two species, a small amount of ferric Me_2BBZ monomer and a majority of strongly antiferromagnetically coupled dimer. The best fit of the data obtained gives a coupling constant of $2J = -300$ cm^{-1} (with $\rho = 93.93\%$). This value is larger than that for most Fe−O−Fe dimers other than porphyrins,[7−9,11] but it is understandable on the basis of the Weibe−Güdel model ($2J_{\text{model}} = -249.05$).[11] On the basis of this model, the large coupling results from its relatively short Fe−O bond distances (Fe−O_{av} = 1.759 Å) and nearly linear Fe−O−Fe bond angle (∠Fe−O−Fe_{av} = 174.45). Further details of the EPR and magnetic studies are provided as Supporting Information.

Table 2. Epoxidation of Styrene in Acetonitrile

catalyst	oxidant	T (°C)	time (h)	yield (%)	TN
1	*m*-CPBA/NMO	−15	1	99	113
1	NaOCl/PPNO	25	14	93	93
$[Mn(Me_2BBZ)Cl]^+$	NaOCl/PPNO	25	14	73	70

The oxo-transfer chemistry of **1** was performed to complete its characterization. While numerous oxo-transfer systems have been identified, the ability of **1** to catalyze such reactions was unclear. Oxo-transfer chemistry has been previously observed for μ-oxo-bridged phthalocyanine complexes, but related μ-oxo-bridged iron porphyrin dimers are generally catalytically inert due to the greater stability of its μ-oxo−diiron unit.[8,12] Hence, following previous studies on μ-oxo-bridged iron−phthalocyanines,[13] **1** was reacted with triphenylphosphine. This reaction, performed under anaerobic conditions, results in loss of the 888 cm^{-1} Fe−O−Fe IR stretch and the formation of a 727 cm^{-1} Ph_3PO band demonstrating that the bridging oxo in the dimeric iron−Me_2BBZ is labile. Interestingly, formation of the oxo bridge appears to be reversible. Anaerobic treatment of the monomeric $[Fe^{II}-(Me_2BBZ)Cl]^+$ complex with Ph_3PO gives rise to the characteristic Fe−O−Fe stretch of the dimer.

It having been demonstrated that oxygen atom transfer reactions are feasible, the next step was to determine whether these reactions could be performed under turnover conditions. The ability of **1** to catalyze the epoxidation of styrene by terminal oxidants was explored under a variety of conditions. Styrene epoxidation at −15 °C in the presence of **1** as catalyst, *m*-CPBA as oxidant, and *N*-methylmorpholine *N*-oxide (NMO) resulted in quantitative conversion of styrene to the corresponding epoxide within 1 h in CH_3CN (Table 2). As has been reported for other systems,[14] the use of excess NMO as an additive is critical for the specific formation of the epoxide. In the absence of NMO, the catalytic epoxidation of styrene with *m*-CPBA results in the formation of benzaldehyde, even without complete conversion of styrene. Control reactions under similar conditions without the catalyst do not give epoxide. A significant solvent effect is also observed. In CH_2Cl_2 at −78 °C, the yield of the epoxide is only 66%, with 11% benzaldehyde side product being obtained.

Although slower, complex **1** can also catalyze the epoxidation of styrene using NaOCl as the terminal oxidant with both high chemoselectivity and reasonable turnover values (93% styrene oxide) when PPNO is used as a chemical additive (Table 2). For comparison, the mononuclear Mn^{II}−Me_2BBZ complex,[2] $[Mn(Me_2BBZ)Cl]^+$, catalyzes the epoxidation reaction under similar conditions although the yield and chemoselectivity are poorer (73% styrene oxide, 11% benzaldehyde). These data may

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suggest that, under turnover conditions, the iron−Me_2BBZ dimer dissociates into monomeric units that serve as the catalytic units. The origin for the difference in the chemoselectivity is unclear, but one possibility is that dimer formation may provide an important pathway for deactivating highly reactive species.

In summary, oxidation of a racemic mixture of monomeric iron−Me_2BBZ atropisomers leads to formation of self-recognized diastereomers, (+,+) and (−,−), of a μ-oxo-bridged diiron(III,III)−Me_2BBZ complex. The structure of **1** reveals that the important factors for this self-recognition are the C_2 symmetry and the inherent nonplanar distortion that provide metallo−bis(benzimidazole)s with their distinct sidedness and atropisomerism, and the differences in the torsional angles that discriminate the two hands upon dimerization. As these same steric features could be used to discriminate chiral ligands and substrates, these results provide indirect support for the potential use of isolated metal−Me_2BBZ atropisomers in chiral recognition and catalysis. Further work to isolate and characterize the individual atropisomers is currently underway.

Acknowledgment. The temperature-dependent magnetization data were collected at the Beckman Institute SQUID facility at the California Institute of Technology. We thank Joshua A. Maurer for his assistance in the SQUID data collection and Dr. Sunney I. Chan of the Department of Chemistry at California Institute of Technology for his insights into the fitting of the EPR and magnetic data. The IR and GC/MS data were collected at the Department of Chemistry Instrumentation Facility, at The Ohio State University. We thank Gordon Renkes for his assistance with the GC/MS instrument and Tomek Fekner for his careful reading of this manuscript. This research was supported by grants from the Hermann Frasch Foundation (Grant 416-HF-97) and the National Science Foundation (CAREER Award No. 9984071), and from a fellowship from the Alfred P. Sloan Foundation (to M.K.C.).

Supporting Information Available: Text and tables providing details of the structure determination and refinement. Coordinates, anisotropic thermal parameters, and bond distances and angles in CIF format. Details of magnetic data (SQUID measurements). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0013781