An Iron(II) Complex with an N_4S Ligand − A Novel Model Compound to Mimic Cytochrome P450 Activity

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Dedicated to Prof. Dr. K. Wieghardt on the occasion of his 60th birthday

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The ligand 2,5-Bis[hydroxybis(2-pyridyl)methyl]thiophene (bhpmt) was designed to mimic the coordination sphere of cytochrome P450. With the ligand's four coplanar nitrogen atoms and an axial sulfur donor group it is the first nonporphyrin model compound to form a similar arrangement. The structure of the corresponding iron(II) perchlorate complex was determined by EXAFS and XPS measurements. The bond lengths of the first coordination sphere are remarkably similar to known porphyrin-based P450 model compounds. It is shown that the iron complex of bhmpt is able to perform epoxidation reactions with open-chain olefins and aqueous hydrogen peroxide (30%) as the oxidizing agent.

Introduction

Iron complexes are widely known in nature and play an essential part as biological redox catalysts in almost all life forms. Especially the heme proteins are of importance. Aside from hemoglobin, a great number of structurally related compounds, such as the cytochromes in the oxidative chain, are known.[1] Designing ligands that can mimic the structural aspects and, consequently, the catalytic properties of an enzyme has been the subject of extensive research in the field of biomimetic chemistry. It is one such model that we would like to report here. As a natural counterpart for our model system we have chosen the ubiquitous enzyme cytochrome P450, one of a class of heme-containing enzymes that catalyze the hydroxylation of C−H bonds, epoxidation of carbon−carbon double bonds, and the oxidation of heteroatoms.[2] Unlike many of the other heme-containing enzymes, P450 features a thiolate function at the apical position of the octahedral iron complex rather than another nitrogen donor group. It appears that thiolate ion ligation of the metal center is the main reason for the different reactivity of P450 compounds compared to other heme-based enzymes.[3] To understand the extraordinary properties of this enzyme many model compounds have been developed to date. While these mostly porphyrin-based complexes can sufficiently mimic the exact steric properties of the natural counterpart, their catalytic activities are limited.[4] So far only the Woggon group has developed a system that is able to perform oxygen insertion with dioxygen into nonactivated C−H bonds. Since the insertion occurs at a side chain of the model compound, the functional properties of P450 cannot be sufficiently mimicked.[4e] Simple, non-porphyrin iron-containing model compounds with an N_4S-donor set are unknown to the best of our knowledge. In contrast to the few known pentadentate ligands that usually carry N_5-donor sets,[5,6] we wanted to introduce a sulfur atom to occupy one axial position in an octahedral metal complex. However, the introduction of a thiolate moiety into a metal complex proves to be difficult, since it readily forms disulfides in the presence of O_2. In nature this problem is circumvented by creating hydrophobic cavities to protect the sulfur atom from oxidation.[4b] Trading stability for higher donor strength, we chose thiophene instead of thiolate as the axial donor group. Here we report the synthesis of the novel ligand 2,5-bis[hydroxybis(2-pyridyl)methyl]thiophene (bhmpt), the iron perchlorate complex of bhmpt, its catalytic properties in the epoxidation of simple olefins, and the structural characterization of its active site.

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Results and Discussion

According to a procedure recently published by Feringa,[6a] who created a similar N_5-ligating system, bhpmt can be synthesized by treating 2,5-thiophenedicarbonyl dichloride with 2-lithiopyridine. However, treatment of 2,5-dilithiothiophene with bis(2-pyridyl) ketone gives much higher yields (Figure 1).

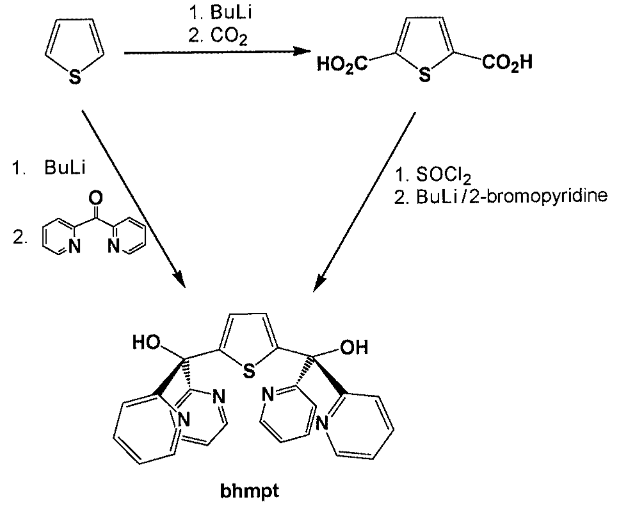

Figure 1. Synthesis of 2,5-bis[hydroxybis(2-pyridyl)methyl]thiophene (bhpmt)

The ligand is well soluble in halogenated solvents, toluene, THF as well as methanol and displays a high stability towards oxidation and hydrolysis.

Reaction of bhpmt with anhydrous iron(II) perchlorate in THF gives the corresponding metal complex. The compound is a yellow solid, paramagnetic and solely soluble in acetonitrile and dimethyl sulfoxide (DMSO). Due to disorder problems we have not been able to solve the crystal structure of the complex. The same problems were observed with the complexes of other divalent metal ions such as Co^{2+}, Ni^{2+} and Zn^{2+}. Only the corresponding copper perchlorate complex of bhpmt gave crystals suitable for X-ray analysis. It would not be reasonable to expect iron to exhibit the same coordination geometry as the copper complex. However, as is shown below, the X-ray data of the copper complex have helped to interpret the XPS and EXAFS data of the iron complex in the solid state and in solution.

The crystal structure of the copper complex shows that the thiophene moiety does not participate in the coordination of the metal center. Instead a dimer of two units of $[Cu(bhmpt)]^{2+}$ is formed, which allows the copper atoms to adopt the preferred square arrangement of four donor atoms. Both copper atoms are coordinated in a nearly planar fashion by three nitrogen atoms and one oxygen atom (Figure 2).

Vapour-pressure osmometric measurements, as well as conductivity measurements, suggest that the dimer is cleaved in solution to give monomers of as-yet-unknown structure.

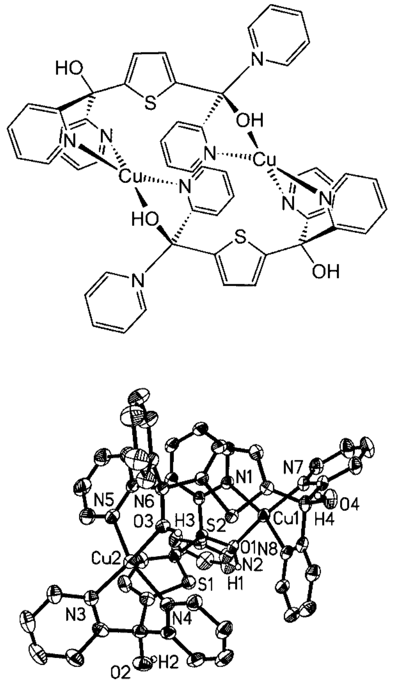

Figure 2. Molecular structure of the cation $[\{Cu(bhpmt)\}_2]^{4+}$; selected bond lengths [Å]: Cu1−O1 1.877(3), Cu1−N1 2.001(3), Cu1−N7 1.980(3), Cu1−N8 2.022(2), Cu1−O33′ 2.716(6) (perchlorate O), Cu2−O3 1.869(2), Cu2−N3 1.974(3), Cu2−N4 2.022(3), Cu2−N5 1.998(3), Cu2−O12 2.691(4) (perchlorate O); ′: $-x$, $2 - y$, $-z$; selected H atoms, perchlorate anions and solvent molecules have been omitted for clarity; two of the perchlorate ions are weakly bonded to the two copper metal ions; by way of moderate hydrogen bonding two THF molecules are bonded to the OH moieties O2 and O4; additional disordered water and THF is situated among the ionic groups; displacement ellipsoids are drawn at the 25% probability level

Since the crystal structure of the corresponding iron complex of bhpmt could not be solved, spectroscopic measurements were used. X-ray photoelectron spectroscopy (XPS) measurements of $[Fe(bhpmt)](ClO_4)_2$ show four equivalent nitrogen atoms with binding energies in the range of coordinated pyridine, whereas for the corresponding copper complex the signal is broadened, indicating different electronic environments for the pyridine groups. According to the crystal structure of $[Cu_2(bhpmt)_2](ClO_4)_4$ the thiophene moiety does not participate in the coordination of the metal center. The XPS signal of thiophene is found at 164.3 eV. For the iron complex this signal is shifted to 164.0 eV. This decrease of binding energy at the sulfur atom is probably due to coordination of the sulfur atom to the iron atom.

The binding of bhmpt to the iron atom was investigated by means of Fe-*K*-edge X-ray absorption spectroscopy (XAS). The iron coordination environment was determined for solid $[Fe(bhpmt)](ClO_4)_2{\cdot}thf$ as well as for the metal complex dissolved in acetonitrile. Comparison of the normalized absorption edges for both samples shows that the step-like edge jump for the dissolved compound appears at lower energies than for the solid complex (Figure 3, separation of about 2−3 eV over the entire edge). Its energetic position is connected to the charge on the absorbing ion,[7]

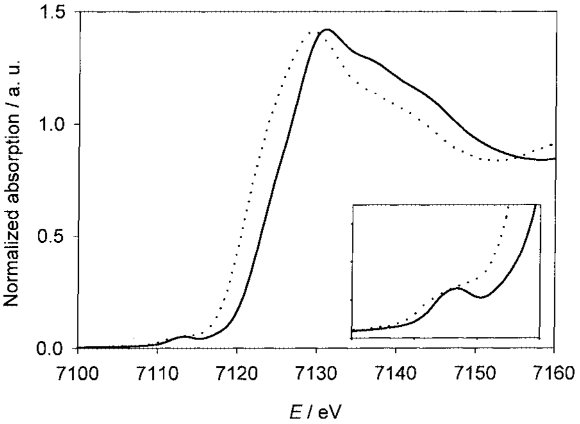

Figure 3. Normalized Fe-*K*-absorption edges of the solid compound (−) and the compound in solution (···); the inset displays the enlarged pre-edge region; abbreviations: a.u. = arbitrary units; *E* = X-ray energy

allowing the assignments of Fe^{II} for the solution and Fe^{III} for the solid-state complex. The Fe^{III} state is presumably a result of aerobic handling of the solid during sample preparation (see Exp. Sect.).

Both edge spectra exhibit a pre-edge peak at about 7113 eV (inset in Figure 3). It is due to a formally dipole-forbidden 1s → 3d electronic transition and its intensity is related to the coordination number and geometry of the iron site.[8] For both complexes the pre-edge peak areas (solid: 10.1 units; dissolved: 9.7 units; 1 unit = 10^{-2} eV) are in between the typical ranges for five- and six-coordinate complexes, indicating a significant distortion from octahedral symmetry.[8,9]

Further information on the iron coordination environment is derived from the extended X-ray absorption fine structure (EXAFS) of the absorption edge. Fourier transformation of the EXAFS signal allows the radial distribution of neighbouring atoms around the central absorbing metal ion to be explored (Figure 4, Table 1).

The structural composition of the first coordination shell of the iron atom is summarized in Table 1. In the solid as well as in the solution sample, the iron atom is coordinated by four nitrogen atoms (solid: 2.13 Å; solution: 2.11 Å) and one sulfur donor (solid: 2.29 Å; solution: 2.27 Å). Thus, the ligand binds in the desired pentadentate fashion with thiophene occupying the apical position (Figure 5). The sixth coordination site is most likely occupied by THF (Fe−O: 1.90 Å) and acetonitrile (Fe−N: 2.21 Å) in the solid state and in solution, respectively. No indication was found that dimerization occurs, as is the case for the corresponding Cu^{II} complex.

Comparison of the obtained data with EXAFS data of a heme-based P450-model compound by Higuchi's group shows very similar bond lengths (Fe−S 2.20 Å, Fe−N 2.00 Å).[4d] This indicates that the structural aspects of P450 can be adequately mimicked even by a simple model compound such as bhmpt in the solid state as well as in solution.

Epoxidation reactions were performed in order to investigate the catalytic activity, and consequently the ability of

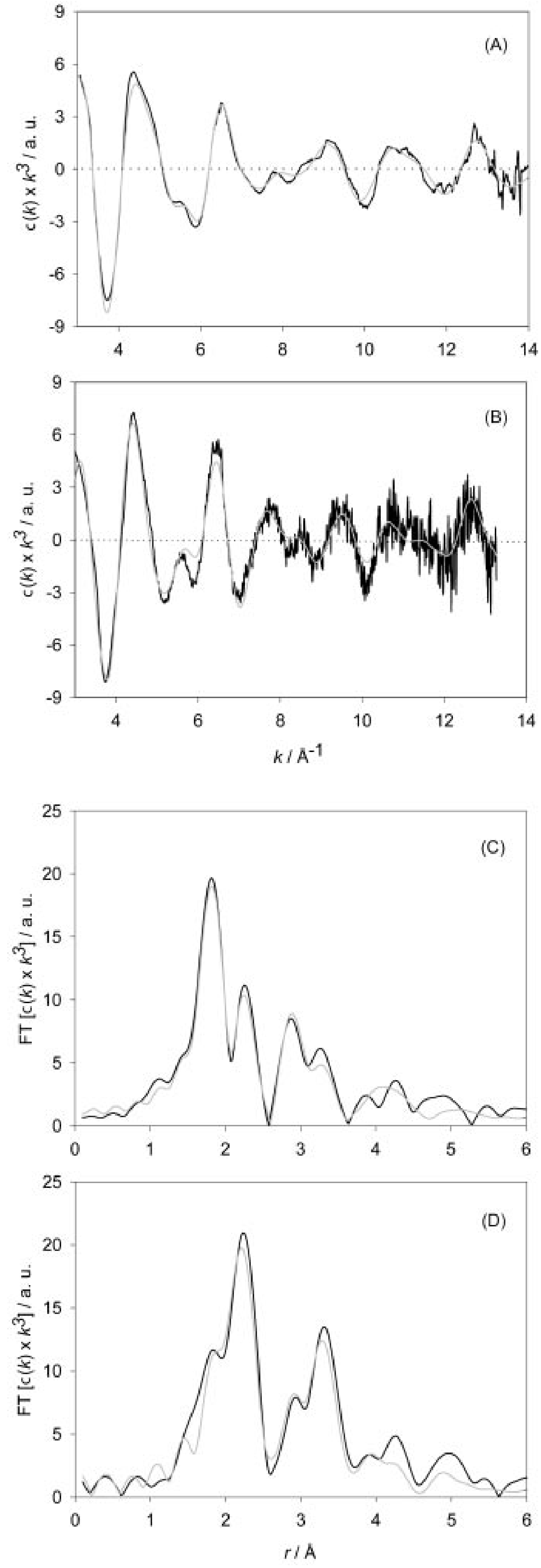

Figure 4. EXAFS (A, B) and corresponding Fourier transforms (C, D) of the solid (A, C) and dissolved (B, D) compound; experimental (black curves) and calculated (gray curves) spectra are compared; abbreviations: a.u. = arbitrary units; χ = EXAFS amplitude; *k* = photoelectron wave number; FT = Fourier transform amplitude; *r* = distance

Table 1. Structural parameters for the first iron coordination sphere, derived from EXAFS analysis

Atom[a]	Solid		Solution	
	r/Å	$2\sigma^2$/Å^2	r/Å	$2\sigma^2$/Å^2
1 O	1.903(2)	0.004(1)	–	–
4 N	2.127(7)	0.036(1)[b]	2.109(8)	0.029(2)[b]
1 N	–	–	2.212(6)	0.003(2)
1 S	2.291(11)	0.036(1)[b]	2.269(19)	0.029(2)[b]
E_F/eV	−15.2(2)		−12.1(4)	
R/%	19.8		35.5	

[a] r: distance; $2\sigma^2$: Debye−Waller parameter; E_F: Fermi energy (related to edge position, see manual of EXCURV98);[10] R: R factor (goodness of refinement).[10] [b] Constrained to have the same value during refinement; values in brackets are the numerical uncertainties (twice the standard deviation) of the last digit.

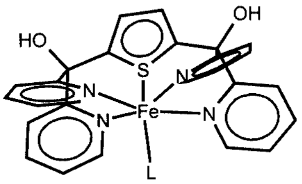

Figure 5. Molecular structure of the P-450 mimic investigated in this study; in the solid L is THF whereas CH_3CN binds to the iron ion in the dissolved complex

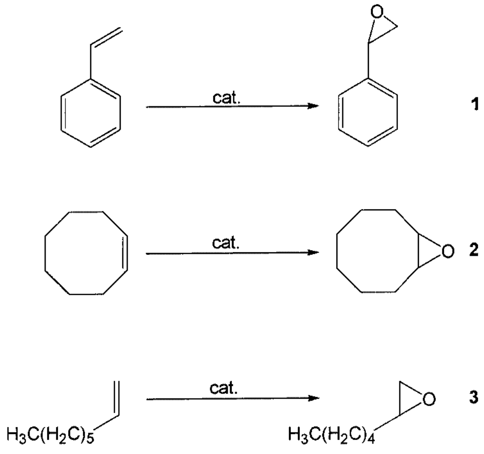

Figure 6. Performed epoxidation reactions

$[Fe(bhpmt)]^{2+}$ to mimic its biological counterpart (Figure 6).

For all reactions the catalyst was charged with a 50-fold excess of the substrate and the same amount of aqueous hydrogen peroxide (30%). The course of the catalytic reaction was monitored by gas chromatography (GC) and the resulting products were identified by gas chromatography/mass spectrometry (GC/MS). Surprisingly, the catalysis with a relatively unreactive olefin such as 1-octene displays similar efficiencies to that of more reactive substrates like styrene and cyclooctene (Figure 7).

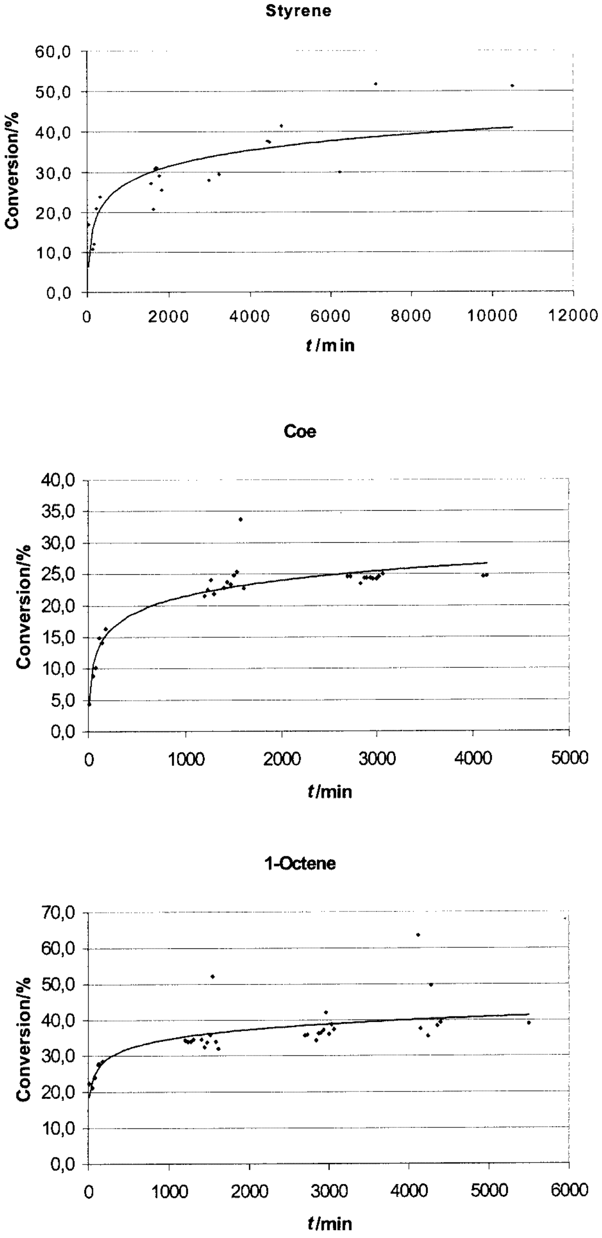

Figure 7. Conversion vs. time plots of the epoxidation reactions with styrene, cyclooctene (coe) and 1-octene

When norbornene is used as a substrate, significantly less epoxide is formed. This leads to the conclusion that the steric demands of the substrate and thus accessibility to the metal center determine the conversion rate, while the electronic properties of the substrate only have a minor effect on the catalysis. Since none of the other model compounds of P450 have been reported to show similar behavior we cannot decide whether this is typical for these types of iron complexes.

The only other iron complex to catalyze the epoxidation of open-chain olefins has been reported by Valentine. In this case, however, the ligand system is based on cyclam, thus having only four nitrogen donor groups. With a turnover of 20 for $[Fe(bhpmt)](ClO_4)_2$, the epoxidation of 1-

octene shows significantly higher turnover numbers based on the iron complex than the one obtained with [Fe(cyclam)](CF_3SO_3)$_2$ which reaches only 7 turnovers (Table 2).[11]

Table 2. Substrates used and resulting conversions to the corresponding epoxides

Substrate	Conversion	Turnover[a]
Styrene	51%	25
1-Octene	40%	20
Cyclooctene	25%	13
Norbornene	10%	5

[a] mmol of epoxide per mmol of catalyst.

The catalytic reactions proceed slowly with moderate conversions of the substrates. After approximately one day, the termination stage of each reaction is reached and the efficiency cannot be increased by further addition of either substrate or hydrogen peroxide. This suggests that the catalyst, which displays an unusually high durability in an aqueous medium for an iron(II) complex, does decompose after a while, forcing the catalytic activity to subside. At present, we do not know the nature or structure of the decomposition products. We believe that the ligand is oxidized after a while, releasing iron perchlorate. This is known to catalyze the decomposition of hydrogen peroxide, which could be another reason for the comparatively low efficiency of the catalyst. When using $Fe(ClO_4)_2$ as the catalyst in a control experiment, no epoxidation product could be detected.

Conclusions

With the iron complex of bhpmt we were able to mimic the structural aspects as well as the catalytic activity of cytochrome P450. We believe the latter is possible due to sulfur ligation of the central atom. Unusually for iron(III) complexes, which mostly form insoluble hydroxides in the presence of water, the metal complex of bhpmt displays a high tolerance for small amounts of water and is able to perform the catalysis with aqueous hydrogen peroxide. We discovered that higher conversion rates are obtained with sterically less demanding (albeit less strained) substrates. Therefore, styrene and 1-octene display conversion rates in the same range, whereas substrates with considerably higher ring strain, such as cyclooctene, are much harder to epoxidize. Norbornene, with the highest steric demand shows hardly any conversion into the corresponding epoxide. This is unlike the reactivity of other epoxidation catalysts such as porphyrin−iron complexes[12] and manganese[13] and chromium[14] complexes of salen-type ligands, where electronic factors play a more important role than the steric factor.

Experimental Section

CAUTION! Although no problems were encountered in this work, transition metal perchlorate complexes with organic ligands are potentially explosive and should be handled with due precaution. All reagents were commercial samples and were used as received.

Materials and Instrumentation: When not stated otherwise, experiments were performed under nitrogen using standard Schlenk techniques and freshly dried solvents. Filtration was done with 1-μm membrane filters (regenerated cellulose, Schleicher & Schuell). Infrared spectra were recorded by using a Bruker IFS 66 FT spectrometer. GC analysis was done with an HP-5890 series II chromatograph with an FID detector and an MSD 5970 integrator. As a standard for gas chromatography 0.8 mL of mesitylene was added to each catalysis experiment. Elemental analyses were performed using a Perkin−Elmer CHN-2400/II elemental analyzer.

2,5-Bis[hydroxybis(2-pyridyl)methyl]thiophene (bhpmt): *n*-Butyllithium (8.0 mL, 3 mmol) was dissolved in *n*-hexane (40 mL) and treated with an equimolar amount of tetramethylethylenediamine (tmeda; 1.5 g). After slow addition of freshly distilled thiophene (0.43 g, 5.1 mmol) in *n*-hexane (50 mL), the reaction mixture was heated to reflux for 1 h. The mixture was then transferred to a flask, containing bis(2-pyridyl) ketone (2.4 g, bis 13 mmol) in diethyl ether, and stirred overnight. After hydrolyzing with iced water and neutralization with hydrochloric acid, the precipitate was filtered off and washed with diethyl ether until a white solid remained. Recrystallization from THF/*n*-hexane yielded 1.1 g (47%). ^1H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 6.95$ (s, 2 H, C_4H_2S), 7.19 (dt, $^3J_{H,H} = 6$, $^4J_{H,H} = 1$ Hz, 4 H, C_5H_4N), 7.94 (dt, $^3J_{H,H} = 8$, $^4J_{H,H} = 2$ Hz, 4 H, C_5H_4N), 7.98 (d, $^3J_{H,H} = 8$ Hz, 4 H, C_5H_4N), 8.49 (d, $^3J_{H,H} = 5$ Hz, 4 H, C_5H_4N) ppm. $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 78.7$ (s, COH), 122.6 (s, C_5H_4N), 122.8 (s, C_5H_4N), 125.9 (s, C_4H_2S), 137.1 (s, C_5H_4N), 147.7 (s, C_5H_4N), 150.6 (s, C_5H_4N), 162.7 (s, C_4H_2S) ppm. IR (KBr): $\tilde{\nu} =$ 3375 br, 1585 vs, 1569 s, 1463 vs, 1432 vs, 1363 br, 1328 m, 1190 s, 1154 m, 1142 m, 1104 s, 1068 m, 967 w, 864 m, 774 s, 749 s, 700 s, 674 s, 662 s, 627 m, 513 w cm^{-1}. UV/Vis (THF): λ_{max} (ε) = 259 nm (22000), 210 nm (28000). MS (FAB+NBA): *m/z* (%) = 453 (61) [M^+ + H], 435 (92) [M^+ − OH], 268 ([M − $py_2COH]^+$). $C_{26}H_{20}N_4O_2S$ (452.5): calcd. C 69.0, H 4.4, N 12.4; found C 68.6, H 3.9, N 11.9.

[Fe(bhpmt)](ClO_4)$_2$·thf: bhpmt (0.36 g, 0.65 mmol) was treated with anhydrous iron(II) perchlorate (0.17 mg, 0.65 mmol) in THF and stirred overnight. The resulting solid was filtered and recrystallized from acetonitrile/THF. Yield 0.31 g (60%). IR (KBr): $\tilde{\nu} =$ 3431 br, 3098 w, 1602 s, 1521 w, 1468 m, 1437 m, 1297 w, 1096 vs, 772 s, 624 s cm^{-1}. Conductivity $\Lambda = 234$ $S \cdot cm^2 \cdot mol^{-1}$ (acetonitrile). $C_{30}H_{28}Cl_2FeN_4O_{11}S$ (779.4): calcd. C 46.2, H 3.6, N 7.2; found C 46.8, H 3.5, N 7.5.

[Cu_2(bhpmt)$_2$](ClO_4)$_4$: The compound was prepared according to the procedure described for the iron complex; bhpmt (0.13 g, 0.29 mmol), copper(II) perchlorate dihydrate (0.11 g, 0.29 mmol), recrystallization from acetonitrile/THF. Yield 0.12 g (80%). IR (KBr): $\tilde{\nu} =$ 3429 br, 1602 s, 1514 w, 1469 m, 1441 m, 1294 w, 1121 vs, 1101 m, 1090 w, 772 s, 627 s cm^{-1}. $C_{64}H_{67}Cl_4Cu_2N_8O_{24.5}S_2$ (1673.2):calcd. C 45.9, H 4.0, N 6.7; found C 42.7, H 3.4, N 7.0.

Crystal Structure Analysis of [Cu_2(bhmpt)$_2$](ClO_4)$_4$·3C_4H_8O·1.5H_2O: $M_r = 1673.26$; crystal dimensions: $0.32 \times 0.45 \times 0.61$ mm, $a = 13.787(3)$ Å, $b = 15.753(2)$ Å, $c = 19.182(4)$ Å, $\alpha = 89.69(2)°$, $\beta = 81.12(2)°$, $\gamma = 65.85(2)°$, $V = 3748.2(12)$ Å^3, $Z =$

2, $\rho_{\text{calcd.}}$ = 1.483 Mg/m^3, triclinic, space group $P\bar{1}$. Stoe IPDS, Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator, T = 20 °C, $\Theta_{\max}$ = 30.31°, $-19 < h < 16$, $-20 < k < 18$, $-27 < l < 27$, 76976 reflections were detected, 20254 independent (R_{int} = 0.0595), 7640 were classified as "observed" with $I > 2\sigma(I)$, μ = 0.847 mm^{-1}, Direct method (SHELXS-97) and difference Fourier syntheses (SHELXL-97), minimizing of $\Sigma w(F_o^2 - F_c^2)^2$ with $w = 1/[\sigma^2(F_o^2) + 0.03P^2]$ and $P = (F_o^2 + 2F_c^2)/3$, 1048 refined parameters, R_1 = 0.0592, wR_2 = 0.1131, $(\Delta/\sigma)_{\max}$ = 0.001, $\Delta\rho_{\max}/\Delta\rho_{\min}$ = 0.615/−0.358 e Å^{-3}. CCDC-190219 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Preparation for the Synthesis of Epoxides: [Fe(bhpmt)]-$(ClO_4)_2$ (8.4 mg, 1.0 µmol) and the substrate (50 µmol) were dissolved in acetonitrile (15 mL) and treated with 30% hydrogen peroxide (50 µL, 50 µmol). This mixture was stirred for 3 d at room temperature. The substrates used and resulting conversions are displayed in Table 2.

XAS Samples: Solution sample: A 3.2 mM solution of Fe(bhpmt)$(ClO_4)_2$ in acetonitrile (75 µL), with 5 vol.% glycerine, was poured into a sample cell of HESAR glass, covered with Kapton windows. Solid sample: In order to avoid "thickness effects" in the X-ray absorption spectrum, [Fe(bhpmt)]$(ClO_4)_2$ (28 mg) in THF was mixed with boron nitride (59 mg, under aerobic conditions) in order to obtain an absorbance less than unity.[15] The mixture was pasted homogeneously into a sample cell of HESAR glass and was sealed with Kapton windows.

XAS Data Collection: Data were collected at the EMBL bending magnet EXAFS beam line D2 at DESY (Hamburg, Germany) using an Si(111) double crystal monochromator and a double focusing mirror. As detectors ionization chambers (absorption mode for solid sample) and a 13-element solid-state Canberra fluorescence detector (fluorescence mode for solution sample) were used. Absolute energy calibration of the spectra was achieved recording Bragg reflections of a static Si(220) crystal in back-reflection geometry.[16] During data collection, the samples were kept in an He closed-cycle cryostat (modified Oxford instruments) at temperatures below 55 K.

XAS Data Analysis: Data reduction such as background removal and extraction of the EXAFS signal was performed using the EXPROG program package (H. F. Nolting, C. Hermes, EMBL Hamburg) and assuming an Fe-K-edge position of E_0 = 7112 eV. EXAFS data were analyzed with EXCURV98,[10] considering multiple scattering from the units of pyridine, tetrahydrofuran, thiophene, and acetonitrile. Pre-edge peak areas were determined by fitting one (solid) or two (solution) Gaussians to the X-ray absorption spectra (solid: 7100−7121 eV; solution: 7100−7118). In addition, a Lorentzian was used as background function (rising edge).

Acknowledgments

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