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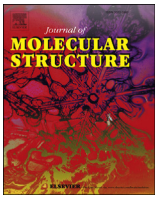

Iron(III) complexes of 2-(1H-benzo[d]imidazol-2-yl)phenol and acetate or nitrate as catalysts for epoxidation of olefins with hydrogen peroxide

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ABSTRACT

Cheap and environmentally friendly Fe(III) catalysts $[Fe(L)_2(CH_3COO)]$ (**1**) and $[Fe(L)_2(NO_3)]\cdot 2CH_3OH$ (**2**) where HL = 2-(1H-benzo[d]imidazol-2-yl)phenol for epoxidation of olefins have been developed. The catalysts have been characterized by elemental analyses, IR, UV–Vis spectroscopy and by X-ray crystallography. The X-ray structures reveal mononuclear compounds having a bidentate acetate or nitrate in **1** and **2**, respectively. Catalytic epoxidations of styrene and cyclohexene have been carried out homogeneously by using 30% aqueous hydrogen peroxide in acetonitrile in the presence of catalytic amounts of **1** or **2**. Yields of the respective epoxides were fair (**1**) to good (**2**) and selectivities were good in all cases although **2** produced two to three times the yield, depending on the substrate, than **1** and higher selectivity as well. A hypothesis for these differences in catalytic efficacy between **1** and **2** that is consistent with mechanistic details of related enzymatic and biomimetic model systems is proposed. Herein we report $[Fe(L)_2(NO_3)]\cdot 2CH_3OH$ (**2**) as the first structurally characterized non-heme iron epoxidation catalyst with a bidentate nitrate ligand.

1. Introduction

In the last decade and a half, biomimetic models of mononuclear non-heme iron-containing enzymes have been studied for reasons that range from the purely academic to the practical [1–3]. Interest in these systems stems from their ability to activate dioxygen or peroxo oxygen atoms and to deliver those atoms to substrates thereby forming epoxides, hydroxylated arenes and oxidized aliphatic C–H bonds. From these studies has come a general understanding of the mechanisms of some of these processes and the probable roles of the various ligands, both innocent and non-innocent, that are bound to the iron center. Reviews by W. Nam in 2007 [4] and in 2015 [5] chronicle advances in this area. Further reviews describe studies revealing underlying principles of the catalytic activity of metalloenzymes and describe application of those principles to development of man-made catalysts for synthetic roles [6,7]. Other studies have looked at underlying electronic structures [8], relationships between structural, electronic and spectroscopic properties [9], tuning of synthetic biomimetic catalyst activity [10], structural effects, including those in the secondary coordination sphere, on catalyst activity [11] and mechanisms of olefin epoxidation by non-heme high-spin iron(III)-acylperoxo species [12]. In addition to illuminating the functioning of various enzymes, some biomimetic model compounds have potential applications in commercial processes [2,13]. These applications are attractive because the iron systems can, in principle, replace existing catalysts consisting of expensive or toxic metal compounds with a "green" alternative [14]. The systems described below derive from our search for catalysts that are functional in partially or entirely aqueous solvents. Such solvents are obviously inherently less polluting or dangerous than some presently in use. We report here syntheses, characterizations, including single crystal X-ray structures, and catalytic olefin epoxidations in

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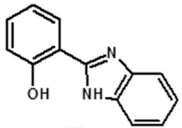
presence of H_2O_2 of two iron(III) complexes derived from 2-(1H-benzo[d]imidazol-2-yl)phenol (HL), a compound that is of interest because of its potential to provide a coordination sphere for iron with some similarities to those in dioxygen activating enzymes.



HL

2. Experimental

2.1. Materials and measurements

All chemicals were of reagent grade, were purchased from Sigma–Aldrich and used without further purification. Solvents were used as received. The benzimidazole-based ligand, 2-(1H-benzo[d]imidazol-2-yl)phenol (HL), was prepared according to the previously reported method [15].

Elemental (C, H and N) analyses were carried out on a Perkin–Elmer 2400II elemental analyzer. Fourier Transform Infrared (FTIR) spectra (4000–400 cm^{-1}) were recorded using KBr disks on a JASCO FTIR-460 Plus spectrophotometer set at 70 scans and 4 cm^{-1} resolution. Electronic absorption spectra were obtained from 1×10^{-5} mol/L solutions in dimethylformamide (DMF) (**1**) and acetonitrile (**2**) by using a JASCO V-530 spectrophotometer. Gas chromatographic analyses were performed with an Agilent Technologies 6890 N network GC system equipped with a fused silica capillary HP-5 column (30 m × 0.32 mm) and a flame ionization detector (FID).

2.2. Synthesis of complexes

2.2.1. [Fe(L)$_2$(CH$_3$COO)] (**1**)

To a stirred methanol solution (10 mL) of HL (0.42 g, 2.0 mmol), a solution of sodium acetate (0.33 g, 4.0 mmol) in the same solvent (10 mL) was added. The resulting solution was added dropwise with stirring to an acetonitrile solution (10 mL) of $Fe(ClO_4)_3 \cdot 6H_2O$ (0.46 g, 1.0 mmol). The color of the solution changed from yellow to dark pinkish brown and a dark brown microcrystalline precipitate appeared within a few minutes. The precipitate was collected by filtration and thoroughly washed with hot acetonitrile and methanol. Yield: 0.22 g (42%). X-ray quality dark brown prismatic crystals of **1** were collected by layering a solution of the compound in dimethylformamide with diethyl ether. *Anal. Calc.* for $C_{28}H_{21}FeN_4O_4$: C, 63.06; H, 3.97; N, 10.50%. Found: C, 62.84; H, 3.79; N, 10.82%. IR (KBr, cm^{-1}): 3432 (w, br), 3058 (w), 1669 (s), 1621 (m), 1599 (s), 1556 (m), 1531 (m), 1478 (s), 1441 (s), 1386 (m), 1317 (m), 1262 (s), 1133 (s), 858 (m), 806 (m), 746 (s), 617 (m). UV–Vis [DMF, λ_{max}, nm (ε, dm^3 $mole^{-1}$ cm^{-1})]: 290 (75,600), 316 (90,500), 330 (87,200), 457 (6600).

2.2.2. [Fe(L)$_2$(NO$_3$)]·2CH$_3$OH (**2**)

To a stirred solution of HL (0.42 g, 2.0 mmol) in methanol (10 mL) was added successively a methanol solution (10 mL) of $Fe(NO_3)_3 \cdot 9H_2O$ (0.40 g, 1.0 mmol) and a solution of triethylamine (0.20 g, 2.0 mmol) in methanol (5 mL). The solution which changed from yellow to dark pinkish brown was stirred for 2 h, filtered and the filtrate was kept undisturbed at room temperature until X-ray quality dark brown crystals of **2** were deposited. These were collected by filtration. Yield: 0.26 g (44%). *Anal. Calc.* for $C_{28}H_{26}FeN_5O_7$: C, 56.01; H, 4.36; N, 11.66%. Found: C, 55.92; H, 4.22; N, 11.85%. IR (KBr, cm^{-1}): 3391 (w, br), 3058 (w), 1623 (m), 1601 (s), 1560 (m), 1517 (m), 1478 (s), 1459 (m), 1444 (s), 1383 (s), 1324 (m), 1305 (m), 1249 (s), 1139 (s), 867 (m), 806 (m), 753 (s), 736 (s), 626 (m). UV–Vis [CH_3CN, λ_{max}, nm (ε, dm^3 $mole^{-1}$ cm^{-1})]: 291 (168,000), 317 (175,000), 328 (173,000), 496 (11,000).

2.3. X-ray crystallography

Single crystals of [Fe(L)$_2$(CH$_3$COO)] (**1**) and [Fe(L)$_2$(NO$_3$)]·2CH$_3$OH (**2**) were coated with oil and mounted on a MiTeGen loop (**1**) or glass fiber (**2**). Intensity data were collected at 153(2) K (**1**) and 100(2) K (**2**) on a Rigaku Saturn 70 diffractometer (**1**) or a Bruker-AXS SMART APEX II diffractometer (**2**) equipped with CCD detectors using graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å). The data for (**1**) were processed *via* the Crystal Clear software suite [16], while for (**2**) this was performed with SAINT [17] and absorption corrections were made with SADABS [18] software packages. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares analysis based on F^2 using the CrystalStructure [19] graphical interface for (**1**), and WINGX software of SHELXTL [20] for (**2**), and with SHELX-97 [21]. Non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed at their geometrically calculated positions with fixed isotropic parameters. Details of crystallographic parameters, data collection and refinements for compounds **1** and **2** are given in Table 1.

2.4. Catalysis

Epoxidation reactions were carried out in a magnetically stirred two-necked round-bottomed flask fitted with a condenser and placed in a temperature controlled oil bath. Typically, one equivalent of the substrate was dissolved in acetonitrile (5 mL) to which was added 0.02 equivalents of the catalyst and the mixture then heated to 60 °C. Aqueous (30%) hydrogen peroxide (equimolar with respect to the substrate) was then added and timing for withdrawal of aliquots was started. Aliquots of 0.100 mL were collected from

Table 1
Crystallographic data for [Fe(L)$_2$(CH$_3$COO)] (**1**) and [Fe(L)$_2$(NO$_3$)]·2CH$_3$OH (**2**).

Parameter	**1**	**2**
Empirical formula	$C_{28}H_{21}FeN_4O_4$	$C_{28}H_{26}FeN_5O_7$
Formula weight	533.35	600.39
T (K)	153(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	*Fdd2*	*Fdd2*
a (Å)	13.773(3)	15.5421(7)
b (Å)	27.460(6)	33.0593(14)
c (Å)	13.201(3)	10.5522(5)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	90.00	90.00
V (Å^3)	4992.8(19)	5421.8(4)
Z	8	8
μ (mm^{-1})	0.646	0.613
λ (Å)	0.71075	0.71075
F(000)	2200	2488
Crystal size (mm^3)	0.24 × 0.15 × 0.14	0.32 × 0.26 × 0.22
D_{calc} (g cm^{-3})	1.419	1.471
No. of data/restraints/params	2556/1/170	2487/1/193
No. of reflns [$I > 2\sigma(I)$]	10,529	15,916
GOF on F^2	1.100	1.055
Final R indices[$I > 2\sigma(I)$]	R_1[a] = 0.0290, wR_2[b] = 0.0775	R_1[a] = 0.0360, wR_2[b] = 0.0967
R indices (all data)	R_1[a] = 0.0291, wR_2[b] = 0.0777	R_1[a] = 0.0391, wR_2[b] = 0.0988

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{½}$.