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Iron(III) aroylhydrazone complexes: Structure, electrochemical studies and catalytic activity in oxidation of olefins

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ABSTRACT

Tridentate Schiff base ligands derived from aromatic aldehydes and benzhydrazide, and their iron complexes $[Fe(L^1)(HL^1)]$ **1**, $[Fe(HL^1)Cl_2(CH_3OH)]\cdot(CH_3OH)$ **2** and $[Fe(HL^2)Cl_2(H_2O)]$ **3** have been prepared and characterized ($H_2L^1 = (E)$-N'-(2-hydroxy-3-methoxybenzylidene)benzohydrazide, $H_2L^2 = (E)$-N'-(5-bromo-2-hydroxybenzylidene)benzohydrazide). The crystal structure of **2** has been determined. The electrochemical properties of these complexes have been investigated by cyclic voltammetric technique in acetonitrile solutions. Electrochemical studies have revealed quasi-reversibility for these compounds. The catalytic potential of these complexes has been tested for the oxidation of cyclooctene using *tert*-butylhydroperoxide (TBHP) as oxidant. The effects of the molar ratio of oxidant to substrate, the temperature, the co-catalyst concentration and the solvent have been studied. Excellent selectivities have been obtained for the epoxidation of cyclohexene, cyclooctene, norbornene, *cis*- and *trans*-stilbene.

1. Introduction

The design of metal catalysts to mimic bio-oxidative activity of P-450 has continued to be an active area of research [1]. There have been numerous reports on the catalytic oxidation of organic substrates by porphyrin complexes [2,3]. Due to the difficulties in modification, the preparation of other planar tetradentate ligands, especially Schiff base [4,5] and amido ligands [6], is highly desirable. The oxidation of hydrocarbons with Schiff base complexes has been a field of academic and industrial interest to analyze the catalytic activity of various metal complexes [7]. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. The development in the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species [8]. Iron-catalyzed systems for C–H oxidation (Gif8 and Fenton chemistry [9], nonheme mimic systems [10–12], olefin epoxidation [5], and the chemistry of Fe-porphyrins [13]) have been summarized in various reports.

The remarkable biological activity of acid hydrazides $R–CO–NH–NH_2$, a class of Schiff base, their corresponding aroylhydrazones, $R–CO–NH–N{=}CH–R'$, and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant interest [14–17]. The coordination compounds of aroylhydrazones have been reported to act as enzyme inhibitors [18] and are useful due to their pharmacological applications [19]. Aroylhydrazones complexes, on the other hand, seem to be a good candidate for catalytic oxidation studies because of their stability to resist oxidation. Investigation into the iron-binding potential of a range of hydrazone derivatives [20–22], as drugs for genetic disorders such as thalassemia, led to the discovery that salicylaldehyde benzoylhydrazone inhibits DNA synthesis and cell growth [23]. This class of diprotic ligand typically acts as tridentate, planar chelate ligand coordinating through the phenolic and amide oxygens and the imine nitrogen. The actual ionization state is dependent upon the conditions and metal employed [24]. With copper(II) in alkaline solution, both the phenolic and amide protons are ionized; in neutral and mild acidic solution the ligands are monoanionic, whereas strongly acidic conditions are necessary to form compounds formulated with a neutral ligand. A binuclear complex of iron(III) with a Schiff base hydrazone derived from 7-chloro-4-hydrazinoquinoline and bridging chloride has been reported [25].

Continuing our studies on catalysis by hydrazone Schiff base manganese complexes [26], we report herein on the synthesis of a series of iron(III) complexes containing substituted aroylhydrazones ligands (Fig. 1) as well as their applications in catalytic epoxidation of olefins with *tert*-butylhydroperoxide.

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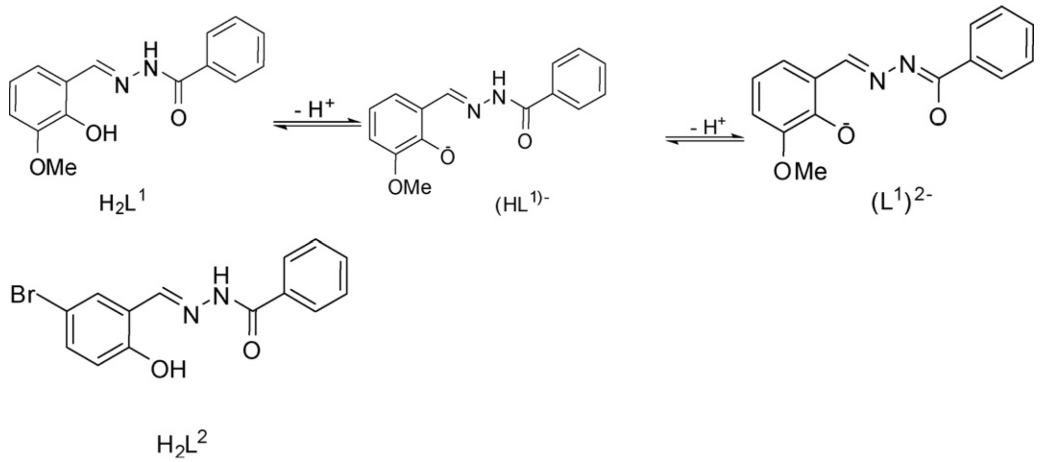

Fig. 1. *In situ* formed H_2L^1 and H_2L^2 ligands.

2. Experimental

2.1. Equipments

The reaction products of oxidation were determined and analyzed by HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320 μm × 0.25 μm) with flame-ionization detector and gas chromatograph–mass spectrometry (Hewlett-Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector). ^{1}H NMR spectra were recorded by use of a Bruker 250 MHz spectrometer. Atomic absorptions were measured by a Varian 220 FS spectrophotometer. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer. IR spectra were recorded using PerkinElmer 597 and Nicolet 510P spectrophotometers. A Thermospectronic model α, UV–vis spectrometer with 1 cm quartz cells was used for recording and storage of UV–vis absorbance spectra.

2.2. Experimental

Voltammetric experiments were performed using a Metrohm computrace voltammetric analyzer model 757 VA. A conventional three-electrode system was used with a polished glassy carbon electrode (area 3.14 mm^2) as working electrode and a platinum wire counter electrode. The reference was an aqueous Ag/AgCl saturated electrode, separated from the bulk of the solution by a bridge with solvent and supporting electrolyte. The solutions in the bridge were changed periodically to avoid aqueous contamination from entering the cell via the Ag/AgCl electrode. Before each experiment the working electrode was cleaned by polishing with alumina 0.05 mm and rinsed thoroughly with distilled water and acetone. The electrolytic medium consisted of 0.1 mol/l tetrabutylammonium perchlorate (TBAP) as supporting electrolyte in acetonitrile and all experiments were carried out at room temperature. The solutions were freshly prepared before use, and were purged with N_2 saturated with solvent for ca. 15 min prior to taking measurements in order to remove dissolved O_2. Voltammograms were recorded in the range from −0.7 to +0.7 V vs. Ag/AgCl.

2.3. Materials

Iron(III) chloride hexahydrate, anhydrous iron(II) chloride, benzhydrazide, 2-hydroxy-3-methoxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde, *tert*-butylhydroperoxide (TBHP) (solution 80% in di-*tert*-butylperoxide) and the olefins were purchased from Merck and Fluka and used as received. Solvents of the highest grade commercially available (Merck) were used without further purification.

2.4. Synthesis of [$Fe^{III}(L^1)(HL^1)$], **1** (H_2L^1 = (E)-N′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide)

Benzhydrazide (0.20 g, 1.47 mmol) and 2-hydroxy-3-methoxybenzaldehyde (0.22 g, 1.47 mmol) were dissolved in methanol (100 ml). A solution of $FeCl_3{\cdot}6H_2O$ (0.40 g, 0.148 mmol) and NaN_3 (0.147 g, 2.26 mmol) in methanol (50 ml) was added to the above solution and refluxed for 3 h. The resulting black-brown solid **1** was filtered off, washed with methanol and dried under air (0.319 g, yield 73%).

IR (KBr, cm^{-1}): 3371 (s), 3170 (s, br), 2785 (w), 1682 (vs), 1620 (s, br), 1396 (s), 1365 (m), 1203 (m), 1026 (m), 779 (m), 702 (m), 609 (s), 509 (m), 409 (m).

2.5. Synthesis of [$Fe(HL^1)Cl_2(CH_3OH)$]·CH_3OH, **2**

Benzhydrazide (0.20 g, 1.47 mmol) and 2-hydroxy-3-methoxybenzaldehyde (0.22 g, 1.47 mmol) were dissolved in methanol (100 ml). A solution of $FeCl_3{\cdot}6H_2O$ (0.40 g, 1.48 mmol) in methanol (50 ml) was added to the above solution and refluxed for 3 h. The resulting black-green solid **3** was filtered off, washed with methanol and dried under air (0.636 g, yield 94%).

IR (KBr, cm^{-1}): 3431 (vs, br), 3231 (s), 2931 (m), 2862 (w), 1600 (vs), 1546 (vs), 1438 (s), 1392 (s), 1315 (m), 1262 (m), 1223 (s), 1092 (s), 746 (w), 708 (m).

2.6. Synthesis of [$Fe(HL^2)Cl_2(H_2O)$], **3** (H_2L^2 = (E)-N′-(5-bromo-2-hydroxybenzylidene)benzohydrazide)

Benzhydrazide (0.20 g, 1.47 mmol) and 5-bromo-2-hydroxybenzaldehyde (0.30 g, 1.49 mmol) were dissolved in methanol (100 ml). A solution of $FeCl_3{\cdot}6H_2O$ (0.40 g, 1.48) in methanol (50 ml) was added to the above solution and refluxed for 3 h. The resulting black-brown solid **2** was filtered off, washed with methanol and dried under air (0.480 g, yield 69%).

IR (KBr, cm^{-1}): 3431 (s, br), 3215 (m), 2923 (m), 2862 (w), 1608 (vs), 1562 (m), 1531 (m), 1500 (m), 1462 (s) 1374 (s), 1346 (m), 1300 (s), 1185 (vs, br), 1092 (s), 715 (m), 654 (m), 600 (m).