



Catalytic oxidation of alcohols and sulfides with hydrogen peroxide using isoindoline and phthalazine-based diiron complexes



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ARTICLE INFO

Article history:

Received 22 April 2014

Received in revised form 18 June 2014

Accepted 25 June 2014

Available online 4 July 2014

Keywords:

Iron

Oxidations

Hydrogen peroxide

Alcohols

Sulfides

ABSTRACT

A series of diiron(III) complexes of 1,3-bis(2'-arylimino)isoindoline, [(Fe(L)Cl)₂O] and 1,4-di-(2'-aryl)aminophthalazine, [Fe₂(μ-OMe)₂(H₂L)Cl₄], including new structurally characterized ligands, 1,4-di-(4'-methyl-2'-thiazolyl)aminophthalazine and 1,4-di-(2'-benzthiazolyl)aminophthalazine, have been characterized, and used as catalysts for the oxidation of *para*-substituted phenyl methyl sulfides and benzyl alcohols. Hammett correlations and kinetic isotope effect experiments support the involvement of electrophilic metal-based oxidants. In case of [(Fe(L^{1,2})Cl)₂O] catalysts, direct correlation has been found between the oxidative and catalase-like activity.

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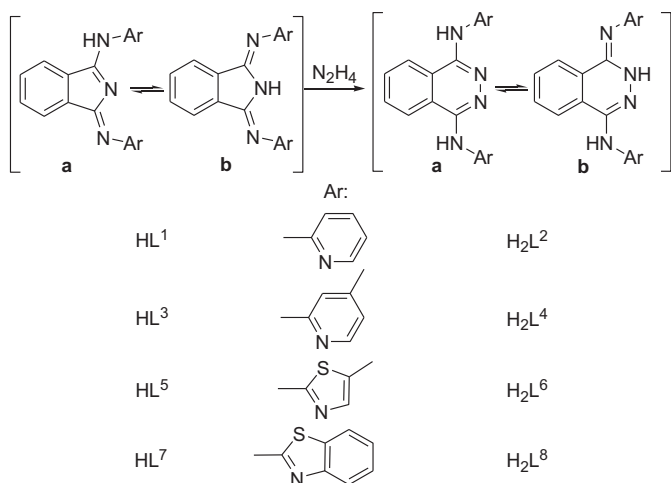
1. Introduction

Development of novel, efficient and inexpensive catalytic system for the oxidation of alcohols and sulfides under mild conditions is an important goal in chemistry. Metal-based oxidation catalysis is a powerful and extremely versatile synthetic tool to afford selectively oxidized products both in homogeneous and in heterogeneous conversions [1–6]. The oxidation of organic sulfides and alcohols by iron complexes along with primary oxidants like iodosobenzene [7], alkyl hydroperoxides [8,9], H₂O₂ [10,11], and molecular oxygen is well established [12]. The chemistry of 1,3-bis(2'-pyridylimino)isoindoline [13–16] and 1,4-di-(2'-pyridyl)aminophthalazine [17,18] ligands exhibited rich metal chemistry, binding a variety of transition metal ions. The latter, that are good tethering units for dinuclear complexes, can directly be synthesized from their 1,3-bis(2'-pyridylimino)isoindoline precursors. In these complexes, it was possible to control the redox potential of the metal center by varying the aryl substituent on the bis-iminoisoindoline moiety as illustrated in Scheme 1.

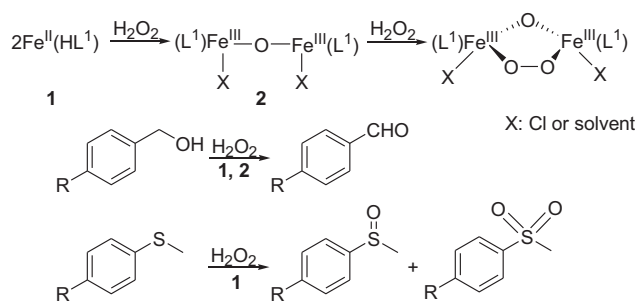
Isoindoline- and phthalazine-based complexes have been used to model enzymatic active sites to explore their biological activity such as: quercetinase [19,20], catecholase [21–23], catechol dioxygenase [24], catalase [25] and SOD [26,27] mimics activity, furthermore they can act as catalysts in various organic transformations [28–30]. We have previously reported the synthesis and crystal structures of a μ-oxido-bridged diiron(III) complex, [Fe₂(μ-O)(L¹)₂Cl₂] (2) and a new iron(II) complex, [Fe(HL¹)(CH₃CN)₃](ClO₄)₂ (1), and their catalytic activity on the oxidation of thioanisoles and benzyl alcohols [31–33]. We have also reported the spectroscopic characterization of a transient green species, Fe^{III}(μ-O)(μ-1,2-O₂)Fe^{III} derived from the reaction of 1 with H₂O₂ upon the formation of 2, which is linked somehow to the observed oxidative reactivity (Scheme 2). More recently a new diiron complex, [Fe₂(μ-OMe)₂(H₂L¹)Cl₄] (3) was prepared and studied its catalytic activity on the oxidation of primary and secondary alcohols with H₂O₂ compared to 2 [34].

In the present work, a series of diiron(III) complexes with the ligands 1,3-bis(2'-arylimino)isoindoline and 1,4-di-(2'-aryl)aminophthalazine have been synthesized and characterized by spectroscopic methods. Single crystals suitable for X-ray crystallography have been obtained in two cases (Scheme 3). New members of this ligand family became available by introducing different functional groups at the imine moiety as shown in Scheme 1.

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Scheme 1. Structure of the isoindoline-based ligands.



Scheme 2. Oxidative reactivity of isoindoline-based iron complexes.

We also report an initial investigation on the catalytic reactivity of the new diiron(III) complexes combined with H₂O₂ that focuses on the oxidation of *para*-substituted thioanisoles and benzyl alcohols with the intention to find a direct correlation between their oxidative and catalase-like activity.

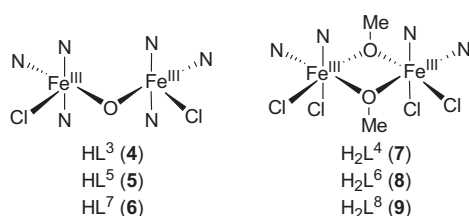
2. Experimental

2.1. Materials

All manipulations were performed under a pure argon atmosphere using standard Schlenk-type techniques unless otherwise stated. Solvents used for the reactions were purified by literature methods [35] and stored under argon. All other chemicals are commercially available and they were used without further purification.

2.2. Analytical and physical measurements

Infrared spectra were recorded on an Avatar 330 FT-IR Thermo Nicolet instrument using samples mullied in KBr pellets. UV–vis



Scheme 3. Structural representation of the synthesized diiron(III) complexes.

spectra were recorded on a Cary 60 spectrophotometer equipped with a fiber-optic probe with 1 cm pathlength. Microanalyses were done by the Microanalytical Service of the University of Pannonia. The crystal evaluations and intensity data collections were performed on a Bruker–Nonius Kappa CCD single-crystal diffractometer (5, 8) using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Crystallographic data and details of the structure determination are given in Table 1, whereas selected bond lengths and angles are listed in Tables 2 and 3. SHELX–2013 [36] was used for structure solution and full matrix least squares refinement on F^2 . CIF files are available in the CCDC database: CCDC 990911 and 990912 (5, 8). GC measurements were performed on a HP 5890 gas chromatograph equipped with a 30 m Supelcowax column.

2.3. Synthesis of 1,4-di-(4'-methyl-2'-thiazolyl)aminophthalazine (H₂L⁶) and 1,4-di-(2'-benzthiazolyl)aminophthalazine (H₂L⁸)

The phthalazine ligands were synthesized according to the method reported for the 1,4-di-(2'-pyridyl)aminophthalazines (H₂L^{2,4}) with small modifications [37,38].

To a refluxing solution of a HL⁵ or HL⁷ (2 mmol) in ~200 mL THF, ~3 mL (~61 mmol) hydrazine monohydrate was added dropwise. The color changed from orange to yellow within 30 min. The mixture was stirred and refluxed overnight (or until ammonia evolution ceased). The volume of THF was reduced to ~20 mL in vacuum, and 30 mL MeOH was added to the hot solution. The crystalline product (H₂L⁶ and H₂L⁸ respectively) was filtered, washed with methanol and vacuum dried.

H₂L⁶: ¹H NMR (DMSO): δ /ppm: 8.52–8.39 (m, 2H), 7.87–7.72 (m, 2H), 7.05 (s, 2H), 2.33 (s, 6H). IR (KBr) cm⁻¹: 3333 s, 3191 s, 3038 s, 1621 s, 1571 s, 1489 m, 1417 m, 1359 s, 1320 m, 1203 w, 1151 m, 1135 m, 1080 w, 961 w, 829 w, 785 m, 763 m, 670 w, 632 w, 588 w, 522 w. UV–vis (DMF) λ_{max} (nm, log ϵ): 430 (3.95), 409 (4.13), 393 (4.09), 307 (3.84), 288 (4.10). C₁₆H₁₄N₆S₂: calcd. C 54.22; H 3.98; N 23.71; found C 54.03; H 4.02; N 23.66.

H₂L⁸: ¹H NMR (DMSO): δ /ppm: 8.67–8.56 (m, 2H), 8.01–7.93 (m, 2H), 7.84 (d, $J = 7.6 \text{ Hz}$, 2H), 7.69–7.52 (m, 2H), 7.38 (t, $J = 8.0, 2\text{H}$), 7.20 (t, $J = 7.6, 2\text{H}$). IR (KBr) cm⁻¹: 3302 w, 3057 w, 2925 w, 1625 m, 1558 s, 1454 w, 1435 m, 1361 s, 1307 w, 1267 w, 1151 m, 1064 w, 1013 w, 911 w, 784 w, 744 m, 717 m, 695 w, 637 w, 588 w, 486 w. UV–vis (DMF) λ_{max} (nm, log ϵ): 428 (4.36), 405 (4.50), 388 (4.42), 290 (4.43), 282 (4.42). C₂₂H₁₄N₆S₂: calcd. C 61.95; H 3.31; N 19.70; found: C 61.89; H 3.28; N 19.52.

2.4. Synthesis of [Fe₂(μ -O)(L^{3,5,7})₂Cl₂] (4,5,6)

Ligand HL³ (1.32 g, 4 mmol) HL⁵ (1.36 g, 4 mmol) or HL⁷ ligand (1.65 g, 4 mmol) was dissolved in 30 mL MeOH, then a solution of FeCl₃ \times 6 H₂O (1.08 g, 4 mmol) in 10 mL MeOH was slowly added, and the solution was refluxed for 8 h under air. A precipitation formed that was filtered and washed with cold MeOH, and ether then dried under high vacuum. The dark purple precipitate was filtered, washed with cold MeOH and ether.

(4) (1.56 g, 91%). IR (KBr) cm⁻¹: 2962 w, 1611 w, 1581 s, 1548 m, 1524 m, 1470 m, 1279 m, 1241 m, 1185 m, 1045 s, 939 m, 819 w, 759 w, 713 m. UV–vis (DMF) λ_{max} (nm, log ϵ): 283 (4.60), 329 (4.47), 368 (4.45), 387 (4.50), 474 (3.83). C₄₀H₃₆Cl₂Fe₂N₁₀O: calcd. C 56.17; H 4.24; N 16.37; found C 55.79; H 4.01; N 16.09.

(5) (1.42 g, 80%). IR (KBr) cm⁻¹: 2962 w, 2921 w, 1548 s, 1530 s, 1460 m, 1311 m, 1241 m, 1185 m, 1110 m, 1091s, 1063 s, 819 w, 782 w, 751 w, 720 m, 526 w. UV–vis (DMF) λ_{max} (nm, log ϵ): 283 (4.51), 392 (4.34), 520 (3.32), 446 (4.31), 474 (4.89), 787 (3.76). C₃₂H₂₄Cl₂Fe₂N₁₀OS₄: calcd. C 43.90; H 2.76; N 16.00; found C 43.26; H 2.94; N 15.51. Crystals suitable for X-ray structural determination were obtained from DMF.

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