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A new iron(III) complex of glycine derivative of amine-chloro substituted phenol ligand: Synthesis, characterization and catechol dioxygenase activity

Iraj Saberikia [a], Elham Safaei [a,*], Mohammad Hossein Kowsari [a], Yong-Ill Lee [b], Patricia Cotic [c], Giuseppe Bruno [d], Hadi Amiri Rudbari [d]

[a] Institute for Advanced Studies in Basic Sciences (IASBS), 45137-66731 Zanjan, Iran
[b] Department of Chemistry, Changwon National University, Changwon 641-773, South Korea
[c] Institute of Mathematics, Physics and Mechanics, University of Ljubljana, Ljubljana, Slovenia
[d] Dipartimento di Chimica Inorganica, Salita Sperone 31, Università di Messina, 98166 Messina, Italy

HIGHLIGHTS

- An iron(III) complex of glycine derivative of chloro-substituted bis(phenol)amine synthesized.
- The complex displayed paramagnetic and metal-centered reduction, and a ligand-centered oxidation.
- The oxygenation cleavage of catechol derivatives with this complex was investigated.

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ABSTRACT

A new iron(III) complex of the glycine derivative of amine-chloro substituted phenol ligand (H_3L^{GDC}) has been prepared and characterized by IR, ^{1}H NMR, UV–Vis spectroscopic techniques, cyclic voltammetry, ESI-MS and magnetic susceptibility studies. X-ray analysis reveals that in iron complex of FeL^{GDC} the iron(III) center has a distorted trigonal bipyramidal coordination sphere and is surrounded by an amine nitrogen, a carboxylate, a water and two phenolate oxygen atoms. The DFT calculations with the UB3LYP/6-311++G** level optimized structure of the complex are in good agreement with experimental X-ray structural data. The variable-temperature magnetic susceptibility indicates that FeL^{GDC} is the paramagnetic high spin iron(III) complex. It has been shown that electrochemical oxidation of this complex is ligand-centered due to the oxidation of phenolate to the phenoxyl radicals. This enzyme mimic utilized molecular oxygen in carrying out the oxidative cleavage of catechols with complete conversion at room temperature.

1. Introduction

Aromatic hydrocarbons are highly toxic environmental pollutants that can be degraded by bacteria under aerobic conditions. The aerobic biodegradation of these compounds is usually initiated by dioxygenases, which catalyze the oxidative cleavage of these compounds with concomitant insertion of both oxygen atoms of molecular oxygen into the aromatic ring of the substrate resulting in ring cleavage [1–3]. This large family of enzymes utilizes similar, mononuclear non-heme iron centers to activate the oxygen molecule to perform oxygenation at lateral positions and a variety of important biological functions [4–8]. Non-heme–iron dependent dioxygenase enzymes which catalyze the oxidative cleavage of catechol substrates are classified according to the different redox states of the iron associated with different reaction mechanisms [9]. The intradiol catechol dioxygenases utilize mononuclear iron(III) centers to catalyze the oxidative cleavage of the carbon–carbon bond between the two phenolic hydroxyl groups, while the extradiol-type enzymes contain a non-heme iron(III) molecule, cleave the adjacent carbon–carbon bond (Scheme 1).

Intradiol-type dioxygenases activate the metal-bound substrate, whereas the extradiol-type dioxygenases activate the O_2 bound to the iron, copper, manganese and magnesium containing dioxygenases have also been isolated [10].

Several bioinorganic modeling studies [9–30] have focused on the structural and spectroscopic characterization of iron(III) complexes of tripodal tetradentate, tetraaza macrocyclic and tetradentate bis(phenolate) ligands [12–14,19–31] as structural and functional models for the catecholate–iron(III) form of catechol dioxygenases. According to these studies, the significance of Lewis

* Corresponding author. Tel.: +98 241 4153200; fax: +98 241 4153232.
E-mail address: safaei@iasbs.ac.ir (E. Safaei).

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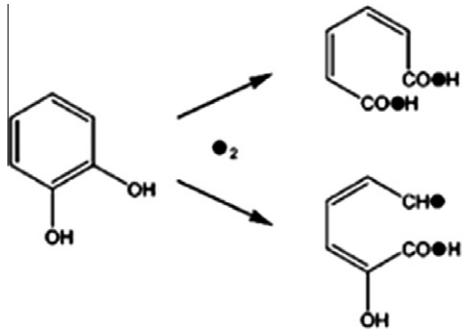
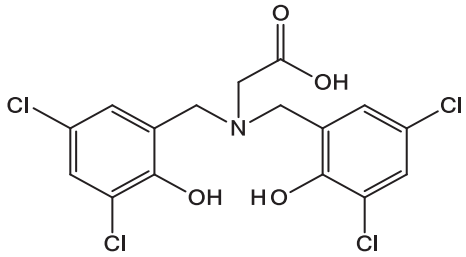


Scheme 1. Scheme of cleavage by intradiol and extradiol dioxygenases [7].



Scheme 2. Structure of [2-(bis(3,5-dichloro-2-hydroxybenzyl) amino) acetic acid] (H_3L^{GDC}).

acidity of iron(III) centers in the dioxygenase reactions have been highlighted [9–20].

In this paper, we report the synthesis, characterization, magnetic and redox properties, and catalytic activity of FeL^{GDC} complex of [N—O]-donor tripodal amine phenol ligand H_3L^{GDC}, 2-(bis-(3,5-dichloro-2-hydroxybenzyl)amino)acetic acid) (Scheme 2) which provide the coordination sphere around iron center. The oxygenation of catechol family with FeL^{GDC} as a functional model for catechol dioxygenases will be investigated with emphasize on the role of chlorine substituents on the catalytic activity of complex.

2. Experimental

2.1. Materials and physical measurements

Reagents or analytical grade materials were obtained from commercial suppliers and used without further purification, except those for electrochemical measurements. Elemental analyses (C, H, N) were performed by were performed by the Elementar, Vario EL III. Fourier transform infrared spectroscopy on KBr pellets was performed on a FT IR Bruker Vector 22 instrument. NMR measurements were performed on a Bruker 400 instrument. UV–Vis absorbance digitized spectra were collected using a CARY 100 spectrophotometer. The electronic spectra of the complex recorded in the CH_2Cl_2 solvent.

The ligand samples were dissolved in acetonitrile (1.0×10^{-4} M) and mixed with deionized water (1:1) just before the mass spectroscopic measurements. The identification of interaction products was performed using Thermo Finigan LCQ advantage ion trap mass spectrometer equipped with electrospray ionization. For sample injections, the instrument syringe pump was used at flow rate of 2 L/min. The instrumental operation conditions were as follows; spray voltage, 4.58 kV; source current, 0.48 A; sheath gas flow rate,19.43 L/min; capillary voltage; 9.44 V, capillary temperature 100 °C, tube lens voltage; 55 V. Experiments were performed in positive-ion mode and optimized by Xcalibur software before the experiments. All MS experiments in this work have been carried out under the optimized instrument conditions. All reported mass spectra are the average of at least 30 consecutive scans.

The mass spectrometry was performed on a QToF Premier (Waters, Manchester, UK) tandem mass spectrometer which had a quadrupole time-of-flight detector with orthogonal acceleration in V mode. The system was operated by MassLynx 4.1 software (Waters-Micromass, Manchester, UK) in positive ion electrospray mode. High purity nitrogen was used as the nebulizer and auxiliary gas, and argon was the collision gas. The nebulizer gas was set to 150 L/h at 150 °C and the cone gas and the source temperatures were set to 20 L/h and 90 °C, respectively. The capillary, extraction, and sample cone voltages were set to 3.0 V, 5.0 V, and 25 V, respectively. The instrument was operated in full-scan mode with QToF data collected between m/z 100–1000, with collision energy of 3 eV. The data were stored in the centroid mode with a scan time of 0.5 s and an inter scan delay of 0.01 s. The MS/MS experiments were performed using collision energies which were optimized for the corresponding analytes. Samples were injected at a flow rate of 5 μL/min. The QToF detector (MCP) was operated at 2100 V.

GC–MS was performed with a Clarus 600 GCMS (Perkin Elmer, Waltham, MA, USA). A 30 m capillary column coated with (5% diphenyl)dimethylpolysiloxane (0.25 mm i.d. and 1 μm film thichness; Elite-5MS, Perkin Elmer, Waltham, MA, USA) was used. The carrier gas was He at a flow 1.0 mL/min. Injection port and transfer line temperature was 270 °C. Samples were injected in methanol. The oven temperature program started at 70 °C (5 min), was raised at 20 °C/min to 200 °C, held for 15 min. and heated at 10 °C/min to 310 °C hold for 5.5 min. The quadrupole mass spectrometer was operated in EI mode (70 eV), scanning between m/z 40 and 520. The ion source temperature was 230 °C.

Magnetic susceptibility were measured from powder samples of solid material in the temperature range 2–300 K by using a SQUID susceptometer (Quantum Design MPMS-XL-5) in a magnetic field of 1000 Oe.

Voltammetric measurements were made with a computer controlled Auto Lab electrochemical system (ECO Chemie, Ultrecht, The Netherlands) equipped with a PGSTA 30 model and driven by GPES (ECO Chemie). A glassy carbon electrode with a surface area of 0.035 cm^2 was used as a working electrode and a platinum wire served as the counter electrode. The reference electrode was an Ag wire as the quasi reference electrode. Ferrocene was added as an internal standard after completion of a set of experiments, and potentials are referenced vs. the ferrocenium/ferrocene couple (Fc^+/Fc).

Diffraction data for FeL^{GDC} was measured on a Bruker–Nonius X8 ApexII diffractometer equipped with a CCD area detector by using graphite-monochromated Mo Kα radiation ($k = 0.71073$) generated from a sealed tube source. Data were collected and reduced by smart and saint software [32] in the Bruker package. The structure was solved by direct methods [33], than developed by least squares refinement on F^2 [34]. All non-H atoms were placed in calculated positions and refined as isotropic with the "riding-model technique". Details concerning collection and analysis are reported in Table 1.

2.2. Preparations

2.2.1. Synthesis of H_3L^{GDC}

The ligand was synthesized according to modified literature procedure [35–39]. As aqueous formaldehyde was one of the reagents, in some cases no added solvent was required beyond what was already present in the reagents solution.

A solution of 2,4-dichlorophenol (7.80 g, 48.00 mmol), 2-aminoacetic acid (1.8 g, 24.00 mmol), and 37% aqueous formaldehyde (3.58 mL, 48.00 mmol) was stirred and refluxed for 48 h. Upon cooling, a large quantity of beige solid was formed. The solvent