Inorganica Chimica Acta 362 (2009) 4699–4705

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Functional model for catecholase-like activity: Synthesis, structure, spectra, and catalytic activity of iron(III) complexes with substituted-salicylaldimine ligands

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A R T I C L E I N F O

Article history:
Received 17 November 2008
Received in revised form 17 June 2009
Accepted 19 June 2009
Available online 27 June 2009

Keywords:
Model of catechol oxidase
Mononuclear iron(III) complexes
Salicylaldimine
Crystal structure
Mössbauer effect

A B S T R A C T

Four new mononuclear iron(III) complexes with the substituted-salicylaldimine ligands, [Fe(L^1)(TCC)] (**1**), [Fe(L^2)(TBC)] (**2**), [Fe(L^3)(TBC)] (**3**) and [Fe(L^4)(TCC)](CH_3CN) (**4**) (HL^1 = N′-(5-OH-salicylaldimine)-diethylenetriamine, HL^2 = (N′-(5-Cl-salicylaldimine)-diethylenetriamine, HL^3 N′-(5-Br-salicyl-aldimine)-dipropylenetriamine, HL^4 = (N′-3,5-Br-salicylaldimine)-dipropylenetriamine, H_2TCC = tetrachlorocatechol, and H_2TBC = tetrabromocatechol), were prepared and characterized by XRD, EPR, and Mössbauer spectroscopy. The coordination sphere of the Fe(III) in complexes **1**–**4** is a distorted octahedral with N_3O_3 donors set which constructed by the Schiff-base ligands and the catecholate substrates of TBC or TCC. The *in situ* prepared Fe(III) complexes [Fe(L^1)Cl_2], [Fe(L^2)Cl_2], [Fe(L^3)(Cl_2)], and [Fe(L^4)Cl_2] in absence of TBC or TCC show a high catecholase-like activity for the oxidation of 3,5-DTBC to the corresponding quinone 3,5-DTBQ.

1. Introduction

The aerobic degradation of the aromatic compounds by oxygen-activating enzymes has been shown to play an important role in the microorganism. The aromatic rings are first hydroxylated to phenol or to catechol (*o*-diphenol), and then oxidized to quinone by tyrosinases or to ring-cleaved products by catechol dioxygenases (Scheme 1). Tyrosinases having two copper ions at their active site that can catalyze the oxidation of monophenols to catechols (creasolase activity) and the oxidation of catechol to *o*-diquinones (catecholase activity) [1–11]. A number of studies on the catecholase-like active model complexes of binuclear copper(II) complexes with the different structural features have been reported [11–38]. On the other hand, the catechol ring-cleavage reactions are catalyzed by catechol dioxygenases [39–55], the catechol dioxygenases are divided into two distinctive types: intradiol and extradiol (Scheme 1) [47–49]. The intradiol-cleaving enzymes contain high-spin iron(III) active center and cleave a C–C bond between the catechol substrates, while the extradiol enzyme contains an iron(II) active site and cleaves a C–C bond adjacent to the two hydroxyl groups of the catechol substrates. Accordingly, the study on the reaction of the intradiol-cleaving enzymes has attracted the intense attention because of the enzyme retains a stable iron(III) state during the catalytic cycle. Several functional models for the intradiol catechol dioxygenase of mononuclear Fe(III) complexes have been synthesized and to gain insight into the mechanism of catechol cleaving [51–74].

In general, the compound of 3,5-di-*tert*-butylcatechol (3,5-DTBC) has been most employed as a substrate on the studies of catalytic activities for catecholase of dinuclear copper (II) complexes and catechol dioxygenase of mononuclear Fe(III) complexes. The oxidation product 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DTBQ), having a maximum electronic absorption spectral band at 400 nm, which was employed in the kinetic study of catecholase activity.

Recently, we have reported the kinetic studies on the functional model Fe(III) complexes for intradiol-cleaving catechol dioxygenase [74]. The observed cleavage products of 3,5-DTBC were identified, but there was no evidence found on the formation of the oxidation product of 3,5-DTBQ. In the course of continue study concerned with the preparation of new Fe(III) complexes for the functional models of the intradiol-cleaving catechol dioxygenases, we have found that the reaction of stoichiometric amount of $FeCl_3$ and Schiff-base (HL^{1-4}) (Scheme 2) with H_2TCC or H_2TBC in CH_3OH and $N(Et)_3$ under air did produced four new mononuclear iron(III) complexes [Fe(L^1)(TCC)] (**1**), [Fe(L^2)(TBC)] (**2**), [Fe(L^3)(TBC)] (**3**) and [Fe(L^4)(TCC)](CH_3CN) (**4**) (HL^1 = N-(5-OH-salicylaldimine)-diethylene-triamine, HL^2 = (N′-(5-Cl-salicylaldimine)-diethylene-triamine, HL^3 = N′-(5-Br-salicylaldimine)-dipropylenetriamine, HL^4 = (N′-3,5-Br-salicylaldimine)-dipropylenetriamine, H_2TCC = tetrachlorocatechol, and H_2TBC = tetrabromocatechol). These Fe(III) complexes **1–4** are structurally similar to that of the inhibitors of catechol-bound protocatechuate 3,4-dioxygenase (3,4-PCD)

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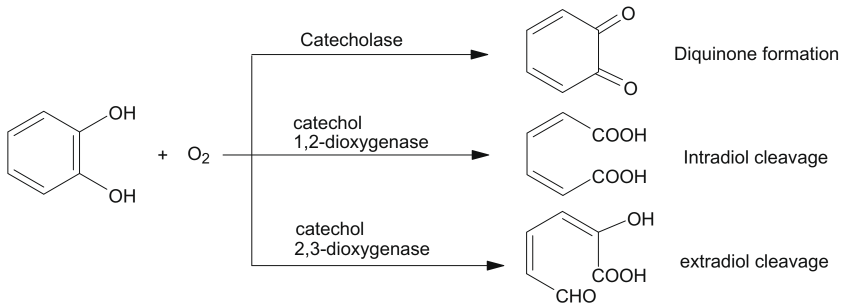
doi:10.1016/j.ica.2009.06.038



Scheme 1. Catecholase and dioxygenase catalyzed aromatic ring cleavage.

[39–49]. Whereas the reaction of the *in situ* prepared iron(III) complexes, [Fe(L^{1-4})Cl_2], with 3,5-DTBC in CH_3OH under air exhibits catecholase activity that produces 3,5-DTBQ. Herewith, we report the synthesis, X-ray crystal structures, ESR, and Mössbauer spectra of mononuclear iron(III) complexes **1–4**. The catecholase activity of 3,5-DTBC of the *in situ* prepared iron(III) complexes, [Fe(L^{1-4})Cl_2], is examined by UV–Vis spectroscopy.

2. Experimental

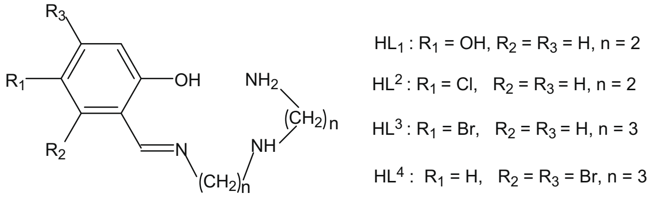
2.1. Materials

All chemicals used were the reagent grade and used as received. 2,5-hydroxy-benzaldehyde, 5-chloro-2-hydroxy-benzaldehyde, 5-bromo-2-hydroxy-benzaldehyde, and 3,5-dibromo-2-hydroxy-benzaldehyde, diethylenetriamine, 3,5-di-tert-butyl-catechol and dipropylenetriamine were purchased from Aldrich Co. Inc. Dipropylenetriamine was purchased from Junsei Co. Tetrachlorocatechol monohydrate and tetrabromocatechol were purchased from Avocado Co. The ligands: N′-(5-OH-salicylaldimine)-diethylenetriamine (HL^1), (N′-(5-Cl-salicylaldimine)-diethylenetriamine (HL^2), and N′-(5-Br-salicyl-aldimine)-dipropylenetriamine (HL^3), (N′-3,5-Br-salicylaldimine)-dipropylenetriamine (HL^4) were prepared by Schiff-base condensation of diethylenetriamine or dipropylenetriamine with the corresponding substituted salicylaldehydes.

2.2. Synthesis of iron(III) complexes

2.2.1. [Fe(L^{1-4})Cl_2]

The iron(III) complexes, [Fe(L^1)Cl2], [Fe(L^2)Cl_2], [Fe(L^3)Cl_2], and [Fe(L^4)Cl_2] were synthesized by the addition of HL^{1-4} (1 mmol) in warming methanol (20 mL) and $FeCl_3$ (162 mg, 1 mmol) in 10 mL of methanol, and then slowly addition triethylamine. The light polycrystalline products were obtained upon cooling overnight. *Anal.* Cacl. for [Fe(L^1)Cl_2], $C_{11}H_{16}Cl_2FeN_3O_2$: C, 37.84; H, 4.59; N, 12.04. Found: C, 38.10; H, 4.37; N, 11.90%. IR (KBr, disc): ν(C=N), 1625 cm^{-1}. *Anal.* Calc. for [Fe(L^2)Cl_2], $C_{11}H_{15}Cl_3FeN_3O$: C, 35.94; H, 4.08; N, 11.43. Found: C, 36.13; H, 3.83; N, 11.48%. IR (KBr, disc): ν(C=N), 1632 cm^{-1}. *Anal.* Calc. for [Fe(L^3)Cl_2], $C_{11}H_{15}BrCl_2FeN_3O$: C, 32.06; H, 3.64; N, 10.20. Found: C, 31.92; H, 3.73; N, 10.35%. IR (KBr, disc): ν(C=N), 1620 cm^{-1}. *Anal.* Calc. for [Fe(L^3)Cl_2], $C_{13}H_{19}BrCl_2FeN_3O$: C, 35.48; H, 4.32; N, 9.55. Found: C, 35.62; H, 4.33; N, 9.45%. IR (KBr, disc): ν(C=N), 1623 cm^{-1}. *Anal.* Calc. for [Fe(L^4)Cl_2], $C_{13}H_{18}Br_2Cl_2FeN_3O$: C, 30.08; H, 3.47; N, 8.10. Found: C, 30.16; H, 3.5; N, 7.81%. IR (KBr, disc): ν(C=N), 1628 cm^{-1}.



Scheme 2. Substituted salicylaldimine ligands.

2.2.2. [Fe(L^1)(TCC)] (*1*)

To a stirred solution of HL^1 (110 mg, 0.5 mmol), $FeCl_3$ (81 mg, 0.5 mmol), and tetrachlorocatechol monohydrate (H_2TCC) (130 mg, 0.5 = mmol) in 20 mL of methanol triethylamine (20 = μL) were added. The solution was further stirred for 30 = min, and dark violet crystals suitable for X-ray analysis of complex **1** were obtained within a few weeks upon slow evaporation of the solution. Yield: 53%. *Anal.* Cacl. for $C_{17}H_{16}Cl_4FeN_3O_4$: C, 38.97; H, 3.08; N, 8.02. Found: C, 38.90; H, 3.17; N, 8.10%. IR (KBr, disc): ν(C=N), 1620 cm^{-1}.

2.2.3. [Fe(L^2)(TBC)] (*2*)

Compound **2** was prepared by the method described above for the preparation of **1**, except using ligand HL^2 instead of HL ^{1}, and H_2TBC instead of H_2TCC. Color: dark violet. Yield: 55%. *Anal.* Calc. for $C_{17}H_{15}Br_4ClFeN_3O_3$: C, 28.35; H, 2.10; N, 5.83. Found: C, 28.13; H, 2.23; N, 5.78%. IR (KBr, disc): ν(C=N), 1639 cm^{-1}.

2.2.4. [Fe(L^3)(TBC)] (*3*)

This compound **3** was synthesized by the same procedure as described for **2**, except using ligand HL^3 instead of HL^2. Color: dark green. Yield: 58%. *Anal.* Calc. for $C_{17}H_{16}Br_5FeN_3O_3$: C, 28.79; H, 2.42; N, 5.30. Found: C, 28.65; H, 2.23; N, 5.45 %. IR (KBr, disc): ν(C=N), 1618 cm^{-1}.

2.2.5. [Fe(L^4)(TCC)] (CH_3CN)(*4*)

Compound **4** also was synthesized by the same procedure as described for **1**, except using ligand HL^4 instead of HL^1.The single crystal product was obtained from the CH_3CN solution. Color: dark green. Yield: 61%. *Anal.* Calc. for $C_{21}H_{21}Br_2Cl_4FeN_4O_3$: C, 34.32; H, 2.88; N, 7.62. Found: C, 34.16; H, 2.81; N, 7.51%. IR (KBr, disc): ν(C=N), 1620 cm^{-1}.

2.3. Physical measurements

Elemental analyses (C, H, N) were determined on a Heraus CHN-O-RAPID analyzer. IR spectra were recorded in the region 400–4000 cm^{-1} on a Bio-Rad FTS40 spectrophotometer with samples as KBr discs. The ^{57}Fe Mössbauer spectra were measured by ^{57}Co(Rh) source on a WissEl Mössbauer system. Both of the source and the sample were kept at 77 K in cryostat equipped with a closed-cycle refrigerator. The isomer shift is relative to α-iron at 295 K. X-band EPR spectra at 77 K for complexes **1–4** in CH_2Cl_2 solution were recorded on a Bruker ESC-160 spectrometer. The electronic spectra for the *in situ* prepared iron(III) complexes [Fe(L^1)Cl_2], [Fe(L^2) Cl_2], [Fe(L^3)Cl_2], and [Fe(L^4)Cl_2] and their adducts