Iron(II)-catecholate complexes of a monoanionic facial $N_3$ ligand: Structural and functional models of the extradiol cleaving catechol dioxygenases

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Two biomimetic iron(II)-catecholate complexes, \([\{Tp^\text{Ph}_2\text{Fe}^\text{III}\text{(CatH)}\}] (1)\) and \([\{Tp^\text{Ph}_2\text{Fe}^\text{III}\text{(DBCH)}\}] (2)\) (where Tp$^\text{Ph}_2$ = hydrotris(3,5-diphenylpyrazole-1-yl)borate, CatH = monoanionic pyrocatecholate and DBCH = monoanionic 3,5-di-tert-butyl catecholate), have been isolated and characterized to study their reactivity towards dioxygen. The single-crystal X-ray structure of (1) reveals a high-spin iron(II) center ligated by the monoanionic facial $N_3$ ligand and a monoanionic catecholate, giving rise to a trigonal bipyramidal coordination geometry. Complex (1) represents the first structurally characterized five-coordinate iron(II)-catecholate complex with an asymmetric bidentate binding motif of monoanionic catecholate. While (1) reacts with dioxygen to form the corresponding iron(III)-catecholate, (2) reacts with dioxygen to give 75 % extradiol and 25 % intradiol cleavage products via an iron(III)-catecholate intermediate species. Complex (2) is a potential functional model of extradiol cleaving catechol dioxygenases.

Keywords: Bioinorganic chemistry, Iron, Oxidative cleavage, Catechol

Oxidative C–C bond cleavage of catechol is catalyzed by nonheme iron enzymes, catechol dioxygenases. These enzymes are found in soil bacteria and play an important role in the biodegradation of aromatic toxic compounds. Catechol dioxygenases are classified into two major categories, extradiol and intradiol cleaving catechol dioxygenases, based on the oxidation state of active site iron and on the position of the C–C bond cleavage. In the active site of extradiol dioxygenases, iron(II) is coordinated by two histidines and one carboxylate donor, either from asparatate or glutamate residue, showing the ‘2-his-1-carboxylate facial triad’ structural motif. The rest of the coordination sites are occupied by water molecules. The extradiol dioxygenases selectively cleave the C2–C3 bond of substrate catechols. The intradiol cleaving dioxygenases use iron(III) in the active site coordinated by two histidines and two tyrosinates and cleave the C1–C2 bond of catechols.

Extensive studies have been carried out using many iron-catecholate model complexes to understand the mechanism of C–C bond cleavage reaction catalyzed by catechol cleaving dioxygenases. Intradiol cleavage of catechol has been reported in most of the model systems, but examples of biomimetic complexes that show extradiol cleavage are limited. However, extradiol selectivity has been observed in iron(III)-catecholate complexes of facial N$_3$ donor ligands. Que et al. have reported the dioxygen reactivity of iron-catecholate complexes of 1,4,7-triazacyclononane (TACN) and 6-Me$_3$-TACN ligands where the highest extradiol selectivity was observed. Very recently, extradiol selective C–C bond cleavage has been reported with model iron(III)-catecholate complexes employing 2-N-1-carboxylate donor ligands that mimic the 2-his-1-carboxylate facial triad motif. In spite of the presence of a large number of model complexes, biomimetic iron(II)-catecholate complexes that mimic the structural and functional aspect of extradiol-cleaving catechol dioxygenases are rare. Que and coworkers have reported the isolation and structural characterization of iron(II)-catecholate complexes of tris(6-methyl-2-pyridylmethyl) amine (6-Me$_3$-TPA) and N,N’-dimethyl-N,N’-bis(6-methyl-2-pyridylmethyl)-trans-1,2-diaminocyclohexane (6-Me$_2$-bpmcn), where a distorted octahedral coordination geometry at the iron(II) center with an asymmetric bidentate binding motif of catecholate was observed. The iron(II) complexes react very rapidly with dioxygen to convert to the corresponding iron(III) complexes and further react slowly with dioxygen to afford intradiol cleavage products.
Iron-tris(pyrazolyl)borates have long been used as bioinspired models since the pyrazole donors of the monoanionic ligand mimic the 2-his-1-carboxylate facial triad. Moro-oka et al. have reported the synthesis and crystal structure of a tetradentate iron(II)-catecholate complex of a sterically hindered ligand, [Fe(II)(Tp)2(CatH)2(DBCH)] (TP = hydrotris(3,5-di-tert-butyl-5-iso-propylpyrazole-1-yl)borate), where a monodentate binding motif of DBCH was observed. However, no oxygenation product was observed. The corresponding iron(III)-catecholate complex has not been reported.

We have been working with a sterically less demanding monoanionic facial N3 ligand, hydrotris(3,5-diphenylpyrazole-1-yl)borate (TPH2), for the synthesis and reactivity study of model complexes for nonheme iron enzymes with the 2-his-1-carboxylate facial triad. We report herein the synthesis and characterization of two iron(II)-catecholate complexes, [(TP)2Fe(II)](DBCH)] and [(TP)2Fe(II)](DBCH)], where CatH = monoanionic pyrocatecholate and DBCH = monoanionic 3,5-di-tert-butyl catecholate. The structural characterization of a five-coordinate iron(II)-catecholate complex (1) is also reported. The reactivity of catecholate complexes with dioxygen and the selective C–C bond cleavage in dioxygen to cause extradiol cleavage although the corresponding iron(II)-catecholate complex has not been reported.

Materials and Methods

All chemicals were purchased from commercial sources and used as received. Solvents were distilled and dried before use. Pyrocatechol and 3,5-di-tert-butyl catechol were recrystallized prior to use. Ligand KTpH2 and Fe(OTf)3·2MeCN were synthesized according to literature procedures. The air-sensitive complexes were synthesized and handled under nitrogen atmosphere in a glove box.

Fourier transform infrared spectroscopy on KBr pellet was performed on a Shimadzu FT-IR 8400S instrument. Solution electronic spectra were recorded on an Agilent 8453 diode array spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyser. Electro-spray mass spectra were recorded with a Waters QTOF Micro YA263 instrument. All room temperature 1H-NMR spectra were collected on a Bruker 500 MHz spectrometer.

Synthesis of the complexes

[(TPH2)Fe(II)](CatH) (1) was prepared as follows: To a suspension of the ligand (0.354 g, 0.5 mmol) in 2 mL methanol, was added a methanolic solution (1 mL) of iron(II) triflate (0.218 g, 0.5 mmol). To the resulting solution, a mixture of pyrocatechol (0.055 g, 0.5 mmol) and triethylamine (70 µL, 0.5 mmol) in methanol (1 mL) were added slowly with constant stirring. The suspension was stirred at room temperature for 20 min to precipitate a white solid. The solid was filtered and washed several times with methanol. X-ray quality single crystals of (1)-2MeOH were isolated by recrystallization of the crude solid from a dichloromethane-methanol solvent mixture. Yield: 0.34 g (76 %). Anal. (%): Calcd for C35H37FeN5O4·2MeOH: C, 70.84; H, 5.27; N, 9.35. Found: C, 70.8; H, 5.1; N, 9.0. IR (KBr): ν = 3352(br), 3059(m), 2606(m), 1597(m), 1545(s), 1499(s), 1477(vs), 1464(vs), 1431(m), 1414(s), 1356(s), 1294(m), 1267(m), 1169(vs), 1099(m), 1009(s), 914(m), 866(m), 814(m), 760(vs), 694(vs), 671(m), 619(m), 569(m), 501(br) cm⁻¹. ESI-MS (positive ion mode, benzene-acetonitrile): m/z = 944.97 (10 %), [(TPH2)Fe(3,5-diphenyl pyrazole)]⁺, 833.95 (50 %), [(TPH2)Fe(CatH)]⁺, 724.97 (30 %), [(TPH2)Fe]⁺, 671.80 (15 %), [(TPH2+2H]⁺, 451.06 (100 %), [(TPH2+3,5-diphenyl pyrazolate)+H]⁺, 221.03 (50 %), [(3,5-diphenyl pyrazole)+H]⁺. 1H NMR (500 MHz, benzene-d6, 295 K): δ = 81.12(br), 68.21(br), 61.47, 60.82, 56.32, 22.44, 15.64, 12.31, 10.32, 7.67–7.32, -15.87, -28.51(br). [(TPH2)Fe(II)](DBCH)] (2) was synthesized according to the protocol described for (1) above, except that 3,5-di-tert-butyl catechol was used instead of pyrocatechol. Yield: 0.40 g (85 %). Anal. (%): Calcd for C35H35BFeN5O2: C, 74.85; H, 5.18; N, 9.03. Found: C, 74.8; H, 5.2; N, 8.9. IR (KBr): ν = 3352(br), 3059(m), 2606(m), 1597(m), 1545(s), 1499(s), 1477(vs), 1464(vs), 1431(m), 1414(s), 1356(s), 1294(m), 1267(m), 1169(vs), 1099(m), 1009(s), 914(m), 866(m), 814(m), 760(vs), 694(vs), 671(m), 619(m), 569(m), 501(br) cm⁻¹. ESI-MS (positive ion mode, benzene-acetonitrile): m/z = 988.97 (10 %), [(TPH2)Fe(3,5-diphenyl pyrazole)]⁺, 877.95 (50 %), [(TPH2)Fe(CatH)]⁺, 742.97 (30 %), [(TPH2)Fe]⁺, 687.80 (15 %), [(TPH2+2H]⁺, 431.06 (100 %), [(TPH2+3,5-diphenyl pyrazolate)+H]⁺, 221.03 (50 %), [(3,5-diphenyl pyrazole)+H]⁺. 1H NMR (500 MHz, benzene-d6, 295 K): δ = 81.12(br), 68.21(br), 61.47, 60.82, 56.32, 22.44, 15.64, 12.31, 10.32, 7.67–7.32, -15.87, -28.51(br).
Analysis of the catechol cleavage products
The iron-catecholate complex (0.05 mmol) was dissolved in 15 mL of oxygen saturated dichloromethane and stirred at room temperature for 12 h under oxygen atmosphere. A greenish-blue solution was formed initially which later changed to light green. The solvent was removed under vacuum and the residue was treated with 3 M hydrochloric acid (10 mL). The organic products were extracted with diethylether (3×15 mL) and the organic fraction was dried over anhydrous sodium sulfate. Removal of the solvent gave the organic products derived from catechol cleavage reaction. The products were analyzed by ESI-MS and 1H-NMR spectroscopy without further purification. The spectral data were compared with the reported data for authentic extradiol and intradiol cleavage products.\(^{22}\) 1H NMR data for 3,5-di-tert-butyl catechol cleavage products (500 MHz, CDCl\(_3\), 295 K): \(\delta = 1.16\) (s, 9H), 1.28 (s, 9H), 6.14 (d, 1H), 6.44 (d, 1H); 4,6-di-tert-butyl-2-pyrene (B): 1.22 (s, 9H), 1.36 (s, 9H), 6.05 (m, 2H); 3,5-di-tert-butyl-2-pyrene (C): \(\delta = 1.22\) (s, 9H), 1.40 (s, 9H), 7.21 (d, 1H), 7.24 (d, 1H).

X-ray crystallographic studies of complex (1)
X-ray single crystal data of (1) were collected at 100 K using Mo-K\(_{\alpha}\) (\(\lambda = 0.7107\) Å) radiation on a Smart Apex diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution/refinement were carried out using the software package of APEX II.\(^{29}\) Crystal structure of (1) was solved by direct method and solved in a routine manner. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically. Crystallographic data of (1) are given in Table 1.

Results and Discussion
The iron(II)-catecholate complexes were synthesized by mixing equimolar amounts of ligand (KTp\(^{Ph2}\)), iron(II) triflate, catechol and triethylamine in methanol at room temperature (Scheme 1). The light yellow complexes show peak at 390 nm in dichloromethane typical for high-spin iron(II) complexes.\(^{30}\) 1H NMR spectra of both the catecholate complexes show relatively sharp, well-resolved and paramagnetically shifted resonances comparable to other high-spin iron(II) complexes of Tp\(^{Ph2}\) ligand.\(^{30}\)

Crystal structure of [(Tp\(^{Ph2}\))Fe\(^{II}\)CatH] (1)
X-ray quality single crystals of (1) were grown from a solvent mixture of dichloromethane and methanol at room temperature under nitrogen atmosphere and crystallized in a triclinic space group

\[
\text{KTP}^{\text{Ph2}} \rightarrow \text{Fe(OHT)}_2, \text{CatH}_2, \text{Et}_3\text{N, MeOH} \rightarrow [(\text{Tp}^{\text{Ph2}})\text{Fe}^{\text{II}}(\text{CatH})] \quad (1)
\]

Syntheses of iron(II)-catecholate complexes

\[
\text{Fe(OHT)}_2, \text{DBCH}_2, \text{Et}_3\text{N, MeOH} \rightarrow [(\text{Tp}^{\text{Ph2}})\text{Fe}^{\text{II}}(\text{DBCH})] \quad (2)
\]

Scheme 1

Table 1 – Crystallographic data for complex (1)

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**Iron(II)-Catecholate Complexes of a Monoanionic Facial N₃ Ligand**

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The molecular structure of the neutral complex, \([\text{Tp}^{\text{Ph}_{2}}\text{Fe}^{\text{II}}(\text{CatH})](1)\), is shown in Fig. 1 and the selected bond parameters are provided in Table 2.

Tab. 2—Selected bond lengths (Å) and angles (°) of (1)

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<th>Bond lengths (Å)</th>
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<td>Fe₁ – N₆</td>
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<tr>
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<td>1.389(8)</td>
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<td>C₅₁ – O₂</td>
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<td>133.8(2)</td>
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<tr>
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<td>88.6(2)</td>
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<tr>
<td>N₄ – Fe₁ – N₆</td>
<td>94.0(2)</td>
</tr>
</tbody>
</table>

The X-ray structure of the neutral complex reveals a five coordinate iron center coordinated by the anionic ligand and a monoanionic catecholate (CatH). Three nitrogen donors from the ligand coordinate to the iron center in facial motif with the Fe₁–N₂, Fe₁–N₄ and Fe₁–N₆ distances of 2.186(6), 2.164(6) and 2.117(6) Å, respectively (Table 2). The average Fe–N distance is comparable with that of reported high-spin iron(II) complexes of Tp³⁺Ph₂ ligand. The catecholate oxygen O₁ binds to the iron center trans to the pyrazole nitrogen N₂ occupying the apical positions with the O₁–Fe₁–N₂ angle of 173.78(17)° (Table 2). The other oxygen atom O₂ from catecholate and two nitrogen donors (N₄ and N₆) from the ligand form the basal plane of the distorted trigonal bipyramidal complex (τ = 0.66). The asymmetric binding of the monoanionic catecholate is evident from the Fe₁–O₁ and Fe₁–O₂ distances of 2.283(5) and 1.925(5) Å, respectively. The Fe–O_cat distances are comparable to those in Fe²⁺(6-Me₃-TPA)(DBCH)ClO₄ (2.268(8) and 1.953(8) Å). The difference in Fe–O_cat distances (Δd = 0.358 Å) in (1) is in good agreement with the reported iron(II)-catecholate complexes. Extensive spectroscopic studies on all the isolated catechol bound extradiol cleaving iron(II) complexes reveals asymmetric binding of catechol to metal centre (Δd = 0.2–0.4 Å). The crystal structure of the substrate bound homoprotocatechuate 2,3 dioxygenases (2,3-HPCD) reveals a penta-coordinate square pyramidal environment of iron(II) with a bidentate monoanionic ligand. The sixth coordination site remains vacant for dioxygen binding. Similar features are observed in the present iron(II)-catecholate complex. Thus, (1) is a very close structural model of extradiol cleaving catechol dioxygenases.

**Dioxygen reactivity of iron-catecholate complexes**

Both the iron (II)-catecholate complexes are sensitive towards dioxygen. The light yellow solutions of (1) and (2) in dichloromethane rapidly transform to greenish-blue species (1a and 2a, respectively) in the presence of dioxygen. The reaction of (2) with dioxygen, however, is much faster as compared to that of (1). The greenish-blue solution

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**Fig. 1**—Molecular structure of the neutral complex, \([\text{Tp}^{\text{Ph}_{2}}\text{Fe}^{\text{II}}(\text{CatH})](1)\). All hydrogen atoms except that attached to B₁ and O₁ have been omitted for clarity.

**Fig. 2**—Solid state packing of (1)-2MeOH showing intermolecular hydrogen bonding interaction between iron(II)-catecholate unit and solvent methanol molecules. All hydrogen atoms except that attached to B₁, O₁ and solvent methanol have been omitted for clarity.
(of 1a) from the reaction of (1) with dioxygen exhibits two broad bands at 600 nm and 780 nm typical for iron(III)-catecholate complexes (Fig. 3). This is in line with the proposal by Que et al. that iron(II)-catecholate complexes are initially converted to the corresponding iron(III)-catecholate species that undergo C–C bond cleavage of catechols upon exposure to dioxygen. The intensity and position of ligand-to-metal charge-transfer bands of (1a) remains unchanged even after several days under oxygen atmosphere. Pyrocatechol was quantitatively recovered by acidic workup of the blue solution. No oxidative C–C bond cleavage of catechol was observed in the reaction of (1) with dioxygen.

The characteristic catecholate-to-iron(III) charge-transfer bands of (2a) are slightly red-shifted to 660 nm and 840 nm (Fig. 4a). The red-shift of the MLCT bands for (2a) with respect to (1a) is due to the presence of electron-donating tert-butyl substituents on the catecholate ring in (2). The positions of the charge-transfer bands of (2a) are very similar to those of [Fe(III)(Tp)iPr2(DBC)] complex.

The LMCT bands in (2a), unlike (1a), slowly decay over a period of 6 h to produce a light green solution (Fig. 4b). The decay of the charge-transfer bands suggests the oxidation of substrate catecholate. To understand the nature of 3,5-di-tert-butyl catechol cleavage products, the reaction mixture was extracted into organic solvent after acid treatment and the organic products were analyzed by 1H NMR spectroscopy. Three catechol-derived products, 3,5-di-tert-butyl-1-oxacyclohepta-3,5-diene-2,7-dione (A), 4,6-di-tert-butyl-2-pyrone (B) and 3,5-di-tert-butyl-2-pyrone (C) were obtained. In the reaction, 25 % A, 22 % B and 53 % C are formed that amount to 75 % extradiol cleavage products of DBCH2 (Scheme 2). Moro-Oka and coworkers have reported that 67 % extradiol cleavage products are formed in the reaction of [Fe(III)(Tp)iPr2(DBC)] with dioxygen. Therefore, the model complex discussed here is an improvement over the reported iron(III)-catecholate complex of Tp+iPr2 ligand.

On the basis of the above experimental observations, it is very clear that initially the iron(II) complexes are converted to the corresponding iron(III)-catecholate species. Complex (1) does not give any catechol cleavage product due to the fact that the pyrocatecholate ring in (1a) is not sufficiently electron rich to initiate dioxygen activation via iron(II)-semiquinone intermediate species. However, the high electron density in the DBC ring of the iron(III)-catecholate species (2a) initiates the dioxygen activation at the iron(II)-semiquinone to form an alkylperoxo intermediate. Bugg et al. have proposed that the alkylperoxo species can undergo rearrangement reaction, depending upon...
the stereoelectronic factors, either via alkenyl migration or via acyl migration to give catechol cleavage products. A pseudoaxial arrangement of the alkylperoxo species leads to an alkenyl migration to form extradiol cleavage products. On the other hand, a pseudoequatorial orientation of the alkylperoxo species favors acyl migration and gives rise to intradiol cleavage products. In the case of (2), alkenyl migration is predominantly operating in the reaction showing extradiol selective cleavage of catechol.

It is important to mention here that iron(II) complexes of TpPh2 ligand has a tendency to get hydroxylated on one of the aromatic rings in the presence of dioxygen and other organic coligands (benzoyl formate, benzoate, phenyl pyruvate, etc.).30,31 Mukherjee et al.36 have recently shown the involvement of a high-spin iron(IV)-oxo intermediate in the hydroxylation process. However, in the reaction of (2) (and 1) with dioxygen, no ring hydroxylated product was observed. This supports the accepted mechanism of the C–C bond cleavage of catechol that does not involve any high valent iron-oxo intermediate species.

Conclusions

We have reported the synthesis, characterization and dioxygen reactivity of two iron(II)-catecholate complexes of a monoanionic facial $N_3$ ligand. The X-ray single crystal structure of one of the iron(II)-catecholate complex (1) shows a facial binding of the tridentate ligand and mimics the 2-his-1-carboxylate facial triad motif of extradiol cleaving catechol dioxygenases. The monoanionic catecholate binds to the iron(II) center in an asymmetric bidentate fashion. To the best of our knowledge, (1) is the first structurally characterized five-coordinate iron(II)-catecholate complex with an asymmetric bidentate binding of the monoanionic catecholate. This is a structural model of the extradiol cleaving catechol dioxygenases. The iron(II)-DBCH complex (2) shows extradiol selective C–C bond cleavage of DBCH and represents a potential functional model of the extradiol cleaving catechol dioxygenases. The results highlight the importance of this ligand in stabilizing five coordinate iron(II)-catecholate model complexes that provide a vacant coordination site properly orientated with respect to the substrate for C–C bond cleavage of catechol.

Supplementary Data

Crystallographic data for (1) have been deposited with the Cambridge Crystallographic Data Centre, under CCDC No. 813452. Copy of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK. Fax: +44 1223-336-033; Email: deposit@ccdc.cam.ac.uk; website: http://www.ccdc.cam.ac.uk.

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and Industrial Research (CSIR), New Delhi, India for fellowships. Crystal structure determination was performed at the DST-funded National Single Crystal Diffractometer Facility in the Department of Inorganic Chemistry, IACS, Kolkata.

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