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# Oxidation versus Dioxygenation of Catechol: The Iron-Bispidine System

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The iron–bispidine-catalyzed oxidation and dioxygenation (catechol dioxygenase activity) [i.e., the oxidation of 3,5-ditert-butylcatecholate (dbc<sup>2–</sup>) by [Fe<sup>II</sup>(L)X<sub>2</sub>]<sup>*n*+</sup> (L = 3,7-dimethyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate methyl ester)] and air (O<sub>2</sub>) was studied experimentally and supported by the analysis of the X-ray crystal structure of [Fe(L·MeOH)(tcc)][B(Ph)<sub>4</sub>] with the deactivated tetrachlorocatecholate tcc<sup>2–</sup> and a DFT-based analysis. The [Fe<sup>II</sup>(L)X<sub>2</sub>]<sup>*n*+</sup>/O<sub>2</sub>/dbc<sup>2–</sup> system catalyzes the intradiol cleavage of dbc<sup>2–</sup> but with a relatively low activity

(5 % yield); most of the substrate is oxidized in a two-electron oxidation to the benzoquinone (dbq) product (48 % yield). The crystallographic and DFT-based theoretical analyses indicate that this is due to the high oxidation potential of the Fe<sup>III</sup> oxidant (fast and efficient electron transfer), that is, the oxidation to the benzoquinone side product is faster, and due to the bonding mode of the catecholate substrate to the Fe<sup>III</sup> oxidant, with little spin density transferred to the catecholate substrate.

# Introduction

Catechol dioxygenases are mononuclear nonheme iron enzymes, and their biochemistry, supported by experimental and computational modeling, has been studied extensively.<sup>[1–4]</sup> Three different reaction channels are possible when dioxygen reacts with a catecholate bound to a nonheme iron center: the oxidation to the *ortho*-quinone (catecholase activity) (i.e., a simple two-electron oxidation), and dioxygenation, which leads to intradiol or extradiol cleavage (see Scheme 1; enzymes that follow the intradiol pathway use Fe<sup>III</sup>, the extradiol enzymes use Fe<sup>II</sup> in their active site). Catechol dioxygenases are isolated from soil bacteria, and the most extensively studied intradiol-cleaving catechol dioxygenase is protocatechuate-3,4-dioxygenase, for which a vast range of structural and mechanistic data are available.<sup>[5]</sup> Various biomimetic systems have been studied, and these have helped to elucidate the catalytic mechanism.<sup>[6–16]</sup>



Scheme 1. Proposed mechanisms for the iron-catalyzed intradiol (a) and the extradiol cleavage (b) of catechol.<sup>[1-4]</sup>

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The biotic and abiotic natural degradation of organic pollutants in the soil,<sup>[17,18]</sup> possible industrial applications for the conversion of aromatic compounds to water-soluble aliphatic products,<sup>[19]</sup> and the transformation of renewable

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biomass resources to fuels and chemicals<sup>[20,21]</sup> by catechol dioxygenases and model compounds continue to attract attention. An interesting recent observation is that volatile halogenated hydrocarbon compounds, which are known to be involved in stratospheric chemistry, in particular in ozone depletion,<sup>[22]</sup> are produced through abiotic natural processes in the soil, which involve Fe<sup>III</sup>, H<sub>2</sub>O<sub>2</sub>, and humic compounds, which have aromatic residues and specifically also catechol groups.<sup>[23]</sup>

We have recently been able to show that the iron-bispidine complex with the same ligand L as used in the present communication leads to the first biomimetic example for the iron-catalyzed halogenation of aliphatic hydrocarbon compounds, and which halogenates with high chemoselectivity.<sup>[24]</sup> Since a possible mechanism to produce volatile halogenated hydrocarbon compounds in the soil might involve the iron-catalyzed degradation of humic compounds (dioxygenation of catechol derivatives) and subsequent ironcatalyzed halogenation of the degradation products, we were interested to test the same catalyst for a possible catechol dioxygenase activity to better understand possible mechanisms for the formation of volatile halogenated hydrocarbons from humic substances. The tetradentate bispidine ligand L, used in this study, is shown in Scheme 2, together with a collection of ligands used in efficient biomimetic catechol dioxygenase reactions. Bispidines are very rigid adamantane derivatives. They were first prepared by Mannich,<sup>[25]</sup> exist in a large variety<sup>[26]</sup> and have been used extensively to enforce specific geometries to metal ions and desirable properties to their complexes.<sup>[27-33]</sup> High-valent iron-bispidine complexes have been found to be particularly interesting due to their high redox potentials<sup>[34,35]</sup> and, consequently, as efficient oxidants and potential oxygenation catalysts.[36-39] The experimental studies of the dioxygenEurjic g/morganic Chemist

ation of 3,5-di-*tert*-butylcatecholate (dbc<sup>2–</sup>) by  $[Fe^{II}(L)-X_2]^{n+}$  and air (O<sub>2</sub>), presented here, are combined with experimental and computational structural work and a DFT-based analysis of the reaction mechanism.



Scheme 2. Structure of the ligand L and other ligands used in catechol dioxygenase modeling.

### **Results and Discussion**

### Syntheses and Structural Properties

The Fe<sup>II</sup> precursor [Fe(L)(OTf)<sub>2</sub>] (OTf = triflate = trifluoromethanesulfonate, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) was prepared by a known procedure,<sup>[40]</sup> and the corresponding Fe<sup>III</sup> tetrachlorocatecholate (tcc<sup>2-</sup>) complex was obtained by ligand exchange in methanol and subsequent air oxidation. The magnetic moment of the catalyst–substrate complex [Fe(L·MeOH)(tcc)][B(Ph)<sub>4</sub>],  $\mu$  = 5.61 BM (Bohr Magneton,  $\mu$ <sub>B</sub>), is only slightly lower than the spin-only value of 5.92 BM for a high-spin d<sup>5</sup> electronic ground state, and this is as expected from the enzyme protocatechuate-3,4-dioxygenase.<sup>[41]</sup> A plot of the experimental structure (single-crystal X-ray diffraction) of [Fe(L·MeOH)(tcc)][B(Ph)<sub>4</sub>] is shown in Figure 1, and selected structural parameters are



Figure 1. (a) ORTEP plot of  $[Fe(L\cdotMeOH)(tcc)]B(Ph)_4$  (ellipsoids are drawn at the 30% probability level, hydrogen atoms and counterions are omitted for clarity). (b) Computed structure of  $[Fe(L)(dbc)]^+$  with the computed spin densities (spin densities: Fe 3.783, N3 0.044, N7 0.038, O8 0.27, O7 0.34, C1 0.094, C2 0.175).

listed in Table 1. The Fe<sup>III</sup>-donor distances are between 1.91–2.27 Å, as expected for high-spin Fe<sup>III</sup>;<sup>[42]</sup> the bond to N7 is, as in other bispidine complexes, significantly longer than the bond to the other tertiary amine. N3 (2.27 versus 2.18 Å).<sup>[26,30]</sup> However, the two Fe<sup>III</sup>–O<sup>catecholate</sup> bonds are with 1.91 and 1.95 Å (trans to N3 and trans to N7, respectively), very similar in length, which is in sharp contrast to the corresponding Jahn-Teller-active CuII complex, in which the Cu<sup>II</sup>-O<sup>catecholate</sup> bond *trans* to N7 is strongly elongated, and for which a second isomer with monodentate catecholate has also been isolated.<sup>[43]</sup> The structure reported here supports our assumption that the generally long bond to N7 is a ligand-enforced structural effect,<sup>[30,44,45]</sup> and this elongation obviously has little influence on the bonding to the bidentate catecholate coligand. The emerging relatively symmetric bonding of catecholate to the Fe<sup>III</sup> center was expected to have a significant influence on the catecholase and dioxygenase activity (vide infra).

Table 1. Structural parameters (distances in Å, angles in °) of  $[Fe(L\cdot MeOH)(tcc)][B(Ph)_4]$  (X-ray diffraction) and  $[Fe(L)(X)]^+$  (DFT, X = tcc, dbc).

		[Fe <sup>III</sup> (L)(tcc)] <sup>+</sup>			[Fe <sup>III</sup> (L)(dbc)] <sup>+</sup>		
	S = 1/2	3/2	5/2	exp.	S = 1/2	3/2	5/2
Fe–N3	2.03	2.11	2.22	2.176(3)	2.03	2.12	2.24
Fe-N7	2.15	2.16	2.29	2.273(4)	2.17	2.16	2.32
Fe-N1	2.00	2.24	2.20	2.103(3)	1.99	2.27	2.20
Fe-N2	2.00	2.24	2.20	2.131(3)	1.99	2.27	2.20
Fe–O8	1.95	1.87	2.03	1.914(3)	1.98	1.90	2.02
Fe-O7	1.96	1.89	2.07	1.946(3)	1.96	1.89	2.07
N3-Fe-N7	88.5	86.8	84.5	80.8(1)	88.3	86.8	83.7
N3-Fe-N1	83.5	78.0	77.2	77.5(1)	83.6	77.8	77.2
N3-Fe-N2	83.5	78.0	77.2	76.8(1)	83.6	77.8	77.2
N3-Fe-O8	176.4	179.4	178.2	171.8(1)	175.8	178.1	176.1
N3-Fe-O7	94.2	94.9	99.5	104.0(1)	93.4	94.1	96.3
N7-Fe-O7	177.3	178.3	176.0	175.1(1)	178.3	179.2	180.0
N1-Fe-N2	166.2	154.9	153.1	153.5(1)	166.2	154.4	153.3
$\Delta G^{[a]} [kJ mol^{-1}]$	50.9	57.3	0.0		56.2	68.2	0.0

[a] All energies quoted refer to the lowest-lying spin state, which was set as the origin.

The structural and electronic properties of the catecholate  $Fe^{III}$  site were also evaluated by a DFT-based structure optimization. The computed structural parameters, also shown in Table 1, are in acceptable agreement with the experimental data.<sup>[46]</sup> As observed experimentally, a high-spin electronic configuration (S = 5/2) is predicted by DFT (the low-spin state (S = 1/2) is significantly higher in energy (50.9 kJmol<sup>-1</sup>); the intermediate-spin state is at 57.3 kJmol<sup>-1</sup>), and this was expected on the basis of the large and rigid ligand cavity.<sup>[26,30]</sup>

## **Catechol Dioxygenase Activity**

Since Fe<sup>III</sup>–bispidine complexes in general are relatively unstable, high-spin [Fe(L)(OTf)<sub>2</sub>] was used as a precatalyst, and the Fe<sup>III</sup>/catecholate species was prepared in situ. The reactive high-spin [Fe(L)(dbc)]<sup>+</sup> complex was obtained by addition of an equimolar amount (stoichiometric reactions) or an excess amount (catalytic reactions, 10 equiv.) of dbc<sup>2-</sup> [addition of the catechol derivative and 2 equiv. of NEt<sub>3</sub> (NEt<sub>3</sub> = triethylamine) in dry and degassed MeCN (MeCN = acetonitrile) as solvent] to a solution of the Fe<sup>II</sup> precursor; the oxidation reaction was then started by the addition of  $O_2$  (1 atm). As usual in catechol dioxygenase studies, after completion the reaction was quenched with HCl (reaction time of approx. 10 h), and the organic products were then extracted into  $Et_2O$  ( $Et_2O$  = diethyl ether) and characterized by GC/GC-MS analyses. Products of the dbc<sup>2-</sup> oxidation and oxygenation (see Scheme 3) in dry MeCN are (a) 3,5-di-tert-butyl-benzoquinone (dbq, the "catechol oxidase" product), (b) muconic acid anhydride (the immediate "catechol dioxygenase" product) (i.e., the muconic acid precursor in dry solution), and (c) traces (at most) of methyl 3,5di-tert-butyl-2-oxofuran-5-carboxylate [derived from lactone formation from the muconate; yields of the stoichiometric reactions (in %) and of the catalytic transformations (TON, TON<sup>max</sup> = 10) are also given in Scheme 3].<sup>[47]</sup> As expected (redox potential, symmetric bonding of the substrate), the iron-bispidine-catalyzed reactions mainly produce the benzoquinone product. On account of the high redox potential of the catalyst, even with  $O_2$  as oxidant, the oxidation of dbc<sup>2-</sup> is efficient but primarily produces the



Scheme 3. The iron-bispidine-based oxidation of H<sub>2</sub>dbc.

benzoquinone (dbq) product. The formation of dbq as the main product also follows experimentally from reaction control of a catalysis experiment by <sup>1</sup>H NMR spectroscopy (see Figure S1 in the Supporting Information).

In a stoichiometric reaction of the Fe<sup>III</sup>-catecholate complex ([Fe<sup>II</sup>(L)(OTf)<sub>2</sub>]/H<sub>2</sub>dbc/NEt<sub>3</sub>, 1:1:2) with O<sub>2</sub> (1 atm; see Figure 2; the immediate formation of [Fe<sup>III</sup>(L)(dbc)]<sup>+</sup> is not shown in this figure), there is a relatively slow and clean monophasic reaction (isosbestic point, pseudo-first-order kinetics), which leads to a decay of the relatively intense electronic transitions at 610 and 910 nm, attributed to Fe<sup>III</sup>-dbc ligand-to-metal charge-transfer (LMCT) transitions and a concomitant increase of a band at 390 nm (absorption of dbq).<sup>[3]</sup> The pseudo-first-order rate constant of dbq formation is  $k_{obs} = 3.43 \times 10^{-4} \text{ s}^{-1}$ , the half-life of the high-spin [Fe<sup>III</sup>(L)(dbc)]<sup>+</sup> complex is  $t_{1/2} = 0.56$  h ( $t_{1/2} =$  $0.693/k_{obs}$ ) and, with the known concentration of O<sub>2</sub> in MeCN ([O<sub>2</sub>] = 8.1 mM),<sup>[48]</sup> the second-order rate constant is  $k_{O_2} = 4.23 \times 10^{-2} \text{ m}^{-1} \text{ s}^{-1}$ . From Figure 2 it also emerges that the rate of decay of the Fe<sup>III</sup>-catecholate complex is close to identical to the rate of formation of dbg ( $k_{obs}$  =  $2.84 \times 10^{-4} \text{ s}^{-1}$  versus  $3.43 \times 10^{-4} \text{ s}^{-1}$ ). On the basis of the selective formation of dbq (90%, catecholase reactivity) and muconic acid anhydride (10%, catechol dioxygenase reactivity, see Scheme 3), it follows that the approximate pseudo-first-order rate for catechol cleavage is  $k_{obs}$  =  $0.38 \times 10^{-2} \text{ m}^{-1} \text{ s}^{-1}$ 



Figure 2. (a) Observed spectral changes in the stoichiometric reaction of the catalyst with dbc ([Fe(L)(OTf<sub>2</sub>)],  $1 \times 10^{-4}$  M; H<sub>2</sub>dbc, 1 equiv.; NEt<sub>3</sub>, 2 equiv.; O<sub>2</sub>, 1 atm; dry MeCN; 298 K). (b) Observed absorption versus time traces of the same experiment at 390 nm (increasing absorption, formation of dbq), and at 610 nm (decreasing absorption, decay of the Fe<sup>III</sup>–catecholate complex) as a function of the time.

Compared to the enzymatic reaction  $(k_{O_2} = 2.5 \times 10^5 \text{ m}^{-1} \text{s}^{-1})^{[49]}$  and other biomimetic reactions (e.g.,

 $k_{O_2} = 3.77 \times 10^{-1} \text{ m}^{-1} \text{ s}^{-1}$  for the decay of [Fe<sup>III</sup>(L-N<sub>4</sub>Me<sub>2</sub>)-(dbc)]<sup>+</sup> in oxygen-saturated MeCN at 25 °C<sup>[8]</sup>), the reactivity of the iron-bispidine-based model system is relatively low. The energy of the LMCT transitions has been correlated to the Lewis acidity of the Fe<sup>III</sup> center (i.e., the ease of electron transfer of the catecholate substrate to the catalytic center has been assumed to be a measure for the catechol dioxygenase activity).<sup>[7,50,51]</sup> With the lower-energy transition at 610 nm, compared to that of [Fe<sup>III</sup>(L-N<sub>4</sub>Me<sub>2</sub>)-(dbc)]<sup>+</sup> at 553 nm, the observed reactivities do not seem to be correlated to the Lewis acidities. The relatively sluggish reaction and the low yield of cleavage versus oxidation product (dioxygenase versus catecholase activity) might rather be due to efficient electron transfer (powerful oxidant), and this was expected on the basis of the high redox potential and efficient outer-sphere electron transfer.<sup>[34]</sup>

#### **DFT-Based Mechanistic Studies**

DFT was used to further analyze the reaction mechanism of the iron-bispidine-catalyzed oxidation of catechol. The experimentally observed and computed structural properties and computed energies of [Fe<sup>III</sup>(L)(dbc)]<sup>+</sup> in the various possible spin states are shown in Table 1. Based on the relative energies, the Fe<sup>III</sup> catalyst has a high-spin electronic configuration (S = 5/2), and the low-spin state (S = 1/2) is significantly higher in energy (56.2 kJ mol<sup>-1</sup>; the intermediate-spin configuration is at 68.2 kJ mol<sup>-1</sup>). This is in agreement with the experimental data of the tcc-based model system (see above), with computational work reported for the enzyme,<sup>[52]</sup> and with a recent DFT-based analysis of another low-molecular-weight model system.<sup>[53]</sup> The computed structural and energetic parameters of  $[Fe^{III}(L)(dbc)]^+$  are similar to those of  $[Fe^{III}(L)(tcc)]^+$ : in their high-spin electronic ground state, the largest deviation in the metal-donor distances is for the relatively weak Fe-N7 bond (0.03 Å). This indicates that the experimental structure of [Fe<sup>III</sup>(L)(tcc)]<sup>+</sup> with the deactivated tcc substrate is a sensible model for the catalytically active  $[Fe^{III}(L)(dbc)]^+$  complex.

Shown in Figure 1 (b) is a plot of the computed structure of [Fe<sup>III</sup>(L)(dbc)]<sup>+</sup> with a visualization of the spin densities. Based on the experimentally observed similarity of the bond lengths from the Fe<sup>III</sup> center to the two catecholate oxygen atoms (O7 and O8), confirmed in the DFT-optimized structures, only little spin density is expected on the catecholate substrate, and this is shown to be distributed symmetrically between the two catecholate carbon atoms C1 and C2 (see Figure 1, b) (i.e., there is only little Fe<sup>II</sup>-semiquinonate (localized radical) as opposed to Fe<sup>III</sup>catecholate character (see Table S3 in the Supporting Information). The expectation therefore is that  $[Fe(L)(dbc)]^+$  is not among the most efficient intradiol-catechol dioxygenase mimics, and this is what was shown by the experiments (see above and Scheme 3). This is amplified by the fact that the bispidine-Fe<sup>III/II</sup> redox potential is relatively high (a result of the large and rigid bispidine cavity<sup>[54]</sup>) [i.e., the driving force for catecholase activity (electron transfer) is large and catechol degradation (intradiol cleavage) therefore is disfavored].

The formation of an alkyl-peroxo-iron(III) intermediate along the reaction coordinate for the intradiol-catechol cleavage (Schemes 1 and 3) leads to two possible isomers of the dioxygen adduct  $[Fe(L)(O_2)(dbc)]^+$  (see Figures S4 and S5, Table S2 in the Supporting Information). The more stable isomer has Fe-OO trans to N7 and is, compared to its isomer (Fe-OO trans to N3), 22.9 kJ mol<sup>-1</sup> more stable in its S = 5/2 spin state; the S = 3/2 state is destabilized by 93.2 kJ mol<sup>-1</sup> for the *trans* to N7 isomer and by 58.5 kJ mol<sup>-1</sup> for the *trans*-to-N3 isomer; the S = 1/2 configuration is at 117.6 kJ mol<sup>-1</sup> for the *trans*-to-N7 isomer and at 107.3 kJ mol<sup>-1</sup> for the *trans*-to-N3 isomer. On the basis of the more stable trans-to-N7 isomer, there are remarkable differences between the preferred S = 5/2 and the higher energy S = 3/2 and S = 1/2 electronic states: (i) in the S =1/2 and S = 3/2 electronic configurations, the catechol C–O bond lengths are 1.40 and 1.39 Å, respectively, and this is typical for a C-O single bond. In the electronic ground state, the two C–O bond lengths are 1.28 Å, thus indicating a distinct carbonyl character; (ii) whereas the Fe(OO)- $C_{catechol}$  distance in the S = 1/2 or S = 3/2 states is at 1.54 Å, thus indicating a relatively strong interaction, in the S =5/2 ground-state electronic configuration the Fe(OO)-C<sub>catechol</sub> distance is significantly longer (2.37 Å) [i.e., there is only a very weak interaction of the iron-bound (activated) dioxygen molecule with the substrate]. As a consequence, in the energetically preferred S = 5/2 electronic state, the spin density on the exo-oxygen atom is +0.70 and on the substrate carbon atom it is -0.07 [i.e., this intermediate (i) has little carbon-based radical character, (ii) has little preference for C-O bond formation, and (iii) is largely Fe<sup>II</sup>benzoquinone in character]. Accordingly, the S = 5/2 state does not lead to the products of the intradiol cleavage and is close to the product of the catecholase reaction (i.e. the two-electron oxidation, which is also observed experimentally). This is in contrast to a recent DFT-based analysis of an efficient intradiol–catechol–dioxygenase model system, in which the two spin states (quartet and sextet) of the peroxo intermediate are very close in energy and which both have Fe<sup>III</sup>–semiquinone character.<sup>[53]</sup> The large structural difference between the two intermediates in the present case (Fe<sup>III</sup>–semiquinone versus Fe<sup>II</sup>–benzoquinone) is the basis for the relatively large energy difference and, unfortunately, is one of the reasons for the inefficiency with respect to dioxygenase activity.

The attack of triplet dioxygen at the high-spin-configured enzyme–substrate complex of protocatechuate-3,4-dioxygenase was analyzed in detail, and the spin-forbidden reaction between triplet dioxygen and singlet catecholate was shown to be initiated by iron-centered redox processes: electrophilic attack by O<sub>2</sub> is facilitated in the Fe<sup>II</sup>–semiquinone intermediate (see Scheme 4).<sup>[52]</sup> This pathway is disfavored in our bispidine complexes with respect to a further iron-based electron transfer and benzoquinone formation.

The simplified reaction coordinate is visualized in Figure 3.<sup>[55]</sup> On the basis of the transformation of the highspin Fe<sup>III</sup>–catecholate complex to [Fe<sup>III</sup>(L)–OH]<sup>+</sup>, the for-



Figure 3. Simplified reaction coordinate on the basis of DFT calculations of the oxygenation of  $[Fe(L)(dbc)]^+$ .<sup>[55]</sup>



Scheme 4. Simplified MO-based scheme to show the spin-allowed pathways for the transfer of three electrons for dioxygenase and catecholase activity (see also Scheme 1 and Scheme 3).<sup>[52]</sup>

mation of muconic acid anhydride is an exergonic process  $(\Delta G = -185.9 \text{ kJ mol}^{-1})$ . On this pathway, the iron center keeps its oxidation state (+III) over the entire process, and the [Fe<sup>III</sup>(L)(O<sub>2</sub>)(dbc)]<sup>+</sup> intermediate in its high energy S = 1/2 and S = 3/2 electronic configurations (172.2 kJ mol<sup>-1</sup>, *trans*-to-N7 isomer) leads to intradiol products. However, the formation of benzoquinone (dbq) on the S = 5/2 spin surface has a much lower-energy intermediate (90.8 kJ mol<sup>-1</sup>, *trans*-to-N3 isomer), and this supports the experimental observations.<sup>[56]</sup>

## Conclusion

The reactivity of the iron-bispidine-based system is lower (up to 2 orders of magnitude) than that of other model complexes, which are up to 5 orders of magnitude less reactive than the natural systems. This is believed to be due to the efficient electron transfer and relatively high redox potential of the bispidine-iron site, which leads to a preference for catecholase over intradiol dioxygenation activity (approx. 90 versus 10%). This is also supported by the observed relatively low energy of the LMCT electronic transitions. Support for the preference for catecholase over catechol dioxygenase activity comes from the DFT-based and the experimental structural analyses, which show that there is only little spin density transferred from the Fe<sup>III</sup> center to the catecholate substrate (i.e. there is little Fe<sup>II</sup>-semiquinonate-localized-radical and primarily Fe<sup>III</sup>-catecholate and Fe<sup>II</sup>-quinone character in the catalytically active form). An important conclusion therefore is that, whereas the iron-bispidine complexes are active halogenation catalysts as well as strong oxidants, they are not very active in catechol dioxygenase. It is not unlikely that catechol and humic acid degradation require a different type of catalytic center than subsequent halogenation of the degradation products.

# **Experimental Section**

General: Chemicals (Aldrich, Fluka) and solvents were of highest possible grade and used as purchased. Mass spectra were obtained with a Bruker ApexQe hybrid 9.4 FT-ICR or Finnigan TSW 700 instrument. Elemental analyses were performed by the analytical laboratories of the chemical institutes of the University of Heidelberg. Product analyses by GC were done with a Varian 3900 instrument equipped with a ZB-1701 column. UV/Vis spectra and kinetic studies were performed at 298 K with a J&M Tidas II spectrophotometer with a quartz cells (path length 10 mm). NMR spectra at 200 MHz (<sup>1</sup>H) were obtained with a Bruker ARX 200 instrument. The solvent was used as internal reference;  $\delta$  in ppm, J in Hz. Electrochemical measurements were conducted with a CH Instruments 660D workstation with a three-electrode setup that consisted of a glassy carbon working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl reference electrode [0.01 M Ag<sup>+</sup>, 0.1 M Bu<sub>4</sub>N(PF<sub>6</sub>)]. The potentials were determined in MeCN and converted versus SCE by adding 290 mV.

Synthesis of the Ligand and the Iron–Bispidine Complexes: The bispidine ligands and the corresponding  $Fe^{II}$  complex  $[Fe^{II}(L)(OTf)_2]$  were prepared as described before.<sup>[40]</sup>



**Oxidative Cleavage of 3,5-Di-***tert***-butylcatechol:** In a typical reaction, 0.1 mmol of [Fe(L)(OTf)<sub>2</sub>] was mixed with 1–10 equiv. of 3,5di-*tert*-butylcatechol in MeCN (10 mL, H<sub>2</sub>O-free, Ar, 298 K), followed by the addition of NEt<sub>3</sub> (2 equiv.). The solution was stirred for a further 5 min, and dioxygen was then bubbled through the solution for 3 min. The reaction was quenched after 9 h with 0.01 M HCl (5 mL), then the organic products were extracted with Et<sub>2</sub>O (5 mL three times) and dried with Na<sub>2</sub>SO<sub>4</sub>. Naphthalene was added as the internal standard, and the mixture was analyzed by GC. The retention for the product peaks were compared with authentic compounds, and their identity was confirmed by GC–MS. All reactions were done in duplicate; the reported data are the average of these reactions. For kinetic studies, the reaction solution was diluted to  $1 \times 10^{-4}$  m based on the iron catalyst.

Synthesis of [Fe(L·MeOH)(tcc)]B(Ph)<sub>4</sub>]: NEt<sub>3</sub> (2 equiv.) was added to a solution with equal amounts of  $[Fe(L)(OTf)_2]$  (1 × 10<sup>-2</sup> M), tetrachlorocatechol (H<sub>2</sub>tcc), and Na[B(Ph)<sub>4</sub>] in MeOH under ambient conditions. Oxidation to iron(III) was immediately observed under air. Blue single crystals were obtained by slow evaporation of the solvent at 0 °C. ESI-MS: calcd. for [Fe(L)(OH<sub>2</sub>)(tcc)]<sup>+</sup>: 756.00107; found: 756.00111. UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max} = 531 \text{ nm}$  ( $\varepsilon_{531} =$ 2190  $\text{M}^{-1}$  cm<sup>-1</sup>), 805 nm ( $\varepsilon_{805} = 980 \text{ M}^{-1}$  cm<sup>-1</sup>). CV: E = -0.03 V versus SCE [0.1 м nBu<sub>4</sub>N(ClO<sub>4</sub>)]. Crystal data: C<sub>54</sub>H<sub>50</sub>BCl<sub>4</sub>FeN<sub>4</sub>O<sub>8</sub>,  $M_r$ =1091.44, 0.400.100.10 mm<sup>3</sup>, monoclinic, space group  $P2_1/n$ , a = 12.1685(10) Å, b = 28.234(2) Å, c = 14.7596(12) Å,  $\beta =$ 94.573(2)°, 5054.8(7) Å<sup>3</sup>, Z = 4, F(000) = 2260, T = 100(2) K,  $\theta$ range 1.8 to 25.0°. Index ranges (indep. set):  $-14 \le h \le 14$ ,  $0 \le k \le 33$ ,  $0 \le l \le 17$ . Reflections measd: 84819, indep.: 8939 ( $R_{int}$ ) = 0.0853). Final R indices  $[I > 2\sigma(I)] R_1 = 0.0635$ ,  $wR_2 = 0.1664$ , GoF = 1.126. Intensity data were collected with a Bruker AXS Smart 1000 CCD diffractometer (Mo-Ka radiation, graphite monochromator,  $\lambda = 0.71073$  Å). Data were corrected for air and detector absorption, Lorentz and polarization effects;<sup>[57]</sup> absorption by the crystal was treated with a semiempirical multiscan method.[58,59] The structure was solved by conventional direct methods,[60,61] and refined by full-matrix least-squares methods based on  $F^2$  against all unique reflections.<sup>[60,61]</sup> All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were input at calculated positions and refined with a riding model.

CCDC-837082 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

**Computational Studies:** All DFT calculations were performed with the Jaguar 6.5 program package<sup>[62]</sup> unless otherwise specified. The B3LYP functional<sup>[63,64]</sup> and LACVP basis set (double  $\zeta$ , with a Los Alamos effective core potential for the Fe center, and 6-31G for the other atoms) were used.<sup>[65]</sup> All intermediates were confirmed by frequency calculations using Gaussian 03.<sup>[66]</sup> Single-point calculations were performed on the B3LYP/LACVP-optimized geometries using the LACV3P++\*\* basis set (LanL2DZ on the Fe center and 6-311++G\*\* on the other atoms). The energies reported are those calculated at the B3LYP/LACV3P++\*\* level and include zero-point and free-energy corrections derived from the B3LYP/ LACVP calculations. A simplified model system was used in all calculations, in which the ester groups on the ligand backbone were replaced by hydrogen atoms.

**Supporting Information** (see footnote on the first page of this article): NMR spectroscopic control of the oxidation reaction; computed structural data and spin densities. Structural parameters (distances in Å, angles in °) of  $[Fe(L\cdotMeOH)(tcc)][B(Ph)_4]$  (X-ray diffraction) and  $[Fe(L)(X)]^+$  (DFT, X = tcc, dbc).

# **FULL PAPER**

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