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Iron(III) Complexes of N_2O and N_3O Donor Ligands as Functional Models for Catechol Dioxygenase Enzymes: Ether Oxygen Coordination Tunes the Regioselectivity and Reactivity

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Table S1. Electrochemical Data [a] for $[Fe(L)Cl_3]$ and [Fe(L)(DBC)Cl] [b] in DMF Solution at 25.0 ± 0.2 °C at a Scan Rate of 50 mV s^{-1} (CV) and 5 mV s^{-1} (DPV)

			$E_{1/2}$ (V)		
Complex	E_{pc} (V)	E_{pa} (V)	CV	DPV	Redox process
$[Fe(L1)Cl_3]$	-0.369	-0.255	-0.312	-0.315	Fe^{III} -Fe^{II}
H_2DBC	-0.290	-0.184	-0.237	-0.259	H_2DBC –DBSQ
	-0.460	-0.380	-0.420	-0.421	Fe^{III} -Fe^{II}
[Fe(L1)(DBC)Cl]	-0.330	-0.178	-0.254	-0.261	DBC^{2-} -DBSQ
$[Fe(L2)Cl_3]$	-0.358	-0.260	-0.309	-0.303	Fe^{III} -Fe^{II}
H2DBC	-0.288	-0.182	-0.239	-0.259	H_2DBC –DBSQ
	-0.466	-0.386	-0.426	-0.420	Fe^{III} -Fe^{II}
[Fe(L2)(DBC)Cl]	-0.288	-0.168	-0.228	-0.243	DBC^{2-} -DBSQ
$[Fe(L3)Cl_3]$	-0.420	-0.274	-0.347	-0.381	Fe^{III} -Fe^{II}
H_2DBC	-0.374	-0.190	-0.282	-0.281	H_2DBC –DBSQ
	-0.480	-0.394	-0.437	-0.439	Fe^{III} -Fe^{II}
[Fe(L3)(DBC)Cl]	-0.368	-0.188	-0.278	-0.277	DBC^{2-} -DBSQ
$[Fe(L4)Cl_3]$	-0.468	-0.286	-0.377	-0.368	Fe^{III} -Fe^{II}
H_2DBC	-0.306	-0.194	-0.250	-0.291	H_2DBC –DBSQ
	-0.464	-0.376	-0.420	-0.419	Fe^{III} -Fe^{II}
[Fe(L4)(DBC)Cl]	-0.380	-0.194	-0.287	-0.281	DBC^{2-} -DBSQ
$[Fe(L5)Cl_3]$	-0.226	-0.120	-0.173	-0.163	Fe^{III} -Fe^{II}
H_2DBC	-	-	-	-	H_2DBC –DBSQ
	-0.198	-0.110	-0.154	-0.143	Fe^{III} -Fe^{II}
[Fe(L5)(DBC)Cl]	-0.252	-0.140	-0.196	-0.181	DBC^{2-} -DBSQ
$[Fe(L6)Cl_3]$	-0.218	-0.126	-0.172	-0.160	Fe^{III} -Fe^{II}
H_2DBC	-	-	-	-	H_2DBC –DBSQ
	-0.220	-0.130	-0.175	-0.159	Fe^{III} -Fe^{II}
[Fe(L6)(DBC)Cl]	-0.268	-0.156	-0.212	-0.187	DBC^{2-} -DBSQ

[Fe(L7)Cl_3]	-0.356	-0.244	-0.300	-0.302	Fe^{III} -Fe^{II}
H_2DBC	-	-	-	-	H_2DBC –DBSQ
	-0.350	-0.222	-0.286	-0.281	Fe^{III} -Fe^{II}
[Fe(L7)(DBC)Cl]	-0.340	-0.220	-0.280	-0.285	DBC^{2-} -DBSQ
[Fe(L8)Cl_3]	-0.370	-0.262	-0.316	-0.297	Fe^{III} -Fe^{II}
H_2DBC	-	-	-	-	H_2DBC -DBSQ
	-0.356	-0.246	-0.301	-0.299	Fe^{III} -Fe^{II}
[Fe(L8)(DBC)Cl]	-0.334	-0.222	-0.278	-0.281	DBC^{2-} -DBSQ

[a] Potential measured vs. Ag(s)/AgNO3 (0.01 M, 0.10 M TBAP); add 0.544 V to convert to NHE.

[b] Generated by adding one equivalent of H2DBC and two equivalents of triethylamine to complex [Fe(L)(Sol)3]3+.

Table S2. Cleavage Products **9** - **15** (Scheme 4) Obtained Upon Oxygenation and Rate of Oxygenation[a] Reactions of Iron(III)-Catecholate Adduct Generated in situ in DMF Solution.

Complexes	Intradiol (%)	Extradiol (%)	Other Products (%)	*E/I* ratio	Reaction rate ($\times 10^{-2}$ $M^{-1}s^{-1}$)
$[Fe(L1)Cl_3]$	16.5 (**12**)	3.1 (**9**, **11**)	1.0 (**14**)	0.19	2.81 ± 0.03
$[Fe(L2)Cl_3]$	10.6 (**12**)	1.8 (**9**, **11**)	-	0.17	2.59 ± 0.04
$[Fe(L3)Cl_3]$	13.4 (**12**)	4.5 (**9**, **11**)	1.3 (**14**)	0.33	2.04 ± 0.01
$[Fe(L4)Cl_3]$	8.1 (**12**)	5.9 (**9**, **11**)	1.0 (**14**) 1.4 (**15**)	0.72	1.81 ± 0.02
$[Fe(L5)Cl_3]$	10.2 (**12**)	3.2 (**9**, **11**)	1.0 (**14**)	0.31	1.26 ± 0.01
$[Fe(L6)Cl_3]$	16.5 (**12**, **13**)	4.0 (**9**, **11**)	1.7 (**14**)	0.24	1.42 ± 0.03
$[Fe(L7)Cl_3]$	16.7 (**12**, **13**)	3.1 (**9**, **11**)	1.8 (**14**)	0.18	0.92 ± 0.05
$[Fe(L8)Cl_3]$	4.9 (**12**)	2.0 (**9**, **11**)	-	0.41	0.94 ± 0.06

[a] $k_{O_2} = k_{obs}/[O_2]$. The solubility of O_2 in DMF is accepted to be 4.86 mM at 25 °C. The kinetic data were obtained by monitoring the disappearance of the lower energy DBC^{2-}-to-iron(III) LMCT band.