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Supplementary Information

Binuclear Cu^{II} Complexes as Catalysts for Hydrocarbon and Catechol Oxidation Reactions with Hydrogen Peroxide and Molecular Oxygen

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Table S1. Experimental and theoretical infrared data (cm^{-1}) for HL1, HL2 and complexes **1** and **2**

	HL1		HL2		Complex **1**		Complex **2**	
Attribution	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
$\nu(NH)_{im}$	3313	3647	-	-	-	-	-	-
$\nu(CH)_{Ar}$	-	-	2928-2638	3219-2977	3134-3037	3072-2941	3072-2941	3071-2958
$\nu(NH)_{sec}$	3124	3498	3288	3484	2909	3240	3240	3297
$\nu(C{=}N)$	1597	1539	1715	1669	1596	1610	1610	1613
$\nu(C{=}C)$	1574-1459	1555	1592-1458	1554	1596-1454	1423	1423	1416
$\delta(O\text{-}H)_{ph}$	1398	1381	1366	1378	-	-	-	-
$\nu(C\text{-}O)$	1277	1295	1258	1297	1275	1259	1259	1259
$\delta(CH)_{Ar}$	748	761	755	763	771	775	775	785
$\nu(Cl\text{-}O)$	-	-	-	-	1130-1028	-	-	-

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Table S2. Torsion angles (°) for complex 1

N(10)-Cu(1)-Cu(2)-N(12)	102.0(2)
O(6)-Cu(1)-Cu(2)-N(12)	–44.7(3)
O(5)-Cu(1)-Cu(2)-N(12)	159.4(3)
N(9)-Cu(1)-Cu(2)-N(12)	–25.5(3)
Cl(3)-Cu(1)-Cu(2)-N(12)	–123.59(19)
N(10)-Cu(1)-Cu(2)-O(5)	–57.3(3)
O(6)-Cu(1)-Cu(2)-O(5)	156.0(3)
N(9)-Cu(1)-Cu(2)-O(5)	175.1(3)
Cl(3)-Cu(1)-Cu(2)-O(5)	77.0(2)
N(10)-Cu(1)-Cu(2)-O(6)	146.7(3)
O(5)-Cu(1)-Cu(2)-O(6)	–156.0(3)
N(9)-Cu(1)-Cu(2)-O(6)	19.2(3)
Cl(3)-Cu(1)-Cu(2)-O(6)	–78.9(2)
N(10)-Cu(1)-Cu(2)-N(7)	–44.3(3)
O(6)-Cu(1)-Cu(2)-N(7)	169.0(3)
O(5)-Cu(1)-Cu(2)-N(7)	13.0(3)
N(9)-Cu(1)-Cu(2)-N(7)	–171.9(3)
Cl(3)-Cu(1)-Cu(2)-N(7)	90.0(2)
N(12)-Cu(2)-O(5)-C(15)	138.5(6)
O(6)-Cu(2)-O(5)-C(15)	–155.1(5)
N(7)-Cu(2)-O(5)-C(15)	18.8(5)
Cu(1)-Cu(2)-O(5)-C(15)	–170.5(6)
N(12)-Cu(2)-O(5)-Cu(1)	–50.9(6)
O(6)-Cu(2)-O(5)-Cu(1)	15.5(2)
N(7)-Cu(2)-O(5)-Cu(1)	–170.6(2)
N(10)-Cu(1)-O(5)-C(15)	–57.8(5)
O(6)-Cu(1)-O(5)-C(15)	154.7(5)
N(9)-Cu(1)-O(5)-C(15)	150.2(10)
Cl(3)-Cu(1)-O(5)-C(15)	54.5(5)
Cu(2)-Cu(1)-O(5)-C(15)	170.3(6)
N(10)-Cu(1)-O(5)-Cu(2)	131.9(2)
O(6)-Cu(1)-O(5)-Cu(2)	–15.6(2)
N(9)-Cu(1)-O(5)-Cu(2)	–20.1(13)
Cl(3)-Cu(1)-O(5)-Cu(2)	–115.75(17)
N(10)-Cu(1)-O(6)-C(27)	137.4(5)
O(5)-Cu(1)-O(6)-C(27)	–145.9(5)
N(9)-Cu(1)-O(6)-C(27)	33.3(5)
Cl(3)-Cu(1)-O(6)-C(27)	–46.6(5)
Cu(2)-Cu(1)-O(6)-C(27)	–161.1(6)
N(10)-Cu(1)-O(6)-Cu(2)	–61.4(4)
O(5)-Cu(1)-O(6)-Cu(2)	15.3(2)
N(9)-Cu(1)-O(6)-Cu(2)	–165.6(2)
Cl(3)-Cu(1)-O(6)-Cu(2)	114.57(18)
N(12)-Cu(2)-O(6)-C(27)	–57.3(6)
O(5)-Cu(2)-O(6)-C(27)	143.0(6)
Cu(1)-Cu(2)-O(6)-C(27)	158.6(7)
N(12)-Cu(2)-O(6)-Cu(1)	144.1(2)
O(5)-Cu(2)-O(6)-Cu(1)	–15.6(2)
N(12)-Cu(2)-N(7)-C(20)	–139.0(5)
O(5)-Cu(2)-N(7)-C(20)	21.7(5)
Cu(1)-Cu(2)-N(7)-C(20)	13.3(6)
N(12)-Cu(2)-N(7)-C(25)	–8.3(5)
O(5)-Cu(2)-N(7)-C(25)	152.4(4)
Cu(1)-Cu(2)-N(7)-C(25)	144.0(4)
N(10)-Cu(1)-N(9)-C(29)	–1.3(5)
O(6)-Cu(1)-N(9)-C(29)	146.2(5)
O(5)-Cu(1)-N(9)-C(29)	150.7(10)
Cl(3)-Cu(1)-N(9)-C(29)	–111.6(5)
Cu(2)-Cu(1)-N(9)-C(29)	134.1(4)
N(10)-Cu(1)-N(9)-C(17)	–132.9(5)
O(6)-Cu(1)-N(9)-C(17)	14.5(5)
O(5)-Cu(1)-N(9)-C(17)	19.0(14)
Cl(3)-Cu(1)-N(9)-C(17)	116.7(5)
Cu(2)-Cu(1)-N(9)-C(17)	2.4(5)
O(6)-Cu(1)-N(10)-C(19)	45.5(7)
O(5)-Cu(1)-N(10)-C(19)	–26.2(5)
N(9)-Cu(1)-N(10)-C(19)	148.8(5)
Cl(3)-Cu(1)-N(10)-C(19)	–130.3(5)
Cu(2)-Cu(1)-N(10)-C(19)	5.9(6)
O(6)-Cu(1)-N(10)-C(30)	–119.2(5)
O(5)-Cu(1)-N(10)-C(30)	169.1(5)
N(9)-Cu(1)-N(10)-C(30)	–16.0(5)
Cl(3)-Cu(1)-N(10)-C(30)	65.0(5)
Cu(2)-Cu(1)-N(10)-C(30)	–158.8(4)

Table S2. Cont.

O(5)-Cu(2)-N(12)-C(16)	34.1(8)
O(6)-Cu(2)-N(12)-C(16)	–29.6(5)
N(7)-Cu(2)-N(12)-C(16)	153.4(5)
Cu(1)-Cu(2)-N(12)-C(16)	–2.8(6)
O(5)-Cu(2)-N(12)-C(13)	–130.9(6)
O(6)-Cu(2)-N(12)-C(13)	165.3(5)
N(7)-Cu(2)-N(12)-C(13)	–11.7(5)
Cu(1)-Cu(2)-N(12)-C(13)	–167.9(4)
C(16)-N(12)-C(13)-C(28)	0.4(7)
Cu(2)-N(12)-C(13)-C(28)	167.9(4)
C(16)-N(12)-C(13)-C(23)	–176.5(5)
Cu(2)-N(12)-C(13)-C(23)	–9.0(8)
C(22)-C(11)-C(15)-O(5)	–178.4(6)
C(22)-C(11)-C(15)-C(21)	2.2(9)
Cu(2)-O(5)-C(15)-C(11)	152.7(5)
Cu(1)-O(5)-C(15)-C(11)	–15.1(8)
Cu(2)-O(5)-C(15)-C(21)	–27.8(8)
Cu(1)-O(5)-C(15)-C(21)	164.4(4)
C(13)-N(12)-C(16)-N(8)	–0.1(7)
Cu(2)-N(12)-C(16)-N(8)	–167.4(4)
C(28)-N(8)-C(16)-N(12)	–0.2(7)
C(29)-N(9)-C(17)-C(24)	167.6(6)
Cu(1)-N(9)-C(17)-C(24)	–55.7(7)
C(30)-N(10)-C(19)-N(14)	0.1(7)
Cu(1)-N(10)-C(19)-N(14)	–166.8(4)
C(31)-N(14)-C(19)-N(10)	–0.1(7)
C(25)-N(7)-C(20)-C(21)	170.3(6)
Cu(2)-N(7)-C(20)-C(21)	–55.6(7)
C(11)-C(15)-C(21)-C(34)	–4.1(9)
O(5)-C(15)-C(21)-C(34)	176.4(5)
C(11)-C(15)-C(21)-C(20)	171.5(6)
O(5)-C(15)-C(21)-C(20)	–7.9(9)
N(7)-C(20)-C(21)-C(34)	–131.1(6)
N(7)-C(20)-C(21)-C(15)	53.3(9)
C(15)-C(11)-C(22)-C(32)	1.0(10)
C(28)-C(13)-C(23)-C(25)	–123.8(7)
N(12)-C(13)-C(23)-C(25)	52.3(8)
N(9)-C(17)-C(24)-C(27)	58.1(8)
N(9)-C(17)-C(24)-C(36)	–123.6(7)
C(20)-N(7)-C(25)-C(23)	179.9(5)
Cu(2)-N(7)-C(25)-C(23)	47.7(7)
C(13)-C(23)-C(25)-N(7)	–73.2(7)
Cu(1)-O(6)-C(27)-C(18)	137.1(5)
Cu(2)-O(6)-C(27)-C(18)	–17.3(9)
Cu(1)-O(6)-C(27)-C(24)	–41.8(8)
Cu(2)-O(6)-C(27)-C(24)	163.8(5)
C(33)-C(18)-C(27)-O(6)	–178.6(6)
C(33)-C(18)-C(27)-C(24)	0.3(10)
C(36)-C(24)-C(27)-O(6)	176.0(6)
C(17)-C(24)-C(27)-O(6)	–5.6(9)
C(36)-C(24)-C(27)-C(18)	–3.0(9)
C(17)-C(24)-C(27)-C(18)	175.4(6)
C(16)-N(8)-C(28)-C(13)	0.5(7)
N(12)-C(13)-C(28)-N(8)	–0.6(7)
C(23)-C(13)-C(28)-N(8)	175.9(6)
C(17)-N(9)-C(29)-C(26)	175.3(6)
Cu(1)-N(9)-C(29)-C(26)	41.3(7)
C(30)-C(26)-C(29)-N(9)	–72.5(7)
C(19)-N(10)-C(30)-C(31)	–0.1(7)
Cu(1)-N(10)-C(30)-C(31)	167.3(4)
C(19)-N(10)-C(30)-C(26)	–177.0(6)
Cu(1)-N(10)-C(30)-C(26)	–9.6(8)
C(29)-C(26)-C(30)-C(31)	–119.2(8)
C(29)-C(26)-C(30)-N(10)	56.8(8)
N(10)-C(30)-C(31)-N(14)	0.0(7)
C(26)-C(30)-C(31)-N(14)	176.4(7)
C(19)-N(14)-C(31)-C(30)	0.0(7)
C(11)-C(22)-C(32)-C(34)	–2.1(10)
C(27)-C(18)-C(33)-C(35)	2.2(11)
C(22)-C(32)-C(34)-C(21)	0.1(10)
C(15)-C(21)-C(34)-C(32)	3.0(10)
C(20)-C(21)-C(34)-C(32)	–172.8(6)
C(18)-C(33)-C(35)-C(36)	–2.0(11)
C(33)-C(35)-C(36)-C(24)	–0.7(12)
C(27)-C(24)-C(36)-C(35)	3.2(10)
C(17)-C(24)-C(36)-C(35)	–175.2(7)

Table S3. Hydrogen bond distances and angles for complex **1** (Å and °)

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(8)-H(8)···Cl(3)#1	0.86	2.29	3.149(5)	173.9
N(14)-H(14)···Cl(4)#2	0.86	2.24	3.089(6)	172.2

Symmetry transformations used to generate equivalent atoms: #1 : x-1/2,y+1/2,z ; #2 : x-1/2,-y+3/2,z-1/2.

Table S4. Experimental (X-ray diffraction data for HL1[23]) and calculated (DFT) main bond distances (Å) and angles (°) for HL1 and HL2

HL1	Exp.	Calc.	HL2	Calc.
N(8)-C(9)	1.70(3)	1.465	N(8)-C(9)	1.462
N(8)-C(7)	1.476(3)	1.468	N(8)-C(7)	1.458
N(14)-C(13)	1.331(3)	1.365	C(14)-C(13)	1.396
N(14)-C(15)	1.359(3)	1.382	C(14)-C(15)	1.395
N(12)-C(11)	1.363(3)	1.385	N(12)-C(11)	1.344
N(12)-C(13)	1.326(3)	1.315	N(12)-C(13)	1.338
C(9)-N(8)-C(7)	113.34(19)	114.55	C(9)-N(8)-C(7)	115.53
C(13)-N(14)-C(15)	107.31(18)	107.21	C(13)-C(14)-C(15)	117.95
C(13)-N(12)-C(11)	105.61(19)	105.72	C(13)-N(12)-C(11)	118.09

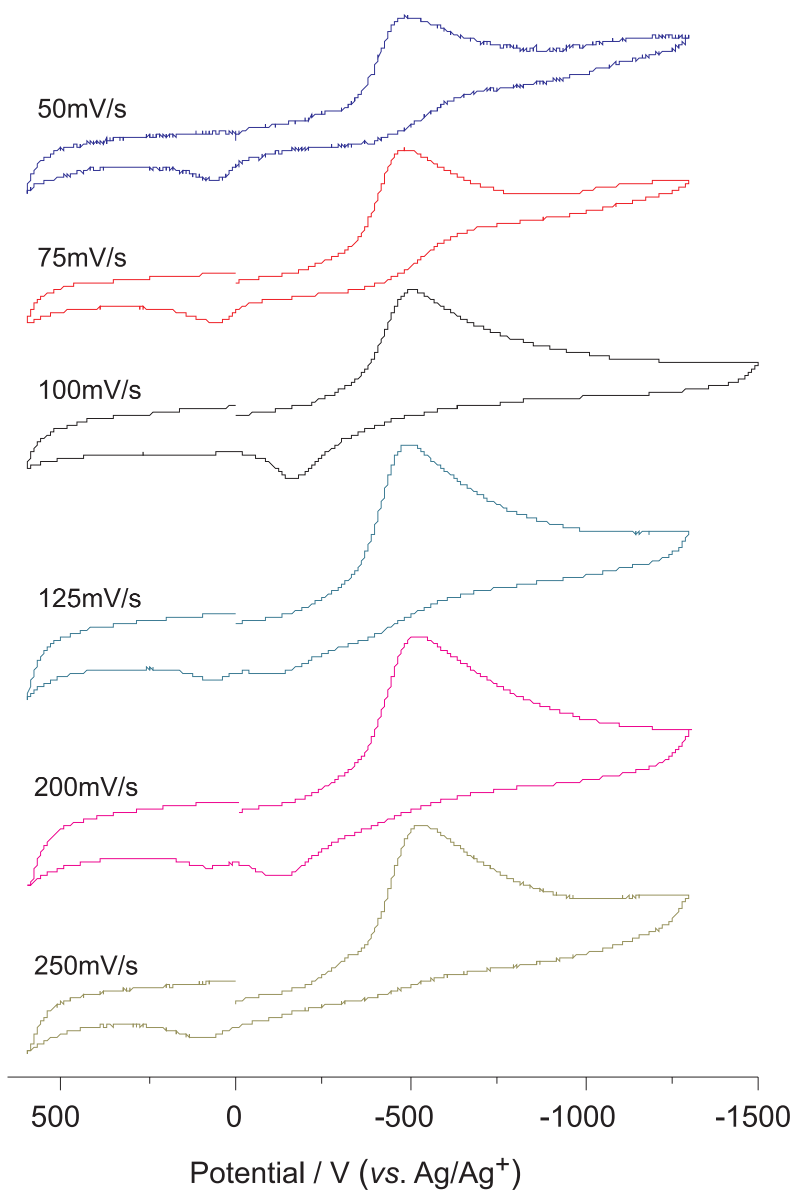

Figure S1. Cyclic voltammograms registered for complex **1** in methanol at different scan rates.

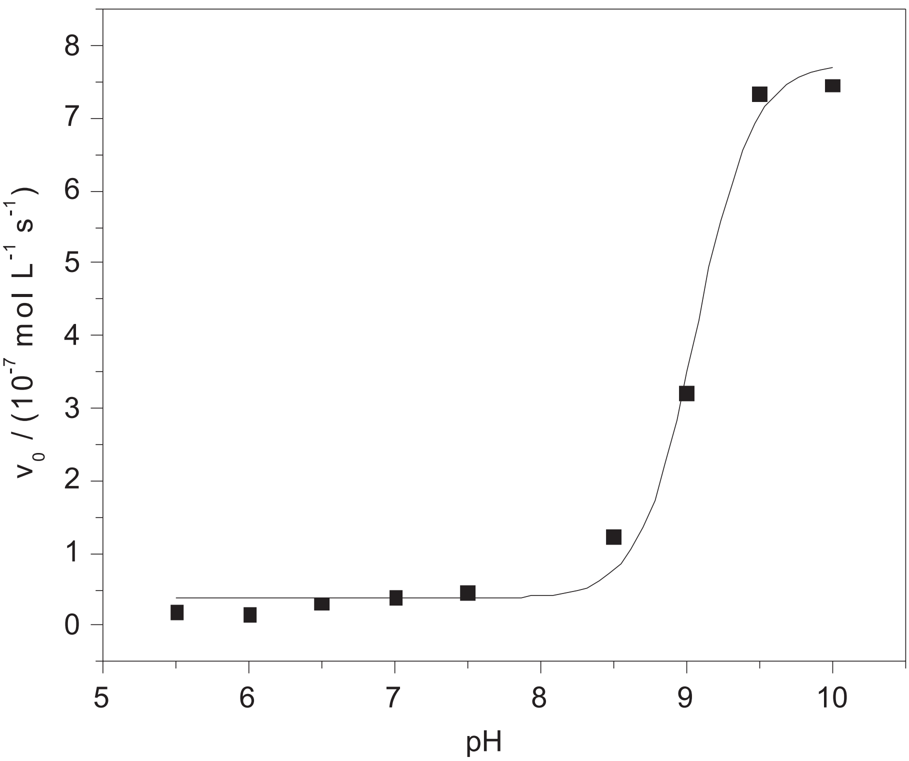

Figure S2. pH dependence for the oxidation of 3,5-dtbc catalyzed by complex **2**, in methanol/water (30:1 v/v) solution. Experimental conditions: $[\mathbf{2}]_{final}$ = 2.4×10^{-5} mol L^{-1}; $[3,5\text{-dtbc}]_{final}$ = 5×10^{-3} mol L^{-1}; $[buffer]_{final}$ = 3×10^{-3} mol L^{-1}; 25 ºC.

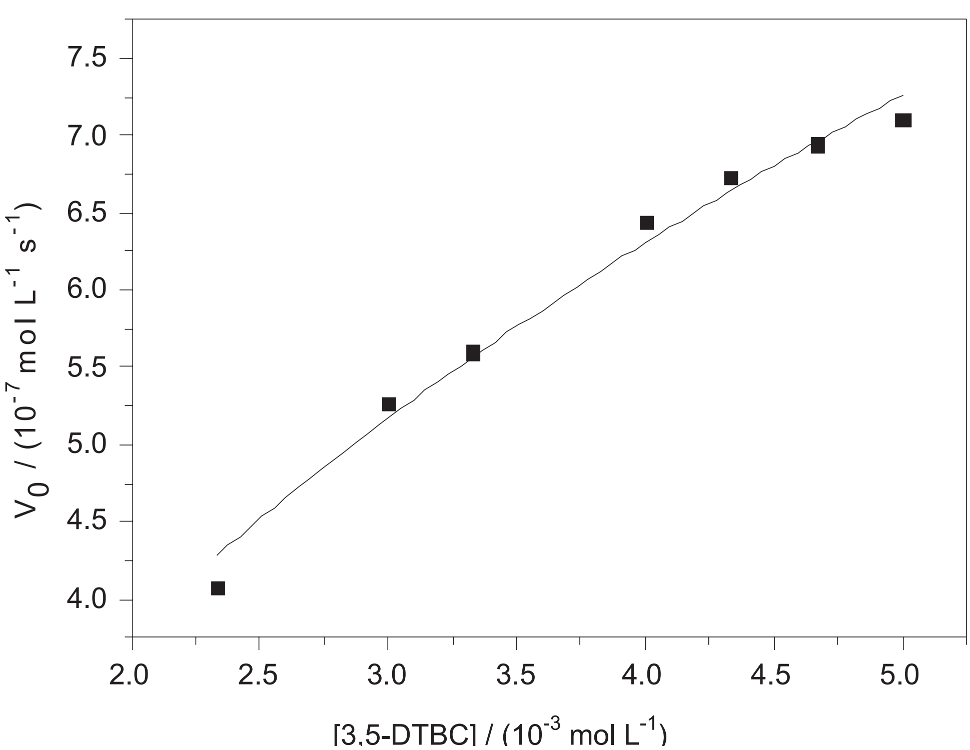

Figure S3. Dependence of the reaction rates on the 3,5-dtbc concentration for the oxidation reaction catalyzed by complex **2**, in methanol/water (30:1 v/v) solution. Experimental conditions: $[\mathbf{2}]_{final}$ = 2.4×10^{-5} mol L^{-1}; $[3,5\text{-dtbc}]_{final}$ = 2.33-5.0 × 10^{-3} mol L^{-1}; $[buffer]_{final}$ = 3×10^{-3} mol L^{-1}; pH 9 (CHES buffer); 25 ºC.