Supplementary information

Comparative Study of the Peroxidase-like Activity of Copper(II) Complexes with N_4 and N_2O_2 Coordination Environments. Application to the Oxidation of Phenol at Moderate Temperature

Joaquín Ferreyra, Claudia Palopoli, Nora Pellegri, Gustavo Terrestre, and Sandra R. Signorella

Contents

Synthesis of copper(II) complexes

N,N'-bis(salicylidene)-1,3-propanediamine (**H_2salpn**). 1,3-Diaminopropane (3.75 mL, 44 mmol) was added to 30 mL of a solution of salicylaldehyde (8.5 mL, 79 mmol) in ethanol and the mixture was left with stirring under reflux for 2.5 h. The crystalline yellow solid was filtered, washed with cold ethanol and hexane, and dried under vacuum. Yield: 7.405 g (26 mmol, 66%). M.p. 49 – 51°C. ^{1}H NMR (Cl_3CD) δ, ppm: 8.38 (s, 2H, H7), 6.84-7.36 (m, 8H, H-ar), 3.72 (t, 4H, H8), 2.12 (q, 2H, H9). ^{13}C NMR (Cl_3CD) δ, ppm: 165.4 (C2), 161.1 (C7), 132.3 (C4), 131.3 (C6), 118.7 (C1), 118.6 (C5), 117.0 (C3), 56.8 (C8), 31.7 (C9). Significant IR bands (ν, cm^{-1}): 1611(C=N), 1273 (C-O).

N,N'-bis(2-pyridinilmethylen)propane-1,3-diamine (**py_2pn**). 2-Pyridinecarboxaldehyde (1.3 mL, 14 mmol) was added to a solution of 1,3-diaminopropane (0.57 mL, 6.8 mmol) in 35 mL of EtOH, and the mixture was left with stirring, under reflux for 24 h. After removal of the solvent at reduced pressure and dried under vacuum the Schiff-base was obtained as a brown oil which was used without further purification. Yield: 1.6527 g (6.5503 mmol, 96%). ^{1}H NMR (Cl_3CD) δ, ppm: 8.65 (m, 2H, H5, J = 4.7 Hz), 8.42 (s, 2H, H6), 8.00 (d, 2H, H2, J = 7.8 Hz), 7.75 (td, 2H, H3, J^1 = 7.8 Hz, J^2 = 1.7 Hz), 7.31 (ddd, 2H, H4, J^1 = 7.8 Hz, J^2 = 5.0 Hz, J^3 = 1.2 Hz), 3.81 (td, 4H, H7, J^1 = 6.9 Hz, J^2 = 1.2 Hz), 2.17 (q, 2H, H8, J = 6.9 Hz). ^{13}C NMR (Cl_3CD) δ, ppm: 161.23 (C6), 154.52 (Ar), 149.37 (Ar), 136.50 (Ar), 124.64 (Ar), 121.21 (Ar), 58.94 (C7), 31.63 (C8). Significant IR bands (ν, cm^{-1}): 3059, 3013, 2926, 2855, 1648 (C=N), 1587/1567/1469/1437 (py).

$[Cu(phen)_2](ClO_4)_2$. The synthesis of this complex was performed following a procedure described previously.[1] 1,10-Phenanthroline monohydrate (0.5024 g, 2.535 mmol) was added to 100 mL of an aqueous solution of 0.68 g of $Cu(ClO_4)_2.6H_2O$ (1.8 mmol) and the mixture was left with stirring under reflux for 4 h. The greenish-blue solid was filtered under reduced pressure, washed with cold water and hexane, and dried under vacuum. Yield: 0.5189 g (0.83 mmol, 66%). Anal. calcd. for $C_{24}H_{16}CuN_4O_8Cl_2$: C 46.3, H 2.6, Cu 10.2, N 9.0 %; Found: C 46.1, H 2.7, Cu 10.3, N 9.2 %. Significant IR bands (ν, cm^{-1}): 1520, 1427, $\nu(ClO_4^-)$ 1065, 845, 718, $\rho(ClO_4^-)$ 619. UV-Vis λ_{max} nm (ε, M^{-1} cm^{-1}) in MeCN: 225 (72000), 269 (58000), 296 (sh), 830 (240). Crystals of $[Cu(phen)_2(MeCN)](ClO_4)_2$ suitable for X-ray diffraction analysis were obtained by slow evaporation of an acetonitrile solution of $[Cu(phen)_2](ClO_4)_2$. Crystals of $[(Cu(phen)_2)Cl]ClO_4$ suitable for X-ray diffraction analysis were formed from a solution of $[Cu(phen)_2](ClO_4)_2$ in 1:5 DMF:buffer borate prepared from boric acid, sodium borate and potassium chloride mixture, after standing in air for several days.

[{Cu(phen)(CH_3CO_2)$_2$}(μ-H_2O)]·H_2O. This compound was obtained following a procedure similar to that described by Devereux et al.[2] $Cu(OAc)_2.H_2O$ (562.6 mg, 2.818 mmol) was added to a solution of 1,10-phenanhroline (510.2 mg, 2.831 mmol) in 25 mL of ethanol, and the resulting mixture was left stirring under reflux for 1 h. After reducing the volume of the mixture to 10 mL under vaccuum, 10 mL of acetone were added. Then, the volume of the mixture was further reduced and a blue precipitate appeared. The solid was filtered under vaccuum, washed with water, acetone and hexane, and dried under vacccuum. Yield: 0,5789 g (1,524 mmol, 54%). Anal. calcd. for $C_{16}H_{14}CuN_2O_4·H_2O$: C 50.6, H 4.2, N 7.4%; Found: C 50.8, H 3.7, N 7.3%. UV-Vis λ_{max} nm (ε, M^{-1} cm^{-1}) in MeCN: 224 (32500), 272 (30500), 708 (300). Significant IR bands (ν, cm^{-1}): $\nu_{as}(AcO^-)$1576; 1515; 1429; $\nu_s(AcO^-)$ 1404; 850; 724. Crystals suitable for X-ray analysis formed by slow evaporation of the reaction mixture.

[Cu(Py_2pn)(ClO_4)$_2$]. This complex was synthesized by a procedure described previously by Ebralidze et al.[3] A solution of 158 mg (0.791 mmol) of $Cu(OAc)_2.H_2O$ in 15 mL of methanol, was added to a solution of py_2pn (200 mg, 0.792 mmol) in 2 mL of methanol, and the mixture was stirred for 2 days at room temperature. Then, 222 mg (1.6 mmol) of $NaClO_4.H_2O$ were added and the complex precipitated from the reaction mixture. The green-bluish solid was filtered, washed with methanol, dichloromethane and hexane, and dried under vacuum. Yield: 0.246 g (0.478 mmol, 60%). Anal. calcd. for $C_{15}H_{16}CuN_4O_8Cl_2$: C 35.00, Cu 12.3, H 3.1 %, N 10.9%; Found: C 34.9%, Cu 12.0, H 2.8%, N 10.7%. UV-Vis λ_{max} nm (ε, M^{-1} cm^{-1}) in MeCN: 288 (15000), 645 (180). Significant IR bands (ν, cm^{-1}): ν(C=N) 1645; 1600/1566/1474/1433 (pyridine ring), $\nu(ClO_4^-)$ 1114, $\rho(ClO_4^-)$ 625.

[Cu(salpn)]. This complex was synthesized by a method similar to that described by Maurya et al.[4] To a solution of 216 mg of $Cu(OAc)_2·H_2O$ (1.062 mmol) in 24 mL of methanol, were added H_2salpn (312 mg, 1.105 mmol), and the mixture was left stirring under reflux for 2 h. The dark-green crystalline solid was filtered, washed with methanol, hexane and dried under vacuum. Yield: 274 mg (0,80 mmol, 75%). Anal. calcd. for $C_{17}H_{16}CuN_2O_2$: C 59.4, H 4.7, Cu 18.7, N 8.2%; Found: C 59.1, H 4.5, Cu 19.1, N 8.2%. UV-Vis λ_{max} nm (ε, M^{-1} cm^{-1}) in MeCN: 229 (43000), 272 (18000), 366 (10000), 608 (245). Significant IR bands (ν, cm^{-1}): 3014, 2900, ν(C=N) 1605, ν(Ar) 1537, 746/725, 596.

[Mn_2(Py_2pn)$_3$(ClO_4)$_2$](ClO_4)$_2$·2H_2O. A deoxygenated solution of py_2pn (152 mg, 0.60 mmol) in 2 mL of CH_2Cl_2 was added to a deoxygenated solution of manganese(II) perchlorate hexahydrate (215 mg, 0.59 mmol) in 2 mL of ethanol, and the mixture was stirred under N_2 and protected from light, for 6 h. The light orange solid was filtered, washed with ethanol,

CH_2Cl_2 and hexane, and dried under vacuum. Yield: 130 mg (0.11 mmol, 50%). Anal. calcd. for $C_{45}Cl_4H_{48}Mn_2N_4O_{16}·2H_2O$: C 41.6, H 4.0, Mn 8.4, N 12.9 %. Found: C 41.2, H 3.9, Mn 8.2, N 12.8 %.

[Mn(salpn)(H_2O)$_2$]ClO_4·H_2O. 445 µL of an aqueous solution of sodium hydroxide 5.31 M (2.36 mmol) were added to a solution of 0.679 g of 1,3-bis(salicylidenamino)propane (2.405 mmol) in 18 mL of methanol/ethanol (1:1). Then, a solution of 832 mg of manganese(II) perchlorate hexahydrate (2.42 mmol) in 3 mL of methanol/ethanol (1:1) was added dropwise, and the reaction mixture was stirred for 2 h at room temperature. After diethyl ether addition, the mixture was stored at 4°C overnight and the green solid was separated by filtration, washed with ice-cold ethanol and dried under vacuum. Yield: 936 mg (1.9 mmol, 79%). Anal. Calcd for $C_{17}ClH_{22}MnN_2O_8·H_2O$: C, 41.8; H, 4.5; Mn, 11.2; N, 5.7%. Found: C, 41.5; H, 4.2; Mn, 10.8; N, 6.1%.

[Mn(3,5-Cl_2-salpn)(H_2O)$_2$]ClO_4·2H_2O. 205 µL of an 5.31 M NaOH aqueous solution (1.09 mmol) were added to a solution of 0.513 g of 1,3-bis(3,5-dichlorosalicylidenamino)propane (1.22 mmol) and 0.442 g of manganese(II) perchlorate hexahydrate (1.21 mmol) in 135 mL of methanol/ethanol (1:1), and the reaction mixture was stirred for 36 h at room temperature. After diethyl ether addition, the greenish solid was separated by filtration, washed with ice-cold ethanol and dried under vacuum. Yield: 535 mg (0.83 mmol, 69%). Anal. Calcd. for $C_{17}Cl_5H_{16}MnN_2O_8·2H_2O$: C, 31.6; H, 3.1; Mn, 8.5; N, 4.4%. Found: C, 31.6; H, 2.6; Mn, 8.4; N, 4.2%.

[Mn(salpn)(µ-O)]$_2$·H_2O. An aqueous solution of 5.31 M NaOH (385 µL, 2.02 mmol) was added to a solution of [Mn(salpn)(H_2O)$_2$](ClO_4)·H_2O (1 g. 2.05 mmol) in methanol (10 mL). The red brown mixture was stirred at room temperature for 48 h. The formed precipitate was filtered and dried under vacuum, and then redissolved in 160 mL of $CHCl_3$, and stirred at room temperature for 1 h. The solid residue of the remaining monomer was filtered out and the filtrate was concentrated in a rotatory evaporator at room temperature. The solid residue was filtered and dried under vacuum. Yield: 569 mg (0.79 mmol, 78%). Anal. Calcd for $C_{34}H_{34}Mn_2N_4O_7$: C 56,7%, H 4,8%, Mn 15,3%, N 7,8%; experimental: C 57,0%, H 4,3%, Mn 14,9%, N 7,7%.

[Mn(3,5-Cl_2-salpn)(µ-O)]$_2$. To a solution of [Mn(3,5-Cl_2salpn)(H_2O)$_2$](ClO_4)·2H_2O (251 mg, 0.389 mmol) in 5 mL of methanol, 73 µL of an aqueous solution of 5.31 M NaOH (0.39 mmol). The reddish-brown mixture was stirred at room temperature for 48 h. The formed solid was filtered and dried under vacuum. Yield: 157 mg (0.16 mmol, 82%). Anal. Calcd for

$C_{34}H_{24}Cl_8Mn_2N_4O_6$: C 41,8%, H 2,5%, Mn 11,2%, N 5,7%; experimental: C 41,5%, H 2,2%, Mn 11,4%, N 5,6%.

Caution! *The perchlorate salts used in this study are potentially explosive and should be handled with care.*

References

1- A.A. Schilt, R.C. Taylor, J. Inorg. Nucl. Chem. 1959, **9**, 211–221.

2- M. Devereux, D. O'Shea, M. O'Connor, H. Grehan, G. Connor, M. McCann, G. Rosair, F. Lyng, A. Kellett, M. Walsh, D. Egan, B. Thati, Polyhedron 2007, **26**, 4073–4084

3- I.I. Ebralidze, G. Leitus, L. J. W. Shimon, Y. Wang, S. Shaik, R. Neumann, Inorg. Chim. Acta 2009, **362,** 4713–4720.

4- M. R. Maurya, S. J. J. Titinchi, S. Chand, Appl. Catal. A Gen. 2002, **228**, 177–187.

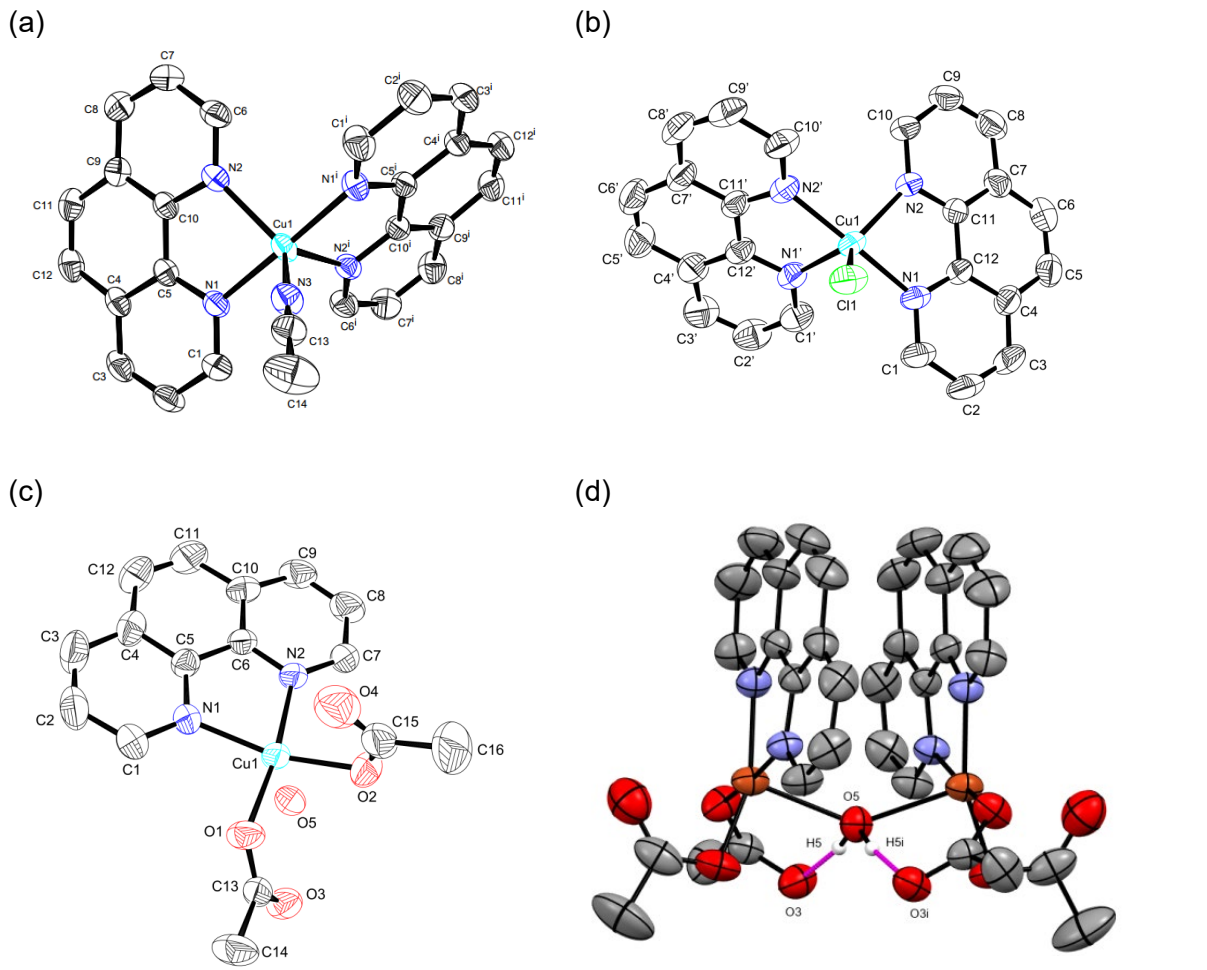

Figure S1. Crystal structures of (a) $[Cu(phen)_2(MeCN)]^{2+}$, (b) $[(Cu(phen)_2)Cl]^{+}$, and asymmetric unit (c) and molecular structure (d) of $[\{Cu(phen)(OAc)_2\}_2\text{-}\mu\text{-}OH_2]$. Symmetry code: i: 1-x, y, 1.5-z

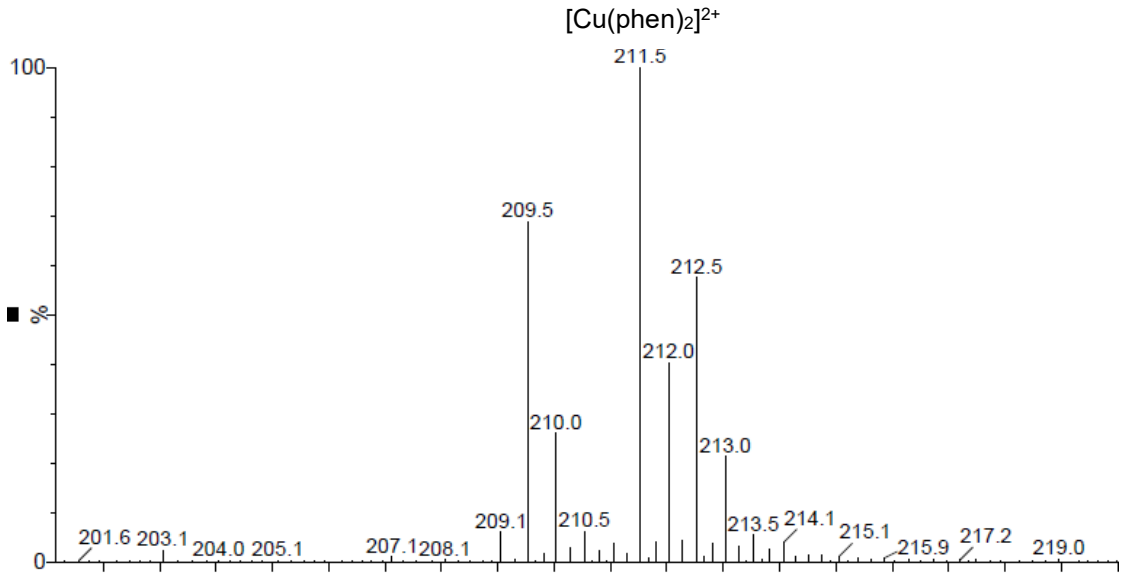

Figure S2. ESI-mass spectrum of $[Cu(phen)_2](ClO_4)_2$ in MeCN

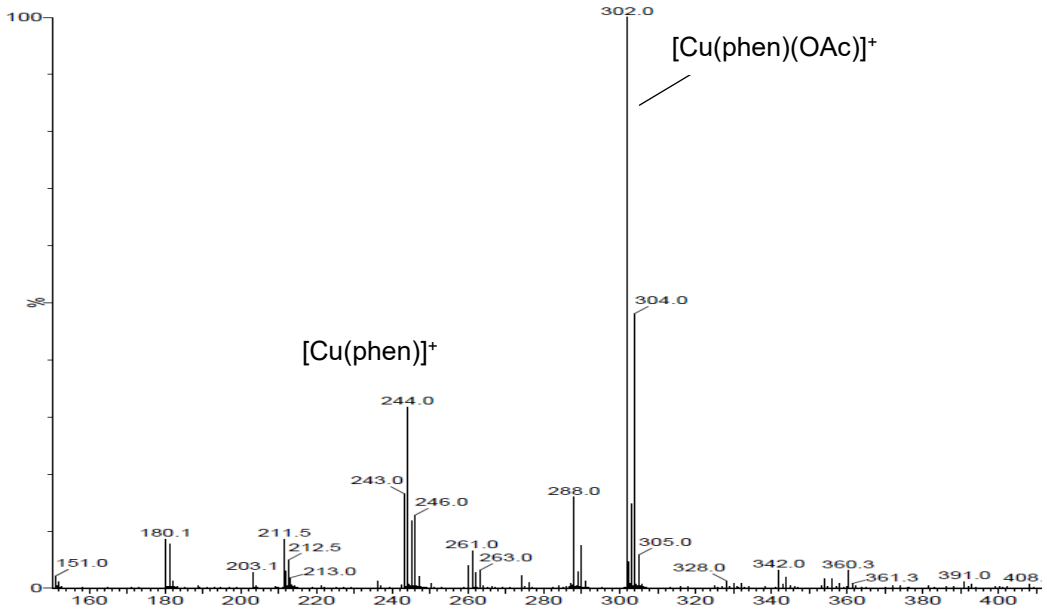

Figure S3. ESI-mass spectrum of [{Cu(phen)(OAc)$_2$}$_2$-μ-OH$_2$] in MeCN

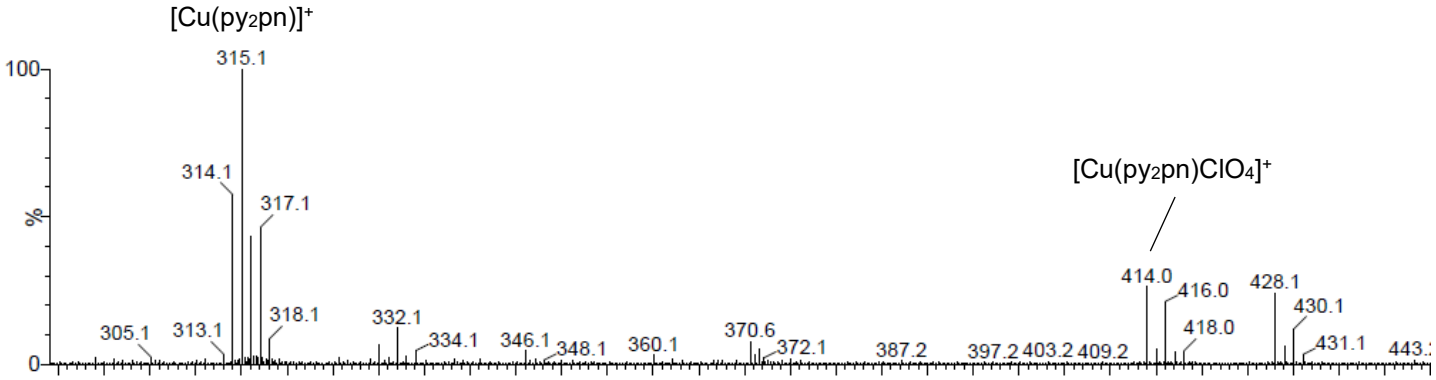

Figure S4. ESI-mass spectrum of [Cu(py$_2$pn)(ClO$_4$)$_2$] in MeOH

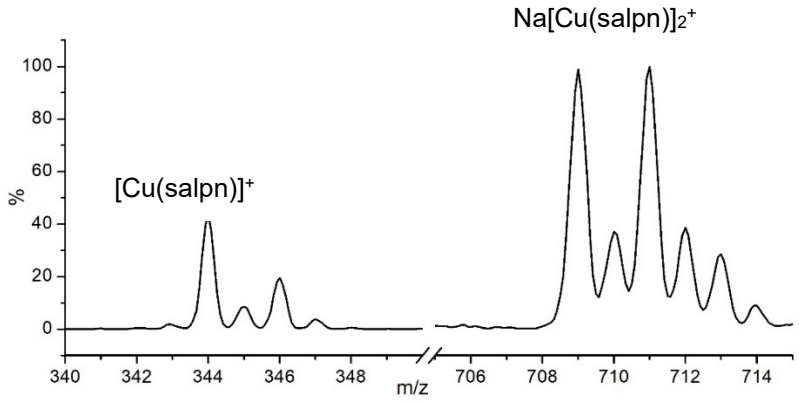

Figure S5. ESI-mass spectrum of [Cu(salpn)] in MeCN

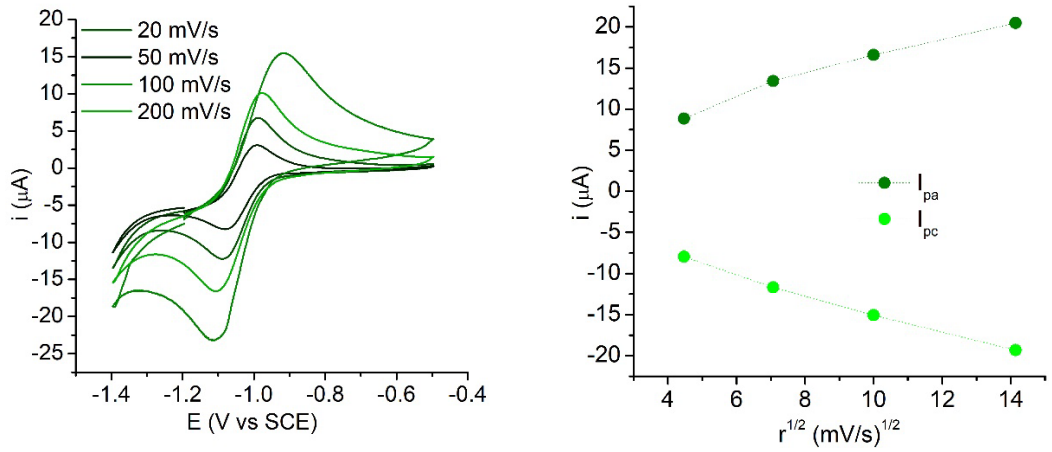

Figure S6. Left: cyclic voltammograms of **[Cu(salpn)]** in MeCN recorded at different scan rates (20-200 mV/s). Right: anodic and cathodic peak currents versus square root of scan rate potential.

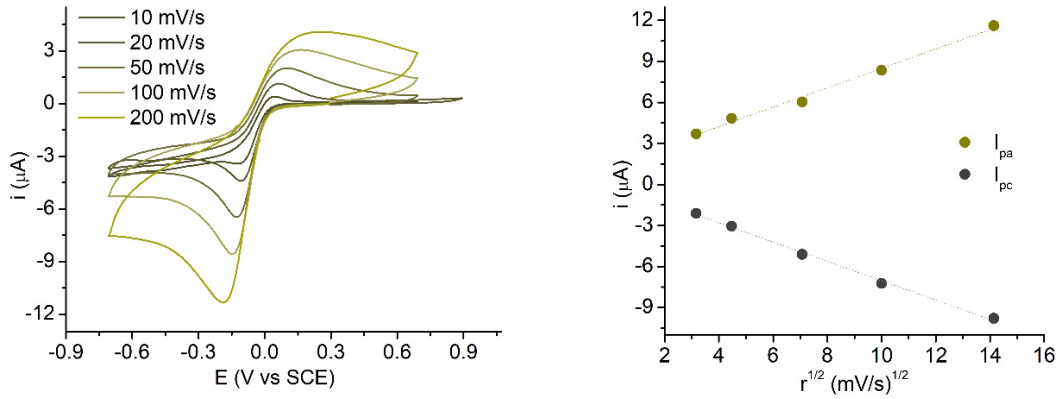

Figure S7. Left: cyclic voltammograms of **[Cu(Py$_2$pn)(ClO$_4$)$_2$]** in MeCN recorded at different scan rates (10-200 mV/s). Right: anodic and cathodic peak currents versus square root of scan rate potential.

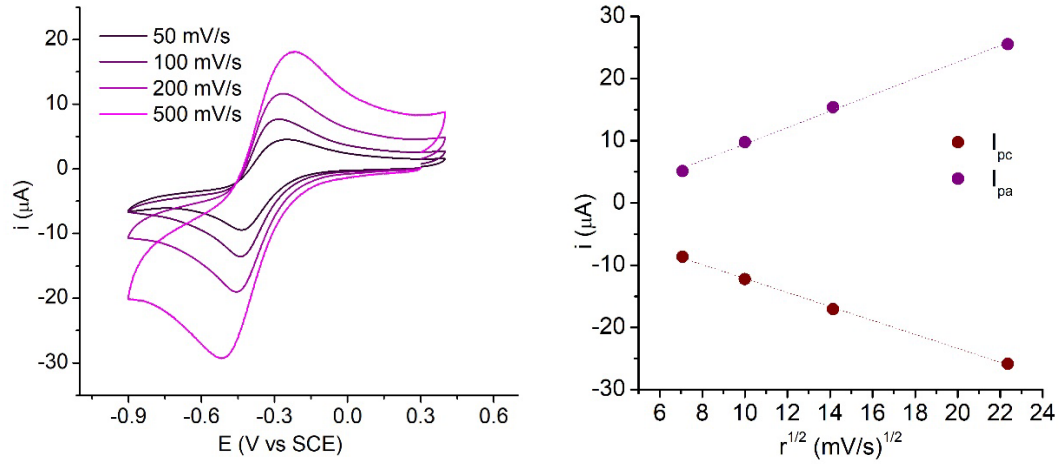

Figure S8. Left: cyclic voltammograms of **[{Cu(phen)(CH$_3$CO$_2$)$_2$}-μ-H$_2$O]** in MeCN recorded at different scan rates (50-500 mV/s). Right: anodic and cathodic peak currents versus square root of scan rate potential.

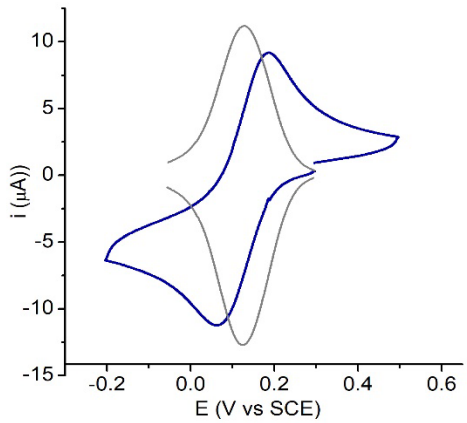

Figure S9. Cyclic and square-wave voltammograms of **$[Cu(phen)_2](ClO_4)_2$** in DMF. Scan rate: 100 mV/s.

Table S1. Crystal data and structure refinement for $[Cu(phen)_2(MeCN)](ClO_4)_2$, $[(Cu(phen)_2)Cl]ClO_4$ and $[\{Cu(phen)(OAc)_2\}_2\text{-}\mu\text{-}OH_2]$

Empirical formula	$C_{26}H_{19}Cl_2CuN_5O_8$	$C_{24}H_{16}Cl_2CuN_4O_4$	$C_{32}H_{30}Cu_2N_4O_9$
Formula weight	663.90	558.85	741.68
Temperature	298(2) K	298(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, C 1 2/c 1	Monoclinic, P 1 21/c 1	Monoclinic, C 1 2/c 1
Unit cell dimensions	a = 19.7423(6) Å, α = 90º	a = 12.6618(7) Å, α = 90º	a = 18.3171(10) Å, α = 90º
	b = 8.6733(3) Å, β = 98.0860(10)º	b = 11.2248(6) Å, β = 111.418(2)º	b = 9.4843(5) Å, β = 100.875(2)º
	c = 15.1399(5)Å, γ = 90º	c = 17.2313(10) Å, γ = 90º	c = 18.8728(10) Å, γ = 90º
Volume	2566.65(15) $Å^3$	2278.6(2)$Å^3$	3219.8(5) $Å^3$
Z, Calculated density	4, 1.718 g/cm^3	4, 1.629 g/cm^3	4, 1.530 g/cm^3
Absorption coefficient	1.123 mm^{-1}	1.234 mm^{-1}	1.381 mm^{-1}
F(000)	1348	1132	1520
Crystal size	0.066 x 0.080 x 0.165 mm	0.053 x 0.112 x 0.235 mm	0.084 x 0.195 x 0.239 mm
Theta range for data collection	2.569 to 25.362 deg	2.506 to 25.359 deg	2.428 to 25.474 deg
Limiting indices	-23<=h<=23, -10<=k<=10, -18<=l<=18	-15<=h<=15, -13<=k<=13, -20<=l<=20	-22<=h<=22, -11<=k<=11, -22<=l<=22
Reflections collected / unique	31316/2335 [R(int) = 0.0468]	26739 / 4174 [R(int) = 0.0774]	35605 / 2971 [R(int) = 0.0429]
Completeness to theta = 25.24	99.5 %	99.9 %	99.9 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2335 / 0 / 193	4174 / 0 / 314	2971 / 1 / 218
Goodness-of-fit on F^2	1.045	1.063	1.103
Final R indices [I>2sigma(I)]	R1 = 0.0358, wR2 = 0.0934	R1 = 0.0605, wR2 = 0.1383	R1 = 0.0383, wR2 = 0.1027
R indices (all data)	R1 = 0.0458, wR2 = 0.1002	R1 = 0.0866, wR2 = 0.1524	R1 = 0.0482, wR2 = 0.1127
Largest diff. peak and hole	0.324 and -0.433 e.$Å^{-3}$	0.654 and -0.706 e.$Å^{-3}$	0.921 and -0.316 e.$Å^{-3}$

Table S2. Selected bond lengths (Å) and angles (º) for $[Cu(phen)_2(MeCN)](ClO_4)_2$, $[(Cu(phen)_2)Cl]ClO_4$ and $[\{Cu(phen)(OAc)_2\}_2\text{-}\mu\text{-}OH_2]$

$[Cu(phen)_2(MeCN)](ClO_4)_2$ $\tau_5 = 0.92$			
Cu1-N1	1.985(2)	N1-Cu1-N2	81.62(8)
Cu1-N3	2.067(3)	N1-Cu1-N3	91.74(6)
Cu1-N2	2.084(2)	N1-Cu1-N2^i	96.56(9)
		N2-Cu1-N3	121.28(6)
		N1-Cu1-N1^i	176.52(12)
		N2-Cu1-N2^i	117.44(12)
$[Cu(phen)_2Cl]ClO_4$ $\tau_5 = 0.8$			
Cu1-N1	1.996(4)	N1-Cu1-Cl1	92.74(13)
Cu1-N2	2.072(4)	N2-Cu1-Cl1	127.56(12)
Cu1-Cl1	2.2939(15)	N1'-Cu1-Cl1	118.79(11)
Cu1-N2'	2.002(4)	N2'-Cu1-Cl1	91.17(12)
Cu1-N1'	2.119(4)	N1-Cu1-N2'	175.41(17)
		N1-Cu1-N2	81.51(15)
		N2-Cu1-N1'	113.64(16)
		N1-Cu1-N1'	95.52(16)
		N2'-Cu1-N1'	80.46(15)
		N2'-Cu1-N2	97.99(15)
$[\{Cu(phen)(OAc)_2\}_2\text{-}\mu\text{-}OH_2]$ $\tau_5 = 0.21$			
O1-Cu1	1.944(2)	O1-Cu1-N1	91.35(10)
O2-Cu1	1.958(2)	O2-Cu1-N1	159.37(12)
Cu1-N2	2.024(2)	O2-Cu1-N2	93.73(10)
Cu1-N1	2.023(3)	O1-Cu1-O2	94.04(11)
Cu1-O5	2.2930(12)	O1-Cu1-N2	172.23(10)
		N1-Cu1-N2	81.30(10)
		O2-Cu1-O5	91.75(11)

	N2-Cu1-O5	85.59(8)
	O1-Cu1-O5	94.32(7)
	N1-Cu1-O5	107.69(10)

Standard deviations in parentheses.

Table S3. Initial rates of p-QI formation for the oxidation of phenol by H_2O_2 catalyzed by $[Cu(py_2pn)]^{2+}$, at **pH 9 and 25ºC**

$[PhOH]_0$ (mM)	**$[H_2O_2]_0$ (mM)**	**[catalyst] (μM)**	**r_0^{QI}(μM/min)**
0.058	3.3	2.6	0.0928
0.058	3.3	2.6	0.0922
0.085	3.3	2.6	0.116
0.085	3.3	2.6	0.110
0.115	3.3	2.6	0.161
0.115	3.3	2.6	0.159
0.231	3.3	2.6	0.229
0.231	3.3	2.6	0.230
0.462	3.3	2.6	0.258
0.462	3.3	2.6	0.275
0.923	3.3	2.6	0.296
0.923	3.3	2.6	0.277
1.62	3.3	2.6	0.300
1.62	3.3	2.6	0.302
2.31	3.3	2.6	0.302
2.31	3.3	2.6	0.296
3.00	3.3	2.6	0.294
3.00	3.3	2.6	0.305
0.265	3.3	0.0	0.0074
0.265	3.3	1.3	0.138
0.265	3.3	2.5	0.240
0.265	3.3	2.5	0.238
0.265	3.3	3.8	0.297
0.265	3.3	3.8	0.301
0.265	3.3	5.0	0.320
0.265	3.3	5.0	0.332
0.265	3.3	10.1	0.366
0.265	3.3	10.1	0.374
0.265	3.3	17.6	0.440
0.265	3.3	17.6	0.437
0.265	3.3	25.2	0.511
0.265	3.3	25.2	0.510
0.265	3.3	32.7	0.624
0.265	3.3	40.3	0.727
0.265	3.3	47.9	0.842
0.265	3.3	45.3	0.799
0.267	0.86	2.6	0.0734
0.267	0.86	2.6	0.0695

0.267	1.7	2.6	0.129
0.267	1.7	2.6	0.141
0.267	2.6	2.6	0.178
0.267	2.6	2.6	0.168
0.267	3.4	2.6	0.200
0.267	3.4	2.6	0.194
0.267	5.2	2.6	0.228
0.267	5.2	2.6	0.237
0.267	8.6	2.6	0.178
0.267	8.6	2.6	0.171
0.267	12.0	2.6	0.161
0.267	12.0	2.6	0.168
0.267	17.2	2.6	0.119
0.267	17.2	2.6	0.127

Table S4. Initial rates of p-QI formation for the oxidation of phenol by H_2O_2 catalyzed by $[Cu(py_2pn)]^{2+}$, at **pH 9 and 50ºC**

$[PhOH]_0$ (mM)	**$[H_2O_2]_0$ (mM)**	**[catalyst] (μM)**	**r_0^{QI}(μM/min)**
0.059	3.3	2.6	2.45
0.059	3.3	2.6	2.48
0.088	3.3	2.6	2.98
0.088	3.3	2.6	2.92
0.119	3.3	2.6	4.60
0.119	3.3	2.6	4.66
0.238	3.3	2.6	6.28
0.238	3.3	2.6	6.31
0.357	3.3	2.6	6.59
0.357	3.3	2.6	6.53
0.476	3.3	2.6	7.94
0.476	3.3	2.6	7.86
0.952	3.3	2.6	8.14
0.952	3.3	2.6	7.78
1.67	3.3	2.6	8.24
1.67	3.3	2.6	8.14
2.38	3.3	2.6	8.20
2.38	3.3	2.6	8.21
0.265	3.3	1.1	2.59
0.265	3.3	1.1	2.44
0.265	3.3	2.3	5.31
0.265	3.3	2.3	5.20
0.265	3.3	3.4	8.45
0.265	3.3	3.4	8.01
0.265	3.3	4.5	12.4
0.265	3.3	4.5	12.9
0.265	3.3	9.0	21.4
0.265	3.3	9.0	22.0
0.265	3.3	15.8	32.8
0.265	3.3	15.8	31.2
0.265	3.3	22.6	38.0
0.265	3.3	22.6	37.5

0.265	3.3	29.4	42.7
0.265	3.3	29.4	43.8
0.265	3.3	36.1	43.7
0.265	3.3	36.1	45.7
0.265	3.3	42.9	46.8
0.265	3.3	42.9	46.0
0.265	0.17	2.7	0.766
0.265	0.17	2.7	0.762
0.265	0.52	2.7	2.85
0.265	0.52	2.7	2.96
0.265	0.86	2.7	4.51
0.265	0.86	2.7	4.57
0.265	1.0	2.7	6.01
0.265	1.0	2.7	5.96
0.265	1.4	2.7	6.68
0.265	1.4	2.7	6.62
0.265	1.7	2.7	7.22
0.265	1.7	2.7	7.39
0.265	2.6	2.7	7.70
0.265	2.6	2.7	7.27
0.265	3.4	2.7	6.79
0.265	3.4	2.7	6.70
0.265	5.2	2.7	5.80
0.265	5.2	2.7	6.27

Table S5. Initial rates of p-QI formation for the oxidation of phenol by H_2O_2 catalyzed by $[Cu(py_2pn)]^{2+}$, at **pH 7 and 25ºC**

$[PhOH]_0$ (mM)	**$[H_2O_2]_0$ (mM)**	**[catalyst] (μM)**	**r_0^{QI}(μM/min)**
0.076	0.27	2.6	0.055
0.076	0.27	2.6	0.056
0.150	0.27	2.6	0.090
0.150	0.27	2.6	0.093
0.300	0.27	2.6	0.121
0.300	0.27	2.6	0.126
0.460	0.27	2.6	0.135
0.460	0.27	2.6	0.135
0.610	0.27	2.6	0.151
0.610	0.27	2.6	0.150
1.20	0.27	2.6	0.180
1.20	0.27	2.6	0.164
2.10	0.27	2.6	0.191
2.10	0.27	2.6	0.192
3.00	0.27	2.6	0.192
3.00	0.27	2.6	0.201
3.90	0.27	2.6	0.197
3.90	0.27	2.6	0.191
0.270	3.3	0.97	0.105
0.270	3.3	0.97	0.109
0.270	3.3	1.6	0.159
0.270	3.3	1.6	0.162

0.270	3.3	2.4	0.157
0.270	3.3	2.4	0.163
0.270	3.3	4.8	0.168
0.270	3.3	4.8	0.171
0.270	3.3	6.6	0.216
0.270	3.3	6.6	0.208
0.270	3.3	13.3	0.225
0.270	3.3	13.3	0.228
0.270	3.3	26.6	0.231
0.270	3.3	26.6	0.234
0.270	3.3	53.2	0.228
0.270	3.3	53.2	0.218
0.260	0.86	2.7	0.091
0.260	0.86	2.7	0.092
0.260	1.3	2.7	0.119
0.260	1.3	2.7	0.120
0.260	1.7	2.7	0.157
0.260	1.7	2.7	0.167
0.260	2.6	2.7	0.179
0.260	2.6	2.7	0.184
0.260	3.4	2.7	0.220
0.260	3.4	2.7	0.235
0.260	5.2	2.7	0.274
0.260	5.2	2.7	0.263
0.260	6.9	2.7	0.285
0.260	6.9	2.7	0.280
0.260	10.3	2.7	0.297
0.260	10.3	2.7	0.287
0.260	13.7	2.7	0.296
0.260	13.7	2.7	0.309

Table S6. Initial rates of p-QI formation for the oxidation of phenol by H_2O_2 catalyzed by $[Cu(py_2pn)]^{2+}$, at **pH 7 and 50ºC**

$[PhOH]_0$ (mM)	**$[H_2O_2]_0$ (mM)**	**[catalyst] (μM)**	**r_0^{QI} (μM/min)**
0.076	0.27	2.7	0.444
0.076	0.27	2.7	0.406
0.152	0.27	2.7	0.632
0.152	0.27	2.7	0.651
0.304	0.27	2.7	0.973
0.304	0.27	2.7	0.925
0.455	0.27	2.7	1.16
0.455	0.27	2.7	1.18
0.607	0.27	2.7	1.28
0.607	0.27	2.7	1.30
1.21	0.27	2.7	1.48
1.21	0.27	2.7	1.52
2.13	0.27	2.7	1.67
2.13	0.27	2.7	1.73
3.04	0.27	2.7	1.69
3.04	0.27	2.7	1.74

3.95	0.27	2.7	1.76
3.95	0.27	2.7	1.82
0.266	3.3	0.16	0.734
0.266	3.3	0.16	0.662
0.266	3.3	0.32	1.03
0.266	3.3	0.32	1.04
0.266	3.3	0.48	1.28
0.266	3.3	0.48	1.32
0.266	3.3	0.65	1.45
0.266	3.3	0.65	1.29
0.266	3.3	0.97	1.77
0.266	3.3	0.97	1.72
0.266	3.3	1.6	2.09
0.266	3.3	1.6	2.19
0.266	3.3	2.4	2.23
0.266	3.3	2.4	2.22
0.266	3.3	3.2	2.64
0.266	3.3	3.2	2.73
0.266	3.3	4.8	2.78
0.266	3.3	4.8	2.72
0.266	3.3	6.5	2.72
0.266	3.3	6.5	2.72
0.267	0.86	2.7	0.943
0.267	0.86	2.7	0.911
0.267	1.3	2.7	1.23
0.267	1.3	2.7	1.23
0.267	1.7	2.7	1.42
0.267	1.7	2.7	1.48
0.267	2.6	2.7	1.80
0.267	2.6	2.7	1.71
0.267	3.4	2.7	2.23
0.267	3.4	2.7	2.19
0.267	5.2	2.7	2.76
0.267	5.2	2.7	2.86
0.267	6.9	2.7	3.17
0.267	6.9	2.7	3.26