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**Figure S1.** SOD activity of [Cu(py<sub>2</sub>pn)]<sup>2+</sup> in the riboflavin-methionine-NBT assay.

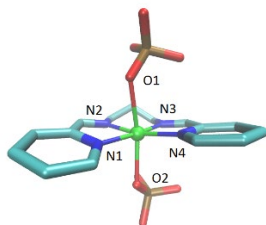
**Figure S2.** ESI-MS spectrum of a 10:1 KO<sub>2</sub>: [Cu(py<sub>2</sub>pn)]<sup>2+</sup> reaction mixture in DMSO.

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**Synthesis of N,N'-bis(2-pyridinylmethyl)propane-1,3-diamine (py<sub>2</sub>pn).** The ligand was prepared as already described.<sup>1</sup> Yield: 94%. <sup>1</sup>H NMR (Cl<sub>3</sub>CD) δ: 8.65 (dd, 2H, *J* = 4.8, 1.4 Hz); 8.42 (s, 2H), 8.00 (d, 2H, *J* = 7.8 Hz), 7.75 (td, 2H, *J* = 7.8, 1.4 Hz), 7.31 (ddd, 2H, *J* = 7.8, 4.8, 1.2 Hz), 3.81 (td, 4H, *J* = 6.9, 1.2 Hz), 2.17 (q, 2H, *J* = 6.9 Hz). <sup>13</sup>C NMR (Cl<sub>3</sub>CD) δ: 161,23, 154,52, 149,37, 136,50, 124,64, 121,21, 58,94, 31,63. Significant IR bands (KBr)  $\nu$  cm<sup>-1</sup>: 3059, 3013, 2926, 2855, 1648, 1587, 1567, 1469, 1437.

**Synthesis of [Cu(py<sub>2</sub>pn)(ClO<sub>4</sub>)<sub>2</sub>]** Py<sub>2</sub>pn (200 mg, 0.792 mmol) dissolved in 2 mL of methanol was added to a solution of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (158 mg, 0,791 mmol) in methanol (15 mL) and the reaction mixture was stirred overnight at room temperature. Then, addition of NaClO<sub>4</sub>·H<sub>2</sub>O (222 mg, 1.6 mmol) caused the formation of a blue-green precipitate, which was collected by filtration, washed with methanol, Cl<sub>2</sub>CH<sub>2</sub> and hexane, and dried under vacuum. Yield: 246 mg (0.478 mmol), 60%. Anal. calcd. for C<sub>15</sub>Cl<sub>2</sub>CuH<sub>16</sub>N<sub>4</sub>O<sub>8</sub>: C 35.00, Cu 12.3, H 3.13 and N 10.88%; Found: C 34.96, Cu 12.0, H 2.75 and N 10.72%. UV-Vis  $\lambda_{\text{max}}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) in DMF: 282 (14840), 626 (102). Significant IR bands (KBr,  $\nu$  cm<sup>-1</sup>): 3048, 2929, 1645, 1603, 1566, 1482, 1433, 1091 ( $\nu_{\text{ClO}_4^-}$ ) and 625 ( $\rho_{\text{ClO}_4^-}$ ). Crystals suitable for X-ray diffraction analysis were obtained by diffusion of ether into a acetonitrile solution of the complex. The stability of the complex was checked by spectrophotometry, in DMF, DMSO and aqueous solutions. In every medium, electronic spectra registered at different times after preparation of solutions showed identical  $\lambda_{\text{max}}$  and molar absorption coefficients.

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



**Table S1.** Selected bond lengths (Å) and bond angles (°) for the DFT optimized structures of Cu(II) and Cu(I) species

Bond length (Å)	Cu(py <sub>2</sub> pn)(ClO <sub>4</sub> ) <sub>2</sub> crystal <sup>2</sup>	[Cu(py <sub>2</sub> pn)(ClO <sub>4</sub> ) <sub>2</sub> ] Calcd.	[Cu(py <sub>2</sub> pn)ClO <sub>4</sub> ] <sup>+</sup> Calcd.	[Cu(py <sub>2</sub> pn)DMF] <sup>2+</sup> Calcd.	[Cu(py <sub>2</sub> pn)O <sub>2</sub> H] <sup>+</sup> Calcd.	[Cu(py <sub>2</sub> pn)] <sup>+</sup> Calcd.	[Cu(py <sub>2</sub> pn)(O <sub>2</sub> H)PhOH] <sup>+</sup> Calcd.
Cu-N(1)	2.024(4)	2.09	2.10	2.16	2.48	2.08	-
Cu-N(2)	1.995(5)	2.05	2.02	2.02	2.08	2.16	2.16
Cu-N(3)	1.995(5)	2.03	2.03	2.05	2.11	2.10	2.11
Cu-N(4)	2.024(4)	2.09	2.05	2.04	2.09	2.11	2.14
Cu-O(1)	2.475(4)	2.56	2.27	2.13	1.92	-	1.96 (Cu-O <sub>hydroperoxide</sub> )
Cu-O(2)	2.475(4)	2.40					1.97 (Cu-O <sub>phenol</sub> )

Dihedral angle (°)	Cu(py <sub>2</sub> pn)(ClO <sub>4</sub> ) <sub>2</sub> crystal	[Cu(py <sub>2</sub> pn)(ClO <sub>4</sub> ) <sub>2</sub> ] Calcd.	[Cu(py <sub>2</sub> pn)ClO <sub>4</sub> ] <sup>+</sup> Calcd.	[Cu(py <sub>2</sub> pn)DMF] <sup>2+</sup> Calcd.	[Cu(py <sub>2</sub> pn)O <sub>2</sub> H] <sup>+</sup> Calcd.	[Cu(py <sub>2</sub> pn)] <sup>+</sup> Calcd.	[Cu(py <sub>2</sub> pn)(O <sub>2</sub> H)PhOH] <sup>+</sup> Calcd.
N(1)-Cu-N(2)	82.6(2)	80.4	81.00	80.15	73.91	80.20	N(2)-Cu-N(3) 85.35
N(1)-Cu-N(3)	171.7(2)	172.94	150.55	136.19	124.47	146.23	N(2)-Cu-N(4) 137.21
N(1)-Cu-N(4)	105.5(2)	106.21	105.44	103.76	99.76	121.42	N(2)-Cu-O <sub>2</sub> H 97.20
N(2)-Cu-N(3)	90.8(3)	92.54	92.1	89.90	89.3	90.13	N(2)-Cu-O(Ph) 112.94
N(2)-Cu-N(4)	171.7(2)	167.31	172.95	169.42	160.48	152.61	N(3)-Cu-N(4) 78.20
N(3)-Cu-N(4)	82.6(2)	80.65	80.88	80.48	79.04	79.87	N(3)-Cu-O <sub>2</sub> H 175.25
O(1)-Cu-O(2)	168.2(3)	163.27	-	-	-	-	N(3)-Cu-OPh 97.16
N(1)-Cu-O(1)	88.0(2)	80.37	88.11	100.47	82.49		N(4)-Cu-O <sub>2</sub> H 173.25
N(2)-Cu-O(1)	91.2(2)	85.87	92.91	99.43	100.99		N(4)-Cu-OPh 97.16
N(3)-Cu-O(1)	97.1(2)	98.91	120.97	123.29	153.01		HO <sub>2</sub> -Cu-OPh 87.63
N(4)-Cu-O(1)	84.8(3)	84.64	90.21	89.60	96.34		

**Table S2.** Initial rates of H<sub>2</sub>O<sub>2</sub> disproportionation in DMF for different initial H<sub>2</sub>O<sub>2</sub> and complex concentrations

[H <sub>2</sub> O <sub>2</sub> ] (mM)	<i>r<sub>i</sub></i> (mM/min) <sup>a</sup>	[Complex] (mM)	<i>r<sub>i</sub></i> (mM/min) <sup>b</sup>
67	0.36 ± 0.04	0.25	0.12 ± 0.01
100	0.53 ± 0.05	0.75	0.35 ± 0.04
133	0.66 ± 0.07	1.00	0.53 ± 0.05
167	0.84 ± 0.08	1.50	1.1 ± 0.1
200	1.05 ± 0.09	1.75	1.6 ± 0.2
300	1.5 ± 0.1	2.00	1.9 ± 0.3
		3.00	4.4 ± 0.6

<sup>a</sup>[complex] = 1 mM; <sup>b</sup>[H<sub>2</sub>O<sub>2</sub>] = 100 mM. [Et<sub>3</sub>N] = 100 mM; T = 25 °C.

**Table S3.** First-order rate constants for [Cu(py<sub>2</sub>pn)OOH]<sup>+</sup> formation at -40°C

[H <sub>2</sub> O <sub>2</sub> ] (M)	<i>k<sub>exp</sub></i> (min <sup>-1</sup> )
0.010	1.2 ± 0.1 × 10 <sup>-1</sup>
0.020	1.7 ± 0.2 × 10 <sup>-1</sup>
0.025	1.9 ± 0.2 × 10 <sup>-1</sup>
0.040	2.2 ± 0.3 × 10 <sup>-1</sup>

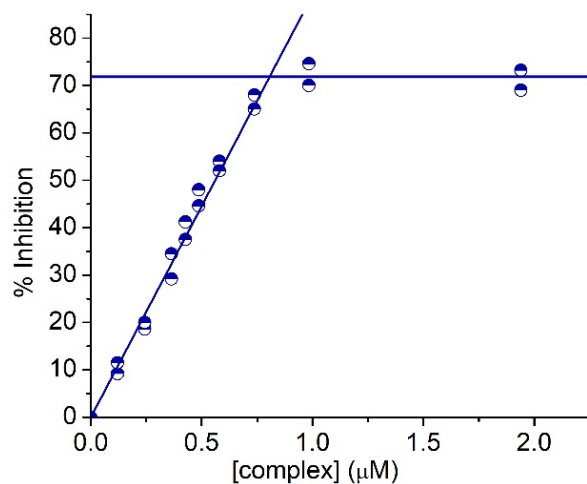
[complex] = 0.95 mM

**Table S4.** Initial rates of *p*-quinonimide formation, at pH 7, for different [complex]<sub>0</sub>, at 50 °C and 25 °C

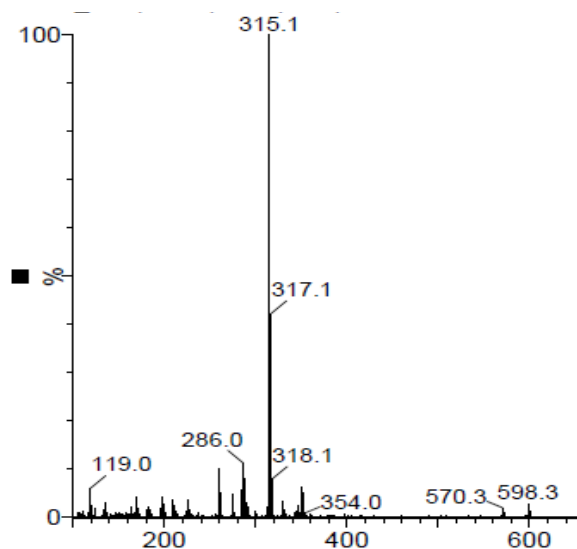
[complex] (μM)	<i>r<sub>i</sub></i> (μM/min) 50 °C	[complex] (μM)	<i>r<sub>i</sub></i> (μM/min) 25 °C
0.10	0.24 ± 0.02	1.13	0.13 ± 0.02
0.18	0.33 ± 0.02	2.66	0.18 ± 0.03
0.23	0.42 ± 0.04	6.64	0.21 ± 0.03
0.30	0.55 ± 0.04	13.3	0.23 ± 0.04
0.36	0.68 ± 0.05	26.6	0.23 ± 0.04
0.53	1.05 ± 0.07	53.1	0.23 ± 0.04
0.67	1.20 ± 0.09		
0.81	1.24 ± 0.09		
1.10	1.30 ± 0.08		
3.46	1.47 ± 0.09		
6.92	1.49 ± 0.09		
13.6	1.56 ± 0.08		
27.3	1.65 ± 0.09		

[phenol] = [H<sub>2</sub>O<sub>2</sub>] = 0.27 mM, [4-APP] = 0.68 mM.

**Figure S1.** SOD activity of  $[\text{Cu}(\text{py}_2\text{pn})]^{2+}$  in the riboflavin-methionine-NBT assay



**Figure S2.** ESI-MS spectrum of a 10:1  $\text{KO}_2:[\text{Cu}(\text{py}_2\text{pn})]^{2+}$  reaction mixture in DMSO



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