Supporting Information

for

O_2 Chemistry of Dicopper Complexes with Alkyltriamine Ligands. Comparing Synergistic Effects on O_2 Binding

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1) Experimental Section

Materials and synthesis

Reagents and solvents used were of commercially available reagent quality unless otherwise stated. Solvents were purchased from SDS. Pentane and CH_2Cl_2 were distilled over CaH_2 under nitrogen. THF was distilled over Na/benzophenone under nitrogen.

Syntheses of ligands L1 and L2

Ligand L1

Ligand **L1** was synthesized as previously described.[1]

Ligand L2

Ligand **L2** was synthesized in a three step synthetic method analogous to **L1** summarized in figure 1.

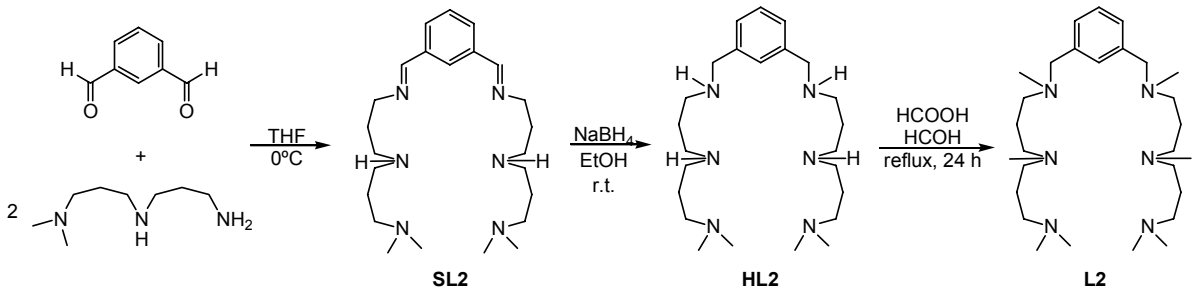

Figure S1. Synthetic method used for **L2** synthesis

SL2.

A solution of N,N-Dimethyldipropylenetriamine (3.6 mL, 20 mmol) in THF (40 mL) is cooled in an ice bath at 0ºC and a solution of isopthalaldehyde (1.34 g, 10 mmols) in THF (20 mL) is added dropwise under vigorous stirring. The mixture is left to attain room temperature and it is stirred for further 5 hours. Then, the solvent is removed under reduced pressure and the resultant product is dried under vacuum to obtain 3.87 g (93 %) of a yellow oil corresponding to **SL2**. FT-IR: 2940 – 2723 (C-H_{sp3}), 1648 (C=N), 1460 (C=C_{arom}) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz, 298 K) δ, ppm: 8.31, 8.27, 7.75 – 7.64, 7.49 – 7.28, 3.98 – 3.90, 3.76 – 3.66, 3.33 – 3.09, 2.75 – 2.66, 2.35 – 2.28, 2.21 – 2.12, 1.92 – 1.82, 1.66 – 1.52. ^{13}C-NMR ($CDCl_3$, 50 MHz, 300 K) δ, ppm: 160.88, 142.97, 142.85, 142.56, 136.53, 129.49, 128.80, 127.40, 127.31, 127.00, 126.43, 126.02, 81.82, 81.63, 81.54, 67.89, 59.74, 58.03, 57.79, 57.68, 52.19, 52.09, 51.86, 51.74, 51.50, 48.38, 48.00, 45.62, 45.49, 45.37, 45.34, 28.07, 27.29, 26.84, 25.554, 24.78, 24.53. The assignation of the NMR spectra of **SL2** is complicated due to the existence of an equilibrium between different isomers in solution as shown in Figure 2. ESI-MS (m/z): 417.0 (100) $[M+H]^+$.

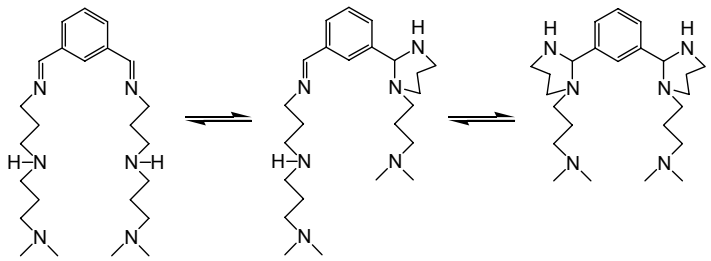

Figure S2. Solution equilibrium of the different isomers of **SL2**

HL2.

3.15 g of **SL2** (7.6 mmols) are dissolved in ethanol absolute (75 mL) and 1.14 g of $NaBH_4$ are slowly added to the stirred mixture directly as a solid. The mixture is stirred for 12 hours and then 10 mL of water are added to destroy the unreacted $NaBH_4$. The solvent is removed under reduced pressure and a mixture of a yellow oil and a white solid is obtained. This mixture is treated with 75 mL of CH_2Cl_2 and 20 mL of water and the aqueous phase is extracted with 2 x 40 mL of CH_2Cl_2. The organic layers are dried over $MgSO_4$ and the solvent is removed to dryness to give 3.13 g (98%) of a yellow oil. FT-IR: 3277 (N-H), 2935 – 2765 (C-H_{sp3}), 1460 (C=C_{arom}) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz, 300 K) δ, ppm: 7.28 – 7.21 (m, 4 H, Ar-**H**), 3.78 (s, 4H, ArC**H$_2$**), 2.73 – 2.62 (m, 12 H, N-C**H$_2$**), 2.31– 2.27 (m, 4 H, N-C**H$_2$**), 2.21 (s, 12 H, N-C**H$_3$**), 1.91 (br.s, 4 H, N-**H**), 1.75 – 1.63 (m, 8 H, C-C**H$_2$**-C). ^{13}C-NMR ($CDCl_3$, 50 MHz, 300 K) δ, ppm: 140.57 (**arC**-CH_2), 128.34, 127.75, 126.56 (**arC**-H), 58.00, 54.01, 48.47, 47.95 (N-**C**H_2-C), 45.49 (N-(**C**H_3)$_2$), 30.30, 28.09 (C-**C**H_2-C). ESI-MS (m/z): 421.0 (100) $[M+H]^+$.

L2.

2.5 g of **L2** (5.9 mmols), HCHO (37%, 25 mL) and HCOOH (85%, 20 mL) are refluxed for 24 h. Then, the solution is cooled and the solvent is removed to obtain a residue which is made basic by the addition of an aqueous solution of NaOH 3M until pH > 14 (~ 25 mL). The resultant suspension is extracted with CH_2Cl_2 (3 x 50 mL), the organic phases are dried over $MgSO_4$ and the solvent is removed under reduced pressure. The product is dried under vacuum to give 2.09 g (98%) of a yellow oil. The product is purified over an alumina column chromatography using dichloromethane:methanol 9:1 as eluent to give 1.31 g of the pure product (46%). FT-IR: 2944 – 2762 (C-H_{sp3}), 1459 (C=C_{arom}) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz, 300 K) δ, ppm: 7.14 – 7.11 (m, 4 H, Ar-**H**), 3.39 (s, 4H, ArC**H$_2$**), 2.31 – 2.23 (m, 16H, N-C**H$_2$**-C), 2.15 – 2.12 (24 H, C**H$_3$**), 1.60 – 1.54 (m, 8H, C-C**H$_2$**-C). ^{13}C-NMR ($CDCl_3$, 50 MHz, 300 K) δ, ppm: 138.98 (**arC**-CH_2), 129.68, 128.00, 127.59 (**arC**-H), 62.24 (Ar-**C**H_2), 57.92, 55.83, 55.78, 55.69 (N-**C**H_2-C), 45.46 (N-(**C**H_3)$_2$), 42.25, 42.16 (N-**C**H_3), 25.58, 25.26 (C-**C**H_2-C). ESI-MS (m/z): 477.2 (100) $[M+H]^+$.

Syntheses of complexes.

$[Cu^{I}_2(L1)](CF_3SO_3)_2$ ($1(CF_3SO_3)_2$). A solution of $Cu(CH_3CN)_4CF_3SO_3$ (160 mg, 0.42 mmols) in THF (1.5 mL) is added dropwise to a stirred solution of **L1** (117 mg, 0.21 mmols) in THF (1 mL). The reaction mixture is stirred for 1 hour to allow the complete precipitation of a fine solid which corresponds to **$1(CF_3SO_3)_2$**. The solvent is decanted and the precipitate is dried under vacuum to yield 170 mg (82 %) of a pale-yellow powder. Anal. Calcd for $C_{36}H_{58}Cu_2F_6N_6O_6S_2$ (MW = 976.10 g/mol): C, 44.30; H, 5.99; N, 8.61; S, 6.57 %. Found: C, 44.25; H, 6.06; N, 8.90; S, 6.98 %. FT-IR: 2863 ($C\text{-}H_{sp3}$), 1475 ($C{=}C_{arom}$), 1247, 1222, 1151, 1026, 634 (CF_3SO_3) cm^{-1}.

$[Cu^{I}_2(L1)](BArF)_2$ ($1(BArF)_2$). To a vigorous stirred mixture of **$1(CF_3SO_3)_2$** (154 mg, 0.16 mmols) in CH_2Cl_2 (1.5 mL) is added a solution of NaBArF (279 mg, 0.31 mmols) in CH_2Cl_2. The mixture is stirred for 2 hours and then filtered through celite to remove the precipitated $NaCF_3SO_3$. The colorless filtrate is layered with pentane and after 5 days white crystals suitable for X-Ray analysis appear. The liquid is decanted and the crystalline material is dried under vacuum to yield 167 mg (44 %). Anal. Calcd for $C_{98}H_{82}B_2Cu_2F_{48}N_6$ (MW = 2404.38 g/mol): C, 48.95; H, 3.44; N, 3.50 %. Found: C, 49.20; H, 3.62; N, 3.40 %. FT-IR: 2857 ($C\text{-}H_{sp3}$), 1473 ($C{=}C_{arom}$), 1609, 1353, 1272, 1113, 901, 670 (BArF) cm^{-1}.

$[Cu^{I}_2(L2)](CF_3SO_3)_2$ ($2(CF_3SO_3)_2$). A solution of $Cu(CH_3CN)_4CF_3SO_3$ (157 mg, 0.42 mmols) in THF (1.5 mL) is added dropwise to a stirred solution of **L2** (99.5 mg, 0.21 mmols) in THF (1 mL). The reaction mixture is stirred for 1 hour to allow the complete precipitation of a fine solid which corresponds to **$2(CF_3SO_3)_2$**. The solvent is decanted and the precipitate is dried under vacuum to yield 156 mg (83 %) of a pale-yellow powder. Anal. Calcd for $C_{30}H_{56}Cu_2F_6N_6O_6S_2{\cdot}2H_2O$ (MW = 938.05 g/mol): C, 38.41; H, 6.45; N, 8.96; S, 6.84 %. Found: C, 38.62; H, 6.65; N, 9.11; S, 6.81 %. FT-IR: 2976 - 2800 ($C\text{-}H_{sp3}$), 1471 ($C{=}C_{arom}$), 1254, 1224, 1143, 1027, 635 (CF_3SO_3) cm^{-1}.

[Cu^{I}_2(L2)](BArF)$_2$ (2(BArF)$_2$). To a vigorous stirred mixture of **2(CF$_3$SO$_3$)$_2$** (88 mg, 0.098 mmols) in CH_2Cl_2 (1.5 mL) is added a solution of NaBArF (173 mg, 0.20 mmols). The mixture is stirred for 2 hours and then filtered through celite to remove the precipitated $NaCF_3SO_3$. The colorless filtrate is layered with pentane and after 5 days pale-orange crystals appear. The liquid is decanted and the crystalline material is dried under vacuum to yield 197 mg (87 %). Anal. Calcd for $C_{92}H_{80}B_2Cu_2F_{48}N_6$ (MW = 2330.30 g/mol): C, 47.42; H, 3.46; N, 3.61 %. Found: C, 47.39; H, 3.69; N, 3.54 %. FT-IR: 2973 - 2869 (C-H_{sp3}), 1465 (C=C_{arom}), 1612, 1354, 1273, 1109, 884, 668 (BArF) cm^{-1}.

[Cu^{I}_2(L2)](SbF$_6$)$_2$ (2(SbF$_6$)$_2$). A solution of $Cu(CH_3CN)_4SbF_6$ (77.4 mg, 0.17 mmols) in THF (1 mL) is added dropwise to a stirred solution of **L2** (39.8 mg, 0.08 mmols) in THF (1 mL). The reaction mixture is stirred for 1 hour to allow the complete precipitation of a fine white solid which corresponds to **2(SbF$_6$)$_2$**. The solvent is decanted, the precipitate is dried under vacuum and the compound is redissolved in CH_2Cl_2. Slow diethyl ether diffusion over this solution affords 64.5 mg of white crystals suitable for X-Ray analysis (72 %). Anal. Calcd for $C_{28}H_{56}Cu_2F_{12}N_6Sb_2 \cdot H_2O$ (MW = 1111.41 g/mol): C, 30.26; H, 5.44; N, 7.56 %. Found: C, 30.21; H, 5.29; N, 7.12 %. FT-IR: 2975 - 2850 (C-H_{sp3}), 1464 (C=C_{arom}), 652 (SbF_6) cm^{-1}.

2) Crystal data for $1(BArF)_2$ and $2(SbF_6)_2$

Table S1. Crystal data for $\mathbf{1(BArF)_2}$ and $\mathbf{2(SbF_6)_2}$

Compound	$\mathbf{1(BArF)_2}$	$\mathbf{2(SbF_6)_2}$
Empirical formula	C98 H82 B2 Cu2 F48 N6	C28 H56 Cu2 F12 N6 Sb2
Formula weight	2404.40	1075.37
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	*P 21/n*	*P21/c*
Unit cell dimensions		
a	13.073(5)Å	16.264(4) Å
alpha	90°	90°
b	27.978(12) Å	15.169(4) Å
beta	96.633(7)°	103.776(4)°
c	13.464 Å	17.642(5) Å
gamma	90°	90°
Volume	4891(3) $Å^3$	4227(2) $Å^3$
Density (calculated)	1.633 Mg/m^3	1.690 Mg/m^3
Absorption coefficient	0.578 mm^{-1}	2.337 mm^{-1}
F(000)	2424	2136
Cell formula units_Z	2	4
Crystal size	0.5 x 0.5 x 0.2 mm	0.08 x 0.05 x 0.02 mm
Theta range for data collection	2.42 to 27.97°	2.04 to 28.34 °
Limiting indices	-17<=h<=17, -36<=k<=36, -17<=l<=17	-21<=h<=21, -20<=k<=20, -23<=l<=23
Reflections collected	69618	62969
Independent reflections	11668 [R(int) = 0.0488]	10415 [R(int)= 0.0351]
Completeness to theta	99.1% (theta = 27.97º)	98.7% (theta = 28.21º)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	11668 / 30 / 749	10415 / 0 / 587
Goodness-of-fit on F^2	1.163	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1057	R1 = 0.0305, wR2 = 0.0772
R indices (all data)	R1 = 0.0716, wR2 = 0.1345	R1 = 0.0370, wR2 = 0.0797
Largest diff. peak and hole	0.801 and -0.667 $e.Å^{-3}$	1.403 and -0.872 $e.Å^{-3}$

Table S2. Selected bond lengths (Å) and angles (º) for **1(BArF)$_2$** and **2(SbF$_6$)$_2$**.

1(BArF)$_2$	**2(SbF$_6$)$_2$**
Cu1-N1 2.007 (3)	Cu1-N1 1.990 (3)
Cu1-N2 2.192 (2)	Cu1-N2 2.120 (3)
Cu1-N3 1.999 (3)	Cu1-N3 1.986 (3)
N1-Cu1-N2 100.98 (10)	Cu2-N4 1.974 (2)
N2-Cu1-N3 102.50 (10)	Cu2-N5 2.100 (3)
N3-Cu1-N1 156.52 (10)	Cu2-N6 1.973 (3)
	N1-Cu1-N2 105.59 (11)
	N2-Cu1-N3 105.08 (10)
	N3-Cu1-N1 148.84 (11)
	N4-Cu2-N5 104.95 (12)
	N5-Cu2-N6 104.34 (15)
	N4-Cu2-N6 150.62 (13)

3) Stopped-flow kinetic measurements for the reaction of $2(BArF)_2$ with O_2

Kinetic measurements were performed using a Hi-Tech Scientific (Salisbury, Wiltshire, UK) SF-43 multi-mixing anaerobic cryogenic stopped-flow instrument combined with a Hi-Tech Scientific Kinetascan diode array rapid scanning unit. All manipulations of the copper(I) complexes and their solutions were done inside a Vacuum Atmospheres or MBraun glove-box filled with argon. Copper(I) solutions of known concentration were placed in Hamilton gas-tight syringes and loaded into the stopped-flow mixing unit. Saturated solutions of O_2 in acetone (8 mM) were prepared by bubbling dry O_2 gas through argon-saturated acetone in a syringe at 293 K for 15 min. Solutions of O_2 with smaller concentrations were prepared by diluting the 8 mM O_2 solution with argon-saturated acetone using graduated gas-tight syringes. The solutions of copper(I) complex in acetone and O_2 in acetone were separately cooled to a low temperature (193-243 K) and mixed in a 1:1 volume ratio. The mixing cell (1 cm) was maintained to $\pm$0.1 K, and the mixing time was ~5-10 ms. Concentrations of all reagents are reported at the onset of the reaction (after mixing) and corrected for the 1:1 dilution. No correction for the temperature contraction of solvent was applied in this work. Dioxygen was always taken in large excess to the copper(I) complex. In all kinetic experiments, a series of 5 - 7 shots gave standard deviations within 5%, with overall reproducibility within 10%. Data analysis was performed with the IS-2 Rapid Kinetics Software (Hi-Tech Scientific) for kinetic traces at a single wavelength or with the Specfit program (BioLogic Science Instruments, Grenoble, France) for global fitting of the spectral changes acquired in a diode array mode.

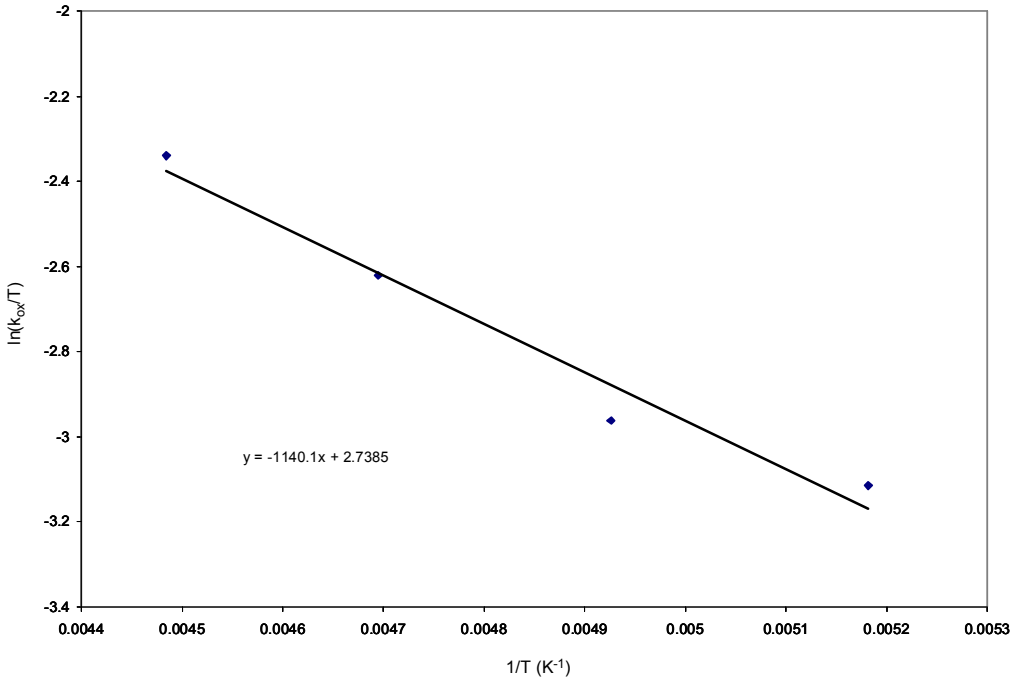

Figure S3. Eyring plot for the reaction of **2(BArF)$_2$** with O_2 in a temperature range from -80ºC to -50ºC. k_{ox} = k(obs)/[O_2], [O_2] = 0.004 M. $\Delta H^{\ddagger}$ = 9.5 ± 2 kJ·mol^{-1}, $\Delta S^{\ddagger}$ = -175 ± 10 J·K^{-1}·mol^{-1}.

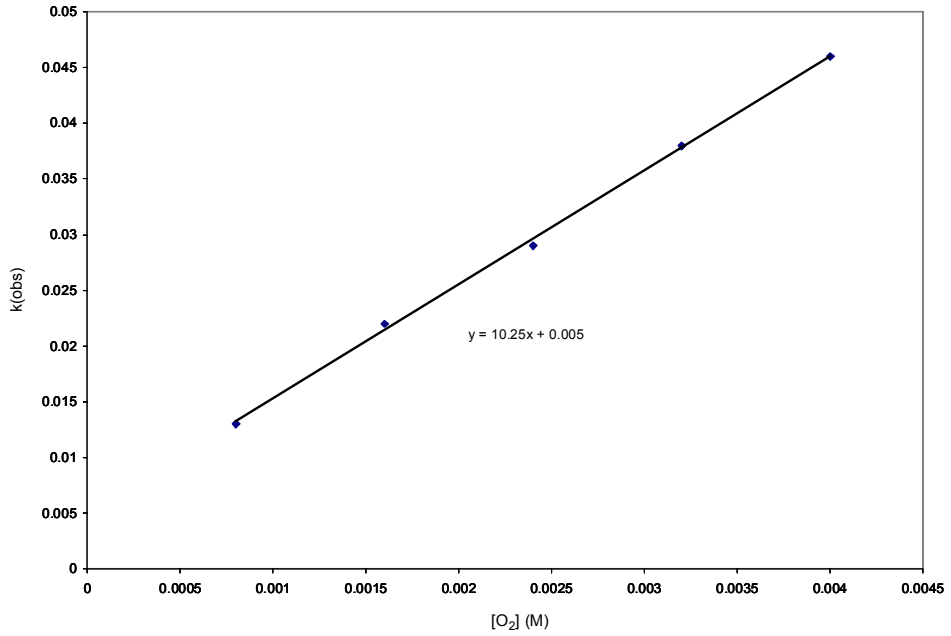

Figure S4. Variation of k(obs) with O_2 concentration (ranging from 0.00075 to 0.004 M) for the reaction of **2(BArF)$_2$** with O_2 at -80ºC. The plot shows a first order dependence in O_2 concentration.

4) Computational details

All geometry optimizations calculations have been performed at the B3LYP level,[2] using the standard 6-31G* basis set[3] with the Gaussian03 package.[4] The geometry optimizations were performed without any symmetry constraints, and the nature of the extrema was checked by analytical frequency calculations. The energies discussed throughout the text are electronic energies without any ZPE corrections.

Table S3. Main geometrical parameters of the DFT calculated structures (distances in Angstroms and angles in degrees)

	$[Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)(L1)]^{2+}$	$[Cu_2(\mu\text{-}O)_2(L1)]^{2+}$	$[Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)(L2)]^{2+}$	$[Cu_2(\mu\text{-}O)_2(L2)]^{2+}$
Cu1···Cu2	3.603	2.810	3.636	2.831
O1-O2	1.443	2.230	1.438	2.227
Cu1-N1	2.326	4.784	2.087	2.014
Cu1-N2	2.026	2.008	2.044	2.001
Cu1-N3	2.101	1.998	2.319	2.714
Cu2-N4	3.303	3.647	2.430	4.500
Cu2-N5	2.013	2.005	2.056	2.014
Cu2-N6	2.016	2.011	2.029	1.998
Cu1-O1	2.039	1.793	2.006	1.810
Cu1-O2	1.892	1.794	1.938	1.805
Cu2-O1	1.894	1.798	1.929	1.790
Cu2-O2	1.942	1.789	1.978	1.800

Table S4. XYZ coordinates and energies of the calculated $[Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)(L2)]^{2+}$ and $[Cu_2(\mu\text{-}O)_2(L2)]^{2+}$ isomers of **3**.

$[Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)(L2)]^{2+}$	**E=-4859.722917 a. u.**			$[Cu_2(\mu\text{-}O)_2(L2)]^{2+}$	**E= -4859.7364318 a. u.**		
Cu	-1.83866600	-0.49542700	-0.09246600	Cu	-0.45413000	-1.52805100	-0.23941200
Cu	1.79655500	-0.49456700	-0.16558000	Cu	2.11338500	-0.37218900	0.05386700
N	-2.48631400	-2.08942600	-1.27305400	N	-1.32433700	-2.26164400	-1.88124900
N	-2.90381800	1.49303200	-0.62969600	N	-4.31571800	0.63679400	0.58880200
N	3.05077200	1.54411300	0.25209600	N	1.44917400	2.23874000	-0.27616000
N	2.81459500	-1.34730600	-1.69951300	N	3.67364800	-0.47268100	-1.21466800
N	-2.89632800	-0.87946900	1.61447200	N	-1.77298500	-2.07823600	1.18042300
N	2.55041700	-1.50853900	1.45641700	N	3.08918800	0.08357900	1.74043300
O	-0.05744600	-0.45988200	-0.85474700	O	0.61873500	-0.78622900	0.98684900
O	0.03446800	-0.17869000	0.55246500	O	1.04503600	-1.16455900	-1.16613600
C	2.70334200	1.78092700	1.68332400	C	0.83400600	2.43165400	1.05820200
C	3.16792100	0.70218900	2.67330900	C	1.79799600	2.29898800	2.24477400
C	2.43136400	-0.64119800	2.67447100	C	2.20273000	0.88429900	2.66737400
H	3.14714200	2.73745300	2.00440700	H	0.35567600	3.42082000	1.11484600
H	1.61707300	1.89632700	1.74248300	H	0.04044800	1.68948500	1.16670400
H	2.99112400	1.11843000	3.67319500	H	1.27138200	2.70157300	3.11983000

H	4.25219800	0.56144100	2.62641000	H	2.66887500	2.95152600	2.12996900
H	1.36105300	-0.45312200	2.80482900	H	1.30736300	0.27975400	2.81958800
H	2.76635300	-1.22603400	3.54429500	H	2.73580900	0.93938800	3.62635600
C	4.17331500	-1.83444800	-1.29021400	C	4.88845800	0.32652500	-0.85406600
C	4.21904200	-2.72490900	-0.04353400	C	5.36671900	0.17496900	0.58407700
C	3.93904000	-2.03429400	1.29743200	C	4.40649000	0.78146000	1.60058300
H	4.79864000	-0.95320900	-1.13502200	H	4.64913900	1.37613300	-1.04863000
H	4.60283900	-2.38593000	-2.13856400	H	5.68844400	0.03892200	-1.54864700
H	3.59065700	-3.61227900	-0.17174300	H	5.62599800	-0.86118500	0.82378300
H	5.24275100	-3.11344500	0.01782800	H	6.30732200	0.73203100	0.66625900
H	4.63589300	-1.20601600	1.42755100	H	4.20363300	1.81490100	1.31751600
H	4.13940600	-2.74256900	2.11487500	H	4.87437400	0.79893600	2.59382100
C	-3.13431600	0.37434000	2.41006300	C	-1.87605400	-1.05336000	2.32596500
C	-3.16671800	2.24778700	0.62896800	C	-3.67929100	0.87949900	1.89554100
C	-3.91672300	1.49426100	1.72566300	C	-3.21557400	-0.36721600	2.67394100
H	-4.12105400	2.23117600	2.51233200	H	-3.04148300	-0.01450600	3.69919900
H	-4.90564200	1.16249500	1.39507700	H	-4.02202600	-1.09929200	2.77624000
H	-2.14731400	0.75433000	2.69466300	H	-1.10230100	-0.30662300	2.13857600
H	-3.65130700	0.08614700	3.33704600	H	-1.57008800	-1.59998400	3.22265200
H	-3.73453100	3.16003900	0.38603300	H	-4.37088100	1.43485400	2.55557200
H	-2.20183400	2.56998100	1.02616600	H	-2.81599600	1.53255800	1.73539400
C	-3.88484400	-2.53134500	-0.99264700	C	-2.77761100	-2.61533300	-1.78423300
C	-4.19362200	-2.79730400	0.48208400	C	-3.16335500	-3.37852300	-0.52514200
C	-4.21200900	-1.56184400	1.38440300	C	-3.13152300	-2.48923800	0.71237100
H	-4.08724600	-3.44164000	-1.57610900	H	-3.03433300	-3.19165800	-2.68199100
H	-5.20729800	-3.21424900	0.51783000	H	-4.20273900	-3.70267800	-0.65236300
H	-4.62143800	-1.83941500	2.36653700	H	-3.63088300	-2.99828700	1.54623200
H	-4.55572300	-1.75480800	-1.37191000	H	-3.34034400	-1.67771000	-1.82095700
H	-3.55204100	-3.58480700	0.89021600	H	-2.58639200	-4.30169600	-0.40561000
H	-4.89687000	-0.82921800	0.95526800	H	-3.66749500	-1.56595500	0.48962100
C	-0.13524000	5.22149500	-0.04416400	C	-2.29189600	4.77599700	-1.28007600
C	1.13159500	4.63864300	0.01712100	C	-1.05876300	4.15097000	-1.47507700
C	-1.20432700	4.50415400	-0.57635900	C	-3.38581300	4.04754900	-0.81294900
C	-1.02173100	3.19187400	-1.04064400	C	-3.27545200	2.67327500	-0.55926200
C	1.34109600	3.34451800	-0.47493600	C	-0.91215400	2.78666700	-1.19429200
C	2.73900500	2.78440800	-0.54622500	C	0.40627300	2.05366900	-1.34645500
C	-2.18198000	2.40689600	-1.60261700	C	-4.51691500	1.90360600	-0.14761400
H	-0.28373300	6.23704400	0.30975400	H	-2.40146400	5.83512900	-1.49323100
H	1.96642100	5.20739400	0.41838800	H	-0.21922900	4.72681700	-1.85488500
H	-2.18450600	4.96988200	-0.63902000	H	-4.33824700	4.54876100	-0.65918100
H	-2.92093600	3.11573900	-2.00329300	H	-5.16963700	2.58200000	0.43131400
H	-1.85189600	1.77699200	-2.43451500	H	-5.08123700	1.65074700	-1.05484600
C	0.25861600	2.63837200	-1.00605300	C	-2.03364400	2.06568200	-0.75760200
H	3.44184400	3.57170800	-0.23493700	H	0.88082700	2.32757900	-2.29455300
H	2.97933100	2.54539600	-1.58807100	H	0.19679800	0.98441000	-1.39932000
H	0.40707300	1.64343000	-1.40903400	H	-1.93703700	1.00076300	-0.55425500
C	2.02161400	-2.48348000	-2.23818100	C	4.00714400	-1.92611900	-1.29264900
C	-2.38033900	-1.71961900	-2.70806300	C	-1.18088300	-1.24630400	-2.97058400
H	2.55566300	-2.96411200	-3.06852900	H	4.78667400	-2.09171300	-2.04553000
H	1.83777600	-3.22944200	-1.46390800	H	4.36976400	-2.29059600	-0.33104000
H	-3.08374400	-0.91979700	-2.94092900	H	-1.72767600	-0.34022300	-2.70070000
H	-2.60532200	-2.58043200	-3.35219600	H	-1.59253700	-1.65173300	-3.90190500
H	1.06493400	-2.10876500	-2.60208800	H	3.10810700	-2.47626000	-1.56912000
H	-1.36721500	-1.37124000	-2.91888100	H	-0.12804800	-1.00776300	-3.10323700
C	2.97636700	-0.36302200	-2.80576600	C	3.23333000	-0.02625500	-2.56941900
H	3.58047100	0.47930700	-2.47002400	H	2.96665500	1.03010200	-2.53347800
H	3.46896800	-0.82835500	-3.66958100	H	4.05010100	-0.17174000	-3.28601600
H	1.99389000	0.00361900	-3.11143800	H	2.36588200	-0.60797800	-2.87470100
C	-1.55458700	-3.22166500	-1.03708300	C	-0.52666600	-3.47008300	-2.24855900
H	-1.61371600	-3.56314700	-0.00344400	H	-0.65737200	-4.25380200	-1.50017600
H	-1.79847000	-4.06688900	-1.69555300	H	-0.85965100	-3.85391400	-3.21957300
H	-0.53868600	-2.88652400	-1.23291900	H	0.52585100	-3.19455400	-2.30359700
C	-4.20144300	1.18966500	-1.28358500	C	2.32356000	3.38130200	-0.60222700

H	-4.02506000	0.80654600	-2.29094400	H	1.78802200	4.34249800	-0.58496400
H	-4.76399800	0.44417400	-0.72205400	H	3.14986700	3.45378100	0.10993000
H	-4.82300500	2.09279600	-1.37366900	H	2.75403500	3.24880400	-1.59935400
C	-2.05002400	-1.75312700	2.47132300	C	3.29397000	-1.24814500	2.38862400
H	-1.82149100	-2.68972000	1.96248900	H	3.94642200	-1.87603400	1.78159000
H	-1.11657300	-1.23640100	2.69439400	H	3.75349300	-1.11961300	3.37550400
H	-2.56466400	-1.98468800	3.41346900	H	2.32647800	-1.73661800	2.49719500
C	1.63577200	-2.66370400	1.65779800	C	-1.03284200	-3.26879300	1.70717000
H	0.61172400	-2.30159100	1.71597400	H	-0.07012600	-2.94188600	2.09917300
H	1.71198900	-3.36115900	0.82260300	H	-1.61028300	-3.75058900	2.50441300
H	1.88916100	-3.20342200	2.58080500	H	-0.86292000	-4.00058900	0.91425900
C	4.52492100	1.41616300	0.12751600	C	-5.64716400	0.02897900	0.76310100
H	4.89215200	0.49719600	0.57702800	H	-6.09182500	-0.16921600	-0.21685700
H	4.80894900	1.41944900	-0.92752100	H	-5.58349300	-0.92016000	1.30143800
H	5.03894800	2.26112900	0.61007000	H	-6.33350000	0.68536400	1.32468700

Table S5. XYZ coordinates and energies of calculated $[Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)(L1)]^{2+}$ and $[Cu_2(\mu\text{-}O)_2(L1)]^{2+}$.

$[Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)(L1)]^{2+}$	**E=-5089.5483291 a. u.**			$[Cu_2(\mu\text{-}O)_2(L1)]^{2+}$	**E=-5089.5736771 a. u.**		
Cu	1.93580400	0.13140800	-0.44666700	Cu	0.20425900	1.40349100	-0.20233000
Cu	-1.53188500	-0.83884500	-0.31027700	Cu	-0.43246500	-1.32597200	-0.00479400
N	2.85285600	-2.00102400	-0.30171400	N	4.37282000	-0.57710000	-1.46150500
N	2.42186700	1.55052200	1.02396500	N	0.36792000	2.74434400	1.26946000
N	-3.54470800	1.76856900	-0.55278900	N	-4.06942000	-1.14412000	-0.20583900
N	-2.64483800	-1.56608100	1.20572500	N	-0.26834900	-2.57561300	1.56268800
N	3.01003300	0.76824100	-2.04259900	N	0.85771400	2.47565500	-1.76909000
N	-2.46837400	-1.36798400	-2.01226500	N	-0.88339800	-2.63615300	-1.45400800
O	0.26266100	-0.38129600	0.27367300	O	0.00584700	0.08771100	1.00067900
O	0.05027800	-0.21327700	-1.14336900	O	-0.21532900	-0.01501600	-1.21581500
C	-2.94766600	2.01954700	-1.88502500	C	-3.83416200	-0.77326100	-1.61693400
C	-3.21676600	0.97209300	-2.98229100	C	-3.18250900	-1.82915400	-2.52893900
C	-2.36863600	-0.30465700	-3.07566100	C	-1.65536800	-1.98718900	-2.59179700
H	-3.32496300	2.98323100	-2.27347800	H	-4.79836800	-0.50551300	-2.08853700
H	-1.86686400	2.13803200	-1.74690000	H	-3.21819300	0.13219600	-1.62050800
H	-2.99754300	1.48160500	-3.92978900	H	-3.42329100	-1.51015400	-3.55177100
H	-4.28285700	0.73926200	-3.05119600	H	-3.68011600	-2.79855100	-2.43453300
H	-1.31155500	-0.02911900	-3.11994700	H	-1.18867200	-1.01335500	-2.74505100
H	-2.61791200	-0.78802900	-4.03187900	H	-1.43854000	-2.60474400	-3.47343500
C	-4.02839100	-1.88747400	0.70821000	C	-1.13832200	-3.79607600	1.44941900
C	-4.10259200	-2.69516900	-0.59097700	C	-0.98484400	-4.60647800	0.16731800
C	-3.86621500	-1.86673900	-1.85666200	C	-1.57111100	-3.89853900	-1.04597400
H	-4.54024700	-0.93325600	0.56179100	H	-2.17405400	-3.45252200	1.53641900
H	-4.55908800	-2.41814000	1.50946800	H	-0.92881100	-4.42989800	2.32013900
H	-3.45653600	-3.57991300	-0.55714200	H	0.04383700	-4.94075600	0.00269100
H	-5.12260700	-3.09094900	-0.66213200	H	-1.56586900	-5.52623500	0.30381000
H	-4.52961900	-1.00343800	-1.83338600	H	-2.60314700	-3.63970600	-0.81996100
H	-4.13036400	-2.45428200	-2.74725900	H	-1.57590100	-4.57051700	-1.91491100
C	3.15416300	2.26352600	-1.99801700	C	0.78237800	3.96478400	-1.60369200
C	2.81497500	2.87603300	0.46208500	C	0.45106500	4.19031500	0.88480000
C	3.77077900	2.84036200	-0.72477200	C	1.35579800	4.50059300	-0.29863700
H	4.02130300	3.88443800	-0.94808800	H	1.40281900	5.59199800	-0.38890600
H	4.72625700	2.36889400	-0.47546400	H	2.38833000	4.17483900	-0.13602400
H	2.15254500	2.68634500	-2.13084800	H	-0.27321600	4.24611400	-1.67664900
H	3.74946700	2.56672700	-2.87067700	H	1.29833900	4.41521800	-2.46091900
H	3.25358300	3.48206800	1.26855900	H	0.77186900	4.74773700	1.77396400
H	1.90003400	3.37956500	0.14675600	H	-0.55913300	4.51739400	0.63600000
C	4.26444600	-2.00991400	-0.79804400	C	4.10050500	0.33202700	-2.57785700
C	4.51257300	-1.33865300	-2.15020700	C	2.62115300	0.78878700	-2.66241400

C	4.38796600	0.18333100	-2.17157900	C	2.32265700	2.06956900	-1.87709800
H	4.61670500	-3.05183800	-0.85513500	H	4.31225800	-0.21897300	-3.49824000
H	5.55902800	-1.55021700	-2.40299500	H	2.37945700	0.96152600	-3.71675600
H	4.81806400	0.56506300	-3.10870800	H	2.85910700	2.90450900	-2.34591700
H	4.87918300	-1.50991200	-0.04123900	H	4.77764100	1.20478900	-2.59092800
H	3.93559000	-1.80418200	-2.95474600	H	1.99232900	-0.02816600	-2.30339900
H	4.99365600	0.58720400	-1.35763200	H	2.69752000	1.98792300	-0.85417200
C	-0.63011000	5.01008500	1.93058300	C	-4.13813700	3.71198800	0.59020800
C	-1.78354600	4.63954500	1.24511500	C	-4.72453300	2.48186900	0.28463400
C	0.35728800	4.06067000	2.18608200	C	-2.88688700	3.76004300	1.20441100
C	0.22328900	2.74254500	1.72449400	C	-2.18943900	2.57195500	1.48349600
C	-1.97022900	3.31612300	0.82005400	C	-4.07667900	1.28376100	0.60913600
C	-3.35452100	2.95947300	0.30804100	C	-4.79973000	-0.03996500	0.46596600
C	1.31987700	1.74923100	2.06018300	C	-0.84650700	2.56778800	2.18093000
H	-0.50833900	6.03069500	2.28038700	H	-4.67110800	4.63337600	0.37596000
H	-2.56403200	5.37575200	1.06917700	H	-5.71092800	2.45590200	-0.17114900
H	1.23973900	4.34673900	2.75269200	H	-2.48046700	4.72284800	1.50294200
H	1.81425100	2.10157800	2.97515900	H	-0.78614100	3.36919400	2.92774300
H	0.91294200	0.75891000	2.26889000	H	-0.70045800	1.61680200	2.69014900
C	-0.95050000	2.38476500	1.03885200	C	-2.81078200	1.34806500	1.19716700
H	-3.77597500	3.84739900	-0.19644800	H	-5.76127700	0.13864000	-0.04772800
H	-3.98224200	2.80201100	1.19476400	H	-5.05331000	-0.39632000	1.47200000
H	-1.08135900	1.36909300	0.69252400	H	-2.30517500	0.42832100	1.46106800
C	3.57901700	0.96467200	1.75185800	C	1.58566700	2.36941000	2.04994500
H	3.26147100	0.04898100	2.25275700	H	1.56311000	1.30284300	2.26982100
H	4.38982900	0.72720200	1.06009600	H	2.48289300	2.59710600	1.47165200
H	3.96253500	1.66323500	2.50857500	H	1.61772000	2.94226900	2.98384100
C	2.02614100	-2.78707300	-1.24804900	C	5.32628500	-1.64073900	-1.79436800
H	0.98067700	-2.72520800	-0.96658400	H	5.39791100	-2.33698100	-0.95284200
H	2.11281100	-2.38573200	-2.25662600	H	4.97447400	-2.20213300	-2.66534400
H	2.33868100	-3.84198100	-1.27118900	H	6.34012700	-1.26284900	-2.01002100
C	-2.78074500	-0.47130100	2.21119600	C	-0.70416000	-1.85936700	2.79825800
H	-3.19714600	0.40784000	1.71973300	H	-1.74549000	-1.55158100	2.68875700
H	-3.44615600	-0.78321400	3.02692000	H	-0.61760800	-2.53430100	3.65796600
H	-1.80378300	-0.22219800	2.62349300	H	-0.07964600	-0.98401800	2.95295100
C	-5.00766200	1.59288800	-0.65162600	C	-4.94253700	-2.32661700	-0.09387300
H	-5.50281800	2.46456400	-1.11251700	H	-5.91453500	-2.18069100	-0.59627900
H	-5.27058200	0.71284600	-1.23795700	H	-4.47887700	-3.21520400	-0.52553300
H	-5.42773100	1.46122700	0.34972900	H	-5.13647400	-2.53461300	0.96242600
C	-1.61107200	-2.49997800	-2.47281300	C	0.47259000	-2.95117600	-2.00094800
H	-1.97155600	-2.88831100	-3.43397800	H	0.39030100	-3.66372000	-2.82966700
H	-0.58621200	-2.14938900	-2.58672800	H	0.93171600	-2.03000000	-2.35860000
H	-1.63027000	-3.31578800	-1.74647100	H	1.10751900	-3.38791600	-1.23031200
C	2.23029300	0.46113800	-3.27621100	C	0.09168800	2.14635000	-3.00612000
H	1.24682800	0.92723200	-3.20187300	H	-0.93446700	2.49983300	-2.88675300
H	2.74836400	0.84996100	-4.16285800	H	0.54427100	2.64612100	-3.87036200
H	2.09812300	-0.61389400	-3.39171300	H	0.07821600	1.07180400	-3.16237600
C	-2.09192500	-2.80321700	1.89938200	C	1.17801400	-3.03550300	1.73990000
C	2.88861300	-2.72686800	1.02533800	C	4.70783700	0.05678500	-0.18660500
C	0.86247500	-1.97983100	4.16945900	C	3.70011000	-0.72458300	3.42026900
C	-0.44646700	-2.20767100	3.74806600	C	2.64065500	-1.61806200	3.23901400
C	1.92218100	-2.13179900	3.27129500	C	4.36718800	-0.19556800	2.31591300
C	-0.69245900	-2.63785400	2.43628700	C	2.24019400	-1.98057200	1.94694800
C	1.70267500	-2.57190300	1.95738500	C	3.98140700	-0.54570800	1.01310000
C	0.38873200	-2.88195700	1.58824600	C	2.92542500	-1.44331700	0.84751100
H	1.05928700	-1.67429600	5.19248700	H	4.02255500	-0.46576500	4.42448500
H	-1.27136300	-2.06206800	4.44035500	H	2.15479000	-2.05640500	4.10711700
H	2.93646000	-1.93385700	3.60996600	H	5.20996300	0.47555400	2.46796700
H	0.18154000	-3.31228200	0.61570300	H	2.67280300	-1.73419800	-0.16827700
H	-2.79203200	-3.05437900	2.70694500	H	1.16555000	-3.71870400	2.59865000

H	-2.12185200	-3.61886300	1.17213400	H	1.42903300	-3.63208300	0.86240900
H	3.77445300	-2.36658900	1.55404700	H	4.46575700	1.12565500	-0.23901000
H	3.06928900	-3.79364300	0.81548600	H	5.79442100	0.02411500	0.00116300

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