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Supplementally Information for

Reactivity of Copper(I) Complexes Supported by Tripodal Nitrogen-containing Tetradentate Ligands toward Gaseous Diatomic Molecules, NO, CO and O_2.

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Experimental

General. Reagents and solvents used in this study, except the ligands and the copper complexes, were commercial products of the highest available purity and were further purified by the standard methods, if necessary.[1] Ligands, tris(2-(pyridin-2-yl)ethyl)amine (tepa),[2] tris- (quinolin-2-ylmethyl)amine (tmqa),[3] tris(pyridin-2-ylmethyl)amine (tmpa),[4] and tris(2-(*N*-tetramethylguanidyl)ethyl)amine (TMG_3tren),[5] and the corresponding copper(I) complexes, [Cu^I(tepa)](OTf),[2] [Cu^I(tmqa)](OTf),[6] [Cu^I(tmpa)(CH_3CN)](OTf),[7] and [Cu^I(TMG_3tren)](OTf),[8] and the copper(II) complex of tepa, [Cu^{II}(tepa)(ONO)](OTf),[9] were synthesized according to the reported procedures. UV–visible spectra were taken on a Jasco V-570 or a Hewlett Packard 8453 photo diode array spectrophotometer equipped with a Unisoku thermostat-cryostat cell holder USP-203 (a desired temperature can be fixed within ±0.5 ºC). Electrochemical measurements (cyclic voltammetry) were performed at 298 K using an Automatic Polarization System HZ-7000 and a HZ-3000 HOKUTODENKO in deaerated acetonitrile containing $TBAPF_6$ (tetrabutylammonium *n*-hexafluorophosphate, 0.10 M) as a supporting electrolyte. A conventional three-electrode cell was used with a glassy carbon working electrode and a platinum wire as a counter electrode. The measured potentials were recorded with respect to Ag/$AgNO_3$ (10 mM). All electrochemical measurements of the copper(I) complexes were carried out under a nitrogen atmosphere. The one-electron oxidation potential values (E_{ox}) (vs Ag/$AgNO_3$) were converted to those vs SCE by adding 0.29 V.[10]

Purification of NO. NO gas (NO(g)) was purchased from Sumitomo Seika Chemicals Co., LTD and purified as the reported method[11] (Figure S1): NO(g) was collected in frozen form in a first trap cooled at 78 K with liquid N_2. Further purification was performed by distillation of frozen NO, which means that frozen NO(g) was warmed up to 193 K with acetone bath and then the sample was collected in a second trap cooled at 78 K with liquid N_2. This second trap was again warmed up to 193 K, and the highly purified NO(g) was collected in a vacuo Schlenk flask with a rubber septum. An NO saturated solution was prepared by bubbling NO(g) into a degassed water (4 mL) in a vial under 1 atm for 10 min. The concentration of NO in water at 298 K was reported as 1.8 mM.[12]

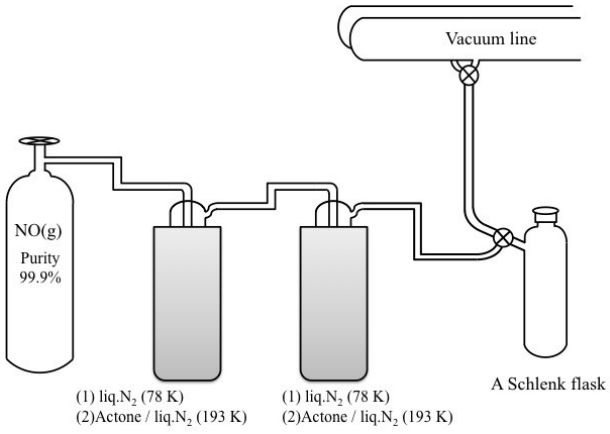

Figure 1. The NO-purification setup

Reactivity of Small Gaseous Molecules. A THF solution containing [Cu^I(**L**)]$^+$ was bubbled with gaseous sample (NO, O_2, CO) for 100 s at 298 K. The UV–vis spectral changes were measured with a photo diode array spectrophotometer. For the reaction of [Cu^I(**L**)]$^+$ and NO, products were characterized by X-ray

structure analysis. After the reaction, remaining NO was removed from the solution and then layered with ether under N_2 atmosphere. Green colour crystals were obtained by slow diffusion after several days at ambient temperature.

X-ray Structure Determination. All single crystals obtained in this study were mounted on a CryoLoop (Hamptom Research Co.) with mineral oil, and all X-ray data were collected on a Rigaku R-AXIS RAPID diffractometer using filtered Mo-$K\alpha$ radiation. The structures were solved by direct method (SIR2011) and expanded using Fourier techniques.[13] Non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2.[14] Hydrogen atoms were attached at idealized positions on carbon atoms and were not refined. All structures in the final stages of refinement showed no movement in the atom positions. The calculations were performed using Olex2 software.[15] Crystallographic parameters are summarized in Table 1.

For $[Cu^{II}(tmqa)(ONO)](CF_3SO_3)$ and $[Cu^{II}(tepa)(ONO)](CF_3SO_3)$, , the alerts related to the ratio of Maximum/Minimum residual density (PLAT094), residual density (PLAT971), and singly bonded carbon (PLAT315) are attributed to unresolved solvent molecules. The alert concerning Missing FCF Reflections (PLAT910), which appears for all complexes, is due to the beam stopper.

Theoretical Calculations. DFT calculations were performed with Gaussian 16 (revision C.02; Gauussian, Inc.). Molecular structures were optimized using the UB3LYP-D3BJ functional with the def2-SVP basis set for all atoms.[16] The grid=ultrafine option in Gaussian 16 was chosen for integral calculation. Solvent effects were considered by employing the polarizable continuum model (PCM) using the integral equation formalism (IEFPCM) approach.[17] The calculations were conducted in acetonitrile with a dielectric constant of 35.688 as implemented in Gaussian. For the optimized geometry, normal coordinate analysis for energy minima were performed to confirm no imaginary frequency. For the $[Cu(tepa)(NO)]^+$ complex, spin doublet and quartet states were calculated, with the quartet state estimated to be unstable by 29.64 kcal mol^{-1}. Similarly, the spin triplet state of $[Cu(tepa)(O_2)]^+$ was calculated to be the ground state, with the spin singlet state lying 24.27 kcal mol^{-1} above it.

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Table S1. Summary of the X-ray Crystallographic Data of Copper(II)-nitrite Complexes.

compound	[Cu(tepa)(ONO)](OTf)	[Cu(tmqa)(ONO)](OTf)	[Cu(TMG$_3$tren)(ONO)](OTf)
Empirical formula	$C_{24}H_{24}CuF_3N_5O_{5.5}S$	$C_{36}H_{25}CuF_3N_6O_5S$	$C_{24}H_{51}CuF_3N_{12}O_5S$
Formula weight	623.08	778.25	740.36
Temperature/K	103	103	103
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	P-1	P-1
a/Å	16.7789(6)	9.5052(6)	11.0382(6)
b/Å	8.1818(3)	13.2148(9)	12.5307(6)
c/Å	20.3388(6)	15.9584(12)	12.7750(7)
α/°	90	66.2124(19)	87.1960(17)
β/°	105.7486(11)	78.309(2)	86.3890(17)
γ/°	90	79.4556(19)	86.0000(14)
Volume/Å^3	2687.35(16)	1784.7(2)	1757.44(16)
Z	4	2	2
ρcalcg/cm^3	1.54	1.448	1.399
μ/mm^{-1}	0.958	0.737	0.748
F(000)	1276	798	782
Crystal size/mm^3	0.4 × 0.2 × 0.05	0.4 × 0.13 × 0.1	0.25 × 0.1 × 0.05
Radiation	MoK_α (λ = 0.71073)	MoK_α (λ = 0.71075)	MoK_α (λ = 0.71073)
2Θ range for data collection/°	6.066 to 54.964	6.136 to 54.964	6.06 to 54.958
Index ranges	-21 ≤ h ≤ 21, -10 ≤ k ≤ 10, -26 ≤ l ≤ 26	-11 ≤ h ≤ 12, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20	-14 ≤ h ≤ 14, -16 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	6156	17707	7994
Independent reflections	6156 [R_{int} = 0.0472, R_{sigma} = 0.0380]	8113 [R_{int} = 0.0263, R_{sigma} = 0.0307]	7994 [R_{int} = 0.0271, R_{sigma} = 0.0325]
Data/restraints/parameters	6156/3/379	8113/30/507	7994/0/455
Goodness-of-fit on F^2	1.07	1.055	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0405, wR_2 = 0.1062	R_1 = 0.0633, wR_2 = 0.1844	R_1 = 0.0316, wR_2 = 0.0814
Final R indexes [all data]	R1 = 0.0550, wR2 = 0.1139	R1 = 0.0674, wR2 = 0.1888	R1 = 0.0374, wR2 = 0.0844
Largest diff. peak/hole / e Å^{-3}	0.89/-0.56	2.80/-0.65	0.60/-0.32

Table S2. Calculated Energies of Small Molecules and Its Complexes (L=tepa).

Compound	*S*	Electronic Energy (Hartree)	Gibbs Free Energy (Hartree)	Solvation*[1] (kcal mol^{-1})	Reaction Energy in Electronic Energy*[2] (kcal mol^{-1})	Reaction Free Energy*[3] (kcal mol^{-1})	XYZ file
CO	0	-113.225741	-113.239753	-0.50	n.d.*[4]	n.d.*[4]	
NO	1/2	-129.789754	-129.80509	-0.39	n.d.*[4]	n.d.*[4]	
O_2	1	-150.205253	-150.221343	-0.12	n.d.*[4]	n.d.*[4]	
N_2O	0	-184.523494	-184.533384	-1.43	n.d.*[4]	n.d.*[4]	
$[LCu]^+$	0	-2673.312203	-2672.945438	-33.31	0	0	1
$[LCuNO]^+$	1/2	-2803.105071	-2802.736794	-34.58	-1.95	7.75	2
$[LCuNO]^+$	3/2	-2803.057824	-2802.686827	-40.55	27.69	33.13	3
$[LCuCO]^+$	0	-2786.545766	-2786.176526	-34.39	-4.91	4.86	4
$[LCuOO]^+$	0	-2823.483951	-2823.113125	-36.97	21.02	30.14	5
$[LCuOO]^+$	1	-2823.522632	-2823.156939	-34.77	-3.25	4.84	6
$[LCuN(O)NO]^+$	0	-2932.903877	-2932.529745	-34.58	-7.63	15.75	7
$[LCuN(O)NO]^+$	1	-2932.900007	-2932.526584	n.c.*[5]	-5.21	n.c.*[5]	8
$[LCu(\mu\text{-NO-}\kappa N)_2CuL]^{2+}$	0	-5606.16085	-5605.392344	-102.95	27.02	32.68	9
$[LCu(O\text{-}N{=}N\text{–}O)CuL]^{2+}$	0	-5606.202753	-5605.428175	n.c.*[5]	0.73	n.c.*[5]	10
$[LCu(O\text{-}N{=}N\text{–}O)CuL]^{2+}$	1	-5606.223300	-5605.448577	-102.89	-12.16	-2.55	11
$[LCu(\mu\text{-}O)CuL]^{2+}$	0	-5420.811590	-5420.890154	n.c.*[5]	545.19	n.c.*[5]	12
$[LCu(\mu\text{-}O)CuL]^{2+}$	1	-5421.688738	-5420.925584	-105.49	-5.22	-13.10	13
$[LCu(ONO)]^+$	1/2	-2878.264566	-2877.887743	-38.79	-66.89	-43.65	14

*[1] Determined by the difference in electronic energies with and without the PCM model. *[2] The electronic energies of starting copper(I) complex is defined as the origin. *[3] The free energies (involving solvation) of starting copper(I) complex is defined as the origin. *[4] not defined. *[5] not calculated.

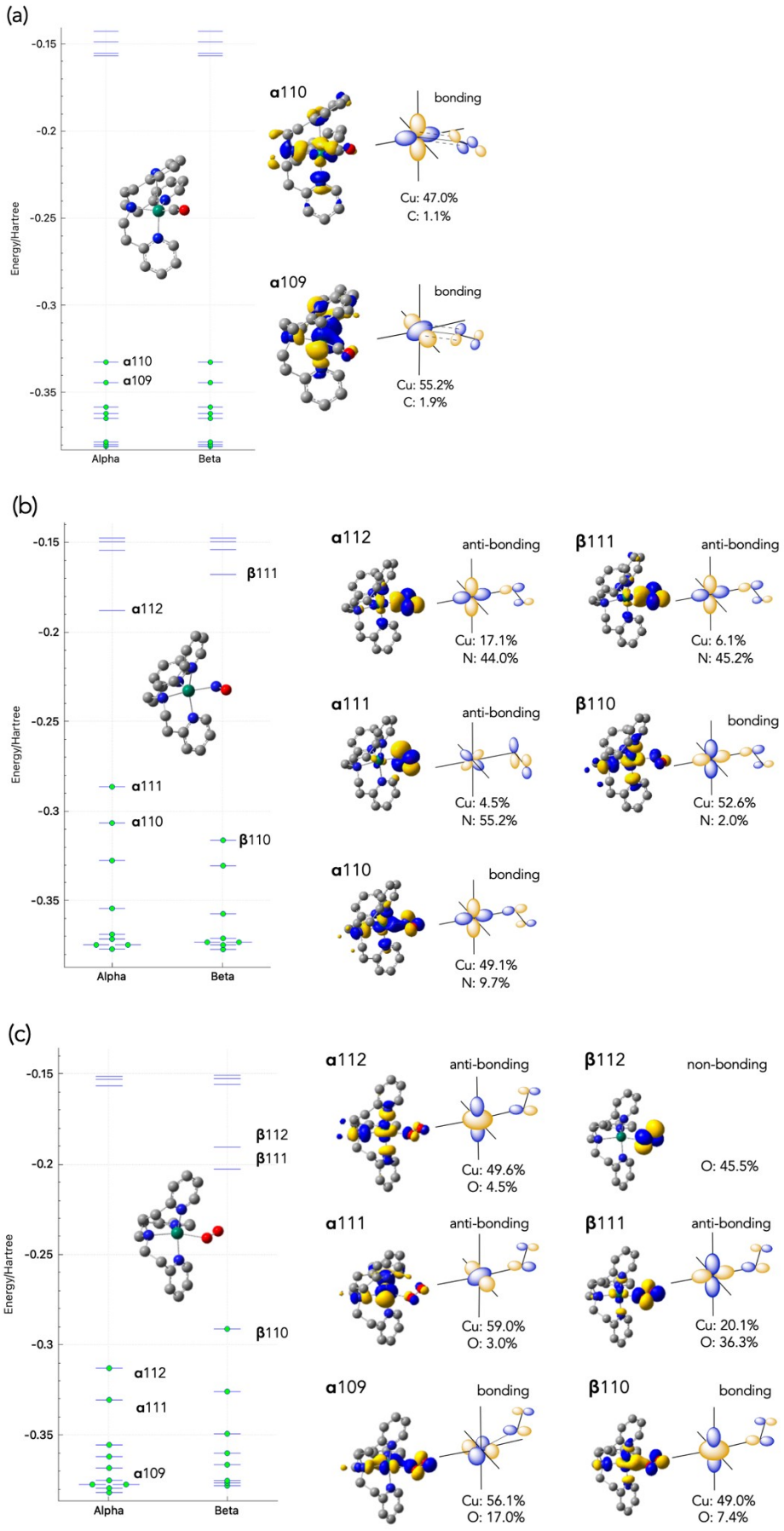

Figure S1. Orbital analysis of (a) $[Cu(tepa)(CO)]^+$, (b) $[Cu(tepa)(NO)]^+$, and (c) $[Cu(tepa)(O_2)]^+$