

Supporting Information

Dioxygen Reactivity of a Copper(I) Complex with a N₃S Thioether Chelate; Peroxo-Dicopper(II) Formation including Sulfur-Ligation

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1. Ligand and Complex(I) Complex $\{[(L^{N3S})Cu]^+\} (1)\}$ Syntheses

2-Ethylthio-*N,N*-bis(pyridin-2-yl)methylethanamine (L^{N3S}): This ligand has in fact been previously reported.^a Our modified prep is as follows: In a round bottom flask 5.40 g (0.033 mol) 2-picolyl chloride hydrochloride (Aldrich) was dissolved in 50 ml *N,N*-dimethylformamide (DMF). Excess $NaHCO_3$ was added to neutralize the amine salt. In a separate flask, 2.17g (0.015 mol) of 2-ethylthio-2-ethylamine hydrochloride (Aldrich) was dissolved in 20 ml DMF and neutralized with $NaHCO_3$. The amine solution was added to the picolyl chloride solution and stirred at 45 °C for 6 days. The orange solution was filtered and the solvent was removed with a high vacuum rotary evaporator. The resulting oil was redissolved in CH_2Cl_2 and any residual DMF and/or $NaHCO_3$ was extracted with 4x200 ml cold water. The organic layer was dried with Na_2SO_4 and rotary evaporated to yield a brown oil. The crude product was purified by column chromatography using 4% MeOH/ CH_2Cl_2 on silica gel to yield a orange/brown oil. (Yield, 80 %) (R_f = 0.55 in 10% MeOH/ CH_2Cl_2 on silica). 1H NMR ($CDCl_3$): δ 8.51 (1 H, py-6, d, J = 4.8 Hz), 7.65 (1 H, py-5, td, J = 7.7 Hz and 1.8 Hz), 7.58 (1 H, py-3, d), 7.14 (1H, py-4, m), 3.85 (4 H, s), 2.82 (2 H, m), 2.70 (2 H, m), 2.44 (2 H, q, J = 7.4 Hz), 1.18 (3 H, t, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 159.6, 149.1, 136.6, 123.1, 122.1, 60.4, 54.0, 29.3, 26.1, 14.9. EI-MS m/z = 265.2 ($M + H^+$).

$[Cu^I(L^{N3S})]ClO_4$ (1): Under an Ar atmosphere, L^{N3S} (0.35 g, 0.0012 mol) in 8 ml MeCN was added with stirring to solid $[Cu(MeCN)_4]ClO_4$ ^b (0.39 g, 0.0012 mol). To the resulting solution was added 5 ml ether to produce a cloudy solution. The solution was filtered to collect a clear, golden yellow solution to which was added 30 ml ether. After a solid precipitated from solution, it was filtered to give 0.22 g (37% yield) of a bright yellow solid. Anal. Calcd for $(C_{16}H_{21}ClCuN_3O_4S)$: C, 42.66; H, 4.70; N, 9.33. Found: C, 42.67; H, 4.61; N, 9.13. 1H NMR (CD_3NO_2): δ 8.8 (2 H, br s), 7.88 (2 H, t, J = 7.4 Hz), 7.49 (4 H, br s), 4.15 (2 H, m), 3.03 (2 H, s), 2.23 (2 H, q, J = 7.4 Hz), 2.08 (2 H, br s), 1.95 (2 H, br s), 1.18 (3 H, t, J = 7.4 Hz).

$[Cu^I(L^{N3S})]B(C_6F_5)_4$ (1): Under an Ar atmosphere L^{N3S} (0.20 g, 0.00074 mol) in 5 ml CH_2Cl_2 was added with stirring to solid $[Cu^I(MeCN)_4]B(C_6F_5)_4$ ^b (0.70 g, 0.00075 mol). The reaction mixture was stirred for 20 minutes and then heptane (10 mL) was added to

the solution until it was cloudy. At this stage the solution was filtered through a medium porosity frit and 70 mL heptane was added to the filtrate to precipitate a slightly brown solid, which was washed thoroughly with 30 mL heptane and then dried overnight under vacuum to give 0.43 g product (57 % yield). Anal. Calcd for (C₄₀H₂₁BCuF₂₀N₃S): C, 46.64; H, 2.06; N, 4.08. Found: C, 47.20; H, 1.59; N, 4.00. ¹H NMR (CD₂Cl₂): δ 8.05 (6 H, br s), 7.87 (2 H, t, *J* = 7.3 Hz), 3.69 (2 H, m), 3.29 (2 H, br s), 2.73 (2 H, br s), 2.14 (2 H, br s), 1.82 (2 H, m), 1.30 (3 H, br).

Note concerning NMR behavior of copper(I) complexes (1): Broadened methylene resonances in copper(I) complexes **1** are likely due to dynamic behavior, as seen in other tripodal tetradentate Cu(I) complexes such as that with the TMPA ligand, see ref. 17 (of the main text) for a leading reference. Apparent upfield shifting of resonances (compared to free ligand) will be discussed elsewhere.

^a Ambundo, E. A.; Deydier, M.-V.; Grall, A. J.; Aguera-Vega, N.; Dressel, L. T.; Cooper, T. H.; Heeg, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1999**, *38*, 4233-4242.; Lazarova, N.; Babich, J.; Valliant, J.; Schaffer, P.; James, S.; Zubieta, J. *Inorg. Chem.* **2005**, *44*, 6763-6770.; Tubbs, K. J.; Fuller, A. L.; Bennett, B.; Arif, A. M.; Berreau, L. M. *Inorg. Chem.* **2003**, *42*, 4790-4791.

^b Liang, H.-C.; Kim, E.; Incarvito, C. D.; Rheingold, A. L.; Karlin, K. D. *Inorg. Chem.* **2002**, *41*, 2209-2212.

2. Peroxo complex $[(L^{N3S})Cu^{II}]_2(\mu-1,2-O_2^{2-})^{2+}$ (**2**) and $[(TPA)Cu^{II}]_2(\mu-1,2-O_2^{2-})^{2+}$ (**3**); UV-Vis Spectrum, plotted versus energy (cm^{-1}).

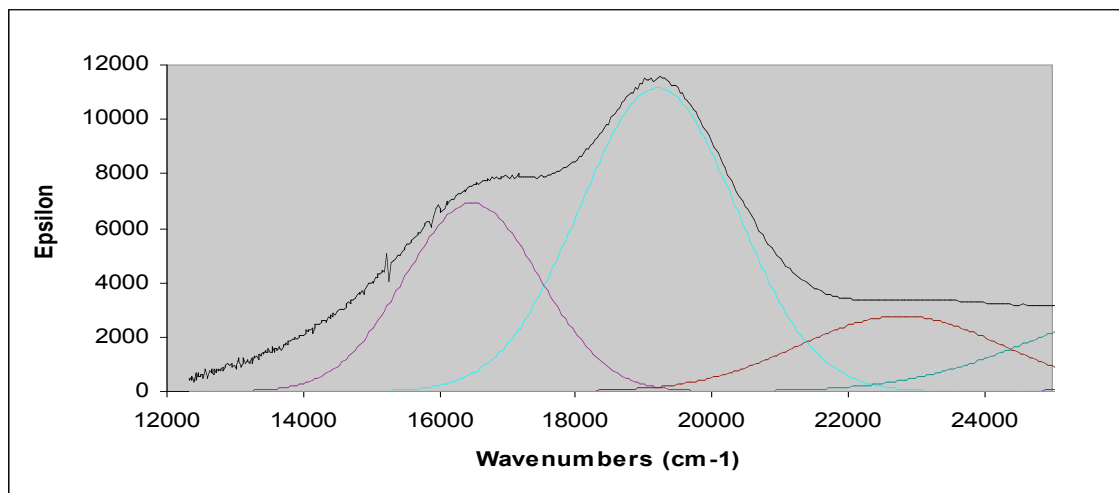


Figure S1. Absorbance spectrum of **3** in dichloromethane.

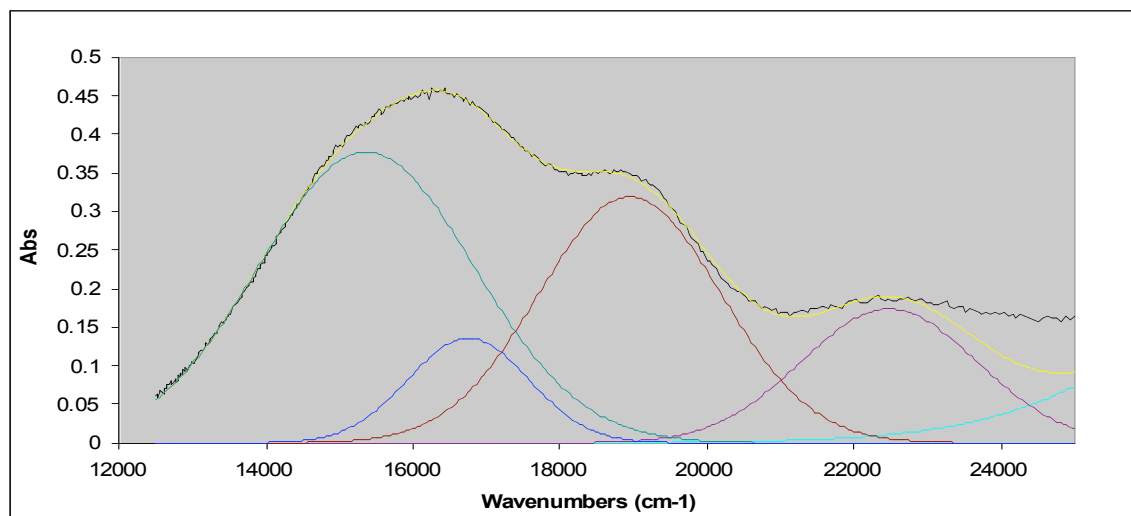


Figure S2. Absorbance spectrum of (**2**), fitted this way based on unpublished rR results.

3. Resonance Raman (rR) Spectroscopy; Experimental

Experimental: Resonance Raman spectroscopy measurements were undertaken on a Princeton Instruments ST-135 back-illuminated CCD detector on a Spex 1877 CP triple monochromator with 1200, 1800, and 2400 grooves/mm holographic spectrograph gratings. Excitation was provided by a tunable Coherent 599 dye laser and Rhodamine 6G dye ($\lambda_{\text{ex}} = 620$) pumped by a Coherent Innova Sabre 25/7DBW Ar⁺ CW ion laser. The spectral resolution was $< 2 \text{ cm}^{-1}$. Sample concentrations were approximately 3mM in Cu₂O₂. Samples were run at 77 K in a liquid N₂ finger Dewar (Wilmad) held in a backscattering geometry. Isotopic substitution was achieved by oxygenating with ¹⁸O₂ (Icon, 99% purity).

4. EXAFS Spectroscopy.

Experimental Section.

The X-ray absorption spectra of **2** were measured at the Stanford Synchrotron Radiation Laboratory on the focused 16-pole 2.0 T wiggler beam line 9-3 under standard ring conditions of 3 GeV and 80-100 mA. A Si(220) double crystal monochromator was used for energy selection. A Rh-coated harmonic rejection mirror and a cylindrical Rh-coated bent focusing mirror were used for beam line 9-3 to reject components of higher harmonics. The solution sample was loaded into a lucite XAS cell with a pre-cooled syringe. The temperature of the solution was maintained below -80 °C during this process. The sample was immediately frozen thereafter and stored under liquid N₂. During data collection, it was maintained at a constant temperature of 10 K using an Oxford Instruments CF 1208 liquid helium cryostat. Fluorescence mode was used to measure data to $k = 13.4 \text{ \AA}^{-1}$. Internal energy calibration was accomplished by simultaneous measurement of the absorption of a Cu-foil placed between two ionization chambers situated after the sample. The first inflection point of the foil spectrum was assigned to 8980.3 eV. Data represented here are an eight-scan average spectrum, which was processed by fitting a second-order polynomial to the pre-edge region and subtracting this from the entire spectrum as background. A three-region spline of orders 2, 3 and 3 was used to model the smoothly decaying post-edge region. The data were normalized by subtracting the cubic spline and by assigning the edge jump to 1.0 at 9000 eV using the *SPLINE* program in the XFIT suite of programs (Dr Paul Ellis SSRL). Theoretical EXAFS signals $\chi(k)$ were calculated using *FEFF* (version 7.0)^{1,2} and fit to the data using EXAFSPAK (G. N. George, SSRL). The structural parameters varied during the fitting process were the bond distance (R) and the bond variance σ^2 , which is related to the Debye-Waller factor resulting from thermal motion, and static disorder. The non-structural parameter E_0 (the energy at which $k = 0$) was also allowed to vary but was restricted to a common value for every component in a given fit. Coordination numbers were systematically varied in the course of the fit but were fixed within a given fit.

Table S1. EXAFS curve fitting results for $[\{(L^{N3S})Cu^{II}\}_2(\mu-1,2-O_2^{2-})](ClO_4)_2$

| Path | Distance (Å) | $\sigma^2 (\text{\AA}^2)^b$ | E_0 (eV) | F^c |
|---------------|----------------|-----------------------------|------------|-------|
| 1 Cu-N/O | 1.89 | 452 | | |
| 3 Cu-N/O | 2.03 | 445 | | |
| 1 Cu-S | 2.41 | 890 | | |
| 4 Cu-C | 2.91 | 870 | -0.04 | 0.04 |
| 10 Cu-C/N-C/N | 3.17 | 870 ^d | | |
| 6 Cu-C/N-C/N | 4.34 | 549 | | |
| 6 Cu-C/N-C/N | 4.76 | 789 | | |

^aEstimated standard deviation for the distances are on the order of $\pm 0.02 \text{ \AA}$. ^bThe σ^2 values are multiplied by 10^5 . ^cError is given by $\Sigma[(\chi_{\text{obsd}} - \chi_{\text{calcd}})^2 k^6] / \Sigma[(\chi_{\text{obsd}})^2 k^6]$. ^d The Debye-Waller factor of the multiple scattering path is linked to its corresponding single scattering path.