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Reduction of Nitrous Oxide to Dinitrogen by a Mixed Valent Tricopper-Disulfido Cluster

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Nitrous oxide (N_2O) is an important greenhouse gas and component of the global nitrogen cycle.[1] Its reduction to dinitrogen (N_2) is thermodynamically favorable ($E° = 1.76$ V), making it attractive as an environmentally benign oxidant, yet its utility in this regard is limited by high kinetic barriers that limit reaction rates. Transition metals facilitate the reduction of N_2O, although in most heterogeneous catalytic systems high temperatures are required[2] and homogeneous processes that operate under mild conditions generally use highly reducing low-valent metal complexes.[3−5] In Nature, conversion of N_2O to N_2 and H_2O is catalyzed under ambient conditions during microbial dentrification by the metalloenzyme nitrous oxide reductase, N_2OR.[6] X-ray crystallographic,[7] spectroscopic, and theoretical studies[8] have identified the active site of N_2OR as a μ-sulfido-tetracopper cluster, without precedent in biology or synthetic chemistry, that cycles through tetracopper(I) and mixed-valent states during catalysis.[9] A provocative mechanism for N_2O reduction has been suggested that involves μ-1,3-coordination and bending of N_2O between two of the copper ions in the fully reduced (all copper(I)) cluster, with the μ-sulfide acting to facilitate electron delocalization during the redox process.[9] Inspired by a desire to test this mechanistic hypothesis and to better understand the properties of the intrinsically novel active site $[(His)_7Cu_4S]$ cluster, multicopper−sulfur complexes supported by N-donor ligands have been targeted for synthesis and characterization.[10] To date, however, none contain reduced copper or react with N_2O. We have resolved these shortcomings and report the characterization of a unique mixed-valent tricopper cluster bridged by disulfide that converts N_2O to N_2 at low temperature. A novel pathway for the reaction is suggested on the basis of theory that has potential implications for understanding the N_2OR enzyme mechanism.

Reaction of Na_2S_2 with $[LCu(CH_3CN)]X$ (L = 1,4,7-trimethyltriazacyclononane, $X = O_3SCF_3^-$ or SbF_6^-)[11] in THF at room temperature over ca. 90 min resulted in the formation of known complex **2a**[11b] or new variant **2b** (Figure 1). The structures and spectroscopic properties of these complexes are similar to each other and to those of others with antiferromagnetically coupled (μ-η^2:η^2-disulfido)dicopper(II) cores.[11b,12] For example, they are EPR silent and exhibit an intense $S_2^{2-} \rightarrow Cu(II)$ charge transfer transition at ∼395 nm (ϵ ∼15 000 M^{-1} cm^{-1}, Figure 1c, red line), excitation into which (λ_{ex} = 406.7 or 457.0 nm) results in resonance enhancement of a peak in the Raman spectrum at ∼431 cm^{-1} ($\Delta^{34}S$ = 19 cm^{-1}) attributable to an S−S stretching mode.

Monitoring the reactions by UV−vis spectroscopy revealed the formation and subsequent decay (at room temperature, $t_{1/2}$ ∼45 min) of an intermediate with λ_{max} = 634 (**1a**) or 631 (**1b**) nm, respectively, the lifetime of which can be extended significantly by lowering the temperature (Figure 1c). For the case of **1b**, crystals suitable for characterization by X-ray diffraction were obtained, although larger scale solid samples for reactivity studies (see below) were more readily isolated for **1a**. The structure of **1b** (Figure 1b) features two $O_3SCF_3^-$ anions associated with a $[L_3Cu_3S_2]^{2+}$ unit. This unit contains a disulfide (S_2^{2-}) bridging the three copper ions in a manner unique in copper chemistry,[10] albeit precedented for other metal ions[13] and analogous to a proposed motif for a peroxide intermediate in dioxygen reduction by copper oxidases.[14] A localized mixed valent $Cu(II)Cu(I)_2$ electronic structure for the $[Cu_3S_2]^{2+}$ core is suggested by metal−ligand bond distances[15] and metal ion coordination geometries, with four-coordinate C_{3v}-distorted tetrahedral Cu1 and Cu2 in the +1 oxidation state and five-coordinate Cu3 in the +2 state.

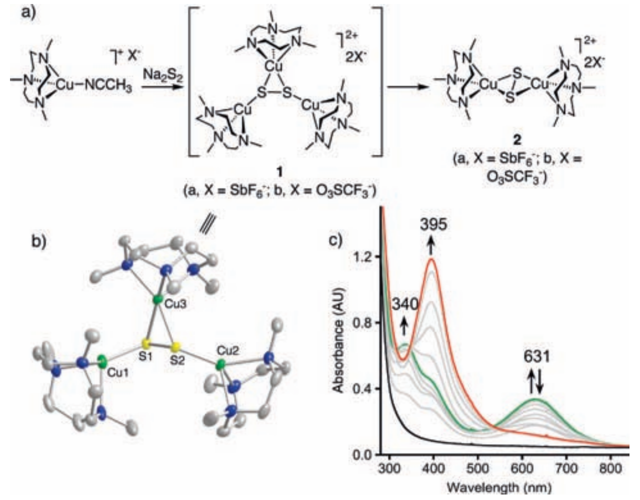

Figure 1. (a) Synthesis of disulfido complexes. (b) X-ray structure of cationic portion of **1b**, with all nonhydrogen atoms shown as 50% thermal ellipsoids. Selected bond distances: Cu1−S1, 2.1416(8) Å; Cu2−S2, 2.1367(8) Å; Cu3−S1, 2.2548(8) Å; Cu3−S2 = 2.2751(8) Å; S1−S2, 2.1267(10) Å. (c) UV/vis spectra obtained during the reaction of $[LCu(MeCN)]O_3SCF_3$ (3.1 mM, black line) with Na_2S_2 in THF. The green line is the spectrum obtained after 90 min at −20 °C (**1b**), which transforms upon warming to rt to **2b** (red line).

In the ESI mass spectrum of **1a** in CH_2Cl_2 (Figure S5) a parent ion envelope with the appropriate isotope pattern for $[L_3Cu_3S_2](SbF_6)^+$ confirms that the trinuclear cluster is retained in solution (calcd *m*/*z* 1003.1463; found 1003.1426). Nonetheless, loss of a $[LCu(I)](SbF_6)$ fragment to yield $[L_2Cu_2S_2]^+$ is facile, as indicated by an intense peak envelope for this species (calcd *m*/*z* = 532.1499; found 532.1521); this observation is relevant to reactivity studies described below. The EPR spectrum of a frozen solution of **1b** (X-band, 3.5K, Figure S4) exhibits an essentially axial signal with slight rhombicity ($g_x = 2.079$, $g_y = 2.024$, $g_z = 2.023$) and a four line hyperfine splitting in g_x due to coupling to

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a single Cu nucleus (A_{Cu} = 138 × 10^{-4} cm^{-1}). The 631 nm absorption band for **1b** resembles (in appearance only; see below) that observed for a mixed-valent form of Cu_Z in N_2OR (λ_{max} = 640 nm) that has been attributed to a S → Cu ligand-to-metal charge transfer (LMCT) transition.[8b,c] Excitation into the 631 nm band for **1b** leads to resonance enhancement of a peak in the Raman spectrum (Figure 2b) at 453 cm^{-1} ($\Delta^{34}S = 19$ cm^{-1}); similar data were observed for **1a**.[16] These results are consistent with assignment of the 631 nm band as a Cu/S_2^{2-} charge-transfer transition and the 453 cm^{-1} peak as a predominantly υ(S−S) mode.

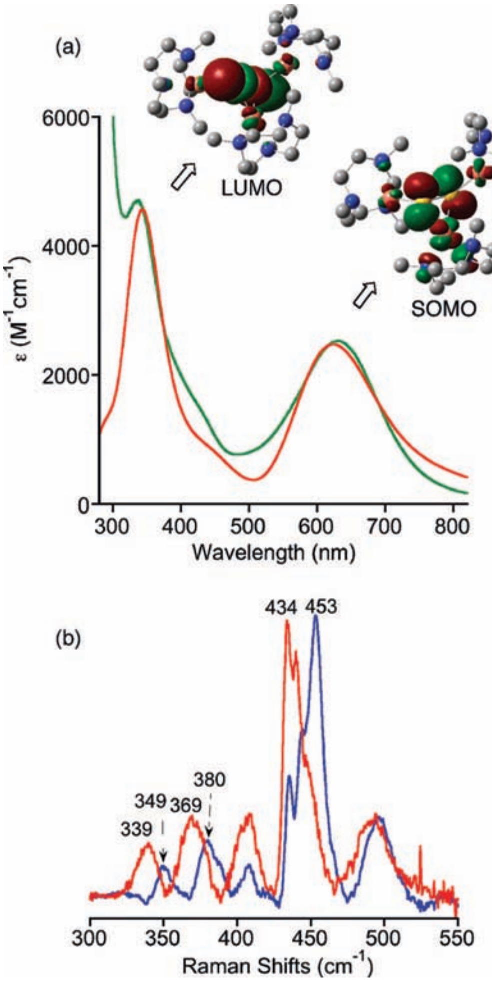

Figure 2. (a) Experimental absorption spectrum of the crude reaction solution containing **1b** obtained upon slow addition of Na_2S_2 (0.5 equiv) to $[LCu(MeCN)]O_3SCF_3$ in THF at −20 °C (green line) and TD-B98 calculated spectrum (red line), with drawings of the acceptor orbitals for the respective features shown. (b) Resonance Raman spectrum obtained from the reaction of $[LCu(MeCN)]O_3SCF_3$ with Na_2S_2 in THF (−196 °C, λ_{ex} = 647.1 nm; ^{32}S, blue line; ^{34}S, red line).

These assignments were investigated further using Density Functional Theory (DFT) calculations. Geometries of the $[L_3Cu_3S_2]^{2+}$ cluster were optimized in the gas phase and including self-consistent reaction-field THF solvation effects. The two optimized geometries were similar and differ little from the single-crystal X-ray structure, except that the S−S bond is longer (2.21 Å) in the computed structures than in the crystal structure (2.13 Å). UV−vis spectra calculated at the time-dependent B98 density functional level of theory were insensitive to choice of structure (computed or X-ray) and showed excellent agreement with the experimental spectrum when computed transitions were blue-shifted by 0.2 eV (Figure 2a; the blue shift is consistent with the tendency for most TD-DFT protocols to underestimate the energy of charge-transfer excitations[17]). Importantly, and in contrast to the assignments for Cu_Z,[8b,c] the absorption near 630 nm can be attributed to a metal-to-ligand charge transfer (MLCT) from the Cu(I) centers into a π* orbital of the S−S bond (SOMO, Figure 2a). Similarly, the peak at ~340 nm originates mainly from an MLCT from the Cu(I) centers into the σ* orbital of the S−S bond (LUMO). With respect to the resonance Raman spectrum, theory predicts an S−S stretch at 406 cm^{-1} and Cu(I)−S stretches at 366 and 347 cm^{-1}. The discrepancy of the S−S stretch with the experimental value is probably due to the elongated S−S bond in the gas-phase optimized structure, which was used for these computations (a frequency of 504 cm^{-1} is predicted when the nonstationary X-ray crystal structure is used). Finally, the calculations show that 71% of the spin density is located on the sulfur atoms and the Cu center coordinated η^2 to the disulfide unit (therefore denoted Cu(II)) with all other atoms having less than 5%.

In addition to converting to **2a** upon warming to room temperature, **1a** in CH_2Cl_2 (or generated in situ in THF) under a He atmosphere at −80 °C slowly ($t_{1/2}$ ~6 h) reacts with excess N_2O to quantitatively (based on **1a**) yield N_2 as determined by GC/MS. In control experiments, identical procedures were followed but either with no complex present or with the complex present but without injecting N_2O; in both cases, N_2 production was not observed. UV−vis spectroscopic changes during the reaction of **1a** with N_2O show bleaching of the 631 nm band and concomitant formation of the features due to **2a** (~60% yield[18]), the identity of which was confirmed by resonance Raman spectroscopy.[11b] In addition, an ESI mass spectrum of the final reaction solution revealed the presence of $\{[L_2Cu_2(OH)_2]SbF_6\}^+$ (calcd m/z 739.1048, found 739.0960).[19,20] Peaks corresponding to this product are not present in the spectrum of the solution resulting from decay of **1a** in the absence of N_2O. We have not been able to isolate $[L_2Cu_2(OH)_2](SbF_6)_2$from the product mixture and suspect that it may not be the primary oxygen-containing copper byproduct of the reduction of N_2O; further experimental mechanistic evaluation is needed to address this issue. Importantly from a mechanistic perspective, the presence of a ~7-fold excess of $[LCu(CH_3CN)](SbF_6)$ in solutions of **1a** in CH_2Cl_2 inhibited both the decomposition of **1a** in the absence of N_2O ($t_{1/2}$ ~ several days at −20 °C) and its reaction with N_2O to form N_2 (40 ± 10% yield after 10 h). These results, in conjunction with the ESI-MS data indicating the feasibility of $[L_2Cu_2S_2]^+$ formation, are consistent with a pre-equilibrium step (eq 1) that generates $[L_2Cu_2S_2]^+$ as the active species in the N_2O activation process, with added LCu(I) shifting the equilibrium to the presumably less reactive trinuclear cluster.

$$[L_3Cu_3S_2]^{2+} \rightleftarrows [L_2Cu_2S_2]^+ + [LCu(I)]^+ \qquad (1)$$

In computational efforts to evaluate this hypothesis, we calculated that the disproportionation shown in eq 1 is endergonic in THF by only 2.7 kcal/mol (with THF bound to $[LCu(I)]^+$). As a result, exhaustive searches at the M06L DFT level for bound complexes and transition-state (TS) structures with N_2O were performed for both $[L_3Cu_3S_2]^{2+}$ and $[L_2Cu_2S_2]^+$. In addition to a number of TS structures found for both clusters with free energies of activation too high to be experimentally relevant (see Supporting Information), we discovered a low-energy ($\Delta G^{\ddagger}$ = 26.6 kcal mol^{-1}) TS structure for $[L_2Cu_2S_2]^+$ that evolves to an oxo-bridged intermediate (not observed experimentally) in an exergonic process (ΔG = −12.5 kcal mol^{-1}, Figures 3 and S13). The nature of the bridging in the

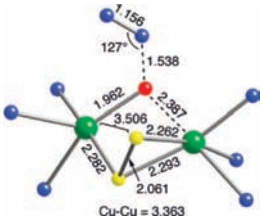

Figure 3. Transition state structure for the N−O bond cleavage computed at the M06L DFT level with selected interatomic distances (Å). C and H atoms of the Me_3tacn ligands are not shown for clarity. Key: green = Cu, blue = N, yellow = S, and red = O.

TS structure, involving only the substrate O atom, differs from the μ-1,3 binding of N_2O proposed for N_2OR by Solomon and co-workers,[9] but the $\Delta G^{\ddagger}$ we compute is similar to their calculated value for the enzyme model (after entropic effects are added to their reported activation potential energies). We were unable to find similar μ-1,3-bridged species for either binuclear or trinuclear clusters; plausible starting structures inevitably dissociated N_2O or relaxed to monodentate coordination.

The ground state of our computed product is a quartet, and this, together with an analysis of its charge and spin density, indicates oxidation of the original Cu(I)/Cu(II) binuclear reactant to a Cu(II)/$-O^{\bullet-}$/Cu(II) product. As has been noted previously,[21] high-spin (triplet) Cu(II)$-O^{\bullet-}$ is preferred over a closed-shell Cu(III)/oxo formalism, and coupling of this fragment with the remaining Cu(II) is ferromagnetic leading to an $S = {}^3/_2$ ground state. In the TS structure, oxidation of the original Cu(I) atom is moderately advanced, but the doublet $S = {}^1/_2$ state remains the ground state. Thus, spin crossing occurs subsequent to commitment to reaction.

We conclude by noting that although the disulfido (S_2^{2-}) unit in complex **1** differs from the sulfido (S^{2-}) ligand in the active site of N_2OR, key properties of Cu_Z are modeled, such as S-bridging between Cu(I) and Cu(II) sites supported by N-donor ligands and superficially similar UV−vis absorption features. Importantly, the complex exhibits reactivity relevant to that of the enzyme, insofar as it converts N_2O to N_2. The finding of N_2O reduction by a discrete copper−sulfur complex under mild conditions is significant, as such reactions have only been observed for Cu oxide surfaces[22] and Cu-doped zeolites[23] at elevated temperatures and for excited-state Cu(I) ions in the gas phase.[24,25] We propose a mechanism involving pre-equilibrium formation of a dicopper complex, which subsequently reduces N_2O via a transition state that features bridging of substrate between the two copper ions through a single O atom. Although previously discounted,[9] the evidence we have obtained suggests that such a pathway may represent a feasible alternative to the mechanism involving μ-1,3-coordination of N_2O proposed previously for the enzyme.

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Supporting Information Available: Materials and Methods, details of X-ray crystallography and calculations, and full citation for ref 1b. This information is available free of charge via the Internet at http://pubs.acs.org/.

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