Synthesis, Characterization and Reactivity of a Dicopper(II) Complex Containing a μ-η^2:η^2 Side-On Bound Disulfido Bridge

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The recent discovery of a Cu_4S cluster at the active site of nitrous oxide reductase (N_2OR), an enzyme that catalyzes the terminal step in bacterial denitrification [$N_2O + 2e^- + 2H^+ \rightarrow H_2O + N_2$], has brought about a surge of interest in copper-sulfur coordination chemistry and spectroscopy. Previously we have reported the first example of a μ-η^1:η^1 end-on disulfide bridged compound synthesized from a Cu(I) complex of the tetradentate ligand TMPA and S_8 (*J. Am. Chem. Soc.*, **2003**, *125*, 1160). Here we report the synthesis of a μ-η^2:η^2 side-on copper disulfide compound $[\{(Me_2N\text{-}MePY2)Cu^{II}\}_2(S_2^{2-})]^{2+}$, **1**, ($Me_2N$-MePY2 is a tridentate pyridyl alkylamine ligand) and its reactivity towards exogenous substrates.

The X-ray crystal structure of **1**-$[B(C_6F_5)_4]_2 \bullet CH_2Cl_2$ shows that each copper ion is 5 coordinate, with three N-donor atoms from the ligand and two S-donor atoms from the μ-η^2:η^2 side-on bound disulfide. Reversible sulfur binding was found by CO ligation to generate $[(Me_2N\text{-}MePY2)Cu^{I}(CO)][B(C_6F_5)_4]$, **2**. Addition of 4 eq. of PPh_3 results in formation of 2eq. of $S{=}PPh_3$ and 2 eq. of $[(Me_2N\text{-}MePY2)Cu^{I}(PPh_3)][B(C_6F_5)_4]$, **3**, whereas addition of 2 eq. PPh_3 results in formation of 2 eq. $S{=}PPh_3$ stoichiometrically. $PhCH_2Br$ does not react with complex **1**. These results indicate the electrophilic nature of the side on Cu_2S_2 core. Addition of the tetradentate ligand TMPA causes immediate formation of our previously reported μ-η^1:η^1 end-on bound disulfide complex $[\{(TMPA)Cu^{II}\}_2(S_2^{2-})]^{2+}$(**4**), thus a disulfide exchange reaction. Further studies including detailed spectroscopic, mechanistic investigation and study of N_2O reduction via copper-sulfur chemistry are underway.