

Reaction of Elemental Sulfur with a Copper(I) Complex Forming a *trans*- μ -1,2 End-On Disulfide Complex: New Directions in Copper–Sulfur Chemistry

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In the past few decades, investigations into copper–sulfur interactions have been of marked interest in the research fields of copper–thiolate chemistry,^{1–5} “blue” copper (Type 1 or the binuclear Cu₂) electron-transfer proteins,^{6–8} other Cu–thiolate proteins,^{9–13} copper monooxygenases,^{14–16} cluster complexes of synthetic or structural interest,^{17,18} dithiolene ligand complexes,^{2,19} compounds with disulfur linkages,^{16,18,20–22} and radiopharmaceuticals.²³ A new focus of interest in copper–sulfur coordination chemistry is derived from the recent discovery of a tetracopper–sulfide cluster at the so-called Cu₂ active site of nitrous oxide reductase (N₂OR), an enzyme that catalyzes the terminal step in bacterial denitrification [N₂O + 2e[−] + 2H⁺ → H₂O + N₂].^{24–28} We report here, in initial studies generating new copper–sulfur chemistry, that [(TMPA)Cu(CH₃CN)]⁺ (**1**)^{29,30} reacts with elemental sulfur (S₈) to generate the *trans*- μ -1,2 end-on disulfide complex [(TMPA)Cu–S–S–Cu(TMPA)]²⁺ (**2**), the first example of a copper complex containing an end-on bridging disulfide ligand.

Complex **2** can be synthesized as either perchlorate or hexafluorophosphate salts, 2-(ClO₄)₂ or 2-(PF₆)₂, respectively, by addition of 1/8 equiv of elemental sulfur (S₈) to a degassed acetonitrile solution of **1**. Addition of S₈ to **1** causes an immediate change in the color of the solution from bright orange to dark blue. A blue solid was precipitated by dropwise addition of diethyl ether, and subsequent recrystallization of 2-(ClO₄)₂ from a concentrated acetone solution afforded deep blue crystals of 2-(ClO₄)₂·(Et₂O)₃; the disulfide formulation was confirmed by X-ray crystallography (Figure 1).³¹ The copper(II) coordination geometry is distorted trigonal bipyramidal, comparable to that of the structurally analogous peroxo dicopper(II) complex [(TMPA)Cu–O–O–Cu(TMPA)]²⁺, formed from the reversible reaction of **1** with O₂.^{30,32} The equatorial ligands are the pyridyl N(2), N(3), and N(4) donors, with the aliphatic amine N(1) and the disulfide sulfur S(1) occupying axial positions.

Kitajima, Fujisawa, and co-workers have presented complementary examples of complexes with μ - η^2 : η^2 side-on coordination of both disulfide and peroxide (see diagram).^{21,33} The Kitajima–Fujisawa μ - η^2 : η^2 side-on disulfide complex was synthesized by thermal decomposition of a thiolate complex via C–S bond cleavage.²¹ This is in stark contrast to the synthesis of the *trans*- μ -1,2 end-on disulfide complex presented here by reaction of **1** with elemental sulfur. The side-on complex contains tridentate copper ligation by a derivatized tris(pyrazolyl)borate ligand.^{21,33} A comparison of S–S and O–O bond lengths, as well as Cu···Cu distances, from both the end-on and the side-on structures of the peroxide and disulfide complexes is presented in Table 1. The S(1)–

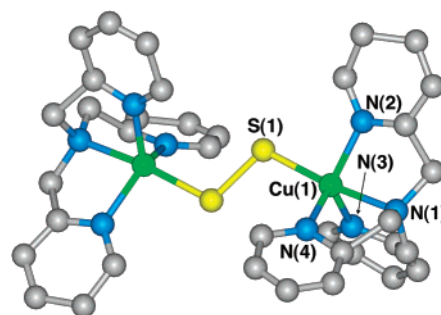


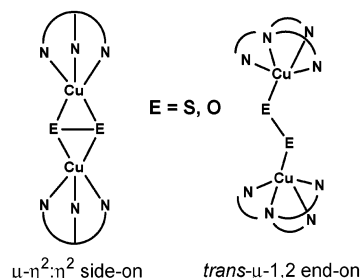
Figure 1. View of the crystal structure of the disulfide complex 2-(ClO₄)₂·(Et₂O)₃. The hydrogens, solvent molecules of crystallization, and perchlorate anions have been removed for clarity. Selected bond lengths (Å): S(1)–S(2) = 2.044(4), Cu(1)–S(1) = 2.280(2), Cu(1)–N(1) = 2.088(5), Cu(1)–N(2) = 2.048(6), Cu(1)–N(3) = 2.091(6), Cu(1)–N(4) = 2.090(6). Selected bond angles (deg): N(1)–Cu(1)–S(1) = 173.69(17), N(2)–Cu(1)–S(1) = 93.54(18), N(3)–Cu(1)–S(1) = 101.02(17), N(4)–Cu(1)–S(1) = 104.9(2), S(1)–S(2)–Cu(1) = 109.75(13).

Table 1. Bond Lengths from End-On and Side-On Structures of Peroxide and Disulfide Complexes

	end-on Cu–S–S–Cu ^a	side-on Cu–S–S–Cu ^b
S–S	2.044(4) Å	2.073(4) Å
Cu···Cu	5.592(2) Å	4.028(3) Å
	end-on Cu–O–O–Cu ^c	side-on Cu–O–O–Cu ^d
O–O	1.432(6) Å	1.412(12) Å
Cu···Cu	4.359(1) Å	3.560(3) Å

^a This work. ^b Reference 21. ^c Reference 32. ^d Reference 35.

S(1A) (2.044 Å) bond length for 2-(ClO₄)₂·(Et₂O)₃ falls into the expected range (2.00–2.07 Å) observed for disulfur complexes with metals other than copper.^{21,34}



The absorption spectrum of 2-(ClO₄)₂·(Et₂O)₃ in acetone at reduced temperatures (Figure S1)³¹ shows low energy features at 573, 649, 857 nm.³⁶ Resonance Raman spectra (Figure 2) of 2-(ClO₄)₂·(Et₂O)₃ excited at 568.2 nm at 77 K in acetonitrile show two vibrational modes at 499 and 316 cm^{−1}, which shift to 490

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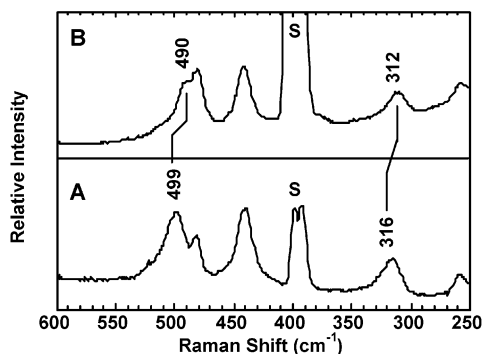


Figure 2. Resonance Raman spectra of $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$ with naturally abundant sulfur (A) and with isotopically enriched ^{34}S (B) in CH_3CN with excitation $\lambda = 568.2\text{ nm}$ at 77 K . "S" denotes CH_3CN solvent bands.

and 312 cm^{-1} (respectively) upon ^{34}S isotope labeling.³⁷ The 499 cm^{-1} mode can be assigned as the S–S stretching vibration on the basis of its frequency and isotope shift.^{38,39} The 316 cm^{-1} mode can be assigned as the symmetric combination of Cu–S stretching vibrations. Similar results were obtained on the crystalline solids of $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$ (Figure S2).^{31,40} The IR spectrum of $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$ has a vibrational feature at 478 cm^{-1} , which is not present in **1** and shifts to 473 cm^{-1} upon ^{34}S labeling (Figure S3).³¹ This vibrational mode can be assigned to the antisymmetric Cu–S stretching vibration which is IR, but not Raman, active due to the C_i symmetry of the molecule. A full spectroscopic comparison of $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$ with that of Kitajima's complex is forthcoming.⁴⁰

There are a number of known metal-disulfide complexes^{34,41,42} with structures that can be classified as side-on, cis end-on, or trans end-on coordination modes. In such species, the discrete S_2^n ($n = 0, -1, -2$) moiety gives rise to a stretching frequency that typically falls within the range from 446 to 725 cm^{-1} depending on the value of n (the higher frequency is attributed to more positive values of n).³⁴ A $\nu(\text{S}=\text{S})$ of 499 cm^{-1} for $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$ (resonance Raman spectroscopy; Figure 2) is higher than that expected for a formal S_2^{2-} moiety.³⁴ The high-frequency stretch for the S–S moiety can be explained by a strong interaction between S_2^{2-} and the Cu^{II} centers, which removes electron density from the S–S π^* antibonding orbital leading to a strengthened S–S bond. The shorter S–S bond in $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$ as compared to that in Kitajima-Fujisawa's side-on disulfide complex (Table 1) reflects the additional contribution of back-bonding into the disulfide σ^* orbital for the latter. This σ^* back-bonding interaction is different for the disulfide complex relative to their peroxide analogues.⁴⁰

The present study shows that elemental sulfur, in reaction with copper(I) complexes, provides an excellent starting point for investigations into new Cu–S chemistry. The dicupric *trans-μ*-1,2 end-on disulfide complex $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$ provides a possible synthon for further explorations into Cu–S chemistry because the disulfide moiety is a potential source of 2 oxidizing equivalents. Future studies with $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$ may potentially lead to the synthesis of small molecule analogues of the tetracopper-sulfide cluster at the Cu_2 active site of nitrous oxide reductase.

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Supporting Information Available: Synthetic details; instrument descriptions; UV–vis of $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$; solid-state resonance Raman spectrum of $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$; IR spectra for **1**, $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$, and the ^{34}S analogue of $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$ (PDF); crystallographic data for

$2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$ (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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