

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

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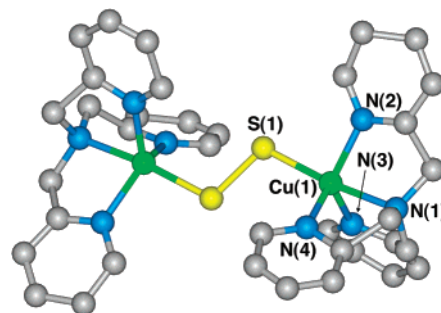
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In the past few decades, investigations into copper–sulfur interactions have been of marked interest in the research fields of copper-thiolate chemistry,<sup>1–5</sup> “blue” copper (Type 1 or the binuclear Cu<sub>2</sub>) electron-transfer proteins,<sup>6–8</sup> other Cu-thiolate proteins,<sup>9–13</sup> copper monooxygenases,<sup>14–16</sup> cluster complexes of synthetic or structural interest,<sup>17,18</sup> dithiolene ligand complexes,<sup>2,19</sup> compounds with disulfur linkages,<sup>16,18,20–22</sup> and radiopharmaceuticals.<sup>23</sup> 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 Cu<sub>2</sub> active site of nitrous oxide reductase (N<sub>2</sub>OR), an enzyme that catalyzes the terminal step in bacterial denitrification [N<sub>2</sub>O + 2e<sup>−</sup> + 2H<sup>+</sup> → H<sub>2</sub>O + N<sub>2</sub>].<sup>24–28</sup> We report here, in initial studies generating new copper–sulfur chemistry, that [(TMPA)Cu(CH<sub>3</sub>CN)]<sup>+</sup> (**1**)<sup>29,30</sup> reacts with elemental sulfur (S<sub>8</sub>) to generate the *trans*- $\mu$ -1,2 end-on disulfide complex [(TMPA)Cu–S–S–Cu(TMPA)]<sup>2+</sup> (**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**·(ClO<sub>4</sub>)<sub>2</sub> or **2**·(PF<sub>6</sub>)<sub>2</sub>, respectively, by addition of 1/8 equiv of elemental sulfur (S<sub>8</sub>) to a degassed acetonitrile solution of **1**. Addition of S<sub>8</sub> 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**·(ClO<sub>4</sub>)<sub>2</sub> from a concentrated acetone solution afforded deep blue crystals of **2**·(ClO<sub>4</sub>)<sub>2</sub>·(Et<sub>2</sub>O)<sub>3</sub>; the disulfide formulation was confirmed by X-ray crystallography (Figure 1).<sup>31</sup> The copper(II) coordination geometry is distorted trigonal bipyramidal, comparable to that of the structurally analogous peroxy dicopper(II) complex [(TMPA)Cu–O–O–Cu(TMPA)]<sup>2+</sup>, formed from the reversible reaction of **1** with O<sub>2</sub>.<sup>30,32</sup> 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  $\mu$ - $\eta^2$ : $\eta^2$  side-on coordination of both disulfide and peroxide (see diagram).<sup>21,33</sup> The Kitajima-Fujisawa  $\mu$ - $\eta^2$ : $\eta^2$  side-on disulfide complex was synthesized by thermal decomposition of a thiolate complex via C–S bond cleavage.<sup>21</sup> This is in stark contrast to the synthesis of the *trans*- $\mu$ -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.<sup>21,33</sup> 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)–



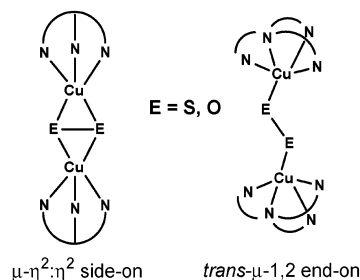
**Figure 1.** Viewed representation of the crystal structure of the disulfide complex **2**·(ClO<sub>4</sub>)<sub>2</sub>·(Et<sub>2</sub>O)<sub>3</sub>. The hydrogens, solvent molecules of crystallization, and perchlorate anions have been removed for clarity. Selected bond lengths (Å): S(1)–S(1A) = 2.044(4), 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(1A)–S(1)–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 <sup>a</sup>	side-on Cu–S–S–Cu <sup>b</sup>
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 <sup>c</sup>	side-on Cu–O–O–Cu <sup>d</sup>
O–O	1.432(6) Å	1.412(12) Å
Cu···Cu	4.359(1) Å	3.560(3) Å

<sup>a</sup> This work. <sup>b</sup> Reference 21. <sup>c</sup> Reference 32. <sup>d</sup> Reference 35.

S(1A) (2.044 Å) bond length for **2**·(ClO<sub>4</sub>)<sub>2</sub>·(Et<sub>2</sub>O)<sub>3</sub> falls into the expected range (2.00–2.07 Å) observed for disulfur complexes with metals other than copper.<sup>21,34</sup>

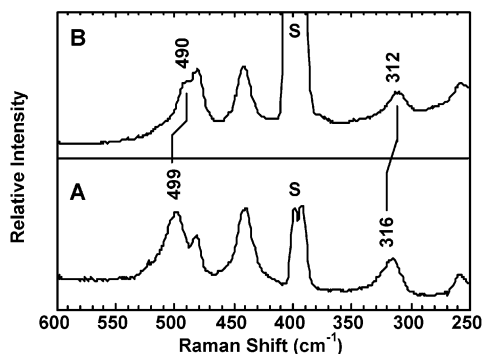


The absorption spectrum of **2**·(ClO<sub>4</sub>)<sub>2</sub>·(Et<sub>2</sub>O)<sub>3</sub> in acetone at reduced temperatures (Figure S1)<sup>31</sup> shows low energy features at 573, 649, 857 nm.<sup>36</sup> Resonance Raman spectra (Figure 2) of **2**·(ClO<sub>4</sub>)<sub>2</sub>·(Et<sub>2</sub>O)<sub>3</sub> excited at 568.2 nm at 77 K in acetonitrile show two vibrational modes at 499 and 316 cm<sup>−1</sup>, 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  $^{34}\text{S}$  (B) in  $\text{CH}_3\text{CN}$  with excitation  $\lambda = 568.2$  nm at 77 K. "S" denotes  $\text{CH}_3\text{CN}$  solvent bands.

and  $312\text{ cm}^{-1}$  (respectively) upon  $^{34}\text{S}$  isotope labeling.<sup>37</sup> The  $499\text{ cm}^{-1}$  mode can be assigned as the S–S stretching vibration on the basis of its frequency and isotope shift.<sup>38,39</sup> The  $316\text{ cm}^{-1}$  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).<sup>31,40</sup> The IR spectrum of  $2\text{-(ClO}_4)_2\cdot(\text{Et}_2\text{O})_3$  has a vibrational feature at  $478\text{ cm}^{-1}$ , which is not present in **1** and shifts to  $473\text{ cm}^{-1}$  upon  $^{34}\text{S}$  labeling (Figure S3).<sup>31</sup> 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.<sup>40</sup>

There are a number of known metal-disulfur complexes<sup>34,41,42</sup> with structures that can be classified as side-on, cis end-on, or trans end-on coordination modes. In such species, the discrete  $\text{S}_2^n$  ( $n = 0, -1, -2$ ) moiety gives rise to a stretching frequency that typically falls within the range from  $446$  to  $725\text{ cm}^{-1}$  depending on the value of  $n$  (the higher frequency is attributed to more positive values of  $n$ ).<sup>34</sup> A  $\nu(\text{S}=\text{S})$  of  $499\text{ cm}^{-1}$  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  $\text{S}_2^{2-}$  moiety.<sup>34</sup> The high-frequency stretch for the S–S moiety can be explained by a strong interaction between  $\text{S}_2^{2-}$  and the  $\text{Cu}^{\text{II}}$  centers, which removes electron density from the S–S  $\pi^*$  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  $\sigma^*$  orbital for the latter. This  $\sigma^*$  back-bonding interaction is different for the disulfide complex relative to their peroxide analogues.<sup>40</sup>

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  $\text{Cu}_Z$  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  $^{34}\text{S}$  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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