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Copper–Sulfur Complexes

Novel Reactivity of Side-On (Disulfido)dicopper Complexes Supported by Bi- and Tridentate Nitrogen Donors: Impact of Axial Coordination**

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The distinctive structure of the [(histidine)$_7$Cu$_4$(μ_4-S)] cluster in the "Cu$_Z$" active site of nitrous oxide reductase[1] and the intriguing proposals for its redox[2] and catalytic reactivity[3] have inspired synthetic model studies aimed at understanding the properties of copper–sulfur complexes supported by N-donor ligands.[4] Of the complexes structurally characterized to date,[5–11] those with end-on (μ-1,2)[9,10] or side-on (μ-η^2:η^2) (disulfido)dicopper(II), $\{Cu_2(S_2)\}^{2+}$, cores are the most common, with examples of the latter having been isolated with tris(pyrazolyl)hydroborate,[11a] bis(pyridyl)methylamine,[11c] β-diketiminate,[11b,d] and anilido-imine[11b,d] ligands. Reactivity studies of $\{Cu_2(S_2)\}^{2+}$ cores supported by tri- or tetradentate pyridylamines have been reported,[9b,11c] and differences between the end- and side-on types were attributed to contrasting nucleophilic and electrophilic character. Further insights into the reactivity of copper–sulfur complexes are needed to understand structure–function relationships among clusters with variable nuclearities and supporting ligands. Ultimately, such fundamental knowledge will facilitate efforts to elucidate possible mechanisms of N$_2$O reduction by Cu$_Z$ and synthetic models.

Herein we report the characterization of two new (μ-η^2:η^2-disulfido)dicopper(II) complexes (**1** and **2**, Figure 1) supported by neutral peralkylated bi- or triamine donors as well as a comparative investigation of their reactivity with a variety of substrates. This study has revealed redox processes previously unseen for copper–sulfur complexes, including phenol, hydroquinone, and catechol oxidations (some involving S-atom insertions), as well as conversion of a $\{Cu_2(\mu$-η^2:η^2-$S_2)\}^{2+}$ core to a $\{Cu_3(\mu$-$S)_2\}^{3+}$ moiety by Cu^I-induced S–S bond scission. The reactivity of the complexes supported by the bi- and triamine donor ligands differs, pointing to interesting influences of supporting ligands on the $\{Cu_2(\mu$-η^2:η^2-$S_2)\}^{2+}$ core properties.

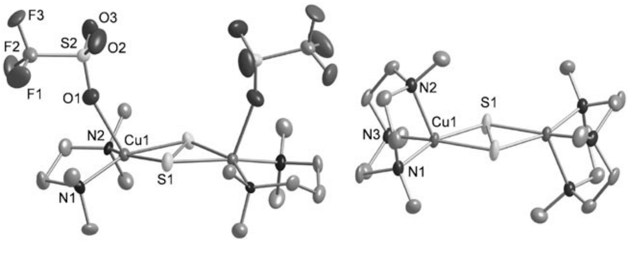

Figure 1. Molecular structures of **1** (left) and the dicationic portion of **2** (right; ellipsoids set at 50% probability, H atoms excluded, only heteroatoms labeled). Selected interatomic distances [Å] for **1**: S1–S1A 2.105(4), Cu1–S1 2.2279(18), Cu1–S1A 2.2406(19), Cu1–N1 2.018(6), Cu1–N2 2.024(6), Cu1–O1 2.344(6), Cu1–Cu1A 3.92. For **2**: S1–S1A 2.165(4), Cu1–S1 2.2037(19), Cu1–S1A 2.2044(18), Cu1–N1 2.012(5), Cu1–N2 2.214(6), Cu1–N3 2.009(6), Cu1–Cu1A 3.84.

Compound **1**, [(Me$_4$pda)$_2$Cu$_2$(O$_3$SCF$_3$)$_2$(μ-η^2:η^2-S$_2$)], was prepared by addition of Na$_2$S$_2$ (0.5 equiv) to a THF solution of Me$_4$pda[12] and Cu(O$_3$SCF$_3$)$_2$ (1:1 molar ratio) and subsequent recrystallization of the resulting orange precipitate from CH$_2$Cl$_2$/pentane. Using an alternative method, green-brown [(Me$_3$tacn)$_2$Cu$_2$(μ-η^2:η^2-S$_2$)](SbF$_6$)$_2$ (**2**) was synthesized by addition of S$_8$ to a CH$_2$Cl$_2$ solution of [(Me$_3$tacn)Cu(MeCN)]SbF$_6$.[12] X-ray structures of the complexes revealed $\{Cu_2(\mu$-η^2:η^2-$S_2)\}^{2+}$ cores with pentacoordinate copper ions in distorted square-pyramidal geometries (Figure 1). Whereas the axial N donors in **2** are disposed in *anti* fashion and the Cu$_2$S$_2$ core is flat, in **1** the axial CF$_3$SO$_3^-$ ligands are *syn* and the Cu$_2$S$_2$ core is puckered (dihedral angle between CuS$_2$ planes 168°). Comparison of the S–S, Cu–Cu, and Cu–S distances in the two complexes indicates that **2** exhibits a greater degree of S–S bond activation and shorter, stronger Cu–S bonds than **1**. As described in a previous analysis,[11d] these differences are consistent with the electron-donating capabilities of their supporting ligands (Me$_3$tacn > Me$_4$pda). Thus, greater electron donation results in more effective Cu^{II} $d_{xy} \rightarrow S_2^{2-}$ σ^* back-bonding[10] and longer S–S, shorter Cu–S, and shorter Cu–Cu distances.

Spectroscopic and electrochemical data provide further support for these notions. Both **1** and **2** are diamagnetic, as revealed by sharp peaks between $\delta = 1$–10 ppm in ^{1}H NMR spectra (RT, CD$_2$Cl$_2$) and, as measured for **1**, EPR silence (X-band, 5 K). Conductivity measurements indicate that **1** is a 1:1 electrolyte in CH$_2$Cl$_2$; thus, dissociation of one O$_3$SCF$_3^-$ ion occurs in solution. UV/Vis spectra (CH$_2$Cl$_2$) exhibit bands with $\lambda_{max} = 370$ nm (**1**, $\varepsilon = 11\,000\,\text{M}^{-1}\text{cm}^{-1}$) or 397 nm (**2**, $\varepsilon = 14\,300\,\text{M}^{-1}\text{cm}^{-1}$) attributable to $S_2^{2-} \rightarrow Cu^{II}$ ligand-to-metal charge transfer (LMCT);[10,11d] the 27-nm shift to longer wavelength (lower energy) for **2** is consistent with the greater electron density provided by its Me$_3$tacn ligands. The relative

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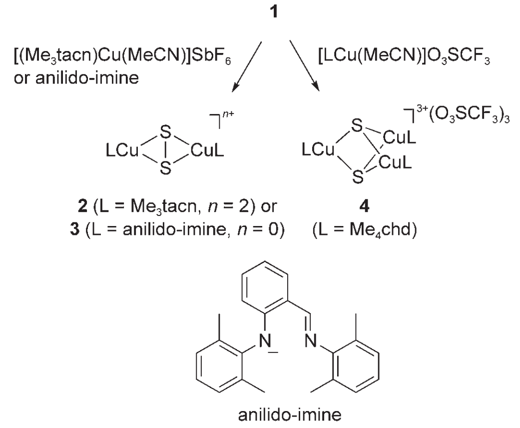
electron-releasing capabilities of the amine ligands are further reflected by the $\tilde{\nu}$(CO) values for their [LCu^I(CO)] complexes, although the difference is small (CH_2Cl_2): 2095 (L = Me_4pda) versus 2091 cm^{-1} (L = Me_3tacn). Resonance Raman spectra (λ_{ex} = 457.9 nm) contain intense, S-isotope sensitive peaks at 485 cm^{-1} (Δ^{34}S = 15 cm^{-1}) and 477 cm^{-1} (Δ^{34}S = 14 cm^{-1}) for **1** and **2**, respectively, that we assign as predominantly $\tilde{\nu}$(S–S) modes. The lower frequency of this feature for **2** than **1** is consistent with their respective S–S bond lengths (greater in **2** than **1**).[13] Finally, irreversible reductions were observed in cyclic voltammograms (0.4 M Bu_4NPF_6 in CH_2Cl_2, vs. $[Fe(C_5H_5)_2]/[Fe(C_5H_5)_2]^+$, 50 mV s^{-1}) of **1** and **2** at −300 mV and −765 mV, respectively, a difference in oxidizing power that correlates with the results of reactivity studies (see below).

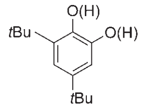
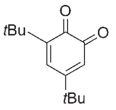
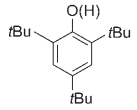
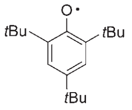
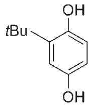
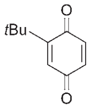
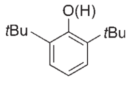
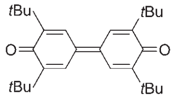
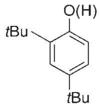
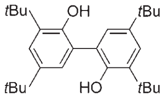
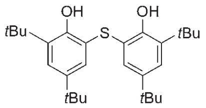
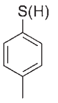
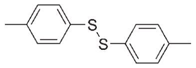
In reactions with PPh_3, CO, benzyl bromide, and 2,6-dimethylphenylisocyanide (ArNC), **1** and **2** behave similarly to each other and to other $\{Cu_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)\}^{2+}$ complexes.[11c,d] Thus, in quantitative reactions sulfur is transferred to PPh_3 to yield S=PPh_3, and sulfur is displaced by CO and ArNC to yield $[LCuCO]^+$ and $[LCuCNAr]^+$, respectively (but no SCNAr is observed[9b,11c]). The compounds are unreactive with benzyl bromide. Complex **1** cleanly converts (greater than 95 % yield) to the evidently more thermodynamically stable $\{Cu_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)\}^{2+}$ complexes **2** and **3** (Scheme 1) upon treatment of **1** in CH_2Cl_2 with $[(Me_3tacn)Cu(MeCN)]SbF_6$ or with a relatively unhindered anilido-imine ligand, respectively. Supporting ligand, redox, and disulfide exchange processes (or a combination thereof) may be involved in these reactions, which are similar to others reported previously.[11b,c]



Scheme 1. Some reactions of compound **1**.

Unique conversions were observed for other reactions of **1**, however (Scheme 1, Table 1). Treatment of **1** in CH_2Cl_2 with $[(Me_4chd)Cu(MeCN)]O_3SCF_3$[12] yielded the known cluster **4**.[5,7] This reaction involves conversion of a $\{Cu_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)\}^{2+}$ core to a $\{Cu_3(\mu\text{-}S)_2\}^{3+}$ unit, which has parallels in copper–oxygen chemistry.[14] Perhaps most interesting are the oxidations of phenolic or phenolate compounds and 4-methylbenzenethiol or -thiolate by **1** (Table 1).[15] In each case, addition of the substrate to a solution of **1** in CH_2Cl_2 caused rapid bleaching of the solution color and deposition of a red-brown precipitate (presumably CuS, although we have not determined the composition of this material). Analysis of the soluble fraction by ^{1}H NMR spectroscopy, ESI-MS, GC–MS, and (for the reaction with 2,4,6-tri-*tert*-butyl phenol) EPR and UV/Vis spectroscopy revealed complete consumption of **1** and formation of the products listed in Table 1. Quantitative recovery of the N-donor ligand (in protonated form, Me_4pdaH^+) was also determined from ^{1}H NMR spectra. From these data and from results of experiments using different molar ratios of the reactants, we deduced that **1** acts as a two-electron oxidizing agent, analogous to bis(μ-oxo)-/peroxodicopper systems.[16] In a particularly intriguing transformation with synthetic potential, substrate oxidation is accompanied by sulfur insertion in the reaction with 2,4-di-*tert*-butylphenol and -phenolate (entry 5).

Table 1: Summary of the results of oxidation reactions of **1**.

Entry	Equiv[a]	Substrate[b]	Product(s)[c]	Yield(s) [%][d]
1	1			> 95
2	2			85 (> 95)
3	1			> 95
4	1			> 95
5	2		 + 	29 (25) 43 (63)
6	2			> 95

[a] Equivalents of substrate that react with **1** according to the reaction stoichiometry. [b] Substrates denoted with −O(H) or −S(H) were used in protonated (e.g. phenol) and deprotonated (e.g. phenolate) forms. [c] Product(s) identified by ^{1}H NMR spectroscopy, ESI-MS, and GC–MS, except the following: entry 2, product identified by UV/Vis and EPR spectroscopy; entry 5, product identified by ^{1}H NMR spectroscopy only. See the Supporting Information for details. [d] For entries 2, 5, and 6, the yields are listed for the phenols, with those for the phenolates in parentheses.

In contrast to the above oxidations observed for **1**, no redox reactions were observed upon treatment of **2** with the representative substrates 3,5-di-*tert*-butylcatechol or 3,5-di-*tert*-butylcatecholate under the same reaction conditions. Also, whereas the UV/Vis features for **1** rapidly (minutes, −20 °C) bleached upon treatment with two equivalents of the protic acid ($(Et_3NH)(BPh_4)$), those for **2** remained unperturbed (1 h, RT). Thus, we surmise that the novel, enhanced reactivity of **1** with phenolic and phenolate compounds is largely a consequence of its greater basicity and higher reduction potential compared to **2**. The availability of an open coordination site for substrate binding may also contribute to the greater reactivity of **1**, as seen in previous studies of the reactivity of μ-η^2:η^2-peroxo- and bis(μ-oxo)dicopper analogues.[17]

In summary, two new complexes with $\{Cu_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)\}^{2+}$ cores have been prepared, and their reactivity with a range of potential substrates has been compared. While observed reactivity with PPh_3, CO, benzyl bromide, and ArNC is akin to that observed for other such $\{Cu_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)\}^{2+}$ complexes, entirely new conversions of **1** with an added copper(I) salt (to give **4**) and with phenolic compounds (to give two-electron-oxidized products) were discovered. The contrasting reactivity of **1** and **2** with $(Et_3NH)(BPh_4)$ and 3,5-di-*tert*-butylcatechol and -catecholate illustrate intriguing supporting-ligand effects on the properties of the $\{Cu_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)\}^{2+}$ core.

Experimental Section

1: A solution of Me_4pda (155 mg, 1.19 mmol) in THF (2 mL) was added to a solution of $Cu(O_3SCF_3)_2$ (431 mg, 1.19 mmol) in THF (10 mL). The reaction was stirred for 30 min and then Na_2S_2 (66 mg, 0.60 mmol) was added to the green-blue solution. The mixture was then stirred for another 2 h, during which time an orange-brown precipitate formed. The precipitate was collected, washed with THF (20 mL), and dried under reduced pressure. The crude material (270 mg) was then dissolved in CH_2Cl_2 (50 mL), filtered through Celite, and the solvent was removed from the filtrate under reduced pressure to yield an orange powder (240 mg, 54 %). ^{1}H NMR (CD_2Cl_2, 500 MHz): $\delta = 1.72$ (t, 4H), 2.94 (s, 24H), 3.72 ppm (t, 8H);[18] ^{13}C NMR (CD_2Cl_2, 75 MHz): $\delta = 21.9$, 48.3, 58.1 ppm;[18] UV/Vis (CH_2Cl_2): λ_{max} (ε) = 254 (4800), 370 nm (11 000 $M^{-1}cm^{-1}$); elemental analysis (%) calcd for $C_{16}H_{36}Cu_2F_6N_4O_6S_4$ (**1**): C 25.63, H 4.84, N 7.47; found: C 25.68, H 5.07, N 7.22.

X-ray crystal structure analysis of **1**: An orange crystal suitable for X-ray diffraction was obtained from a CH_2Cl_2 solution by slow diffusion of pentane at −20 °C. Crystal data: $C_{16}H_{36}Cu_2F_6N_4O_6S_4$, M_r = 749.81, orthorhombic, space group *Fdd*2, $a = 12.8236(9)$, $b = 47.649(3)$, $c = 9.6062(7)$ Å, $V = 5869.7(7)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.697$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 173(2)$ K, crystal dimensions $0.3 \times 0.3 \times 0.2$ mm^3, $\mu(Mo_{K\alpha}) = 1.810$ mm^{-1}, $\theta = 1.71$–25.03°, 7424 measured reflections, 2219 independent reflections ($R_{int} = 0.0611$), R_1 ($I > 2\sigma(I)$) = 0.0477, wR_2 ($I > 2\sigma(I)$) = 0.1034, GOF = 1.077, 176 parameters, final difference map within 0.499 and −0.522 e Å^{-3}.

2: Elemental sulfur (10 mg, 0.31 mmol) was added to a solution of $[(Me_3tacn)Cu(MeCN)]SbF_6$[19] (160 mg, 0.31 mmol) in CH_2Cl_2 (20 mL). The reaction was stirred for 3 h, filtered through Celite, and the solvent was removed under reduced pressure. The green-brown powder obtained was washed with pentane (2 × 10 mL), extracted with CH_2Cl_2 (3 × 10 mL), and the solvent was removed under reduce pressure to yield **2** as a green-brown powder (188 mg, 60 %). ^{1}H NMR (CD_2Cl_2, 300 MHz): $\delta = 2.95$ (s, 12H), 2.83 ppm (s, 9H); ^{13}C NMR (CD_2Cl_2, 75 MHz): $\delta = 55.9$, 48.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 269 (5800), 397 nm (14 300 $M^{-1}cm^{-1}$); elemental analysis (%) calcd for $C_{18}H_{42}Cu_2N_6S_2Sb_2F_{12}$ (**2**): C 21.51, H 4.16, N 8.21; found: C 21.65, H 4.21, N 8.36.

X-ray crystal structure analysis of **2**: A brown crystal suitable for X-ray diffraction was obtained from a concentrated solution in CH_2Cl_2 at −20 °C. Crystal data: $C_{18}H_{42}Cu_2N_6S_2 \cdot 2(F_6Sb)$, M_r = 1005.28, triclinic, space group $P\bar{1}$, $a = 8.0091(8)$, $b = 9.3236(9)$, $c = 12.2143(12)$ Å, $\alpha = 110.840(4)$, $\beta = 100.412(5)$, $\gamma = 92.959(5)$°, $V = 831.69(14)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.007$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 173(2)$ K, crystal dimensions $0.4 \times 0.3 \times 0.3$ mm^3, $\mu(Mo_{K\alpha}) = 3.082$ mm^{-1}, $\theta = 1.83$–25.05°, 2864 measured reflections, 2864 independent reflections ($R_{int} = 0.028$), R_1 ($I > 2\sigma(I)$) = 0.0473, wR_2 ($I > 2\sigma(I)$) = 0.1118, GOF = 1.089, 195 parameters, final difference map within 2.092 and −1.290 e Å^{-3}. CCDC-657470 and 657471 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) K. Brown, M. Tegon, M. Prudencio, A. S. Pereira, S. Besson, J. J. Moura, I. Moura, C. Cambillau, *Nat. Struct. Biol.* **2000**, *7*, 191 – 195; b) T. Haltia, K. Brown, M. Tegoni, C. Cambillau, M. Saraste, K. Mattila, K. Djinovic-Carugo, *Biochem. J.* **2003**, *369*, 77 – 88.

[2] For example, see: a) T. Rasmussen, B. C. Berks, J. N. Butt, A. J. Thomson, *Biochem. J.* **2002**, *364*, 807 – 815; b) V. S. Oganesyan, T. Rasmussen, S. Fairhurst, A. J. Thomson, *Dalton Trans.* **2004**, 996 – 1002.

[3] a) P. Chen, S. I. Gorelsky, S. Ghosh, E. I. Solomon, *Angew. Chem.* **2004**, *116*, 4224 – 4233; *Angew. Chem. Int. Ed.* **2004**, *43*, 4132 – 4140; b) J. M. Chan, J. A. Bollinger, C. L. Grewell, D. M. Dooley, *J. Am. Chem. Soc.* **2004**, *126*, 3030 – 3031; c) S. I. Gorelsky, S. Ghosh, E. I. Solomon, *J. Am. Chem. Soc.* **2006**, *128*, 278 – 290; d) S. Ghosh, S. I. Gorelsky, S. DeBeer George, J. M. Chan, I. Cabrito, D. M. Dooley, J. J. G. Moura, I. Moura, E. I. Solomon, *J. Am. Chem. Soc.* **2007**, *129*, 3955 – 3965; e) E. Solomon, R. Sarangi, J. Woertink, A. Augustine, J. Yoon, S. Ghosh, *Acc. Chem. Res.* **2007**, *40*, 581 – 591.

[4] J. T. York, I. Bar-Nahum, W. B. Tolman, *Inorg. Chim. Acta* **2007**, DOI: 10.1016/j.ica.2007.06.047.

[5] E. C. Brown, J. T. York, W. E. Antholine, E. Ruiz, S. Alvarez, W. B. Tolman, *J. Am. Chem. Soc.* **2005**, *127*, 13752 – 13753.

[6] J. T. York, E. C. Brown, W. B. Tolman, *Angew. Chem.* **2005**, *117*, 7923 – 7926; *Angew. Chem. Int. Ed.* **2005**, *44*, 7745 – 7748.

[7] J. T. York, I. Bar-Nahum, W. B. Tolman, *Inorg. Chem.* **2007**, *46*, 8105 – 8107.

[8] Y. Lee, A. A. N. Sarjeant, K. D. Karlin, *Chem. Commun.* **2006**, 621 – 623.

[9] a) M. E. Helton, P. Chen, P. P. Paul, Z. Tyeklar, R. D. Sommer, L. N. Zakharov, A. L. Rheingold, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2003**, *125*, 1160 – 1161; b) D. Maiti, J. S. Woertink, M. A. Vance, A. E. Milligan, A. A. Narducci Sarjeant, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2007**, *129*, 8882 – 8892.

[10] P. Chen, K. Fujisawa, M. E. Helton, K. D. Karlin, E. I. Solomon, *J. Am. Chem. Soc.* **2003**, *125*, 6394 – 6408.

[11] a) K. Fujisawa, Y. Moro-oka, N. Kitajima, *J. Chem. Soc. Chem. Commun.* **1994**, 623 – 624; b) E. C. Brown, N. W. Aboelella, A. M. Reynolds, G. Aullón, S. Alvarez, W. B. Tolman, *Inorg. Chem.* **2004**, *43*, 3335 – 3337; c) M. E. Helton, D. Maiti, L. N. Zakharov, A. L. Rheingold, J. A. Porco, Jr., K. D. Karlin, *Angew. Chem.* **2006**, *118*, 1156 – 1159; *Angew. Chem. Int. Ed.* **2006**, *45*, 1138 – 1141; d) E. C. Brown, I. Bar-Nahum, J. T. York, N. W. Aboelella, W. B. Tolman, *Inorg. Chem.* **2007**, *46*, 486 – 496.

[12] Abbreviations: Me_4pda = *N,N,N′,N′*-tetramethylpropanediamine, Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane, Me_4chd = *N,N,N′,N′*-tetramethyl-*trans*-1(*R*),2(*R*)-diaminocyclohexane.

[13] The relationship between the S–S separation and $\tilde{\nu}$(S–S) may be quantified by Badger's rule, as described in reference [11d]. From the observed S–S distances, the predicted $\tilde{\nu}$(S–S) values are 481 cm^{-1} (**1**) and 444 cm^{-1} (**2**). The value for **1** is in excellent agreement with that observed by Raman spectroscopy. We attribute the poorer agreement for **2** to the more complicated set of features in the 400–500 cm^{-1} region of the spectrum for this compound arising from coupling of vibrational modes (i.e. the strong peak at 477 cm^{-1} is likely not a pure S–S stretch).

[14] a) M. Taki, S. Teramae, S. Nagatomo, Y. Tachiu, T. Kitagawa, S. Itoh, S. Fukuzume, *J. Am. Chem. Soc.* **2002**, *124*, 6367 – 6377; b) S. Itoh, S. Fukuzumi, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2081 – 2095.

[15] No reaction was observed (by NMR spectroscopy) upon treatment of **1** in CD_2Cl_2 with 9,10-dihydroanthracene, THF, or aniline (RT, 2–4 h).

[16] E. A. Lewis, W. B. Tolman, *Chem. Rev.* **2004**, *104*, 1047 – 1076.

[17] a) V. Mahadevan, J. L. DuBois, B. Hedman, K. O. Hodgson, T. D. P. Stack, *J. Am. Chem. Soc.* **1999**, *121*, 5583 – 5584; b) V. Mahadevan, M. J. Henson, E. I. Solomon, T. D. P. Stack, *J. Am. Chem. Soc.* **2000**, *122*, 10249 – 10250; c) A. P. Cole, V. Mahadevan, L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Inorg. Chem.* **2005**, *44*, 7345 – 7364.

[18] Because of peak broadening (presumably arising from fluxionality of the propylene backbone), we were unable to assign the coupling constants in the ^{1}H NMR spectrum. Also, we were unable to identify the CF_3 signal in the ^{13}C NMR spectrum owing to the relatively low solubility of **1** in CD_2Cl_2.

[19] The $O_3SCF_3^-$ salt of this complex has been reported: A. P. Cole, V. Mahadevan, L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Inorg. Chem.* **2005**, *44*, 7345 – 7364.