Inorganic Chemistry
COMMUNICATION
pubs.acs.org/IC

Dangling Thiyl Radical: Stabilized in $[PPh_4]_2[(bdt)W^{VI}(O)(\mu\text{-}S)_2Cu^{I}(SC_6H_4S^{\bullet})]$

Moumita Bose, Golam Moula, Ameerunisha Begum, and Sabyasachi Sarkar*

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India

Supporting Information

ABSTRACT: The synthesis, crystal structure, and spectroscopic characterization of $[PPh_4]_2[(bdt)W(O)(S_2)Cu(SC_6H_4S^{\bullet})]$ (**3**; bdt = benzenedithiolate) relevant to the active site of carbon monoxide dehydrogenase are presented. Curiously, in **3**, the copper(I) benzenemonothiolate subcenter possesses a dangling thiyl radical that is stabilized by a disulfido-bridged oxo tungsten dithiolene core. The benzenedithiolate ligand, which is generally bidentate in nature, acts as a bidentate and also as a monodentate in **3**. The formation of an unusual dangling thiyl radical has been magnetically and spectroscopically identified and has been supported by the density functional theory level of calculation.

A transient thiyl radical intermediate is formed in ribonucleotide reductase originating from a cysteine residue in *Escherichia coli*.[1] The ribonucleoside triphosphate reductase from *Lactobacilllus leichmanii* is shown to represent a kinetically competent thiyl radical coupled to cob(II)alamin.[2,3] The stability of a thiyl radical is raised by π conjugation when bridged with the metal d orbitals in a dimeric compound.[4] In a metal-coordinated terminal thiyl radical, $\{M-S^{\bullet}R\}$, the weak M−S bond dissociates, yielding a transient dangling, uncoordinated thiyl radical that dimerizes to form a disulfide bond.[5] It has also been shown that hexanuclear copper(I) thionein under irradiation generated a stable thiyl radical.[6] Searching a stable dangling thiyl radical is a fascinating challenge. Serendipity struck our luck to isolate such a species that is described herein. In carbon monoxide dehydrogenase (CODH) of the aerobic bacterium *Oligotropha carboxidovorans*, the copper-containing molybdoflavoprotein possesses a unique heterometallic Mo−μ-S−Cu dinuclear core (Figure 1).[7,8]

In its proposed catalytic oxidation of carbon monoxide (CO), the role of copper is envisaged to support the insertion of CO within the μ-S−Cu bond with the entire load of redox shuffle on the central molybdenum from Mo^{VI} to Mo^{IV}. Curiously, no role of the terminal cysteine bound as $Cu-S_{cys}$ is noted, although all of the atoms in the $\{Mo-\mu\text{-}S-Cu-S_{cys}\}$ frame are capable of participating in some concerted redox reaction. The heterometallic core structure of CODH has thrown a challenge to engineer a similar atomic assembly as a model.[9,10] Tatsumi and co-workers synthesized the active-site analogue by the reaction of dithiolate with a preorganized dinuclear $\{Mo-(\mu\text{-}S)_2-Cu\}$ diamond core.[9] Such bimetallic Mo−Cu core-containing complexes are known albeit not flanked by dithiolene coordination.[11] The other rational approach to create such a heterometallic core structure is to start with a dithiolene Mo/W moiety as the precursor and reacting it with a copper thiolate fragment. Holm et al. followed this route to synthesize the tungsten analogue of Tatsumi's complex by interaction of a stable monodithiolene {tungsten oxo, sulfido} complex with copper thiolate.[9,10,12] As expected, $[(bdt)Mo^{VI}OS_2Cu^{I}SPh]^{2-}$ (**1**) and $[(bdt)W^{VI}OS_2Cu^{I}S[2,6\text{-bis}(2,4,6\text{-triisopropylphenyl})\text{phenyl}]]^{2-}$ (**2**) (bdt = benzenedithiolate) complexes are found to be structurally similar.[9,10] The use of a monodithiolene {molybdenum(VI) oxo, sulfido} complex as the precursor in such a reaction is difficult because of the inherent instability of the starting {molybdenum(VI) oxo, sulfido} complex where the intramolecular redox reaction between molybdenum(VI) and the coordinated sulfido ligands leads to ready dimerization.[13] To extend our understanding in such chemistry, we followed the strategy of Tatsumi using a $\{W-(\mu\text{-}S)_2-Cu\}$ core as the precursor dimetallic frame and unexpectedly isolated the title product, $[PPh_4]_2[(bdt)W^{VI}(O)(S_2)Cu^{I}(SC_6H_4S^{\bullet})]$ (**3**), with a dangling thiyl radical. The tricoordinated copper(I) of the precursor dimetallic frame is linked to only one of the thiolate sulfurs of the dithiolene (bdt) ligand to yield **3**. **3** was synthesized by reacting either $[O_2W^{VI}S_2Cu^{I}(CN)]^{2-}$ (**4**) or $[O_2W^{VI}S_2Cu^{I}(SPh)]^{2-}$ (**5**) with bdt (Scheme 1).[14] Its X-ray crystal structure shows a $\{(bdt)M(\mu\text{-}S)_2Cu\}$ (M = W) core that is present in **1** (M = Mo) or in **2** (M = W) (Figure 2).[15] However, copper in **3** retains tricoordination, utilizing unicoordination from another bdt and leaving free another uncoordinated sulfur of the bdt ligand.

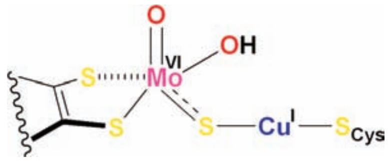
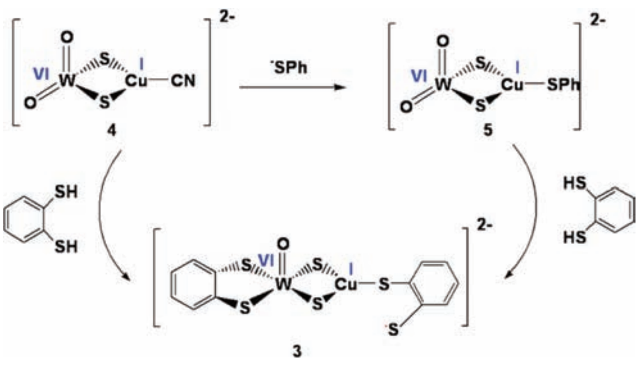


Figure 1. Active-site structure of oxidized [MoCu]-CODH based on X-ray crystallography.[7].

The presence of two counter-monocations in these complexes suggests an overall 2− charge on each of the anions of **1**−**3**, which is consistent with the assignment of the formal oxidation state of an individual metal like $\{M^{VI}Cu^{I}\}$ (M = Mo, W) in the heterometal core. In **3**, the trigonal-planar copper atom is coordinated by one sulfur atom of the bdt ligand. Surprisingly, the other −SH group of the bdt ligand remained uncoordinated. Counting the overall charge on **3**, this −SH group should not be present in anionic form, and in the absence of any ν(SH) in the IR and Raman spectral studies, the entity of the uncoordinated

Received: February 7, 2011
Published: March 31, 2011

Scheme 1. Synthesis of 3



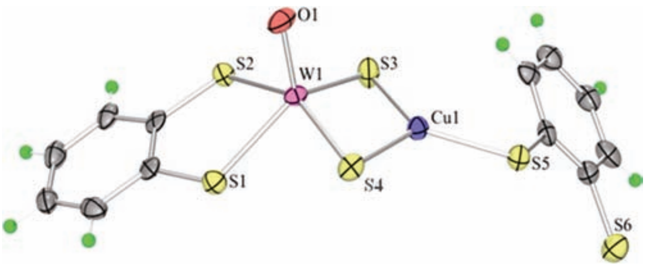


Figure 2. ORTEP view of the anion of **3**, with 50% probability thermal ellipsoids.

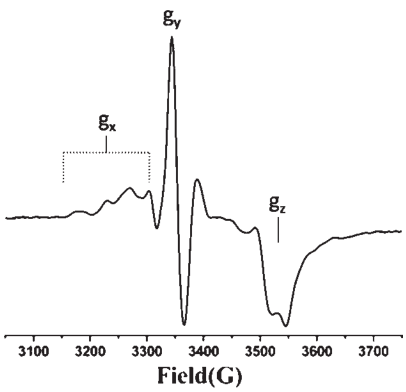


Figure 3. Solid-state EPR (120 K) of complex **3**.

sulfur of the bdt ligand became puzzling.[16,17] Interestingly, **3** is paramagnetic ($\mu_{\mathrm{eff}} = 1.56\ \mu_{\mathrm{B}}$), as measured by the Evans method.[18] Its electron paramagnetic resonance (EPR) spectrum (Figure 3) shows an anisotropic signal at $g_x = 2.08$, $g_y = 2.01$, and $g_z = 1.91$. This EPR signal may best be described as originating from a sulfur-centered (thiyl) radical ($g_y = 2.01$) along with $^{63}\mathrm{Cu}^{\mathrm{I}}$ hyperfine broadening near g_z from the moiety $\{\mathrm{Cu^{I}SPhS^{\bullet}}\}$. A similar EPR profile showing the interaction of copper(I) with a radical in $\mathrm{Cu^{I}NO}$ is documented.[19−21]

Complex **3** shows a reversible cyclic voltammetric reduction at −0.6 V (vs Ag/AgCl), and it displays an electronic absorption band at 1200 nm. These are due to the presence of the thiyl radical (Supporting Information).

It is important to note that the tricoordinated copper(I) is constrained to approach the dangling thiyl sulfur to enhance its coordination number to four because of the hindrance in the rotation of the latter. The structural skeleton of **3** (and also for **1** and **2**) shows the planar phenyl ring (attached to the thiol group, {Cu−S−C(Ph)}) with an angle close to 110° for **3** (113° for **1** and 108° for **2**). Figure 4a presents a view of **3** to show the disposition of the {OW−(μ-S)$_2$−Cu−S5} core aligned with the uncoordinated S6 (thiyl sulfur of bdt) in one plane. Such a rigid arrangement would not allow S6 to participate in bonding with $\mathrm{Cu^{I}}$. An apparent free rotation of the phenyl plane on the monodentate bdt along $\mathrm{Cu^{I}}$−S5−Ph−S6 could have allowed S6 to get close to Cu for bonding. However, the rigid disposition (Figure 4a) is caused by the S5−S6 interaction, as shown in HOMO−8 (Figure 4b).

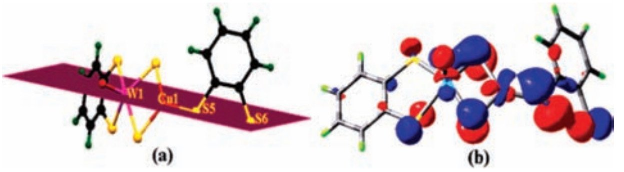


Figure 4. Constraint imposed by S5−S6 interaction restricted rotation of bdt, thus preventing Cu−S6 bond formation.

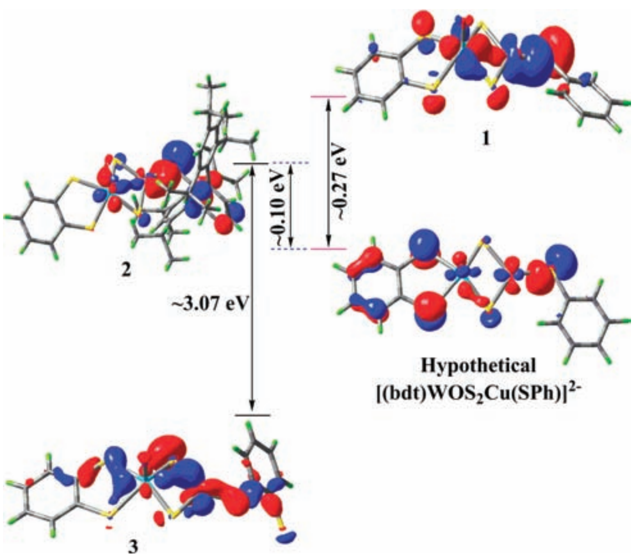


Figure 5. Relative energy (not to scale) and overlap in the respective HOMO−4 for the M−Cu (M = Mo, W) bond in **1** and **2**. Such an overlap is missing in HOMO−4 (and all of the bonding orbital) for the hypothetical $[(\mathrm{bdt})\mathrm{W^{VI}OS_2Cu^{I}(SPh)}]^{2-}$. For **3**, the corresponding metal−metal-bonded orbital, HOMO−21, is much stabilized compared to **1** or **2**.

The density functional theory (DFT) calculation (the RO-B3LYP method) showed that most of the spin density is located at the S6 atom (54%) and at the S5 atom (24%).[22] It is also important to note the presence of a metal−metal (M−Cu) bond in all of these complexes, imparting stability to the heterobimetallic core. Figure 5 presents the relative stability of the respective HOMOs related to the metal−metal bond in complexes **1**−**3**. The extra stabilization in **3** is noted. For the nonformation of $[(\mathrm{bdt})\mathrm{W^{VI}OS_2Cu^{I}(SPh)}]^{2-}$ analogous to **1** and **2**, its computed HOMO−4 does not involve any metal−metal (W−Cu) bond (Figure 5). This may be the reason that the tungsten analogue of

1 with a {Cu−SPh} moiety could not be isolated. This work thus showed the rare dissimilarity in the reactivity between similar molybdenum and tungsten compounds.

In summary, we have shown that complex **3** is described as a species containing a stable dangling thiyl radical. The orbital overlap as shown by DFT between both the sulfurs of the dithiolene of the bdt thus locks the rotation of the phenyl ring, thereby separating the thiyl sulfur and the copper center apart for bonding. Energetically such an arrangement stabilizes over the expected thiophenolato-coordinated complex.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Materials, methods, details of synthesis, spectral, electrochemical, and analytical data of **3**−**5**, computational details, crystal data of **5**, and CIF files of **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: abya@iitk.ac.in.

■ ACKNOWLEDGMENT

M.B. and G.M. thank the Council of Scientific and Industrial Research, New Delhi, India, for the award of doctoral fellowships. A.B. thanks the Department of Science & Technology, New Delhi, India, for the award of a fast track scheme for young scientists.

■ REFERENCES

(1) Himo, F.; Siegbahn, P. E. M. *Chem. Rev.* **2003**, *103*, 2421.

(2) Licht, S.; Gerfen, G. J.; Stubbe, J. *Science* **1996**, *271*, 477.

(3) Booker, S.; Licht, S.; Broderick, J.; Stubbe, J. *Biochemistry* **1994**, *33*, 12676.

(4) Springs, J.; Janzen, C. P.; Darensbourg, M. Y.; Calabrese, J. C.; Krusic, P. J.; Verpeaux, J. N.; Amatore, C. *J. Am. Chem. Soc.* **1990**, *112*, 5789.

(5) Kimura, S.; Bill, E.; Bothe, E.; Weyhermuller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2001**, *123*, 6025.

(6) Sievers, C.; Deters, D.; Hartmann, H. J.; Weser, U. *J. Inorg. Biochem.* **1996**, *62*, 199.

(7) Dobbek, H.; Gremer, L.; Kiefersauer, R.; Huber, R.; Meyer, O. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 15971.

(8) Gnida, M.; Ferner, R.; Gremer, L.; Meyer, O.; Meyer-Klaucke, W. *Biochemistry* **2003**, *42*, 222.

(9) Takuma, M.; Ohki, Y.; Tatsumi, K. *Inorg. Chem.* **2005**, *44*, 6034.

(10) (a) Groysman, S.; Majumdar, A.; Zheng, S. L.; Holm, R. H. *Inorg. Chem.* **2010**, *48*, 1082. (b) Gourlay, C.; Nielsen, D. J.; White, J. M.; Knottenbelt, S. Z.; Kirk, M. L.; Young, C. G. *J. Am. Chem. Soc.* **2006**, *128*, 2164.

(11) (a) Müller, A.; Dartmann, M.; Römer, C.; Clegg, W.; Sheldrick, G. M. *Angew. Chem., Int. Ed.* **1981**, *20*, 1060. (b) Gheller, S. T.; Hambley, T. R.; Rodgers, J. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1984**, *23*, 2519. (c) Acott, S. R.; Garner, D.; Nicholson, J. R.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 713. (d) Maiti, B. K.; Pal, K.; Sarkar, S. *Inorg. Chem. Commun.* **2004**, *7*, 1027.

(12) Groysman, S.; Wang, J. J.; Tagore, R.; Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 12794.

(13) Groysman, S.; Holm, R. H. *Biochemistry* **2009**, *48*, 2310.

(14) Synthetic details of **3**−**5** are in the Supporting Information.

(15) Crystal data for **3**: recorded at 293 K with Mo Kα radiation (0.71073 Å), $C_{60}H_{48}CuOP_2S_6W$, M_r = 1286.67, crystal dimensions 0.03 mm × 0.02 mm × 0.02 mm, triclinic, space group $P\bar{1}$, $a = 10.773(5)$ Å, $b = 10.935(5)$ Å, $c = 23.724(5)$ Å, $\alpha = 79.498(5)°$, $\beta = 86.561(5)°$, $\gamma = 77.836(5)°$, $V = 2685.6(18)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.591$ g cm^{-3}, $\mu = 2.870$ mm^{-1}, $2\theta_{max} = 52°$. Of a total of 14898 reflections collected, 10260 were independent ($R_{int} = 0.0310$). The structure was solved by direct methods and refined by full-matrix least squares on F^2 using *SHELXL* (Sheldrick, 1997). Final R1 [$I > 2\sigma(I)$] = 0.0457 and wR2 = 0.1384 (all data), GOF = 1.091.

(16) Free bdtH_2 displays ν(SH) at 2538 and 2560 cm^{-1}.[17]

(17) Griffith, W. P.; Koh, T. Y. *Spectrochim. Acta* **1995**, *51*, 253.

(18) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(19) Chatgilialoglu, C.; Bertrand, M. P.; Ferreri, C.; Alfassi, Z. B. *Sulfur-centered radicals in organic synthesis, S-centered Radicals*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1999; p 311.

(20) Andrzejewska, E.; Zuk, A.; Pietrzak, J.; Krzyminiewski, R. *J. Polym. Sci.* **1978**, *16*, 2991.

(21) Usov, O. M.; Sun, Y.; Grigoryants, V. L.; Shapleigh, J. P.; Scholes, C. P. *J. Am. Chem. Soc.* **2006**, *128*, 13102 and references cited therein.

(22) See the Supporting Information for full references.