Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 6347–6349 **6347**
DOI: 10.1021/ic900956k

Enhanced Electronic Coupling in a Molecular Pair of Dimolybdenum Units Bridged by a Tetrathioterephthalate Dianion

Mei Juan Han, Chun Y. Liu,* and Peng Fei Tian

Department of Chemistry, Tongji University, Shanghai 200092, People's Republic of China

Received May 15, 2009

Two covalently bonded dimolybdenum units have been assembled with a tetrathioterephthalate dianion (tttp^{2-}), yielding the first full S-donor dimetal molecular dyad $[Mo_2(DAniF)_3](S_2CC_6H_4CS_2)[Mo_2(DAniF)_3]$ (DAniF = *N*,*N*′-di-*p*-anisylformamidinate). This linear molecule has a $Mo_2\cdots Mo_2$ separation of 12 Å as determined by X-ray crystallographic analysis. Large potential separations ($\Delta E_{1/2}$) for the successive oxidations of the two dimetal centers and greatly red-shifted metal-to-ligand charge-transfer absorption have been observed as compared to the terephthalate and dithioterephthalate analogues. In addition, further electrochemical oxidations result in a pair of quasi-reversible two-electron redox waves separated by ca. 250 mV.

Starting with the Cruetz−Taube ion, $\{[Ru(NH_3)_5](pyrazine)[Ru(NH_3)_5]^{5+}\}$, various bridged dinuclear metal complexes, generally designated as A (acceptor)−B (bridging)−D (donor), have long been of interest for the study of electronic coupling interactions.[1] Recently, research in this area has been sparked again, mainly because of the potential that elegantly designed metal-containing molecular chains may be used as electronic devices, such as molecular wires, switches, and rectifiers,[2] in conformance with the trend toward minimization of electronic equipment.[3] By taking advantage of metal complex units as electronic donors and/or acceptors, the dyad molecules are electronically addressable, optically active, and/or magnetically interactive. These properties provide a basis upon which fascinating molecular functions may be established.[4]

A relatively new approach to this area is to employ two equatorially linked dimetal units by a suitable linker. Quadruply bonded Mo_2 and W_2 units have been commonly used as the electron donor/acceptor because of their well-defined electronic configuration and redox activity. A variety of dicarboxylate linkers have been employed to assemble two dimetal building blocks, giving molecules a so-called "dimer of dimers" with a general formula $[M_2](O_2CXCO_2)[M_2]$, where $[M_2]$ represents a dimetal building block supported by auxiliary ligands.[5] However, the O-donor linker is, in general, not desirable in that it offers weak coupling between two metal centers. Thus, significant efforts have been made in searching for proper connectors that are capable of optimizing the metal-to-metal electronic interaction.[6]

It is generally recognized that a narrow energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) would lead to strong electronic coupling interaction. In the system of the "dimer of dimers", this can be realized by replacing the O donor with an S while the remaining part of the bridging ligand stays unchanged. An S donor is less electronegative than O, which increases the energy of the metal-based HOMO while lowering the ligand-based LUMO (π^*). This has been proven both experimentally and theoretically in previous work on the partially S-substituted dithiooxamidate derivative as compared to the corresponding oxamidate analogue.[6d] Enhanced electronic communication has also been observed in the dimetal (M = Mo and W) complex system, where a terephthalate linker is replaced by a dithioterephthalate.[6c] Speaking of a full S-donor ligand, the low-dimensional metal complexes derived from a tetrathiooxalate

---

*To whom correspondence should be addressed. E-mail: cyliu06@mail.tongji.edu.cn.

(1) (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988. (b) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086. (c) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (d) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. *J. Chem. Rev.* **2001**, *101*, 2655.

(2) (a) Liang, W.; Shores, M. P.; Bockrath, M.; Long, J. R.; Park, H. *Nature* **2002**, *417*, 725. (b) Robertson, N.; McGowan, C. A. *Chem. Soc. Rev.* **2003**, *32*, 96. (c) Chae, D. H.; Berry, J. F.; Jung, S.; Cotton, F. A.; Murillo, C. A.; Yao, Z. *Nano Lett.* **2006**, *6*, 165. (d) Ren, T. *Organometallics* **2005**, *24*, 4854. (e) Mahapatro, A. K.; Ying, J.; Ren, T.; Janes, D. B. *Nano Lett.* **2008**, *8*, 2131.

(3) (a) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541. (b) Nitzan, A.; Ratner, M. A. *Science* **2003**, *300*, 1384. (c) Joachim, C.; Ratner, M. A. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 8801.

(4) (a) Xu, G.-L.; Crutchley, R. J.; DeRosa, M. C.; Pan, Q.-J.; Zhang, H.-X.; Wang, X.; Ren, T. *J. Am. Chem. Soc.* **2005**, *127*, 13354. (b) Hamon, P.; Justaud, F.; Cador, O.; Hapiot, P.; Rigaut, S.; Toupet, L.; Ouahab, L.; Stueger, H.; Hamon, J.-R.; Lapinte, C. *J. Am. Chem. Soc.* **2008**, *130*, 17327.

(5) For example, see: (a) Cotton, F. A.; Donahue, J. P.; Murillo, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 5436. (b) Chisholm, M. H.; Patmore, N. J. *Acc. Chem. Res.* **2007**, *40*, 19. (c) Burdzinski, G. T.; Chisholm, M. H.; Chou, P.-T.; Chou, Y.-H.; Feil, F.; Gallucci, J. C.; Ghosh, Y. T.; Gustafson, L.; Ho, M.-L.; Liu, Y.; Ramnauth, R.; Turro, C. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 15247.

(6) (a) Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Villagrán, D.; Wang, X. *J. Am. Chem. Soc.* **2003**, *125*, 13564. (b) Cotton, F. A.; Murillo, C. A.; Villagrán, D.; Yu, R. *J. Am. Chem. Soc.* **2006**, *128*, 3281. (c) Chisholm, M. H.; Patmore, N. J. *Dalton Trans.* **2006**, 3164. (d) Cotton, F. A.; Li, Z.; Liu, C. Y.; Murillo, C. A. *Inorg. Chem.* **2007**, *46*, 7840.

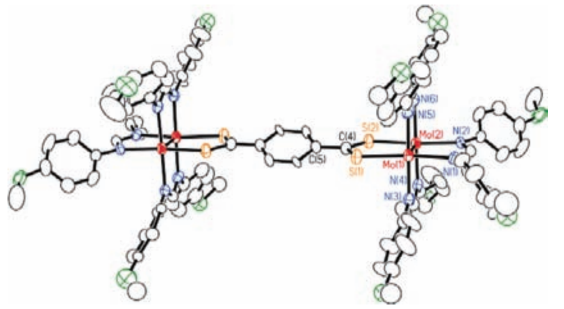


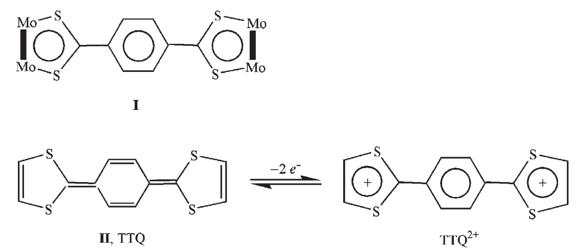
Figure 1. Core structure of **1** with displacement ellipsoids drawn at the 40% probability level. Selected bond distances (Å): Mo(1)−Mo(2), 2.103 (1); Mo−S (av), 2.443[2]; C(4)−C(5), 1.487(8). $Mo_2 \cdots Mo_2$ separation: 12.24 Å.

dianion (tto^{2-})[7] have shown attractive conductive functionalities because of the facilitated electron-hopping pathway. For the same reason, a tetrathioterephthalate dianion (tttp^{2-}) is expected to be a qualified linker that should promote enhanced electronic communication between the linked metal centers. This recognition has led to the first transition-metal tttp complex reported recently;[8] however, given the resultant insoluble zigzag coordination polymers, the electronic properties of this intriguing chalcognide bridging ligand were not examined. Thus, prior to this work, the preparation of metal−tttp dyads, along with the physical study in terms of its functionality of being an electronic bridge, has been an unachieved objective.[6c]

Herein we report the synthesis, structure, and spectroscopic and electrochemical properties of the first dimolybdenum pair linked by a tttp^{2-}, or $[Mo_2(DAniF)_3]_2(\mu\text{-}S_2CC_6H_4CS_2)$ (**1**), where DAniF = *N*,*N*′-di-*p*-anisylformamidinate. Owing to the two electron-rich dimetal coordination units, enhanced electronic coupling and multiple-electron redox processes have been observed.

Compound **1** was prepared by a straightforward procedure. Dimolybdenum precursor $Mo_2(DAniF)_3(O_2CCH_3)$ was mixed with dipiperidinium salt of tetrathioterephthalate[9] in a molar ratio of 2:1 in tetrahydrofuran (THF)/ethanol, producing a dark-green solid of **1** in good yield.[10] The single-crystal structure of **1** is shown in Figure 1.[11] The two Mo_2 units are symmetry-related and have a metal−metal bond distance of 2.103(1) Å, slightly longer than 2.09 Å for the dicarboxylate analogues. The two [Mo_2] units are spaced by the linker by 12.24 Å. The central *p*-phenylene group is not coplanar with the two Mo−Mo vectors but deviates from their mean plane by 27.1°. The bond distance of C(4)−C(5) is 1.487(8) Å, slightly but significantly shorter than a C−C single bond.

Scheme 1. **I**, the Schematic Core of **1** Showing the Metal−Organic Hybridized Conjugated System, and **II**, with TTQ Sharing a Similar Structural Scaffold with **1**[a]



[a] The heavy lines linking two Mo atoms represent metal−metal multiple covalent bonds. The dication TTQ^{2+} possesses an isoelectronic conjugated π system with that of **1**.

In **1**, the Mo_2 unit is coordinated by an S_2C bridging group of the tttp dianion, resulting in a five-membered chelating ring (Mo_2S_2C). Within the Mo_2S_2C moiety, orbital conjugation of δ (Mo_2) with p (S) is invoked. Thus, in terms of Hückel's $4n + 2$ π-electron rule, the cyclic pentakis (dimetaldithiolene) should be considered a pseudoaromatic system with two δ electrons involved. With two such coordination units connected by a *p*-phenyl group, the aromatic core structure of **1** can be schematically represented as **I** (Scheme 1). It is interesting to note that tetrathioquinodimethane (TTQ, **II**), a linear organic tetrathiolene molecule, has a molecular scaffold similar to that of the core of **1**. In earlier work, the TTQ-type compounds were studied as electron donors for conductive charge-transfer complexes.[9,12] As is well-known, many low-dimensional conjugated multisulfur molecules such as tetrathiafulvalene (TTF) are the building blocks of exciting electric and magnetic solids.[13] Unfortunately, the TTQ family, unlike TTF, was not intensively studied because of its extreme air sensitivity as documented.[12] Significantly, tetrametallic complex **1** has an isoelectronic conjugated π system resembling that of the dication TTQ^{2+} with three aromatic units,[12b] as shown in Scheme 1.

As shown in Figure 2, the electronic absorption spectrum of **1** exhibits a shoulder at 386 nm and an intense absorbance at 715 nm. While the first absorbance is attributable to the $\delta \rightarrow \delta^*$ transition of the [Mo_2] units, the second band is due to a metal-to-ligand (linker) charge-transfer (MLCT). It should be noted that the MLCT absorption appears at 492 nm for the terephthalate analogue $[Mo_2(DAniF)_3]_2(\mu\text{-}O_2CC_6H_4CO_2)$[5a] and at 645 nm for the dithioterephthalate analogue $[Mo_2(Bu^tCO_2)_3]_2(\mu\text{-}SOCC_6H_4COS)$.[6c] Steady increases of the wavelengths of the MLCT absorption bands are observed as the O donors on the parent terephthalate linker are

---

(7) (a) Kubo, K.; Nakao, A.; Yamamoto, H. M.; Kato, R. *J. Am. Chem. Soc.* **2006**, *128*, 12358. (b) Pullen, A. E.; Zeltner, S.; Olk, R.-M.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1997**, *36*, 4163.

(8) Neofotistou, E.; Malliakas, C. D.; Trikalitis, P. N. *Inorg. Chem.* **2007**, *46*, 8487.

(9) Ueno, Y.; Bahryand, M.; Okawara, M. *Tetrahedron Lett.* **1977**, 4607.

(10) Preparation of $[Mo_2(DAniF)_3](S_2CC_6H_4CS_2)[Mo_2(DAniF)_3]$ (**1**): A yellow solution of $Mo_2(DAniF)_3(O_2CCH_3)$ (0.102 g, 0.10 mmol) in 10 mL of THF was mixed with dipiperidinium tetrathioterephthalate (0.020 g, 0.05 mmol) in 10 mL of ethanol. After stirring for 2 h, a green microcrystalline product formed, which was filtered and washed with ethanol (2 × 5 mL). Yield: 0.0714 g (67%). Diffusion of ethanol into a dichloromethane solution of the product affords green needle-shaped crystals. ^1H NMR ($CDCl_3$, ppm): 8.50 (s, 2H, −NCHN−), 8.33 (s, 4H, −NCHN−), 8.30 (s, 4H, aromatic H), 6.67 (d, 16H, aromatic H), 6.64 (d, 16H, aromatic H), 6.57 (d, 8H, aromatic H), 6.56 (d, 8H, aromatic H), 3.73 (s, 24H, $-OCH_3$), 3.67 (s, 12H, $-OCH_3$). Anal. Calcd for $C_{98}H_{94}Mo_4N_{12}O_{12}S_4$ (**1**): C, 53.81; H, 4.42; N, 7.84. Found: C, 53.98; H, 4.80; N, 7.52.

(11) Single-crystal X-ray data for $\mathbf{1}\cdot 2.6CH_2Cl_2\cdot 1.5CH_3CH_2OH$ were collected at 293(2) K on a Bruker SMART 1000 CCD area detector system. Structure determination and refinement were carried out using the *SHELXS-97* and *SHELXL-97* programs. Crystal data: $M = 2429.63$, triclinic, space group $P\bar{1}$, $a = 10.458(4)$ Å, $b = 13.999(5)$ Å, $c = 20.600(8)$ Å, $\alpha = 77.172(5)°$, $\beta = 79.503(5)°$, $\gamma = 74.101(5)°$, $Z = 1$, $V = 2804.4(2)$ Å^3. The structure was refined on F^2 and converged for 11 541 unique reflections and 648 parameters to give R1 = 0.1082 and wR2 = 0.1388 and a GOF of 0.963.

(12) (a) Ueno, Y.; Nakayama, A.; Okawara, M. *J. Chem. Soc., Chem. Commun.* **1978**, 74. (b) Yamashita, Y.; Kobayashi, Y.; Miyashi, T. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1052.

(13) (a) Ferraris, J. P.; Cowan, D. O.; Walatka, V., Jr.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. (b) Shibaeva, R. P.; Yagubskii, E. B. *Chem. Rev.* **2004**, *104*, 5347.

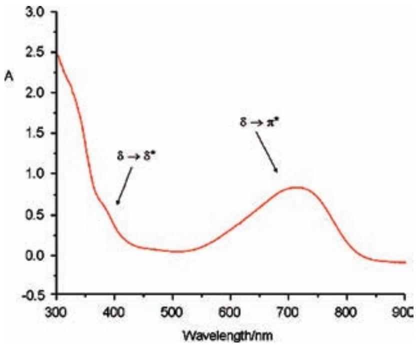


Figure 2. Electronic absorption spectrum of **1** in a CH_2Cl_2 solution at room temperature.

stepwise substituted by S atoms. Therefore, it is indicative that for **1** there exists a smaller energy gap between the metal-based HOMO (*δ*) and ligand-based LUMO (*π**) in comparison with the dicarboxylate-linked and partially S-substituted analogues. According to the electron-hopping mechanism, the unoccupied low-lying orbital from the linker plays a critical role in facilitating electron transfer from metal to metal.

Compound **1** also shows unusual redox behavior. Electrochemical oxidation of the dicarboxylate-linked analogues typically presents a one-electron redox couple because of the conversion of M_2^{4+} to M_2^{5+} (M = Mo, W) or vice versa. As shown in Figure 3, the cyclic voltammogram (CV) of **1** displays two redox couples, each consisting of two well-resolved quasi-reversible waves. According to their current ratio, the low potential couple belongs to the one-electron process but the high potential waves are due to two-electron processes. The two successive one-electron oxidations occur at 0.500 and 0.700 V, respectively, in the potential region where oxidation of dimolybdenum units is normally observed for linked dimolybdenum pairs, and the potential separation ($\Delta E_{1/2}$) is 200 mV. It should be noted that the $\Delta E_{1/2}$ value measured for the terephthalate-bridged analogue is 100 mV.[5a] The reported potential separation for $[Mo_2(Bu^t\text{-}CO_2)_3]_2(\mu\text{-}SOCC_6H_4COS)$ is 184 mV.[6c] The increased $\Delta E_{1/2}$ dictates that in **1** strong electronic communication is established between the two dimetal centers. Compound **1** has a $Mo_2 \cdots Mo_2$ separation 1 Å longer than that of its counterpart $[Mo_2]$(terephthalate)$[Mo_2]$ (ca. 11.2 Å), with weaker electrostatic interaction being imposed upon the dimetal centers. Therefore, the enhancement of the coupling effect for **1** should be attributed to the optimized electronic resonance of the metal center with the tetrathio linker, which consequently increases the extent of electron delocalization over the entire molecule.[14] Strong electronic communication for **1** is also manifested as a comparison is made between **1** and $[Mo_2]$(oxalate)$[Mo_2]$. The oxalate derivative has a $\Delta E_{1/2}$ value of 204 mV, approximately the same as that of the compound investigated, although it has a much shorter $Mo_2 \cdots Mo_2$ separation (ca. 7 Å).[5a] In this case, coulombic force makes a great contribution to the electronic communication as measured by $\Delta E_{1/2}$, but does not account for the electron delocalization. From this point of view, substitution of an O donor by S for the bridging ligand is an efficient way to facilitate intramolecular electron transfer without shortening the path. Therefore, this approach is particularly applicable for long-range electronic coupling interactions. Although the two-electron redox processes are not well understood at this time, it appears that the two electron-rich coordination units of the molecule are responsible for this unusual electrochemical behavior. Given the similar $\Delta E_{1/2}$ values for both of the two redox pairs, it seems that the two-electron processes are coupled by the same physical origin as the single-electron waves. Nevertheless, it is evident that, compared with other members of this complex family, compound **1** is capable of sustaining a high degree of positive charge.

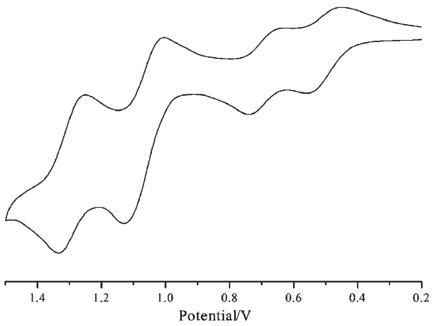


Figure 3. CV for **1** in a CH_2Cl_2 solution with potentials vs Ag/AgCl, a scan rate of 100 mV/s, and 0.1 M Bu_4NPF_6 as the electrolyte. $E_{1/2}(0/1+)$ and $E_{1/2}(1+/2+)$ are 0.500 and 0.700 V, respectively, and $E_{1/2}(2+/4+)$ and $E_{1/2}(4+/6+)$ are 1.070 and 1.300 V, respectively. Under the same conditions, $E_{1/2}$ for the Fc/Fc^+ couple appeared at 0.54 V.

In summary, we have synthesized, structurally characterized, and studied the first dimolybdenum dyad having a tetrathio linker, $[Mo_2](S_2CC_6H_4CS_2)[Mo_2]$. By introduction of S donors onto the linker, long-range electronic coupling and multiple electron redox processes have been observed. Therefore, this work provides an advance for the development of metal-containing conducting molecules.

Acknowledgment. We thank the National Science Foundation of China and the Shanghai Education Committee for financial support.

Supporting Information Available: X-ray crystallographic data for $\mathbf{1}\cdot 2.6CH_2Cl_2\cdot 1.5CH_3CH_2OH$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(14) Evans, C. E. B.; Naklicki, M. L.; Rezvani, A. R.; White, C. A.; Kondratiev, V. V.; Crutchley, R. J. *J. Am. Chem. Soc.* **1998**, *120*, 13096.