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Photochemic Isomerization of a Dinuclear Molybdenum Complex with Ethylene-1,2-Dithiolate and Disulfur Ligands: X-ray Structures of the Two Isomers

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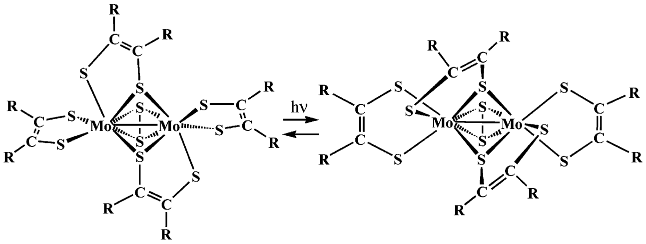
A photochromic complex with disulfur and dimethyl-ethylene-1,2-dithiolate ligands, $[Mo_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Me_2)_2(S_2C_2Me_2)_2]$ (**3**), was synthesized and characterized. Photoirradiation of **3** with visible light resulted in the formation of the isomer (**3′**). The electronic spectrum of **3′** has a new intense peak in the near infrared region, and in the dark, the spectrum returns to that of **3**. X-ray structural analyses of $\mathbf{3}\cdot C_6H_6$ and **3′** revealed a large conformational change of the bridging dithiolate ligands: the two ligands in **3′** come very close to each other compared to those in $\mathbf{3}\cdot C_6H_6$. Crystal data: $\mathbf{3}\cdot C_6H_6$, monoclinic, space group *C*2/*c*, $a = 15.193(4)$ Å, $b = 14.287(3)$ Å, $c = 14.685(4)$ Å, $\beta = 105.30(1)°$, $V = 3074(1)$ Å^3, $Z = 4$; **3′**, monoclinic, space group *C*2/*c*, $a = 21.5400(8)$ Å, $b = 9.5232(5)$ Å, $c = 13.9828(2)$ Å, $\beta = 118.924(1)°$, $V = 2510.5(2)$ Å^3, $Z = 4$. ^{1}H NMR spectra of **3** (3.06, 3.05, 1.66, and 1.31 ppm) and **3′** (2.90, 2.75, 2.14, and 1.97 ppm) are also reported: each spectrum has four signals due to methyl groups, which accords well with the fact that each of the molecules, $\mathbf{3}\cdot C_6H_6$ and **3′**, has a crystallographic 2-fold axis.

Photochemistry of metal complexes is of great current interest. The field is very wide, and many kinds of metal atoms and ligands are the targets of research.[1,2] We have reported on the photochromism of the dinuclear molybdenum and tungsten complexes with diphenyl-ethylene-1,2-dithiolate and disulfur ligands, $[M_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Ph_2)_2(S_2C_2Ph_2)_2]$ (M = Mo (**1**),[3] M = W[4]) (Scheme 1), together with the nonphotochromic complexes $[M_2(\mu\text{-}S_2)_2(\mu\text{-}S_4)(S_2C_2Ph_2)_2]$ (M = Mo (**2**),[3] M = W[4]). Metal dithiolate complexes have attracted much attention due to their versatility.[5] No photochromic complexes, however, have been reported for dinuclear metal complexes having dithiolate ligands, and it is very interesting to find out the structure of the photoirradiated species.

Scheme 1. Photochromic Isomerization of Dinuclear Molybdenum Complexes (R = Ph, Me)



The replacement of the phenyl groups in **1** by methyl groups gave a much more photosensitive photochromic complex, $[Mo_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Me_2)_2(S_2C_2Me_2)_2]$ (**3**), and the X-ray structures of **3** and its isomer obtained with photoirradiation to **3** were successfully determined by X-ray crystallography, which will be reported here.

Complex **3** was prepared from $Na_2[Mo_2(\mu\text{-}S)_2O_2(cys)_2]\cdot 5H_2O$,[6] acyloin, and P_4S_{10}.[7] On exposure to halogen-lamp

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(1) Roundhill, D. M. *Photochemistry and Photophysics of Metal Complexes*; Fackler, J. P., Jr., Ed.; Modern Inorganic Chemistry; Plenum Press: New York, 1994.

(2) For example: (a) Bevilacqua, J. M.; Eisenberg, R. *Inorg. Chem*. **1994**, *33*, 2913−2923. (b) Kato, M.; Kawano, M.; Taniguchi, H.; Funaki, M.; Moriyama, H.; Sato, H.; Matsumoto, K. *Inorg. Chem*. **1992**, *31*, 26−35. (c) Adamson, A. W. *Coord. Chem. Rev*. **1993**, *125*, 1−12. (d) Fanghänel, E.; Poleschner, H. *Z. Chem*. **1979**, *19*, 192−193. (e) Vogler, A.; Kunkely, H. *Inorg. Chem*. **1988**, *27*, 504−507. (f) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc*. **1981**, *103*, 1258−1261.

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(4) Shibahara, T.; Nishiura, K.; Tsuboi, M.; Akashi, H.; Sakane, G. *Chem. Lett*. **2001**, 1002−1003.

(5) For example: (a) Sugimori, A. *J. Photochem. Photobiol. C* **2000**, *1*, 33−56. (b) Falaras, P.; Mitsopoulou, C.-A.; Argyropoulos, D.; Lyris, E.; Psaroudakis, N.; Vrachnou, E.; Katakis, D. *Inorg. Chem*. **1995**, *34*, 4536−4542. (c) Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *J. Am. Chem. Soc*. **1966**, *88*, 5174−5179. (d) McCleverty, J. A.; Locke, J.; Ratcliff, B.; Wharton, E. J. *Inorg. Chim. Acta* **1969**, *3*, 283−286. (e) Bravard, D. C.; Newton, W. E.; Huneke, J. T.; Yamanouchi, K.; Enemark, J. H. *Inorg. Chem*. **1982**, *21*, 3795−3798. (f) McCleverty, J. A. *Prog. Inorg. Chem*. **1968**, *10*, 49−221. (g) Ueyama, N.; Oku, H.; Kondo, M.; Okamura, T.; Yoshinaga, N.; Nakamura, A. *Inorg. Chem*. **1996**, *35*, 643−650. (h) Lim, B. S.; Donahue, J. P.; Holm, R. H. *Inorg. Chem*. **2000**, *39*, 263−273. (i) Hille, R. *Chem. Rev*. **1996**, *96*, 2757−2816. (j) Johnson, M. K.; Lee, D. C.; Adams, M. W. W.; *Chem. Rev*. **1996**, *96*, 2817−2839.

(6) Shibahara, T.; Akashi, H. *Inorg. Synth*. **1992**, *29*, 254−260.

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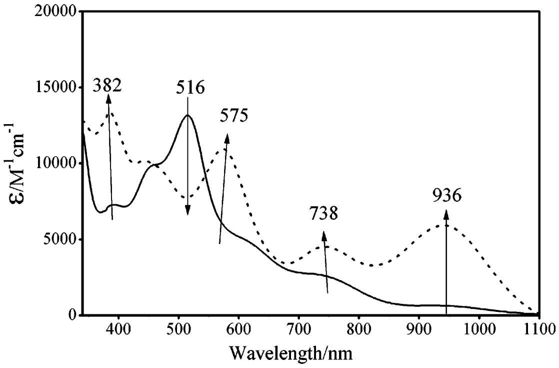

Figure 1. Electronic spectra of photochromic molybdenum complexes in CH_2Cl_2: **3** before halogen-lamp light exposure (—) and **3′** after halogen-lamp light exposure (···).

light, the solution of **3** in dichloromethane changes from red to pale gray-red. The spectral change is shown in Figure 1: the spectrum in the visible region changes very much, and a new peak appears in the near-infrared region. In the dark, the spectrum returns to the original one in 6 h at room temperature and remains unchanged for more than a week in a freezer (−15 °C). The feature of the spectral change of **3** is very similar to that of **1** in the appearance of a new intense peak in the near-infrared region on exposure to light. Complex **3**, however, is much more sensitive to light than **1**. In addition, the spectrum of the irradiated species of **3** returns much more slowly to the original one (in 6 h as stated above) than that of **1** does (in 5 min).

The high sensitivity of **3** toward light and the high stability of the photoirradiated species (**3′**) enabled us to obtain crystals of **3′**. Irradiation of **3** in dichloromethane with halogen-lamp light was followed by addition of hexane. Storage of the resultant solution in a freezer (−15 °C) gave crystals. Recrystallization of **3** from benzene solution gave crystals suitable for X-ray crystallography. The structures of **3**·C_6H_6 and **3′** were determined by X-ray crystallography,[8,9] and ORTEP figures are shown in Figures 2 and 3, respectively. The complex **3**·C_6H_6 has a 2-fold axis that passes through the midpoints of the two S atoms (μ-S_2) and the two molybdenum atoms, and the conformation is close to that[5e] of **1** except that **3**·C_6H_6 has methyl groups and **1** has phenyl groups (see also Scheme 1). Complex **3′** also has a crystallographic 2-fold axis.

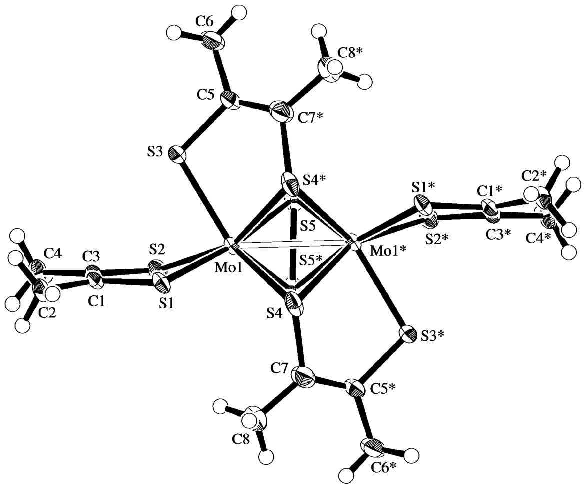

Figure 2. ORTEP drawing of **3**·C_6H_6. Benzene of crystallization was omitted for clarity. Selected bond distances (Å) and angles (deg): Mo1−Mo1*, 2.7874(8); Mo1−S1, 2.3757(9); Mo1−S2, 2.3830(9); Mo1−S3, 2.4485(9); Mo1−S4, 2.4690(9); Mo1−S4*, 2.4670(9); Mo1−S5, 2.4904(9); Mo1−S5*, 2.4291(9); S5−S5*, 2.124(2); S1−Mo1−S2, 80.86(4); S3−Mo1−S4*, 77.76(3); Mo1−S4−Mo1*, 68.76(3); Mo1−S5−Mo1*, 69.01(3).

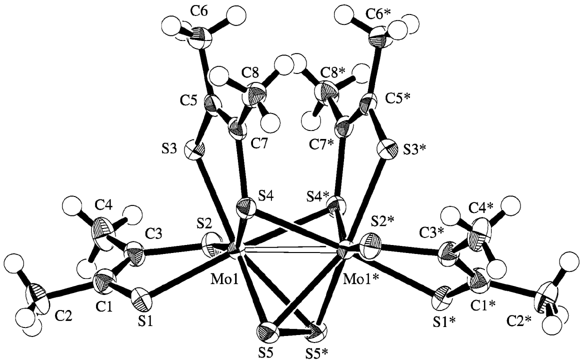

Figure 3. ORTEP drawing of **3′**. Selected bond distances (Å) and angles (deg): Mo1−Mo1*, 2.7605(7); Mo1−S1, 2.368(1); Mo1−S2, 2.410(1); Mo1−S3, 2.401(1); Mo1−S4, 2.414(1); Mo1−S4*, 2.515(1); Mo1−S5, 2.484(1); Mo1−S5*, 2.502(1); S5−S5*, 2.026(2); S1−Mo1−S2, 81.39(4); S3−Mo1−S4, 79.16(4); Mo1−S4−Mo1*, 68.09(3); Mo1−S5−Mo1*, 67.23(3).

A large conformational change is evident for the dithiolate ligands between **3**·C_6H_6 and **3′**. The nonbridging dithiolate ligand shifts from approximately perpendicular to the μ-S_2 ligand in **3**·C_6H_6 to parallel in **3′**, and the bridging dithiolate ligand shifts from approximately parallel to the μ-S_2 ligand in **3**·C_6H_6 to perpendicular in **3′**. The two bridging ligands in **3′** come very close to each other compared to those in **3**·C_6H_6. Both complexes **3**·C_6H_6 and **3′** exhibit a bend of the S−C−C−S ligand plane away from the S−Mo−S plane.[10] Remarkable changes are also observed in some bond

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(7) Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *Inorg. Chem.* **1965**, *4*, 1615−1617. The reaction mixture of 3-hydroxy-2-butanone (0.83 g, 9.4 mmol) and diphosphorous pentasulfide (3.0 g, 6.7 mmol) in toluene (16 mL) was refluxed at 110 °C for 3 h under a dinitrogen atmosphere, and the resultant solution was filtered. The following procedures were done in the dark. To the filtrate were added ethanol (5.0 mL) and $Na_2[Mo_2(\mu\text{-}S)_2O_2(cys)_2]\cdot5H_2O$ (0.104 g, 0.533 mmol) in water (4 mL), the mixture was kept standing in a room temperature for a day with stirring, and then, the resultant suspension was filtered. From the filtrate, the photochromic complex **3** (red, third band; yield 10%) was obtained by column chromatographic separation (*n*-hexane and dichloromethane) together with a mononuclear complex $[Mo(S_2C_2Me_2)_3]$ (green, first band; yield 5%): the precipitate contains a nonphotochromic dinuclear complex $[Mo_2(\mu\text{-}S_2)_2(\mu\text{-}S_4)(S_2C_2Me_2)_2]$ (violet; yield 1%). The solid sample of **3** was obtained by the addition of hexane to the solution. Anal. Found (Calcd for $Mo_2S_{10}C_{16}H_{24}$): C, 26.42 (26.36); H, 3.41 (3.32).

(8) Crystal data for **3**·C_6H_6: formula $Mo_2S_{10}C_{22}H_{30}$, fw 806.96, monoclinic; space group *C*2/*c*, $a = 15.193(4)$ Å, $b = 14.287(3)$ Å, $c = 14.685(4)$ Å, $\beta = 105.30(1)°$, $V = 3074(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.743$ g cm^{-3}, μ(Mo Kα) = 15.06 cm^{-1}, R1 (R_w) = 0.042 (0.122), 2947 reflections with $I > 2.0\sigma(I)$ and 169 variable parameters. Intensity data were collected at −160 °C.

(9) Crystal data for **3′**: formula $Mo_2S_{10}C_{16}H_{24}$; fw 728.85, monoclinic, space group *C*2/*c*, $a = 21.5400(8)$ Å, $b = 9.5232(5)$ Å, $c = 13.9828(2)$ Å, $\beta = 118.924(1)°$, $V =$, 2510.5(2) Å^3, $Z = 4$, D_{calcd} 1.93 g cm^{-3}, μ(Mo Kα) = 18.33 cm^{-1}, R1 (R_w) = 0.036 (0.081) for 1967 reflections with $I > 2.0\sigma(I)$ and 127 variable parameters. Intensity data were collected at −160 °C.

(10) Campbell, S.; Harris, S. *Inorg. Chem.* **1996**, *35*, 3285−3288. Bending angles: (a) **3**·C_6H_6, nonbridging dithiolate ligands, 22.53(9)°, bridging dithiolate ligands, 36.87(9)°; (b) **3′**, nonbridging dithiolate ligands, 22.2(1)°, bridging dithiolate ligands, 16.2(1)°.

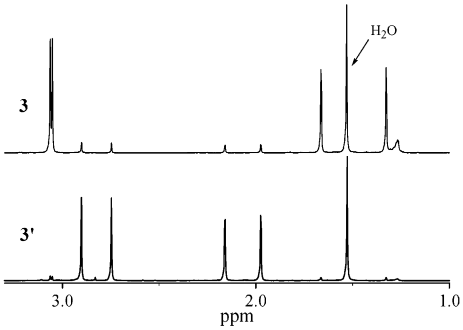

Figure 4. ^{1}H NMR spectra of **3** and **3′** in CH_2Cl_2 at 25 °C.

distances between **3**·C_6H_6 to **3′**: Mo−S (bridging dithiolate ligands, monoligating) distances in **3′** are shorter than those in **3**·C_6H_6; Mo−S (bridging dithiolate ligands, diligating) distances in **3′** are classified into two groups (long and short), while those in **3**·C_6H_6 are virtually identical; S−S (μ-S_2) distance in **3′** is shorter than that in **3**·C_6H_6.

We believe that this is the first example of photochromic isomeric pairs of dithiolate metal complexes characterized by X-ray crystallography. To our knowledge, the only reaction that might be associated with **3** is the photochemical isomerization of $[Cp^*_2Mo_2(S)_2(\mu\text{-}S)_2]$ to $[Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2]$ and $[Cp^*_2Mo_2(S)_2(\mu\text{-}S_2)]$.[11] The reason the irradiated species of **1** is much more short-lived is explained by the bulkiness of the phenyl groups compared to that of methyl groups: more bulky phenyl groups prevent the two bridging dithiolate ligands in **1** from coming close and, therefore, from taking the similar structure to that of **3′**.

^{1}H NMR spectra of **3** and **3′** in dichloromethane, respectively, are shown in Figure 4. Each spectrum has four signals due to methyl groups, which accords well with the fact that each of the molecules, **3**·C_6H_6 and **3′**, has a crystallographic 2-fold axis.

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Supporting Information Available: Tables of X-ray crystallographic data in pdf and CIF formats for **3**·C_6H_6 and **3′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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