Photochromism of Dinuclear Molybdenum Complexes with Disulfur and Ethylene-1,2-dithiolate Ligands

Takashi Shibahara,* Nobuaki Iwai, Mari Sasaki, and Genta Sakane
Department of Chemistry, Okayama University of Science, 1-1 Ridai-cho, Okayama 700

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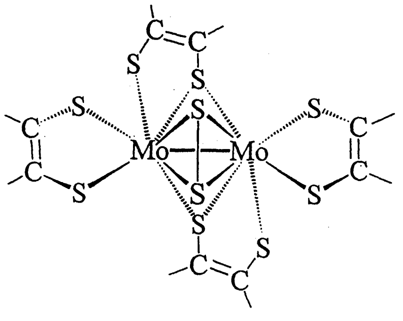
Photochromism was found out for a dinuclear molybdenum complex $[Mo_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Ph_2)_2(S_2C_2Ph_2)_2]$ (**1**), and a similar complex $[Mo_2(\mu\text{-}S_2)_2(\mu\text{-}S_4)(S_2C_2Ph_2)_2]$ (**6**) was found to show no photochromic property. On exposure to sunlight and halogen-lamp light, the color of solution of **1** changes from red-purple to gray. In the dark the color returns to red-purple.

We have recently reported the reaction of incomplete cubane-type molybdenum aqua clusters $[Mo_3(\mu_3\text{-}S)(\mu\text{-}X)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (X=O, S) with acetylene to produce aqua clusters with alkenedithiolate ligands $[Mo_3(\mu_3\text{-}S)(\mu\text{-}X)(\mu\text{-}S_2C_2H_2)(H_2O)_9]^{4+}$.[1] As an extension of the chemistry, we found a photochromic dinuclear molybdenum complex $[Mo_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Ph_2)_2(S_2C_2Ph_2)_2]$ (**1**). Although photochemistry of metal complexes has often been reported, no photochromic complexes have been reported to our knowledge for this type of dinuclear molybdenum complexes.[2]



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The reaction of incomplete cubane-type molybdenum cluster $[Mo_3S_4Cl_4(H_2O)_2(PPh_3)_3]\cdot 3THF$ (**2**) with diphenylacetylene in acetonitrile resulted in decomposition of the Mo_3S_4 core. Thus, when diphenylacetylene (0.028 g) was added to an acetonitrile solution (30 mL) containing **2** (0.050 g; $C_2Ph_2/\mathbf{2} = 5$), a series of color changes occurred: green-yellow → brown → green brown → red-brown.[3] Two kinds of crystalline products were isolated:[4] photochromic dinuclear molybdenum complex **1** (red purple)[5] and a trigonal prismatic mononuclear complex $[Mo(S_2C_2Ph_2)_3]$ (**3**) (dark green),[6] and these structures have been determined by X-ray structural analyses.

Schrauzer and co-workers reported the preparation of $[Mo_2S_2(S_2C_2Ph_2)_4]$ (**4**) from $MoCl_5$, benzoin, and P_4S_{10}, and gave the estimated structure of $[Mo_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]$ in 1966.[7] McCleverty and co-workers reported the preparation of $[Mo_2S_4(S_2C_2Ph_2)_2]$ (**5**) from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, benzoin, and P_4S_{10}, and gave the estimated structure of $[Mo_2(\mu\text{-}S)_4(S_2C_2Ph_2)_2]$ in 1969.[8] Using the same starting materials as those used by McCleverty et al., Newton, Enemark, and co-workers reported the preparation of the dinuclear complexes **1**, $\mathbf{1}\cdot 1.5CH_2Cl_2$ (**1'**), and **5** in 1982,[9] and described the X-ray structure of **1'**,[9] but no photo-chemistry.

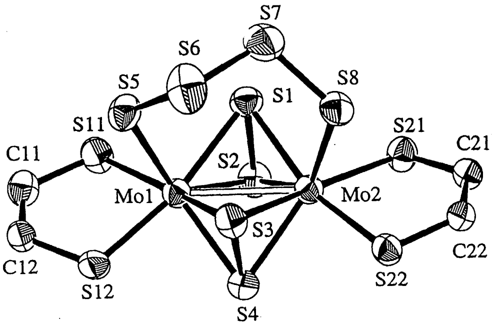

Figure 1. ORTEP drawing of **6**. selected bond distances (Å): Mo1-Mo2, 2.786; Mo1-S1, 2.469(4); Mo1-S2, 2.451(4); Mo2-S1, 2.430(3); Mo2-S2, 2.443(3); Mo1-S3, 2.424(3); Mo1-S4, 2.439(4); Mo2-S3, 2.454(4); Mo2-S4, 2.438(4); Mo1-S5, 2.462(4); Mo2-S8, 2.454(4); Mo1-S11, 2.380(3); Mo1-S12, 2.341(3); Mo2S21, 2.375(3); Mo2-S22, 2.3653(3); S1-S2, 2.043(5); S3-S4, 2.050(5); S5-S6-2.055(6); S6-S7, 2.074(6); S7-S8, 2.062(5). Phenyl groups are omitted for clarity.

Following the procedure by Newton, Enemark, and co-workers, we obtained three species after column chromatographic separation: **1'**, a novel dinuclear complex $[Mo_2(\mu\text{-}S_2)_2(\mu\text{-}S_4)(S_2C_2Ph_2)_2]$ (**6**; the structure is reported here),[10] and the mononuclear complex **3**. We did not find the dinuclear complex **5**. The complex **6** (Figure 1) has a $\mu\text{-}S_4$ ligand, and no report has appeared on complexes with $\mu\text{-}S_4$ so far, though complexes with terminal S_4 ligands have already been reported.[11] No appreciable difference was observed in the corresponding Mo-Mo, Mo-S, and S-S distances between **1'** and **6**. The peak positions (770sh, 650sh, 542, 460 nm) of the electronic spectrum of **1'** obtained by us (Figure 2) are rather different from those reported by Newton, Enemark, and co-workers (750, 655, 533, 474 nm in CH_2Cl_2).[12] As they noted,[9] slight difference in the synthetic procedure might give different species, or the use of chromatography might be indispensable for the separation of complexes with similar structure. Both factors may be operative.

On exposure to sunlight and halogen-lamp light, solution of **1'** (or **1**) in CH_2Cl_2 changes from red-purple to gray: peak positions are at 965, 770sh, 560, 415sh nm, the effective wave-length region being 580-620 nm. The peak at 542 nm disappears and two peaks appear: a peak at 560 nm in visible region and a broad peak at 965 nm in near infrared region. In the dark the color returns to original red-purple in a few minutes in room temperature, and much slower in an ice bath.

It is very interesting that compound **1** having $\mu\text{-}S_2$, $\mu\text{-}S_2C_2Ph_2$, and $S_2C_2Ph_2$ ligands shows photochromism, while

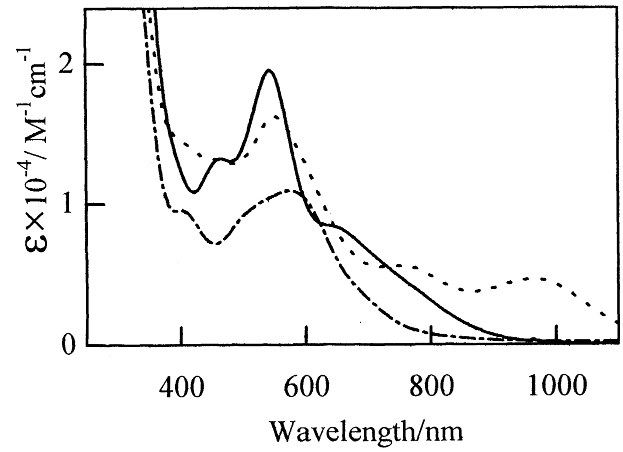

Figure 2. Electronic spectra of dinuclear molybdenum complexes in CH_2Cl_2.

———— **1** before sunlight exposure.

········ **1** after sunlight exposure.

·—·—·—· **6** before and after sunlight exposure.

compound **6** having μ-S_2, μ-S_4, and $S_2C_2Ph_2$ ligands does not. Isomerization or deformation of the molecule **1** might be the cause of the photochromism, but we cannot specify it at present. We are also planning to characterize metal complexes with 1,2-dithiolene and sulfur (S_n) ligands on photochromism.

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References and Notes

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3 Addition of an equivalent amount of C_2Ph_2 also caused the series of color change, though the reaction was slower.

4 Manual separation or column chromatographic separation on a column on silica gel was necessary for complete separation: yields are very low (less than 1%).

5 Crystal data for **1**: Formula $Mo_2S_{10}C_{56}H_{40}$, M_w = 1255.41, orthorhombic, space group P_{bca}, a = 30.892(2)Å, b = 18.887(3) Å, c = 17.995(2) Å, V = 10499(3) Å^3, Z = 8, D_c = 1.550 g cm^{-3}, $R(R_w)$= 6.3(6.4)% for 1853 reflections ($I \geq 3.0\sigma(I)$).

6 Details to be published elsewhere.

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10 Crystal data for **6**: Formula $Mo_2S_{12}C_{28}H_{20}$, Mw = 933.07, monoclinic, space group $P2_1/c$, a = 12.765(3)Å, b = 21.102(7) Å, c = 12.614(2) Å, V = 3389(1) Å^3, β = 94.11(2)°, Z = 4, D_c = 1.829 g cm^{-3}, $R(R_w)$ = 6.0 (7.3)% for 3086 reflections ($I \geq 2.0\sigma(I)$).

11 For example, D. Coucouvanis, A. Toupadakis, S.-M. Koo, and A. Hadjikyriacou, *Polyhedron*, **8**, 1705 (1989), and the references therein.

12 We got the same species **1'** as Newton, Enemark, and co-workers did and this has been supported by a single crystal X-ray analysis.