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

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Novel photochromic and non-photochromic ethylene-1,2-dithiolato dinuclear tungsten complexes, $[W_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Ph_2)_2(S_2C_2Ph_2)_2]$ (**2a**) and $[W_2(\mu\text{-}S_2)_2(\mu\text{-}S_4)(S_2C_2Ph_2)_2]$ (**2b**), respectively, were synthesized and characterized.

Investigation into complexes with ethylene-1,2-dithiolate ligands started very actively in 1960’s in the field of bioinorganic chemistry.[1] Recently the complexes have received a renaissance through the finding that many molybdenum and tungsten redox enzymes have ethylene-1,2-dithiolatate moieties connecting pterin and phosphate groups as cofactors.[2–8] However photochromism of ethylene-1,2-dithiolate complexes has not been fully developed.[9]

We have recently reported that the ethylene-1,2-dithiolato dinuclear molybdenum complex $[Mo_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Ph_2)_2\text{-}(S_2C_2Ph_2)_2]$ (**1a**) is photochromic, but the complex $[Mo_2(\mu\text{-}S_2)_2(\mu\text{-}S_4)(S_2C_2Ph_2)_2]$ (**1b**) shows no photochromism, though **1b** has the same and additional ligands as **1a** does.[10]

It is interesting to compare the molybdenum complexes with corresponding congeneric tungsten ones. We describe here the preparation, X-ray structures and characterization of the photochromic and non-photochromic dinuclear tungsten dithiolato complexes $[W_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Ph_2)_2(S_2C_2Ph_2)_2]$ (**2a**) and $[W_2(\mu\text{-}S_2)_2(\mu\text{-}S_4)(S_2C_2Ph_2)_2]$ (**2b**), respectively. No photochromic dinuclear tungsten complexes with dithiolate ligands have been reported so far.

The novel tungsten complexes **2a** and **2b** were obtained by the similar procedures to those described for the molybdenum complexes **1a** and **1b**. The reaction mixture of benzoin (20 g) and P_4S_{10} (20 g) in 1,4-dioxane (120 mL) was refluxed for 2 h under a dinitrogen atmosphere, and the resultant solution was filtered. To the filtrate was added $(NH_4)_2WS_4$ (6.3 g) in water (80 mL), and the mixture was refluxed further for 1.5 h under a dinitrogen atmosphere, and then filtered. From the filtrate the dinuclear complexes **2a** (deep red) and **2b** (red) were separated column chromatographically, together with a mononuclear tungsten complex $[W(S_2C_2Ph_2)_3]$ (**2c**, green).[11] During the chromatographic separation, the column was covered with black paper to protect from light.

The tungsten complexes **2a** and **2b** are isomorphous with the molybdenum complexes **1a** and **1b**, respectively,[12] and the X-ray structures are shown in Figures 1(**2a**) and 2(**2b**). The synthesis and characterization of **2c** were reported more than three decades ago,[13] and the X-ray structural determination was made very recently.[6]

The tungsten complex **2a** shows photochromism. Exposure of halogen-lamp light to the solution of **2a** in dichloromethane caused a decrease of the peak at 505 nm and an appearance of a new peak at 850 nm (Figure 3) with no distinct color change, and in the dark the spectrum returns to the original one in a few hours at room temperature, while a distinct color change of **1a** was observed: from red-purple to green via gray, returning to the original color in a few minutes at room temperature. Contrarily, neither **2b** nor **1b** shows photochromism.

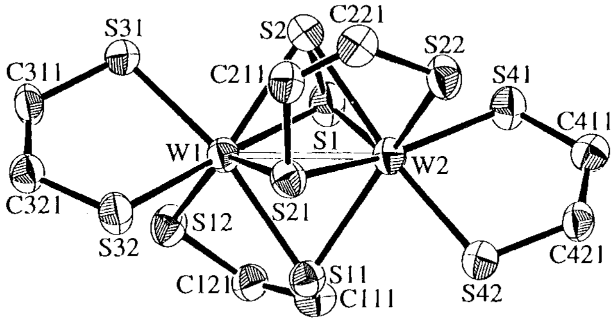

Figure 1. ORTEP drawing of **2a**. Selected bond distances (Å): W1-W2, 2.7923(4); W1-S1, 2.503(2): W1-S2, 2.429(2); W1-S11, 2.463(2); W1-S12, 2.427(2); W1-S21, 2.465(2); W1-S31, 2.363(2); W1-S32, 2.362(2); W2-S1, 2.440(2); W2-S2, 2.495(2); W2-S11, 2.473(2); W2-S21, 2.457(2); W2-S22, 2.439(2); W2-S41, 2.358(2); W2-S42, 2.360(2); S1-S2, 2.057(3). Phenyl groups are omitted for clarity.

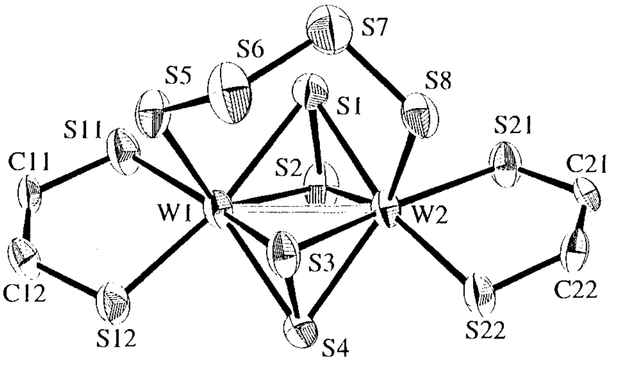

Figure 2. ORTEP drawing of **2b**. Selected bond distances (Å): W1-W2, 2.7913(7); W1-S1, 2.477(4); W1-S2, 2.456(4); W2-S1, 2.434(4); W2-S2, 2.443(4); W1-S3, 2.430(4); W1-S4, 2.450(4); W2-S3, 2.458(4); W2-S4, 2.445(4); W1-S5, 2.444(4); W2-S8, 2.443(4); W1-S11, 2.375(4); W1-S12, 2.343(4); W2-S21, 2.370(3); W2-S22, 2.361(4); S1-S2, 2.059(6); S3-S4, 2.072(6); S5-S6-2.056(6); S6-S7, 2.081(7); S7-S8, 2.055(6). Phenyl groups are omitted for clarity.

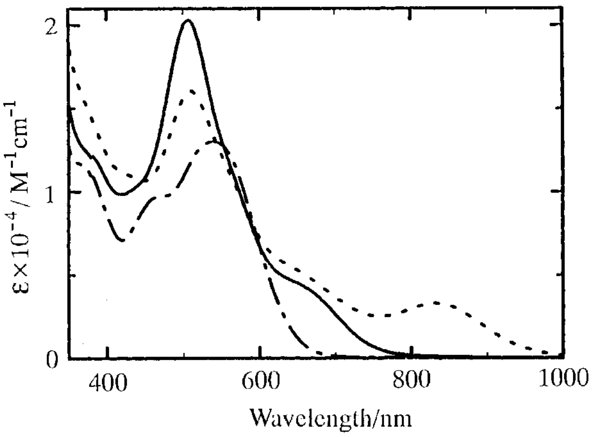

Figure 3. Electronic spectra of dinuclear tungsten complexes in CH_2Cl_2. ———— : **2a** before light exposure; ········ : **2a** after light exposure; —·—·—· : **2b** before and after light exposure.

The tungsten complex **2a** is sensitive even to the light of a fluorescent lamp for indoor lighting, and is less stable to light than the molybdenum complex **1a** is: continuous irradiation of the fluorescent light to the complex **2a** in dichloromethane for a week causes color change from deep red to green, which indicates degradation of **2a** and formation of **2c**, while the molybdenum complex **1a** remains unchanged under the same condition. The longer lifetime of the photo-exited state of **2a** compared to that of **1a** may be responsible for the easier degradation of **2a**.

Holm and coworkers reported the preparation, characterization, and X-ray structures of $[W_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]^{2-}$ (**3**)[6] and $[Mo_2(\mu\text{-}S)_2(S_2C_2Me_2)_4]^{2-}$ (**4**)[7] obtained from $(Et_4N)_2$-$[WS(S_2C_2Ph_2)_2]$ and tropylium hexafluorophosphate and from $[Mo(CO)_2(S_2C_2Me_2)_2]$ and Na_2S, respectively, where they referred to no photochromism of these species. Moreover, very recently we have succeeded in the reduction of **1a** to give $[Mo_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]^{2-}$ (**5**), and found that the reduced species **5** did not show any photochromism.[14] Accordingly, the complex **3** can be considered as a reduced species of **2a**.

Density functional theory (DFT) has predicted that the presence of the bridged dithiolate ligand in the molybdenum complex **1a** is most probably responsible to the photochromic properties.[15] Therefore, both the bridged dithiolate ligands and the μ-S_2 moieties in **1a** and **2a** seem to play important roles in the photochromism.

We are trying to find out structures of the photo-activated species of **1a** and **2a**.

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11 Anal. of **2a**. Calcd for $W_2S_{10}C_{56}H_{40}$: C, 48.00; H, 2.88%. Found: C, 48.15; H, 2.84%. Anal. of **2b**. Calcd for $W_2S_{12}C_{28}H_{20}$: C, 30.33; H, 1.82%. Found: C, 29.39; H, 1.85%.

12 Crystal data for **2a**: Formula, $W_2S_{10}C_{56}H_{40}$, MW = 1401.2, orthorhombic, space group *Pbca* (#61), a = 30.909(4) Å, b = 18.912(3) Å, c = 17.959(3) Å, V= 10497(4) Å^3, Z = 8, D_{calc} = 1.773 g cm^{-3}, R (R_w) = 0.030 (0.028). Crystal data for **2b**: Formula $W_2S_{12}C_{28}H_{20}$, MW = 1108.9, monoclinic, space group $P2_1/c$(#14), a = 12.7613(4) Å, b = 21.153(1) Å, c = 12.5887(5) Å, β = 94.109(3)°, Z = 4, V= 3389.5(2) Å^3, D_{calc} = 2.173 g cm^{-3}, R (R_w) = 0.063 (0.096).

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