Redox Chemistry of Dinuclear Molybdenum Dithiolene Complexes. Interconversion of the Bridging Disulfide and Sulfides

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The redox properties of a photochromic dinuclear molybdenum complex, $[Mo_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Ph_2)_2(S_2C_2Ph_2)_2]$ (**1**), were examined. Conventional and thin-layer cyclic voltammetric measurements showed that **1** undergoes two-electron reduction followed by chemical reactions to give $[Mo_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]^{2-}$ (**2**), which was structurally characterized by X-ray crystallography. The overall two-electron oxidation product of **2** was converted to **1** via formation of four bonds.

The chemistry of molybdenum-sulfur complexes has been expanded markedly during last two decades in connection with bioinorganic[1] and catalytic[2] aspects. In a series of synthetic and structural studies of di-, tri- and tetra-nuclear sulfur-bridged molybdenum complexes, we have found that the dinuclear complex, $[Mo_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Ph_2)_2(S_2C_2Ph_2)_2]$ (**1**),[3] exhibited photochromism.[4] As an extension of our sulfur-bridged dinuclear molybdenum chemistry, we describe the chemically and electrochemically unique redox properties for the reduction of **1** and the oxidation of $[Mo_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]^{2-}$ (**2**), which is the reduction product of **1**.

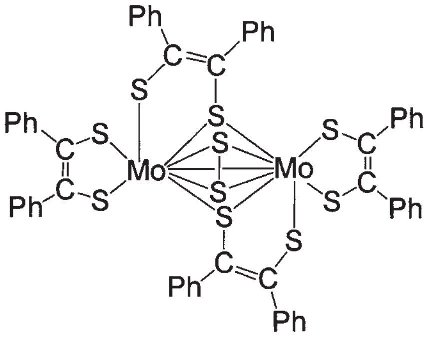

Figure 1. Structure of the photochromic dinuclear molybdenum complex, $[Mo_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Ph_2)_2(S_2C_2Ph_2)_2]$ (**1**).

Figure 2A shows cyclic voltammograms of **1** on a platinum disk electrode in dichloromethane at 25 °C. A negative potential scan initiated at 0 V gives a diffusion-controlled reduction peak around −0.7. Bulk controlled potential coulometric and thin-layer cyclic voltammetric measurements reveal that the number of electrons for the reduction is two. No appreciable reoxidation peak corresponding to the reduction peak appears around −0.6 V on the reverse scan even with a scan rate of $100\,V\,s^{-1}$. The chemically irreversible reduction proceeds in an EC mechanism[5] involving a fast chemical reaction. The EC product is the complex **2**, a salt of which was chemically synthesized and structurally characterized (vide infra). The two-electron reduction of **1** may occur first at two molybdenum centers corresponding to the reduction of $Mo^{V}{}_2$ to $Mo^{IV}{}_2$ from the theoretical results using ab initio and hybrid DFT programs.[6] The reduced $Mo^{IV}{}_2$ species, in which disulfide and two dithiolene ligands bridge the two molybdenum centers, is followed by chemical steps involving an intramolecular transfer of two electrons from two molybdenum(IV) to μ-disulfide. The fast chemical reaction process consists of: (1) molybdenum-molybdenum bond cleavage, (2) cleavage of two bonds consisting of molybdenum and bridging dithiolene sulfur and (3) reductive cleavage of bridging disulfide to give two bridging sulfides. These three bond cleavage steps deform the structure of $[Mo^{IV}{}_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Ph_2)_2(S_2C_2Ph_2)_2]^{2-}$ to give the stable centrosymmetric complex **2**.

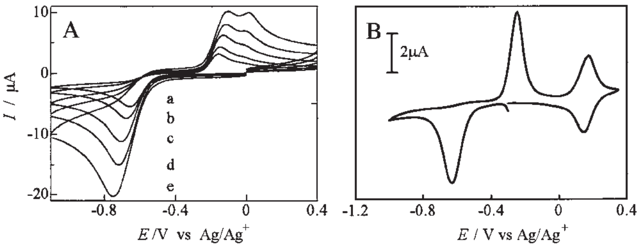

Figure 2. Conventional (A) and thin-layer (B) cyclic voltammograms of 0.2 mM **1** in dichloromethane containing 0.1 M Bu_4NPF_6 with a scan rate of A-a) 0.1, b) 0.2, c) 0.5, d) 1.0, e) $2.0\,V\,s^{-1}$and B) $2\,mV\,s^{-1}$. Reversible redox couple appeared at 0.2 V in B is ferrocene/ferrocenium couple.

A reverse positive potential scan in cyclic voltammograms of the complex **1** gives two oxidation peaks. The peak current ratio of the second oxidation peak around 0 V to the first one around −0.2 V is significantly dependent on the scan rate. The relative second oxidation peak current increases with the scan rate up to $50\,V\,s^{-1}$ and the current ratio becomes close to unity above $v = 50\,V\,s^{-1}$. The complex **2** is consecutively oxidized by one electron to give $[Mo_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]^{-}$ and $[Mo_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]$, respectively. The electrochemical overall two-electron oxidation product $[Mo_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]$ is rapidly converted into the original complex **1** through the bond formation processes, which are in complete contrast to the bond cleavage processes in the reduction of the complex **1**.

Figure 2B shows a thin-layer cyclic voltammetry[7] of **1** with a scan rate of $2\,mV\,s^{-1}$ in dichloromethane. A cathodic potential scan initiated at −0.3 V gives a symmetrical reduction peak with a peak potential of −0.63 V. The peak area corresponding to the charge passed is double that of the oxidation and rereduction peaks for ferrocene that is known to show a reversible one-electron redox. Thus, the reduction process is confirmed to be two electrons. The absence of reoxidation peaks corresponding to the reduction on the reverse positive potential scan indicates again that the reduction process proceeds in an EC mechanism. A symmetrical oxidation peak appears at -0.25 V that corresponds to the potential for the first oxidation peak in conventional cyclic voltammetry. The peak area of the oxidation peak is almost equal to that of the reduction peak. Thus, the oxidation is an overall two-electron process consisting of an ECEC mechanism, in which the chemical reaction product accompanied with the first one-electron oxidation is favorably oxidized with additional one electron at this potential within the time window of thin-layer cyclic voltammetry. The second scan cycle shows the almost identical voltammogram to the first cycle voltammogram. The overall two-electron oxidation product is converted to the original complex **1**. Thus the total electrode reaction is represented as a square two-electron ECEC mechanism.

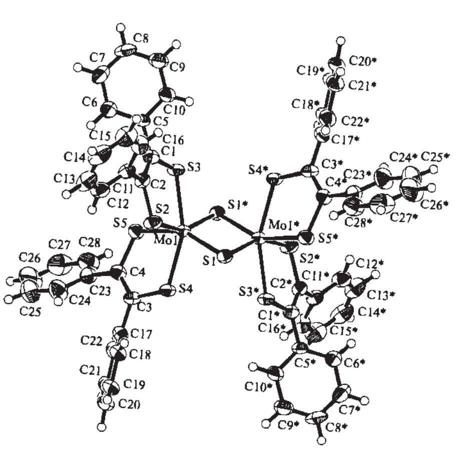

Figure 3. Structure of bis(μ-sulfide) complex **2**. Selected bond distances (Å): Mo1–Mo1*, 3.046(1); Mo1–S1, 2.337(2); Mo1–S1*, 2.329(2); Mo1–S2, 2.435(2); Mo1–S3, 2.405(2); Mo1–S4, 2.406(2); Mo1–S5, 2.437(2), C1–C2, 1.364(9); C3–C4, 1.370(9), and bond angles (°): S1–Mo1–S1*, 98.50(5); Mo1–S1–Mo1*, 81.50(5); S2–Mo1–S3, 78.60(6); S4–Mo1–S5, 78.78(6).

In order to identify the chemical structure of **2**, we have attempted a preparative scale chemical reduction using an appropriate reducing agent. KO_2 reduction in the presence of small amounts of ethanol and stoichiometric amounts of 18-crown-6 to KO_2 afforded the pure crystals of the compound $[K(18\text{-Crown-}6)]_2[Mo_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]\cdot(18\text{-Crown-}6)\cdot 3CH_2Cl_2$ (**2′**).[8] The x-ray structure of the anion of **2′** is shown in Figure 3. Two bis(dithiolato) molybdenum moieties, $Mo(S_2C_2Ph_2)_2$'s, are bridged by two μ-S, and a crystallographic inversion center resides on the midpoint of Mo1 and Mo1*: The two molybdenum and two μ-S atoms are coplanar. The Mo-Mo distance (3.046(1) Å) in **2′** is much longer than those in molybdenum metal (2.72 Å) and in the relevant complex $[Mo_2(\mu\text{-}S_2)(\mu\text{-}S_2C_2Ph_2)_2(S_2C_2Ph_2)_2]\cdot 1.5CH_2Cl_2$ (**1′**) (2.778(1) Å).[3] Therefore, a direct Mo-Mo bond may not exist. The Mo–S (terminal dithiolene) distances (2.405–2.437 Å) are slightly longer than those (2.353–2.382 Å) in **1′**. Two potassium ions are in two of the three 18-crown-6 molecules, respectively, and there is one free 18-crown-6 and three free dichloromethane molecules. The analogous and isostructural molybdenum complex ion, $[Mo_2(\mu\text{-}S)_2(S_2C_2Me_2)_4]^{2-}$ and tungsten complex ion, $[W_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]^{2-}$, have been very recently synthesized utilizing an oxidative dimerization of $[M^{IV}(S_2C_2Ph_2)_2(CO)]$ (M = Mo,[9] W[10]), respectively. Also $[Mo_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)_4]^{2-}$ has been prepared from $[Mo_2S_{10}/S_{12}]^{2-}$ or $[Mo_2S_4(CS_4)_2]^{2-}$ and $MeO_2CC\equiv CCO_2Me$.[11]

The presence of bridging dithiolene and bridging disulfide ligands may be an important factor for photochromism because no photochromic properties are observed in CH_2Cl_2 for the complex ion **2** and $[Mo_2(\mu\text{-}S_2)_2(\mu\text{-}S_4)(S_2C_2Ph_2)]$.[4]

Even if the oxidation process proceeds through the EEC and/or ECEC processes, the overall two-electron reduction-oxidation is formally described in terms of the bridging sulfide/disulfide redox couple. The structurally characterized interconversion involving the four bond cleavages upon reduction and the four bond formations upon oxidation is the first example and helps us to better understand the molybdenum-sulfur redox chemistry[1] in bioinorganic fields.

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8 For desolvated species $[K(18\text{-Crown-}6)]_2[Mo_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]\cdot(18\text{-Crown-}6)$, yield: 63%, elemental analysis (calcd.): C% 53.34(52.70); H% 5.22(5.38), vis. λ/nm(ε): 469(15300); 574(15200); 704(13000), FAB-mass$^-$: 1226(M^-). Uv-vis spectrum of **2′** is consitent with that of electrolytic reduction product of **1** and the multi-scan thin-layer cyclic voltammogram of **2′** is almost same as that of **1**.

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