Binuclear Molybdenum(V)porphyrins Bridged by Benzenediolate or Naphthalenediolate Dianion: Cooperative Coordination Equilibrium of Two Molybdenum Centers Involving Electron Transfer

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(Received September 12, 1996)

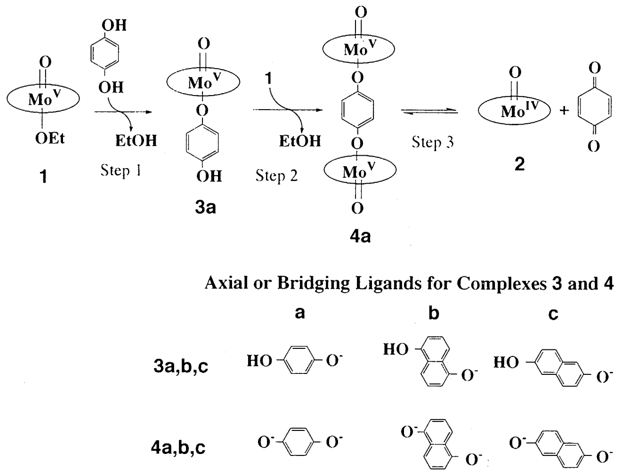
The reactions of molybdenumporphyrin and an aromatic diol were studied. A cooperative coordination of two hydroxyl groups to molybdenum centers was confirmed.

Binuclear complexes of redox-active metal centers linked by a π-conjugated bidentate ligand have attracted attention concerning intramolecular electron transfer process,[1,2] biochemical catalysis,[3] and molecular switches or molecular wires.[4] A bidentate ligand in which two coordination sites are connected by a conjugated π system is expected to be a mediator in the transmission of stimulation from one metal center to the other. The authors found that coordination of aromatic diols at one coordination site to a molybdenum porphyrin stimulated simultaneous coordination of the other site.

The present letter describes formation of binuclear complexes bridged by benzenediolate or naphthalenediolate dianions, and a cooperative manner of two coordination sites of the ligand.

Figure 1(A) shows a time course of UV-vis spectral change for the reaction of oxoethoxomolybdenum(V)tetraphenylporphyrin, Mo^{V}(tpp)(O)(OEt), **1**, (1.11 x 10^{-5} M, M = mol/dm^{-3}) and 1 eq. (0.5 mole/(1 mole of **1**)) of 1,4-benzenediol at 20.0 °C. The spectrum changed gradually with isosbestic points. The product was assigned to a one electron reduced species, **2**.[5,6] Complexes studied are abbreviated as shown in Scheme. The complex **1** was completely reduced to the complex **2** by 1 eq. of 1,4-benzenediol in one day. Isosbestic points indicate that the first step of the reaction is rate-determining and intermediate(s) does not accumulate.

Scheme 1.



In the reaction of **1** with 1 eq. of 1,5-naphthalenediol, the Soret, α, and β bands shifted to 461, 589 and 630 nm, respectively, with isosbestic points, at 20.0 °C. The resulted complex was attributed to a binuclear complex, **4b**. As the temperature was raised, the molybdenum in complex **4b** was reduced slowly to afford the complex **2** and attained an equilibrium with **2**. The final molar ratio of the complex **2** to **4b**

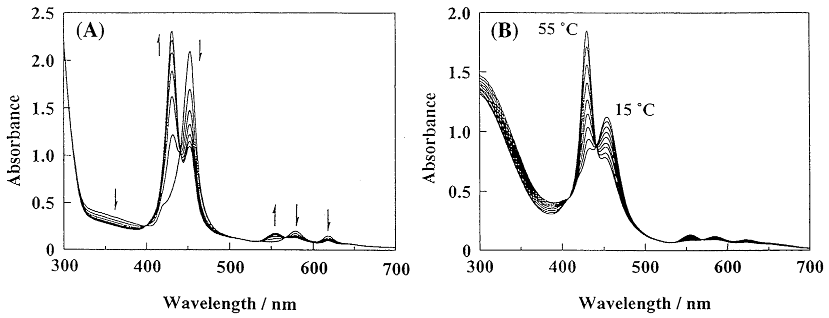


Figure 1. (A). UV-vis absorption spectral change of **1** (1.11 x 10^{-5} mol dm^{-3}) after addition of 1 eq. of 1,4-benzenediol in benzene in an atmosphere of nitrogen at 20.0 °C. Curves show spectra at 0.5, 10, 20, 30, 40, 50, and 60 min after addition of the diol. (B). Temperature-dependence of UV-vis absorption spectra of **2** (1.09 x 10^{-4} mol dm^{-3}) in the presence of 160 eq. of *p*-benzoquinone in toluene in an atmosphere of nitrogen at every 5 °C from 15 to 55 °C.

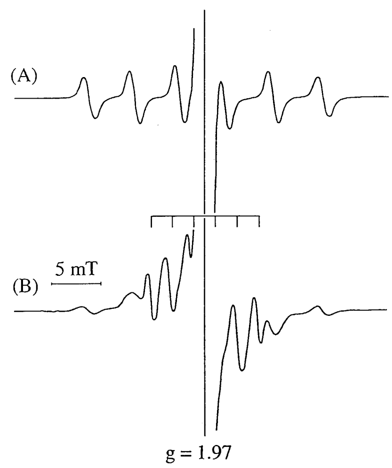


Figure 2. ESR spectra of **1**, in toluene (A), and in the presence of 1 eq. of 1,5-naphthalenediol in toluene under nitrogen (B).

depended on the temperature. The reaction of **4b** to **2** is simultaneous reduction of two molybdenum centers and elimination of quinone. A similar equilibrium was observed when **2** (1.09×10^{-4} M) was mixed with 160 eq. of *p*-benzoquinone. Figure 1(B) shows a thermochromic change in the absorption spectrum. At lower temperatures, the binuclear complex **4a** was formed in preference to **2**. As the temperature was raised, spectrum changed with isosbestic points to one attributable to **2**. The equilibrium was immediately established as the temperature was changed. The similar fast equilibrium was confirmed for the system of **2** and 2,6-naphthoquinone.

The interaction between two molybdenum atoms across the bridging ligand in **4** was examined in the ESR spectra as shown in Figure 2. The complex **1** showed a characteristic signal for mononuclear Mo^V complexes at room temperature and the signal consisted of a strong central line and six hyperfine lines coupled at 46.3×10^{-4} cm^{-1}.[7,8] Upon addition of 1 eq. of 1,5-naphthalenediol, the spectrum was changed to a characteristic spectrum of a binuclear Mo^V complex with a hyperfine coupling constant of 21.0×10^{-4} cm^{-1}. The hyperfine coupling constant demonstrates that two unpaired electrons in two Mo^V centers are fast exchanged across the bridging ligand.[2,9] The similar ESR spectrum was also obtained for the mixture of the complex **2** and *p*-benzoquinone under high concentration conditions (1×10^{-3} M) and assigned to the binuclear complex **4a** bridged by 1,4-benzenediol dianion .

Above observations allow us to postulate a reaction mechanism for reduction of molybdenum(V)porphyrins by benzenediols or naphthalenediols. The reaction process is divided into three steps as shown in Scheme; Step 1: The ethoxo ligand of **1** is substituted by a hydroxyarenolate monoanion affording **3** through a proton transfer from arenediol to **1**. Step 2 : A binuclear complex, **4** bridged by arenediol dianion is formed by ligand substitution of the residual **1** with unreacted hydroxyl group of hydroxyarenolato ligand of **3**. Step 3 : The complex **3** gives **2** and quinone by intramolecular electron transfer from bridging diolate to two Mo^V centers. The reduction of Mo^V to Mo^{IV} takes place in this step.

In the reduction of **1** by 1 eq. of 1,4-benzenediols, the reaction rates for each step, v_1, v_2, and v_3 are in the order of $v_1 \leq v_2 << v_3$, and the absorption bands due to the complex **3** and **4**, therefore, can not be detected in the reaction process. The above mechanism is supported by the reaction of **1** and 1,2-benzenediol. The reaction of **1** and 1,2-benzenediol gave only a mononuclear complex.[3a] The formation of a binuclear complex was sterically inhibited. These observations indicate clearly that the reduction of molybdenum center proceeds *via* the binuclear complex.

There were no evidence for forming a mononuclear intermediate in the forward and reverse reactions between **4** and **2**. The complex **2** did not react with 2,6-di-*t*-butyl-*p*-benzoquinone, in which one coordination site is blocked by two *t*-butyl groups. These facts convince that the formation of binuclear complexes with quinones is not stepwise and that the formation of two Mo-O bonds proceeds in the cooperative manner of two coordination sites of the quinones. The cooperation of two coordination sites is mediated by a change in the π electronic structure of the ligand.

The equilibrium constants, $K = [\mathbf{4}] / [\mathbf{2}]^2$ [quinone] were photometrically evaluated for the case of 1,4-benzenediol, 1,5- and 2,6-naphthalenediols as 2×10^7 (40.0 °C), 1×10^{10} (39.8 °C), and 2×10^{12} mol^{-2} dm^6 (38.2 °C), respectively. These results satisfactorily explained the coordination equilibrium assumed in the Scheme. The 1,4-benzenediol system had the considerably small constant. The reaction of the complex **1** and 1,4-benzenediol, therefore, did not permit to detect the binuclear complex **4a** in dilute conditions, because **4a** dissociates immediately to form **2**. The large equilibrium constants for 2,6- and 1,5-naphthoquinone reflect the lower LUMO energy than that of 1,4-benzoquinone.[10]

To our knowledge, the above result is one of the successful examples of the cooperative bond-formation and cleavage at two coordination sites involving inner sphere electron transfer, *i.e.*, the bond formation or cleavage at one coordination site synchronously stimulates the other one through the π conjugate system. As demonstrated by ESR spectra, two unpaired electrons of the binuclear complex are fast exchanged across the bridging π-conjugated ligand. The cooperation of two coordination centers results from a change in the conjugate system and the fast electron transport. This behavior may play a central role of electron transport as "molecular wire".

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