Chain and Discrete Dimer Complexes of Molybdenum(II) Trifluoroacetate Axially Coordinated by *p*-Quinones, $[Mo_2(O_2CCF_3)_4(2,6\text{-}Me\text{-}BQ)]_n$ (2,6-Me-BQ=2,6-dimethyl-*p*-benzoquinone) and $[Mo_2(O_2CCF_3)_4(2,6\text{-}t\text{-}Bu\text{-}BQ)_2]$ (2,6-*t*-Bu-BQ=2,6-di-*t*-butyl-*p*-benzoquinone)

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(Received July 3, 1995)

A chain complex $[Mo_2(O_2CCF_3)_4(2,6\text{-}Me\text{-}BQ)]_n$ (2,6-Me-BQ = 2,6-dimethylbenzoquinone) and a bis *p*-quinone adduct complex $[Mo_2(O_2CCF_3)_4(2,6\text{-}t\text{-}Bu\text{-}BQ)_2]$ (2,6-*t*-Bu-BQ = 2,6-di-*t*-butyl-*p*-benzoquinone) have been prepared and characterized by X-ray crystal structure analyses, ^{13}C-NMR spectrum, and cyclic voltammetry. The effect of alkyl groups R (= Me, *t*-Bu) at the 2,6-positions of the *p*-benzoquinone on the structures of the complexes have been discussed.

Recently much interest has been devoted to the unique physical properties of the polymeric transition metal complexes constructed by the combination of metal complexes and bridging ligands.[1] In order to produce such properties, the interaction of metal-ligand and metal-metal through the ligand is important. In the previous paper,[2] we introduced *p*-quinone as the bridging ligand and isolated a complex, $[Mo_2(O_2CCF_3)_4AQ]_n$ (**1**) (AQ = 9,10-anthraquinone), in which $Mo_2(O_2CCF_3)_4$ dimers are linked by the axial coordinations of AQ to form a chain structure. The X-ray structural data revealed a discernible interaction between $Mo_2(O_2CCF_3)_4$ and AQ. Unfortunately the chain complex **1** is insoluble in common organic solvent (such as benzene and alkyl halides) and we could not perform the solution studies. In this study, we have tried to prepare discrete bis *p*-quinone adduct of $Mo_2(O_2CCF_3)_4$, which may be expected to be soluble in organic solvent, by preventing the one carbonyl oxygen from the coordination due to steric hindrance of the alkyl groups at the 2,6-positions of *p*-benzoquinone. In the case of R = Me, a chain complex $[Mo_2(O_2CCF_3)_4(2,6\text{-}Me\text{-}BQ)]_n$ (**2**) (2,6-Me-BQ = 2,6-dimethyl-*p*-benzoquinone) has been formed. On the other hand, we have successfully isolated the desired bis *p*-benzoquinone adduct, $[Mo_2(O_2CCF_3)_4(2,6\text{-}t\text{-}Bu\text{-}BQ)_2]$ (**3**) (2,6-*t*-Bu-BQ = 2,6-di-*t*-butyl-*p*-benzoquinone), by introducing *t*-buthyl groups at the 2,6-positions.

The complexes **2** and **3** were prepared by adding an excess of the *p*-quinones in benzene into a benzene solution of $Mo_2(O_2CCF_3)_4$ under Ar. Anal. $[Mo_2(O_2CCF_3)_4(2,6\text{-}Me\text{-}BQ)]_n$ (**2**); Found: C, 24.70; H, 1.02%. Calcd for $C_{16}H_8F_{12}Mo_2O_{10}$: C, 24.63; H, 1.03%. $[Mo_2(O_2CCF_3)_4(2,6\text{-}t\text{-}Bu\text{-}BQ)_2]$ (**3**); Found: C, 39.58; H, 3.65%. Calcd for $C_{36}H_{40}F_{12}Mo_2O_{12}$: C, 39.87; H, 3.72%.

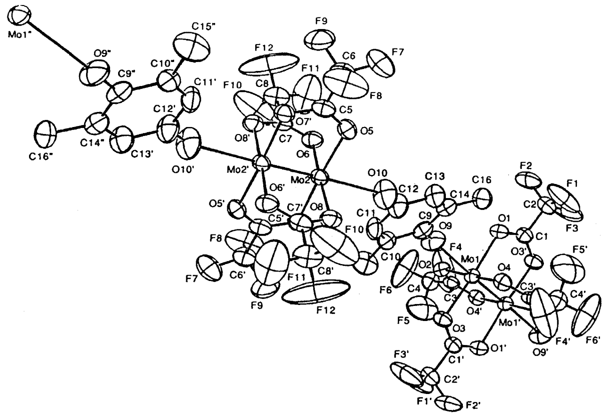

Figure 1. Perspective view of the portion of the chain of **2**. Selected interatomic distances (*l*/Å) and angles (ϕ/°): Mo1-Mo1' 2.108(1), Mo1-O1 2.128(8), Mo1-O2 2.117(7), Mo1-O3 2.127(8), Mo1-O4 2.117(7), Mo1-O9 2.619(9), Mo2-Mo2' 2.111(1), Mo2-O5 2.122(7), Mo2-O6 2.130(7), Mo2-O7 2.117(7), Mo2-O8 2.128(7), Mo2-O10 2.60(1), Mo1'-Mo1-O9 173.6(2), Mo1-O9-C9 152.6(7), Mo2'-Mo2-O10 175.7(2), Mo2-O10-C12 141.7(8).

In Figure 1, the crystal structure of **2** is shown.[3] $Mo_2(O_2CCF_3)_4$ is axially coordinated by 2,6-Me-BQ to form a chain structure. The characteristic point of the structure is that two kinds of $Mo_2(O_2CCF_3)_4$ units exist in the chain. The crystallographic inversion centers are located in the centers of the both dimer units. The axial positions of the (Mo1-Mo1') dimer unit are occupied by the carbonyl oxygens adjacent to the methyl groups at the 2,6-positions, O9 and O9'. On the other hand, the axial positions of the (Mo2-Mo2') dimer unit are occupied by the carbonyl oxygens at the 4-position of the 2,6-Me-BQ, O10 and O10'. The similarity in the axial coordination distances, Mo1-O9=2.619(9) Å, Mo2-O10=2.60(1), shows that there is no substantial difference in the coordination abilities of these carbonyl oxygens of the *p*-quinone. Moreover, the similarity in the Mo-Mo distances, Mo1-Mo1'=2.108(1) Å, Mo2-Mo2'=2.111(1) Å, shows that the axial coordinations effect is almost the same for the dimer units; the Mo-Mo distance of the parent complex $Mo_2(O_2CCF_3)_4$ is 2.090(4) Å.[4]

In Figure 2, the crystal structure of **3** is shown.[3] It is clearly shown that the bulkiness of the *t*-butyl groups of the *p*-quinone

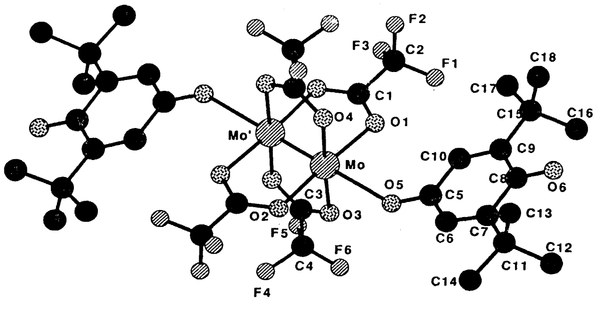

Figure 2. Perspective view of **3**. Selected interatomic distances (*l*/Å) and angles (ϕ/°): Mo-Mo 2.117(1), Mo-O1 2.129(5), Mo-O2 2.125(5), Mo-O3 2.124(5), Mo-O4 2.115(5), Mo-O5 2.568(6), Mo'-Mo-O5 179.0(1), Mo-O5-C5 140.6(5).

prevents the coordination of the carbonyl oxygen adjacent to the 2,6-alkyl groups to form the bis *p*-quinone adduct of the dimer $Mo_2(O_2CCF_3)_4$. The crystallographic inversion center exists in the center of the dimer. The carbonyl oxygen at the 4-position, O5, is axially coordinated to the Mo atom with the distance of 2.568(6) Å. The Mo-Mo bond distance is 2.117(1) Å, being elongated by 0.027 Å by the axial coordinations.

The complex **3** is soluble in chloroform and dichloromethane. In the ^{13}C-NMR spectrum of the $CDCl_3$ solution, the signal for the carbonyl carbon at the 4-position was detected at 194.1 ppm, which is 5.1 ppm lower field compared with the signal position for the carbon of free *p*-quinone. Such a large shift was not observed for the carbonyl carbon adjacent to the *t*-butyl groups; (187.3 ppm for **3** and 187.7 ppm for free *p*-quinone). This is the evidence for the existence of the interaction between the Mo_2 dimer and the *p*-quinone, and shows that the axial coordination of the *p*-quinone occurs in solution as in the crystal structure.

The CV (cyclic voltammetry) measurement was also performed in CH_2Cl_2 solution. The result is shown in Figure 3. 2,6-*t*-Bu-BQ itself has two well-resolved redox couples at -0.80 and -1.45 V (*vs.* SCE), however, in the case of **3**, a reduction peak and a shoulder peak occur at -0.80 V and -0.50 V (*vs.* SCE), respectively, and the corresponding anodic peak does not appear. Alternatively, an oxidation peak occurs at 1.0 V (*vs.* SCE); the oxidation wave at ~1.5 V (*vs.* SCE) may be due to the oxidation of $Mo_2(O_2CCF_3)_4$. Although detailed analyses are necessary to explain the CV feature, this result may be correlated with the interaction between the Mo_2 dimer and the *p*-quinone.[5]

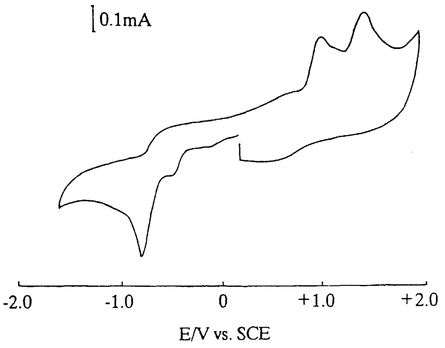

Figure 3. The cyclic voltammogram of **3** in CH_2Cl_2 at a glassy carbon electrode: scan rate=100 mV/s, [complex]=1.0×10^{-3} mol dm^{-3}, [$(n\text{-}Bu)_4NClO_4$]=0.1 mol dm^{-3}.

The present work was partially supported by a Grant-in Aid for Scientific Research No. 06740508 from the Ministry of Education, Science and Culture.

References and Notes

1 e.g., O. Schneider, J. Metz, and M. Hanack, *Mol. Cryst. Liq. Cryst.*, **81**, 273 (1982); J. P. Collman, J. T. McDevitt, C. R. Leidner, G. T. Yee, J. B. Torrance, and W. A. Little, *J. Am. Chem. Soc.*, **109**, 4606 (1987); A. Caneschi, D. Gatteschi, R. Sessoli, and P. Ray, *Acc. Chem. Res.*, **22**, 392 (1989); H. O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean, and O. Kahn, *Science*, **261**, 447 (1993).

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3 Crystal Data for **2**: $Mo_2F_{12}O_{10}C_{16}H_8$ F.W.=780.10, monoclinic, space group $P2_1/c$, a=15.117(4), b=18.634(3), c=8.856(3) Å, β=105.89(1)°, V=2399(1) Å^3, Z=4, D_m=2.13, D_c=2.16 g cm^{-3}, μ(Mo-$K\alpha$)=11.60 cm^{-1}, F(000)=1504, T=298 K, R=0.060, R_w=0.067. A total of 6844 reflections were measured in the range $2\le2\theta\le59°$; 3266 with $I\ge3\sigma(I)$ were assumed as observed. For **3**: $Mo_2F_{12}O_{12}C_{36}H_{40}$, F.W.=1084.56, orthorhombic, space group Pbcn, a=11.5887(9), b=14.316(1), c=26.697(2) Å, V=4429.2(6) Å^3, Z=4, D_m=1.63, D_c=1.63 g cm^{-3}, μ(Mo-$K\alpha$)=6.546 cm^{-1}, F(000)=2176, T=298 K, R=0.038, R_w=0.055. A total of 3677 reflections were measured in the range $2\le2\theta\le49°$; 2384 with $I\ge3\sigma(I)$ were assumed as observed. For the determination of both structures, intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-$K\alpha$ radiation. The structures were solved by the direct methods and refined by the full-matrix least-squares methods using MolEN program package.

4 F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, **1**, 161 (1971).

5 The CV experiment was also performed for 2,6-*t*-Bu-BQ by adding $Mo_2(O_2CCF_3)_4$ to the solution of 2,6-*t*-Bu-BQ. The oxidation waves of the two redox couples of 2,6-*t*-Bu-BQ gradually faded with increasing the concentration of $Mo_2(O_2CCF_3)_4$, and finally, the same cyclic voltammogram as that of **3** was obtained at the ratio of 2,6-*t*-Bu-BQ:$Mo_2(O_2CCF_3)_4$=1:0.5.