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A Chain Compound Built Up by Alternated Arrangement of Molybdenum(II) Trifluoroacetate Dimer and 9,10-Anthraquinone

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Reaction of molybdenum(II) trifluoroacetate, $Mo_2(O_2CCF_3)_4$ and 9,10-anthraquinone (AQ) gave a chain complex, $[Mo_2(O_2CCF_3)_4 \cdot AQ]_n$. The complex has been characterized by X-ray structural analysis, IR, ESR, and reflectance spectra.

Using bridging ligands is much effective for controlling the arrangement of metal complexes to form polynuclear structure. In the previous paper, we reported linear arrangement of metal-metal bonds by the combination of molybdenum(II) acetate ($Mo_2(O_2CCH_3)_4$) and bidentate ligand, pyrazine, 4,4'-bipyridine, or 1,4-diazabicyclo[2.2.2]octane.[1] The X-ray structural analysis of the bipyridine complex showed that the $Mo_2(O_2CCH_3)_4$ skeltons are arranged by the bridging ligands to form a linear chain structure. On the other hand, Kerby et al. reported zigzag chain polymers consisting of molybdenum(II) acetate and more flexible bidentate ligand, 1,2-bis(dimethylphosphino)ethane or tetramethylethylenediamine.[2] These complexes do not show any different property from the starting materials probably due to the essential weakness of the axial coordination.

Recently Chisholm et al. have prepared tetranuclear complexes, $[M_2(O_2C\text{-}t\text{-}Bu)_3]_2(\mu\text{-}L)$ (M=Mo, W) and reported that an electronic coupling mainly occurs through the bridging ligand even in the case of the M_2 subunits located closely with parallel mode, $M{\equiv}M \quad M{\equiv}M$.[3] That is, the interaction through the bridging ligand plays an important role for the coupling. In this study, we introduce *p*-quinone as a potential ligand having such an ability. Since the *p*-quinone is an electron acceptor, we expect the interaction through its energetically low-lying LUMO. Here, the polymer complex $[Mo_2(O_2CCF_3)_4 \cdot AQ]_n$ (AQ=9,10-anthraquinone) (**1**) is presented.

The complex **1** was obtained as follows. A solution of 9,10-anthraquinone (32 mg, 0.15 mmol) in dry benzene (15 ml) was added to a solution of $Mo_2(O_2CCF_3)_4$ (100 mg, 0.15 mmol) in dry benzene (15 ml) under argon. After stirring the solution for 0.5 h at room temperature, a precipitate was filtered, washed with benzene, and dried in vacuo. Anal. Found: C, 31.38; H, 1.16%. Calcd for $C_{22}H_8F_{12}Mo_2O_{10}$: C, 31.01; H, 0.95%.

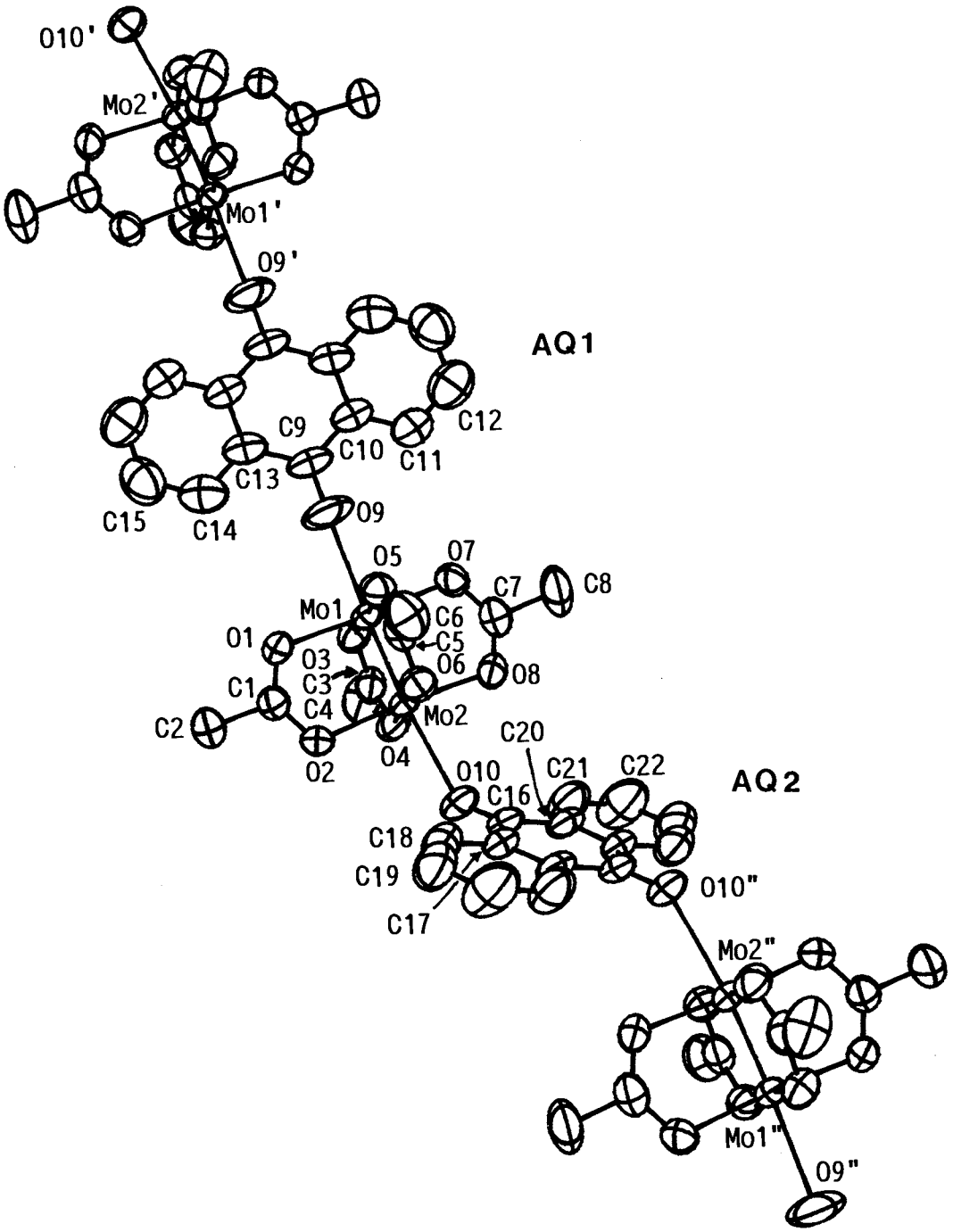

Fig. 1. ORTEP view of a stepped chain structure of $[Mo_2(O_2CCF_3)_4 \cdot AQ]_n$. Selected bond distances (l/Å) and angles (ϕ/°) are: Mo1-Mo2 2.107(1), Mo1-O1 2.116(4), Mo1-O3 2.110(5), Mo1-O5 2.115(5), Mo1-O7 2.114(4), Mo1-O9 2.478(6), Mo2-O2 2.119(4), Mo2-O4 2.118(5), Mo2-O6 2.135(5), Mo2-O8 2.119(4), Mo2-O10 2.532(5); O1-Mo1-O3 90.5(2), O1-Mo1-O5 89.5(2), O1-Mo1-O7 176.9(2), O3-Mo1-O5 176.2(2), O3-Mo1-O7 89.8(2), O5-Mo1-O7 90.1(2), Mo1-O9-C9 178.7(7), O2-Mo2-O4 90.9(2), O2-Mo2-O6 88.7(2), O2-Mo2-O8 175.8(2), O4-Mo2-O6 176.8(2), O4-Mo2-O8 90.1(2), O6-Mo2-O8 90.1(2), Mo2-O10-C16 136.7(5). Crystallographic inversion centers exist in the center of each AQ molecule. Fluorine atoms of CF_3 groups are omitted for clarity.

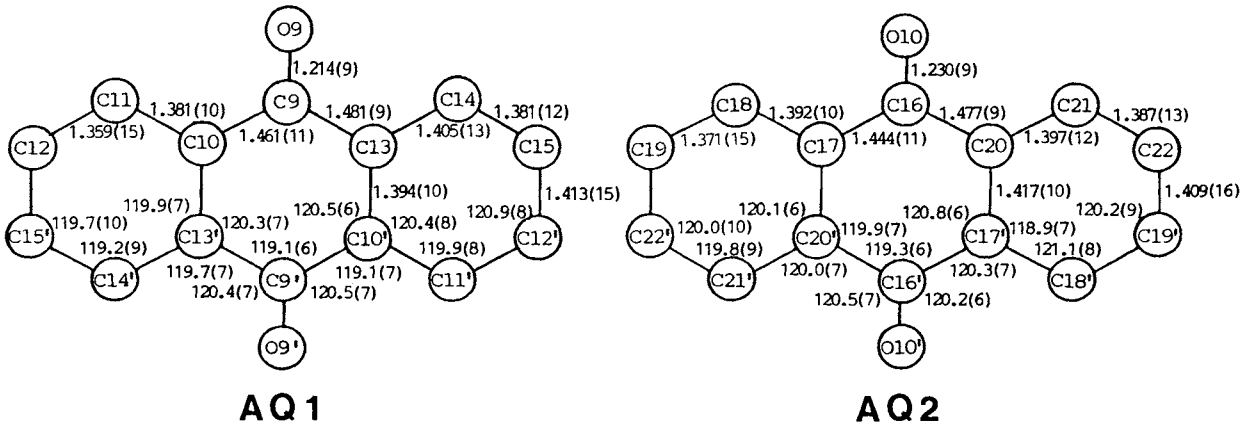

Fig. 2. Numbering of atoms and bond lengths (l/Å) and angles (ϕ/°) of AQ1 and AQ2.

The X-ray structural analysis of **1**[4] has shown that a chain structure is built up by two kinds of bridges of 9,10-anthraquinone, AQ1 and AQ2. As shown in Fig. 1, AQ1 links $Mo_2(O_2CCF_3)_4$ with a linear mode, ∠Mo1-O9-C9=178.7(7)°, and AQ2 bridges with a tilting mode, ∠Mo2-O10-C16 =136.7(5)°. The tilting mode of AQ2 bridge leads to a stepped chain structure. The bond distances (Mo-O(AQ)) of the axial ligations by AQ1 and AQ2 are 2.478(6) and 2.532(5) Å, respectively. The Mo-Mo bond length is 2.107(1) Å, slightly increased from the parent complex $Mo_2(O_2CCF_3)_4$ (2.090(4) Å).[5] The average Mo-O(O_2CCF_3) distances are 2.114(5) Å for Mo1 and 2.123(5) Å for Mo2, which are also slightly longer than that for $Mo_2(O_2CCF_3)_4$ (2.06(2) Å).[5]

For comparison of the two AQ molecules in the chain, the bond distances and angles of AQ1 and AQ2 are listed in Fig. 2. The structural feature of AQ1 is almost identical with the AQ molecule itself reported in the literature.[6] Contrarily, the structural feature of AQ2 is somewhat different. The bond distance of C=O is lengthened by 0.017 Å. The existence of non-equivalent AQ molecules in the chain can be also detected in the IR spectrum. As shown in Fig. 3, two absorptions ascribed to C=O stretching band are observed at 1660 and 1680 cm^{-1}. We have assigned the higher frequency absorption to C=O of AQ1 and the lower to that of AQ2 since the ν(C=O) absorption of free 9,10-anthraquinone is observed at 1678 cm^{-1}.[7] The structural perturbation on AQ2 may be due to the axial coordination to $Mo_2(O_2CCF_3)_4$ and causes the shift to the lower frequency. This interpretation is consistent with the relationship between the bond order and the vibration frequency of the carbonyl group; the C=O stretching band shifts to the lower frequency with decrease of the bond order.[7] The electronic structure of AQ2 may be affected

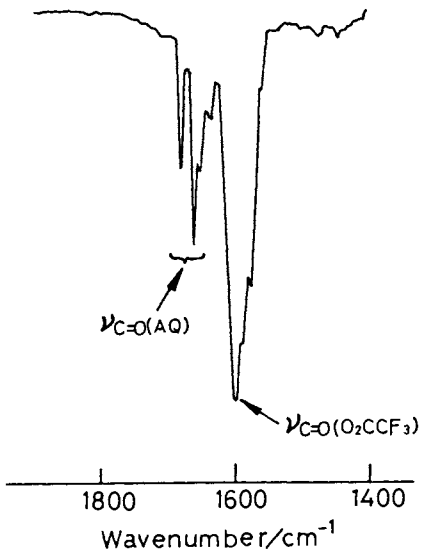

Fig. 3. IR spectrum (in KBr) of $[Mo_2(O_2CCF_3)_4 \cdot AQ]_n$ in the carbonyl region.

by the adjacent $Mo_2(O_2CCF_3)_4$ moiety and some interaction between AQ2 and $Mo_2(O_2CCF_3)_4$ may occur. However, it is not clear for the reason why such a structural variation occurs only for AQ2.

Diffused reflectance spectrum of **1** shows the absorption band corresponding to the δ-δ* transition as a shoulder around 440 nm [$Mo_2(O_2CCF_3)_4$ shows this band at 434 nm].[8] In addition, **1** is ESR silent at room temperature. These results show that significant change of the electronic state of the Mo_2 core does not occur on the polymer formation.

In the present work, it has been demonstrated that the *p*-quinone acts as a bridging ligand to link the dimer units, $Mo_2(O_2CCF_3)_4$. Moreover, a structural perturbation in the bridging AQ molecule has been observed. This result implies an interaction between the dimer unit and bridging ligand. However, this interaction is too weak to have a significant effect on the electronic structure of the Mo_2 core. In order to achieve the significant interaction between the dimer units, it is desirable to use stronger oxidizing agent as the bridging ligand. Such efforts are in progress.

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4) Crystal data for **1**: $Mo_2F_{12}O_{10}C_{22}H_8$, F.W.=852.2, monoclinic, space group $P2_1/c$, a=10.920(4), b=16.239(3), c=16.565(7) Å, β=107.85(2)°, V=2796.1(17) Å^3, Z=4, D_m=2.04, D_c=2.03 g cm^{-3}, μ(Mo-Kα)=10.05 cm^{-1}, crystal dimensions 0.56×0.56×0.34 mm^3. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using a graphite-monochromated Mo-Kα radiation. A total of 4836 reflections ($1 \le 2\theta \le 48°$) were collected, of which independent 3784 reflections with $I \ge 3\sigma(I)$ were considered as observed. The structure was solved by direct methods and refined by the full-matrix least-squares methods. The refinement converged at R=0.045 and R_w=0.048. All the calculations were performed on a Micro-VAX II computer with the SDP program package.

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