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Structure and Properties of a Compound Formed by the Reaction of Molybdenum(II) Trifluoroacetate with 4,4'-Bipyridine

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The reaction of molybdenum(II) trifluoroacetate with 4,4'-bipyridine (bpy) in acetonitrile gave a pale yellow compound. The X-ray structural analysis of the compound showed that it consists of linear-chains formulated as $[Mo_2(O_2CCF_3)_4 \cdot bpy]_n$ and $Mo_2(O_2CCF_3)_4 \cdot (bpy)_2$ dimers in the crystal.

The use of bridging ligands is much effective for controlling the arrangement of metal complexes to form polynuclear structure. Recently, some metal-containing polymers prepared by this method have shown the remarkable properties in electrical conduction and magnetism.[1] However, the number of such metal-containing polymers is still limited. Therefore, it is important to prepare new types of polymers by the combination of metal complexes and bridging ligands.

Previously, we reported that the combination of molybdenum(II) acetate ($Mo_2(O_2CCH_3)_4$) and 4,4'-bipyridine (bpy) gave a linear-chain compound, $[Mo_2(O_2CCH_3)_4 \cdot bpy]_n \cdot [THF]_n$ (**1**), in which $Mo_2(O_2CCH_3)_4$ and bpy are alternately arranged.[2] Our interests have been devoted to the effect of substituent groups of the dimer unit on the polymer structure. During the course of the study, we found that the reaction of molybdenum(II) trifluoroactate ($Mo_2(O_2CCF_3)_4$) and bpy gave the product of $Mo_2(O_2CCF_3)_4$: bpy = 3 : 4 in spite of the similar condition as that for preparation of **1**.[3] The X-ray structural analysis of the compound ($(Mo_2(O_2CCF_3)_4)_3 \cdot (bpy)_4$ (**2**)) showed that the crystal consists of polymer chains formulated as $[Mo_2(O_2CCF_3)_4 \cdot bpy]_n$ and discrete bis bpy adduct dimers, $Mo_2(O_2CCF_3)_4 \cdot (bpy)_2$. To our knowledge, such coexistence of polymer chains and discrete dimers in the crystal is unprecedented. Here, we present the preparation, X-ray crystal structure, and some spectral properties of **2**.

The compound **2** was obtained as follows. A solution of 4,4'-bipyridine (94 mg, 0.60 mmol) in acetonitrile (5 ml) was added to a solution of $Mo_2(O_2CCF_3)_4$ (200 mg, 0.31

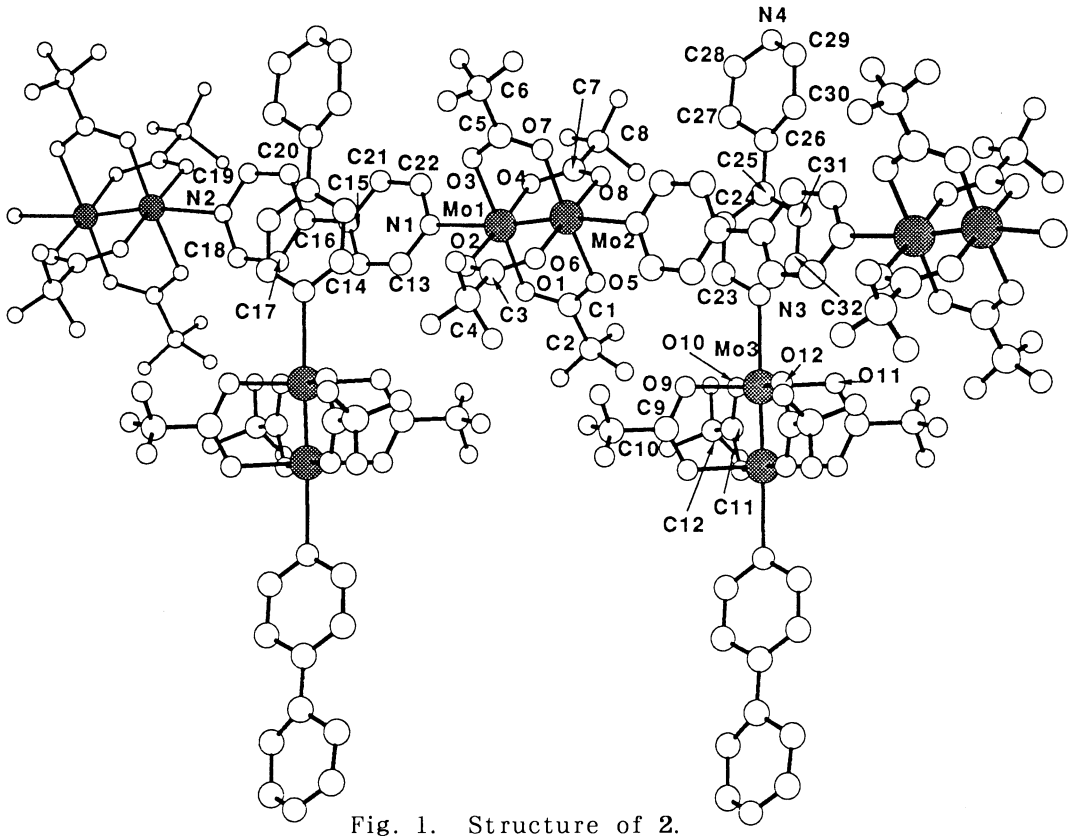

Fig. 1. Structure of 2.

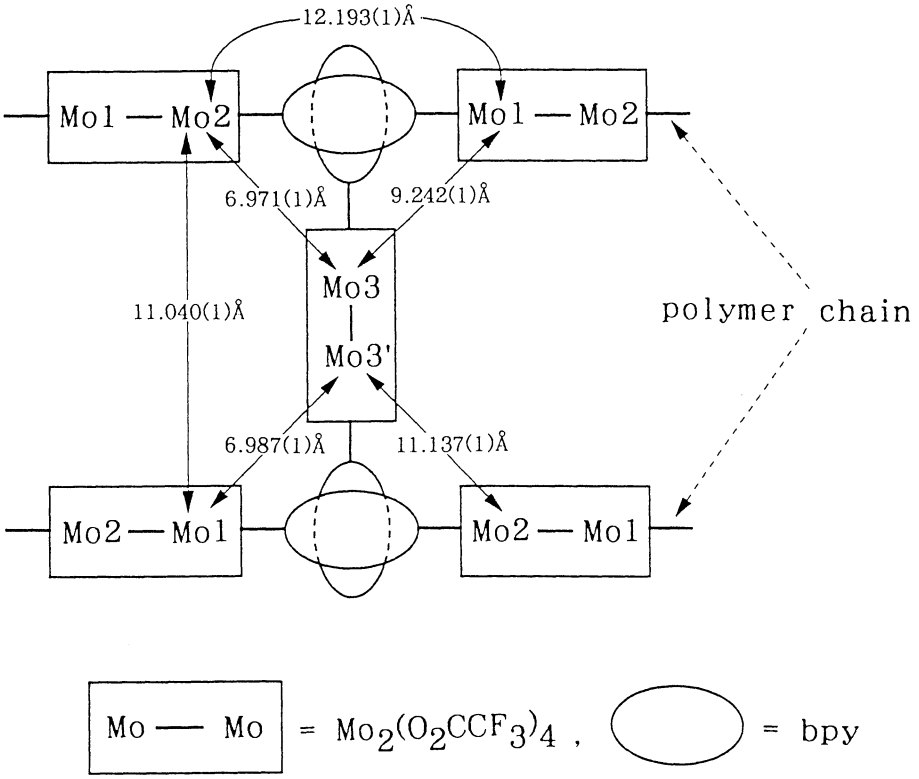

Fig. 2. Correlation between the $Mo_2(O_2CCF_3)_4$ cores.

mmol) in acetonitrile (5 ml) under argon. After stirring the solution for 1 h at room temperature, a precipitate appeared, which was filtered, washed with acetonitrile, and dried in vacuo. The yield was 230 mg. Anal. Found: C, 30.46; H, 1.18; N, 4.50%. Calcd for $C_{32}H_{16}F_{18}Mo_3N_4O_{12}$: C, 30.07; H, 1.26; N, 4.38%.

Crystal structure[4] of **2** is shown in Fig. 1. The discrete dimers $Mo_2(O_2CCF_3)_4 \cdot (bpy)_2$ are located between the infinite chains of $[Mo_2(O_2CCF_3)_4 \cdot bpy]_n$. The correlation between the $Mo_2(O_2CCF_3)_4$ cores is schematically shown in Fig. 2. The chain formed by alternating $Mo_2(O_2CCF_3)_4$ and bpy shows good linearity, ∠Mo1-Mo2-N2=166.2(2)°, ∠Mo2-Mo1-N1=168.0(2)°. The bpy links the $Mo_2(O_2CCF_3)_4$ with the distances of 2.546(8) Å (for Mo2-N2) and 2.569(8) Å (for Mo1-N1). The Mo-Mo bond distance is 2.128(1) Å, lengthened by 0.038 Å on the axial coordination (The Mo-Mo distance in $Mo_2(O_2CCF_3)_4$ is 2.090(4) Å).[5]

The discrete dimer unit, $Mo_2(O_2CCF_3)_4 \cdot (bpy)_2$ has a crystallographic inversion center in the center of the molecule. The bpy is axially coordinated to $Mo_2(O_2CCF_3)_4$ core with the distance of 2.530(9) Å. The Mo-Mo bond distance is 2.124(1) Å, which is comparable with that of the corresponding dimer unit in the chain.

The structural parameters of $Mo_2(O_2CCH_3)_4$,[6] $Mo_2(O_2CCF_3)_4$,[5] and their adduct complexes[2,7,8] are listed in Table 1. The axial coordination for $Mo_2(O_2CCF_3)_4$ is stronger than that for $Mo_2(O_2CCH_3)_4$; the Mo-N distances for $Mo_2(O_2CCF_3)_4$ are 0.06 - 0.2 Å shorter than those for $Mo_2(O_2CCH_3)_4$. This may be due to the presence of electron-withdrawing fluorine atoms on the carboxylate, which enhances the metal acidity and leads to strengthening the ligand-Mo bond. Moreover, on the axial ligation, Mo-Mo and Mo-O(carboxylate) distances of $Mo_2(O_2CCF_3)_4$ are more elongated than those of $Mo_2(O_2CCH_3)_4$.

The solid-state Raman spectrum[9] of **2** shows a Mo-Mo stretching band at 369

Table 1. Structural parameters of $Mo_2(O_2CCH_3)_4$, $Mo_2(O_2CCF_3)_4$, and their adduct complexes

	Mo-Mo (Å)	Mo-O (Å)	Mo-N (Å)	Mo-Mo-N (°)	Ref.
$Mo_2(O_2CCH_3)_4$	2.0934(8)	2.119(5)[a]			6)
$[Mo_2(O_2CCH_3)_4 \cdot bpy]_n \cdot [THF]_n$ (1)	2.103(1)[a]	2.120(6)[a]	2.621(8)[a]	169.2(2)[a]	2)
$[Mo_2(O_2CCH_3)_4 \cdot tmed]_n$[b]	2.103(1)	2.119(2)[a]	2.729(2)	170.5(1)	7)
$Mo_2(O_2CCF_3)_4$	2.090(4)	2.06(2)[a]			5)
$Mo_2(O_2CCF_3)_4 \cdot (py)_2$	2.129(2)	2.116(6)[a]	2.548(8)	171.0(2)	8)
$(Mo_2(O_2CCF_3)_4)_3 \cdot (bpy)_4$ (2)					This work
chain unit	2.128(1)	2.120(8)[a]	2.557(8)[a]	167.1(2)[a]	
dimer unit	2.124(1)	2.127(7)[a]	2.530(9)	166.4(2)	

a) mean values. b) tmed = tetramethylethylenediamine.

cm^{-1}, significantly lower than that of $Mo_2(O_2CCF_3)_4$ (ν_{Mo-Mo} = 394 cm^{-1}). The shift is explained with the elongation of the Mo-Mo bond on the axial ligation.

In the diffuse reflectance spectrum of **2**, the $\delta - \delta^*$ transition observed at 430 nm in $Mo_2(O_2CCF_3)_4$[8] is red-shifited and appears as a shoulder at ~450 nm. The red-shift is relatively larger than that observed in **1**. This may be also explained with the difference in the lengthening of the Mo-Mo bond length.

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3) The reaction with pyrazine (pyz) or 1,4-diazabicyclo[2.2.2]octane (dabco) gave the compounds of $Mo_2(O_2CCF_3)_4$: L = 1 : 1 (L = pyz, dabco). They are presumed to be the chain structure as shown for **1**.

4) Crystal Data for **2**: $Mo_3F_{18}O_{12}N_4C_{32}H_{16}$, F.W.=1278.28, triclinic, space group $P\bar{1}$, a=12.452(4), b=19.735(8), c=8.818(3) Å, α=91.31(3), β=97.54(3), γ=89.17(3)°, V=2147.5(14) $Å^3$, Z=2, D_m=1.95, D_c=1.98 g cm^{-3}, μ(Mo-Kα)=9.78 cm^{-1}, crystal dimensions 0.60×0.45×0.10 mm^3. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using a graphite-monochromated Mo-Kα radiation. A total of 6716 reflections were collected, of which independent 4970 reflections with $I > 3\sigma(I)$ were considered as observed. The structure was solved by the direct method and refined by full-matrix least-square method. The refinement converged at R=0.065 and R_w=0.068. All the calculations were performed on a Micro-VAX II computer with the SDP program package.

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