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Chain Compound of Molybdenum(II) Pivalate Bridged by 4,4′-Bipyridine

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Synopsis. A chain complex, $[Mo_2\{O_2CC(CH_3)_3\}_4\,bpy]_n$ (bpy=4,4′-bipyridine), was prepared by the reaction of molybdenum(II) pivalate ($Mo_2\{O_2CC(CH_3)_3\}_4$) and bpy. An X-ray crystal analysis showed that the chain structure is formed by alternating $Mo_2\{O_2CC(CH_3)_3\}_4$ and bpy.

Recently, much interest has been devoted to polymeric transition-metal complexes bridged by a ligand regarding their physicochemical properties.1) In spite of the increased interest, the variety of the polymeric complexes is still limited because of a synthetic problem. It is thus important to produce new types of polymeric transition-metal complexes. In view of such importance, we initiated a study of the polymeric complex $[M_2(O_2CR)_4L]_n$ (L=bidentate bridging ligand), in which the axial positions of $M_2(O_2CR)_4$ are occupied by donor atoms of the bridging ligands to give the polymer structure.2—5) In a previous paper, we reported that the reaction of $Mo_2(O_2CCF_3)_4$ and bpy (4,4′-bipyridine) in acetonitrile gave the 3:4 complex $\{Mo_2(O_2CCF_3)_4\}_3(bpy)_4$ **(1)**, whose X-ray analysis showed that the crystal consists of polymer chains formulated as $[Mo_2(O_2CCF_3)_4bpy]_n$ and discrete bis bpy adduct dimers, $Mo_2(O_2CCF_3)_4(bpy)_2$.5) On the other hand, a combination of $Mo_2(O_2CCH_3)_4$ and bpy affords the intended 1:1 complex,2) though the crystal comprises the polymer chains and THF molecules used as a solvent. Thus, the complex is formulated as $[Mo_2(O_2CCH_3)_4bpy]_n \cdot n$THF **(2)**. These results show that the choice of the substituent R is important for controlling the crystal structure in combination with $Mo_2(O_2CR)_4$ and bpy.

In this study we used molybdenum(II) pivalate ($Mo_2\{O_2CC(CH_3)_3\}_4$, i.e., R=*t*-butyl) as $Mo_2(O_2CR)_4$ in order to investigate the substituent effect on the crystal structure. The reaction gave a 1:1 complex, $[Mo_2\{O_2CC(CH_3)_3\}_4bpy]_n$ **(3)**. A perspective view of a portion of the chain, $[Mo_2\{O_2CC(CH_3)_3\}_4bpy]_{n'}$ is shown in Fig. 1. The chain structure is formed by alternating $Mo_2\{O_2CC(CH_3)_3\}_4$ and bpy. Two crystallographically independent $Mo_2\{O_2CC(CH_3)_3\}_4$ exist in the chain. The bpy ligand is weakly coordinated to $Mo_2\{O_2CC(CH_3)_3\}_4$ with distances of 2.665(6) Å (for Mo1–N1) and 2.679(7) Å (for Mo2–N2). The Mo–Mo bond lengths are 2.092(1) Å (for Mo1–Mo1′) and 2.099(1) Å (for Mo2–Mo2′), slightly increased from the parent complex, $Mo_2\{O_2CC(CH_3)_3\}_4$ (2.088(1) Å,6b) 2.087(1) Å6c)). The most noticeable point of **3** is that the crystal consists of only chains of $[Mo_2\{O_2CC(CH_3)_3\}_4bpy]_n$. In the case of **1** and **2**, $Mo_2(O_2CCF_3)_4(bpy)_2$ dimers or THF molecules are located in the space between the infinite chains of $[Mo_2(O_2CR)_4bpy]_n$ ($R=CF_3$, CH_3). In **3**, the bulky *t*-butyl group of $Mo_2\{O_2CC(CH_3)_3\}_4$ might play an important role in filling up the space in the crystal.

In Table 1, Raman and diffuse reflectance spectral data with structural parameters (Mo–Mo, Mo–N distances) for **1**, **2**, **3**, and their parent complexes, $Mo_2(O_2CR)_4$, are listed. The Mo–Mo stretching bands of **1**, **2**, and **3** appear at lower wave numbers compared with those of their parent complexes. The shift of the bands corresponds to the elongation of the Mo–Mo bond. The elongation results from an axial coordination of bpy to the Mo_2 dimer. In **1**, electron-withdrawing fluorine atoms on the carboxylate may enhance the metal acidity and lead to a relatively strong bpy–Mo bond. On the other hand, in **3**, which has an electron donating *t*-butyl group on the carboxylate, the bpy–Mo distance is the largest. In the diffuse reflectance spectra of **1**—**3**, the δ–δ^* transition is red-shifted on the axial coordination, and appears as a shoulder at 440—450 nm. The shift is also consistent with the elongation of the Mo–Mo bond.

Experimental

Preparation. Molybdenum(II) pivalate was prepared by a method described in the literature.6a)

$[Mo_2\{O_2CC(CH_3)_3\}_4bpy]$ (3). A solution of bpy (52 mg, 0.33 mmol) in 5 ml of acetonitrile was added to a solution of molybdenum(II) pivalate (100 mg, 0.17 mmol) in 5 ml of acetonitrile under Ar, and was stirred for 1 h at room temperature. After leaving the solution at −3 °C overnight, separated orange crystals were collected by filtration and dried in vacuo. Anal. Found: C, 47.84; H, 5.73; N, 3.80%. Calcd for $C_{30}H_{44}Mo_2N_2O_8$: C, 47.88, H, 5.89, N, 3.72%.

Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Yanako CHN CORDER MT-5. Raman spectra were obtained on a JASCO R-800 spectrometer in the solid state with 514.5 nm excitation. The electronic spectra were measured with a Shimadzu UV-3100 spectrophotometer.

X-Ray Crystal Structure Analysis. The unit-cell parameters and intensities were measured on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) at 25±1 °C. The intensity date were collected by the ω–2θ scan technique and corrected for Lorentz-polarization effects, but not for absorption.

Crystal Data: $C_{30}H_{44}Mo_2N_2O_8$, F.W.=752.57, triclinic, $P\bar{1}$; a=11.844(5), b=17.167(7), c=10.378(4) Å, α=101.71(3), β=115.55(2), γ=72.62(3)°, V=1810(1) Å^3, D_m=1.40,

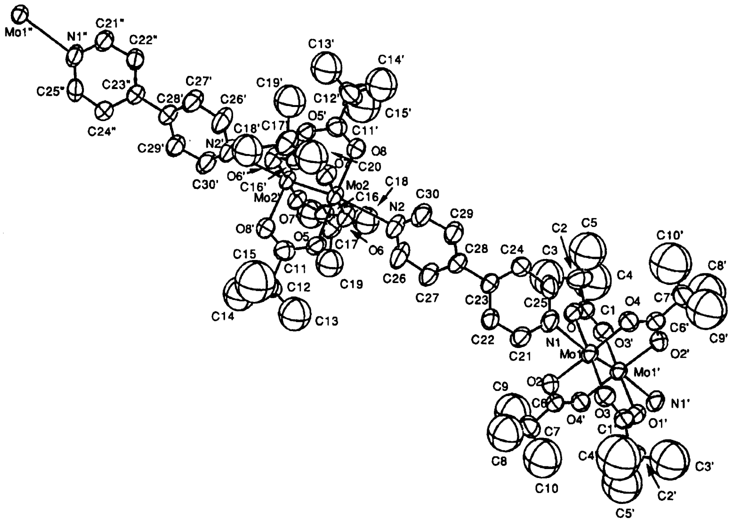

Fig. 1. Perspective view of portion of the chain $[Mo_2\{O_2CC(CH_3)_3\}_4bpy]_n$. Selected bond distances (l/Å) and angles (ϕ/°) are Mol–Mol′ 2.092(1), Mol–O1 2.111(6), Mol–O2 2.109(8), Mol–O3 2.114(6), Mol–O4 2.108(8), Mol–N1 2.665(6), Mo2–Mo2′ 2.099(1), Mo2–O5 2.122(7), Mo2–O6 2.116(5), Mo2–O7 2.111(5), Mo2–O8 2.108(7), Mo2–N2 2.679(7), Mol′–Mol–N1 170.4(2), Mo2′–Mo2–N2 168.9(2).

Table 1. Raman and Diffuse Reflectance Spectral Data and Structural Parameters of **1**, **2**, **3**, and Their Parent Complexes $Mo_2(O_2CR)_4$

Complex	Raman ν(Mo–Mo)	Reflectance $\lambda_{max}(\delta–\delta^*)^{b)}$	Mo–Mo	Mo–N	Ref.
	cm^{-1}	nm	Å	Å	
$Mo_2(O_2CCF_3)_4$	394	430	2.090(4)		7
$\{Mo_2(O_2CCF_3)_4\}_3(bpy)_4$ (**1**)	369	445sh			5
Polymer chain			2.128(1)	2.557(8)$^{c)}$	
Discrete dimer			2.124(1)	2.530(9)	
$Mo_2(O_2CCH_3)_4$	403	440	2.0934(8)		8
$[Mo_2(O_2CCH_3)_4bpy]_n \cdot n$THF (**2**)	392	445sh	2.103(1)$^{c)}$	2.621(8)$^{c)}$	2
$Mo_2\{O_2CC(CH_3)_3\}_4^{a)}$	403	435	2.088(1)		6b
$[Mo_2\{O_2CC(CH_3)_3\}_4bpy]_n$ (**3**)	390	440sh	2.096(1)$^{c)}$	2.672(7)$^{c)}$	This work

a) Three polymorphs (α, β, γ form) are known (see Ref. 6c). The structural datum for α form is listed.
b) sh=shoulder. c) mean values.

Table 2. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B/Å$^{2\ a)}$	Atom	x	y	z	B/Å$^{2\ a)}$
Mol	0.92122(7)	0.00300(5)	0.40109(7)	3.87(2)	C10	1.316(2)	0.063(2)	0.376(3)	20(1)*
Mo2	0.04580(7)	0.44655(4)	-0.44576(8)	3.80(2)	C11	0.1468(8)	0.4488(5)	−0.6570(9)	4.9(2)
O1	0.8221(5)	0.1148(4)	0.4736(6)	5.0(2)	C12	0.229(1)	0.4192(7)	−0.745(1)	8.5(3)
O2	1.0051(5)	0.0610(4)	0.3165(6)	4.7(2)	C13	0.338(2)	0.351(1)	−0.692(2)	12.3(5)*
O3	1.0096(5)	−0.1088(4)	0.3160(6)	4.8(2)	C14	0.236(2)	0.482(1)	−0.807(2)	13.0(6)*
O4	0.8275(5)	−0.0543(4)	0.4738(6)	4.8(2)	C15	0.144(2)	0.372(2)	−0.882(3)	19.0(9)*
O5	0.1637(5)	0.4036(3)	−0.5642(6)	4.7(2)	C16	0.1791(7)	0.5781(5)	−0.2997(9)	4.4(2)
O6	0.1880(5)	0.5045(3)	−0.2871(6)	4.6(2)	C17	0.2805(9)	0.6200(6)	−0.186(1)	5.5(3)
O7	−0.0896(5)	0.3821(3)	−0.5977(6)	4.4(2)	C18	0.314(1)	0.5953(9)	−0.039(2)	9.9(4)*
O8	−0.0662(5)	0.4832(3)	−0.3221(6)	4.7(2)	C19	0.399(1)	0.587(1)	−0.215(2)	10.3(4)*
N1	0.7009(7)	0.0319(5)	0.1705(7)	5.1(2)	C20	0.238(1)	0.711(1)	−0.187(2)	11.1(5)*
N2	0.2042(7)	0.3203(5)	−0.2911(8)	5.6(2)	C21	0.7121(8)	0.0551(6)	0.0634(9)	5.2(3)
C1	0.8756(8)	0.1409(5)	0.6026(9)	5.0(2)	C22	0.6141(8)	0.1077(6)	−0.0331(9)	4.8(2)
C2	0.796(1)	0.2124(7)	0.667(1)	7.4(4)	C23	0.4985(7)	0.1391(5)	−0.0198(8)	3.9(2)
C3	0.767(2)	0.286(1)	0.597(2)	17.1(8)*	C24	0.4850(8)	0.1143(6)	0.0912(9)	5.0(2)
C4	0.869(3)	0.239(2)	0.806(3)	22(1)*	C25	0.5897(9)	0.0614(6)	0.1820(9)	5.8(3)
C5	0.680(2)	0.198(2)	0.646(3)	18.9(9)*	C26	0.3265(9)	0.3185(6)	−0.242(1)	6.6(3)
C6	1.1171(8)	0.0723(5)	0.3968(9)	4.7(2)	C27	0.4244(8)	0.2604(6)	−0.157(1)	5.6(3)
C7	1.1871(9)	0.1064(6)	0.339(1)	6.1(3)	C28	0.3940(7)	0.2002(5)	−0.1155(9)	4.1(2)
C8	1.131(2)	0.100(1)	0.182(2)	16.9(8)*	C29	0.2664(8)	0.2000(6)	−0.169(1)	5.3(3)
C9	1.173(2)	0.190(2)	0.377(3)	18.2(9)*	C30	0.1753(9)	0.2609(6)	−0.257(1)	6.1(3)

a) Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$. Starred atoms were refined isotropically.

$D_c=1.38$ g cm^{-3}, $Z=2$, $\mu(\text{Mo }K\alpha)=7.18$ cm^{-1}, $R=0.054$, $R_w=0.063$. 5987 Reflections were measured in the range $2.0\leq2\theta\leq49.0°$; 4106 with $I\geq3\sigma(I)$ were assumed as observed. The structure was solved by direct methods and refined by the full-matrix least-squares method. All of the non-hydrogen atoms, besides methyl carbon atoms of the pivalate, were refined with anisotropic thermal parameters. Hydrogen atoms were inserted at their calculated positions and fixed at their positions. The weighting scheme $w=1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$ was employed.

All of the calculations were carried out on a Micro VAXII computer using an SDP program package.[9] The atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 2. The anisotropic thermal parameters of non-hydrogen atoms, the atomic coordinates and the thermal parameters of the hydrogen atoms, and F_o-F_c tables have been deposited as Document No. 67065 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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