CHEMISTRY LETTERS, pp. 1753-1756, 1990.

Linear Chain Compounds of Molybdenum(II) Acetate Dimer Linked by Linear-bidentate Ligands, Pyrazine, 4,4'-Bipyridine, and 1,4-Diazabicyclo[2.2.2]octane

Makoto HANDA,* Kenichi KASAMATSU, Kuninobu KASUGA,
Masahiro MIKURIYA,[†] and Toshinori FUJII[†]
Department of Chemistry, Faculty of Science, Shimane University,
Nishikawatsu, Matsue 690
[†]Department of Chemistry, School of Science, Kwansei Gakuin University,
Uegahara, Nishinomiya 662

Linear chain compounds, $[Mo_2(O_2CCH_3)_4 \cdot L]_n$(L=pyrazine, 4,4'-bipyridine, 1,4-diazabicyclo[2.2.2]octane) have been prepared and characterized. The linear chain structure of alternating $Mo_2(O_2CCH_3)_4$ units and bridging ligands L was confirmed by an X-ray structural analysis of the bpy complex.

Much interest has been devoted to the low dimensional metal-containing polymers for their physicochemical properties.$^{1)}$ However, the variety of the species is not so extensive and practically converged into d^8 metal systems because they are essentially built up by stacks of planar complexes. Hanack et al. proposed a useful approach for the polymer formation; they prepared a new type of one-dimensional conductors by arranging alternately metal phthalocyanine units and linear-bidentate ligands with π-electrons.$^{2)}$ If this approach is applied for controlling the arrangement of the metal-metal bond units, chemistry of new type metal clusters or linear chain compounds will be expected. For the metal unit, $Mo_2(O_2CR)_4$ is feasible because it easily allows axial coordination and its metal-metal bond is one of the most characterized ones.$^{3-6)}$ Up to date, such structures by the combination of $M_2(O_2CR)_4$ and the linear-bidentate ligands have been reported for Cr$^{7)}$ and Rh$^{8)}$ systems. As for Mo system, quite recently, zigzag chains of $Mo_2(O_2CCH_3)_4$ units linked by nonlinear-bidentate ligands, 1,2-bis(dimethylphosphino)ethane(dmpe) and tetramethylethylenediamine(tmed) have been reported.$^{9)}$ In the present study, we prepared the linear chain compounds by the reaction of molybdenum(II) acetate and the excess of bidentate ligand, pyrazine(pyz), 4,4'-bipyridine(bpy), or 1,4-diazabicyclo-[2.2.2]octane(dabco). The good linearity of the chain was confirmed by an

X-ray structural analysis of the bpy complex.

The compounds were prepared by adding an about five times excess of the corresponding ligands dissolved in THF into the THF solution of $Mo_2(O_2CCH_3)_4$ under an argon atmosphere. Anal. $[Mo_2(O_2CCH_3)_4\cdot pyz]_n$ (**1**); Found: C, 28.52; H, 3.06; N, 5.69%. Calcd for $C_{12}H_{16}Mo_2N_2O_8$: C, 28.36; H, 3.17; N, 5.51%. $[Mo_2(O_2CCH_3)_4\cdot bpy]_n\cdot[THF]_n$ (**2**); Found: C, 40.10; H, 4.32; N, 4.31%. Calcd for $C_{22}H_{28}Mo_2N_2O_9$: C, 40.26; H, 4.30; N, 4.27%. $[Mo_2(O_2CCH_3)_4\cdot dabco]_n$ (**3**); Found: C, 31.41; H, 4.75; N, 5.38%. Calcd for $C_{14}H_{24}Mo_2N_2O_8$: C, 31.13; H, 4.48; N, 5.19%.

Orange crystals of **2**, suitable for an X-ray structural analysis, were obtained by diffusing together THF solutions of $Mo_2(O_2CCH_3)_4$ and bpy in an H-shaped tube under an argon atmosphere.

All the complexes have the stoichiometry $Mo_2(O_2CCH_3)_4$:L=1:1 (with a THF molecule of crystal solvent in the case of L=bpy), and are presumed to be the desired linear chain structure. The chain structure was confirmed by the X-ray analysis of **2**.[10] The crystal contains two crystallographically independent chains (designated as A and B hereafter) and THF. There is no remarkable structural difference between A and B, so the portion of A is depicted in Fig. 1. The chains elongated by alternating $Mo_2(O_2CCH_3)_4$ and bpy show good linearity, ∠Mo(A)'-Mo(A)-N(A)=169.4(2)° and ∠Mo(B)'-Mo(B)-N(B)=169.0(2)°. The chain A is parallel to the b axis, however B extends at the angle, 145.9° for the b axis. Crystallographic inversion centers are located at the midpoints of Mo-Mo bonds and C-C bonds linking the two pyridine rings of bpy molecules. The Mo-Mo bond lengths are 2.103(1) (for A)

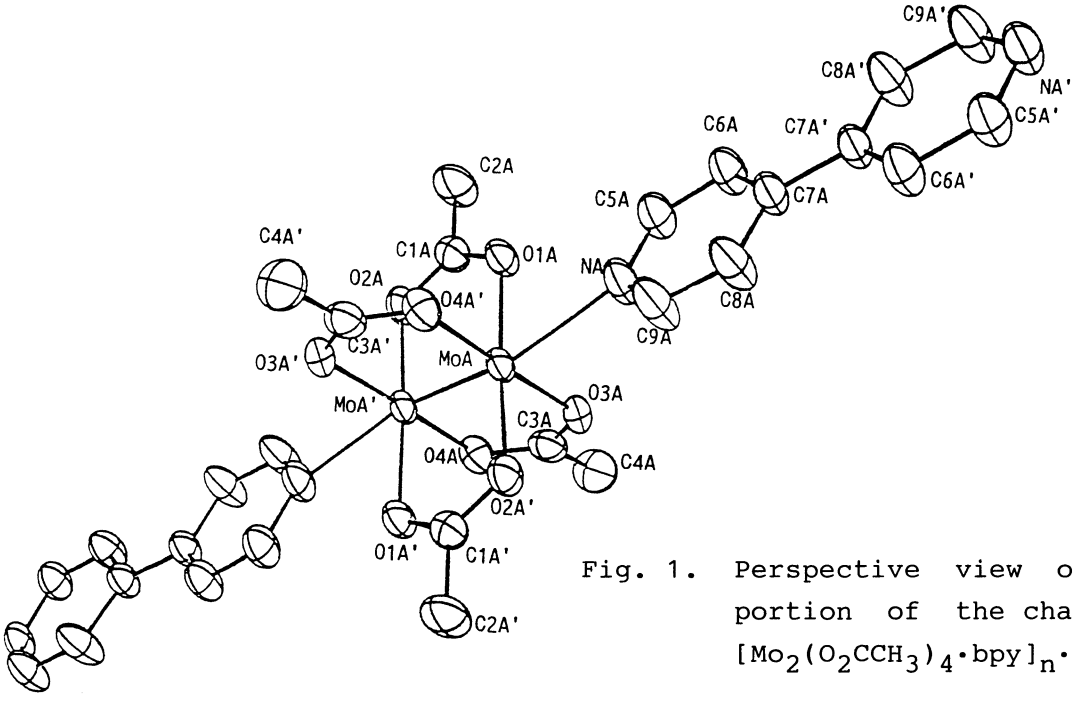

Fig. 1. Perspective view of the portion of the chain A of $[Mo_2(O_2CCH_3)_4\cdot bpy]_n\cdot[THF]_n$ (**2**).

and 2.104(1) Å (for B) and Mo-O are 2.109(6) – 2.138(5) Å. These values are comparable to those of $Mo_2(O_2CCH_3)_4$.[11)] The bpy links the $Mo_2(O_2CCH_3)_4$ units with a Mo-N distance of 2.619(8) (for A) and 2.624(7) Å (for B), and the linearity of the ligand gives the linear chain structure in contrast to $[Mo_2(O_2CCH_3)_4\cdot dmpe]_n$ and $[Mo_2(O_2CCH_3)_4\cdot tmed]_n$.[9)]

In the solid state Raman spectra, which were obtained using 5145 Å exciting radiation, Mo-Mo stretching bands of the present complexes appear at 398 cm^{-1} for **1**, and 392 cm^{-1} for **2** and **3**, respectively, slightly lower than that of $Mo_2(O_2CCH_3)_4$.[3)] The shifts are small compared with that of a bis pyridine adduct $Mo_2(O_2CCF_3)_4(py)_2$, in which the band at 397 cm^{-1} of $Mo_2(O_2CCF_3)_4$ is shifted to 367 cm^{-1} by the axial ligation.[4)] It is due to the difference in the lengthening of the Mo-Mo distance accompanied by the axial ligation; the Mo-Mo bond length is increased from 2.090 Å to 2.129 Å in $Mo_2(O_2CCF_3)_4(py)_2$, while that for **2** is stretched only by 0.01 Å.

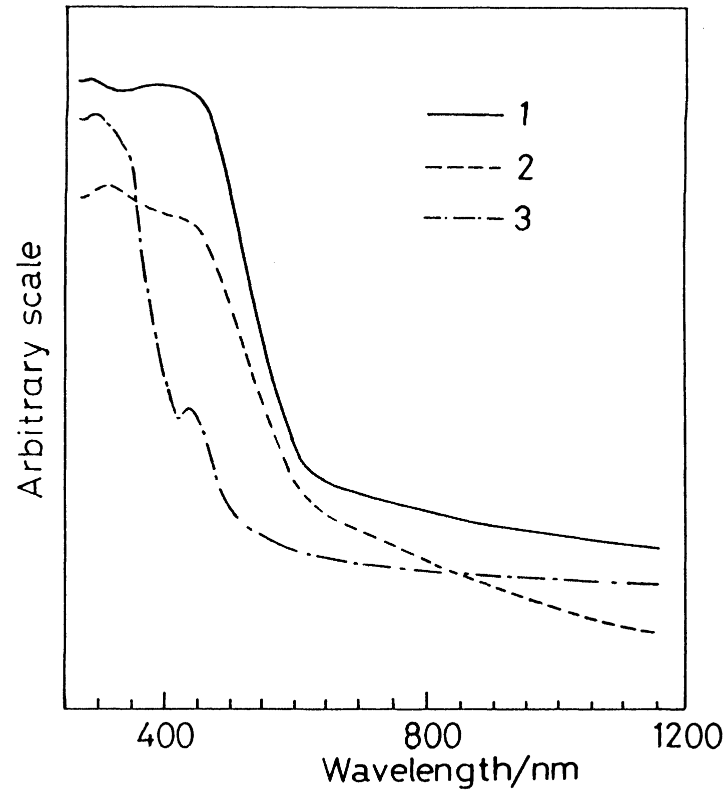

Fig. 2. Reflectance spectra of **1-3**.

Diffuse reflectance spectra of the present complexes show the 23 000 cm^{-1} band[6)] observed in $Mo_2(O_2CCH_3)_4$ and its related compounds as a peak at 22 600 cm^{-1} for **3** and shoulders near 22 000 cm^{-1} for **1** and **2** (Fig. 2). This band has been assigned to a $\delta - \delta^*$ transition based on the metal-metal bond.[6)] The present results show the existence of the metal-metal bond in the chain, however there seems to be no remarkable interaction between the metal-metal bonds.

In this work, the linear arrangement of the metal-metal bonds was obtained by the use of the bridging linear-bidentate ligands. The next problem is to give the one-dimensional properties to this type of polymers by means of increasing the interaction between the metal-metal bond units. Such efforts, e.g. partial oxidations or modifications of bridging ligands, are in progress.

This work was supported by a Grant-in-Aid for Scientific Research (No. 1740352) from the Ministry of Education, Science and Culture.

References

1) For example, "Extended Linear Chain Compounds," ed by J. S. Miller, Plenum, New York (1982), Vols. 1-3.
2) O. Schneider and M. Hanack, Mol. Cryst. Liq. Cryst., 81, 273 (1982) and references therein.
3) W. K. Bratton, F. A. Cotton, M. Debeau, and R. A. Walton, J. Coord. Chem., 1, 121 (1971); J. San Filippo, Jr. and H. J. Sniadoch, Inorg. Chem., 12, 2326 (1973); A. P. Ketteringham and C. Oldham, J. Chem. Soc., 1973, 1067.
4) F. A. Cotton and J. G. Norman, Jr., J. Am. Chem. Soc., 94, 5697 (1972).
5) J. G. Norman, Jr., H. J. Kolari, H. B. Gray, and W. C. Trogler, Inorg. Chem., 16, 987 (1977); J. L. Templeton, Prog. Inorg. Chem., 26, 211 (1979).
6) W. C. Trogler and H. B. Gray, Acc. Chem. Res., 11, 232 (1978); M. C. Manning, G. F. Holland, D. E. Ellis, and W. C. Trogler, J. Phys. Chem., 87, 3083 (1983); F. A. Cotton and R. A. Walton, "Multiple Bonds Between Metal Atoms," Wiley, New York (1982).
7) F. A. Cotton and T. R. Felthouse, Inorg. Chem., 19, 328 (1980).
8) F. A. Cotton and T. R. Felthouse, Inorg. Chem., 20, 600 (1981).
9) M. C. Kerby, B. W. Eichhorn, J. A. Creighton, and K. P. C. Vollhardt, Inorg. Chem., 29, 1319 (1990).
10) Crystal data for (**2**): $C_{22}H_{28}Mo_2N_2O_9$=656.35, triclinic, space group $P\bar{1}$, a=12.351(6), b=14.434(8), c=8.472(5) Å, α=107.13(3), β=110.08(3), γ=66.56(5)°; V=1279.4 Å^3, Z=2, D_m=1.71, D_c=1.70 gcm^{-3}, μ(Mo-Kα)=10.1 cm^{-1}, crystal dimensions 0.25×0.28×0.38 mm^3. Intensity data were collected on an Enraf-Nonius CAD-4 automated four-circle diffractometer using graphite-monochromated Mo-Kα radiation. Of the 4410 ($2<2\theta<48°$) measured the unique 3426 reflections with $I>3\sigma(I)$ were considered as observed. The structure was solved by the direct method and refined by the full-matrix least-squares method. All the non-hydrogen atoms except for THF were refined with anisotropic thermal parameters. The THF molecule was included in the full-matrix refinement with a disorder model. The refinement converged at R=0.052 and R_w=0.064. All the calculations were performed on a Micro-VAX II computer with the SDP program package.
11) F. A. Cotton, Z. C. Mester, and T. R. Webb, Acta Crystallogr., Sect. B, 30, 2768 (1974).

(Received June 28, 1990)