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A New Route to Synthesize Dinuclear Mo(I) Complexes Containing SR Bridges: Synthesis and Structure of $Mo_2(CO)_8(SCH_2CO_2Et)_2$

BOTAO ZHUANG*, LIANGREN HUANG, LINGJIE HE, YU YANG and JIAXI LU

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, China

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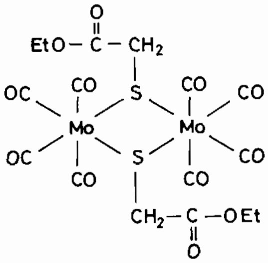
Dinuclear molybdenum(0, I) complexes containing SR bridges $[Mo_2(CO)_8(SR)_2]^{n-}$ ($n = 1, 0$) are of interest because of their interesting electrochemistry and variety of reactivity [1–3], as well as their containing Mo–SR which is relevant to enzymes, especially nitrogenase.

The first dinuclear Mo(I) complex, $Mo_2(CO)_8(SBu^t)_2$, was synthesized in 1981 from the reaction of $Mo(SBu^t)_4$ with high pressure carbon monoxide [4]. Using this reaction, the Mo(I) dinuclear complexes, with R being a ligand other than Bu^t, have not been obtained because the starting materials $Mo(SR)_4$ for this preparative reaction have not been synthesized except for $Mo(SBu^t)_4$. A new route to synthesize dinuclear molybdenum(I) complexes has been investigated. Herein we report the synthesis and structure of a new dinuclear Mo(I) complex, $Mo_2(CO)_8(SCH_2CO_2Et)_2$ (**1**).



1

Experimental

Synthesis of 1

One equivalent of the dinuclear Mo(0) complex, $[Et_4N]_2[Mo_2(CO)_8(SCH_2CO_2Et)_2]$ (**2**) [2] and of I_2 react in hexane at room temperature for 5 h resulting in a mixture of a green solution and a gray residue. After filtration and concentration, a green microcrystalline product $Mo_2(CO)_8(SCH_2CO_2Et)_2$ (**1**) was obtained. *Anal.* Calc. for $MoC_8H_7SO_6$: C, 29.36; H, 2.14; Mo, 29.33. Found: C, 30.01; H, 2.44; Mo, 28.90%. IR (KBr pellet): ν(C=O) 2090(s), 1990(s), 1988(s), 1952(s) cm^{-1}; δ(Mo–CO) 562(m), 548(m) cm^{-1}. The absence of the characteristic absorption of the Et_4N^+ cation is consistent with the formulation of **1** with Mo atoms present in the +1 oxidation state.

Crystal Data

1 crystallizes in the orthorhombic, space group *Pbca* with $a = 8.681(1)$, $b = 18.881(2)$, $c = 14.512(2)$ Å; $V = 2379(1)$ Å^3; $Z = 4$; $R_1 = 0.077$, $R_2 = 0.083$.

Intensity Measurement, Structural Determination and Refinement

Single crystals were obtained from the hexane solution of **1** and a green thin plate-like crystal of dimensions 0.025 × 0.2 × 0.2 mm was selected for X-ray diffraction. 846 independent reflections with $I \geqslant 3\sigma(I)$ were collected on a CAD4 diffractometer with Mo Kα radiation in the range of $1° \leqslant \theta \leqslant 24°$ by using $\theta/2\theta$ scans. Data reduction, an empirical absorption and decay correction were performed as above. The systematic absences $0kl(k \neq 2n)$, $h0l(l \neq 2n)$ and $hk0(h \neq 2n)$ uniquely determined the space group in the orthorhombic system as *Pbca*. The structure was solved by direct method and difference Fourier techniques and refined by full matrix least-squares procedures with anisotropic thermal parameters for all nonhydrogen atoms.

Results and Discussion

Oxidation of $[Et_4N]_2[Mo_2(CO)_8(SR)_2]$ (R = Ph, Bu^t and CH_2CO_2Et), which are conveniently prepared from $Mo(CO)_6$ [1–3] by iodine in hexane at ambient temperature affords dinuclear Mo(I) complexes $Mo_2(CO)_8(SR)_2$ almost quantitatively.

$$[Et_4N]_2[Mo_2(CO)_8(SR)_2] + I_2 \longrightarrow Mo_2(CO)_8(SR)_2 + 2Et_4NI \qquad (1)$$

From reaction (1), the dinuclear Mo(I) complexes $Mo_2(CO)_8(SR)_2$ containing various thiol ligands as bridges can be prepared with facility in contrast to the method reported by M. Kamasta *et al.* [4] which is limited to the preparation of the Bu^t complex, $Mo_2(CO)_8(SBu^t)_2$, so far. Not only the hexane but also the other noncoordinating solvents such as toluene might be used in this preparative reaction according to the convenience of the isolation of the desired products. Noteworthily, a compound containing a Mo–N bond, $Mo_2(CO)_6(SR)_2(MeCN)_2$, may be obtained if MeCN is used as solvent in the preparative reaction [5].

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*Author to whom correspondence should be addressed.

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TABLE I. Positional and Thermal Parameters (e.s.d.s) for $Mo_2(CO)_8(SCH_2CO_2Et)_2$

Atom	x	y	z	B_{eq}
Mo	0.1449(2)	0.0177(1)	0.0471(1)	2.82(3)
S	−0.0157(7)	−0.0861(3)	0.0748(4)	3.0(1)
C(1)	0.294(3)	−0.029(1)	0.135(2)	5.5(6)
O(1)	0.378(3)	−0.053(1)	0.190(2)	10.4(6)
C(2)	0.295(2)	0.100(1)	0.049(2)	4.9(6)
O(2)	0.375(2)	0.1467(9)	0.057(2)	7.7(6)
C(3)	0.275(3)	−0.025(1)	−0.055(2)	4.6(5)
O(3)	0.349(3)	−0.050(1)	−0.111(2)	8.4(6)
C(4)	0.033(5)	0.063(1)	0.152(2)	8(1)
O(4)	−0.029(3)	0.092(1)	0.213(1)	7.2(6)
C(5)	0.080(3)	−0.165(1)	0.022(2)	3.6(5)
C(6)	0.207(3)	−0.192(1)	0.083(2)	4.0(6)
O(5)	0.329(2)	−0.207(1)	0.052(2)	7.2(5)
O(6)	0.166(2)	−0.2009(9)	0.169(1)	5.3(4)
C(7)	0.287(3)	−0.224(2)	0.231(2)	6.2(7)
C(8)	0.216(4)	−0.233(2)	0.325(2)	10(1)

TABLE II. Bond Distances (Å) and Bond Angles (°) (e.s.d.s) in $Mo_2(CO)_8(SCH_2CO_2Et)_2$

Mo−Mo	2.939(1)	C(2)−O(2)	1.133(10)
Mo−S	2.438(2)	C(3)−O(3)	1.136(12)
Mo−S	2.459(2)	C(4)−O(4)	1.180(14)
Mo−C(1)	2.023(11)	C(5)−C(6)	1.500(13)
Mo−C(2)	2.026(10)	C(6)−O(5)	1.197(11)
Mo−C(3)	2.033(12)	C(6)−O(6)	1.304(11)
Mo−C(4)	1.992(14)	O(6)−C(7)	1.452(11)
S−C(5)	1.870(9)	C(7)−C(8)	1.51(2)
C(1)−O(1)	1.162(11)		
S−Mo−S	106.23(7)	C(1)−Mo−C(4)	90.9(5)
S−Mo−C(1)	84.7(3)	C(2)−Mo−C(3)	87.4(5)
S−Mo−C(2)	168.8(4)	C(2)−Mo−C(4)	88.9(5)
S−Mo−C(3)	96.7(3)	C(3)−Mo−C(4)	175.3(6)
S−Mo−C(4)	86.5(4)	Mo−S−Mo	73.77(6)
S−Mo−C(1)	167.4(3)	S−C(5)−C(6)	110.7(6)
S−Mo−C(2)	84.3(3)	C(5)−C(6)−O(5)	120(1)
S−Mo−C(3)	86.6(3)	C(5)−C(6)−O(6)	114.2(9)
S−Mo−C(4)	95.9(3)	O(5)−C(6)−O(6)	125(1)
C(1)−Mo−C(2)	85.2(4)	C(6)−O(6)−C(7)	115.8(9)
C(1)−Mo−C(3)	85.9(4)	O(6)−C(7)−C(8)	107.1(9)

The positional and thermal parameters with estimated standard deviations of **1** are listed in Table I and the bond distances and angles of the anion of **1** are shown in Table II. The molecular structure of the anion of **1** is depicted in Fig. 1. As shown in Fig. 1, **1** is centrosymmetric, the geometry of each Mo(I) atom is a distorted octahedral with a large SMoS angle of 106.23(7)° and small equatorial CMoC angle of 85.2(4)°. The average Mo−C (equatorial) distance of 2.025(2) Å, Mo−C (axial) distance of 2.01(2) Å and Mo−S distance of 2.45(1) Å are comparable to the corresponding parameters (2.01, 2.05 and 2.48 Å) of the analog, $Mo_2(CO)_8(SBu^t)_2$ [4].

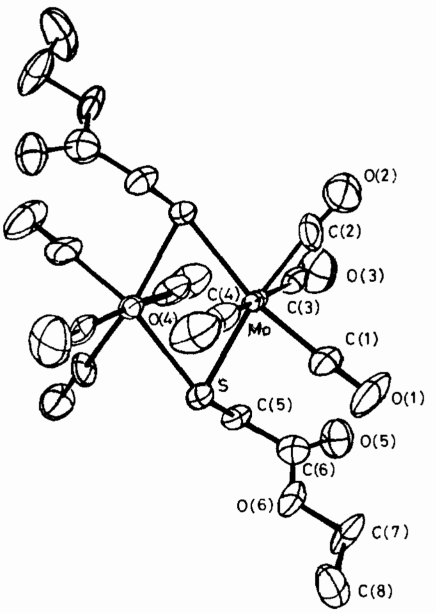

Fig. 1. The molecular configuration of $Mo_2(CO)_8(SCH_2CO_2Et)_2$.

Obviously, the fact that **1** possesses a longer axial Mo−C bond distance of 2.033(12) Å leads to an easier substitution of CO of **1** by coordinating solvents such as MeCN. The Mo−Mo distance of **1** is 2.939(1) Å. Formation of this single Mo−Mo bond meets the requirement to keep an 18-electron configuration around each Mo atom for stabilization and the Mo−Mo distance of **1** is somewhat shorter than that of $Mo_2(CO)_8(SBu^t)_2$ (2.984(2) Å), due to the different electronegativity of the Bu^t ligand from the CH_2CO_2Et ligand. Taking account of the structure of the Mo(0) dinuclear complex $[Mo_2(CO)_8(SCH_2CO_2Et)_2]^{2-}$ with a nonbonding Mo···Mo distance of 3.939(1) Å [2], the bonding of Mo−Mo and the different configuration of the bimetallic center of MoS_2Mo in **1** confirm our previous speculation that the two electron character of dinuclear Mo(0) complexes $[Mo_2(CO)_8(SR)_2]^{2-}$ derives from creation or cleavage of a metal−metal single bond coupled with structural rearrangement in a bridged bimetallic center [1].

References

1 B.-T. Zhuang, J. W. McDonald, F. A. Schultz and W. E. Newton, *Organometallics, 3,* 943 (1984).
2 B.-T. Zhuang, L.-R. Huang, Y. Yang and J.-X. Lu, *J. Struct. Chem., 4,* 103 (1985).
3 B.-T. Zhuang, L.-R. Huang, L.-J. He, W.-Z. Cheng, Y. Yang and J.-X. Lu, *Huaxue Xuebao (Acta Chim. Sin.),* (1986) in press.
4 M. Kamata, T. Yoshida and S. Otsuka, *J. Am. Chem. Soc., 103,* 3572 (1981).
5 B.-T. Zhuang, L.-R. Huang, Y. Yang and J.-X. Lu, *Inorg. Chim. Acta, 116,* L41 (1986).