Inorganica Chimica Acta, 116 (1986) L41–L43

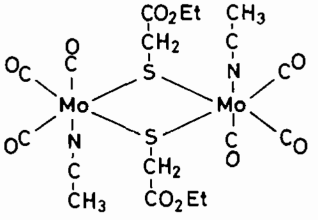
Synthesis and Structure of a Dinuclear Mo(I) Complex Containing Mo–N, $Mo_2(CO)_6(SCH_2CO_2Et)_2(CH_3CN)_2$

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

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

(Received January 24, 1986)

The results derived from the EXAFS studies on the FeMo cofactor [1] have been interpreted as an indication of the existence, besides the iron and sulfur atoms, of 2–3 oxygen (or nitrogen) atoms at 2.10 Å around the molybdenum atoms in this cofactor. In order to better understand the microenvironment of the Mo site in this FeMo cofactor and thereby more satisfactorily interpret the EXAFS data a study of Mo complexes containing Mo–O(N) bonds has attracted widespread interest among cluster chemists. A dinuclear Mo(I) complex containing CH_3CN coordinated to each Mo atom has been isolated from an oxidation of dinuclear Mo(0) complexes [2]. Herein we report the synthesis and structure of $Mo_2(CO)_6(SCH_2CO_2Et)_2(CH_3CN)_2$ (**1**).



1

Experimental

Synthesis

$[Et_4N]_2[Mo_2(CO)_8(SCH_2CO_2Et)_2]$ (**2**) [3, 4] was reacted with an equivalent amount of I_2 in CH_2CN at room temperature for 24 h. Analytically pure green microcrystalline product **1** was obtained after filtration, washing and drying in vacuum. *Anal.* Found: C, 32.28; H, 3.06; N, 4.80; S, 9.05. Calcd. for $C_{18}H_{20}S_2O_{10}N_2Mo_2$: C, 31.76; H, 2.94; N, 4.12; S, 9.41%. The IR spectrum of **1** shows two absorptions at 2270 and 2300 cm^{-1}, which are the characteristic frequencies of C≡N [5]. Four strong bands (1980, 1940, 1870, 1860 cm^{-1}) in the CO stretching region, divided into two groups, and the absence of the characteristic absorption of the Et_4N^+ cation are consistent with the formulation of **1** with Mo atoms present in the +1 oxidation state.

Crystal Data

1 crystallizes in the monoclinic space group, $P2_1/n$ with $a = 9.156(1)$, $b = 9.806(2)$, $c = 15.206(2)$ Å; $\beta = 107.78(1)°$; $Z = 2$.

Intensity Measurements, Structural Determination and Refinement

Single crystals of **1** were grown from acetonitrile and the intensities were collected on a CAD4 diffractometer in the range $1 \leqslant \theta \leqslant 25°$ by using the ω–2θ scan technique. The structure was solved by direct and Fourier methods and was refined to $R_1 = 0.047$, $R_2 = 0.055$ by full-matrix least-squares method for 1748 independent reflections with $I > 3\sigma(I)$. The final positional and thermal parameters with estimated standard deviations are listed in Table I.

Results and Discussion

The bond distances and bond angles of **1** are given in Table II. The centrosymmetrical molecular configuration of **1** is depicted in Fig. 1. The geometry around each Mo atom is a distorted octahedral with

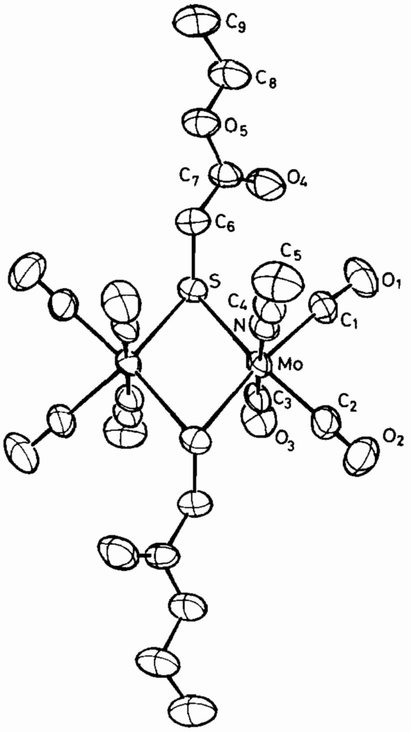


Fig. 1. The molecular configuration of $Mo_2(CO)_6(SCH_2CO_2Et)_2(CH_3CN)_2$ (**1**).

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

TABLE I. Positional and Thermal Parameters for $Mo_2(CO)_6(SCH_2CO_2Et)_2(CH_3CN)_2$ with Estimated Standard Deviations

Atom	x	y	z	B_{eq}
Mo	0.39811(6)	0.38923(6)	0.01278(4)	2.60(1)
S	0.5590(2)	0.3866(2)	−0.0901(1)	3.05(3)
O(1)	0.1107(6)	0.3530(7)	0.0916(4)	7.1(2)
O(2)	0.3536(8)	0.0772(6)	−0.0254(5)	7.2(2)
O(3)	0.6396(6)	0.2674(6)	0.1854(3)	5.4(1)
O(4)	0.8307(7)	0.3403(6)	−0.1612(4)	6.9(1)
O(5)	0.8636(6)	0.1279(5)	−0.1073(3)	4.4(1)
N	0.2220(6)	0.4638(6)	−0.1145(4)	3.3(1)
C(1)	0.2219(8)	0.3695(8)	0.0660(5)	4.2(2)
C(2)	0.3646(8)	0.1918(8)	−0.0169(5)	4.2(2)
C(3)	0.5511(8)	0.3169(8)	0.1221(4)	3.6(2)
C(4)	0.1309(8)	0.4952(7)	−0.1799(4)	3.6(2)
C(5)	0.0155(10)	0.5365(10)	−0.2635(5)	5.8(2)
C(6)	0.7191(8)	0.2713(7)	−0.0442(5)	3.5(2)
C(7)	0.8108(8)	0.2548(8)	−0.1107(5)	3.6(2)
C(8)	0.9594(9)	0.0979(9)	−0.1667(5)	5.1(2)
C(9)	1.0074(11)	−0.0438(10)	−0.1516(6)	6.2(2)
				B_{iso}
H(1)	0.029(10)	0.391(8)	0.249(5)	6.8(0)
H(2)	0.034(10)	0.472(8)	−0.316(5)	6.8(0)
H(3)	0.041(10)	0.609(8)	−0.286(5)	6.8(0)
H(4)	0.679(8)	0.177(7)	−0.029(4)	4.7(0)
H(5)	0.790(8)	0.278(7)	0.008(4)	4.7(0)
H(6)	1.040(9)	0.171(8)	−0.147(5)	6.1(0)
H(7)	0.892(9)	0.119(7)	−0.230(5)	6.1(0)
H(8)	1.030(10)	−0.072(9)	−0.093(5)	7.4(0)
H(9)	1.095(10)	−0.080(9)	−0.192(5)	7.4(0)
H(10)	0.907(10)	−0.119(9)	−0.165(5)	7.4(0)

TABLE II. Bond Distances (Å) and Bond Angles (°) in $Mo_2(CO)_6(SCH_2CO_2Et)_2(CH_3CN)_2$ with Estimated Standard Deviations

Distances			
Mo–Mo′	2.966(1)	C(3)–O(3)	1.159(8)
Mo–S	2.455(2)	N–C(4)	1.129(8)
Mo–S′	2.467(2)	C(4)–C(5)	1.440(11)
Mo–N	2.230(5)	S–C(6)	1.814(7)
Mo–C(1)	2.024(7)	C(6)–C(7)	1.508(10)
Mo–C(2)	1.990(8)	C(7)–O(4)	1.188(8)
Mo–C(3)	1.950(7)	C(7)–O(5)	1.330(8)
C(1)–O(1)	1.130(8)	O(5)–C(8)	1.469(9)
C(2)–O(2)	1.132(9)	C(8)–C(9)	1.454(13)
Angles			
Mo–S–Mo′	74.10(5)	C(1)–Mo–C(3)	94.4(3)
S–Mo–S′	105.90(5)	C(2)–Mo–C(3)	82.0(3)
S–Mo–N	82.29(14)	Mo–C(1)–O(1)	175.8(7)
S–Mo–C(1)	164.0(2)	Mo–C(2)–O(2)	173.5(7)
S–Mo–C(2)	85.8(2)	Mo–C(3)–O(3)	176.6(7)
S–Mo–C(3)	97.2(2)	Mo–N–C(4)	176.7(6)
S′–Mo–N	95.12(15)	N–C(4)–C(5)	179.4(8)
S′–Mo–C(1)	85.7(2)	S–C(6)–C(7)	111.0(5)
S′–Mo–C(2)	165.0(2)	C(6)–C(7)–O(4)	125.8(7)

(continued)

TABLE II. *(continued)*

Angles			
S′–Mo–C(3)	87.1(2)	C(6)–C(7)–O(5)	110.1(6)
N–Mo–C(1)	85.7(3)	O(4)–C(7)–O(5)	124.1(7)
N–Mo–C(2)	95.8(3)	C(7)–O(5)–C(8)	116.2(6)
N–Mo–C(3)	177.8(2)	O(5)–C(8)–C(9)	107.6(8)
C(1)–Mo–C(2)	84.9(3)		

TABLE III. Selected Structural Parameters for Cluster Complexes 1 and 2

	1	2
MoSMo	74.10(5)°	99.20(5)°
SMoS	105.90(5)°	80.80(5)°
Mo–S	2.455(2) Å, 2.467(2) Å	2.586(1) Å, 2.587(1) Å
Mo···Mo	2.966(1) Å	3.939(1) Å
Number of M–M	1	0

a large SMoS angle of 105.95(5)° and a small equatorial C_1MoC_2 angle of 84.91(3)°. The internuclear Mo . . . Mo distance is 2.966(1) Å. This obvious metal–metal bonding meets the requirement of an 18 electron configuration about each Mo atom for stabilization, thus accounting for a distortion of the configuration of the MoS_2Mo unit (see Table III). Compared with the molybdenum(0) complex $[Mo_2(CO)_8(SCH_2CO_2Et)_2]^{2-}$ (2) [3] the bond lengths of C–O are somewhat shorter on account of the fact that the oxidation of Mo(0) to Mo(I) decreases the electron backdonation to the vacant π^* orbitals of the carbonyls. It is noteworthy that such a complex **1** with a CH_3CN ligand coordinated to each Mo atom has not been found in the literature except the one mentioned in our previous work [2], particularly in view of the fact that the coordination of acetonitrile as a substrate of N_2-ase might be useful in understanding the function of N_2-ase in biological nitrogen fixation. The C–N bond length of 1.129(2) Å in **1** indicates that the C–N triple bond has not been activated at all, in contrast to the trinuclear Mo(IV) compound $\{Mo_3(\mu_3\text{-}X)(\mu\text{-}S)_3[\mu\text{-}S_2P(OEt)_2][S_2P(OEt)_2]_3(H_2O)\}$ (X = S, O) (**3**), which obviously activates the coordinated CH_3CN, resulting in the dimeric cyclic condensation of CH_3CN into an imidazole ring [6]. In light of the difference in activation of CH_3CN ligands between **1** and **3**, it appears that polynuclear clusters are capable of activating certain small-molecule substrates compared with mononuclear and/or dinuclear ones.

Interestingly enough, substitution of carbonyls by CH_3CN is somehow correlated to the formation of a Mo–Mo bond and to the increase in the oxidation state of Mo, as well as to the influence of metal–metal bonding on the reactivities of cluster compounds. As a matter of fact, the Mo(0) complexes $[Mo_2(SR)_2(CO)_8]^{2-}$ (R = Ph, Bu^t) exhibit a greater affinity for CO and are less susceptible to solvolytic reaction [2], whereas the Mo(I) compound $Mo_2(CO)_8(SCH_2CO_2Et)_2$ with Mo–Mo bonding possesses a longer axial Mo–CO bond length of 2.069 Å [7]* therefore allowing an easier substitution of CO.

References

1 B. K. Burgess, S.-S. Yang, C.-B. You, J.-G. Li, G. D. Friesn, N.-H. Pan, E. I. Stiefel and W. E. Newton, in A. H. Gibson and W. E. Newton (eds.), 'Current Perspectives in Nitrogen Fixation', 1981, p. 71.

2 B.-T. Zhuang, J. W. McDonald, F. A. Schultz and W. E. Newton, *Organometallics, 3,* 943 (1984).

3 B.-T. Zhuang, L.-R. Huang, Y. Yang and J.-X. Lu, *J. Struct. Chem.,* in press.

4 B.-T. Zhuang, L.-R. Huang, L.-J. He, W.-Z. Cheng, Y. Yang and J.-X. Lu, *Huaxue Xuebao (Acta Chim. Cinica),* in press.

5 L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules', 3rd edn., Chapman and Hall, London, 1975, p. 295.

6 J.-L. Huang, M.-Y. Shang, S.-F. Lu and J.-X. Lu, *J. Struct. Chem., 3,* 129 (1984).

7 B.-T. Zhuang, L.-R. Huang, Y. Yang and J.-X. Lu, unpublished results.

---

*Crystal data of $Mo_2(CO)_8(SCH_2CO_2Et)_2$. Space group *Pbca*, a = 8.681(1), b = 18.881(2), c = 14.512(2) Å, R_1 = 0.083, R_2 = 0.092 for 904 independent reflections.