Structure of $[Et_4N]_2[Mo_2(CO)_8(\mu\text{-}SPh)_2]$ and Structural Chemistry of Dinuclear Molybdenum(0,I) Carbonyl Complexes Containing Thiolato Bridges

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(Received April 6, 1988; revised August 3, 1988)

Abstract

The crystal and molecular structure of the dinuclear molybdenum(0) carbonyl complex containing thiophenyl bridges, $[Et_4N]_2[Mo_2(CO)_8(\mu\text{-}SPh)_2]$ (1) was determined from three-dimensional X-ray data. 1 crystallizes in the triclinic, space group $P\bar{1}$ with $a = 9.841(2)$, $b = 9.921(4)$, $c = 11.848(2)$ Å; $\alpha = 81.80(3)°$, $\beta = 85.64(2)°$, $\gamma = 82.06(3)°$; $V = 1038.9\text{-}(6)$ Å^3; $Z = 1$; $R = 0.068$ for 3228 independent reflections with $I \geqslant 3\sigma(I)$. A planar MoS_2Mo bimetallic framework with a large Mo...Mo distance of 4.069-(1)·Å which obviously indicates the absence of Mo–Mo bonding was contained in the centrosymmetric structure of the anion of 1, $[Mo_2(CO)_8(\mu\text{-}SPh)_2]^{2-}$. Studying the structure of 1 and comparing 1 with $[Et_4N]_2[Mo_2(CO)_8(\mu\text{-}SCH_2CO_2Et)_2]$ (2), $Mo_2(CO)_8(\mu\text{-}SCH_2CO_2Et)_2$ (3), $Mo_2(CO)_6(\mu\text{-}SCH_2\text{-}CO_2Et)_2(MeCN)_2$ (4) and $Mo_2(CO)_6(\mu\text{-}SPh)_2(MeCN)_2$ (5), the structural chemistry of dinuclear molybdenum(0,I) carbonyl complexes containing thiolato bridges and the relevance to their properties and electrochemistry were discussed.

Introduction

The current interest in the chemistry [1] of molybdenum with thiolato ligands has grown rapidly due to the known presence of Mo–S bonding in a variety of molybdoenzymes, among them nitrogenase. A great many Mo–S bond-containing complexes of molybdenum in a high oxidation state including iron–molybdenum–sulfur cluster compounds [2], which are concerned as a modelling compound of the molybdenum-site in nitrogenase have been investigated. With molybdenum in the middle oxidation state the first SR-containing dinuclear Mo(III) complex, $[(C_5H_5Mo)_2(SMe)_2]_2{}^n$ ($n = 0, +1$), was synthesized and characterized by King [3] and Connelly and Dahl [4]. Since then several studies on related compounds have appeared in the literature, but still very little research on the

molybdenum–SR-containing complexes with molybdenum in the low oxidation state, which might be useful for understanding the molybdenum-site in enzymes and for building the iron–molybdenum–sulfur cluster (the moiety postulated to be present in N_2-ase [5]), has been reported. Recently, we have synthesized a series of dinuclear molybdenum(0) carbonyl complexes containing thiolato bridges, $[Et_4N]_2[Mo_2(CO)_8(SR)_2]$ (R = Ph, Bu^t, CH_2CO_2Et and $C_6H_5CH_2$) [6–9] and have isolated the related molybdenum(I) dinuclear complexes, $Mo_2(CO)_{8-n}\text{-}(SR)_2L_n$ (R = Ph, Bu^t, CH_2CO_2Et and $C_6H_5CH_2$; $n = 0, 2$; L = MeCN, Ph_3P) [10–12] from the oxidation of dinuclear molybdenum(0) complexes $[Et_4\text{-}N]_2[Mo_2(CO)_8(SR)_2]$, in different solvents. Studies on the chemistry of these complexes indicating their interesting two-electron character and variety of reactivity have prompted us to explore their structural chemistry. We have given some preliminary reports about the complexes, $[Et_4N]_2[Mo_2\text{-}(CO)_8(SCH_2CO_2Et)_2]$, $Mo_2(CO)_8(SCH_2CO_2Et)_2$, $Mo_2(CO)_6(SCH_2CO_2Et)_2(MeCN)_2$, and $Mo_2(CO)_6\text{-}(SPh)_2(MeCN)_2$. Herein we report the structure of the phenothiolate-bridged dinuclear molybdenum(0) carbonyl complex $[Et_4N]_2[Mo_2(CO)_8(\mu\text{-}SPh)_2]$ (1), summarize the structural chemistry of dinuclear molybdenum(0,I) carbonyl thiolato-bridged complexes and discuss the relationship between their structures and properties.

Experimental

Materials and Methods

All synthetic procedures, crystal growth and preparation of the sample for X-ray determination were carried out under a nitrogen atmosphere using the Schlenk technique and degassed solvents. The single crystal selected for data collection was sealed in a glass capillary under nitrogen. Acetonitrile was distilled from CaH_2 and isopropanol was dried by magnesium methoxide. Hexane was commercial. Molybdenum hexacarbonyl was purchased from Fluka. NaSPh was prepared by the reaction of stoichiometric amounts of NaOMe and PhSH in

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methanol, followed by evaporation to dryness, trituration of the residue with diethyl ether and filtration.

Routine characterization: infrared spectra were measured on a Perkin-Elmer 577 Spectrophotometer in the range of 200 to 400 cm^{-1} by using KBr pellets. Elemental analysis for carbon, hydrogen and nitrogen were determined on a Carlo Erba Strumentazion Elemental Analyzer-MOD 1106.

Preparation of [Et$_4$N]$_2$[Mo$_2$(CO)$_8$(μ-SPh)$_2$] (1)

2.13 g of NaSPh were reacted with 2.66 g of anhydrous Et$_4$NCL in 160 ml MeCN at 45 °C for 3 h resulting in a slurry reaction mixture. This resulting slurry was then filtered onto 4.26 g of solid molybdenum hexacarbonyl and the resulting reaction mixture was stirred at 45 °C for 4 h. After cooling to room temperature and filtration, the resulting filtrate was evaporated under vacuum to 50 ml and 150 ml of isopropanol was added. 4.7 g of yellow microcrystalline product 1 was obtained by filtration, washed with MeCN/i-PrOH (1:4 v/v), i-PrOH and hexane by turns, and dried *in vacuo. Anal.* Calc. for C$_{18}$H$_{25}$NMoO$_4$S: C, 48.32; H, 5.59; N, 3.13; Mo, 21.48; S, 7.16. Found: C, 48.22; H, 5.69; N, 3.20; Mo, 21.28; S, 7.30%. IR (KBr pellet): 2000(m), 1900(s), 1840(s), 1770(s) (ν(MoC—O)); 577(m), 543(m), 600(m), 639(m) (δ(Mo—C—O)) and 359(m) (ν(Mo—C)) cm^{-1}.

X-ray Structural Determination of [Et$_4$N]$_2$-[Mo$_2$(CO)$_8$(μ-SPh)$_2$] (1)

A single crystal (light yellow color) of 1 with dimensions of 0.25 × 0.25 × 0.50 mm was grown from the mixed solvent MeCN/i-PrOH (1:1 v/v). 1 crystallizes in the triclinic, space group P$\bar{1}$ with a = 9.842(2), b = 9.921(4), c = 11.848(2) Å; α = 81.80(3)°, β = 85.64(2)°, γ = 82.06(3)°; Z = 1; V = 1038.9(6) Å^3; D_c = 1.430 g/cm^3.

X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromator Mo Kα radiation (λ = 0.71073 Å) in the range of 1° ⩽ θ ⩽ 25° using the θ—2θ scan technique. After correction for Lorentz and polarization (LP) effects and for anisotropic attenuation, the 3228 independent refractions ($I \geqslant 3\sigma(I)$) collected were used in the structural analysis. The preliminary structure solved by the heavy atom method was refined by Fourier synthesis and full-matrix least-squares resulting in obtaining the parameters of all the atoms in the unit cells. Hydrogen atoms participate in the calculation of the structure factor. The final cycle of the full-matrix least-squares refinement included 226 variable anisotropic temperature factors for all non-hydrogen atoms converged (the largest parameter shift is 0.57 times its e.s.d.) at R_1 = 0.069 and R_2 = 0.091. The final positional and thermal parameters with estimated standard deviations are

listed in Table 1. The bond distances and bond angles are shown in Tables 2 and 3. The structure of the anion of 1 is depicted in Fig. 1.

Preparation and X-ray Structural Determination of [Et$_4$N]$_2$[Mo$_2$(CO)$_8$(μ-SCH$_2$CO$_2$Et)$_2$] (2), Mo$_2$(CO)$_8$(μ-SCH$_2$CO$_2$Et)$_2$ (3), Mo$_2$(CO)$_6$(μ-SCH$_2$CO$_2$Et)$_2$(MeCN)$_2$ (4) and Mo$_2$(CO)$_6$(μ-SPh)$_2$(MeCN)$_2$ (5)

See refs. 9–12. Selected bond distances and bond angles of these four complexes are listed in Tables 4 and 5.

TABLE 1. Positional and Thermal Parameters of [Et$_4$N]$_2$-[Mo$_2$(CO)$_8$(SPh)$_2$] (1)^a

Atom	x	y	z	B_{eq}
Mo	0.02384(6)	0.32555(5)	0.10602(4)	3.27(1)
S	−0.1185(2)	0.5679(2)	0.1255(1)	3.58(4)
C(1)	0.1391(8)	0.1496(7)	0.0696(6)	4.2(2)
C(2)	−0.0381(8)	0.2551(7)	0.2777(6)	4.6(2)
C(3)	−0.1633(8)	0.2478(9)	0.1121(6)	5.2(2)
C(4)	0.1912(8)	0.3990(8)	0.1279(6)	5.1(2)
O(1)	0.2073(6)	0.0445(5)	0.0502(5)	6.1(2)
O(2)	−0.0686(8)	0.2048(6)	0.3805(5)	7.0(2)
O(3)	−0.2680(7)	0.2023(8)	0.1325(7)	9.3(2)
O(4)	0.2804(6)	0.4305(8)	0.1522(6)	9.7(2)
C(5)	−0.0919(7)	0.6641(7)	0.2302(6)	3.7(1)
C(6)	−0.0761(8)	0.8030(7)	0.2043(6)	4.6(2)
C(7)	−0.0738(9)	0.8780(8)	0.2928(7)	5.2(2)
C(8)	−0.0823(9)	0.8159(8)	0.4058(7)	5.4(2)
C(9)	−0.0929(9)	0.6758(8)	0.4321(6)	5.3(2)
C(10)	−0.0980(8)	0.6001(8)	0.3453(6)	4.7(2)
N	0.4205(6)	0.7880(7)	0.2909(6)	5.1(2)
C(11)	0.3391(9)	0.6602(9)	0.3467(8)	5.8(2)
C(12)	0.441(1)	0.5278(9)	0.3323(9)	7.3(3)
C(13)	0.3004(8)	0.9097(9)	0.3140(7)	5.5(2)
C(14)	0.357(1)	1.047(1)	0.2702(9)	7.5(3)
C(15)	0.510(1)	0.780(1)	0.153(1)	8.8(3)
C(16)	0.428(1)	0.758(1)	0.0798(9)	10.3(4)
C(17)	0.526(1)	0.806(1)	0.350(1)	9.6(3)
C(18)	0.463(1)	0.815(1)	0.489(1)	11.8(3)

^{a}e.s.d.s given in parentheses.

TABLE 2. Bond Distances (°) of [Mo$_2$(CO)$_8$(SPh)$_2$]$^{2-}$

Mo—S	2.599(1)	C(6)—C(7)	1.378(6)
Mo—S	2.617(1)	C(7)—C(8)	1.366(7)
Mo—C(1)	1.945(4)	C(8)—C(9)	1.389(7)
Mo—C(2)	1.920(4)	C(9)—C(10)	1.377(6)
Mo—C(3)	2.064(5)	N—C(11)	1.514(6)
Mo—C(4)	2.012(5)	N—C(13)	1.537(6)
C(1)—O(1)	1.157(5)	N—C(15)	1.512(7)
C(2)—O(2)	1.178(5)	N—C(17)	1.515(8)
C(3)—O(3)	1.102(6)	C(11)—C(12)	1.525(8)
C(4)—O(4)	1.123(6)	C(13)—C(14)	1.483(8)
C(5)—S	1.787(4)	C(15)—C(16)	1.458(11)
C(5)—C(6)	1.385(6)	C(17)—C(18)	1.508(13)
C(5)—C(10)	1.401(6)	Mo...Mo	4.069(1)

TABLE 3. Bond Angles (°) of $[Et_4N]_2[Mo_2(CO)_8(SPh)_2]$ (1)

S–Mo–S	77.45(3)	C(6)–C(5)–C(10)	118.8(4)
S–Mo–C(1)	173.0(1)	C(5)–C(6)–C(7)	120.4(4)
S–Mo–C(2)	101.4(1)	C(6)–C(7)–C(8)	120.6(4)
S–Mo–C(3)	89.3(2)	C(7)–C(8)–C(9)	119.9(4)
S–Mo–C(4)	89.7(1)	C(8)–C(9)–C(10)	120.0(4)
S–Mo–C(1)	95.6(1)	C(5)–C(10)–C(9)	120.1(4)
S–Mo–C(2)	176.3(1)	C(11)–N–C(13)	106.9(4)
S–Mo–C(3)	97.2(1)	C(11)–N–C(15)	109.4(5)
S–Mo–C(4)	90.9(2)	C(11)–N–C(17)	111.9(4)
C(1)–Mo–C(2)	85.6(2)	C(13)–N–C(15)	110.7(4)
C(1)–Mo–C(3)	90.6(2)	C(13)–N–C(17)	109.4(5)
C(1)–Mo–C(4)	91.1(2)	C(15)–N–C(17)	108.5(6)
C(2)–Mo–C(3)	86.3(2)	N–C(11)–C(12)	114.4(4)
C(2)–Mo–C(4)	85.6(2)	N–C(13)–C(14)	115.8(4)
C(3)–Mo–C(4)	171.5(2)	N–C(15)–C(16)	116.7(6)
S–C(5)–C(6)	121.6(3)	N–C(17)–C(18)	118.4(6)
S–C(5)–C(10)	119.4(3)	Mo–S–C(5)	113.9(2)
Mo–S–Mo	102.55(5)	Mo–S–C(5)	115.3(2)
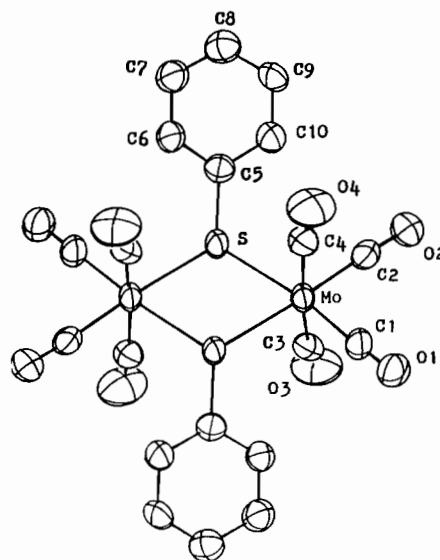
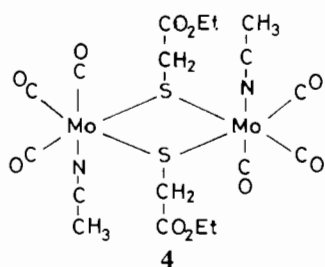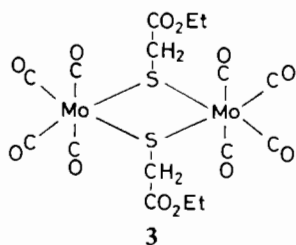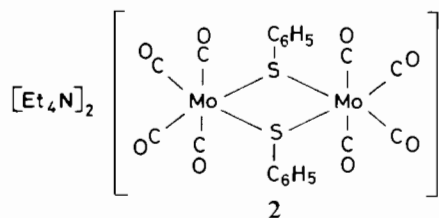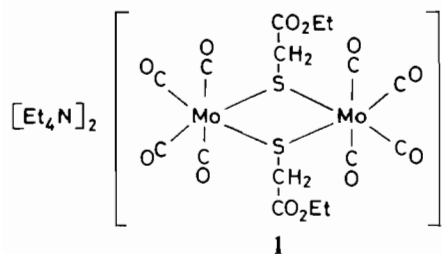Fig. 1. Structure of the anion of 1, $[Mo_2(CO)_8(SPh)_2]^{2-}$.

TABLE 4. Selected Structural Parameters of MoS_2Mo Frameworks in Mo(0) and Mo(I) Dimers

Complexes	MoSMo (°)	SMoS (°)	Mo–S (Å)	Mo–Mo (Å)
$[Et_4N]_2[Mo_2(CO)_8(SPh)_2]$ (1)	102.55(5)	77.45(3)	2.608	4.069
$[Et_4N]_2[Mo_2(CO)_8(SCH_2CO_2Et)_2]$ (2)	99.20(5)	80.80(5)	2.587	3.939
$Mo_2(CO)_8(SCH_2CO_2Et)_2$ (3)	73.77(7)	106.23(7)	2.449	2.939
$Mo_2(CO)_8(SBu^t)_2$ (6)	73.9	106.1(2)	2.48	2.984
$Mo_2(CO)_6(SCH_2CO_2Et)_2(MeCN)_2$ (4)	74.10(5)	105.90(5)	2.461	2.966
$Mo_2(CO)_6(SPh)_2(MeCN)_2$ (5)	74.20(4)	105.80(4)	2.469	2.9782

TABLE 5. Selected Structural Parameters of Mo Terminal Ligands of Mo(0) and Mo(I) Dimers[a]

Complexes	C'MoC' (°)	Mo–C' (Å)	Mo–C" (Å)	Mo–N (Å)
$[Et_4N]_2[Mo_2(CO)_8(SPh)_2]$ (1)	85.6(2)	1.945(4) 1.920(4)	2.064(1) 2.012(5)	
$[Et_4N]_2[Mo_2(CO)_8(SCH_2CO_2Et)_2]$ (2)	87.79(25)	1.954(6) 1.937(6)	2.027(6) 2.025(6)	
$Mo_2(CO)_8(SCH_2CO_2Et)_2$ (3)	85.2(4)	2.023(11) 2.026(10)	2.033(12) 1.992(14)	
$Mo_2(CO)_8(SBu^t)_2$ (6)	81.45(5)	2.01	2.05	
$Mo_2(CO)_6(SCH_2CO_2Et)_2(MeCN)_2$ (4)	84.93(3)	2.024(7) 1.990(8)	1.950(7)	2.230(5)
$Mo_2(CO)_6(SPh)_2(MeCN)_2$ (5)	87.1(3)	2.019(6) 2.002(6)	1.950(4)	2.217(3)

[a]C', equatorial carbonyl; C", axial carbonyl.

[Et$_4$N]$_2$ ... (structure **1**: [Mo$_2$(CO)$_8$(μ-SCH$_2$CO$_2$Et)$_2$]$^{2-}$)

1

[Et$_4$N]$_2$ ... (structure **2**: [Mo$_2$(CO)$_8$(μ-SPh)$_2$]$^{2-}$)

2

(structure **3**)

3

(structure **4**)

4

(structure **5**)

5
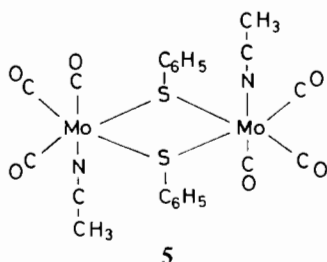
Results and Discussion

Structure of [Et$_4$N]$_2$[Mo$_2$(CO)$_8$(μ-SPh)$_2$] (1)

1 consists of three discrete structural fragments, two Et$_4$N$^+$ cations and an anion [Mo$_2$(CO)$_8$(μ-SPh)$_2$]$^{2-}$ which is comprised of two equivalent Mo atoms, each bonded to four terminal carbonyls and two bridging phenyl mercapto ligands. As shown in Tables 1–3 and Fig. 1, the anion of **1**, [Mo$_2$(CO)$_8$(μ-

SPh$_2$]$^{2-}$, is centrosymmetric and the geometry of each molybdenum(0) atom is a distorted octahedra consisting of two coordinated sulfur atoms and four coordinated carbon atoms with a small SMoS angle of 77.45(3)° and equatorial CMoC angle of 85.6(2)°. The large Mo...Mo distance of 4.069(1) Å implied non-bonding of metal...metal which meets the requirement of an 18-electron configuration about each Mo atom for stabilization. The bimetal core unit MoS$_2$Mo is a plane with a Mo–S bond distance of 2.608 Å which is a little longer than that in the core unit of the CH$_2$CO$_2$Et-analog, [Mo$_2$(CO)$_8$(μ-SCH$_2$-CO$_2$Et)$_2$]$^{2-}$, of **2**. The dihedral angle of 43.5° between the MoS$_2$Mo core plane and the benzene ring plane indicated that the conjunction of the lone pair of electrons on sulfur and the π-electrons of the phenyl ring is impossible. Due to the stereo-hindrance of the phenyl rings, **1** possesses a larger MoSMo angle (102.55°) and a longer Mo...Mo distance (4.069 Å) compared with the analog [Mo$_2$(CO)$_8$(μ-SCH$_2$CO$_2$-Et)$_2$]$^{2-}$, of which the MoSMo angle and Mo...Mo distance are 99.20° and 3.939 Å, respectively. The four carbonyls coordinated to each molybdenum atom are unequal in the Mo–C bond distances. The axial Mo–C distance (2.038 Å) is longer than the equatorial one (1.933 Å), so the C–O distance of the equatorial carbonyl is obviously different from that of the axial carbonyl.

Structure of Dinuclear Molybdenum(0,1) Carbonyl Complexes Containing Thiolato-bridges, [Mo$_2$(CO)$_8$-(μ-SR)$_2$]$^{2-}$, Mo$_2$(CO)$_8$(μ-SR)$_2$ and Mo$_2$(CO)$_6$(μ-SR)$_2$(MeCN)$_2$

The characteristic feature of both the Mo(0) dimer, [Mo$_2$(CO)$_8$(μ-SR)$_2$]$^{2-}$, and the Mo(1) dimer, Mo$_2$(CO)$_8$(μ-SR)$_2$ and Mo$_2$(CO)$_6$(μ-SR)$_2$(MeCN)$_2$, (R = Ph, Bu^t, CH$_2$CO$_2$Et and CH$_2$C$_6$H$_4$CH$_2$SH [13] is the existence of a planar bimetallic MoS$_2$Mo framework which is important for the electron transfer character of these complexes and might be a reactive fragment [14] for the sysnthesis of a polynuclear metal cluster like the structural unit MS$_2$M postulated as an essential unit of the active center in N$_2$-ase [15]. In Mo(0) dimers, as indicated by the structures of [Mo$_2$(CO)$_8$(μ-SPh)$_2$]$^{2-}$ and [Mo$_2$(CO)$_8$-(μ-SCH$_2$CO$_2$Et)$_2$]$^{2-}$, the planar MoS$_2$Mo framework with a long Mo...Mo distance possessed nearly the same dimension in bond distance and bond angle and the coordinated carbonyls on each Mo(0) atom divided into two groups due to *trans*-effect, the axial Mo–C bond distances are significantly different from the equatorial ones leading to the short and long adjacent C–O bond distances (1.112 and 1.167 Å). This is consistent with the separation of ν(MoC–O) in the IR spectra of the Mo(0) dimers (for **1**, 2000-(m), 1900(s), 1840(s) and 1770(s); for **2**, 1980(m), 1875(s), 1830(s) and 1770(s)) and is the reason why both **1** and **2** exhibit similar reactivity in being

oxidized to related Mo(I) dimers chemically and electrochemically. For the Mo(I) dimers, as shown by the structural data of $Mo_2(CO)_8(SCH_2CO_2Et)_2$ (3), $Mo_2(CO)_6(SCH_2CO_2Et)_2(MeCN)_2$ (4), $Mo_2(CO)_6$-$(SPh)_2(MeCN)_2$ (5) and $Mo_2(CO)_8(SBu^t)_2$ (6) [16] listed in Tables 4 and 5, the planar MoS_2Mo frameworks with short Mo...Mo distances, which indicated the existence of metal–metal bonding and were significantly different from the ones in the Mo(0) dimers, basically have the same bond distances and angles. With an obvious difference from Mo(0) dimers, the Mo–C bond distances of the four carbonyls coordinated to each Mo(I) atom in Mo(I) dimers without any MeCN (3 and 7 for example) are nearly equal resulting in the fact that the four strong absorption peaks assigned to $\nu(MoC–O)$ in the range of 1600 to 2000 cm^{-1} are very close to each other in the IR spectra of Mo(I) dimers, Mo_2-$(CO)_8(SR)_2$ [12]. For instance, the $\nu(MoC–O)$ of $Mo_2(CO)_8(SCH_2CO_2Et)_2$ are 2090, 1990, 1988 and 1952 cm^{-1} [11]. However, coordination of the MeCN molecule to the Mo(I) atom causes a decrease in the opposite Mo–C bond distance in $Mo_2(CO)_6$-$(SR)_2(MeCN)_2$ and thus it is more difficult to replace another axial carbonyl by the third acetonitrile molecule. This explains why the oxidation of $[Mo_2(CO)_8(SR)_2]^{2-}$ by I_2 in MeCN affords pure $Mo_2(CO)_6(SR)_2(MeCN)_2$ in high yield and no 4MeCN-substituted product, $Mo_2(CO)_4(SR)_2(MeCN)_4$, is isolated [12]. Taking into account the Mo–SR bond distances in those Mo(0) and Mo(I) dimers shown in Table 4 it could be suggested that the Mo–S bond distances are mainly dependent upon the oxidation states of the molybdenum atoms in the complexes. The higher is the oxidation state of molybdenum, the shorter the Mo–S bond distance becomes.

According to the discussion mentioned above we can come to the conclusion that the configuration of the planar MoS_2Mo frameworks in those dinuclear molybdenum(0,I) carbonyl complexes containing thiolato bridges, $[Mo_2(CO)_{8-x}(SR)_2$-$L_x]^{n-}$ (R = aryl or alkyl; L = MeCN; x = 2; and n = 0,2) is mainly dependent on the oxidation state of Mo and less dependent on the R ligands in the complexes. The complexes with the Mo atoms in the same oxidation state nearly possess the same configuration of the bimetallic MoS_2Mo framework resulting in the similarity of their reactivity including their redox chemistry though their ligands R are very different. This also demonstrates the important influence of valence electrons on molecular geometry [5].
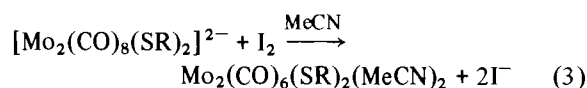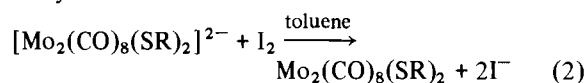
Relationship of Two-electron Transfer Character with the Configuration-change of Planar MoS₂Mo Framework with Formation of a Metal–Metal Bond

A very interesting and characteristic electrochemical behavior of the dinuclear Mo(0) carbonyl complexes containing SR bridges is the two-electron transfer character, *i.e.* these complexes undergo reversible two-electron oxidation in a single step [6, 7, 9]

$$[Mo_2(CO)_8(SR)_2]^{2-} \rightleftharpoons [Mo_2(CO)_8(SR)_2]^0 + 2e^- \quad (1)$$
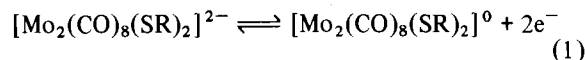
In fact, the oxidated product, Mo(I) dimers Mo_2-$(CO)_8(SR)_2$ and $Mo_2(CO)_6(SR)_2(MeCN)_2$, may be isolated from the chemical oxidation of Mo(0) dimers with iodine in toluene and MeCN, respectively.

$$[Mo_2(CO)_8(SR)_2]^{2-} + I_2 \xrightarrow{\text{toluene}} Mo_2(CO)_8(SR)_2 + 2I^- \quad (2)$$

$$[Mo_2(CO)_8(SR)_2]^{2-} + I_2 \xrightarrow{\text{MeCN}} Mo_2(CO)_6(SR)_2(MeCN)_2 + 2I^- \quad (3)$$

Mo(I) dimers can also be reduced to Mo(0) dimers by a chemical reductant such as Et_4NBH_4 in acetonitrile.

Taking into account the structural data of the bimetallic MoS_2Mo frameworks of the Mo(0) and Mo(I) complexes, it is obvious that the two-electron transfer character relates closely to the configuration-change of the MoS_2Mo framework with creation or cleavage of the Mo–Mo bond. Mo(0) dimers $[Mo_2$-$(CO)_8(SCH_2CO_2Et)_2]^{2-}$ and $[Mo_2(CO)_8(SPh)_2]^{2-}$, for example, possess large MoSMo angles (99.55° and 102.55°), long Mo–S bond distances (2.587 and 2.608 Å) and non-bonding Mo...Mo distances (3.939 and 4.069 Å), but the Mo(I) dimers $Mo_2(CO)_8$-$(SCH_2CO_2Et)_2$ and $Mo_2(CO)_6(SPh)_2(MeCN)_2$ have small MoSMo angles (73.77° and 74.20°), short Mo–S bond distances (2.469 and 2.449 Å) and bonding Mo–Mo distances (2.939 and 2.979 Å). That is, $Mo^0_2 \rightarrow Mo^I_2$ two-electron oxidation is accompanied by contractions in the MoS_2Mo framework of ~26° in the MoSMo angle, 0.1 Å in the Mo–S bond distance and 1.0 Å in the Mo...Mo distance indicating a significant configuration-change. Noteworthily, in contrast to the case of phosphido-bridged complexes, $Fe_2(CO)_6(PPh_2)_2/[Fe_2(CO)_6$-$(PPh_2)_2]^{2-}$, which have a highly non-planar FeP_2Fe core in neutral $Fe_2(CO)_6(PPh_2)_2$ and a planar FeP_2Fe in the dianion $[Fe_2(CO)_6(PPh_2)_2]^{2-}$ and almost the same Fe–P distances in both neutral and dianion species (2.233 and 2.280 Å) [17, 18], the MoS_2Mo frameworks in both Mo(0) and Mo(I) dimers are planar and the Mo–S bond distance of the Mo(I) dimer is 0.138 Å shorter than that of the Mo(0) dimer (Table 4). It would appear that the way the interconversion of the Mo(0) and Mo(I) dimer is involved in the accompaning two-electron transfer is different from that of $[Fe_2(CO)_6$-$(PPh_2)_2]^{2-}$ and $Fe_2(CO)_6(PPh_2)_2$. In phosphido-bridged iron complexes, the change of configuration

of the FeP_2Fe cores involves planar and non-planar changes during the two-electron redox of the complexes, but for the thiolato-bridged molybdenum complexes, the configuration-change of the MoS_2Mo frameworks occurs in the same plane. We therefore speculate the existence of a resonance between structure **A** and structure **B** in solution as shown below.
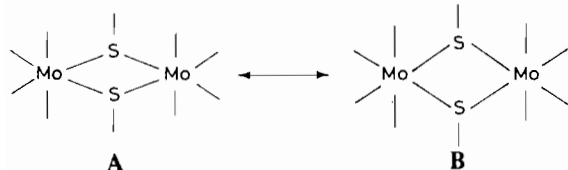
Structure **A** has the same size as the Mo(0) dimer and Structure **B** exhibits the same bond distances and angles as the Mo(I) dimer. Obviously, it is easy to interconvert between structure **A** and structure **B** if the two sulfur atoms move ~0.6 Å away or towards one another in the MoS_2Mo plane. In terms of the results derived from a theoretical study on $[Cr_2(CO)_8(\mu\text{-}PH_2)_2]^z$ (z = 2+, 0, 2−) by Shaik and co-workers [19], the electronic structure of d^6–d^6 complexes, $[Mo_2(CO)_8(\mu\text{-}SR)_2]^{2-}$, should similarly be $\pi^2\delta^{*2}\delta^2\pi^{*2}\sigma^2\sigma^{*2}$ and the occupied π^* and σ^* levels, especially the σ^* level, rise sharply with a decrease of the MoSMo bridging angle θ. So the conversion of structure **A** to structure **B** with a decrease of angle θ would lead to the rise of the occupied σ^* level and thus the electrons filled in the σ^* orbital become unstable and can be taken out easily resulting in the two-electron oxidation of the Mo(0) dimer to the Mo(I) dimer accompanied by formation of the Mo—Mo bond in order to satisfy the 18-electron configuration around each d^5 Mo atom, if certain conditions such as the presence of oxidant (I_2 for example) or electrolysis are provided. This speculation enables a plausible explanation of the facile nature of the two-electron transfer between $Mo_2(CO)_8(SR)_2$ and $[Mo_2(CO)_8(SR)_2]^{2-}$ to be made, although the existence of the resonance of structure **A** and structure **B** remains to be confirmed.

Acknowledgements

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