

New molybdenum–sulfur–oxygen complexes containing the O_3MoS_3 unit: synthesis, structure, X-ray photoelectron spectra and electrochemistry of a novel mixed-valence dinuclear Mo complex, $[Et_4N]_2[Mo_2(CO)_3(S,O-C_6H_4-1,2)_3]$

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Abstract

The reaction of molybdenum hexacarbonyl with *o*-hydroxyphenylthiolate and air-treated *o*-hydroxyphenylthiolate in acetonitrile affords a new dinuclear molybdenum–sulfur–oxygen complex containing the O_3MoS_3 unit, $[Et_4N]_2[Mo_2(CO)_3(S,O-C_6H_4-1,2)_3]$ (**1**). **1** was characterized by routine elemental analysis and spectroscopy, and the crystal and molecular structure of **1** was studied by X-ray crystallography. $1 \cdot C_3H_7OH$ crystallizes in the monoclinic, space group $P2_1/c$, with $a = 13.310(2)$, $b = 19.572(3)$, $c = 17.580(2)$ Å, $\beta = 103.78(1)^\circ$, $Z = 4$, $V = 4447.9(22)$ Å³, $R = 0.072$ and $R_w = 0.082$. The anion of **1**, $[Mo_2(CO)_3(S,O-C_6H_4-1,2)_3]^{2-}$, has a pseudo- C_3 axis through two molybdenum atoms which possess trigonal prism and distorted octahedron geometries. The Mo...Mo distance in **1** is 3.168(2) Å. The interesting O_3MoS_3 structural unit with an average Mo–S bond distance of 2.32 Å and Mo–O bond distance of 2.06 Å is comparable with the XAS (X-ray absorption spectroscopy) data of the first coordination sphere of Mo atom in iron molybdenum cofactor (FeMo-co) isolated from nitrogenase. X-ray photoelectron spectra of **1** show the existence of two different oxidation states of Mo atoms in **1**. A cyclic voltammetry (CV) study on **1** indicated that the electrochemistry on the two metal centers is different. The synthetic reaction, possible reactivity and possible oxidation states of Mo atoms are discussed.

Introduction

Since the EPR and Mössbauer studies [1–2] on the MoFe protein indicated that the active site of nitrogenase comprises a Fe–Mo–S aggregate and the XAS (X-ray absorption spectroscopy) [3–6] results revealed that the environment of the Mo site in and after extrusion from the MoFe–protein matrix contains two to three oxygen atoms at 2.10–2.12 Å, three to five sulfur atoms at 2.37 Å and three to four iron atoms at 2.68–2.70 Å, the investigation on the chemistry of Mo–Fe–S clusters and Mo–S complexes in order to approach the structure of the active center of nitrogenase has received increasing attention in the literature. A great many Mo–Fe–S cluster compounds including linear and cubane-like clusters have been synthesized and studied as model compounds [7–9] and a few Mo–S–O complexes, which reflect the XAS data of the first coordination sphere of the Mo atom in FeMo-co of N_2 -ase [10, 11] have

been reported. We report here the synthesis, structure, XPS (X-ray photoelectron spectra) and electrochemistry of a novel mixed-valence dinuclear Mo–S–O complex with the MoS_3O_3 structural unit, $[Et_4N]_2[Mo_2(CO)_3(S,O-C_6H_4-1,2)_3]$ (**1**).

Experimental

Materials and methods

All reactions and measurements were performed in a dry nitrogen atmosphere by using Schlenk techniques. MeCN and isopropanol were dried by distillation with CaH_2 and $Mg(OMe)_2$, respectively, and all solvents were deoxygenated before use. $Mo(CO)_6$ and Et_4NCl were purchased from Fluka and 2-mercaptophenol from Merck-Schuchardt.

Sodium *o*-hydroxyphenylthiolate was prepared by reaction of stoichiometric amount of 2-mercaptophenol and NaOMe in MeOH followed by evaporation to dryness, trituration of the residue with diethyl ether, and filtration.

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Infrared spectra (IR, values in cm^{-1}) were recorded on a Perkin-Elmer 577 instrument.

Cyclic voltammetry measurements were carried out with a three electrode cell using 0.1 M Bu_4NBF_4 as the supporting electrolyte and MeCN as the solvent. The working electrode was a glassy carbon disk ($A = 0.0804 \text{ cm}^2$). The reference electrode was an aqueous SCE separated from the sample solution by a salt bridge. Solutions were blanketed with nitrogen. The potentiostat was a CV-1B from BAS (Bioanalytical Systems).

Elemental analysis were carried out on Carlo Erba Strumentazione elemental analyzer MOD 1106.

X-ray photoelectron spectra were measured on a NP-3G model X-ray photoelectron spectrometer from Shenyang Scientific Instrument Factory of the Chinese Academy of Sciences. The instrumental deviation is less than 0.05 eV. The Mg $K\alpha$ X-ray line at 1253.6 eV was used for excitation and the X-ray power supply was run at 15 kV and 10 mA. All samples were run as powder dusted onto gallium in a nickel through supported by a molybdenum holder and under vacuum (4×10^{-9} Torr). All measurements were referenced to the Ag line. For comparison the Mo(0) dimer $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_8(\text{SPh})_2]$ [12, 13] has been measured under identical conditions.

Synthesis of $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_3(\text{S}, \text{O}-\text{C}_6\text{H}_4-1,2)_3]$ (1)

A mixture of sodium *o*-hydroxyphenylthiolate (0.4 g, 2.7 mmol) and sodium methoxide (0.14 g, 2.3 mmol) in 80 ml MeCN was stirred at $\sim 50^\circ\text{C}$ under air for 24 h. The resulting reaction mixture was degassed and a mixture of solid $\text{Mo}(\text{CO})_6$ (0.71 g, 2.7 mmol), Et_4NCl (0.9 g, 5.4 mmol) and sodium *o*-hydroxyphenylthiolate (0.2 g, 1.35 mmol) was added. The reaction mixture was stirred at $\sim 50^\circ\text{C}$ under N_2 for 24 h forming a deep red solution with some white precipitate in it. After cooling to room temperature and filtering, the deep red filtrate was concentrated under vacuum to 30 ml, and 30 ml isopropanol was added. A total of 0.60 g red crystalline product (1) was obtained by filtering, and washing with isopropanol; yield 50% (based on $\text{Mo}(\text{CO})_6$ used). *Anal.* Calc. for $\text{C}_{37}\text{H}_{52}\text{N}_2\text{Mo}_2\text{O}_6\text{S}_3$: C, 48.89; H, 5.72; N, 3.08; Mo, 21.15; S, 10.57. Found: C, 48.41; H, 5.16; N, 2.75; Mo, 20.87; S, 10.14%. IR (KBr): 1908s, 1760s, 1740s, 620m, 640m, 375m cm^{-1} .

Synthetic reaction with variation of reaction conditions

(a) A mixture of sodium *o*-hydroxyphenylthiolate (0.89 g) and Et_4NCl (1.99 g) in ~ 50 ml MeCN was stirred at $\sim 50^\circ\text{C}$ under N_2 overnight resulting in a yellow solution with a white precipitate in it. This slurry was filtered onto solid $\text{Mo}(\text{CO})_6$ (1.06 g) and

the resulting reaction mixture was stirred at 50°C under N_2 for 24 h. After cooling to room temperature and filtering, the filtrate was evaporated under vacuum to 25 ml, and 30 ml isopropanol was added. A total of 0.85 g yellow microcrystalline product 2 which was recognized to be the Mo(0) dimer $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_8(\text{S}-\text{C}_6\text{H}_4\text{OH})_2]$ [14] by IR, elemental analysis and X-ray crystallography, was obtained.

(b) To a solution of sodium *o*-hydroxyphenylthiolate in MeOH (generated by reaction of 0.26 g NaOMe with 0.5 ml 2-mercaptophenol in 15 ml MeOH) was added a solution of 0.54 g of Et_4NCl in 60 ml MeCN. The resulting mixture was stirred at $50\text{--}55^\circ\text{C}$ under O_2 overnight. Then the resulting reaction mixture was degassed and 0.85 g of solid $\text{Mo}(\text{CO})_6$ was added. This mixture was stirred at $50\text{--}55^\circ\text{C}$ under N_2 for 24 h. After filtering, concentration, and addition of isopropanol neither 1 nor 2, but a new red product, of which the characterization and X-ray structure determination are in progress, was obtained.

X-ray structure determination

A summary of crystal data, intensity collection information and structure refinement parameters is presented in Table 1. Diffraction experiments were performed at $\sim 23^\circ\text{C}$ with an Enraf-Nonius CAD4 four circle automatic diffractometer using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Computer program were those of the SDP/VAX (Enraf-Nonius) [15].

A black rhombic crystal of $1 \cdot \text{C}_3\text{H}_7\text{OH}$ grown from a mixed-solvent of MeCN and isopropanol was mounted on a glass fiber, wrapped with gel. The final orientation matrix and unit cell parameters were determined from 25 machine-centered reflections having $24^\circ < 2\theta < 26^\circ$. Data reduction including Lorentz and polarization correction was carried out. An empirical absorption correction based on intensity profiles of six reflections over a range of settings (Ψ) of the diffraction vectors was applied to the data. A total of 8405 reflections was collected. Systematic absences $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) unambiguously established the space group in the monoclinic system as $P2_1/c$.

The structure was solved by direct methods procedure using the program MULTAN of the SDP/VAX. A total of 32 phase sets was produced by using 403 reflections (minimum E of 1.93). After the heavy atom fragment of the structure was located from an E -map prepared from the phase set with probability statistics: absolute figure of merit is 1.17, residual is 5.85 and Ψ_0 is 2.637; the rest of the non-hydrogen atoms were found from subsequent Fourier electron density difference maps. Isotropic refinement

of all the non-hydrogen atoms converged to a R value of 0.087. At this point all the atoms were assigned to anisotropic temperature factors. All hydrogen atoms were not included in the structure factor calculations. The structure was refined in full-matrix least-squares were the function minimized was $\sum w(|F_o| - |F_c|)^2$, and the weight w defined as per the Kilean and Lawrence method with terms of 0.020 and 1.0 [16]. The final cycle of refinement (using anisotropic temperature factors for all non-hydrogen atoms) included 487 variable parameters and converged with the final R value of 0.072 and the weighted R_w of 0.082, and all parameter shifts were less than 1.30σ . The standard deviation of an observation of unit weight was 1.35. There were 24 correlation coefficients greater than 0.50. The highest peak in the final difference Fourier had a height of $0.81 \text{ e}/\text{\AA}^3$, with an estimated error based on ΔF [17] of 0.14; the minimum negative peak had a height of $-0.67 \text{ e}/\text{\AA}^3$. The final positional and thermal parameters with estimated standard deviations are listed in Table 2.

TABLE 1. Summary of crystal data, intensity collection and structure refinement parameters for $1 \cdot \text{C}_3\text{H}_7\text{OH}$

Formula	$\text{C}_{40}\text{H}_{60}\text{Mo}_2\text{N}_2\text{O}_7\text{S}_3$
Molecular weight	969.01
a (Å)	13.310(2)
b (Å)	19.572(3)
c (Å)	17.580(2)
β (°)	103.78(1)
Crystal system	monoclinic
V (Å ³)	4447.9
Z	4
D_{calc} (g/cm ³)	1.45
Space group	$P2_1/c$
Crystal dimensions (mm)	$0.35 \times 0.30 \times 0.13$
Radiation	Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$)
Absorption coefficient μ (cm ⁻¹)	7.3
Scan mode	θ - 2θ
Scan speed: min., max. (°/min)	1.0, 5.0
Scan range	$0.45 + 0.35 \tan \theta$
Data collected	$2\theta = 50.0$ ($+h, +k, \pm l$)
Unique data	8405
Data used in refinement with $I > 3\sigma(I)$	2760
No. non-hydrogen atoms in asymmetric unit	54
No. variables	487
Phasing technique	direct methods
R^a	0.072
R_w^a	0.082

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

TABLE 2. Positional parameters and their e.s.d.s for all the non-hydrogen atoms in $1 \cdot \text{C}_3\text{H}_7\text{OH}$

Atom	x	y	z	B (Å ²)
Mo(1)	0.6710(1)	0.10476(8)	0.69198(9)	3.75(4)
Mo(2)	0.9142(1)	0.12394(8)	0.74154(9)	3.85(4)
S(1)	0.5516(4)	0.1913(3)	0.6884(3)	5.4(1)
S(2)	0.5817(4)	0.0675(3)	0.5689(3)	5.4(1)
S(3)	0.5772(4)	0.0325(3)	0.7545(3)	5.7(1)
O(1)	0.7681(8)	0.1852(6)	0.7348(6)	4.1(3)
O(2)	0.7902(8)	0.0936(6)	0.6369(6)	4.1(3)
O(3)	0.7892(9)	0.0623(6)	0.7758(6)	4.5(3)
O(10)	1.049(1)	0.2233(8)	0.6747(8)	8.6(5)
O(20)	1.080(1)	0.0185(7)	0.7299(9)	8.4(5)
O(30)	1.064(1)	0.1628(8)	0.8968(7)	7.4(4)
C(1)	0.995(1)	0.187(1)	0.698(1)	5.2(5)
C(2)	1.016(1)	0.0592(9)	0.734(1)	5.4(5)
C(3)	1.005(1)	0.147(1)	0.840(1)	5.4(5)
C(11)	0.740(1)	0.2509(8)	0.7409(8)	3.2(4)
C(12)	0.632(1)	0.262(1)	0.7195(9)	4.6(5)
C(13)	0.592(2)	0.330(1)	0.726(1)	6.0(6)
C(14)	0.661(2)	0.382(1)	0.748(1)	7.0(6)
C(15)	0.768(2)	0.3686(9)	0.767(1)	6.2(6)
C(16)	0.810(1)	0.3032(9)	0.765(1)	4.6(5)
C(21)	0.784(1)	0.0723(9)	0.5649(9)	4.1(5)
C(22)	0.685(1)	0.0547(8)	0.5232(8)	3.1(4)
C(23)	0.665(2)	0.0271(9)	0.4450(9)	4.8(5)
C(24)	0.751(2)	0.018(1)	0.412(1)	5.4(5)
C(25)	0.850(2)	0.0338(9)	0.4569(9)	5.2(5)
C(26)	0.869(2)	0.0591(9)	0.534(1)	5.0(5)
C(31)	0.777(2)	0.0163(9)	0.829(1)	5.1(5)
C(32)	0.676(1)	-0.0031(9)	0.828(1)	4.9(5)
C(33)	0.654(2)	-0.053(1)	0.882(1)	5.7(6)
C(34)	0.740(2)	-0.078(1)	0.938(1)	7.6(7)
C(35)	0.843(2)	-0.056(1)	0.941(1)	6.9(6)
C(36)	0.866(2)	-0.008(1)	0.8846(9)	5.6(6)
N(1)	0.744(1)	0.1794(9)	0.0006(8)	6.2(5)
C(41)	0.664(2)	0.120(1)	-0.038(1)	9.9(8)
C(42)	0.594(2)	0.103(1)	0.019(1)	10.8(8)
C(43)	0.684(3)	0.241(1)	0.016(1)	12(1)
C(44)	0.618(2)	0.273(1)	-0.070(2)	12(1)
C(45)	0.801(3)	0.154(2)	0.084(1)	14(1)
C(46)	0.867(2)	0.088(1)	0.077(1)	13.3(9)
C(47)	0.813(2)	0.186(2)	-0.060(1)	15(1)
C(48)	0.894(2)	0.251(1)	-0.021(2)	10.8(9)
N(2)	0.235(1)	0.1576(9)	0.394(1)	8.7(5)
C(51)	0.276(2)	0.225(1)	0.426(1)	9.5(8)
C(52)	0.358(2)	0.219(2)	0.508(2)	16(1)
C(53)	0.326(2)	0.112(1)	0.383(2)	11.0(9)
C(54)	0.375(2)	0.144(1)	0.322(1)	11.9(8)
C(55)	0.165(2)	0.181(1)	0.318(1)	12(1)
C(56)	0.103(2)	0.109(2)	0.290(2)	17(1)
C(57)	0.199(2)	0.116(1)	0.457(2)	17(1)
C(58)	0.102(2)	0.155(2)	0.478(2)	18(1)
O	0.409(2)	0.333(1)	0.333(1)	13.7(7)
C(61)	0.318(3)	0.423(2)	0.346(2)	17(1)
C(62)	0.332(2)	0.380(2)	0.293(3)	18(1)
C(63)	0.278(3)	0.360(2)	0.216(2)	15(1)

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

Results and discussion

*Synthetic reaction of [Et₄N]₂[Mo₂(CO)₃(S,O-C₆H₄)₃]
(1)*

The reaction of Mo(CO)₆ with the mixture of *o*-hydroxyphenanthiolate and air-treated *o*-hydroxyphenanthiolate in warm MeCN affords the mixed-valence dinuclear Mo complex [Et₄N]₂[Mo₂(CO)₃(S,O-C₆H₄-1,2)₃] (1). It is evident that this synthetic reaction involves a redox process, in which Mo(0) in Mo(CO)₆ is oxidized by air-treated *o*-hydroxyphenanthiolate because 1 contains the Mo atom, in a higher oxidation state than zero, and the ligands (O,S-C₆H₄-1,2)²⁻, which keep the feature of the benzene rings. In terms of the formation of the catecholate complexes of high oxidation state metal ions from a reaction of M(CO)₆ (M = Mo, W) with *o*-benzoquinone [18–20], it is reasonable to conjecture that the air-treated *o*-hydroxyphenanthiolate is an *o*-thiobenzoquinone which can serve as a two-electron oxidizing agent with the concomitant generation of [O,S-C₆H₄-1,2]²⁻. Thus it is obvious that the oxidation of Mo(CO)₆ by two *o*-thiobenzoquinones and the substitution of carbonyls of Mo(CO)₆ by the concomitant generated [S,O-C₆H₄-1,2]²⁻ and an additional *o*-hydroxyphenanthiolate lead to the formation of the MoO₃S₃ moiety, [Mo(S,O-C₆H₄-1,2)₃]²⁻, which coordinates to another Mo(CO)₆ forming 1. So, both *o*-hydroxyphenanthiolate and air-treated *o*-hydroxyphenanthiolate are essential for the formation of 1 and control of the air-treated *o*-hydroxyphenanthiolate is very important for reaching high yield. As a matter of fact, only a Mo(0)–SR complex [[Mo₂(CO)₈(S-C₆H₄OH)₂]²⁻ was isolated when *o*-hydroxyphenanthiolate without any air treatment was used in the synthetic reaction. In this case, the *o*-hydroxyphenanthiolate, as a monodentate ligand, directly reacted with Mo(CO)₆ affording Mo(0)–SR complexes with the planar MoS₂Mo unit [12–14, 21] and neither Mo(0)–SR complexes nor 1 was obtained if only air-treated *o*-hydroxyphenanthiolate was used.

Structure of [Et₄N]₂[Mo₂(CO)₃(S,O-C₆H₄-1,2)₃] (1) and the interesting MoO₃S₃ unit

The selected bond distances and bond angles of 1 are given in Table 3. In a crystallographically asymmetry unit there are four fragments, one anion [Mo₂(CO)₃(S,O-C₆H₄-1,2)₃]²⁻, two cations Et₄N⁺ and a solvent (isopropanol) molecule. The packing diagram of these fragments is shown in Fig. 1. The cations Et₄N⁺ and the solvent molecule have their expected unexceptional geometry and will not be considered further. The structure of the anion of 1, [Mo₂(CO)₃(S,O-C₆H₄-1,2)₃]²⁻, is depicted in Fig. 2. As is shown in Fig. 2 and Table 3, the anion of 1

TABLE 3. Selected bonds distances (Å) and angles (°) of 1 · C₃H₇OH^a

Mo(1)–Mo(2)	3.168(2)
Mo(1)–S(1)	2.314(6)
Mo(1)–S(2)	2.324(5)
Mo(1)–S(3)	2.328(6)
Mean ^b	2.322(6)
Mo(1)–O(1)	2.06(2)
Mo(1)–O(2)	2.06(2)
Mo(1)–O(3)	2.06(2)
Mean	2.059(2)
Mo(2)–O(1)	2.26(2)
Mo(2)–O(2)	2.24(1)
Mo(2)–O(3)	2.26(1)
Mean	2.25(1)
Mo(2)–C(1)	1.91(3)
Mo(2)–C(2)	1.88(3)
Mo(2)–C(3)	1.92(2)
Mean	1.90(1)
S(1)–C(12)	1.75(2)
S(2)–C(22)	1.77(2)
S(3)–C(32)	1.76(2)
Mean	1.761(8)
O(1)–C(11)	1.36(2)
O(2)–C(21)	1.32(2)
O(3)–C(31)	1.33(2)
Mean	1.33(1)
O(10)–C(1)	1.15(2)
O(20)–C(2)	1.18(2)
O(30)–C(3)	1.16(2)
Mean	1.16(2)
C(11)–C(12)	1.41(2)
C(11)–C(16)	1.38(3)
C(12)–C(13)	1.44(2)
C(13)–C(14)	1.38(3)
C(14)–C(15)	1.42(3)
C(15)–C(16)	1.40(2)
(C21)–C(22)	1.40(3)
C(21)–C(26)	1.38(2)
C(22)–C(23)	1.44(3)
C(23)–C(24)	1.42(2)
C(24)–C(25)	1.40(3)
C(25)–C(26)	1.41(2)
C(31)–C(32)	1.40(2)
C(31)–C(36)	1.43(2)
C(32)–C(33)	1.43(2)
C(33)–C(34)	1.41(3)
C(34)–C(35)	1.43(3)
C(35)–C(36)	1.46(2)
Mean	1.41(2)
S(1)–Mo(1)–S(2)	90.5(2)
S(1)–Mo(1)–S(3)	90.9(2)
S(2)–Mo(1)–S(3)	92.0(2)
Mean	91.1(6)

(continued)

TABLE 3. (continued)

S(1)–Mo(1)–O(1)	79.5(3)
S(2)–Mo(1)–O(2)	79.0(4)
S(3)–Mo(1)–O(3)	79.7(3)
Mean	79.5(3)
S(1)–Mo(1)–O(2)	131.8(3)
S(1)–Mo(1)–O(3)	136.0(3)
S(2)–Mo(1)–O(1)	135.8(3)
S(2)–Mo(1)–O(3)	132.4(3)
S(3)–Mo(1)–O(1)	130.6(3)
S(3)–Mo(1)–O(2)	135.9(3)
Mean	134(2)
O(1)–Mo(1)–O(2)	76.5(4)
O(1)–Mo(1)–O(3)	75.0(4)
O(2)–Mo(1)–O(3)	75.5(4)
Mean	75.7(6)
O(1)–Mo(2)–O(2)	69.0(4)
O(1)–Mo(2)–O(3)	67.5(4)
O(2)–Mo(2)–O(3)	68.3(4)
Mean	68.3(6)
O(1)–Mo(2)–C(1)	101.2(6)
O(1)–Mo(2)–C(3)	105.8(6)
O(2)–Mo(2)–C(1)	102.8(6)
O(2)–Mo(2)–C(2)	99.7(7)
O(3)–Mo(2)–C(2)	104.4(7)
O(3)–Mo(2)–C(3)	103.3(6)
Mean	103(2)
O(1)–Mo(2)–C(2)	167.7(6)
O(2)–Mo(2)–C(3)	171.1(6)
O(3)–Mo(2)–C(1)	167.3(6)
Mean	169(2)
C(1)–Mo(2)–C(2)	85.7(8)
C(1)–Mo(2)–C(3)	85.1(9)
C(2)–Mo(2)–C(3)	84.8(8)
Mean	85.3(4)
Mo(1)–S(1)–C(12)	101.8(7)
Mo(1)–S(2)–C(22)	100.7(6)
Mo(1)–S(3)–C(32)	101.5(7)
Mean	101.4(5)
Mo(1)–O(1)–Mo(2)	94.0(4)
Mo(1)–O(2)–Mo(2)	95.0(4)
Mo(1)–O(3)–Mo(2)	94.6(4)
Mean	94.6(4)
Mo(1)–O(1)–C(11)	126(2)
Mo(2)–O(1)–C(11)	139(2)
Mo(1)–O(2)–C(21)	128(2)
Mo(2)–O(2)–C(21)	137(2)
Mo(1)–O(3)–C(31)	125(1)
Mo(2)–O(3)–C(31)	140(1)
Mean	133(6)
Mo(2)–C(1)–O(10)	176(2)
Mo(2)–C(2)–O(20)	180(2)
Mo(2)–C(3)–O(30)	175(2)
Mean	178(2)
O(1)–C(11)–C(12)	114(2)
O(1)–C(11)–C(16)	124(2)
O(2)–C(21)–C(22)	115(2)

(continued)

TABLE 3. (continued)

O(2)–C(21)–C(26)	125(2)
O(3)–C(31)–C(32)	117(2)
O(3)–C(31)–C(36)	119(2)
Mean	119(4)
S(1)–C(12)–C(11)	118(1)
S(1)–C(12)–C(13)	123(2)
S(2)–C(22)–C(21)	119(1)
S(2)–C(22)–C(23)	120(1)
S(3)–C(32)–C(31)	116(1)
S(3)–C(32)–C(33)	121(2)
Mean	119(2)
C(12)–C(11)–C(16)	122(2)
C(11)–C(12)–C(13)	119(2)
C(12)–C(13)–C(14)	119(3)
C(13)–C(14)–C(15)	120(2)
C(14)–C(15)–C(16)	123(3)
C(11)–C(16)–C(15)	117(2)
C(22)–C(21)–C(26)	120(2)
C(21)–C(22)–C(23)	122(2)
C(22)–C(23)–C(24)	117(2)
C(23)–C(24)–C(25)	119(2)
C(24)–C(25)–C(26)	124(2)
C(21)–C(26)–C(25)	118(2)
C(32)–C(31)–C(36)	123(2)
C(31)–C(32)–C(33)	122(2)
C(32)–C(33)–C(34)	116(2)
C(33)–C(34)–C(35)	123(3)
C(34)–C(35)–C(36)	122(3)
C(31)–C(36)–C(35)	115(3)
Mean	121(3)

*Numbers in parentheses are e.s.d.s in the least significant digits from inverse of least-squares matrix. For the cation in **1**, the eight N–C bonds are within the range 1.49(3)–1.62(3) Å with a mean value of 1.54(4) Å and the C–C bonds are within the range 1.52(4)–1.70(4) Å with a mean value of 1.61(6) Å. The twelve C–N–C angles are within the range 99(2)–125(3)° with a mean value of 109(8)° and the N–C–C angles are within 99(2)–113(2)° with a mean value of 108(5)°. For the isopropanol molecular in the crystal, the O–C bond is 1.43(4) Å and the two C–C bonds are 1.30(5) and 1.42(5) Å, respectively, the two O–C–C angles are 106(5) and 115(3)°, respectively, and the C–C–C angle is 137(5)°. For the cations and solvent molecular scatter estimate has been obtained as follows: $s = [(\sum X_i^2 - NX^2)/(N-1)]^{1/2}$ where X_i is the value of an individual bond or angle and X is the mean value for the N equivalent bond lengths or angles. The standard deviation from the mean, σ , is reported, $\sigma = [\sum X_i^2 - NX^2]^{1/2}/N$.

possesses a pseudo- C_3 axis through the two molybdenum atoms. The geometry around one Mo atom is a trigonal prism with three sulfur atoms and three oxygen atoms from three bidentate (*S,O*- C_6H_4 -1,2) ligands. The three oxygen atoms, as three bridging ligands, are also linked to the another Mo atom which has three terminal carbonyls resulting in a distorted octahedron geometry. Thus, the overall coordination geometry of the anion of **1** can be

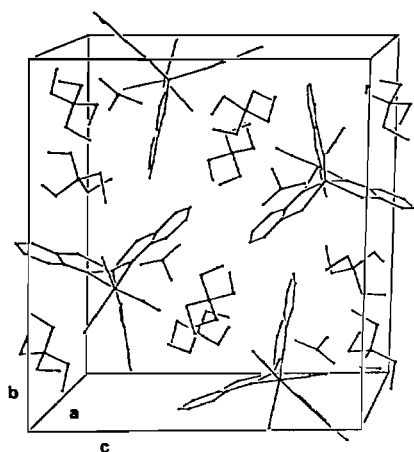


Fig. 1. Packing diagram for $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_3(\text{S},\text{O}-\text{C}_6\text{H}_4-1,2)_3] \cdot \text{C}_3\text{H}_7\text{OH}$.

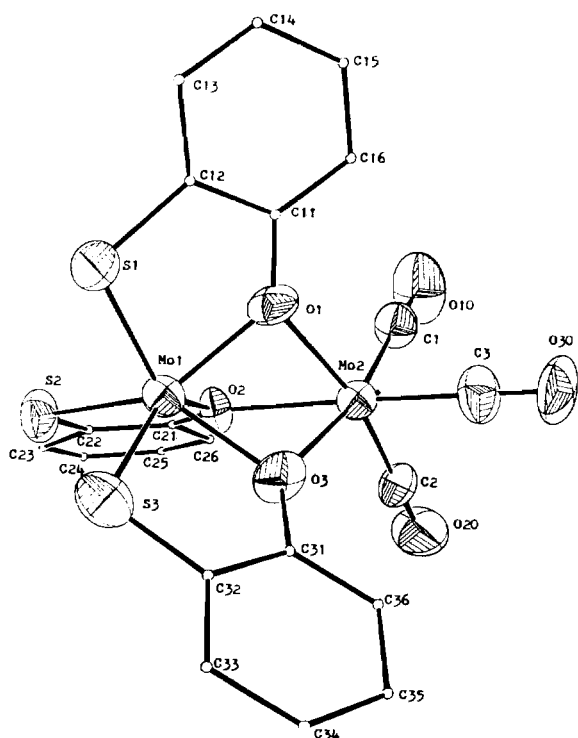


Fig. 2. The molecular structure of the anion $[\text{Mo}_2(\text{CO})_3(\text{S},\text{O}-\text{C}_6\text{H}_4-1,2)_3]^{2-}$ showing the atom labelling scheme. Thermal ellipsoids are drawn by ORTEP [22] and represent 50% probability surfaces. The ellipsoids for the phenyl rings have been drawn artificially small for clarity.

described as a trigonal prism and a distorted octahedron sharing a face. The Mo-Mo bond distance of 3.168(2) Å indicates the existence of a weak Mo-Mo interaction. Mo-C-O angles of 176(2)–177(2)° show the linear coordination of the terminal carbonyls. The fact that the two Mo atoms of 1 are located at two different coordination environments

and the Mo-O_b bond distances for the two Mo atoms are unequal (2.06 and 2.248 Å) probably reflects that the two molybdenum atoms are in two different oxidation states. Taking the Mo-S (2.32 Å), Mo-C (1.90 Å), C-O (1.15 Å) bond distances and $\nu(\text{Mo}-\text{C})$ (375 cm⁻¹), $\nu(\text{MoC}-\text{O})$ (1900, 1760, 1740 cm⁻¹) of 1 into account, it is obvious that each of the two Mo atoms in 1 is not the average value, Mo²⁺ according to the formula of 1. In fact, the appearance of the two couples of 3d^{5/2} and 3d^{3/2} peaks in XPS of 1 provides evidence for the existence of two different valencies of the Mo atoms in 1 (see below). Three (S,O-C₆H₄-1,2) ligands in 1 retain their aromatic feature with a C-C bond distance of 1.42 Å and C-C-C bond angle of 120° as well as a C-O bond distance of 1.34 Å which are expected for a catecholate ligand [23].

It is worth pointing out that to our knowledge this is the first example of a complex containing the Mo atom coordinated by 3SR and 3OR ligands forming the O₃MoS₃ unit of which the Mo-S and Mo-O bond distances of 2.32 Å and 2.06 Å, respectively are comparable with the data [5, 6] obtained from XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) studies on FeMo-co of nitrogenase (Table 4).

Interestingly, in view of the existence of the lone pair of electrons on S atoms in 1, the S atoms of 1, will be able to coordinate to another metal moiety. In fact, a trinuclear Mo-O-S complex

TABLE 4. Comparison of the selected structural data of 1 with the EXAFS data of the as isolated FeMo-co

	FeMo-co	1
Mo-S (Å)	2.37	2.32
No. of S	3	3
Mo-O (Å)	2.10	2.06
No. of O	3	3

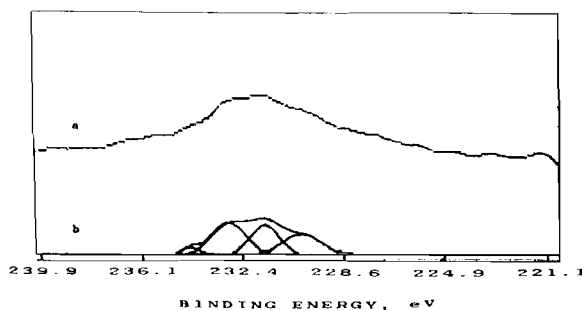


Fig. 3. (a) XPS of $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_3(\text{S},\text{O}-\text{C}_6\text{H}_4-1,2)_3]$; (b) the result of curve fitting for XPS of 1.

$[\text{Mo}_3(\text{CO})_7(\text{S},\text{O}-\text{C}_6\text{H}_4-1,2)_3]^{2-}$ formed by coordination of the S atoms of **1** to a $\text{Mo}(\text{CO})_4$ moiety has been isolated. Thus it is possible to introduce the Fe atom into **1** forming Mo–Fe–S–O modelling compounds because, like $\text{Fe}(\text{II})\text{L}_2^-$, the $\text{Mo}(\text{CO})_4$ moiety could complex with MoS_4^{2-} or WS_4^{2-} resulting in a series of Mo–Mo(W)–S complexes [25, 26] which is similar to the linear Fe–Mo–S modelling compound [7].

X-ray photoelectron spectra (XPS) of 1 and the existence of two different oxidation states of Mo atoms

The XPS of **1** and its result of curve fitting are shown in Fig. 3 and Table 5. Two couples of peaks at 230.08/232.79 and 231.43/234.21 eV ($3d^{5/2}/3d^{3/2}$) observed in XPS of **1** indicate that the two Mo atoms in the O_3MoS_3 and O_3MoC_3 units of **1** are in two different oxidation states and neither of them is Mo^{2+} , the average formal oxidation state according to the formula of **1**. Comparing with the XPS data of a known dinuclear Mo(0) complex $[\text{Et}_4\text{N}]_2-$

TABLE 5. Result parameters of XPS of $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_3(\text{S},\text{O}-\text{C}_6\text{H}_4-1,2)_3]$ (**1**) and dinuclear Mo(0) complex $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_8(\text{SPh})_2]$

Complexes	Binding energies (eV)	
	$3d^{3/2}$	$3d^{5/2}$
$[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_3(\text{S},\text{O}-\text{C}_6\text{H}_4-1,2)_3]$	232.79 234.21	230.08 231.43
$[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_8(\text{SPh})_2]$	231.34	228.14

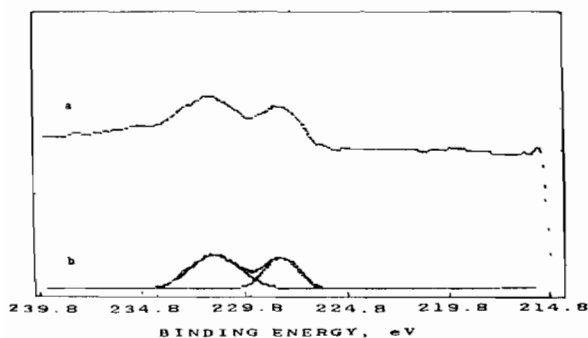


Fig. 4. (a) XPS of $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_8(\text{SPh})_2]$; (b) the result of curve fitting for XPS of $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_8(\text{SPh})_2]$.

* $[\text{Et}_4\text{N}]_2[\text{Mo}_3(\text{S},\text{O}-\text{C}_6\text{H}_4-1,2)_3(\text{CO})_7]$ crystallizes in the triclinic, space group $P\bar{1}$ with $a = 13.801(2)$, $b = 14.163(3)$, $c = 12.157(2)$ Å; $\alpha = 93.18(2)$, $\beta = 98.01(3)$, $\gamma = 83.32(2)^\circ$; $Z = 2$; $R = 0.046$, two Mo–Mo bonds are 3.1843(3) and 3.2145(3) Å, respectively [24].

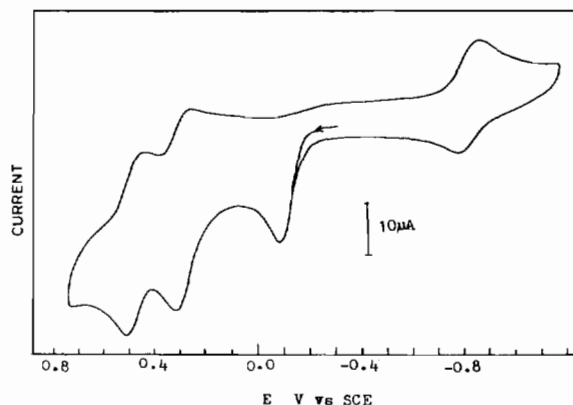


Fig. 5. Cyclic voltammogram of $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_3(\text{S},\text{O}-\text{C}_6\text{H}_4-1,2)_3]$ in acetonitrile. Scan rate: 100 mV/s. Concentration of $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_3(\text{S},\text{O}-\text{C}_6\text{H}_4-1,2)_3]$: 0.0017 M.

TABLE 6. Redox potential (V) for the redox process of $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_3(\text{S},\text{O}-\text{C}_6\text{H}_4-1,2)_3]$

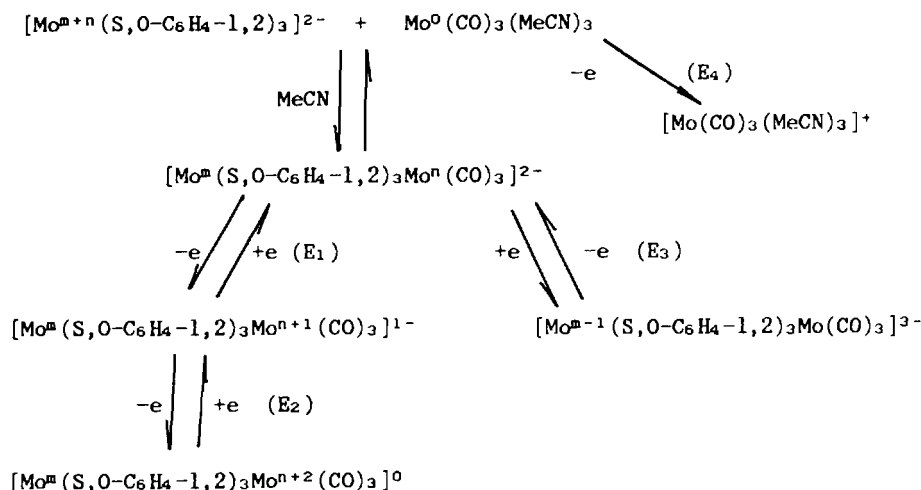
No.	E_{pa}	E_{pc}	$E_{1/2}^a$ (V vs. SCE)
1	+0.32	+0.24	+0.28 (E1)
2	+0.53	+0.45	+0.49 (E2)
3	-0.78	-0.87	-0.83 (E3)
4	-0.09 (E4)		

$$^a E_{1/2} = (E_{pc} + E_{pa})/2.$$

$[\text{Mo}_2(\text{CO})_8(\text{SPh})_2]$ [12, 13] of which only a couple of peaks at 231.34/228.14 eV ($3d^{3/2}/3d^{5/2}$) was observed (Fig. 4), it is obvious that the binding energies of the two couple peaks in **1** are higher than that in $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\text{CO})_8(\text{SPh})_2]$. This fact demonstrates the absence of the Mo(0) atom in **1** and excludes the possibility of the two Mo atoms in **1** being in the 0 and 4+ oxidation states. Therefore, the two oxidation states of n , m for the two Mo atoms in **1** should be

$$0 < n < +2, +2 < m < +4 \text{ and } m + n = 4$$

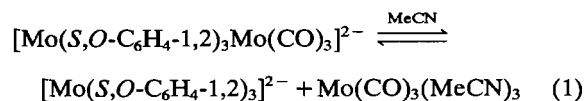
Considering the shorter Mo–O (compared with the other Mo atom in **1**) and Mo–S (compared with the Mo(II) complex $\text{Mo}(\text{CO})_2(\text{S}_2\text{CN}-i\text{-Pr})_2$ [27]), it is easy to figure out that the Mo atom of the O_3MoS_3 unit is in the higher oxidation state and the Mo atom of O_3MoC_3 is in the low oxidation state. It is also reasonable to consider the stabilization of the Mo atom in the low oxidation state by coordination of carbonyls. Noteworthy, the fact that the oxidation state of the Mo atom in the O_3MoC_3 unit is higher than zero indicates the existence of charge transfer in **1** because the Mo atom of O_3MoC_3 unit should be zero valence Mo in terms of the synthetic reaction of **1**.



Scheme 1.

Cyclic voltammetry of [Et₄N]₂[Mo₂(CO)₃(S,O-C₆H₄-1,2)₃] (**1**)

1 exhibits a rich electrochemistry. The cyclic voltammetry of **1** in MeCN at carbon electrode is shown in Fig. 5 and the redox potentials are given in Table 6. As shown in Fig. 5 there are three redox couples at -0.83 , $+0.28$ and $+0.49$ V versus SCE and an irreversible oxidation peak at -0.09 V versus SCE. According to their peak separation ΔE value of $80\text{--}90$ mV and their peak current parameters $i_p/(v^{1/2}\text{a.c.})$ which are comparable with the one observed for ferrocene under identical conditions, the three redox couples belong to a one-electron transfer process. In conjunction with the fact that the XPS result of **1** indicates the two Mo atoms of **1** are in two different oxidation states, and the structure of **1** shows two Mo atoms of **1** in two different coordination environments, it is plausible that the three redox couples are derived from the redox which occurs on two different Mo centers of **1** and it is possible that the couple at negative potential reflects the redox that occurs on the higher oxidation state Mo atom of the O₃MoS₃ unit, and the other two at positive potentials result from the redox of the O₃MoC₃ center. Referring to the CV of the dinuclear Mo(0)-S,S-C₆H₄-1,2 compound [28] and the mononuclear Mo(0)-dtc complex [29], the irreversible oxidation peak of **1** could be imagined as oxidation of a low valence Mo species from decomposition or dissociation of **1**. Thus, the CV behavior of **1** shown in Fig. 5 could be explained by Scheme 1. It is reasonable to assume that the dissociation of **1** takes place and equilibrium (1) is established in MeCN, according to the synthetic reaction discussed above, and the low valence Mo species Mo(CO)₃(MeCN)₃ undergoes irreversible oxidation at -0.09 V versus SCE (E4).



On positive going scan, **1** undergoes a reversible one-electron oxidation to form $[\text{Mo}^{\text{m}}(\text{S}, \text{O}-\text{C}_6\text{H}_4-1,2)_3\text{Mo}^{\text{n}+1}(\text{CO})_3]^{-}$ and $[\text{Mo}^{\text{m}}(\text{O}, \text{S}-\text{C}_6\text{H}_4-1,2)_3\text{Mo}^{\text{n}+2}(\text{CO})_3]^0$ successively with loss of electrons from the Mo atom of the O₃MoC₃ center of **1** at potentials E1 and E2. On negative-going scan, **1** undergoes a reversible reduction to form $[\text{Mo}^{\text{m}-1}(\text{S}, \text{O}-\text{C}_6\text{H}_4-1,2)_3\text{Mo}^{\text{n}}(\text{CO})_3]^{3-}$ at E3 by addition of one electron to the Mo atom of the O₃MoS₃ center of **1**.

Referring to the irreversible reduction of mononuclear catecholato-tungsten(VI) [30] and the irreversible oxidation of the catecholate ligand [31], the possibility that the redox couples at E1, E2 and E3 are derived from the high valence Mo species, which came from the dissociation of **1**, or the catecholate can obviously be excluded.

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