Inorganica Chimica Acta, *160* (1989) 229–234

Synthesis, Structure and Electrochemical Behavior of a New Dinuclear Mo(0) Carbonyl Complex with Two μ^2-Thiolato Ligands, $[Et_4N]_2[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]$

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(Received September 1, 1988; revised December 19, 1988)

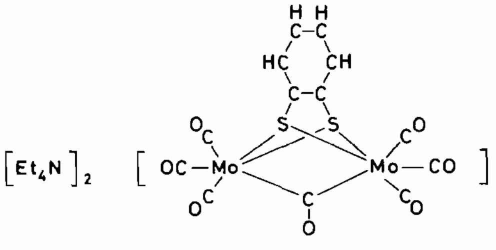
Abstract

A new dinuclear molybdenum(0) carbonyl complex with μ^2-thiolato ligands $[Et_4N]_2[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]$ (**1**) has been synthesized by the reaction of tetraethylammonium benzene-1,2-dithiolate with molybdenum hexacarbonyl in acetonitrile, and characterized by routine elemental analysis and spectroscopy. The crystal and molecular structure of **1** has been determined by X-ray crystallography. Single crystals of **1** grown from a mixture solvent of acetonitrile and isopropanol crystallize in the orthogonal, space group *Pnma* (#62) with $a = 31.081(5)$, $b = 9.582(5)$, $c = 11.557(6)$ Å; $V = 3441.9$ Å^3; $Z = 4$; $R_1 = 0.045$, $R_2 = 0.058$. **1** possesses two thiolato- and one carbonyl-ligand bridges, and the MoS_2Mo ring consisting of two SR bridges adopts the 'butterfly' conformation in *syn-exo* geometry with a Mo–Mo bond distance of 2.9801(8) Å, Mo–S–Mo bond angle of 70.65(4)° and dihedral angle (between two MoSMo planes) of 96.54°. A cyclic voltammetry study indicated that **1** exhibited irreversible one-electron oxidation behavior which is very different from that observed in the complexes $[Mo_2(CO)_8(SR)_2]^{2-}$ containing a planar MoS_2Mo ring.

Introduction

Our recent research on a series of dinuclear molybdenum(0) carbonyl complexes containing thiolato-bridges, $[Mo_2(CO)_8(SR)_2]^{2-}$ (R = Ph, Bu^t, $C_6H_5CH_2$, CH_2CO_2Et), lead to the discovery that those complexes exhibit an interesting two-electron transfer character and possess a planar MoS_2Mo bimetallic core center [1–6]. In order to approach the relevance of the electrochemical behavior to the MoS_2Mo bimetallic framework in those complexes, an attempt to build the dinuclear molybdenum(0) carbonyl complexes containing a non-planar MoS_2Mo bimetallic core center by bidentate dithiolate ligands has been the focus of our work.

By using a benzene-1,2-dithiolate ligand, a new dinuclear molybdenum(0) carbonyl complex with a non-planar $Mo(\mu\text{-}S,S\text{-}C_6H_4\text{-}1,2)Mo$ bimetallic core in *syn-exo* geometry, $[Et_4N]_2[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]$ (**1**), has been obtained and investigated. Herein we report the synthesis, structure and electrochemical behavior of the complex **1**.



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Experimental

Materials and Methods

Acetonitrile was distilled with CaH_2 and isopropanol was dried by magnesium methoxide. Hexane was commercial. Molybdenum hexacarbonyl, ferrocene and benzene-1,2-dithiol were purchased from Fluka. Sodium benzene-1,2-dithiolate was prepared by the reaction of stoichiometric amounts of NaOMe and benzene-1,2-dithiol in methanol, followed by evaporation to dryness, trituration of the residue with diethyl ether and filtration. $[Et_4N]_2[Mo_2(CO)_8(SBu^t)_2]$ was prepared by the literature method [1, 2].

All synthetic procedures, crystal growth and preparation of the sample for X-ray structure determination and for cyclic voltammetric measurement were carried out under nitrogen atmosphere by using Schlenk technique and degassed solvents.

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0020-1693/89/$3.50

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Routine characterization: infrared spectra were measured on a Perkin-Elmer 577 spectrophotometer in the range 200 to 4000 cm^{-1} using KBr pellets. Elemental analysis for carbon, hydrogen and nitrogen were carried out on a Carlo Erba Strumentazion Elemental Analyzer-MOD 1106.

Preparation of $[Et_4N]_2[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]$ *(1)*

A mixture of solid sodium benzene-1,2-dithiolate (0.75 g, 4.03 mmol) and tetraethylammonium chloride (1.33 g, 7.97 mmol) in 70 ml of acetonitrile was stirred at ~53 ℃ for 5 h. The resulting slurry then was filtered onto 2.10 g of solid molybdenum hexacarbonyl (7.95 mmol) and the mixture was stirred at 50–53 ℃ for 20 h resulting in a brown solution. After cooling to room temperature and filtration, the resulting solution was evaporated under vacuum to 35 ml and 40 ml of isopropanol was added. Then this solution was allowed to stand at 4 ℃ for two days and a light brown crystalline product **1** (0.7 g) was precipitated and collected by filtration, washed with MeCN–isopropanol (1:4 vol./vol.), isopropanol and hexane by turns, and dried *in vacuo*. *Anal.* Calc. for $C_{29}H_{44}N_2Mo_2O_7S_2$, C, 44.16; H, 5.58; N, 3.55; Mo, 24.37; S, 8.12. Found: C, 44.30; H, 5.07; N, 3.01; Mo, 24.08; S, 8.17%. IR (Kbr pellet): seven strong absorption bands (2000, 1890, 1870, 1835, 1798, 1755 and 1740 cm^{-1}) in the range of 1600–2000 cm^{-1} are assigned to νCO.

X-ray Structural Determination of $[Et_4N]_2[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]$ *(1)*

A single crystal sample of **1** with dimensions of 0.30 × 0.25 × 0.25 mm was grown from mixed solvents of MeCN and i-PrOH. **1** crystallizes in the orthogonal, space group *Pnma*, with $a = 31.801(5)$, $b = 9.582(5)$, $c = 11.557(6)$ Å; $V = 3441.9$ Å^3; $D_c = 1.52$ g/cm^3; $Z = 4$.

The X-ray diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 computer controlled Kappa Axis diffractometer with graphite monochromator Mo Kα radiation ($\lambda = 0.71073$ Å) in the range of $\theta < 26°$ using the ω–2θ scan technique. After correction for Lorentz and polarization effects and linear absorption attenuation and empirical absorption of the Psi scan technique, only 2476 independent refractions ($I > 3\sigma(I)$) corrected were used for the structure analysis.

The structure was solved by the Patterson heavy-atom method which revealed the positions of the molybdenum and sulfur atoms. All the positions of non-hydrogen atoms were revealed by subsequent difference Fourier syntheses and refined by full-matrix least-squares. Hydrogen atoms were not included in the calculations. The cations are disorderly arranged about a mirror plane and their occupancy factors are taken as 0.5 during calculations. The final cycle of refinement included 293 variable parameters and converged (largest parameter shift was 0.68 times its e.s.d.) with unweighted and weighted agreement factors of

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.045 \quad \text{and}$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.058$$

The weight w is defined as per the Killean and Lawrence method [7] with terms of 0.020 and 1.0.

The set of computer programs used in the crystallographic calculations was SDP/VAX (Enraf-Nonius and B. A. Frenz and Associates, Inc.).

The final positional and thermal parameters with estimated standard deviations are listed in Table 1.

TABLE 1. Positional and thermal parameters of $[Et_4N]_2$-$[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]$ (1)^a

Atom	x	y	z	B_{eq} (Å^2)^b
Mo(1)	0.88270(2)	0.2500(0)	0.73333(5)	3.31(1)
Mo(2)	0.88154(2)	0.2500(0)	0.99118(5)	3.33(1)
S	0.92711(4)	0.4136(1)	0.8601(1)	3.85(3)
O	0.7891(2)	0.2500(0)	0.8822(5)	9.5(3)
O(1)	0.8247(1)	0.0247(4)	0.6220(3)	5.2(1)
O(2)	0.9301(2)	0.2500(0)	0.5005(6)	10.4(3)
O(3)	0.8353(1)	0.4795(5)	1.1321(4)	6.2(1)
O(4)	0.9483(2)	0.2500(0)	1.1985(6)	7.0(2)
C	0.8265(3)	0.2500(0)	0.8988(8)	5.7(2)
C(1)	0.8461(2)	0.1089(6)	0.6664(4)	3.7(1)
C(2)	0.9124(3)	0.2500(0)	0.5896(8)	5.6(2)
C(3)	0.8524(2)	0.3957(7)	1.0788(5)	4.0(1)
C(4)	0.9260(3)	0.2500(0)	1.1203(7)	4.1(2)
C(5)	0.9764(2)	0.3228(6)	0.8750(4)	3.7(1)
C(6)	1.0147(2)	0.3983(7)	0.8914(4)	5.4(1)
C(7)	1.0536(2)	0.3228(7)	0.9092(5)	5.9(2)
N(1)	0.2385(2)	0.2500(0)	0.1219(5)	3.6(1)
N(2)	0.0779(2)	0.2500(0)	0.5380(6)	4.0(1)
C(11)	0.2411(4)	0.352(1)	0.2248(8)	5.4(3)
C(12)	0.1990(4)	0.341(2)	0.124(1)	7.4(3)
C(13)	0.2399(4)	0.347(1)	0.0156(8)	5.6(3)
C(14)	0.2763(4)	0.355(1)	0.122(1)	6.9(3)
C(15)	0.2420(3)	0.2500(0)	0.3429(6)	9.2(3)
C(16)	0.1562(3)	0.2500(0)	0.1253(9)	10.9(4)
C(17)	0.2359(3)	0.2500(0)	0.8980(7)	9.2(3)
C(18)	0.3212(3)	0.2500(0)	0.1229(9)	12.5(4)
C(21)	0.1092(4)	0.327(1)	0.625(1)	6.5(3)
C(22)	0.0321(3)	0.2500(0)	0.5866(9)	8.7(3)
C(23)	0.0815(4)	0.176(1)	0.418(1)	6.7(3)
C(24)	0.0866(4)	0.100(1)	0.525(1)	6.4(3)
C(25)	0.1577(3)	0.201(2)	0.596(1)	9.3(5)
C(26)	0.0176(4)	0.427(1)	0.588(1)	9.8(4)
C(27)	0.0505(4)	0.2500(0)	0.3258(9)	9.8(3)
C(28)	0.0862(5)	0.023(1)	0.639(1)	11.1(4)

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

Electrochemical Measurements

Cyclic voltammetry (CV) experiments were carried out with a three electrode cell using 0.1 M Bu_4NBF_4 as the supporting electrolyte and acetonitrile as solvent. The working electrode was glassy carbon disk ($A = 0.0804$ cm^2). The reference electrode was an aqueous SCE separated from the sample solution by a salt bridge, and the solution for measurement was deoxygenated and blanketed with nitrogen. The potentiostat is CV-1B from BAS (Bioanalytical System).

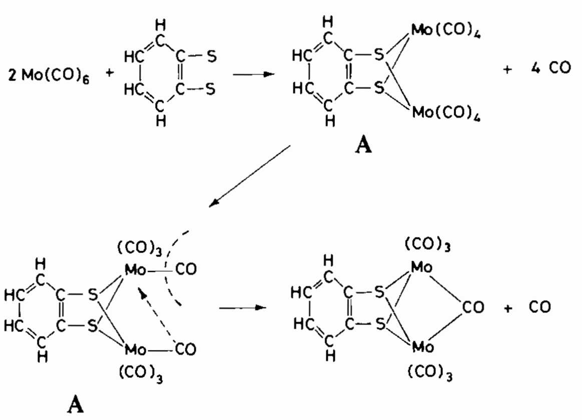
For comparison, the CV of ferrocene and $[Et_4N]_2[Mo_2(CO)_8(SBu^t)_2]$ was measured under identical conditions.

Results and Discussion

Synthesis of $[Et_4N]_2[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]$ (1)

1 was prepared by the reaction of molybdenum hexacarbonyl with benzene-1,2-dithiolate in acetonitrile at 50 °C for 20 h. This preparative reaction is quite similar to that of the dinuclear molybdenum(0) complexes $[Mo_2(CO)_8(\mu\text{-SR})_2]^{2-}$ [1–3, 8] except for using bidentate dithiolate instead of monodentate thiolate but the configuration of the formed products was very different. This indicated that the sort of thiolate such as mono- or bidentate ligands is very important for building the complexes with different structure types, and it also could be predicted that the use of different kinds of bidentate thiolates might lead to another type of product. As a matter of fact, the reaction of $Mo(CO)_6$ with *o*-xylyl-α,α′-dithiolate afforded $[Mo_2(CO)_8(SCH_2C_6H_4CH_2SH)_2]^{2-}$ [9] and another two products which are different from **1** in terms of their IR spectra and elemental analysis. **1** is quite sensitive to air, therefore an anaerobic technique is necessary for synthesizing **1** in higher yield.

In the light of the fact that $Mo(CO)_6$ reacted with thiolate SR^- [1–6] and $S_2CNEt_2^-$ [10], for example, resulting in the $Mo(CO)_4$ unit containing products, it appears that the formation of **1** could be suggested as following this scheme.



The reaction of one benzene-1,2-dithiolate molecule with two $Mo(CO)_6$ molecules affords an 'intermediate' species **A**, which comprises two $Mo(CO)_4$ units bridged by one bidentate dithiolate ligand, via a substitution of two carbonyls in each of the two $Mo(CO)_6$ by a benzene-1,2-dithiolate at first and then the 'intermediate' **A** loses one CO from its one $Mo(CO)_4$ unit and turns simultaneously a terminal CO of its other $Mo(CO)_4$ unit to a bridging CO which links the two Mo atoms for stabilization (see below) leading to the final product **1**.

Structure of $[Et_4N]_2[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]$ (1)

The bond distances and bond angles are listed in Tables 2 and 3 respectively, and the molecular structure of the anion of **1** is depicted in Fig. 1. **1** comprises two Et_4N^+ cations and an anion, $[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]^{2-}$, with Mo(0) atoms. Only half a molecule is contained in a crystallographically unsymmetrical unit. As is shown in Fig. 1, the anion of **1** has a mirror plane which contains a bridging CO, two Mo atoms and two terminal carbonyls, and the two Mo(0) atoms, around each of which the geometry is a distorted octahedron, are linked by two sulfur atoms from a benzene-1,2-dithiolate ligand and one carbon atom from a bridging CO ligand resulting in a short Mo–Mo bond distance of 2.980(8) Å which in addition to the MoSMo angle of 70.65° indicates the existence of Mo–Mo interaction. Coordination about each Mo is completed by three terminal carbonyls. Unlike the Mo(0) dimer analog $[Mo_2(CO)_8(SR)_2]^{2-}$ (R = Ph (**2**), CH_2CO_2Et (**3**)) [2, 8], which possess a MoS_2Mo planar bimetallic center, the anion of **1** contains a non-planar MoS_2Mo bimetallic center adopting the 'butterfly' conformation, which provides the first example of a *syn-exo* form [11] of dinuclear molybdenum(0) complexes with two μ^2-thiolato ligands, on account of the requirement of the structure of the benzene-1,2-dithiolate ligand which maintains the normal C–S bond distance of

TABLE 2. Selected bond distances (Å) of $[Et_4N]_2[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]$ (**1**)

Mo(1)–Mo(2)	2.9801(8)	O(4)–C(4)	1.138(8)
Mo(1)–S	2.553(1)	C(5)–C(5)	1.396(9)
Mo(1)–C	2.592(8)	C(5)–C(6)	1.406(6)
Mo(1)–C(1)	1.929(5)	C(6)–C(7)	1.427(6)
Mo(1)–C(2)	1.900(8)	C(7)–C(7)	1.401(1)
Mo(2)–S	2.602(1)	N(1)–C(11)	1.539(8)
Mo(2)–C	2.018(9)	N(1)–C(12)	1.50(2)
Mo(2)–C(3)	1.950(6)	N(1)–C(13)	1.55(1)
Mo(2)–C(4)	2.036(8)	N(1)–C(14)	1.55(1)
S–C(5)	1.772(4)	N(2)–C(21)	1.58(2
O–C	1.177(9)	N(2)–C(22)	1.532(8)
O(1)–C(1)	1.166(5)	N(2)–C(23)	1.56(2)
O(2)–C(2)	1.167(8)	N(2)–C(24)	1.47(2)
O(3)–C(3)	1.143(5)		

TABLE 3. Selected bond angles (°) of $[Et_4N]_2[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]$ (1)

Mo(2)–Mo(1)–S	55.43(3)	S–Mo(2)–C(4)	93.2(2)
Mo(2)–Mo(1)–C	41.7(4)	C–Mo(2)–C(3)	83.2(2)
Mo(2)–Mo(1)–C(1)	113.3(1)	C–Mo(2)–C(4)	164.8(3)
Mo(2)–Mo(1)–C(2)	151.6(2)	C(3)–Mo(2)–C(3)	91.6(3)
S–Mo(1)–S	75.84(5)	C(3)–Mo(2)–C(4)	86.3(2)
S–Mo(1)–C	86.7(1)	Mo(1)–S–Mo(2)	70.65(4)
S–Mo(1)–C(1)	168.6(1)	Mo(1)–S–C(5)	102.8(1)
S–Mo(1)–C(1)	96.8(1)	Mo(2)–S–C(5)	96.8(1)
S–Mo(1)–C(2)	103.8(2)	Mo(1)–C–Mo(2)	79.5(3)
C–Mo(1)–C(1)	84.2(2)	Mo(1)–C–O	123.1(5)
C–Mo(1)–C(2)	166.6(3)	Mo(2)–C–O	157.5(6)
C(1)–Mo(1)–C(1)	89.0(2)	Mo(1)–C(1)–O(1)	177.5(3)
C(1)–Mo(1)–C(2)	86.3(2)	Mo(1)–C(2)–O(2)	179.1(6)
Mo(1)–Mo(2)–S	53.92(3)	Mo(2)–C(3)–O(3)	178.7(5)
Mo(1)–Mo(2)–C	58.8(3)	Mo(2)–C(4)–O(4)	174.6(6)
Mo(1)–Mo(2)–C(3)	121.7(1)	S–C(5)–C(5)	119.4(1)
Mo(1)–Mo(2)–C(4)	136.5(2)	S–C(5)–C(6)	119.6(4)
S–Mo(2)–S	74.19(5)	C(5)–C(5)–C(6)	121.1(3)
S–Mo(2)–C	98.9(2)	C(5)–C(6)–C(7)	118.5(5)
S–Mo(2)–C(3)	97.1(1)	C(6)–C(7)–C(7)	120.5(3)
S–Mo(2)–C(3)	171.3(1)		

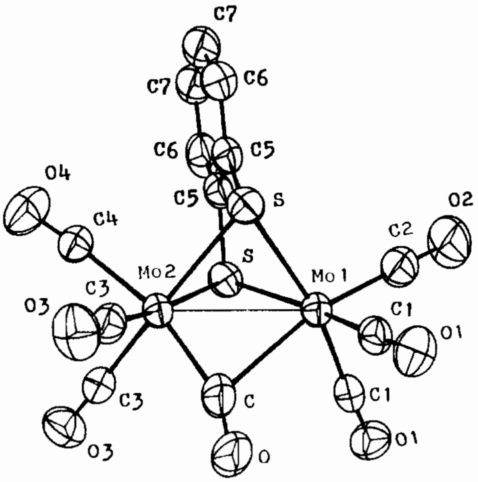


Fig. 1. Structure of the anion of 1, $[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]^{2-}$.

1.772(4) Å and normal S–C(5)–C(6) bond angle of 119.6(4)°. The dihedral angle between the two MoSMo planes is 96.54°. The Mo–S bond distance (av. 2.577 Å) of **1** is comparable with that observed in some other Mo(0) dimers [2, 8, 9, 12] (see Table 4) although the configuration of their MoS_2Mo bimetallic centers is very different. This indicates that the Mo–S bond distance is mainly dependent upon the oxidation state of the Mo atoms in those complexes.

Noteably, the fact that the folding of $Mo(\mu\text{-}S)_2$-Mo bridges with a Mo–Mo bond in **1** was accompanied by the formation of a carbonyl bridge resulting in an 18-electron configuration around each Mo(0) atom implies that the folding of $Mo(\mu\text{-}S)_2Mo$ bridges with the presence of Mo–Mo bonding leads to the unstabilization of the $Mo(CO)_4$-unit-containing Mo(0) dimer, 'intermediate' **A** mentioned above, because the 18-electron rule is no longer satisfied. Interestingly, taking notice of the structural data of the carbonyl bridge it is easy to find that the bridging CO unsymmetrically links two Mo(0) atoms with two different Mo–C bond distances (Mo(1)–C, 2.592(8) and Mo(2)–C, 2.018(9) Å). The value of the short Mo(2)–C bond distance is still close to that of the terminal Mo–C bond distance in the $Mo(CO)_4$ unit [10]. This is just the evidence of the conversion of a terminal CO on one $Mo(CO)_4$ unit to a bridging CO.

Owing to a *trans* effect, the different Mo–C bond distances of the bridging CO obviously result in the two different Mo–C bond distances of the two terminal CO (Mo(1)–C(2), 1.900(8) and Mo(2)–C(4), 2.036(8) Å). In addition, considering other four terminal carbonyls which possess two sets of Mo–C bond distances (1.929(5) and 1.950(6) Å) there correspondingly are five kinds of C–O bond distances (1.177(9), 1.166(5), 1.167(8), 1.143(5) and 1.138(8) Å for C–O, C(1)–O(1), C(2)–O(2), C(3)–O(3) and C(4)–O(4) respectively) in **1**. In terms of these bond length data and the structure shown in Fig. 1, the seven carbonyls of **1** are in different environments. This is consistent with the fact that the IR spectra of **1** have seven strong absorption peaks in the range of 2000 to 1600 cm^{-1} which are assigned to ν(C–O).

Taking into account the importance of the planar MoS_2Mo bimetallic unit to the reversible two-electron transfer character in dinuclear Mo(0) thiolato-bridged complexes mentioned in our previous paper [8], it

TABLE 4. Selected structural parameters of some dinuclear molybdenum(0) carbonyl complexes with thiolato-bridges

Complexes	Mo–S–Mo (Å)	Mo–S (Å)	Mo...Mo (Å)	Reference
$[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]^{2-}$	70.65(4)	2.553(1) 2.602(1)	2.9801(8)	this work
$[Mo_2(CO)_8(SPh)_2]^{2-}$	102.55(5)	2.599(1) 2.617(1)	4.069(1)	8
$[Mo_2(CO)_8(SCH_2C_6H_4CH_2SH)_2]^{2-}$	99.3(1)	2.605(4) 2.578(3)	3.949(3)	9
$[Mo_2(CO)_8(SC_6H_4OH)_2]^{2-}$	102.12(2)	2.6155(7) 2.6200(7)	4.0722(4)	12
$[Mo_2(CO)_8(SCH_2CO_2Et)_2]^{2-}$	99.20(5)	2.586(1) 2.587(1)	3.939(1)	2

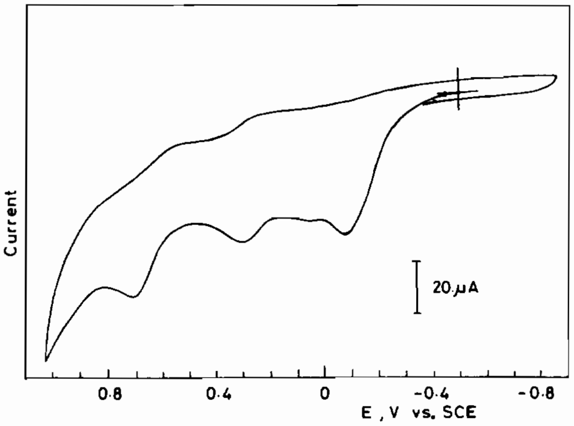


Fig. 2. Cyclic voltammogram of 1 in MeCN: sample concentration, 0.002 M; scan rate, 100 mV/s.

might be expected that 1 with a non-planar MoS_2Mo unit would not exhibit the same electrochemical behavior as the complexes with a planar MoS_2Mo unit. As a matter of fact, the CV study on 1 indicated that 1 underwent irreversible electrochemical oxidation (see below).

Preliminary Cyclic Voltammetry Study on $[Et_4N]_2[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]$ (1)

The cyclic voltammogram of 1 at carbon electrode in MeCN is shown in Fig. 2. 1 displays an irreversible oxidation peak at −0.08 V *versus* SCE and another two oxidation peaks at 0.34 and 0.72 V *versus* SCE, which seem to have two corresponding reduction waves at 0.29 and 0.57 V *versus* SCE. For the first irreversible oxidation peak the voltammetric peak current parameter ($i_p/v^{1/2}AC$) of 747 A cm $s^{1/2}$ $V^{-1/2}$ mol^{-1} roughly indicated that 1 underwent a one-electron irreversible oxidation at −0.08 V *versus* SCE, because under identical conditions the peak current parameters of 688 A cm $s^{1/2}$ $V^{-1/2}$ mol^{-1} and 1482 A cm $s^{1/2}$ $V^{-1/2}$ mol^{-1} were observed for the one-electron oxidation of ferrocene and the two-electron oxidation of $[Et_4N]_2[Mo_2(CO)_8(SBu^t)_2]$ respectively.

As was mentioned in our previous papers [1–3], $[Mo_2(CO)_8(SR)_2]^{2-}$ (R = Ph, CH_2CO_2Et) underwent a two-electron reversible oxidation in one step at potential −0.4 V *versus* SCE

$$[Mo_2(CO)_8(SR)_2]^{2-} \rightleftharpoons [Mo_2(CO)_8(SR)_2]^0 + 2e^-$$

It is easily seen that the electrochemical behavior of 1 is very different from that of $[Mo_2(CO)_8(SR)_2]^{2-}$. The difference in their electrochemical characters is undoubtedly derived from the different structure, in particular, the configuration of the bimetallic center MoS_2Mo of 1 and $[Mo_2(CO)_8(SR)_2]^{2-}$, because it is impossible that 1 with a non-planar MoS_2Mo unit and a carbonyl bridge could be oxidated to the Mo(I) dimer, $[Mo_2(CO)_7(S,S\text{-}C_6H_4\text{-}1,2)]^0$, in the way $[Mo_2(CO)_8(SR)_2]^{2-}$, which contains a planar MoS_2Mo unit, performed [8]. The fact that 1 exhibited an irreversible oxidation at −0.08 V *versus* SCE suggests that a chemical reaction leading to the formation of some new species takes place as soon as 1 undergoes a one electron oxidation. The other two oxidation peaks at 0.34 and 0.72 V *versus* SCE with the corresponding reduction waves at 0.29 and 0.57 V *versus* SCE might be evidence of the formation of a new species in the chemical reaction.

Supplementary Material

Observed and calculated structure factors are available from the author on request.

Acknowledgements

We would like to acknowledge the grants from the National Natural Science Foundation of China and the Science Foundation of Chinese Academy of Sciences in support of this research.

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