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Formations and electrochemical behavior of mononuclear and binuclear molybdenum dithiolene complexes with nitrosyl ligands: Evidence for the formation of a coordinatively unsaturated species [Cp*Mo(NO)(dithiolene)]

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Abstract

The one-pot reaction of [Cp*Mo(NO)(CO)$_2$] with elemental sulfur and dimethyl acetylenedicarboxylate (C_2Z_2 (Z = COOMe)) gave the [2+2] cycloadduct of the mononuclear molybdenum dithiolene complex [Cp*Mo(NO)($S_2C_2Z_2$)(C_2Z_2)] (**1**), and some binuclear complexes:[Cp*Mo(NO)($S_2C_2Z_2$)]$_2$ (**2**), [Cp*$_2$Mo$_2$(NO)$_2$S$_2$($S_2C_2Z_2$)] (**3**) and [Cp*Mo(NO)S$_2$]$_2$ (**4**). The reaction of [Cp*Mo(NO)(Cl)(μ-Cl)]$_2$ with O=C{S_2C_2(COOMe)$_2$} in the presence of sodium methoxide also produced complex **2** and the paramagnetic Cp*Mo bisdithiolene complex [Cp*Mo($S_2C_2Z_2$)$_2$] (**5**, Z = COOMe). The structures of complexes **1**–**5** were determined by X-ray crystal structure analysis. The nitrosyl ligands of complexes **1**–**4** showed a linear coordination to the molybdenum center (the Mo–N–O bond angles = 169–174°), and their N–O bond lengths were 1.17–1.20 Å. In the binuclear complexes **2**–**4**, two nitrosyl ligands were placed at *cis*-position. Complexes **1** and **2** were characterized by cyclic voltammetry and spectroelectrochemistry (visible and IR). The electrochemical reduction of the dimeric complex **2** formed the monomeric dithiolene complex [Cp*Mo(NO)($S_2C_2Z_2$)]$^-$ (**X**$^-$) whose lifetime was several minutes. When the anion **X**$^-$ was electrochemically oxidized, the coordinatively unsaturated species **X** was generated, but it was immediately dimerized to afford the original dimeric complex **2**. The reduction of the complex **1** included the elimination of the bridged DMAD moiety (C_2Z_2) to give the anion **X**$^-$.

Keywords: Molybdenum; Dithiolene; Mononuclear; Nitrosyl; X-ray structure; Electrochemistry

1. Introduction

A mononuclear molybdenum dithiolene complex [1] is a very interesting compound not only in coordination chemistry but also inorganic biochemistry, because such a complex has an active molybdenum center for some oxo-transfer reactions [2–4], and the molybdenum cofactors (Moco) also involve a mononuclear molybdenum dithiolene moiety. Garner et al. have reported the half-sandwich type of the mononuclear cobalt dithiolene complex [CpCo(dithiolene)] (Cp = η^5-cyclopentadienyl) with heterocycles (e.g. pterin) which are related to the chemistry of Moco [5]. On the other hand, most of CpMo dithiolene complexes are binuclear [6] such as Cp/dithiolene ratio 2:2 complexes, which are formulated as [CpMo(dithiolene)]$_2$ (Chart 1(a)) [7]. Mononuclear CpMo dithiolene complexes

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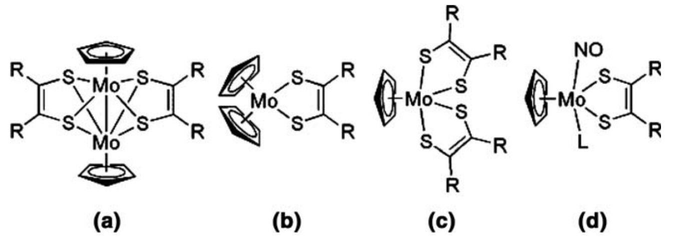


Chart 1.

have been also reported: most cases are the sandwich type of molybdocene dithiolene complex (Cp/dithiolene 2:1 complexes) of the general formula $[Cp_2Mo(dithiolene)]^n$ ($n = +1$ [8] and 0 [9]) (Chart 1(b)), but the mononuclear CpMo dithiolene complexes are rare. Fourmigué et al. have reported the CpMo bisdithiolene complexes $[CpMo(dithiolene)_2]^n$ ($n = 0, -1$) (Cp/dithiolene 1:2 complexes, Chart 1(c)), [10]. McCleverty and James have reported the mononuclear Cp^*Mo dithiolene complexes $[Cp^*Mo(NO)(I)(dithiolene)]^-$ and $[Cp^*Mo(NO)(P(OPh)_3)(dithiolene)]$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) having a nitrosyl ligand [11]. These are corresponding to Cp/dithiolene 1:1 complexes (Chart 1(d)). In other cases, the mononuclear Cp^*Mo dithiolene complex with the aminocarbyne ligand $[Cp^*Mo(CO)(\equiv CNEt_2)(dithiolene)]$ and its derivative with the aminomethylene ligand $[Cp^*Mo(Cl)(=CHNEt_2)(dithiolene)]$ were also reported [12].

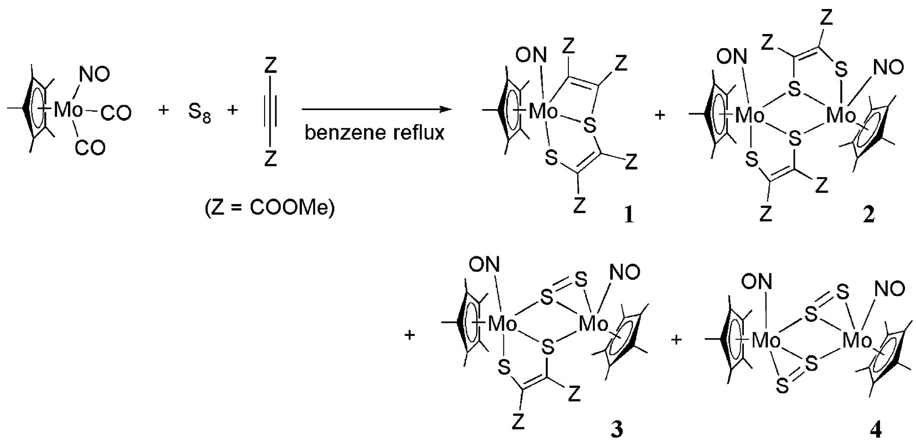
In this work, the synthesis of the mononuclear Cp^*Mo dithiolene complex is our target, and the monomeric complex $[Cp^*Mo(NO)(CO)_2]$ was used as a starting material. We have developed the syntheses of the monomeric dithiolene complexes [CpM(dithiolene)] (M = Co and Rh) by using the one-pot reaction; $[CpCo(CO)_2]$ (or [CpRh(cod)] (cod = 1,5-cyclooctadiene)) with elemental sulfur and activated alkynes [13]. This paper reports on the one-pot reaction of $[Cp^*Mo(NO)(CO)_2]$ with elemental sulfur and dimethyl acetylenedicarboxylate (DMAD). This reaction resulted in the novel mononuclear molybdenum dithiolene complex $[Cp^*Mo(NO)(S_2C_2Z_2)(C_2Z_2)]$ (Z = COOMe) and some binuclear dithiolene complexes having nitrosyl ligands. The X-ray structures and the electrochemical behavior of the mononuclear and binuclear molybdenum dithiolene complexes are investigated. We discuss here the formation of the coordinatively unsaturated mononuclear species $[Cp^*Mo(NO)(dithiolene)]$ as a reactive intermediate. In addition, the syntheses of molybdenum dithiolene complexes from the binuclear complex $[Cp^*Mo(NO)(Cl)(\mu\text{-}Cl)]_2$ are described.

2. Results and discussion

2.1. Formations of molybdenum dithiolene complexes from $[Cp^*Mo(NO)(CO)_2]$

$[Cp^*Mo(NO)(CO)_2]$, elemental sulfur, and DMAD (C_2Z_2 (Z = COOMe)) reacted in refluxing benzene for 72 h to give $[Cp^*Mo(NO)(S_2C_2Z_2)(C_2Z_2)]$ (**1**, 7% yield), $[Cp^*Mo(NO)(S_2C_2Z_2)]_2$ (**2**, 5% yield), $[Cp^*_2Mo_2(NO)_2S_2(S_2C_2Z_2)]$ (**3**, 4% yield) and a trace amount of $[Cp^*Mo(NO)S_2]_2$ (**4**). Although this reaction was very complicated, isolable products were carefully separated by silica gel column chromatography. Only complexes **1**–**4** were isolated and characterized (Scheme 1). A main product in this reaction was complex **1**. Complexes **1**–**3** were well obtained in a long time reaction (72 h), because the starting material $[Cp^*Mo(NO)(CO)_2]$ was completely used.

In these products, only complex **1** was a mononuclear dithiolene complex. The ^1H NMR spectrum of complex **1** showed four different signals of the COOMe proton, and the mass spectrum indicated the 1:1 formula ($M^+ = 611$) of one molecular DMAD (C_2Z_2) and $[Cp^*Mo(NO)(S_2C_2Z_2)]$. These results suggest the structure of an [2+2] cycloadduct of the molybdenum dithiolene complex **1** (Scheme 1); we earlier reported some examples of the [2+2] cycloadduct $[(C_nR_n)M(S_2C_2Z_2)(C_2Z_2)]$ that are formed by the reactions of DMAD with the 16-electron coordinatively unsaturated metal dithiolene complexes $[CpRh(S_2C_2Z_2)]$ [14] and $[(\eta^6\text{-}C_6H_6)Ru(S_2C_2Z_2)]$ (Z =



Scheme 1.

COOMe) [15]. Hidai et al. have reported the [2+2] cycloadduct of iridium dithiolene complex [Cp*Ir($S_2C_2Z_2$)(C_2Z_2)] [16]. Similarly, we propose that the reaction of the coordinatively unsaturated molybdenum species [Cp*Mo(NO)($S_2C_2Z_2$)] (**X**) with DMAD also provides complex **1**. The species **X** was not isolated in this reaction, but the EI^+ mass spectrum of complex **1** showed a strong positive fragment which corresponding to X^+ ($X^+ = 469$ ([1^+−DMAD])).

Complex **2** involved a binuclear complex having two molydadithiolenes and nitrosyl ligands. The ^1H NMR spectrum of complex **2** indicated two different signals of the COOMe proton. The EI^+ mass spectrum of complex **2** showed the dimolybdenum isotope pattern, and the parent ion is corresponding to the dimer of **X**. The fragment ion X^+ having a strong intensity was also detected. Analogous complexes to complex **2** have been reported: King and Bisnette reported the binuclear molybdenum dithiolene-complex [CpMo(NO){$S_2C_2(CF_3)_2$}]$_2$ starting from [CpMo(NO)$(CO)_2$] with bis(trifluoromethyl)dithiete $S_2C_2(CF_3)_2$ [17], and McCleverty and James reported [CpMo(NO){$S_2C_2(CN)_2$}]$_2$ which they obtained from [[CpMo(NO)(I)(μ-I)]$_2$] with Na_2{$S_2C_2(CN)_2$} [11]. In addition, complex **3** was a binuclear complex having one molydadithiolene structure, and another molybdenum center did not make a dithiolene ring. The binuclear sulfide complex **4** is a known compound: Herberhold et al. reported that the reaction of [Cp*Mo(NO)I_2] with H_2S results in complex **4** [18].

The reaction of the sulfide complex **4** with DMAD in refluxing benzene also gave the dithiolene complex **2**, but the yield was very low. In general, a metal sulfide complex reacts with an alkyne to produce dithiolene complexes [19]. On the other hand, we propose another formation route for complex **2** which is a dimerization of the monomeric dithiolene complex [Cp*Mo(NO)($S_2C_2Z_2$)] (**X**), because only a small amount of complex **2** was obtained from complex **4** with DMAD. Coordinatively unsaturated metal dithiolene complexes are well-known, and some of them can be dimerized due to their unsaturation. Such dimerizations have been reported in [CpCo(bdt)] (bdt = 1,2-benzenedithiolate) [20], [Cp*Rh (bdt)], [Cp*Rh(mnt)] (mnt = maleonitrile-1,2-dithiolate), [Cp*Rh(dmit)] (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) [21], [(η^6-C_6R_6)Ru(bdt)] and [(η^6-C_6R_6)Ru{S_2C_2-$(COOMe)_2$}] [15,22].

2.2. Formations of molybdenum dithiolene complexes from [Cp*Mo(NO)(Cl)(μ-Cl)]$_2$

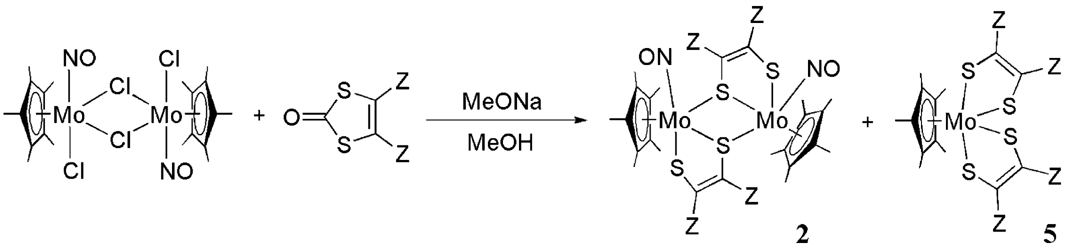
Dimethyl 1,3-dithiol-2-one-4,5-dicarboxylate O=C{S_2-$C_2(COOMe)_2$} reacted with sodium methoxide in methanol, and the initially colorless solution was changed to yellow. The molybdenum chloride complex dimer [Cp*Mo(NO)(Cl)(μ-Cl)]$_2$ was added into this solution, and then complex **2** (15% yield, main product) and a trace amount of the bisdithiolene complex [Cp*Mo($S_2C_2Z_2$)$_2$] (**5**, Z = COOMe) were obtained (Scheme 2).

The ligand exchange reaction between the chloride ligand and the dithiolene ligand produces complex **2**. The coordinatively unsaturated species [Cp*Mo(NO)($S_2C_2Z_2$)] (**X**) was not obtained in this reaction. The ligand exchange reactions of [Cp*M(Cl)(μ-Cl)]$_2$ (M = Rh, Ir) or [(η^6-C_6R_6)Ru(Cl)(μ-Cl)]$_2$ with a dithiolene ligand have been reported in many cases. These reactions often produce the coordinatively unsaturated species of the monomeric dithiolene complexes [Cp*M(dithiolene)] (M = Rh, Ir) [21b,21c,23,24] or [(η^6-C_6R_6)Ru(dithiolene)] (C_6R_6 = C_6H_6 [25], p-C_6H_4(Me)(i-Pr) [25], C_6Me_6) [15,22] in a solid state or in a solution. Therefore, we conclude that the unsaturated molybdenum species **X** is less stable than those of the Rh, Ir and Ru dithiolene complexes.

2.3. X-ray structures of molybdenum dithiolene complexes

The structures of complexes **1–5** were determined by X-ray structure analyses. Figs. 1–5 show the ORTEP drawing (the thermal ellipsoids show 50% probability) together with the selected bond lengths and angles, and Table 1 includes the summary of the bond lengths and the mean deviation from the molybdadithiolene plane. The crystal data are summarized in Table 2. All complexes have four-legged piano-stool geometries. In the nitrosyl complexes **1–4**, the N–O bond lengths of nitrosyl ligand were 1.17–1.20 Å (Table 1), and the Mo–N–O bond angles were 169–174°, which indicate a linear coordination of the nitrosyl ligand to the molybdenum center. These coordination modes of the nitrosyl ligand are similar to those of the usual organometallic nitrosyl complexes [26].

Complex **1** has one nitrosyl ligand, the five-membered molybdadithiolene ring, and the bridging DMAD moiety (Fig. 1). The C=C bond length in the molybdadithiolene



Scheme 2.

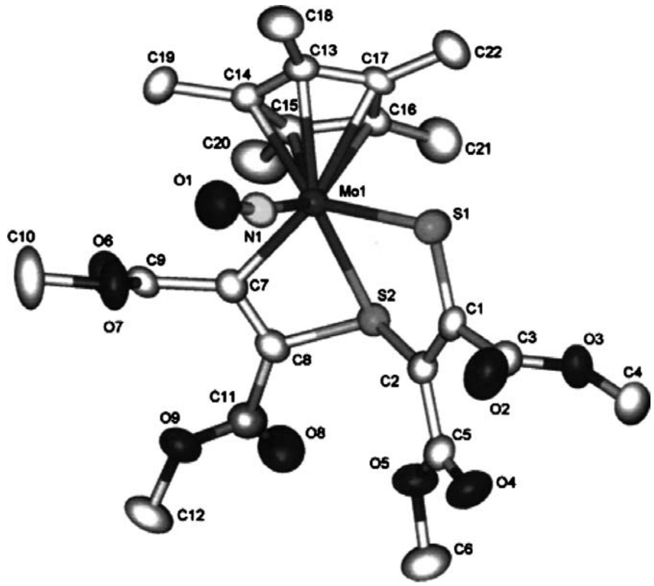


Fig. 1. The ORTEP drawing of $[\mathrm{Cp^*Mo(NO)\{S_2C_2(COOMe)_2\}\{C_2(COOMe)_2\}}]$ (**1**). The hydrogen atoms are not shown for the sake of simplicity. Selected bond lengths (Å): Mo1–S1 = 2.494(1), Mo1–S2 = 2.560(1), S1–C1 = 1.714(4), S2–C2 = 1.759(5), C1–C2 = 1.347(6), Mo1–C7 = 2.167(4), Mo1–N1 = 1.780(4), S2–C8 = 1.781(4), N1–O1 = 1.192(5), C7–C8 = 1.307(6). Selected bond angles (°): S1–Mo1–S2 = 78.50(4), Mo1–S1–C1 = 103.6(2), Mo1–S2–C2 = 102.1(2), S1–C1–C2 = 126.1(3), S2–C2–C1 = 117.8(3), Mo1–N1–O1 = 170.2(3).

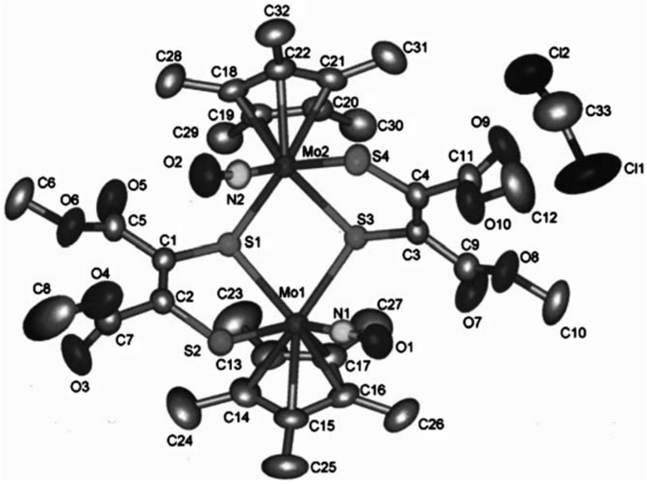


Fig. 2. The ORTEP drawing of $[\mathrm{Cp^*Mo(NO)\{S_2C_2(COOMe)_2\}}]_2(\mathrm{CH_2Cl_2})$ ($\mathbf{2}\cdot\mathrm{CH_2Cl_2}$). The hydrogen atoms are not shown for the sake of simplicity. Selected bond lengths (Å): Mo1–S1 = 2.5214(9), Mo1–S2 = 2.4391(9), Mo1–S3 = 2.5140(9), Mo1–N1 = 1.780(3), S1–C1 = 1.778(4), S2–C2 = 1.741(4), C1–C2 = 1.336(5), N1–O1 = 1.199(5), Mo2–S3 = 2.5385(9), Mo2–S4 = 2.433(1), Mo2–S1 = 2.501(1), Mo2–N2 = 1.797(3), S3–C3 = 1.782(4), S4–C4 = 1.735(4), C3–C4 = 1.339(5), N2–O2 = 1.180(4). Selected bond angles (°): S1–Mo1–S2 = 80.98(3), Mo1–S1–C1 = 105.4(1), Mo1–S2–C2 = 106.6(1), S1–C1–C2 = 119.9(3), S2–C2–C1 = 124.9(3), Mo1–N1–O1 = 173.2(3), S3–Mo2–S4 = 81.06(3), Mo2–S3–C3 = 105.2(1), Mo2–S4–C4 = 107.0(1), S3–C3–C4 = 120.1(3), S4–C4–C3 = 124.7(3), Mo2–N2–O2 = 174.0(3), Mo1–S1–Mo2 = 96.23(3), Mo1–S3–Mo2 = 95.48(3).

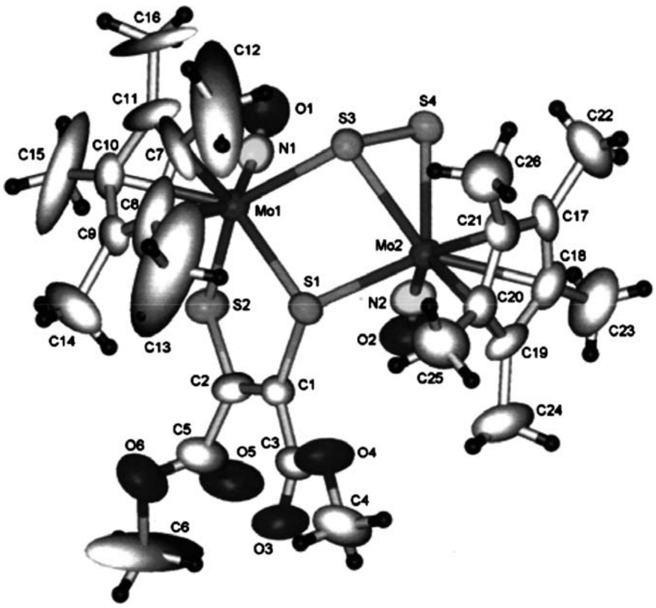


Fig. 3. The ORTEP drawing of $[\mathrm{Cp^*_2Mo_2(NO)_2S_2\{S_2C_2(COOMe)_2\}}]$ (**3**). Selected bond lengths (Å): Mo1–S1 = 2.536(3), Mo1–S2 = 2.429(3), Mo1–S3 = 2.503(3), Mo1–N1 = 1.77(1), S1–C1 = 1.77(1), S2–C2 = 1.73(1), C1–C2 = 1.35(2), N1–O1 = 1.20(2), Mo2–S3 = 2.494(3), Mo2–S4 = 2.417(4), Mo2–S1 = 2.500(3), Mo2–N2 = 1.81(1), N2–O2 = 1.17(1), S3–S4 = 2.034(5). Selected bond angles (°): S1–Mo1–S2 = 80.7(1), Mo1–S1–C1 = 104.9(4), Mo1–S2–C2 = 107.5(4), S1–C1–C2 = 120(1), S2–C2–C1 = 123(1), Mo1–N1–O1 = 172.1(9), S3–Mo2–S4 = 48.9(1), Mo2–N2–O2 = 169(1), Mo1–S1–Mo2 = 90.7(1), Mo1–S3–Mo2 = 91.7(1).

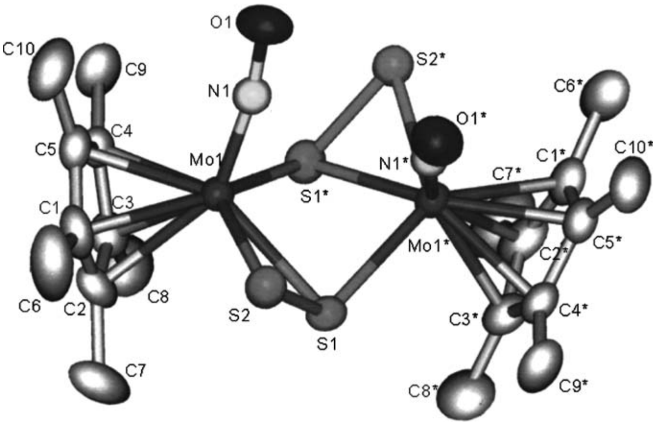


Fig. 4. The ORTEP drawing of $[\mathrm{Cp^*Mo(NO)S_2}]_2$ (**4**). The half of all atoms (marked as *) was found by a symmetry expansion. The hydrogen atoms are not shown for the sake of simplicity. Selected bond lengths (Å): Mo1–S1 = 2.520(1), Mo1–S2 = 2.439(1), Mo1–N1 = 1.781(3), N1–O1 = 1.191(4), S1–S2 = 2.052(1). Selected bond angles (°): Mo1–S1–S2 = 63.50(4), Mo1–S2–S1 = 67.65(4), S1–Mo1–S2 = 48.85(3), Mo1–N1–O1 = 170.1(3).

ring (C1–C2 = 1.347(6) Å) is longer than that in the bridging DMAD (C7–C8 = 1.307(6) Å). This can be explained by the π-electron delocalization in the molybdadithiolene ring. This tendency has been observed also in the DMAD adduct of the rhodium dithiolene complex $[\mathrm{CpRh(S_2C_2Z_2)(C_2Z_2)}]$ (Z = COOMe) [14]. The mean deviation from the molybdadithiolene plane in complex **1** is 0.28020 Å. This result indicates that the molybdadithiolene ring is not planar.

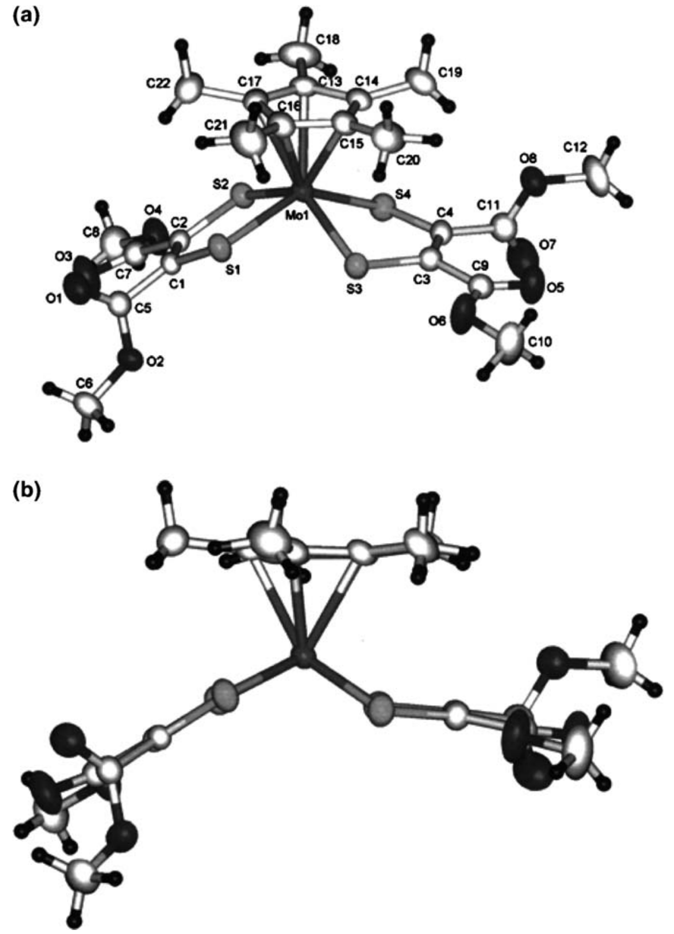


Fig. 5. The ORTEP drawings of [$Cp^*Mo\{S_2C_2(COOMe)_2\}_2$] (**5**): (a) The view showing the all non-hydrogen atoms, and (b) the view showing the planes of two molybdadithiolenes. Selected bond lengths (Å): Mo1–S1 = 2.387(1), Mo1–S2 = 2.362(1), Mo1–S3 = 2.371(1), Mo1–S4 = 2.396(1), S1–C1 = 1.714(4), S2–C2 = 1.739(4), S3–C3 = 1.733(4), S4–C4 = 1.718(4), C1–C2 = 1.345(6), C3–C4 = 1.357(6). Selected bond angles (°): S1–Mo1–S2 = 81.92(4), Mo1–S1–C1 = 107.6(1), Mo1–S2–C2 = 108.6(1), S1–C1–C2 = 122.0(3), S2–C2–C1 = 119.6(3), S3–Mo1–S4 = 81.29(4), Mo1–S3–C3 = 104.1(1), Mo1–S4–C4 = 103.2(1), S3–C3–C4 = 119.8(3), S4–C4–C3 = 121.1(3).

Complex **2** is the binuclear complex consisting of two nitrosyl ligands and two molybdadithiolene rings (Fig. 2). The crystal of complex **2** includes one molecule of dichloromethane. Two nitrosyl ligands are placed at *cis*-position to each other. The similar *cis*-location of two nitrosyl ligands has been reported in [$CpMo(NO)\{S_2C_2(CF_3)_2\}]_2$ [11,17]. The mean deviations from the molybdadithiolene planes are 0.1299 (Mo1 plane) and 0.0985 Å (Mo2 plane). Complex **3** is the binuclear complex having two nitrosyl ligands and one molybdadithiolene ring (Fig. 3). The mean deviation from the molybdadithiolene plane is 0.1304 Å. Complex **4** is the binuclear sulfide complex without a C_2Z_2 moiety (Fig. 4). In complexes **3** and **4**, two nitosyl ligands are also located at *cis*-position. The structure of the Mo2–S3–S4 core in complex **3** is similar to that the Mo1–S1–S2 core in complex **4** (Figs. 3 and 4).

Complex **5** is the molybdenum complex including one Cp^* ligand and bisdithiolene moiety (Fig. 5(a) and (b)). This complex formally has d^1 molybdenum center (Mo^V). The Mo–S bond lengths (Mo1–S1 = 2.387(1) and Mo1–S2 = 2.362(1) Å) are shorter than those of complexes **1**–**4** (Table 1). The reason may be a high valence molybdenum center in complex **5**, and there are strong π-electron donations [27] from the sulfur atom of the dithiolene ligand to the electron poor, high valency-molybdenum center in complex **5**. Complex **5** showed an ESR response ($g = 2.0104$ in Fig. 6) which is attributed to the d^1 molybdenum spin: the molybdenum of $I = 0$ (natural abundance 75%) and the molybdenum of $I = 2/5$ ($a = 1.67$ mT, natural abundance 25%).

Fourmigué et al. already reported the Cp^*M bisdithiolene complexes [$Cp^*M(dmit)_2]^n$ (M = Mo [10] and W [28]; $n = -1$ and 0). According to their articles, when the complex is the monoanion [$Cp^*M(dmit)_2]^-$ ($M = d^2$ metal), two metalladithiolene rings are planar, however, in the neutral complex [$Cp^*M(dmit)_2]^0$ ($M = d^1$ metal), one of the two metalladithiolene rings is distorted. The similar distortion of metalladithiolene plane has been observed in the

Table 1
Bond lengths (Å) in the molybdenum dithiolene complexes **1**–**5**

Compound	**1**	**2** · (CH_2Cl_2)	**3**	**4**	**5**
Mo1–S1	2.494(1)	2.5214(9)	2.536(3)	2.520(1)	2.387(1)
Mo1–S2	2.560(1)	2.4391(9)	2.429(3)	2.439(1)	2.362(1)
S1–C1	1.714(4)	1.778(4)	1.77(1)	–	1.714(4)
S2–C2	1.759(5)	1.741(4)	1.73(1)	–	1.739(4)
C1–C2	1.347(6)	1.336(5)	1.35(2)	–	1.345(6)
N1–O1	1.192(5)	1.199(5)	1.20(2)	1.191(4)	–
Mo2(Mo1)–S3	–	2.5385(9)	2.494(3)	–	2.371(1)
Mo2(Mo1)–S4	–	2.433(1)	2.417(4)	–	2.396(1)
S3–C3	–	1.782(4)	–	–	1.733(4)
S4–C4	–	1.735(4)	–	–	1.718(4)
C3–C4	–	1.339(5)	–	–	1.357(6)
N2–O2	–	1.180(4)	1.17(1)	–	–
Mean deviation (Å) from molybdadithiolene plane	0.28020	0.1299,$^{(a)}$ 0.0985$^{(b)}$	0.1304	–	0.0482,$^{(c)}$ 0.2760$^{(d)}$

The mean deviations (Å) from: (a) Mo1–S1–S2–C1–C2, (b) Mo2–S3–S4–C3–C4, (c) Mo1–S1–S2–C1–C2, and (d) Mo1–S3–S4–C3–C4 planes.

Table 2
Crystallographic data of the molybdenum dithiolene complexes **1**–**5**

Compound	**1**	**2** · (CH_2Cl_2)	**3**	**4**	**5**
Formula	$C_{22}H_{27}MoNO_9S_2$	$C_{33}H_{44}Mo_2N_2O_{10}S_4Cl_2$	$C_{26}H_{36}Mo_2N_2O_6S_4$	$C_{20}H_{30}Mo_2N_2O_2S_4$	$C_{22}H_{27}MoO_8S_4$
Formula weight (g mol^{-1})	609.52	1019.74	792.70	650.59	643.63
Crystal color	Orange	Green	Brown	Greenish brown	Brown
Crystal habit	Block	Needle	Block	Block	Block
Crystal size (mm)	0.09 × 0.06 × 0.04	0.15 × 0.10 × 0.06	0. 09 × 0.06 × 0.04	0.12 × 0.09 × 0.09	0. 12 × 0.09 × 0.09
Crystal system	Orthorhombic	Monoclinic	Triclinic	Tetragonal	Monoclinic
Space group	$P2_12_12_1$ (#19)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P4_12_12$ (#92)	$P2_1/n$ (#14)
a (Å)	12.3522(5)	8.4632(2)	8.3110(4)	9.1955(2)	8.4755(5)
b (Å)	12.4802(5)	16.7221(4)	10.8012(5)	9.1955(2)	25.3725(11)
c (Å)	16.7327(7)	30.1930(8)	18.9456(11)	30.1323(11)	12.6053(7)
α (°)			80.80(2)		
β (°)		94.8968(4)	79.91(1)		101.6891(8)
γ (°)			73.260(13)		
V ($Å^3$)	2579.5(2)	4257.4(2)	1592.6(1)	2547.90(12)	2654.5(2)
Z	4	4	2	4	4
D_{calc} (g cm^{-3})	1.569	1.591	1.653	1.696	1.610
μ (Mo Kα) (cm^{-1})	7.19	9.62	10.89	13.30	8.52
T (K)	296	296	296	296	296
$2\theta_{max}$ (°)	55.0	55.0	55.0	54.9	55.0
Unique data (R_{int})	5900 (0.038)	9555 (0.027)	6924 (0.045)	2907 (0.032)	6063 (0.035)
Number of observations	3678	5937	3355	2585	3104
Number of variables	343	522	397	151	343
R_1, wR_2 [$I > 3.00\sigma(I)$]	0.030, 0.024	0.033, 0.042	0.059, 0.075	0.027, 0.029	0.029, 0.025
Goodness-of-fit on F^2	1.068	0.914	0.937	1.381	1.146
Largest difference peak and hole (e $Å^{-3}$)	0.99 and −0.36	0.80 and −0.75	1.38 and −1.19	0.51 and −0.51	0.53 and −0.35

$R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

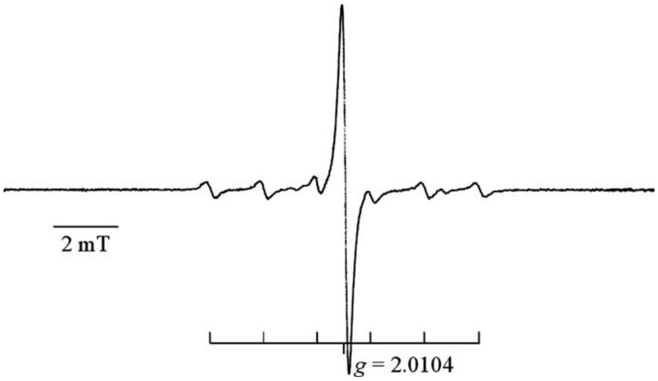


Fig. 6. ESR spectrum of the bisdithiolene complex **5** in toluene solution at room temperature.

paramagnetic dithiolene complexes $[Cp^*_2M(dmit)]^+$ ($M = Mo, W$) [8]. Complex **5** showed such remarkable distortion in one of two molybdadithiolene planes (Fig. 5(b)).

2.4. Electrochemical behavior of molybdenum dithiolene complexes

Fig. 7(a)–(c) exhibits the cyclic voltammograms (CVs) of complexes **1** and **2**. In the reduction process, complex **1** showed a one-step irreversible wave at −1.70 V (Fig. 7(a)), and complex **2** showed two-step irreversible waves at −1.76 V and −2.14 V, respectively (Fig. 7(b)). These results indicate that the reduced species of complexes **1** and **2** are unstable on the time scale of CV measurement ($v = 100$ mV s^{-1}). In the CV of complex **1**, when the potential was scanned to positive after the reduction, a reoxidation wave appeared at −1.06 V (Fig. 7(a)). A similar

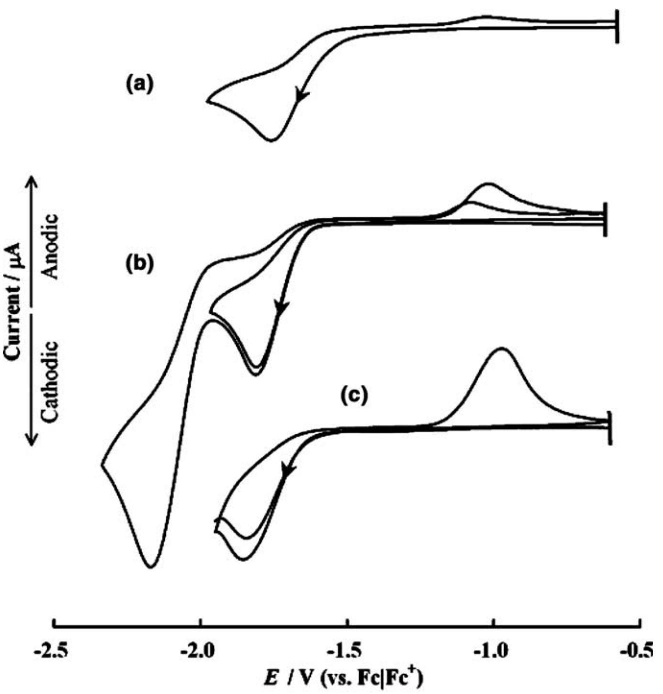


Fig. 7. Cyclic voltammograms of 1 mM solutions in dichloromethane containing TBAP of (a) complex **1**, (b) complex **2** ($v = 100$ mV s^{-1}, $\sigma = 1.6$ mm Pt disk) and (c) complex **2** ($v = 5$ mV s^{-1}, Pt mesh in an OTTLE cell).

reoxidation wave also appeared after the first reduction of complex **2** (Fig. 7(b)). Therefore, the electrochemical reductions of complexes **1** and **2** provide the same species. Fig. 7(c) exhibits the CV with a slow scan rate (5 mV s^{-1}) of complex **2** in an optically transparent thin-layer electrode (OTTLE) cell. The cathodic current in a first reduction was almost the same as the anodic one in a reoxidation wave, and the identical electrochemical behavior was almost repeated in the CV of a multiple scan (Fig. 7(c)). Namely, a reversible redox reaction can be recognized in the overall process, and we can consider the reversible ECEC reaction mechanism (electrochemical square scheme), which is shown in Scheme 3.

The visible absorption spectra during electrolysis were measured by using the OTTLE cell. Fig. 8(a) shows the spectral changes during the first reduction of complex **2** at −1.75 V. The spectra were remarkably changed with an isosbestic point around 430 nm. After 2 min, the potential changed to −0.5 V for a reoxidation. The spectrum was almost recovered to the original spectrum of complex **2** with the same isosbestic point (Fig. 8(b)). These results suggest that complex **2** is converted to another species after a reduction (EC), but the species reforms the original complex **2** by a reoxidation (EC). Therefore, the ECEC reaction mechanism is overall reversible (Scheme 3). However, when the reduction electrolysis was performed for over 2 min, the spectrum of complex **2** did not recover well even after a reoxidation. This result indicates that the lifetime of a reduced species is several minutes. We assume that the reduced species is the mononuclear molybdenum dithiolene complex $[Cp^{*}Mo(NO)\{S_2C_2(COOMe)_2\}]^-$ (**X**$^-$) (Scheme 3).

The IR absorption spectra of complex **2** during OTTLE-electrolysis were measured. Fig. 9(a) shows the IR spectrum before electrolysis: there was a stretching vibration at 1653 cm^{-1} which is attributed to the N–O bond, and stretching vibrations at 1701 and 1732 cm^{-1} based on two different C–O moieties in the COOMe groups. When complex **2** was reduced at −1.75 V, the N–O vibration shifted to 1506 cm^{-1}, and the single signal of C–O vibration was observed at 1711 cm^{-1} (Fig. 9(b)). The former result shows that an electron density at the NO ligand was higher than those of complex **2**, and the latter result also suggests the formation of the mononuclear species **X**$^-$ by the reduction of complex **2**, because the two COOMe groups in **X**$^-$ are formally equivalent. The monomer and dimer structural changes of dithiolene complexes have been reported. The electrochemical oxidations of the mononuclear cobalt dithiolene complex [Cp*Co(dddt)] (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) [29] and the mononuclear ruthenium dithiolene complex $[(C_6H_6)Ru\{S_2C_2(COOMe)_2\}]$ [15] undergo dimerizations. This process is a unique case, because the reduction of a dimeric dithiolene complex gives a monomer.

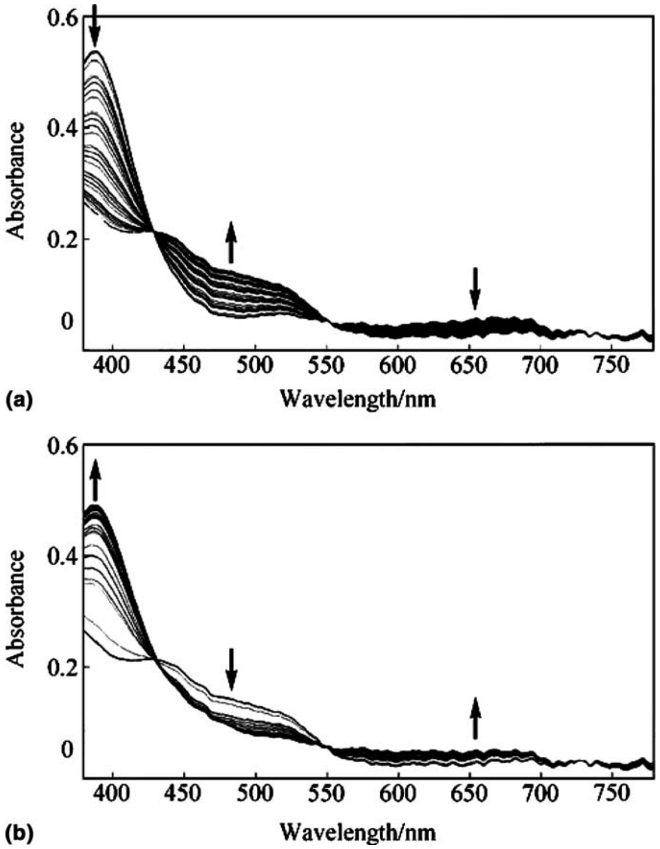
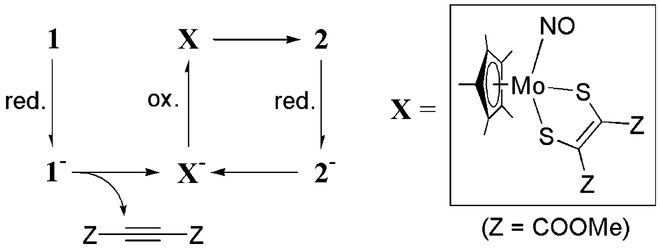


Fig. 8. Spectral changes in a visible region of complex **2** during (a) reduction (−1.75 V, sampling time 2 min, sampling interval 4 s); (b) reoxidation (−0.5 V, sampling time 2 min, sampling interval 4 s) after reduction. The spectra were measured in dichloromethane solution containing TBAP.



Scheme 3.

Similarly, we see that the reduction of the [2+2] cycloadduct **1** also produced species **X**$^-$ according to the CV in Fig. 7(a). The bridging DMAD moiety is formally eliminated by a reduction (Scheme 3). We have reported many examples of the electro-reductive dissociations of metal dithiolene adducts: the alkylidene- and imido-bridged cobalt dithiolene complexes eliminate those bridged moieties by a reduction [30], and the square-planar nickel dithiolene adduct eliminates simple olefins [31], norbornadiene [32], *o*-quinodimethane [32b], and benzyl radical [33] by a reduction. The reduction behavior of complexes **1** and **2** is summarized in Scheme 3. The reduction and reoxidation behavior of complex **2** are considered as an electrochemical square scheme [34].

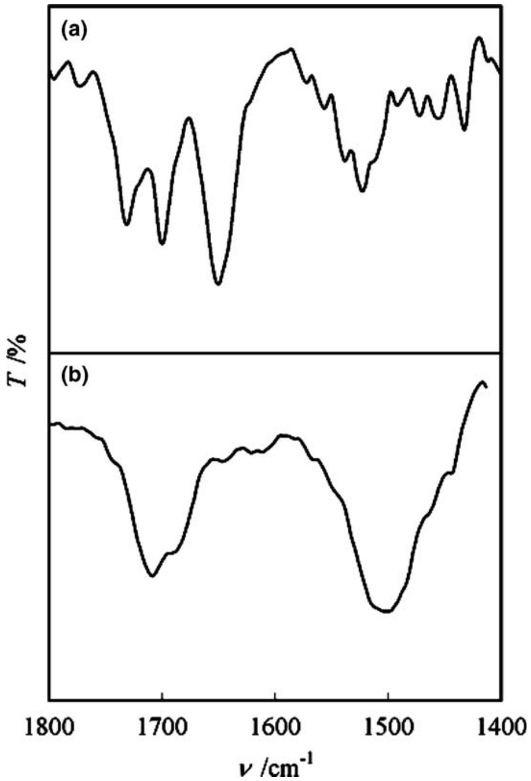


Fig. 9. IR spectral changes of complex **2** in an OTTLE cell: (a) before electrolysis and (b) after reduction at −1.75 V for 2 min. The spectra were measured in dichloromethane solution containing TBAP.

2.5. Conclusion

This paper has reported the formation procedures and structures of some mononuclear and binuclear molybdenum dithiolene complexes by using the starting materials [Cp*Mo(NO)(CO)$_2$] and [Cp*Mo(NO)(Cl)(μ-Cl)]$_2$. The one-pot reaction of [Cp*Mo(NO)(CO)$_2$] with elemental sulfur and DMAD formed the [2+2] cycloadduct of molybdenum dithiolene complex [Cp*Mo(NO)(S$_2$C$_2$Z$_2$)(C$_2$Z$_2$)] (**1**, Z = COOMe) as a new Cp/dithiolene 1:1 complex included in Chart 1(d), the binuclear complexes [Cp*Mo(NO)-(S$_2$C$_2$Z$_2$)]$_2$ (**2**, Cp/dithiolene 2:2 complex in Chart 1(a)), [Cp*$_2$Mo$_2$(NO)$_2$S$_2$(S$_2$C$_2$Z$_2$)] (**3**) and [Cp*Mo(NO)S$_2$]$_2$ (**4**). We assumed that the reaction of the coordinatively unsaturated molybdenum dithiolene species [Cp*Mo(NO)-(S$_2$C$_2$Z$_2$)] (**X**) with DMAD forms the [2+2] cycloadduct **1**. We have reported that the coordinatively unsaturated cobalt dithiolene complex [CpCo(S$_2$C$_2$X$_2$)] reacts not only with nucleophiles (e.g. diazo compound [35] and azide compound [36]) but also with electrophiles such as DMAD [14,15] and tetracyanoethylene oxide (TCNEO) [37] to afford the coordinatively saturated adducts. We conclude that the [2+2] cycloadduct **1** is produced due to unsaturation of species **X**. However, the unsaturated species **X** is extremely unstable. We assume that the stability of the unsaturated metal dithiolene species depends on the metal center [15]. Although the π-electron delocalization and the aromatization in the metalladithiolene ring occasionally alleviate their unsaturation, in this case of molybdenum, the strong π-acceptability of nitrosyl ligand provably causes continued instability of the unsaturated molybdenum center in **X**.

Although the isolation of species **X** was not possible in this work, it was detected by the EI$^+$ mass spectra of the adduct **1** and the binuclear complex **2**. This result indicates that an electron impact induces the elimination of DMAD from adduct **1** and the monomerization of complex **2**. In addition, the species **X** can be generated electrochemically. The reduction of the binuclear complex [Cp*Mo(NO)(S$_2$C$_2$Z$_2$)]$_2$ (**2**) gives the mononuclear complex [Cp*Mo(NO)(S$_2$C$_2$Z$_2$)]$^-$ (**X**$^-$), and the oxidation of **X**$^-$ forms the neutral species **X**. The species **X** has a short lifetime, and it immediately reforms the original binuclear complex **2**. Some examples of the electro-oxidative dimerization of a mononuclear metal dithiolene complex have been reported [15,29,38,39]. Our case is the electro-reductive monomerization of a binuclear metal dithiolene complex.

3. Experimental

3.1. General remarks

All reactions were carried out under an argon atmosphere by means of standard Schlenk techniques. Solvents were purified by Na-benzophenone distillation before use. [Cp*Mo(NO)(CO)$_2$] [40] and [Cp*Mo(NO)(Cl)(μ-Cl)]$_2$ [41] were synthesized by the literature methods. Dimethyl 1,3-dithiol-2-one-4,5-dicarboxylate O═C{S$_2$C$_2$(COOMe)$_2$} was obtained from the reaction of dimethyl 1,3-dithiol-2-thione-4,5-dicarboxylate (from Tokyo Kasei Kogyo Co., Ltd.) with Hg(OAc)$_2$ [42]. Silica gel (Wakogel C-300) was supplied from Wako Pure Chemical Industries, Ltd. Mass and IR spectra were recorded on a JEOL JMS-D300 and a Shimadzu Model FTIR 8600PC spectrometer, respectively. NMR spectra were measured with a JEOL LA500 spectrometer. Elemental analyses were determined by using a Shimadzu PE2400-II instrument. HPLC treatment was performed with LC-908 (column type: AJLH332-018, column length: 120 cm, solvent: CHCl$_3$) produced by Japan analytical industries corporation.

3.2. Formations of mononuclear and binuclear molybdenum dithiolene complexes

3.2.1. One-pot reaction of [Cp*Mo(NO)(CO)$_2$] with S$_8$ and DMAD

[Cp*Mo(NO)(CO)$_2$] (208 mg, 0.654 mmol), S$_8$ (85 mg, 2.66 mmol), and DMAD (1.52 mL, 12.5 mmol) reacted in refluxing benzene (40 mL) for 72 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica gel, eluent = dichloromethane). [Cp*Mo(NO)(S$_2$C$_2$Z$_2$)(C$_2$Z$_2$)] (**1**, orange solid, 7% yield), [Cp*Mo(NO)(S$_2$C$_2$Z$_2$)]$_2$ (**2**, green solid, 5% yield), [Cp*$_2$Mo$_2$(NO)$_2$S$_2$(S$_2$C$_2$Z$_2$)] (**3**, brown solid, 4%

yield) and $[Cp^*Mo(NO)S_2]_2$ (**4**, greenish-brown solid, trace amount) were obtained. The complexes were further purified by HPLC and by a recrystallization from dichloromethane/*n*-hexane. The spectroscopic data of products are as follows.

*3.2.1.1. $[Cp^*Mo(NO)\{S_2C_2(COOMe)_2\}\{C_2(COOMe)_2\}]$ (**1**).* Red solid. Mass (EI^+, 70 eV) *m*/*z* (relative intensity) 611 ([M^+], 17), 580 ([$M^+{-}OMe$], 11), 469 ([$M^+{-}C_2(COOMe)_2$], 98), 469 ([$M^+{-}C_2(COOMe)_2{-}NO$], 100). ^1H NMR ($CDCl_3$, 500 MHz, vs. TMS) $\delta = 1.93$ (s, 15H, C_5Me_5), 3.73 (s, 3H, COO*Me*), 3.77 (s, 3H, COO*Me*), 3.82 (s, 3H, COO*Me*), 3.85 (s, 3H, COO*Me*). IR (KBr disk) 1728, 1655, 1435, 1250 cm^{-1}. HR-mass (EI^+, 70 eV) Calc. for $C_{22}H_{27}MoNO_9S_2$: 611.0181. Found: 611.0174.

*3.2.1.2. $[Cp^*Mo(NO)\{S_2C_2(COOMe)_2\}]_2$ (**2**).* Green solid. Mass (EI^+, 70 eV) *m*/*z* (relative intensity) 934 ([M^+], 17), 904 ([$M^+{-}NO$], 11), 469 ([$M^+/2$], 98), 439 ([$M^+/2{-}NO$], 100). ^1H NMR ($CDCl_3$, 500 MHz, vs. TMS) $\delta = 1.85$ (s, 30H, C_5Me_5), 3.68 (s, 6H, COO*Me*), 3.84 (s, 6H, COO*Me*). IR (KBr disk) 1732, 1703, 1649, 1526, 1518, 1431, 1238 cm^{-1}. Anal. Calc. for $C_{33}H_{44}Cl_2Mo_2N_2O_{10}S_4$: C, 38.87; H, 4.35; N, 2.75. Found: C, 39.11; H, 4.54; N, 3.02%.

*3.2.1.3. $[Cp^*_2Mo_2(NO)_2S_2\{S_2C_2(COOMe)_2\}]$ (**3**).* Brown solid. Mass (EI^+, 70 eV) *m*/*z* (relative intensity) 792 ([M^+], 17), 762 ([$M^+{-}NO$], 9), 732 ([$M^+{-}2NO$], 41), 590 ([$Cp^*{}_2Mo_2S_4$], 100). ^1H NMR ($CDCl_3$, 500 MHz, vs. TMS) $\delta = 1.84$ (broad, 30H, C_5Me_5), 3.67 (s, 3H, COO*Me*), 3.82 (s, 3H, COO*Me*). IR (KBr disk) 1736, 1724, 1641, 1246 cm^{-1}. Anal. Calc. for $C_{26}H_{36}Mo_2N_2O_6S_4$: C, 39.39; H, 4.58; N, 3.53. Found: C, 39.45; H, 4.75; N, 3.25%.

3.2.2. Reaction of $[Cp^*Mo(NO)(Cl)(\mu\text{-}Cl)]_2$ with dimethyl 1,3-dithiol-2-one-4,5-dicarboxylate

Dimethyl 1,3-dithiol-2-one-4,5-dicarboxylate $O{=}C\{S_2C_2(COOMe)_2\}$ (35 mg, 0.15 mmol) was treated with an equivalent of sodium methoxide in methanol solution (10 mL) at room temperature. The initially colorless solution was changed to yellow after 1 h. The dichloromethane solution (20 mL) of $[Cp^*Mo(NO)(Cl)(\mu\text{-}Cl)]_2$ (50 mg, 0.075 mmol) was added into this solution. The reaction mixture was further stirred at room temperature for 17 h. After the solvent was removed under reduced pressure, the residue was extracted by dichloromethane/water, and the organic layer was separated by column chromatography (silica gel, eluent = dichloromethane). The complexes were further purified by HPLC and by a recrystallization from dichloromethane/*n*-hexane. Complex **2** (15% yield), and the bisdithiolene complex $[Cp^*Mo(S_2C_2Z_2)_2]$ (**5**, brown solid, trace amount) were obtained.

*3.2.2.1. $[Cp^*Mo\{S_2C_2(COOMe)_2\}_2]$ (**5**).* Brown solid. Mass (FAB^+, 70 eV) 645 ([M^+]). Anal. Calc. for $C_{22}H_{27}MoO_8S_4$: C, 41.05; H, 4.23. Found: C, 41.20; H, 4.33%.

3.3. X-ray diffraction study

Single crystals of complexes **1**–**5** were obtained by a recrystallization from the dichloromethane solutions and then vapor diffusion of *n*-hexane into these solutions. A single crystal was mounted on the top of a thin glass fiber. The measurement was made on a Rigaku MERCURY diffractometer with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Half of all atoms in complex **4** were observed by a symmetry expansion. Hydrogen atoms were refined using the riding model. All the calculations were carried out using the Crystal Structure crystallographic software package. The crystal data complexes **1**–**5** are summarized in Table 2.

3.4. Electrochemical measurements

All electrochemical measurements were performed under an argon atmosphere. Solvents for electrochemical measurements were dried with a 4 Å molecular sieve before use. A platinum wire served as a counter electrode, and the reference electrode is Ag/AgCl (3 mol dm^{-3} aqueous NaCl solution) corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium (Fc/Fc^+) couple.

3.4.1. CV measurements

The Model CV-50W instrument from BAS Co. was used for CV measurements. The CV measurements were done in 1 mmol dm^{-3} dichloromethane solutions of complexes **1** and **2** containing 0.1 mol dm^{-3} tetra-*n*-butylammonium perchlorate (TBAP) at 25 °C. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode.

3.4.2. Visible and IR absorption spectral measurements during electrolysis

The visible absorption spectra during electrolysis were obtained for 1 mmol dm^{-3} dichloromethane solution of complex **2** containing 0.1 mol dm^{-3} TBAP at 25 °C in an optically transparent thin-layer electrode (OTTLE, thin-layer thickness = 0.4 mm) cell [43] by using a Photal MCPD-7000 rapid scan spectrometer. The working electrode was a piece of stationary platinum mesh in the thin-layer form. The IR absorption spectra during electrolysis were obtained for 5 mmol dm^{-3} dichloromethane solution of complex **2** containing 0.3 mol dm^{-3} TBAP at 25 °C in an OTTLE cell (thin-layer thickness = 0.2 mm) designed originally by Hartl et al. [44], and the IR spectra was recorded by using a Jasco FT-IR-8000 spectrometer. The working electrode was a piece of stationary platinum mesh in the thin-layer form.

3.5. ESR measurements

ESR spectra were recorded on a JEOL X-band JES-3X ESR spectrometer. Microwave frequencies and the magnetic field were directly determined by using a microwave counter, ADVANTEST TR5212, and a field measurement unit, JEOL NMR field meter ES-FC-5, respectively. The 5 mmol dm^{-3} toluene solution of complex **5** was used for the ESR measurement.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 297228 (**1**), 297229 (**2**), 297230 (**3**), 297231 (**4**) and 297232 (**5**). Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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