Electrical and Spectroscopic Properties of Bis(dmit)oxomolybdenum(2−) (dmit = 4,5-dimercapto-1,3-dithiole-2-thionate) Anion Complexes and the Oxidized Analogs

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(Received August 30, 1988)

Abstract

$[NBu^n_4]_2[MoO(dmit)_2]$ (1) (dmit = 4,5-dimercapto-1,3-dithiole-2-thionate; $C_3S_5^{2-}$) and $[NMA]_2[MoO(dmit)_2]$ (2) (NMA = *N*-methylacridinium) were prepared. The $[MoO(dmit)_2]^{2-}$ anion with a square pyramid geometry around the molybdenum atom is electrochemically reversibly oxidized at +0.12 V (*versus* SCE) to form the stable $[MoO(dmit)_2]^-$ anion. By reactions of 1 with iodine in the presence of $[MNA][ClO_4]$ and with the tetrathiafulvalenium cation ($TTF^{+\bullet}$) were isolated $[NMA]_{0.9}[MoO(dmit)_2]$ (3) and $[TTF][MoO(dmit)_2]$ (4), respectively. By reactions of 1 with 7,7,8,8-tetracyano-*p*-quinodimethane and with hydrogen iodide in acetonitrile were obtained complexes formulated as $[NBu^n_4]_{0.15}[MoO(dmit)_2]$ (5) and $[NBu^n_4]_{0.25}[MoO(dmit)_2]$ (6), respectively. Although complexes 1–3 are essentially insulators, 4–6 behave as semiconductors with conductivities 1.1×10^{-5}, 7.3×10^{-3}, and 5.1×10^{-4} S cm^{-1} at 25 °C for compacted pellets, respectively. IR, ESR, electronic and X-ray photoelectron spectra of the complexes are discussed.

Introduction

Electrically conducting metal complexes with sulfur-rich dithiolene ligands have been recently studied [1–4], in which electrical conduction is expected to occur through two- or three-dimensional pathways constructed from intermolecular sulfur–sulfur contacts. Dmit–metal complexes (dmit = 4,5-dimercapto-1,3-dithiole-2-thionate; $C_3S_5^{2-}$) are of much interest from the standpoint of the intermolecular S–S contacts in planar $[M(dmit)_2]^{n-}$ (M = Ni, Pd, and Pt; n = 0.3–2.0) complexes [4–6]. Particularly, $[TTF][Ni(dmit)_2]_2$ (TTF = tetrathiafulvalenium) [5] and $[NMe_4][Ni(dmit)_2]_2$ [6] were reported to become superconductors. Although nonplanar dmit–metal complexes are also expected to have intermolecular S–S contacts and to construct new packings of the complexes in the crystal phase, few studies on them have been reported to date [7, 8].

In the course of our study on electrically conducting, nonplanar dmit–metal complexes [7–9], we have found a stable redox process of the $[MoO(dmit)_2]^{2-}$ anion with square-pyramid geometry and have isolated some complexes containing the oxidized anions. This paper reports electrical properties of these complexes as well as IR, ESR, electronic, and X-ray photoelectron spectroscopies of them.

Experimental

Materials

4,5-Bis(benzoylthio)-1,3-dithiole-2-thione [10], $[pyridinium]_2[MoOCl_5]$ [11], and $[TTF]_3[BF_4]_2$ [12] were prepared according to the literatures. $[NMA][ClO_4]$ (NMA = the *N*-methylacridinium cation) was prepared by the reaction of [NMA]I with $Mg[ClO_4]_2$ in water and recrystallized from acetone.

Preparation of $[MoO(dmit)_2]^{2-}$ Anion Complexes

$[NBu^n_4]_2[MoO(dmit)_2]$ (1) was prepared according to the literature [9].

To an acetone (30 cm^3) solution of $[NMA][ClO_4]$ (60 mg, 200 μmol) was added an acetone (30 cm^3) solution of 1 (100 mg, 100 μmol). A brown solid of $[NMA]_2[MoO(dmit)_2]\cdot 0.5Me_2CO$ (2) precipitated immediately, which was collected by filtration, washed with acetone and dried *in vacuo* (74% yield).

Preparation of $[NMA]_{0.9}[MoO(dmit)_2]$ (3)

To an acetonitrile (5 cm^3) solution of 1 (50 mg, 50 μmol) was added an acetonitrile (2 cm^3) solution of iodine (3.2 mg, 25 μmol), followed by addition of an acetonitrile (2 cm^3) solution of $Ag[ClO_4]$ (10.4 mg, 50 μmol). After a precipitate of AgI was filtered off, the filtrate was added to an acetonitrile (5 cm^3) solution of $[NMA][ClO_4]$ (44 mg, 150 μmol). A

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precipitate of $[NMA]_{0.9}[MoO(dmit)_2]$ (**3**) formed immediately, was collected by centrifugation, washed with acetonitrile and dried *in vacuo* (88% yield).

Preparation of [TTF][MoO(dmit)₂] (4)

To an acetonitrile (60 cm^3) solution of $[TTF]_3[BF_4]_2$ (95 mg, 1.2 mmol) was added **1** (120 mg, 1.2 mmol) dissolved in acetonitrile (30 cm^3). A precipitate of **4** formed immediately, was collected by centrifugation, washed with acetonitrile and dried *in vacuo* (98% yield based on **1**).

Preparation of $[NBu^n{}_4]_x[MoO(dmit)_2]$ (x = 0.15 and 0.25)

To an acetonitrile (30 cm^3) solution of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (41 mg, 200 μmol) was added an acetonitrile (10 cm^3) solution of **1** (100 mg, 100 μmol) and the solution was allowed to stand overnight at room temperature. A resulting black precipitate formulated as $[NBu^n{}_4]_{0.15}[MoO(dmit)_2]$ (**5**) was collected by centrifugation, washed with acetonitrile and dried *in vacuo* (38% yield).

To an acetonitrile (10 cm^3) solution of **1** (100 mg, 100 μmol) was added 20 molar amounts of HI dissolved in acetonitrile. A black solid formulated as $[NBu^n{}_4]_{0.25}[MoO(dmit)_2]$ (**6**) immediately precipitated, was washed with acetonitrile and dried *in vacuo* (66% yield).

Melting points and elemental analyses for the complexes obtained are listed in Table 1.

Physical Measurements

Electronic absorption, powder reflectance [13], ESR [14], and IR spectra [15] were measured as described elsewhere. X-ray photoelectron spectra were obtained by irradiating the complexes with Mg Kα X-rays (240 W) at 298 K using a Shimazu-ESCA 750 photoelectron spectrometer with the computer analyser ESCA PAC 760, and were calibrated with the carbon $1s_{1/2}$ photoelectron peak (285 eV). The peak shift caused by charge-up effect was corrected with the silicon $2s_{1/2}$ peak (149 eV) [16]. The error of the binding energy determination was estimated to be 0.1 eV. Electrical resistivities of compacted pellets were measured by the conventional two-probe technique [17].

Results and Discussion

As was reported in the previous paper [9], the $[MoO(dmit)_2]^{2-}$ anion assumes a square pyramid geometry around the molybdenum atom and is electrochemically reversibly oxidized at $E_{1/2}{}^0 = +0.12$ V (*versus* SCE) ($\Delta E = E_{cp} - E_{ap} = 60$ mV). By an oxidation reaction of complex **1** with iodine in the presence of $Ag[ClO_4]$ and $[NMA][ClO_4]$ complex **3** was isolated, the $[MoO(dmit)_2]^{2-}$ anion being essentially, formally one-electron oxidized. Similarly, oxidation of **1** with the tetrathiafulvalenium cation affords **4** which contains also the $[MoO(dmit)_2]^-$ anion together with the $TTF^{+\cdot}$ radical cation as described below. Both complexes **3** and **4** show an intense IR band at 935 and 930 cm^{-1}, respectively, attributable to the Mo=O stretching which is close to that (930 cm^{-1}) of **1**. Thus, the $[MoO(dmit)_2]^-$ anion also seems to have a square pyramid geometry quite similar to that of the $[MoO(dmit)_2]^{2-}$ anion [9].

Complexes **1** and **2** show the C=C stretching band of the dmit ligand at 1440 cm^{-1}, while **3** and **4** exhibit this band at 1370 and 1350 cm^{-1}, respectively. Such noticeable low-frequency shifts of this band on the oxidation of the anion suggest that oxidation occurs essentially on the dmit ligand rather than the metal center [15]. In addition, **4** shows a ν(C=C) stretching band due to the $TTF^{+\cdot}$ radical cation at 1470 cm^{-1} [18, 19].

TABLE 1. Melting Points and Elemental Analyses of the Molybdenum–dmit Complexes

No.	Complex	Melting point (decomp.) (°C)	Found (calc.) (%)		
			C	H	N
1	$[NBu^n{}_4]_2[MoO(dmit)_2]$	170–173	45.82 (46.12)	7.36 (7.33)	2.82 (2.83)
2	$[NMA]_2[MoO(dmit)_2]0.5Me_2CO$	169–172	45.95 (46.24)	3.04 (3.04)	2.88 (2.95)
3	$[NMA]_{0.9}[MoO(dmit)_2]$	>190	31.49 (32.86)	1.73 (1.59)	1.92 (1.86)
4	$[TTF][MoO(dmit)_2]$	>185	20.38 (20.33)	0.65 (0.57)	
5	$[NBu^n{}_4]_{0.15}[MoO(dmit)_2]$	177–180	19.23 (19.22)	0.69 (1.04)	0.66 (0.40)
6	$[NBu^n{}_4]_{0.25}[MoO(dmit)_2]$	175–180	21.40 (21.25)	1.74 (1.60)	0.68 (0.62)

NMA = *N*-methylacridinium, TTF = tetrathiafulvalenium.

TABLE 2. IR ν(C=C) and ν(Mo=O) Frequencies (cm^{-1})^a and Binding Energies (eV) of Mo $3d_{3/2}$ Electrons of the Mo–dmit Complexes

Complex	ν(C=C)	ν(Mo=O)	Binding energies (Mo $3d_{3/2}$)
1	1440	930	232.5
2	1440	910	232.7
3	1370	910	233.0
4	1350	935	232.4
5	1300		232.2
6	1300		233.1

^{a}Measured in KBr disks.

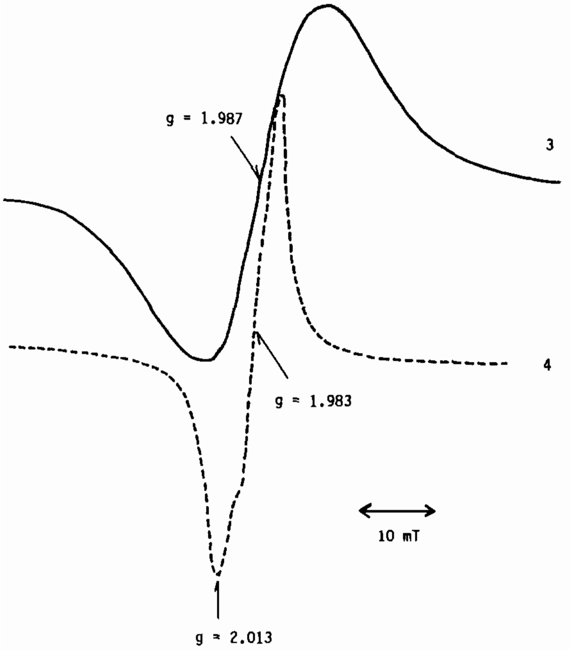

Fig. 1. Powder ESR spectra of 3 and 4 at room temperature.

Binding energies of molybdenum $3d_{3/2}$ electrons determined by X-ray photoelectron spectroscopy are almost unvaried for complexes **1**, **2**, **3** and **4** (see Table 2), which is in accordance with the above-described ligand-centered oxidation on **3** and **4**.

In contrast to the ESR-silence of complexes **1** and **2**, complexes **3** and **4** exhibit intense ESR signals at $g = 1.987$ and 1.983, respectively, although **4** accompanies with the signal (apparently $g = 2.013$) due to the $TTF^{+\bullet}$ radical cation ($g_{max} = 2.016$, $g_{int} = 2.009$, $g_{min} = 2.003$) [20] (see Fig. 1). Moreover, the ESR spectrum of an acetonitrile solution containing equimolar amounts of **1** and iodine at room temperature shows an isotropic signal at $g = 1.987$ which has six satellites due to the hyperfine couplings with $^{95/97}Mo$ nuclei with $I = 5/2$ [$a(^{95/97}Mo) = 28.2 \times 10^{-4}$ cm^{-1}] [9].

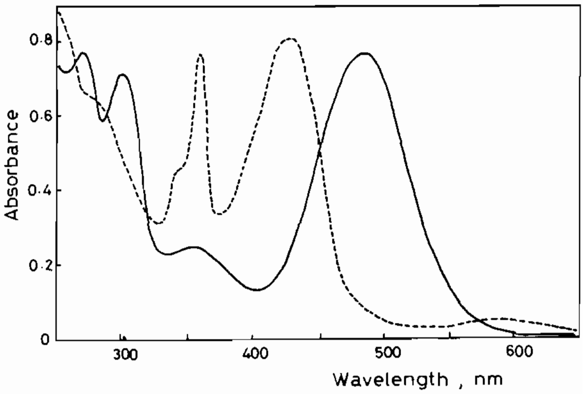

Fig. 2. Electronic absorption spectra of 1 (7.1×10^{-5} mol dm^{-3}) (——) and of 3 (7.6×10^{-5} mol dm^{-3}) (----) in acetonitrile.

Figure 2 shows the electronic absorption spectra of **1** and **3** in acetonitrile. The intense bands at 300 and 485 nm observed for **1** are reasonably assigned to local excitations of the dmit ligand, as were observed for Na_2dmit (316 and 514 nm in methanol) and $[NBu^n_4]_2[Zn(dmit)_2]$ (300 and 530 nm in acetonitrile) [21]. On the other hand, the corresponding bands occur at 280 and 430 nm for complex **3**, which are essentially the same as bands observed on the electrochemical oxidation of **1** [9]. Complexes **1**, **2** and **3** show powder reflectance spectra corresponding to the solution absorption spectra, suggesting no significant molecular interaction in the solid state. Moreover, complex **4** gives an intense reflectance band at 790 nm which is due to $TTF^{+\bullet}/TTF^{+\bullet}$ charge transfer transition [22].

Complex **1** reacts with TCNQ in acetonitrile to give a black solid of **5** in which the anion moiety seems to be further oxidized. The IR ν(C=C) band of the dmit ligand occurs around 1300 cm^{-1}, which is rather close to those of $[M(dmit)_2]^{\delta-}$ ($\delta < 1$; M = Ni, Pd, and Pt) complexes with high conductivities (1250–1290 cm^{-1}) [15]. Since the IR ν(Mo=O) band has not been observed around 900 cm^{-1}, the configuration around the molybdenum atom of **5** seems to be different from the square pyramid geometry, presumably a Mo–O–Mo linkage being formed as described below. The powder reflectance spectrum of **5** as well as the absorption spectrum in *N,N*-dimethylformamide is displayed in Fig. 3. The band observed at 370 nm is reasonably assigned to the local excitation of the dmit ligand in the further oxidized complex. A broad band around 800 nm may be assigned to a charge transfer transition from dmit–sulfur to molybdenum, as was reported for $[MoO(S\text{-}2,4,6\text{-}Pr^i_3C_6H_2)_4]$ (803 nm) [23]. The broad band at 480 nm which is not observed for both the $[MoO(dmit)_2]^{2-}$ and $[MoO(dmit)_2]^-$ anions is likely ascribed to a Mo–O–Mo linkage based on the bands reported for $[Mo_2O_3(S_2COR)_4]$ (R = Me, Et, Pr^i, Bu^n

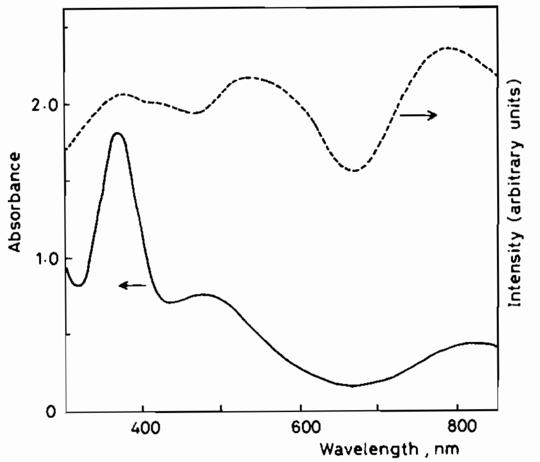

Fig. 3. Electronic absorption (9.2×10^{-5} mol dm^{-3} in *N,N*-dimethylformamide) (——) and powder reflectance spectrum (- - - -) of **5**.

and Bu^i) [24, 25]. The complex shows an isotropic, intense ESR signal at $g = 2.008$. The reaction of **1** with HI (or HBr) in acetonitrile also has yielded a black solid of **6**. The IR, electronic reflectance and ESR spectra are essentially the same as those of **5**. Moreover, binding energies of molybdenum $3d_{3/2}$ electrons for these complexes are essentially the same as those of the other Mo–dmit complexes (see Table 2). To investigate the formation process of **5** and **6**, we have measured ESR spectra of acetonitrile solutions containing **1**/TCNQ and **1**/HBr. The former solution has revealed a signal due to the TCNQ$^{-\bullet}$ anion radical together with signals of oxidized molybdenum species. Since the signal of the TCNQ$^{-\bullet}$ radical anion obscures other signals, Fig. 4 shows the ESR spectrum of the latter solution. The signal at $g = 1.989$ indicates the formation of the [MoO(dmit)$_2$]$^-$ anion in the system. This signal gradually decreases in its intensity with time and concomitantly the intensity of the signal at $g = 2.008$ relatively increases, which corresponds to the signal of complex **6**. This finding suggests that [MoO(dmit)$_2$]$^{2-}$ is further oxidized via [MoO(dmit)$_2$]$^-$ to form complex **6** (and **5**).

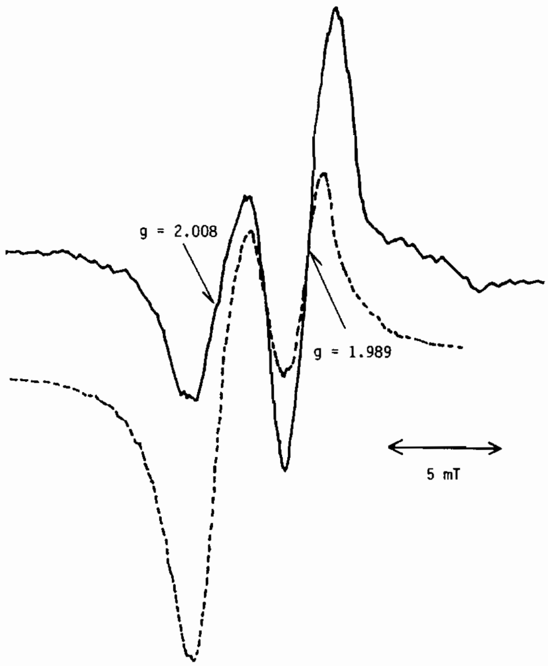

Fig. 4. ESR spectra of an equimolar mixture of **1** and HBr in acetonitrile at room temperature: measured immediately (——) and in 15 min after mixing (- - - -).

TABLE 3. Electrical Conductivities ($\sigma_{25\,°C}$) and Activation Energies (E_a) of the Mo–dmit Complexes[a]

Complex	$\sigma_{25\,°C}$ (S cm^{-1})	E_a (eV)
1	$<10^{-10}$	
2	$<10^{-10}$	
3	6.7×10^{-9}	0.54
4	1.1×10^{-5}	0.31
5	7.3×10^{-3}	0.18
6	5.1×10^{-4}	0.19

[a]Measured for compacted pellets.

Electrical conductivities (σ) at 25 °C and activation energies (E_a) for the complexes measured for compacted pellets are summarized in Table 3. Complexes **1** and **2** are essentially insulators, because the anions are located separately through the cations in the crystals, as was revealed for the crystal structure of **1** [9]. The other complexes behave as typical semiconductors in the temperature range from −30 to +55 °C. Although complex **3** is in a one-electron dmit-centered oxidized state, it has also very small conductivity, probably because the geometry of the anion is considered to be quite similar to that of **1** and there is no effective interaction between the dmit ligands. On the other hand, **4** exhibits somewhat large conductivity. It contains the TTF$^{+\bullet}$ radical cation, which may construct a conduction pathway. The conductivity of this complex is relatively large for a TTF$^{+\bullet}$ radical cation simple salt. This may be caused by a columnar structure of the TTF$^{+\bullet}$ radical cations, as was reported for [TTF][Rh(CO)$_2$Cl$_2$] [20] and [dibenzotetrathiafulvalenium][SnEt$_2$Cl$_3$] [26] ($\sigma_{25\,°C} = 2.1 \times 10^{-4}$ and 3.3×10^{-5} S cm^{-1} for crystals, respectively). Complexes **5** and **6** exhibit higher conductivities, which may come from electrical conduction pathways constructed from an intermolecular contact through the Mo–O–Mo linkage and/or a dmit–dmit interaction through sulfur atoms as reported for some dmit–metal complexes [4–8, 21] may result in the higher conduction.

Acknowledgement

This work has been partially supported by a Miyashita Research grant, for which we thank the Material Research Foundation.

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