

Preparation and properties of oxometallate complexes with sulfur-rich dithiolate ligands, $[M(O)(C_8H_4S_8)_2]^{2-}$ ($M = V(IV)$ and $Mo(IV)$) salts, and high electrical conductivity of their oxidized species

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Received 15 February 2000; accepted 3 April 2000

Abstract

Penta-coordinate oxometallate complexes with sulfur-rich dithiolate ligands, $[NEt_4]_2[V(O)(C_8H_4S_8)_2]$, $[N\text{-methylpyridinium}]_2[V(O)(C_8H_4S_8)_2]$, and $[NEt_4]_2[Mo(O)(C_8H_4S_8)_2]$ ($C_8H_4S_8^{2-} = 2\text{-}\{(4,5\text{-ethylenedithio})\text{-}1,3\text{-dithiole-}2\text{-ylidene}\}\text{-}1,3\text{-dithiole-}4,5\text{-dithiolate(}2\text{-)}$), were prepared by reactions of $V(O)(acac)_2$ ($acacH = \text{acetylacetonone}$) or $[pyridinium]_2[Mo(O)Cl_5]$ with $Na_2C_8H_4S_8$ in ethanol in the presence of NEt_4Cl or $N\text{-methylpyridinium iodide}$. They exhibited oxidation potentials at -0.27 ± 0.14 V (vs. SCE), and were reacted with iodine, 7,7,8,8-tetracyano-*p*-quinodimethane or the decamethylferrocenium cation in benzonitrile to afford oxidized species, $[V(O)(C_8H_4S_8)_2]$, $[NEt_4]_{0.2}[V(O)(C_8H_4S_8)_2]$, $[NEt_4]_{0.3}[Mo(O)(C_8H_4S_8)_2]$, and $[Fe(C_5Me_5)_2]_{0.05}[Mo(O)(C_8H_4S_8)_2]$, and a reaction of suspension of powdered $[N\text{-methylpyridinium}]_2[V(O)(C_8H_4S_8)_2]$ with an excess amount of iodine in hexane gave $[N\text{-methylpyridinium}]_2[V(O)(C_8H_4S_8)_2](I_3)_2$. In the oxidized species occurred the $C_8H_4S_8$ ligand-centered oxidation. They exhibited electrical conductivities of $0.11\text{--}5.5$ S cm^{-1} measured for compacted pellets at room temperature. The electronic states of the oxovanadium(IV) and oxomolybdenum(IV) complexes and their oxidized species are discussed on the basis of electronic absorption, powder reflectance, IR and ESR spectra. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Oxovanadium complexes; Oxomolybdenum complexes; Dithiolate complexes; Oxidation; Electrical conductivity

1. Introduction

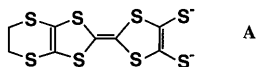
Planar metal complexes with sulfur-rich dithiolate ligands have attracted much attention to high electrical conductivities of their partially oxidized species. Many C_3S_5 -metal complexes ($(C_3S_5^{2-} = 4,5\text{-disulfanyl-}1,3\text{-dithiole-}2\text{-thionate (}2\text{-)})$) exhibit high electrical conductivities and especially $[M(C_3S_5)_2]$ -type complexes ($M = Ni(II), Pd(II), Pt(II), \text{ and } Au(III)$) behave as good electrical conductors, some of which are well-known as

superconductors [1–5]. Non-planar C_3S_5 -metal complexes have also been explored as electrical conductors having electron-conduction pathways constructed with unique molecular packing in the solid state. Some $[M(C_3S_5)_3]$ -type complexes ($M = V(IV), Re(IV), Mo(IV)$ and $W(IV)$) exhibited high electrical conductivities [6–9].

Metal complexes with more sulfur-rich dithiolate ligands as an extended π -electron delocalized system are expected to form better electrical conductors because of the formation of more effective electron-conduction pathways through more S–S interactions in the solid state [10–16]. Some oxidized metal complexes with $C_8H_4S_8^{2-}$ ($2\text{-}\{(4,5\text{-ethylenedithio})\text{-}1,3\text{-dithiole-}2\text{-ylidene}\}\text{-}1,3\text{-dithiole-}4,5\text{-dithiolate(}2\text{-)}$; **A**) ligand showed high electrical conductivities:

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planar $[M(C_8H_4S_8)_2]$ -type complexes ($M = Ni(II)$, $Pt(II)$, and $Au(III)$) [12–14] and non-planar $[Co(\eta^5-C_5H_5)(C_8H_4S_8)]^+$ [17] and $[Ti(\eta^5-C_5H_5)(C_8H_4S_8)_2]^{n+}$ ($n < 1$) complexes [18]. Previously non-planar, penta-coordinate oxometallate complexes, $[M(O)(C_3S_3)_2]^{2-}$ ($M = V(IV)$ [19] and $Mo(IV)$ [20,21]) salts, were prepared. Their oxidized species, however, exhibited low electrical conductivities. On the other hand, the oxometallate complexes having the $C_8H_4S_8$ ligand are expected to become good electrical conductors with effective electron conduction pathways owing to many $S \cdots S$ interactions in the solid state.

This paper reports preparation of $[M(O)(C_8H_4S_8)_2]^{2-}$ ($M = V(IV)$ and $Mo(IV)$) complexes having a penta-coordinate geometry and their electrochemical and spectroscopic properties. Electrical conductivities of their oxidized species are discussed based on their electronic states and molecular interactions in the solid state.

2. Experimental

2.1. Preparation of $[NEt_4]_2[V(O)(C_8H_4S_8)_2]$ (**1**)

All the following reactions were performed under argon atmosphere. $C_8H_4S_8(CH_2CH_2CN)_2$ [14] (100 mg, 0.21 mmol) was dissolved with stirring to an ethanol (15 cm³) solution containing sodium metal (23 mg, 1.0 mmol) under supersonic waves. An ethanol (5 cm³) solution of $V(O)(acac)_2$ ($acacH = acetylaceton$) (40 mg, 0.15 mmol) and NEt_4Cl (210 mg, 0.70 mmol) was added to the resulting red–brown solution of $Na_2[C_8H_4S_8]$. After stirring the solution for 3 h, brown solids of **1** were obtained, which were collected by filtration, washed with water, methanol and diethyl ether, and dried in vacuo (74% yield). Anal. Calc. for $C_{32}H_{48}N_2OS_{16}V$: C, 36.93; H, 4.65; N, 2.69. Found: C, 36.90; H, 4.64; N, 2.76%.

2.2. Preparation of $[N\text{-methylpyridinium}]_2[V(O)(C_8H_4S_8)_2]$ (**2**)

$C_8H_4S_8(CH_2CH_2CN)_2$ (230 mg, 0.50 mmol) was dissolved with stirring into a methanol solution (20 cm³) containing sodium metal (120 mg, 5.0 mmol). The resulting solution was reacted with a methanol (10 cm³) solution of $V(O)(acac)_2$ (72 mg, 0.27 mmol) in the presence of *N*-methylpyridinium iodide (180 mg, 0.80 mmol) to afford brown solids of **2** immediately. They were collected by filtration, washed with methanol, and dried in vacuo (70% yield). Anal. Calc. for $C_{28}H_{24}N_2OS_{16}V$: C, 34.72; H, 2.50; N, 2.89. Found: C, 34.54; H, 2.54; N, 2.95%.

2.3. Preparation of $[NEt_4]_2[Mo(O)(C_8H_4S_8)_2]$ (**3**)

$C_8H_4S_8(CH_2CH_2CN)_2$ (280 mg, 0.60 mmol) was dissolved in an ethanol (20 cm³) solution containing sodium metal (150 mg, 6.5 mmol) under supersonic waves. To the resulting red solution of $Na_2[C_8H_4S_8]$ was added with stirring an ethanol (15 cm³) solution of $[N\text{-methylpyridinium}]_2[Mo(O)Cl_5]$ [22] (140 mg, 0.30 mmol), followed by addition of an ethanol (15 cm³) solution of NEt_4Cl (210 mg, 0.70 mmol). Brown solids of **3** precipitated immediately, which were collected by filtration, washed with water and ethanol, and dried in vacuo (40% yield). Anal. Calc. for $C_{32}H_{48}MoN_2OS_{16}$: C, 35.40; H, 4.46; N, 2.58. Found: C, 35.70; H, 4.39; N, 2.73%.

2.4. Preparation of $[V(O)(C_8H_4S_8)_2]$ (**4**)

To a benzonitrile (50 cm³) solution of **1** (58 mg, 0.056 mmol) was added with stirring a benzonitrile (10 cm³) solution of iodine (73 mg, 0.29 mmol) to afford immediately black solids of **4**. They were collected by centrifugation, washed with benzonitrile, dichloromethane and acetone, and dried in vacuo (70% yield). Anal. Calc. for $C_{16}H_8OS_{16}V$: C, 24.63; H, 1.03. Found: C, 24.80; H, 1.20%.

2.5. Preparation of $[NEt_4]_0.2[V(O)(C_8H_4S_8)_2]$ (**5**)

A tetrahydrofuran (10 cm³) solution of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (63 mg, 0.31 mmol) was added with stirring to a benzonitrile (50 cm³) solution of **1** (58 mg, 0.056 mmol) and the solution was stirred for 15 min. The black solids of **5** obtained were collected by centrifugation, washed with benzonitrile and tetrahydrofuran, and dried in vacuo (75% yield). Anal. Calc. for $C_{17.6}H_{12}N_{0.2}OS_{16}V$: C, 26.22; H, 1.50; N, 0.35. Found: C, 25.79; H, 1.58; N, 0.38%.

2.6. Preparation of $[N\text{-methylpyridinium}]_2[V(O)(C_8H_4S_8)_2]$ **I**₆ (**6**)

To a hexane (100 cm³) solution containing iodine (130 mg, 0.50 mmol) was added finely powdered **2** (97 mg, 0.10 mmol) and the suspended solution was stirred for 8 h at room temperature. The resulting solids of **6** were collected by filtration, washed with hexane, and dried in vacuo (70% yield). Anal. Calc. for $C_{28}H_{24}I_6N_2OS_{16}V$: C, 19.44; H, 1.40; N, 1.62. Found: C, 19.53; H, 1.40; N, 1.70%.

2.7. Preparation of $[NEt_4]_{0.3}[Mo(O)(C_8H_4S_8)_2]$ (**7**)

A benzonitrile (10 cm³) solution of iodine (67 mg, 27 mmol) was added with stirring to a benzonitrile (50 cm³) solution of **3** which immediately produced black

microcrystals of **7**. They were collected by centrifugation, washed with acetone, and dried in vacuo (78% yield). Anal. Calc. for $C_{18.4}H_{14}MoN_{0.3}OS_{16}$: C, 25.57; H, 1.63; N, 0.49. Found: C, 25.35; H, 1.52; N, 0.67%.

2.8. Preparation of $[Fe(C_5Me_5)_2]_{0.05}[Mo(O)(C_8H_4S_8)_2]$ (**8**)

To a benzonitrile (50 cm³) solution of **3** (120 mg, 0.011 mmol) was added with stirring a benzonitrile (10 cm³) solution of $[Fe(C_5Me_5)_2][BF_4]$ [23] (94 mg, 0.23 mmol) to afford immediately black microcrystals of **8**. They were collected by centrifugation, washed with

acetone, and dried in vacuo (57% yield). Anal. Calc. for $C_{17}H_{9.5}Fe_{0.05}MoOS_{16}$: C, 24.26; H, 1.14. Found: C, 24.38; H, 1.35%.

2.9. Physical measurements

IR, ESR [7], electronic absorption, powder reflectance [24], and X-ray photoelectron spectra [17] were measured as described previously. Electrospray ionization (ESI) mass spectra were also obtained as described previously [9], using the spectrometer, Kansai University. Cyclic voltammograms were measured in benzonitrile using $[NBu_4][ClO_4]$ as an electrolyte, and electrical conductivities of the complexes were measured at room temperature for compacted pellets by the conventional two-probe method as described previously [25].

3. Results and discussion

3.1. Spectroscopic and electrochemical properties of complexes **1** and **3**

Fig. 1 shows the negative-ion ESI mass spectra of complex **1** dissolved in acetonitrile–benzonitrile (2:1) solution and of **3** in acetonitrile. The peaks around $m/z = 780$ and 826 ($z = -1$) are due to $[V(O)(C_8H_4S_8)_2]^-$ and $[Mo(O)(C_8H_4S_8)_2]^-$ anions, respectively. The calculated mass spectra on the isotope distribution of these cation species are in good agreement with the observed spectra having the mass interval of 1.0. $[M(O)(C_8H_4S_8)_2]^{2-}$ ($M = V(IV)$ and $Mo(IV)$) anions are oxidized by one-electron through the electrolysis at the electrospray inlet, owing to low oxidation potentials of these anion species, as described below. The appearance of one-electron oxidized species of the complexes in the ESI mass spectra was also observed for some $C_8H_4S_8$ –metal complexes: $[Pt(C_8H_4S_8)_2]^{2-}$ [14], $Co(\eta^5-C_5H_5)(C_8H_4S_8)$ [17] and $Ru(bpy)_2(C_8H_4S_8)$ complexes [24].

Fig. 2 shows the electronic absorption spectrum of **1** in benzonitrile and the powder reflectance spectrum. The appreciable absorption band at 440 nm is ascribed to π – π^* transition of the $C_8H_4S_8$ ligand, as observed for other $C_8H_4S_8$ –metal complexes [24,25]. Complex **3** also showed the π – π^* band at 460 nm in benzonitrile. The reflectance spectrum of **1** shows a broad intense band at the longer wavelength 920 nm, which suggests some interactions among the $[V(O)(C_8H_4S_8)_2]^{2-}$ anions through some non-bonded S–S contacts in the solid state. The similar bands at a longer wavelength were also observed for the solid state spectra of $[V(O)(C_3S_5)_2]^{2-}$ complexes [19]. The powder reflectance spectrum of **3** also showed a broad band at 900 nm, which was not observed for the solution spectrum. This is due to a molecular interaction among the $[Mo(O)(C_8H_4S_8)_2]^{2-}$ anion moieties.

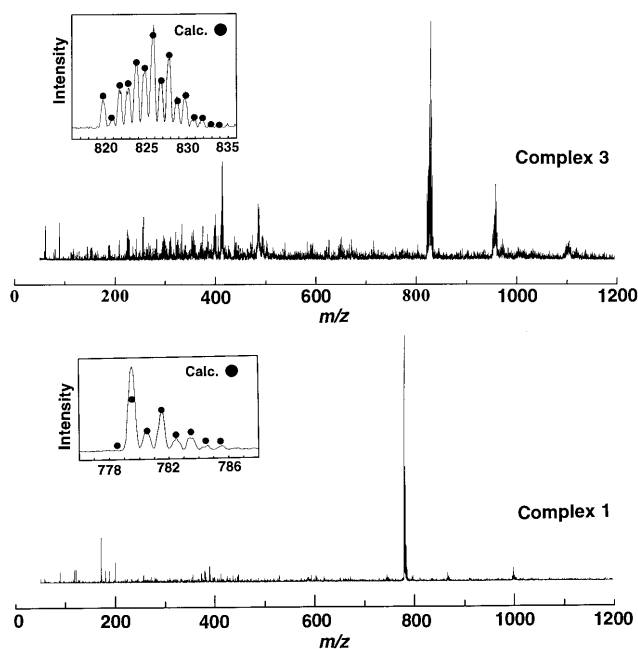


Fig. 1. Negative-ion ESI mass spectra of complexes **1** in acetonitrile–benzonitrile (2:1) and **3** in acetonitrile. In the enlarged spectra, the calculated intensities (●) based on the isotopic distribution of the $[M(O)(C_8H_4S_8)_2]^{2-}$ ($M = V(IV)$ and $Mo(IV)$) species are shown.

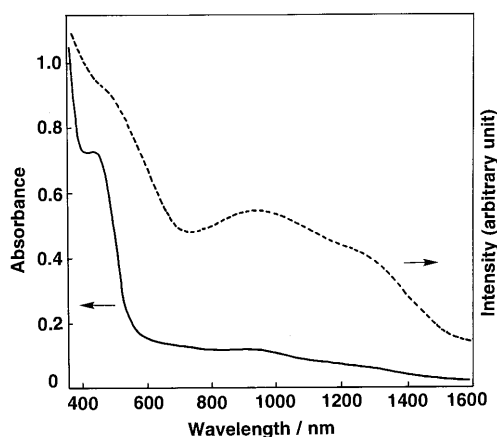


Fig. 2. Electronic absorption spectrum of **1** (2.0×10^{-4} mol dm⁻³) in benzonitrile (—) and the powder reflectance spectrum (---).

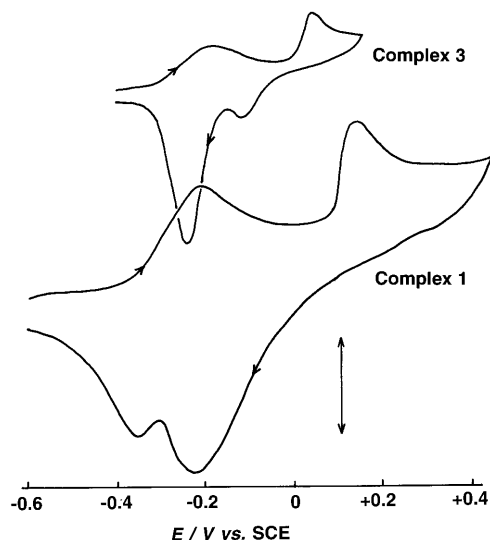


Fig. 3. Cyclic voltammograms of **1** (1.0×10^{-3} mol dm $^{-3}$) and **3** (1.0×10^{-3} mol dm $^{-3}$) in benzonitrile. Supporting electrolyte: 0.02 and 0.1 mol dm $^{-3}$ [NBu $_4^+$][ClO $_4^-$] for **1** and **3**, respectively. Sweep rate: 100 mV s $^{-1}$.

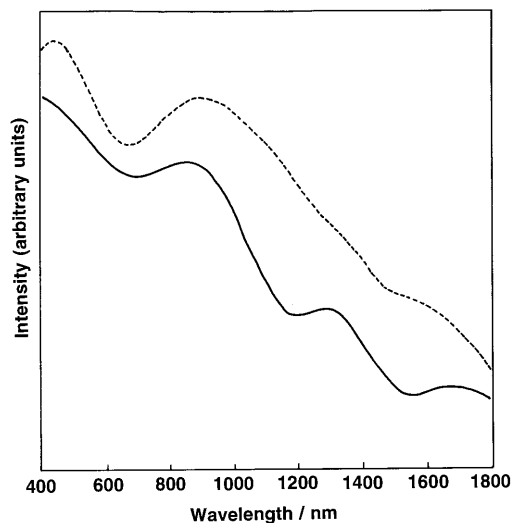


Fig. 4. Powder reflectance spectra of **4** (—) and **7** (---).

Fig. 3 shows the cyclic voltammograms of complexes **1** and **3** measured in benzonitrile. Oxidation peaks at -0.21 and -0.18 V (vs. SCE) observed for **1** and **3** correspond to $[M(O)(C_8H_4S_8)_2]^{2-/-1-}$ redox processes ($M = V(IV)$ and $Mo(IV)$, respectively). Furthermore, the second oxidation processes $[M(O)(C_8H_4S_8)_2]^{1-/-0}$ occur at $+0.14$ and $+0.04$ V (vs. SCE), ($M = V(IV)$ and $Mo(IV)$, respectively). The first oxidation potentials for these present complexes are appreciably lower than those of corresponding $[M(O)(C_3S_3)_2]^{2-}$ complexes: $M = V(IV)$, $+0.19$ V [19] and $M = Mo(IV)$, $+0.15$ V (vs. SCE) [20]. Other $C_8H_4S_8$ -metal complexes ($[NBu_4^+][Au(C_8H_4S_8)_2]$ [13], $[NBu_4^+][Pt(C_8H_4S_8)_2]$ [14], and $Co(\eta^5-C_5H_5)(C_8H_4S_8)$ [17]) were also found to be

oxidized at lower potentials than the corresponding C_3S_3 -metal complexes.

3.2. Oxidation of $[M(O)(C_8H_4S_8)_2]^{2-}$ complexes ($M = V(IV)$ and $Mo(IV)$)

Both the $[V(O)(C_8H_4S_8)_2]^{2-}$ and $[Mo(O)(C_8H_4S_8)_2]^{2-}$ complexes having low oxidation potentials were oxidized by some oxidizing agents to afford over one-electron oxidized species **4–8**. The oxovanadium(IV) complex with the low oxidation potential can be also oxidized even by TCNQ. Complex **6** obtained by the iodine-doping of the solid-liquid reaction is likely to have the I_3^- ion, as observed for several iodine-oxidized $C_8H_4S_8$ -metal complexes [14,24,25]. Thus, it is formally two-electron oxidized species.

The oxidized complexes **4** and **5** exhibit almost isotropic ESR signals at $g = 2.005$ and 2.009 (peak-to-peak linewidth, 0.9 and 2.3 mT), respectively. These complexes are almost two-electron oxidized species containing a small amount of paramagnetic $[M(O)(C_8H_4S_8)_2]^-$ anions. The anions are surrounded by diamagnetic $[M(O)(C_8H_4S_8)_2]^0$ species, resulting in a sharp signal. The signals observed at $g = 2.005$ and 2.009 are ascribed to the radical species of the $C_8H_4S_8$ ligand, as observed for partially oxidized $C_8H_4S_8$ -metal ($M = Pt(II)$, $Co(III)$, $Ti(IV)$ and $Zr(IV)$) [13,17,18,25,26] and C_3S_3 -metal ($M = Re(IV)$, $Mo(IV)$, $W(IV)$ and $Au(III)$) complexes [7,8,27].

The $C_8H_4S_8$ ligand-centered oxidation observed for the present oxovanadium- and oxomolybdenum-complexes are consistent with the XPS and IR results. The binding energy of the vanadium $2p_{3/2}$ electrons for the oxidized species **4** determined by XPS is 516.9 eV, which is larger than that (515.8 eV) for the unoxidized species **1**. This finding suggests that the oxidized species is in the diamagnetic vanadium(V) state. In accordance with this, complex **4** has shown a $V=O$ stretching IR band at 991 cm $^{-1}$, which is higher by 38 cm $^{-1}$ than that of **1**. The binding energies of the molybdenum $3d_{3/2}$ electrons for the oxidized species **7** and **8** are 232.6 and 232.3 eV, respectively. These values are essentially the same as that (232.8 eV) for the unoxidized complex **3**, which suggests the diamagnetic molybdenum(IV) state for the oxidized complexes. The $Mo=O$ stretching IR bands for **7** and **8** have been observed at 913 cm $^{-1}$, which is very close to the frequency (917 cm $^{-1}$) for the unoxidized complex **3**. Since the $[Mo(O)(dbt)_2]^{2-}$ ($dbt = \text{benzene-1,2-dithiolate}$) complex showed a high frequency shift (25 cm $^{-1}$) of the $Mo=O$ stretching band upon the molybdenum oxidation[28], this finding is consistent with the $C_8H_4S_8$ ligand-centered oxidation for **7** and **8**, as observed also for the oxidized $[Mo(O)(C_3S_3)_2]$ complexes [21].

Powder reflectance spectra of the oxidized species **4** and **7** are displayed in Fig. 4. Unoxidized complexes **1**

and **3** show broad bands around 900 nm due to molecular interactions through S⋯S non-bonded contacts in the solid state (Fig. 2), while these oxidized species give broad bands at a longer wavelength. These findings indicate further molecular interactions through S⋯S non-bonded contacts caused by the ligand-oxidation, which result in the formation of effective electron-conduction pathways, as described below.

3.3. Electrical conductivities of the oxidized species of complexes

Complexes **1** and **2** are essentially an insulator (electrical conductivities of the compacted pellets, $< 10^{-8}$ S cm $^{-1}$ at room temperature). The oxidized species, however, exhibit high electrical conductivities, which are listed in Table 1. These oxidized complexes exhibit appreciably high electrical conductivities compared with those of the oxidized species of the corresponding $[M(O)(C_3S_5)_2]^{2-}$ ($M = V(IV)$ and $Mo(IV)$) complexes; especially, the conductivities of the molybdenum species **7** and **8** are much higher than those (6.7×10^{-9} – 7.3×10^{-3} S cm $^{-1}$) of the oxidized $[Mo(O)(C_3S_5)_2]^{n-}$ ($n < 1$) complexes [19–21]. The conductivity of complex **6** obtained by the iodine-doping procedure is rather low compared with those of the other species, which is due to an inadequate molecular rearrangement for the formation of electron-conduction pathways owing to the oxidation reaction of the anion moieties in the presence of the cations in the solid state. However, it is greatly higher than that (5.2×10^{-7} S cm $^{-1}$) of $[N\text{-methylpyridinium}]_2[V(O)(C_3S_5)_2]_{4.2}$ obtained by the iodine-doping procedure [19]. Such high electrical conductivities of

Table 1
Electrical conductivities (σ)^a of the oxidized complexes

Complex	σ_{RT} (S cm $^{-1}$)	Complex	σ_{RT} (S cm $^{-1}$)
4	0.12	7	0.29
5	7.2×10^{-3}	8	5.9
6	9.0×10^{-4}		

^a Measured for compacted pellets at room temperature.

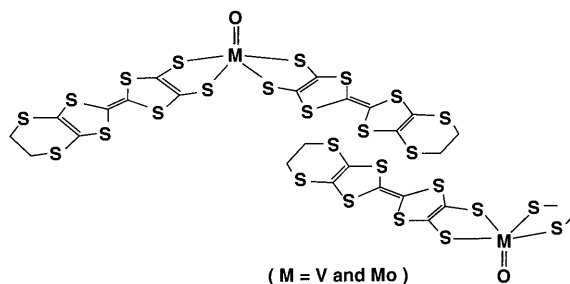


Fig. 5. A possible molecular array of the oxidized $[M(O)(C_8H_4S_8)_2]$ moieties with some non-bonded S⋯S contacts among the $C_8H_4S_8$ ligands.

the oxidized $[M(O)(C_8H_4S_8)_2]^{n-}$ ($M = V(IV)$ and $Mo(IV)$; $n < 1$) complexes come from an effective molecular interaction through S⋯S contacts, as is seen in a possible molecular array shown in Fig. 5. This is based on a square pyramidal geometry of the complexes, as was clarified for the molecular structure of the $[Mo(O)(C_3S_5)_2]^{2-}$ complex [20]. The oxidized $[M(\eta^5-C_5H_5)(C_8H_4S_8)_2]^{n+}$ ($M = Ti(IV)$ and $Zr(IV)$; $n < 1$) complexes having a similar non-planar geometry around the metal ion also exhibited high electrical conductivities (10^{-1} S cm $^{-1}$) [18,26]. Thus, the $C_8H_4S_8$ ligand is of greater advantage for a molecular interaction through S⋯S contacts in the solid state compared with the C_3S_5 ligand. This was also observed for some $C_8H_4S_8$ -metal complexes [14,17,24,25].

Acknowledgements

We are grateful to Professor S. Suzuki (Graduate School of Science, Osaka University) for measurement of ESR spectra, and to Dr I. Kawafune (Osaka Municipal Technical Research Institute) for measurement of X-ray photoelectron spectra. This research was supported in part by Grant-in-Aids for Scientific Research (No. 11120228 and No. 11136223) from Ministry of Education, Science, Sports and Culture, Japan.

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