Preparation and Spectroscopic Properties of the $[\text{Re}_2(\text{C}_3\text{S}_4\text{Se})_5]^{2-}$ Anion Complex and Electrical Conductivities of the Oxidized Species $[\text{C}_3\text{S}_4\text{Se}_2]^{2-} = 1,3$-Dithiole-2-selone-4,5-dithiolate(2-) \\
Takashi Maikawa$^a$, Motohiro Nakano$^a$, Ryuichi Arakawa$^a$, \newline Gen-etsu Matsubayashi$^{a*}$, Wasuke Mori$^b$ \\
$^a$ Department of Applied Chemistry, Faculty of Engineering, Osaka University, 1–1 Machikaneyama, Toyonaka, Osaka 560, Japan \newline $^b$ Department of Chemistry, Faculty of Science, Osaka University, 1–1 Machikaneyama, Toyonaka, Osaka 560, Japan \\

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Dinuclear Complexes, Rhenium(IV) Complexes, Dithiolate, Magnetic Susceptibility, Electrical Conductivity \\

The dinuclear rhenium(IV) complexes with the $\text{C}_3\text{S}_4\text{Se}$-ligand $[1,3$-dithiole-2-selone-4,5-dithiolate(2-)], $[\text{PPPh}_3]_2[\text{Re}_2(\text{C}_3\text{S}_4\text{Se})_5]$ (1) and $[\text{NEt}_4]_2[\text{Re}_2(\text{C}_3\text{S}_4\text{Se})_5]$ (2), were prepared. Complex 2 was oxidized by a reaction with $[\text{Fe}(\text{C}_5\text{H}_5)_3][\text{PF}_6]$ or $[\text{TTF}][\text{BF}_4]_2$ (TTF = the tetra(thia)fulvalenium radical cation) and by the current-controlled electrolysis to yield $[\text{NEt}_4]_x[\text{Re}_2(\text{C}_3\text{S}_4\text{Se})_5]$ ($x = 0.15$ and 0.5) and $[\text{TTF}][\text{Re}_2(\text{C}_3\text{S}_4\text{Se})_5]$. The compounds exhibit electrical conductivities of $3.3 \times 10^{-3}$ – $9.3 \times 10^{-4}$ S cm$^{-1}$ for compact pellets at room temperature. Electrochemical and spectroscopic properties of the complexes are discussed on the basis of cyclic voltammetry and ESR, XPS and IR spectra as well as the magnetic susceptibility of the TTF salt.

Introduction \\
Metal complexes with the $\text{C}_3\text{S}_4\text{Se}$-ligand $[1,3$-dithiole-2-thione-4,5-dithiolate(2-)] have attracted much interest because of high electrical conductivities and superconductivity of their oxidized species $[1$–$4]$. Electron-conduction pathways in the solid state often originate from two-dimensional molecular interactions through sulfur-sulfur contacts. Based on the standpoint that bulky $\text{C}_3\text{S}_4\text{Se}$-metal complexes can afford new electron-conduction pathways constructed with two- or three-dimensional molecular interactions through S-S contacts, we have been investigating $\text{C}_3\text{S}_4\text{Se}$-metal complexes with octahedral geometries and found high electrical conductors of these complexes $[5$–$11]$. Particularly, our recent study on the dinuclear rhenium complexes with the $\text{C}_3\text{S}_4\text{Se}$-ligand $[1,3$-dithiole-2-selone-4,5-dithiolate(2-)] having the selone group as the terminal ligand revealed possible effective conduction pathways even among the bulky anion moieties $[12]$. Substitution of the $\text{C}_3\text{S}_4\text{Se}$-ligand with the selenium atom is expected to lead to new molecular interactions of the metal-complex anion moieties through the selenium atoms having extended orbitals. Metal complexes with some selenium-containing $\text{C}_3\text{S}_4\text{Se}$ ligands were prepared $[13]$, and some nickel(II) complexes with the $\text{C}_3\text{S}_4\text{Se}$ ligand having the selone group were reported to exhibit high electrical conductivities $[14,15]$. This paper reports on the preparation and spectroscopic properties of dinuclear rhenium complexes with the $\text{C}_3\text{S}_4\text{Se}$ ligand $[1,3$-dithiole-2-selone-4,5-dithiolate(2-)] having the selone group as well as on electrical conductivities of the oxidized species.

Experimental \\
Materials \\
4,5-Bis(benzoyl)-1,3-dithiole-2-selone $[14]$ and $[\text{NBu}_4]^+_2[\text{Re}_2\text{Cl}_8]_2$ $[16]$ were prepared according to the literature. $[\text{Fe}(\text{C}_5\text{H}_5)_3][\text{PF}_6]$ $[6]$ and tris(tetra(thia)fulvalenium) bis(tetrafluoroborate) $[\text{TTF}][\text{BF}_4]_2$ $[17]$ were prepared as described previously.

Preparations \\
$[\text{PPPh}_3]_2[\text{Re}_2(\text{C}_3\text{S}_4\text{Se})_5]$ (1) and $[\text{NEt}_4]_2[\text{Re}_2(\text{C}_3\text{S}_4\text{Se})_5]$ (2) \\\nAll the following reactions were performed under a nitrogen atmosphere. $[\text{NBu}_4]^+_2[\text{Re}_2\text{Cl}_8]_2$ (500
mg, 44 μmol) was added to a methanol (100 cm³) solution containing 4,5-bis(benzoyl)-1,3-dithiole-2-selone (120 mg, 260 μmol) and sodium metal (18 mg, 790 μmol), and the reaction mixture was stirred for 1 h at 60 °C. It was filtered and [PPh₄]Br (500 mg, 1.2 mmol) was added to the filtrate. The filtrate was allowed to stand for 1 h at room temperature to yield a dark brown solid. It was collected by filtration and recrystallized from a mixture of dichloromethane and ethanol (1:1 v/v) to afford black microcrystals of 1 (53% yield).

**Analysis for C₆₃H₄₀P₇Re₇S₂O₇Se₅ (2267.5)**
Calcd C 33.37 H 1.78%,
Found C 33.08 H 1.85%.

Similarly, Na₂[C₃S₄Se], obtained by the reaction of sodium with 4,5-bis(benzoyl)-1,3-dithiole-2-selone in methanol, was reacted with [NBu₄]₂[Re₂Cl₈]. Addition of an excess amount of [NET₄]Br to the reaction mixture afforded a dark brown solid. It was collected by filtration and recrystallized from a mixture of acetone and ethanol (1:1 v/v) to give dark brown microcrystals of 2 (30% yield).

**Analysis for C₁₆₂H₄₀N₂O₇Re₂S₂O₇Se₅ (1849.2)**
Calcd C 20.14 H 2.18 N 1.51%,
Found C 20.54 H 2.44 N 1.59%.

[**TTF**][Re₂(C₃S₄Se)₅] (3)
An acetonitrile (25 cm³) solution of [**TTF**]₃[BF₄]₂ (32 mg, 41 μmol) was added with stirring to an acetonitrile (40 cm³) solution of 2 (30 mg, 16 μmol). A black solid of 3 precipitated immediately, which was collected by centrifugation, washed with acetonitrile and diethyl ether, and dried in vacuo (87% yield).

**Analysis for C₂₁H₄₄N₁O₇Re₂S₂O₇Se₅ (1793.1)**
Calcd C 14.07 H 0.22%,
Found C 13.70 H 0.24%.

[**NET₄**]₀.₅[Re₂(C₃S₄Se)₅] (4)
To an acetonitrile (40 cm³) solution of 2 (30 mg, 16 μmol) was added with stirring an acetonitrile (10 cm³) solution of [Fe(C₅H₅)₂][PF₆] (16 mg, 48 μmol). A black solids of 3 precipitated, which were collected by centrifugation, washed with acetonitrile and diethyl ether, and dried in vacuo (89% yield).

**Analysis for C₁₆₂H₈₀N₂O₇Re₂S₂O₇Se₅ (1609.2)**
Calcd C 11.88 H 0.45 N 0.41%,
Found C 12.01 H 0.19 N 0.13%.

**Physical measurements**

Electronic absorption [18] and X-ray photoelectron spectra (XPS) [19] were measured as described previously. The ¹³C NMR spectra of the [Re₂(C₃S₄Se)₅]²⁻ anion were measured using [NBu₄]₂[Re₂(C₃S₄Se)₅] with suitable solubility in dichloromethane-d₂ as described previously [12]. IR spectra were measured on a Perkin-Elmer 983G spectrophotometer for KBr disks. ESR spectra were recorded on JEOL ME-2X and JES-FEIX spectrometers and calibrated with signals of MnO₂. The electrospray ionization (ESI) mass spectrum of 1 dissolved in acetonitrile was obtained as described previously [12]. The magnetic susceptibility of 3 was measured in the temperature range 4.2–300 K under the magnetic field of 500 mT using an MPMS SQUID-magnetometer of Quantum Design Co. at the Faculty of Science, Osaka University. Electrical resistivities of the complexes were measured for compacted pellets at room temperature by the conventional two-probe method. The cyclic voltammogram of 1 was recorded in dichloromethane using [NBu₄][ClO₄] as an electrolyte, as described previously [20].

**Results and Discussion**

The electrospray ionization mass spectrum of 1 dissolved in a mixture of acetonitrile and dichloromethane (1:1 v/v) gave a single peak at 794 m/z (z = -2), as illustrated in Fig. 1. This suggests the dinuclear form (A) for the [Re₂(C₃S₄Se)₅]²⁻ anion, which is similar to the [Re₂(C₃S₅)₅]²⁻ anion as confirmed by the X-ray structural analysis [12]. This form of the anion moiety was confirmed by the ¹³C NMR signals of [NBu₄]₂[Re₂(C₃S₄Se)₅] dissolved in dichloromethane-d₆: three C=Se signals at 207.14, 207.68 and 210.13 ppm with the intensities of ca. 2:1:2 and five C=C signals at 152.88,
Fig. 1. The negative ion ESI mass spectrum of complex 1 dissolved in a mixture of acetonitrile and dichloromethane (1:1 v/v).

Fig. 2. Cyclic voltammogram of complex 1 (1.0 x 10^-3 mol dm^-3) in dichloromethane at room temperature; 0.1 mol dm^-3 [NBu^4][ClO_4], sweep rate 0.01 V s^-1.

HOMO energy levels. On the other hand, the [Re_2(C_3S_4Se)_5]^{2/-} and [Re_2(C_3S_4Se)_5]^{3/-} couples occur at E^0 = -0.30 and -0.63 V (vs SCE), respectively, which are somewhat higher than the reduction potentials of the [Re_2(C_3S_5)_5]^{2/-} anion (E^0 = -0.38 and -0.72 V vs SCE). These findings indicate that the LUMO energy levels of the [Re_2(C_3S_4Se)_5]^{2/-} anion are lowered compared with those of the [Re_2(C_3S_5)_5]^{2/-} anion.

Fig. 3 shows the electronic absorption spectrum of complex 1 together with that of [PPh_4]^2- [Re_2(C_3S_5)_5] in dichloromethane. Both the bands due to π-π* transitions [21,22] of the C_3S_4Se-li-
gand observed around 450 nm and due to metal-ligand charge transfer transitions [10,11,23] at 670 nm appear at longer wavelengths for complex 1 than for the corresponding C₃S₅-complex. This reflects the lowered LUMO energy level of the [Re₂(C₃S₄Se)₅]²⁻ anion compared with the [Re₂(C₃S₅)₅]²⁻ anion based on the similar HOMO levels of these anions, as described above.

Fig. 4 shows the spectral change of a dichloromethane solution containing complex 1 and various amounts of [Fe(C₅H₅)₂][PF₆] as an oxidant. Upon the addition of the oxidant to an equimolar amount of the [Re₂(C₃S₄Se)₅]²⁻ anion, the σ-π* bands in the region of 450 - 550 nm shift to the somewhat higher energy region, and the metal-ligand charge transfer band at 670 nm decays, a broad band concomitantly occurring around 800 nm. These findings indicate the occurrence of the oxidized [Re₂(C₃S₅)₅]²⁻ anion species. Upon further addition of the oxidant, however, all the bands appreciably lessen in their intensities due to the precipitation of the [Re₂(C₃S₄Se)₅]⁰ species.

Complex 2 was oxidized by the TTF⁺ radical cation, the [Fe(C₅H₅)₂]⁺ cation and the current-controlled electrolysis to afford complexes 3, 4 and 5, respectively. The binding energies (41.5 and 41.6 eV for 3 and 4, respectively) of Re 4f⁷/² electrons for these oxidized species determined by XPS were essentially the same as that of 2 (41.3 eV). These findings suggest a ligand-centered oxidation, as was observed for the oxidized [Re₂(C₃S₅)₅]²⁻ species [12] and many oxidized C₃S₅-metal complexes [6,10,23]. The IR C=C stretching frequency of the C₃S₄Se-ligand observed at 1340 cm⁻¹ for 1 and 2 occurred at 1300 cm⁻¹ for 3-5, as compared to 1340 cm⁻¹ for the [Re₂(C₃S₅)₅]²⁻ complexes, and at 1270 and 1300 cm⁻¹ for the oxidized [Re₂(C₃S₅)₅]²⁻ (0<n<1) species [12]. The oxidized species 4 and 5 exhibited a broad ESR signal at g = 2.00 (the peak-to-peak line width = 27 mT) due to the oxidized C₃S₄Se-ligand. The samples contain small amounts of the paramagnetic [Re₂(C₃S₄Se)₅]²⁻ anion, which is surrounded by the diamagnetic [Re₂(C₃S₄Se)₅]⁰ species. Complex 3 showed rather sharp ESR signals due to the [Re₂(C₃S₄Se)₅]⁰ anion (the line width = 2 mT) and the TTF⁺ radical cation (the line width = 1.5 mT) at g = 2.01. This is similar to ESR spectra of [TTF]²[V(C₃S₅)₃] [5], [TTF][Au(C₃S₅)₂] [23] and [TTF][Re₂(C₃S₅)₅] [12]. The magnetic susceptibility of 3 was measured over the temperature range 4.2-300 K (Fig. 5). The susceptibility of 1.62 x 10⁻³ cm³ mol⁻¹ at 300 K corresponds to the effective magnetic moment of 1.97 μB, which is considerably lower as compared with the value (2.45 μB) for two unpaired electrons of the anion and the cation and rather close to that (1.73 μB) for one unpaired electron. This result suggests the presence of a one-electron oxidized [Re₂(C₃S₄Se)₅]²⁻ anion together with the essentially dimerized TTF⁺ radical cations. The susceptibility obeys essentially the Curie-Weiss law \[μ_0M/μ = 0.870/\left(T + 238\right)\] in the temperature range 150–300 K, indicating a strong antiferromagnetic interaction among the paramagnetic anion moieties. Below
100 K a phase transition seems to occur, resulting in an increase of the susceptibility.

Complexes 1 and 2 have very small electrical conductivities ($3.2 \times 10^{-9}$ and $7.2 \times 10^{-8}$ S cm$^{-1}$, respectively) as measured for compact pellets at room temperature. However, the oxidized species exhibit high conductivities: $6.0 \times 10^{-3}$, $3.3 \times 10^{-3}$ and $9.3 \times 10^{-4}$ S cm$^{-1}$ (compact pellets, at room temperature) for 3, 4 and 5, respectively. The ligand-centered oxidation probably leads to extended S-S and/or S-Se nonbonded contacts even among the bulky anion moieties in the solid state, which constructs effective electron-conduction pathways. Although this effect of the molecular interactions on the conductivity also seems to be generally similar to that of the $[\text{Re}_2(C_3\text{S}_5)_5]$ complexes (conductivities $= 10^{-3} - 10^{-2}$ S cm$^{-1}$) [12], no appreciable positive effects by the introduction of the selenium atom into the $C_3\text{S}_5$-moiety are observed for the present complexes.

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