Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Preparations, Structures and Electrical Conductivities of Oxidized Bulky $[M(C_3S_5)_3]$-Type Anion Complexes $[C_3S_5{}^{2-}$ = 4,5-Disulfanyl-1,3-Dithiole-2-Thionate(2-)]

Gen-Etsu Matsubayashi [a] , Motohiro Nakano [a] , Hatsue Tamura [a] & Kazuhiro Natsuaki [a]

[a] Department of Applied Chemistry, Faculty of Engineering, Osaka University, 1-16, Machikancyama, Toyonaka, Osaka, 560

To cite this article: Gen-Etsu Matsubayashi, Motohiro Nakano, Hatsue Tamura & Kazuhiro Natsuaki (1997): Preparations, Structures and Electrical Conductivities of Oxidized Bulky $[M(C_3S_5)_3]$-Type Anion Complexes $[C_3S_5{}^{2-}$ = 4,5-Disulfanyl-1,3-Dithiole-2-Thionate(2-)], Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 296:1, 245-253

To link to this article: http://dx.doi.org/10.1080/10587259708032324

Mol. Cryst. Liq. Cryst., 1997, Vol. 296, pp. 245–253
Reprints available directly from the publisher
Photocopying permitted by license only

PREPARATIONS, STRUCTURES AND ELECTRICAL CONDUCTIVITIES OF OXIDIZED BULKY [M(C_3S_5)$_3$]-TYPE ANION COMPLEXES [$C_3S_5^{2-}$ = 4,5-DISULFANYL-1,3-DITHIOLE-2-THIONATE(2-)]

GEN-ETSU MATSUBAYASHI,* MOTOHIRO NAKANO,
HATSUE TAMURA, AND KAZUHIRO NATSUAKI
Department of Applied Chemistry, Faculty of Engineering, Osaka University,
1-16, Machikaneyama, Toyonaka, Osaka 560

This paper is dedicated to Professor Fumio Ogura and Professor Yusei Maruyama on the occasion of their retirements from Hiroshima University and from Institute for Molecular Science, respectively.

(Received 19 July 1996; In final form 17 September 1996)

Abstract. Several [M(C_3S_5)$_3$]$^{n-}$ (M = V(IV), Mo(IV), W(IV); n = 2 and M = Nb(V), Re(V); n = 1) anion complexes were prepared. They exhibited low oxidation potentials of +0.145 - +0.76 V *vs*. SCE. They were oxidized by reactions with iodine, [Fe(C_5Me_5)$_2$]$^+$, [Fe(C_5H_5)$_2$]$^+$, and the TTF$^{\cdot+}$ radical cation, as well as the electrolysis, in organic solvents to afford oxidized [M(C_3S_5)$_3$]$^{m-}$ ($0 < m < 1$) species having electrical conductivities of 6.0×10^{-5} - 1.5×10^{-1} S cm^{-1} measured for compacted pellets at room temperature. X-ray crystal structures of the [M(C_3S_5)$_3$]$^{2-}$ (M = Mo, W) complexes and the one-electron-oxidized [M(C_3S_5)$_3$]$^-$ (M = V, W) species as well as ESR and X-ray photoelectron spectra of the oxidized species are discussed.

Keywords: Dithiolate, C_3S_5, metal complex, structure, electrical conductivity

INTRODUCTION

Metal complexes with sulfur-rich ligands have attracted much attention as electrically conducting molecular compounds. Oxidized planar metal complexes with the 4,5-disulfanyl-1,3-dithiole-2-thionate(2-) ligand ($C_3S_5^{2-}$) are known to become good electrical conductors.[1-3] High electrical conductivities of them come from formation of effective electron-conduction pathways constructed with molecular interactions through sulfur-sulfur non-bonded contacts among the ligands in the solid state.

Non-planar bulky molecules may be often considered to be ineffective for their molecular packings in the crystals. However, C_3S_5-metal complexes with bulky geometries are expected to afford new types of molecular packing with S-S interactions leading to two- or three-dimensional electron-conduction pathways in their oxidized species. We have prepared several $[M(C_3S_5)_3]^{n-}$ (M = V(IV),[4] Mo(IV),[5,6] W(IV)[7]; n = 2 and M = Nb(V), Re(V)[7]; n = 1) anion complexes and have observed raised electrical conductivities for their oxidized species.[4-8] In this paper, preparations of the oxidized $[M(C_3S_5)_3]^{m-}$ ($0 < m < 1$) anion complexes, structures of some species, their ESR and X-ray photoelectron spectra and electrical conductivities are described.

EXPERIMENTAL

A reaction of VCl_3 or $ReCl_5$ with $[NBu^n_4]_2[Zn(C_3S_5)_2]$ in methanol or ethanol gave $[NBu^n_4]_2[V(C_3S_5)_3]$ or $[NBu^n_4][Re(C_3S_5)_3]$, while a reaction of VCl_3 or $ReCl_5$ with $Na_2C_3S_5$ in methanol afforded mainly $[VO(C_3S_5)_2]^{2-}$ or $[ReO(C_3S_5)_2]^-$ anion complexes.[4,7] $[NBu^n_4][Nb(C_3S_5)_3]$ was obtained by a reaction of $NbCl_5$ with $Na_2C_3S_5$ in methanol in the presence of NBu^n_4Br, while $NbCl_5$ reacted with $[NBu^n_4]_2[Zn(C_3S_5)_2]$ in acetonitrile to give the dinuclear complex, $[NBu^n_4]_2$-$[Nb_2(S_2)_2(C_3S_5)_4]$.[8] A reaction of WCl_6 with $Na_2C_3S_5$ in ethanol in the presence of NBu^n_4Br yielded $[NBu^n_4]_2[W(C_3S_5)_3]$. A similar reaction of $MoCl_5$ with $Na_2C_3S_5$ in methanol yielded $[NBu^n_4]_2[Mo(C_3S_5)_3]$ in a low yield, together with a large amount of $[NBu^n_4]_2[MoO(C_3S_5)_3]$.[5,6]

Reactions of $[NBu^n_4]_2[M(C_3S_5)_3]$ with $[Fe(C_5Me_5)_2][BF_4]$ in acetonitrile afforded $[Fe(C_5Me_5)_2][M(C_3S_5)_3]$ as dark blue and black crystals for M = W and Mo, respectively. Reactions of $[NBu^n_4]_2[M(C_3S_5)_3]$ with iodine, $[Fe(C_5H_5)_2][PF_6]$ or $[TTF]_3[BF_4]_2$ ($TTF^{\cdot+}$ = the tetrathiafulvalenium radical cation) afforded black microcrystals of $[NBu^n_4]_x[M(C_3S_5)_3]$ (M = W and Mo; x = 0.05 - 0.4). Controlled-current electrolysis of a dichloromethane or an acetonitrile solution containing $[NBu^n_4]_2[M(C_3S_5)_3]$ (M = W or Mo) and $[NBu^n_4][ClO_4]$ as an electrolyte yielded black microcrystals of $[NBu^n_4]_{0.3}[W(C_3S_5)_3]$ and $[NBu^n_4]_{0.8}[Mo(C_3S_5)_3]$, respectively.[6] The oxidized molybdenum- and tungsten-complexes which were obtained by reactions with various oxidants and by the electrolysis are listed in Table 2 for the electrical conductivities (see below).

The $[V(C_3S_5)_3]^{2-}$ anion complex was oxidized by the N-methylphenazinium cation (NMP^+) to afford $[NMP]_2[V(C_3S_5)_3]$ containing the one-electron-oxidized $[V(C_3S_5)_3]^-$ anion and moieties of the $NMP^{\cdot}$ radical / the NMP^+ cation.[4] A reaction of the $[V(C_3S_5)_3]^{2-}$ anion complex with $[TTF]_3[BF_4]_2$ in acetonitrile afforded $[TTF]_2$-

[$V(C_3S_5)_3$] having moieties of neutral TTF / the TTF$^{\cdot +}$ radical cation and the [$V(C_3S_5)_3$]$^-$ anion.[4] The [$V(C_3S_5)_3$]$^{2-}$ complex was reacted with [$Fe(C_5H_5)_2$][PF_6] in acetonitrile to give [$Fe(C_5H_5)_2$][$V(C_3S_5)_3$] (the one-electron-oxidized species). Similarly, a reaction of the complex with [$Fe(C_5H_4Me)_2$][PF_6], [$Fe(C_5Me_5)_2$][PF_6] or [$Ni(C_5H_5)_2$][PF_6] in acetonitrile afforded [$Fe(C_5H_4Me)_2$]-, [$Fe(C_5Me_5)_2$]- and [$Ni(C_5H_5)_2$][$V(C_3S_5)_3$].[9] These oxidized complexes contain the one-electron-oxidized [$V(C_3S_5)_3$]$^-$ anion.

Oxidation of the [$Re(C_3S_5)_3$]$^-$ anion complex by iodine or [$Fe(C_5H_5)_2$][PF_6] in dichloromethane afforded essentially one-electron-oxidized [$Re(C_3S_5)_3$]$^{n-}$ ($n = 0.05$ and 0.1) species.[7] [NBu^n_4][$Nb(C_3S_5)_3$] was also oxidized by the [$Fe(C_5H_5)_2$]$^+$ cation in acetonitrile or the TTF$^{\cdot +}$ radical cation in acetone to afford [NBu^n_4]$_{0.05}$-[$Nb(C_3S_5)_3$] and [TTF][$Nb(C_3S_5)_3$], which were identified by elemental (C,H and N) analyses.

Cyclic voltammograms,[10] electronic absorption, ESR and X-ray photoelectron spectra[6] were measured, as described previously. Electrical conductivities of the complexes were measured for the compacted pellets by the conventional two-probe method.[11]

RESULTS AND DISCUSSION

The [$M(C_3S_5)_3$]$^{n-}$-type anions ($n = 1$, M = Nb and Re; $n = 2$, M = V, Mo and W) are likely to have distorted octahedral or trigonal prismatic geometry around the metal ion. Figure 1 illustrates the molecular structure of the anion of [NBu^n_4]$_2$[$W(C_3S_5)_3$].[6] The structure of the anion indicates three C_3S_5 ligands coordinated to the metal ion. The S_3 (coordinated sulfur atoms) triangles are twisted with respect to each other by an average

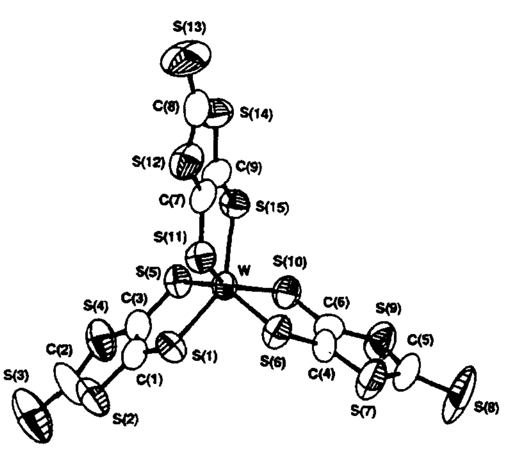

FIGURE 1 Molecular geometry of the anion of [NBu^n_4]$_2$[$W(C_3S_5)_3$] together with the atom-labeling scheme.[6]

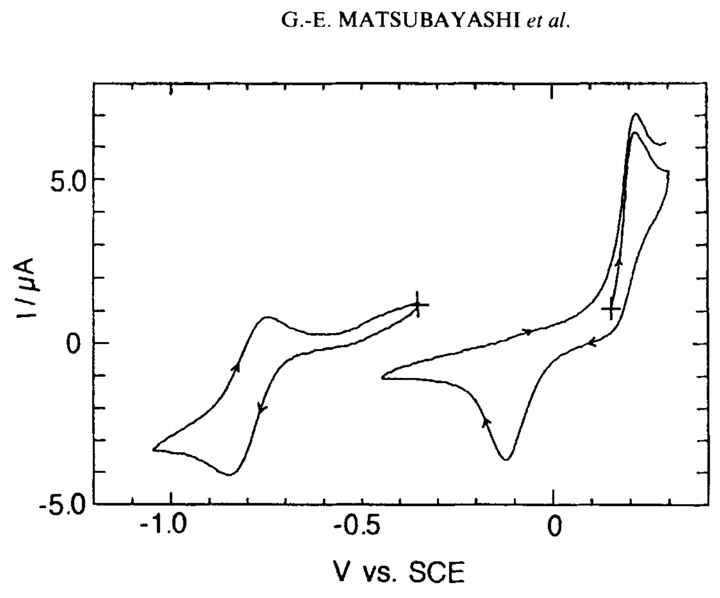

FIGURE 2 Cyclic voltammogram of $[NBu^n_4][Nb(C_3S_5)_3]$ (1.0×10^{-3} mol dm^{-3}) in dichloromethane; 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$, sweep rate 100 mV s^{-1}.

of 16°(twist angle, ϕ), assuming a distorted trigonal prismatic coordination around the metal ion. This is very close to that of $[NBu^n_4]_2[Mo(C_3S_5)_3]$ (average ϕ = 11°). There are no significant close atom-atom contacts among cation/anions for these complexes.

The cyclic voltammogram of $[NBu^n_4][Nb(C_3S_5)_3]$ in dichloromethane is shown in Fig. 2. The $[Nb(C_3S_5)_3]^-$ anion is irreversibly oxidized at +0.24 V *vs.* SCE, whereas the quasi-reversible $[Nb(C_3S_5)_3]^{2-}/[Nb(C_3S_5)_3]^-$ redox wave is observed at -0.80 V *vs.* SCE. The $[Re(C_3S_5)_3]^-$ anion is also irreversibly oxidized at +0.76 V *vs.* SCE in dichloromethane.[7] On the other hand, the $[Mo(C_3S_5)_3]^{2-}$ and $[W\text{-}(C_3S_5)_3]^{2-}$ anions are stably oxidized at lower potentials; reversible $[M(C_3S_5)_3]^{2-}/[M(C_3S_5)_3]^-$ redox waves are observed at +0.145 and +0.185 V *vs.* SCE and reversible $[M(C_3S_5)_3]^-/[M(C_3S_5)_3]^0$ redox waves at +0.38 and +0.325 V *vs.* SCE in dimethylformamide, respectively.[6] The reversible $[V(C_3S_5)_3]^{2-}/[V(C_3S_5)_3]^-$ and $[V(C_3S_5)_3]^-/[V\text{-}(C_3S_5)_3]^0$ redox processes also occur at +0.15 and +0.65 V vs. SCE in acetonitrile.[4]

Since these $[M(C_3S_5)_3]$-type anion complexes have low oxidation potenials, reactions of them with some oxidants afford oxidized species. Reactions of the $[M(C_3S_5)_3]^{2-}$ (M = V, Mo and W) complexes with the $[Fe(C_5Me_5)_2]^+$ cation give one-electron-oxidized species $[Fe(C_5Me_5)_2][M(C_3S_5)_3]$. Oxidation of these complexes with iodine, the $[Fe(C_5H_5)_2]^+$ cation or the $TTF^{\cdot +}$ radical cation leads to further oxidized $[M(C_3S_5)_3]^{n-}$ ($n < 1$) species. Oxidation of the $[M(C_3S_5)_3]^-$ (M = Nb and Re) anions with iodine or the $[Fe(C_5H_5)_2]^+$ cation yields essentially one-electron-

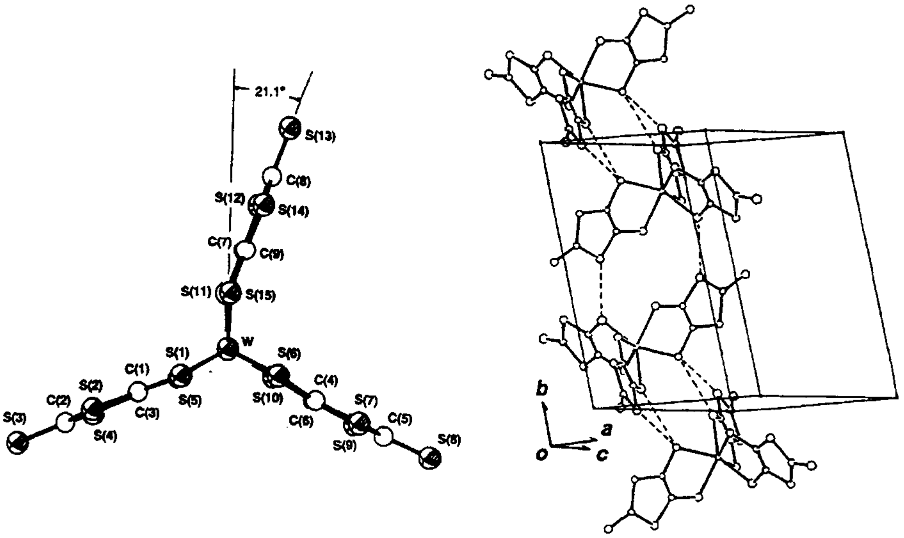

FIGURE 3 Molecular geometry of the anion of [Fe(C_5Me_5)$_2$][W(C_3S_5)$_3$] and packing diagram of the anion. Dashed lines show sulfur-sulfur non-bonded contacts (< 3.7 Å).[6]

oxidized [M(C_3S_5)$_3$]$^{n-}$ (n ~ 0) species.

Crystal structures for the following one-electron-oxidized [M(C_3S_5)$_3$]$^-$ (M = W and V) complexes have been clarified. Figure 3 shows the geometry of the anion of [Fe(C_5Me_5)$_2$][W(C_3S_5)$_3$] and the packing diagram of the anion moieties.[6] The anion with a WS_6 core assumes a regular trigonal prismatic geometry (the S-W-S twist angle, 0°), which resembles those of [Mo($S_2C_2H_2$)$_3$]^0 [12] and [Mo($S_2C_6H_4$)$_3$]^0 species.[13] The S(1)-S(5) and the S(6)-S(10) ligand planes are almost straight extended outside from the center of the core, while the S(11)-S(15) plane is caused appreciably bent on the S(11) and S(15) atoms. This is caused by the intermolecular, non-bonded S-S contacts of this ligand moiety through the S(11) and S(14) atoms forming an interaction chain of the anion. The packing diagram of the anions exhibits some intermolecular S-S non-bonded contacts (< 3.7 Å, dashed lines). One-dimensional molecular interaction among the anions is deduced in spite of the bulky geometry of the anion. In the crystal structure of [NMP]$_2$[V(C_3S_5)$_3$] containing the one-electron-oxidized [V(C_3S_5)$_3$]$^-$ anion, a two-dimensional molecular interaction through S-S non-bonded contacts (< 3.7 Å) is observed among the oxidized C_3S_5-ligands of the anion moieties.[4] The [V(C_3S_5)$_3$]$^-$ anion assumes a distorted octahedral geometry for the VS_6 core. These molecular interactions through the S-S contacts lead to electron-conduction pathways for these oxidized complexes.

The presence of one-electron-oxidized [W(C_3S_5)$_3$]$^-$ species in [Fe(C_5Me_5)$_2$]-

$[Mo(C_3S_5)_3]$ is shown in an intense ESR signal (g = 1.988) in solution and a broad signal (g = 2.0) in the solid state.[6] The broad powder ESR signal (the peak-to-peak linewidth = 90 mT) is likely caused by the above-mentioned molecular interaction of the paramagnetic anion species through S-S non-bonded contacts. This is also the same for the powder ESR signal of $[Fe(C_5Me_5)_2][Mo(C_3S_5)_3]$. $[NBu^n_4]_{0.05}[Nb(C_3S_5)_3]$ also gives a broad signal (g = 2.011, the linewidth = 25 mT), showing some interactions of the paramagnetic oxidized species. The $[Re(C_3S_5)_3]^{n-}$ (n = 0.05 and 0.1) complexes exhibit a rather sharp, approximately isotropic powder ESR signals (g = 2.013, the linewidth = 7.4 mT).[7] The $[M(C_3S_5)_3]^{n-}$ (M = Mo and W; n < 1) complexes also show sharp powder ESR signals (g = 1.988, the linewidth = 1.5 mT). These complexes are essentially two-electron-oxidized species, containing a small amount of the paramagnetic $[M(C_3S_5)_3]^-$ anion. The one-electron-oxidized anion moieties are surrounded by the diamagnetic $[M(C_3S_5)_3]^0$ species, which resembles the situation of the $[M(C_3S_5)_3]^-$ anion in solution.[6]

The valence states of the metal atoms of the oxidized C_3S_5-metal complexes can be deduced from binding energies of electrons of the metal atom determined by X-ray photoelectron spectra. The binding energy of V $2p_{3/2}$ electrons of $[NBu^n_4]_2$-$[V(C_3S_5)_3]$ is 523.3 eV, while some one-electron-oxidized $[V(C_3S_5)_3]^-$ complexes exhibit binding energies of 523.2 - 523.7 eV.[4,9] These findings indicate that the V(IV) state remains upon the oxidation of these complexes because of the ligand-centered oxidation. For the oxidized $[Re(C_3S_5)_3]^{n-}$ (n = 0.05 and 0.1) complexes the binding energies of Re 4f electrons are also close to those of the $[Re(C_3S_5)_3]^-$ complex.[7] This is also the same for the binding energies of Nb 3d electrons of the $[Nb(C_3S_5)_3]^{0.05-}$ and $[Nb(C_3S_5)_3]^-$ complexes. Thus, the oxidized species is considered to have the Re(V) and Nb(V) states together with the oxidized C_3S_5-ligands. The ligand-centered oxidation was also deduced based on X-ray photoelectron spectra for the partially oxidized $[M(C_3S_5)_2]^{m-}$ (M = Ni, Pd and Pt; m < 2), [14] $[Fe(C_3S_5)_2]^{n-}$ [10] and $[Au(C_3S_5)_2]^{n-}$ (n < 1) complexes.[15]

Electrical conductivities of the $[M(C_3S_5)_3]^{n-}$ (M = V, Nb; n $\leq$ 1) complexes measured for compacted pellets at 25 °C, together with those of $[NBu^n_4]_2[V(C_3S_5)_3]$ and $[NBu^n_4][Nb(C_3S_5)_3]$, are listed in Table I. Although the $[NBu^n_4]_2[V(C_3S_5)_3]$ and $[NBu^n_4][Nb(C_3S_5)_3]$ are essentially an insulator, their oxidized complexes exhibit appreciable increase in the conductivities and the oxidized vanadium complexes behave as semiconductors in the temperature range of -30 to 25 °C. The electron conduction of these oxidized species is likely to occur through conduction pathways constructed with sulfur-sulfur non-bonded contacts among the C_3S_5-ligands, as observed for the crystal structure of $[NMP]_2[V(C_3S_5)_3]$.[4] The $TTF^{\cdot+}$ radical cation complex behaves as a good electrical conductor. This seems to come from electron-conduction pathways constructed with S-S contacts among the TTF/$TTF^{\cdot+}$ and the oxidized $[V(C_3S_5)_3]^-$

TABLE I Electrical conductivities (σ) of the [$M(C_3S_5)_3$] (M = V and Nb) anion complexes measured for compacted pellets at 25°C.

Complex	σ / S cm^{-1}	Lit.
[NBu^n_4]$_2$[$V(C_3S_5)_3$]	4.5×10^{-10}	3
[$Fe(C_5H_5)_2$][$V(C_3S_5)_3$]	1.2×10^{-5}	8
[$Fe(MeC_5H_4)_2$][$V(C_3S_5)_3$]	2.5×10^{-6}	8
[$Ni(C_5H_5)_2$][$V(C_3S_5)_3$]	4.7×10^{-4}	8
[NMP]$_2$[$V(C_3S_5)_3$]	2.8×10^{-5}	3
[TTF]$_2$[$V(C_3S_5)_3$]	1.0×10^{-2}	3
[NBu^n_4][$Nb(C_3S_5)_3$]	7.5×10^{-8}	This work
[NBu^n_4]$_{0.05}$[$Nb(C_3S_5)_3$]	2.4×10^{-5}	This work
[TTF][$Nb(C_3S_5)_3$]	6.1×10^{-6}	This work

moieties. The crystal structure of [BEDT-TTF]$_3$[$V(C_3S_5)_3$]$_2$ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene) prepared by the electrolysis was reported to reveal more effective molecular interaction networks for the electron-conduction constructed with short S-S contacts within the BEDT-TTF stacks and among the C_3S_5-ligands and C_3S_5-ligand-BEDT-TTF. This results in a high conductivity (σ_{RT} = 3 S cm^{-1}) of this complex.[16]

Table 2 summarizes electrical conductivities of the oxidized [$M(C_3S_5)_3$]$^{n-}$ (M = Mo, W, Re; n < 1) complexes measured for compacted pellets at room temperature, together with those of [$M(C_3S_5)_3$]$^{2-}$ (M = Mo and W) and [$Re(C_3S_5)_3$]$^-$ complexes. One-electron-oxidized [$M(C_3S_5)_3$]$^-$ (M = Mo and W) complexes exhibit raised conductivities (10^{-4} - 10^{-5} S cm^{-1}). The electron-conduction pathways come from molecular interactions through some S-S contacts, as observed for the crystal structure of [$Fe(C_5Me_5)_2$][$W(C_3S_5)_3$]. Some further oxidized complexes and the [$Re(C_3S_5)_3$]$^{n-}$ (n = 0.05 and 0.1) complexes behave as good electrical conductors with high conductivities (1.1×10^{-1} - 3.3×10^{-3} S cm^{-1}). Although crystal structures of them have not yet clarified, more effective molecular packings affording higher conductivities are expected in spite of the bulky anion geometries. The [$M(C_3S_5)_3$]$^{2-}$ (M = Mo and W) anion complexes can be further oxidized beyond the one-electron oxidized state to become good electrical conductors with more effective interligand S-S contacts for the electrical conduction.

TABLE 2 Electrical conductivities (σ) of $[M(C_3S_5)_3]$ (M = Mo, W, and Re) anion complexes measured for compacted pellets at room temperature.

Complex	σ / S cm^{-1}	Oxidant	Lit.
$[NBu^n_4]_2[Mo(C_3S_5)_3]$	3.0×10^{-8}		5
$[NBu^n_4]_2[W(C_3S_5)_3]$	6.0×10^{-8}		5
$[NBu^n_4][Re(C_3S_5)_3]$	1.8×10^{-8}		6
$[Fe(C_5Me_5)_2][Mo(C_3S_5)_3]$	1.1×10^{-4}	$[Fe(C_5Me_5)_2][BF_4]$	5
$[Fe(C_5Me_5)_2][W(C_3S_5)_3]$	6.0×10^{-5}	$[Fe(C_5Me_5)_2][BF_4]$	5
$[NBu^n_4]_{0.3}[Mo(C_3S_5)_3]$	1.5×10^{-1}	I_2	4
$[NBu^n_4]_{0.15}[W(C_3S_5)_3]$	1.3×10^{-3}	I_2	5
$[NBu^n_4]_{0.4}[Mo(C_3S_5)_3]$	6.1×10^{-3}	$[Fe(C_5H_5)_2][PF_6]$	5
$[NBu^n_4]_{0.3}[W(C_3S_5)_3]$	3.3×10^{-3}	$[Fe(C_5H_5)_2][PF_6]$	5
$[NBu^n_4]_{0.05}[Mo(C_3S_5)_3]$	4.2×10^{-2}	$[TTF]_3[BF_4]_2$	5
$[NBu^n_4]_{0.2}[W(C_3S_5)_3]$	1.1×10^{-3}	$[TTF]_3[BF_4]_2$	5
$[NBu^n_4]_{0.8}[Mo(C_3S_5)_3]$	1.6×10^{-7}	Electrolysis	5
$[NBu^n_4]_{0.3}[W(C_3S_5)_3]$	1.1×10^{-2}	Electrolysis	5
$[NBu^n_4]_{0.05}[Re(C_3S_5)_3]$	2.2×10^{-2}	I_2	6
$[NBu^n_4]_{0.1}[Re(C_3S_5)_3]$	4.6×10^{-3}	$[Fe(C_5H_5)_2][PF_6]$	6

CONCLUSION

Bulky $[M(C_3S_5)_3]^{n-}$-type (M = Nb and Re, n = 1; M = V, Mo and W, n = 2) anion complexes having non-planar distorted octahedral or trigonal prismatic geometries around the metal ions are oxidized at low potentials. The oxidized C_3S_5-metal complexes exhibit more effective molecular interactions due to the S-S non-bonded contacts, which act as electron-conduction networks. Thus, they exhibit raised electrical conductivities and some of them behave as good electrical conductors with high conductivities because of more effective electron-conduction pathways constructed with S-S contacts of the ligands even if they have bulky geometries around the metal ions.

REFERENCES

1. G. Matsubayashi, Rev. Heteroatom Chem., Myu: Tokyo, 4, 171 (1991).
2. P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R.A. Clark, and A. E.

Underhill, Coord. Chem. Rev., 110, 115 (1991).

3. R.-M. Olk, B. Olk, W. Dietzsch, R. Kirmse, and W. Hoyer, Coord. Chem. Rev., 117, 99 (1992).
4. G. Matsubayashi, K. Akiba, and T. Tanaka, Inorg. Chem., 27, 4744 (1988).
5. G. Matsubayashi, K. Douki, and H. Tamura, Chem. Lett., 1251 (1992).
6. G. Matsubayashi, K. Douki, H. Tamura, M. Nakano, and W. Mori, Inorg. Chem., 32, 5990 (1993).
7. G. Matsubayashi, T. Maikawa, and M. Nakano, J. Chem. Soc., Dalton Trans., 2995 (1993).
8. G. Matsubayashi, K. Natsuaki, M. Nakano, and H. Tamura, to be published.
9. K. Akiba, G. Matsubayashi, and T. Tanaka, Inorg. Chim. Acta, 165, 245 (1989).
10. S. Tanaka and G. Matsubayashi, J. Chem. Soc., Dalton Trans., 2837 (1992).
11. K. Ueyama, G. Matsubayashi, and T. Tanaka, Inorg. Chim. Acta, 87, 143 (1984).
12. A. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinlich, J. Am. Chem. Soc., 87, 579 (1965).
13. M. J. Benett, M. Cowie, J. L. Martin, and J. Takats, J. Am. Chem. Soc., 95, 7504 (1973).
14. Y. Sakamoto, G. Matsubayashi, and T. Tanaka, Inorg. Chim. Acta, 113, 137 (1986).
15. G. Matsubayashi and A. Yokozawa, J. Chem. Soc., Dalton Trans., 3535 (1990).
16. W. E. Broderick, E. M. McGhee, M. R. Godfrey, B. M. Hoffman, and J. A. Ibers, Inorg. Chem., 28, 2902 (1989).