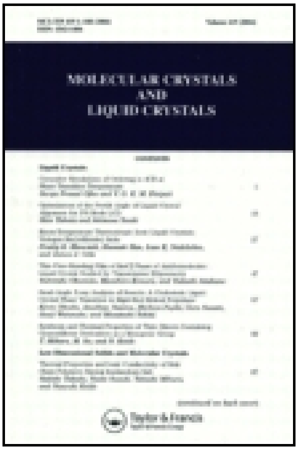

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Electrical Conductivities of Oxidized η^5-Cyclo-Pentadienyl-Metal Complexes with $C_8H_4S_8$ Ligand

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Electrical Conductivities of Oxidized η^5-Cyclo-Pentadienyl-Metal Complexes with $C_8H_4S_8$ Ligand

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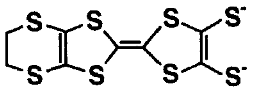
$Co(\eta^5\text{-}C_5H_5)(C_8H_4S_8)$, $Ti(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)$, $[NMe_4][Ti(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2]$, and $[NMe_4][Zr(\eta^5\text{-}C_5H_5)(C_8\text{-}H_4S_8)_2]$ [$C_8H_4S_8{}^{2-}$ = 2-{(4,5-ethylenedithio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate(2-)] were prepared. They exhibited low oxidation potentials [-0.23 – +0.45 V (*vs.* SCE)] for the $C_8H_4S_8$ ligand oxidation and were oxidized by iodine or 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) to afford $[Co(\eta^5\text{-}C_5H_5)\text{-}(C_8H_4S_8)](I_3)$, $[Ti(\eta^5\text{-}C_5H_5)_2(C_8H_4S_8)](I_3)$, $[Ti(\eta^5\text{-}C_5H_5)\text{-}(C_8H_4S_8)_2](I_3)_{0.3}$, $[Ti(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2](TCNQ)_{0.3}$, and $[Zr\text{-}(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2]$. These oxidized species showed electrical conductivities of $0.19 - 1.0 \times 10^{-4}$ S cm^{-1} at room temperature for compacted pellets.

Keywords: dithiolene complexes; cobalt(III) complexes; titanium(IV) complexes; zirconium(IV) complexes; electrical conductivity

INTRODUCTION

Metal complexes with sulfur-rich dithiolate ligands often become good molecular electrical conductors. Oxidized planar C_3S_5-metal complexes of the $[M(C_3S_5)_2]^{n-}$ type [$C_3S_5{}^{2-}$ = 4,5-disulfanyl-1,3-dithiole-2-thionate



A

(2-) ; M = Ni(II), Pd(II), Pt(II), and Au(III); n < 1] exhibited high electrical conductivities and some Ni(II) and Pd(II) complexes were reported to be superconductors.[1,2] S..S nonbonded contacts between the ligands often form effective electron-conduction pathways in the solid state. The $C_8H_4S_8^{2-}$ dithiolate ligand [$C_8H_4S_8^{2-}$ = 2-{(4,5-ethylenedithio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate(2-); **A**] and related ligands as a further π-electron delocalized system also afford metal complexes with high electrical conductivities.[3-9] Metal complexes having both these sulfur-rich ligands and organic groups may form new electrical conductors as molecular inorganic-organic composites having columnar and/or layered structures.

In this work, some η^5-C_5H_5-metal [M = Co(III), Ti(IV) and Zr(IV)] complexes with the $C_8H_4S_8$ ligand have been prepared and their properties and electrical conductivities of their oxidized species have been studied.

EXPERIMENTAL

$Na_2C_8H_4S_8$ produced by the reaction of $C_8H_4S_8(CH_2CH_2CN)_2$ (**1**)[5] with NaOEt in ethanol was reacted with Co(η^5-C_5H_5)(CO)I_2 in ethanol to give Co(η^5-C_5H_5)($C_8H_4S_8$) (**2**).[10] Ti(η^5-C_5H_5)$_2$Cl$_2$ was reacted with $Li_2C_8H_4S_8$ obtained by the reaction of **1** with MeLi in THF to afford Ti(η^5-C_5H_5)$_2$($C_8H_4S_8$) (**3**). [NMe_4]$_2$[$C_8H_4S_8$] obtained by the reaction of **1** with Me_4NOH in THF was reacted with Ti(η^5-C_5H_5)Cl$_3$ in THF to give [NMe_4][Ti(η^5-C_5H_5)($C_8H_4S_8$)$_2$] (**4**). The reaction of [NMe_4]$_2$[$C_8H_4S_8$] with Zr(η^5-C_5H_5)Cl$_3$ in THF afforded [NMe_4][Zr(η^5-C_5H_5)($C_8H_4S_8$)$_2$] (**5**).

Complexes **2** and **3** were reacted with excess amounts of iodine in dichloromethane to give [Co(η^5-C_5H_5)($C_8H_4S_8$)](I_3) (**6**) and [Ti(η^5-C_5H_5)$_2$($C_8H_4S_8$)](I_3) (**7**). The reaction of **4** with excess amounts of iodine and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) yielded [Ti(η^5-C_5H_5)($C_8H_4S_8$)$_2$](I_3)$_{0.3}$ (**8**) and [Ti(η^5-C_5H_5)($C_8H_4S_8$)$_2$]-(TCNQ$^{\cdot-}$)$_{0.3}$ (**9**), respectively. Both the reactions of **5** with iodine in dichloromethane and with TCNQ in THF afforded [Zr(η^5-C_5H_5)-($C_8H_4S_8$)$_2$] (**10**). Compositions of the complexes were determined by

CHN elemental analyses. The presence of the I_3^- ion was confirmed by the Raman spectra (ν(I-I-I), 111[10] and 112 cm^{-1}).

Cyclic voltammograms of **2** - **5** were measured using$[NBu^n_4][ClO_4]$ or $[NBu^n_4][PF_6]$ as an electrolyte, as described previously.[11] Electrical conductivities were measured at room temperature for compacted pellets by the conventional two-probe method.[12]

RESULTS AND DISCUSSION

Cyclic voltammograms of complexes **2** (measured in N,N-dimethylformamide), **3** (in dichloromethane), **4** (in acetone) and **5** (in acetone) exhibited oxidation peaks at +0.45, +0.54, -0.14, and -0.04 V (vs. SCE), respectively, which correspond to the oxidation of the $C_8H_4S_8$ ligand center. They were reacted with iodine to give oxidized species, and particularly **4** and **5** were oxidized even by TCNQ because of their low oxidation potentials, as described below.

The electronic absorption spectrum of complex **4** in acetone exhibits a band ascribed to a π - π* transition of the $C_8H_4S_8$ ligand at 330 nm, as observed for $Na_2[C_8H_4S_8]$, $[NBu^n_4][Au(C_8H_4S_8)_2]$[4] and $[NBu^n_4]_2$-$[Pt(C_8H_4S_8)_2]$.[5] Furthermore, the complex shows ligand-to-metal π - d charge transfer (LMCT) bands at 594 and 826 nm (Fig. 1). The LMCT bands appeared at 530 nm for **2** (in dichloromethane),[11] at 456 nm for **3** (in dichloromethane) , and at 456 nm for **5** (in acetone). Electronic absorption spectra of **4** in acetone in the presence of various amounts of iodine as an oxidant are also illustrated in Fig. 1. Adding some amounts of iodine to the solution of **4** changes to its spectrum with the isosbestic point at 780 nm, finally giving the bands at longer wavelengths due to the one-electron oxidized $[Ti(\eta^5\text{-}C_5H_5)(C_8H_4S_8)_2]^0$ species. Complexes **2**, **3** and **5** also showed the spectra of the one-electron oxidized species with addition of the oxidant. These stable states of the oxidized complexes are in contrast to the rapid destruction of one-electron oxidized species of $Co(\eta^5\text{-}C_5H_5)(C_3S_5)$[13] and $Ti(\eta^5\text{-}C_5H_5)_2(C_3S_5)$.[14]

Complexes **2** and **3** were reacted with iodine to afford one-electron oxidized species **6** and **7** containing the I_3^- ion. On the other hand, oxidation of **4** by iodine and TCNQ yielded formally 0.7-electron oxidized

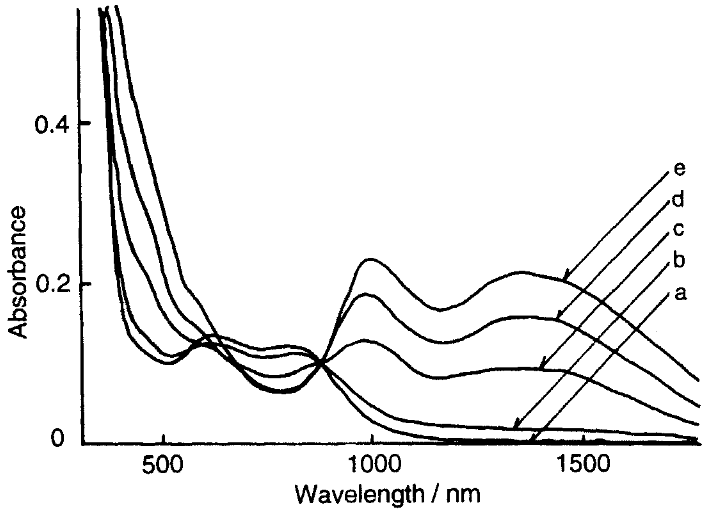


FIGURE 1 Electronic absorption spectra of **4** (2.0 x 10^{-5} mol dm^{-3}) in acetone in the presence of iodine. Concentration of iodine (mol dm^{-3}): (a) 0; (b) 3.0 x 10^{-6}; (c) 6.0 x 10^{-6}; (d) 9.0 x 10^{-6}; (e) 3.0 x 10^{-5}.

species **8** and **9**, respectively. This is also similar to the oxidation of **5** to form the one-electron oxidized species **10**. Oxidized species **6** - **9** showed an intense, sharp isotropic powder ESR signals at g = 2.003 -2.007 (peak-to-peak line width, 1.4 -3.5 mT). The signals are ascribed to the radical species of the $C_8H_4S_8$ ligand moiety, as observed for partially oxidized $C_8H_4S_8$-metal [M = Pt(II)[5] and Mo(IV)[15]] and C_3S_5-metal [M = Au(III),[3] W(IV)[16] and Re(IV)[17]] complexes with the sulfur-rich ligand-centered oxidation. However, complex **10** showed a very weak ESR signal, which may be due to the dimer formation of the oxidized moieties, as observed for the oxidized $[Au(C_8H_4S_8)_2]^0$ species.[3] Powder reflectance spectra of the oxidized complexes showed bands at longer wavelengths compared with the original complexes, as illustrated for **4** and its oxidized species **8** in Fig. 2. This suggests some molecular interactions through S..S contacts in the solid state.

Electrical conductivities of the oxidized complexes measured for compacted pellets at room temperature are shown in Table 1. Although complexes **2** - **5** are essentially insulators, all the oxidized species behave as semiconductors. In these cyclopentadienyl-metal complexes having a

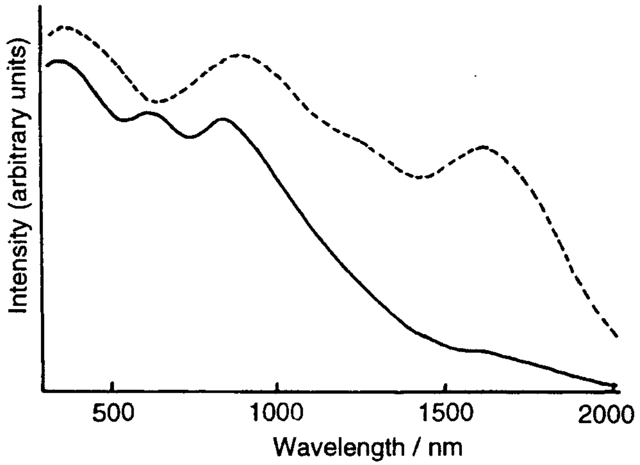


FIGURE 2 Powder reflectance spectra of **4** (——) and the oxidized species **8** (- - - -).

non-planar geometry, the $C_8H_4S_8$ ligand moiety leads to the formation of effective electron-conduction pathways through S..S contacts in the solid state. Although complex **7** is likely to have a similar arrangement of the $C_8H_4S_8$ ligand moieties, as assumed for **6**,[10] **7** has two C_5H_5 groups, resulting in somewhat lower electrical conductivity. On the other hand, complexes **8** and **9** exhibit high electrical conductivities, as well as **6**. These metal complexes with two $C_8H_4S_8$ ligands have a penta-coordinate geometry around the Ti(IV) ion and assume good electron-conduction pathway can be

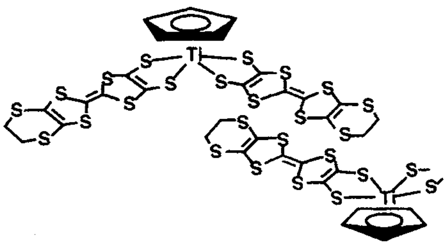


FIGURE 3 Assumed molecular array for the oxidized species **8** and **9** in the solid state.

TABLE 1 Electrical conductivities (σ)*

Complex	σ_{RT} / S cm^{-1}
6	0.19
7	2.9×10^{-3}
8	0.16
9	0.12
10	1.0×10^{-4}

* Measured for compacted at room temperature pellets.

constructed through S..S contacts (Fig. 3). Other penta-coordinate oxometallate complexes with two $C_8H_4S_8$ ligands, $[M(O)(C_8H_4S_8)_2]^{n-}$ [M = V(IV) and Mo(IV); n < 1], also have exhibited high electrical conductivities (0.11 - 5.5 S cm^{-1} for compacted pellets).[15]

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