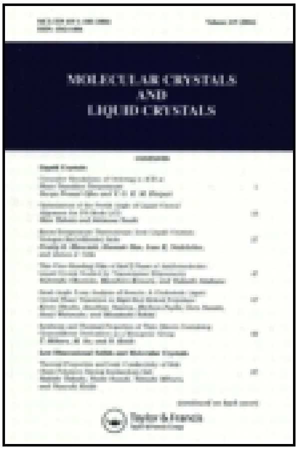

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Synthesis and Electrical Conductivities of Some Metal Complexes with the Extended Dithiolato Ligand Having a C_8S_8 Skeleton

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SYNTHESIS AND ELECTRICAL CONDUCTIVITIES OF SOME METAL COMPLEXES WITH THE EXTENDED DITHIOLATO LIGAND HAVING A C_8S_8 SKELETON

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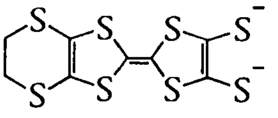
ABSTRACT The new dithiolato ligand with an extended π-electron system, $C_8H_4S_8{}^{2-}$ (2-[(4,5-ethylenedithio)-1,3-dithiole-2-ylidene]-1,3-dithiole-4,5-dithiolate) was synthesized and $[NBu^n{}_4][Au(C_8H_4S_8)_2]$ and $Pt(C_8H_4S_8)(SEt_2)_2$ prepared. Redox potentials of these complexes were determined. Their oxidized species and $Na_{1.5}[Ni(C_8H_4S_8)_2]$ exhibit electrical conductivities of 0.06 - 17 S cm^{-1} at room temperature for compacted pellets.

INTRODUCTION

Oxidized planar C_3S_5-metal complexes [$C_3S_5{}^{2-}$ = the 4,5-dimercapto-1,3-dithiole-2-thionato(2-) ligand] are known to become good electrical conductors,[1-3] and some C_3S_5-nickel(II) and -palladium(II) complexes exhibit superconductivity at low temperature.[4,5] They have effective electron-conduction pathways constructed with molecular interactions through sulfur-sulfur nonbonded contacts in the solid state. In metal complexes with more sulfur-rich dithiolato ligands having an extended π-electron system are expected effective molecular interaction through S-S contacts, accompanied with diminished on-site Coulomb repulsions. $Ni[S_2C_2S_2C_2S_2C_2(CF_3)_2]_2$,[6] $[Ni(S_2C_2S_2)]_n$[7] and $[Ni(S_2C_2S_2C_2S_2C_2S_2)]_n$[8] behave as electrical conductors. In this work, the 2-[(4,5-ethylenedithio)-1,3-dithiole-2-ylidene]-1,3-dithiole-4,5-dithiolato(2-) ligand ($C_8H_4S_8{}^{2-}$, abbreviated as etdt^{2-}) was newly synthesized, their metal complexes [M = Ni(II), Pt(II) and Au(III)] were prepared, and spectroscopies and electrical conductivities of the oxidized etdt-metal complexes studied.



etdt^{2-}

EXPERIMENTAL

4,5-Bis(p-acetoxybenzylthio)-1,3-dithiole-2-one prepared by the modified procedure of the literature[9,10] was reacted with 4,5-ethylenedithio-1,3-dithiole-2-thione in triethylphosphite under a reflux condition to give 4,5-bis(p-acetoxybenzylthio)-1,3-dithiole-2-[(4,5-ethylenedithio)-1,3-dithiole-2-ylidene] [$(p\text{-}AcOC_6H_4CH_2)_2$etdt].[11]

Na_2etdt was formed by the reaction of sodium metal with $(p\text{-}AcOC_6H_4CH_2)_2$etdt in methanol. A reaction of Na_2etdt with $NaAuCl_4 \cdot 2H_2O$ in methanol in the presence of $[NBu^n{}_4]Br$ afforded $[NBu^n{}_4][Au(etdt)_2]$ (**1**). A reaction of cis-$PtCl_2(Et_2S)_2$ with Na_2etdt in methanol gave $Pt(etdt)(Et_2S)_2$ (**2**). On the other hand, a reaction of cis-$PtCl_2(Me_2S)_2$ dissolved in dichloromethane with Na_2etdt in methanol in the presence of $[NBu^n{}_4]Br$ afforded $[NBu^n{}_4]_{0.4}[Pt(etdt)_2]$ (**3**). A reaction of Na_2etdt with $NiCl_2 \cdot 2H_2O$ in methanol gave $Na_{1.5}[Ni(etdt)_2]$ (**4**). Complex **1** dissolved in methanol and complex **2** in benzonitrile were oxidized by iodine to yield $[NBu^n{}_4]_{0.05}[Au(etdt)_2]$ (**5**) and $Pt(etdt)I_{1.8}$ (including a small amount of Et_2S) (**6**).

Cyclic voltammograms and spectroscopies of the complexes were measured as described elsewhere.[11] The hypothetical structure of the $[Ni(etdt)_2]^{2-}$ ion was optimized by the PM3 method using the MOPAC 93 program.[12] Extended Hückel MO calculations for $[Ni(etdt)_2]^{2-}$ and $[Ni(C_3S_5)_2]^{2-}$ species were carried out using the program package CACAO ver. 4.0.[13]

RESULTS AND DISCUSSION

Cyclic voltammograms of complexes **1** and **2** are illustrated in Figure 1. The former exhibits a quasi-reversible wave

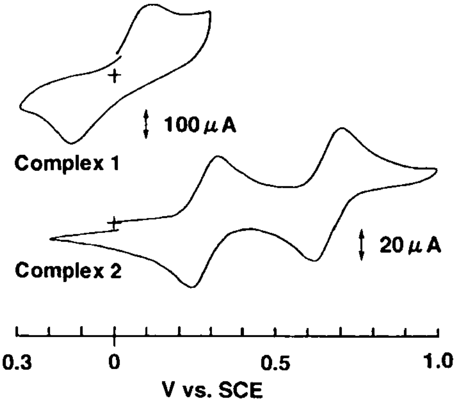


FIGURE 1 Cyclic voltammograms of complex **1** in N,N-dimethylformamide (1.0×10^{-3} mol dm^{-3}) and complex **2** in benzonitrile (1.0×10^{-3} mol dm^{-3}), 0.1 mol dm^{-3} $[NBu^n{}_4][ClO_4]$; scan rate 0.1 V s^{-1}.

due to the $[Au(etdt)_2]^- \rightarrow [Au(etdt)_2]^0$ process at +0.12 V(vs. SCE) as an oxidation peak potential. This is considerably low compared with the oxidation peak potential (+0.72 V vs. SCE) of the $[Au(C_3S_5)_2]^-$ anion,[14] indicating easy oxidation of the present complex. The reversible waves of the latter complex show somewhat higher oxidation potentials (0.32 and 0.70 V vs. SCE), which are in contrast to the $[Pt(C_3S_5)_2]^{2-}$ anion (-0.08 and +0.11 V vs. SCE).[15] The $[Ni(etdt)_2]^{2-}$ species seems to have a considerably low oxidation potential, since the reaction of Na_2etdt and $NiCl_2$ resulted in a precipitation of the oxidized species (complex **4**).

The binding energies of Au $4f_{7/2}$ and $4f_{5/2}$ electrons of the one-electron oxidized species **5** determined by XPS were 86.2 and 89.9 eV, respectively, which were essentially the same as those of **1**. This finding suggests that the ligand-centered oxidation occurs in **5**, as were observed for several $[M(C_3S_5)_2]^{n-}$ (M = Au(III),[14] Ni(II) and Pt(II);[15] n < 1) complexes. One of ν(C=C) stretching frequencies of the etdt ligand of **1** observed at 1500 cm^{-1} occurred at 1450 cm^{-1} for the oxidized species **5**. This is also consistent with the ligand-centered oxidation, as observed for oxidized C_3S_5-metal complexes.[14-17] This complex showed no ESR signal, although it contains essentially the $[Au(etdt)_2]^0$ species. This is suggestive of any association of the paramagnetic oxidized species, as pointed out for the finding that no ESR signal was observed for $[Au(C_2H_4S_2C_2S_2)_2]^0$.[18]

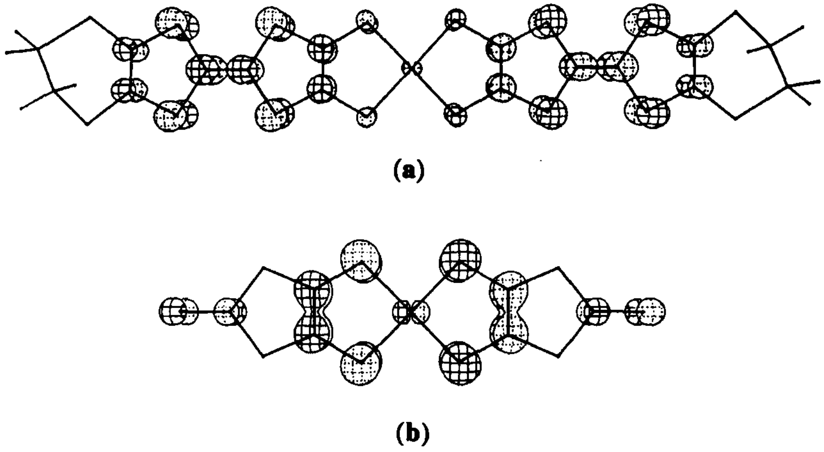
Although complexes **1** and **2** are essentially an insulator, oxidized species **3** - **6** behave as semiconductors with high DC conductivities of 17 - 0.06 S cm^{-1} at room temperature measured for compacted pellets. The conductivities are summarized in Table 1. Activation energies for the electrical conduction of **4**, **5** and **6** were determined to be 21, 14, and 80 meV, respectively. In particular, very low activation energies of **4** and **5** determined for compacted pellets may suggest the possibility of metallic properties in the crystals.

TABLE I Electrical conductivities (σ) and activation energies (E_a)

Complex	σ_{RT} / S cm^{-1}	E_a / eV
1	9.4×10^{-9}	
3	0.2	
4	17	0.014
5	2.8	0.021
6	0.062	0.08

* Measured at room temperature for compacted pellets.

They are essentially two-electron oxidized species where the HOMO makes up the conduction band. Based on square-planar geometries of the $[Ni(etdt)_2]^{2-}$ anion similar



(a)

(b)

FIGURE 2 HOMO forms of (a) $[Ni(etdt)_2]^{2-}$ and (b) $[Ni(C_3S_5)_2]^{2-}$ anions

to that of the $[Ni(C_3S_5)_2]^{2-}$ anion, extended Huckel MO calculations[13] of these anions exhibited HOMO forms,which are illustrated in Figure 2. Large amplitudes of calculated HOMO envelopes on sulfur atoms coordinating to the nickel(II) ion observed for $[Ni(C_3S_5)_2]^{2-}$ are diminished in the $[Ni(etdt)_2]^{2-}$ species. The charge carriers are delocalized through the whole moiety of the etdt ligand. The MO calculation indicates the nearly degenerated HOMO and NHOMO levels with the energy splitting of 0.1 V. This nearly two-fold degeneracy may induce a multi-Fermi surface system on the partial oxidation. In the etdt complex the amplitudes on the coordinating sulfur atoms are rather decreased and the π-electrons are extensively delocalized through the ligand

compared with those of the C_3S_5-complex. This leads to effective sulfur-sulfur interactions between adjacent $[M(etdt)_2]$ anion moieties.

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