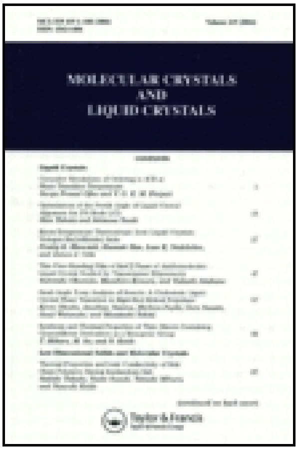

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Preparation and Properties of Gold Complexes with TTF Dithiolato Ligands

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Preparation and Properties of Gold Complexes with TTF Dithiolato Ligands

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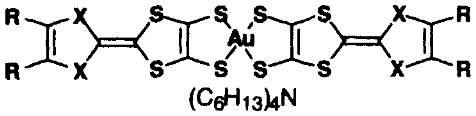
Several gold(III) complexes with TTF dithiolato ligands have been prepared as the tetrahexylammonium salts. The cyclic voltammograms in DMF showed two or three pairs of redox waves. X-Ray structure analysis of $Ph_4P{\cdot}Au(eodt)_2{\cdot}(DMF)_2$ reveals that the $Au(eodt)_2$ anion takes a significantly folded chair conformation. Charge-transfer salts of $Au(dt)_2$ derivatives with TCNQ showed high conductivity ($\sigma_{rt} = 10^0$-10^1 S cm^{-1} on a compressed pellet).

Keywords: bis(dithiolene) complex; tetrathiafulvalene; gold complex; electrical conductivity; X-ray structure analysis

INTRODUCTION

Metal complexes with TTF-dithiolato ligands $M(dt)_2$, where dt is 2-(1,3-dithiol-2-ylidene)-1,3-dithiole-4,5-dithiolate, have recently received considerable attention as d-π composite materials for molecular metals and molecular magnetic conductors.[1] However, most anionic $M(dt)_2$ complexes are readily oxidized to form insoluble neutral complexes due to presence of strongly electron-donating TTF moieties. We have noted the gold complexes $Au(dt)_2^-$ because it should tougher against oxidation than the other anionic $M(dt)_2$ ones considering the fact that the oxidation potentials of Au(dmit)$_2$$^-$[2] and Au(dddt)$_2$$^-$[3] are more positive than the corresponding Ni complexes. Furthermore, square planarity of Au(III) complexes similar to Ni(II) and Pd(II) ones is promising for development of highly conducting molecular materials. Inspite of the interest for Au(dt)$_2$ complexes mentioned above, only the bis(ethylenedithio) derivative has been prepared as the tetrabutylammonium salt.[1c] In these Proceedings, we report herein preparation, structure and properties of Au(dt)$_2$ derivatives with various substituents on TTF moieties.

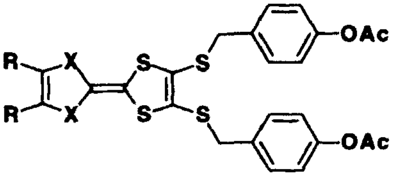


X = S, R = H, Au(dt)$_2$
X = S, R = SMe, Au(tmdt)$_2$
X = S, 2R = -O(CH$_2$)$_2$O-, Au(eodt)$_2$
X = Se, R = H, Au(ds)$_2$

RESULTS AND DISCUSSION

Synthesis and Electrochemistry

The reaction of bis(*p*-acetoxybenzyl)-TTF (or STF) derivatives[4] (**1**, **2**) with an excess of NaOMe (8 equiv. mol) in THF-MeOH (1:1, v/v) at room temperature, followed by treatment with (n-$C_6H_{13})_4NBr$, and then with $NaAuCl_4\cdot 2H_2O$ afforded the target (n-$C_6H_{13})_4N\cdot Au(dt)_2$



1: X = S, R = H, SMe,
2R = -O(CH$_2$)$_2$O-
2: X = Se, R = H

TABLE 1. Redox Potentials of Au(dt)$_2$ Derivatives in DMF (V vs. SCE, 25 °C)

Compound	E_{m1}[a]	E_4	E_{m2}[b]	E_5
$(n\text{-}C_6H_{13})_4N\cdot Au(dt)_2$	+0.13[c]	+0.91[c]		+0.95[c]
$(n\text{-}C_6H_{13})_4N\cdot Au(tmdt)_2$	+0.22[c]		+0.88[c]	
$(n\text{-}C_6H_{13})_4N\cdot Au(chdt)_2$	+0.02[c]		+0.86[c]	
$(n\text{-}C_6H_{13})_4N\cdot Au(ds)_2$	+0.16[c]		+1.01[c]	

[a] $E_{m1} = (E_1+E_2+E_3)/3$. [b] $E_{m2} = (E_4+E_5)/2$. [c] Irreversible step. Anodic peak potential.

derivatives in 11-54% yields. The cyclic voltammograms of $(n\text{-}C_6H_{13})_4N\cdot Au(dt)_2$ derivatives in DMF consists of two or three pairs of irreversible redox waves (TABLE 1).[5] Considering that there are five redox-active sites in these complexes, that is two TTFs and one gold bis(dithiolene), these waves may correspond to multi-electron transfer processes. Comparison of peak currents of each redox wave suggests the first redox corresponds to three-electron transfer.

Crystal Structure of $Ph_4P\cdot Au(eodt)_2\cdot(DMF)_2$

When a DMF solution of $(n\text{-}C_6H_{13})_4N\cdot Au(eodt)_2$ had been kept for a week at room temperature in the presence of an excess of Ph_4PBr, single crystals of the corresponding tetrakis(triphenyl)phosphonium salt were obtained as brown plates.[6] FIGURE 1 shows ORTEP drawing and atomic numbering scheme of the $Au(eodt)_2^-$ determined by X-Ray structure analysis.[6] The Au(eodt)$_2$ anion takes a chair conformation folded at S3 and S4 (S9 and S10). The dihedral angle between two planes composed of S1-S2-S3-S4 (S9-S10-S11-S12) and S3-S4-S5-S6 (S7-S8-S9-S10) is 12.8° (19.1°). In contrast, the AuS_4^- core is almost planar. The crystal includes two DMF molecules used as the solvent for crystallization in a unit cell. As shown in FIGURE 2, the Au(eodt)$_2$ anions are orthogonally arranged in the bc plane. On the other hand,

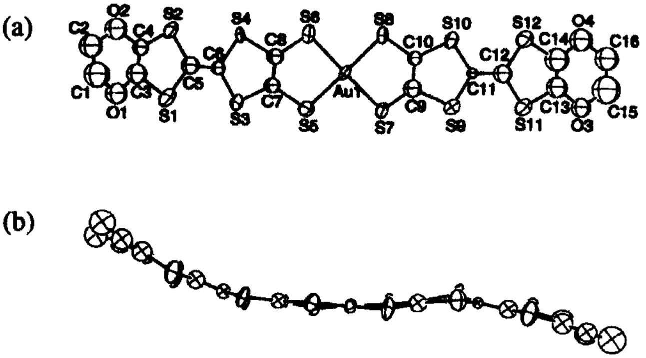


FIGURE 1. (a) ORTEP drawing and atomic numbering scheme of Au(eodt)$_2$ anion in Ph$_4$P·Au(eodt)$_2$·(DMF)$_2$ and (b) side view.

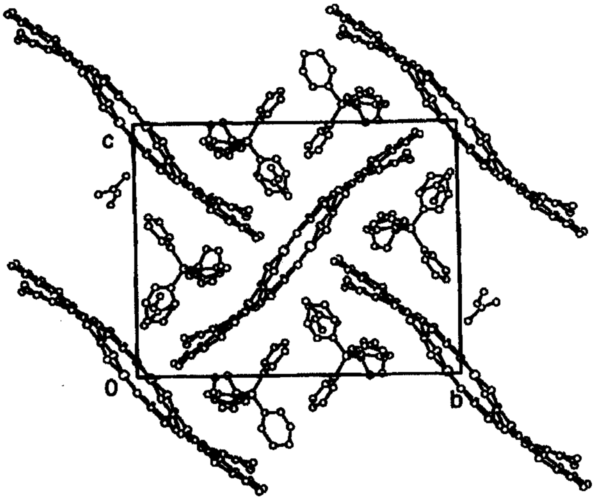


FIGURE 2. Crystal structure of Ph$_4$P·Au(eodt)$_2$·(DMF)$_2$ viewed onto the *bc* plane.

they form sheet-like networks along the a-axis. There are many side-by-side S···S contacts less than the sum of the van der Waals radii (3.7 Å) between adjacent molecules along the a axis, the shortest one being 3.53(2) Å.

Electrical Properties of Conducting Materials

When $(n\text{-}C_6H_{13})_4N{\cdot}Au(dt)_2$ derivatives were treated with an excess of TCNQ, overoxidations occur and the corresponding TCNQ complexes were obtained. The ν_{CN} value (2180 cm^{-1}) in IR spectra indicates the TCNQ molecules are completely reduced to $TCNQ^{-\cdot}$ for all the complexes. Therefore, the $Au(dt)_2$ derivatives are partially oxidized in all cases. As shown in TABLE 2 most complexes exhibited high conductivity ($\sigma_{rt} = 10^0\text{-}10^1$ S cm^{-1}) on a compressed pellet. Though they showed semiconductive temperature dependence of resistivity, their activation energies (E_a = 0.024-0.051 eV) were very low. Therefore, they are expected to metallic behavior on a single crystal.

TABLE 2. Electrical Conductivity of the TCNQ complexes of $Au(dt)_2$ and $Au(ds)_2$.

Donor	D : A[a]	σ_{rt} / S cm^{-1} [b]	Ea / eV
$Au(dt)_2$	2 : 1	7.7	0.032
$Au(tmdt)_2$	6 : 1	10	0.038
$Au(eodt)_2$	4 :1	4.8	0.064
$Au(chdt)_2$	4 : 1	1 2x 10^{-3}	0.11
$Au(ds)_2$	2 :1	29	0.024

[a] Determined based on elemental analysis. [b] Measured on a compressed pellet by a four-probe technique.

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[5] Satisfactory cyclic votammogram of $(n\text{-}C_6H_{13})_4N\cdot Au(eodt)_2$ could not be obtained owing to association with chemical reaction.

[6] Crystal data: monoclinic, space group $P2_1/n$, $a = 12.384(8)$, $b = 23.482(7)$, $c = 18.876(8)$ Å, $\beta = 99.01(4)°$, $V = 542194)°$, $Z = 4$, $R(R_w) = 0.111(0.136)$ for 2494 observed ($[I \geq 2\sigma(I)]$) reflections from 7415 unique data.