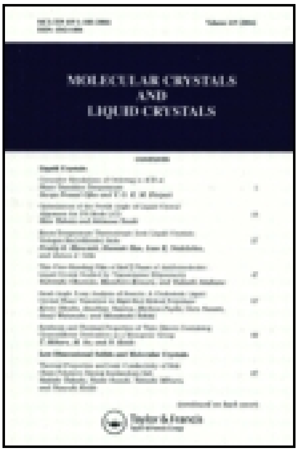

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Preparation and Properties of Metal Complexes with TTP-Dithiolate Ligands

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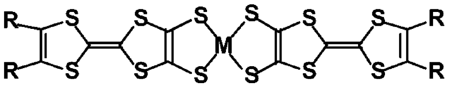
Several copper and platinum complexes with TTP (2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) dithiolato ligands, Cu(ttpdt)$_2$ (**1**) and Pt(ttpdt)(bpy) (**2**), have been prepared. The tetrakis(ethylthio) and tetrakis(hexylthio) derivatives of neutral Cu(ttpdt)$_2$ showed relatively high conductivity of σ_{rt} = 10^{-2} S cm^{-1} on compressed pellets. On the other hand, radical cation salts of **1** and **2** exhibited moderate conductivity of σ_{rt} = 10^{-2} –10^{-4} S cm^{-1}.

Keywords: dithiolene complex; tetrathiapentalene; cyclic voltammetry; electrical conductivity

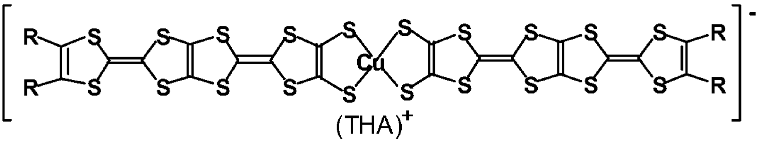
INTRODUCTION

Transition metal complexes with 1,2-dithiolene ligands have received considerable attention since discovery of molecular superconductors based on M(dmit)$_2$ exhibit superconductivity at low temperatures[1]. Recently, synthesis of metal dithiolene complexes with extended π-system M(dt)$_2$, in which

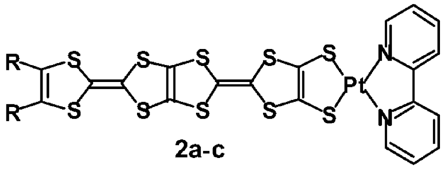


M(dt)$_2$

strongly electron-donating tetrathiafulvalene (TTF) moiety exists in the ligand, have been reported by several groups for the purpose of developing d-π cooperative systems as well as conducting component of molecular metals[2]. In this connection, metal complexes with more extended π-electron system as a ligand are of interest to explore exotic conducting materials. We have synthesized bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (TTP) and its derivatives[3], and have found they afford a large number of metallic radical cation salts stable down to low temperatures[4]. In these Proceedings, we report preparation and properties of metal complexes with TTP dithiolate ligand, Cu(ttpdt)$_2$ (**1**) and Pt(ttpdt)(bpy) (**2**)[5].



THA · **1a-c**



2a-c

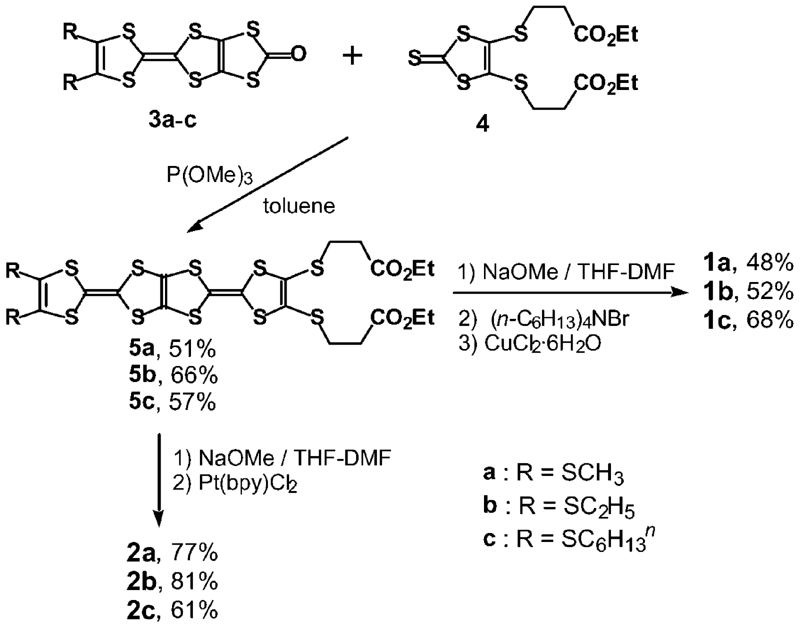
a : R = SCH_3
b : R = SC_2H_5
c : R = SC_6H_{13}-*n*

RESULTS AND DISCUSSION

Synthesis

The synthesis was achieved as shown in Scheme 1. The compound **3a-c** and 1,3-dithiol-2-thione with dithiolate protecting group **4** was cross-coupled with trimethyl phosphite in refluxing toluene to afford the corresponding TTP derivative (**5a-c**) in 48-68% yields. The reaction of **5** with sodium methoxide in THF-DMF followed by

SCHEME 1



treatment with tetrahexylammonium bromide and copper(II) dichloride gave Cu(ttpdt)$_2$ as a tetrahexylammonium (THA) salt (48-68% yields). On the other hand, Pt(ttpdt)(bpy) derivatives were obtained by treatment of **5** with sodium methoxide and then with Pt(II)(bpy)Cl$_2$ in THF-DMF (61-81% yields).

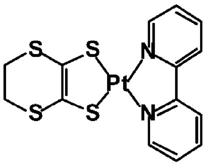
Electrochemistry of **2c**

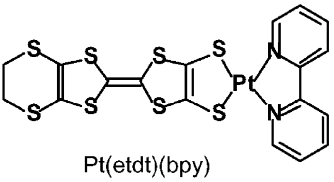
Among the obtained metal complexes, cyclic voltammetry of the platinum complex **2c** has been carried out. The redox potentials of **2c** are listed in Table 1 together with its related compounds. Cyclic voltammogram of **2c** in benzonitrile consists of three-pairs of irreversible waves. Comparison of peak currents indicates that the redox wave at the highest voltage region corresponds to two-electron transfer. The first oxidation potential (0.18 V) is almost the same as

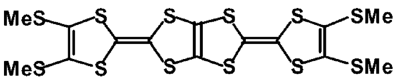
TABLE 1 Redox Potentials of **2c** and Related in Benzonitrile (V vs. SCE 25 °C)

Donor	E_1	E_2	E_3	E_4
2c	0.18*	0.71*	1.11*	
Pt(dddt)(bpy)	0.34*			
Pt(etdt)(bpy)	0.20*	0.80*		
TTM-TTP	0.53	0.72	0.99	1.11

* Irreversible step. Anodic peak potentials.


Pt(dddt)(bpy)


Pt(etdt)(bpy)


TTM-TTP

that of Pt(etdt)(bpy) (0.20 V)[5] but is lower by 0.16 and 0.35 V than those of Pt(dddt)(bpy) (0.34 V) and TTM-TTP (0.53 V)[3a], respectively. Based on the above results, it is considered that the positive charge formed by the first oxidation mainly distributes on both dithiolene moiety and the attached 1,3-dithiole ring. On the other hand, the second oxidation potential (0.71 V) is lower by about 0.1 V than that of Pt(etdt)(bpy) (0.80 V) and comparable to that of TTM-TTP (0.72 V). This result indicates that the second oxidation occurs in the TTP moiety other than the 1,3-dithiol-2-ylidene contributing the first redox process.

Electrical Property of Conducting Materials

Oxidation of **1a**-**c** with NO_2SbF_6 in THF has afforded neutral complexes of **1b** and **1c**, and SbF_6 salt of **1a**, respectively. The room temperature conductivity of those materials is 10^{-2} S cm^{-1} on compressed pellets (Table 2). The conductivity of neutral materials of

TABLE 2 Electrical Conductivity of Conducting Complexes (Donor)(Acceptor)$_X$

Donor	Anion	D : A [a]	σ_{rt} / S cm^{-1} [b]	E_a / eV
1a	SbF_6	2 : 1	2.4×10^{-2}	0.091
1b	-	neutral	6.2×10^{-2}	0.051
1c	-	neutral	6.6×10^{-2}	0.22
2a	SbF_6	1 : 1	7.4×10^{-3}	0.17
	I_3		1.0×10^{-4}	-
2b	SbF_6	1 : 1	4.8×10^{-2}	0.18
	I_3		9.2×10^{-3}	0.18
	TCNQ	3 : 2	2.1×10^{-3}	0.12
2c	SbF_6	1 : 1	1.2×10^{-3}	0.20
	I_3		1.9×10^{-2}	0.15
	TCNQ	3 : 1	3.6×10^{-2}	0.12

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

1b and **1c** may be regarded to be relatively high considering that they have bulky ethylthio or hexylthio groups. Temperature dependence of resisitivity reveals they are semiconductors with activation energies of 0.051-0.22 eV. On the other hand, oxidation of the unsymmetrical complexes **2a**-**c** has been carried out by use of NO_2SbF_6, TCNQ and I_2 as oxidants. The conductivity of the obtained salts is 10^{-2} - 10^{-4} S cm^{-1} at room temperature on compressed pellets. They exhibited semiconducting temperature dependence of resistivity with activation energy of 0.12-0.20 eV.

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