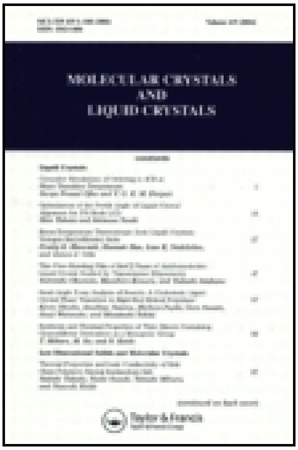

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Syntheses and physical properties of metal complex conductors with extended ttf ligands

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SYNTHESES AND PHYSICAL PROPERTIES OF METAL COMPLEX CONDUCTORS WITH EXTENDED TTF LIGANDS

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Metal complexes based on extended TTF (tetrathiafulvalene) ligands, $[M(dmdt)_2]^{2-}$, $[M(tmdt)_2]^{2-}$ (dmdt = dimethyltetrathiafulvalenedithiolate, tmdt = trimethylenetetrathiafulvalenedithiolate) (M = Ni, Pd, Pt, etc) were synthesized. The newly developed nickel complexes such as $[Ni(dmdt)_2]^{2-}$ and $[Ni(tmdt)_2]^{2-}$ are easily oxidized to neutral state by electrochemical oxidation and the microcrystals of these neutral complexes exhibit high conductivity (100–500 Scm^{-1}). The crystal structure of $[Ni(tmdt)_2]$, one of these neutral complexes, was finally determined, which supports the metallic behavior of resistivity of this neutral metal complex.

Keywords: organic conductor; metal complex; extended TTF dithiolato ligand; neutral metal; one component metal

INTRODUCTION

Molecular conductors based on organic compounds have been developed with the increasing of molecular variations. The extension of π conjugated systems will be one of the effective strategy to find new metallic compounds. Metal complexes with extended TTF ligands also have extended π conjugated systems, and multiple redox property. Therefore, the effort to realize the metal complex conductors with the extended TTF ligands have

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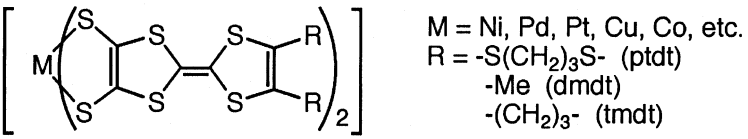


SCHEME 1

been made in these years [1–6]. Although the metal complexes with extended TTF ligands have large molecular sizes (molecular lengths are over 20 Å) and have many peripheral chalcogens, they are able to dissolve in conventional organic solvents. It is because the metal complexes are obtained as anionic species. Additionally, there are several interests to apply the metal complexes for molecular conductors, such as the introduction of magnetic metal, the variation of coordination geometry, etc. In this paper, we report the syntheses of metal complexes based on extended TTF (tetrathiafulvalene) ligands, $[M(dmdt)_2]^{2-}$ and $[M(tmdt)_2]^{2-}$ (dmdt = dimethyltetrathiafulvalenedithiolate, tmdt = trimethylenetetrathia-fulvalenedithiolate) (M = Ni, Pd, Pt, etc). The crystal structure and electrical transporting property of neutral $[Ni(tmdt)_2]$ is also mentioned.

SYNTHESIS

All of the synthetic procedures were carried out under a strictly inert atmosphere with the Schlenk technique. The synthesis of ligand moieties with the cyanoethyl-protecting group was performed according to the reported [7] and its derived methods. The synthetic procedure of $[Ni(tmdt)_2]$ was described in the following paragraphs, and the other metal complexes were also obtained by the almost similar methods.

2,3-Bis(2-cyanoethylsulfanyl)-6,7-trimethylenetetrathiafulvalene: $tmdt(C_2H_4CN)_2$ 3

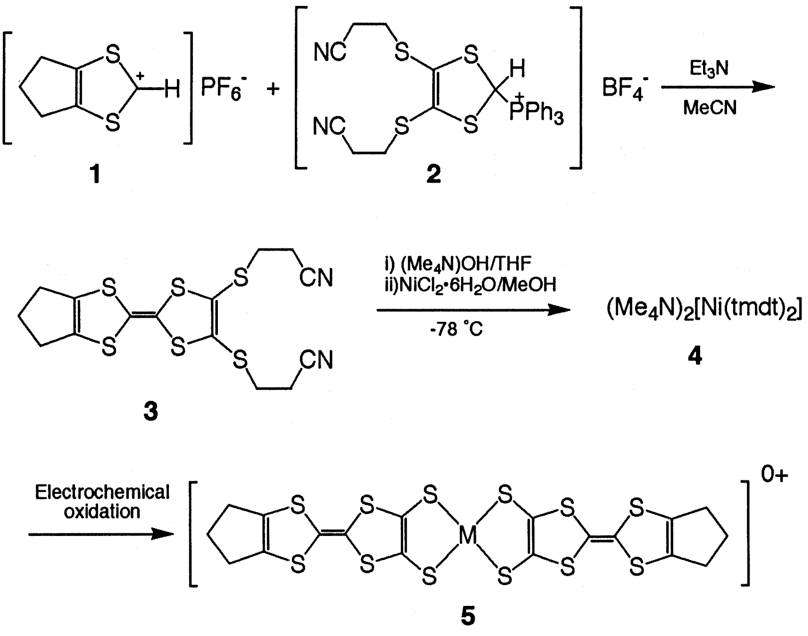
Triethylamine (6.5 ml) was added to an acetonitrile solution (120 ml) of 4,5-trimethylene-1,3-dithiolium hexafluorophosphate **1** (1.16 g) 4.0 mmol and triphenyl[4,5-bis(2′ -cyanoethylsulfanyl)-1,3-dithiol-2-yl]phosphonium tetrafluoroborate **2** (2.51 g, 4.0 mmol). The yellow mixture gradually turned to an orange solution. After stirring the solution for 1 hour, the solvent was removed by evaporation. The purification by silica-gel-column chromatography (CH_2Cl_2) gave 1.25 g of yellow needle crystals **3** (75% yield).

$(Me_4N)_2[Ni(tmdt)_2]$ 4

The coordination of ligands to metals was performed at low temperature. The tmdt ligand **3** (200 mg, 0.48 mmol) was dissolved in THF (7 ml) at −78°C and methanol solution of 25% $(Me_4N)OH$ (1.0 ml, 2.7 mmol) was added to the solution. The mixture was warmed to room temperature gradually, and the orange solution turned to a reddish suspension. After cooling down to −78°C again, $NiCl_2{\cdot}6H_2O$ (11.5 mg, 0.24 mmol) dissolved in methanol solution (3 ml) was dropped to the reddish suspension. When the suspension was stirred over night and slowly warmed up to room temperature, the corresponding metal complexes **4** (180 mg, 91% yield) could be obtained after filtration.

Neutral $[Ni(tmdt)_2]$ 5

Black plate crystals of neutral $[Ni(tmdt)_2]$ were obtained electrochemically from acetonitrile solution containing $(Me_4N)_2[Ni(tmdt)_2]$ in H-shape glass cells with Pt electrodes by applying a 0.2 μA current for 20 days. The obtained crystals were insoluble in conventional organic solvents and stable in air. The composition was determined by electron probe X-ray



SCHEME 2 Synthesis of neutral $[Ni(tmdt)_2]$.

microanalysis and elemental analysis. The crystal structure determination was made on a Rigaku MERCURY CCD system at 123 K to collect a sufficient number of reflections, because a crystal size was too small ($0.1 \times 0.05 \times 0.03\,\mathrm{mm}^3$) for a conventional X-ray diffraction experiment. The lattice constants are as follows: $a = 6.376(3)$ Å, $b = 7.359(1)$ Å, $c = 12.012(7)$ Å, $\alpha = 90.384(7)^\circ$, $\beta = 96.688(4)^\circ$, $\gamma = 103.587(4)^\circ$, $V = 543.7(4)$ Å^3 with space group $P\bar{1}$. Non-hydrogen atoms were refined anisotropically. The final R-value based on the 5905 reflections [$I > 2.0\ \sigma(I)$] was 0.069.

RESULTS AND DISCUSSION

The molecular structure of $[\mathrm{Ni(tmdt)_2}]$ is exhibited in Figures 1a–1c. The Ni-S distances are 2.179(1) and 2.175(1) Å, and the S-Ni-S angle is 92.29(4)° at 123 K. The good planar ligand coordinates to the nickel metal in ideal square planar geometry, therefore, the $[\mathrm{Ni(tmdt)_2}]$ molecule shows an almost completely planarity. Except for hydrogen atoms, the most deviated atom distance from the molecular plane is no more than 0.33 Å, even when the molecular plane is defined by only the nickel and neighboring four sulfur atoms.

This good molecular planarity is effective to pack the $[\mathrm{Ni(tmdt)_2}]$ molecules closely. As shown in Figure 1a, the $[\mathrm{Ni(tmdt)_2}]$ molecules make layers by side-by-side contacts. The closest Ni$\cdots$Ni distance is 6.376(3) Å, which is found between the molecules of [000] and [100] symmetry. There exist many short S$\cdots$S contacts within the sum of the van der Waals radii (3.350(2)–3.675(2) Å), which are illustrated as broken lines in Figure 1a. Particularly, the atom distances between the sulfurs coordinating to the nickel and sulfurs of neighbor molecules are very short (3.350(2)–3.451(2) Å). The molecular overlap is also close, as shown in Figures 1b and 1c. There are two types of overlap mode, and half of the molecules are overlapped in both cases. The averaged interplanar distance between the molecules of [000] and [111] symmetry is 3.346 Å and molecules of [000] and [101] symmetry is 3.677 Å. There also exists short S$\cdots$S contacts 3.715(2) and 3.752(2) Å, respectively, which are represented as dotted lines in Figure 1c.

These distinctive structural features are reflected on the electrical transporting property. Neutral $[\mathrm{Ni(tmdt)_2}]$ shows $4 \times 10^2\ \mathrm{S\,cm^{-1}}$ of room temperature conductivity and metallic temperature dependence, The calculated band structure based on tight binding methods suggests the existence of three-dimensional Fermi surfaces [8].

In spite of neutral compounds, the other complexes also show high conductivities at room temperature: $[\mathrm{Ni(dmdt)_2}]$ ($4\text{–}5 \times 10^2\ \mathrm{S\,cm^{-1}}$),

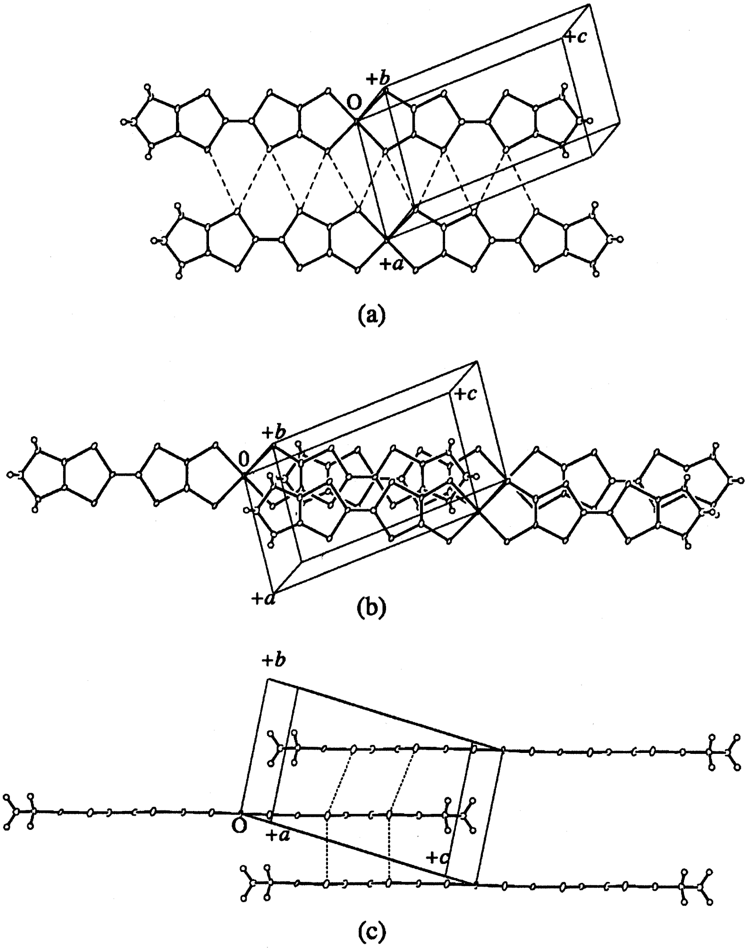


FIGURE 1 Crystal structures of neutral [Ni(tmdt)$_2$]. (a) Side-by-side molecular arrangement viewed along the perpendicular axis to the molecular plane. (b) Projection view of molecular overlap mode (c) Side view of Figure 1b, which shows the ideal planarity of the molecular arrangement.

[Pd(dmdt)$_2$] (1×10^2 S cm^{-1}), [Co(dmdt)$_2$] (0.1–0.3 S cm^{-1}), [Cu(dmdt)$_2$] (2×10^1 S cm^{-1}), [Ni(ptdt)$_2$] (3–7 S cm^{-1}), and [Co(tmdt)$_2$] (1–2 S cm^{-1}). Regardless of central metals or ligands, the neutral metal complexes with extended TTF ligands show novel aspects of metal complex conductors in the future.

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