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Highly Conducting Transition Metal Complexes Derived from the DMIT-Ligand

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HIGHLY CONDUCTING TRANSITION METAL COMPLEXES DERIVED FROM THE DMIT-LIGAND

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Abstract The nature of the metal M (M = Ni, Pd, Pt) plays a predominant role in determining the transport properties and the structure of the $TTF[M(dmit)_2]_x$ series.

INTRODUCTION

It has been well established that, in order to maintain the metallic state for a molecular metal system down to very low temperatures, effective interstack electronic coupling is needed among other things to avoid Peierls transition.[1] The use of sulfur atoms on the periphery of the molecular units as a means of extending the π electron system and promoting interstack coupling is one of the possible strategy. We report here the results obtained for the $TTF[M(dmit)_2]_x$ series (H_2dmit = 4,5-dimercapto-1,3-dithiole-2-thione; M = Ni or Pd, x = 2; M = Pt, x = 3). It will be shown that such systems approach the objective of a "true 3-D molecular metal" much more closely than any previous examples and that the nature of M plays a predominant role in determining the transport properties and the structure of these highly conducting transition metal complexes.

RESULTS

Crystals of the $TTF[M(dmit)_2]_x$ complexes have been obtained

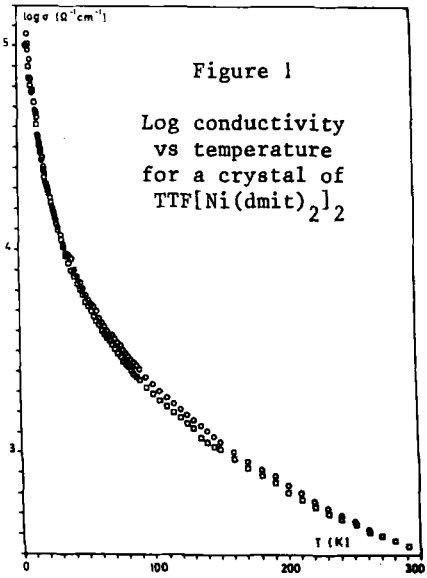

Figure 1

Log conductivity vs temperature for a crystal of $TTF[Ni(dmit)_2]_2$

by slow interdiffusion of acetonitrile solutions of $(TTF)_3(BF_4)_2$ and $(n\text{-}Bu_4N)[M(dmit)_2]$. We have recently reported [2] that the nickel complex analogue, $TTF[Ni(dmit)_2]_2$ exhibits a metal-like conductivity temperature dependence down to 4 K, with a conductivity at room temperature of *ca.* 300 Ω^{-1} cm^{-1} and at 4 K of over 10^5 Ω^{-1} cm^{-1} (Figure 1). A uniform segregated stacking arrangement of the constituent TTF and $Ni(dmit)_2$ units is observed in which close intermolecular contacts involving sulfur atoms on both types of molecules occur mainly between units in adjacent stacks, leading to a three-dimensional network of closely spaced molecules (Figure 2).

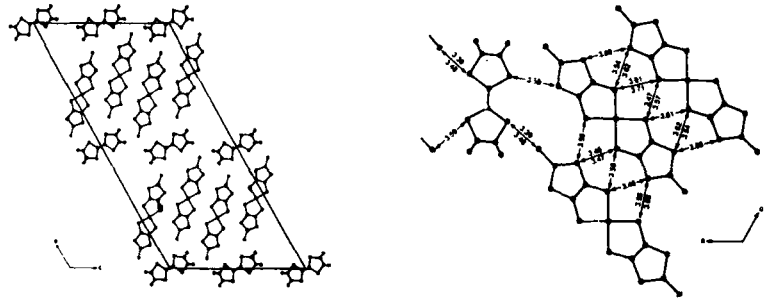

Figure 2. Crystal structure of $TTF[Ni(dmi)_2]_2$

The $TTF[Pd(dmit)_2]_2$ complex analogue has the same 1:2 stoichiometry and powder diagrams indicate that this compound is isostructural to the nickel complex. The room temperature conductivity is still higher, ca. 700 Ω^{-1} cm^{-1}.

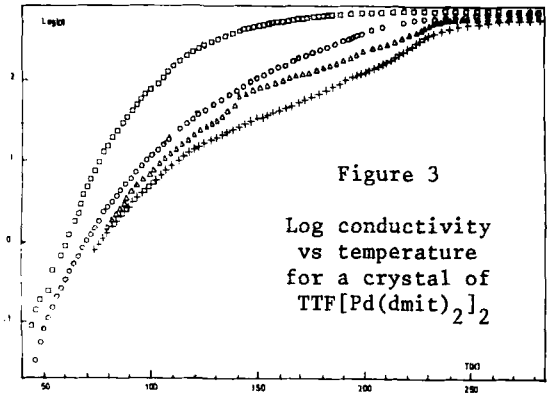

Figure 3

Log conductivity vs temperature for a crystal of $TTF[Pd(dmit)_2]_2$

The palladium complex exhibits a quasi-metallike conductivity temperature dependence down to 220 K (σ_{220K} = 720 Ω^{-1} cm^{-1}) (Figure 3). This quasi-metallic behavior is maintained on cooling and warming cycling as long as the temperature remains higher than 220 K. Below this temperature, the crystals undergo an irreversible metal-to-insulator transition and exhibit a semi-conducting behavior on subsequent temperature cycling. However, the room temperature conductivity returns to its initial value.

The properties and structure of the platinum member of the series are quite different: (i) the stoichiometry is now 1:3, $TTF[Pt(dmit)_2]_3$; (ii) these crystals exhibit a thermally activated conductivity (Figure 4;

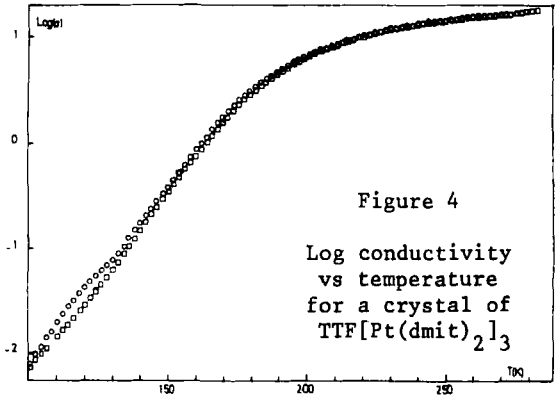

Figure 4

Log conductivity vs temperature for a crystal of $TTF[Pt(dmit)_2]_3$

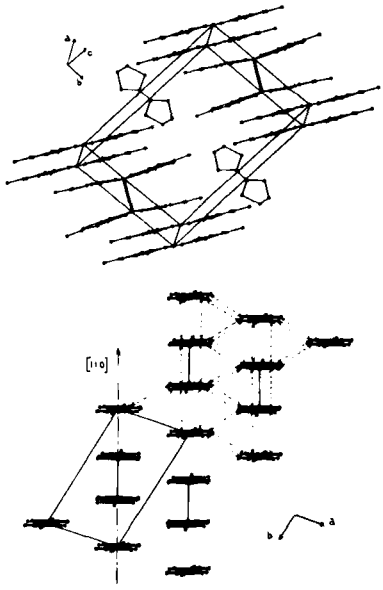

Figure 5
Crystal structure of $TTF[Pt(dmit)_2]_3$

E_a = 0.03 to 0.2 eV); (iii) the semi-conducting behavior is reflected in the structure, which consists of non-uniform stacks of $Pt(dmit)_2$ units comprising alternate monomer and dimer molecules, and of uniform stacks of TTF with large stacking distances (6.31 Å) (Figure 5).

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