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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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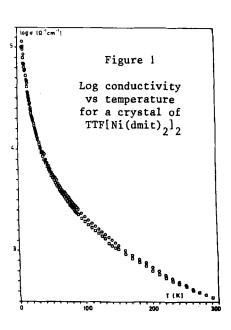
Abstract The nature of the metal M (M = Ni, Pd, Pt) plays a predominant role in determining the transport properties and the structure of the TTF[M(dmit)₂] series.

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. 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 $_2$ dmit = 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) $_2$] $_{\mathbf{x}}$ complexes have been obtained



by slow interdiffusion of acetonitrile solutions of $(TTF)_3(BF_4)_2$ and $(n-Bu_4N) [M(dmit)_{2}]$. We have recently reported 2 that the nickel complex analogue, TTF[Ni(dmit)], exhibits a metal-like conductivity temperature dependence down to 4 K, with a conductivity at room temperature of <u>ca.</u> 300 Ω^{-1} cm⁻¹ and at 4 K of over $10^5~\Omega^{-1}$ cm⁻¹ (Figure 1). A uniform segregated stacking arrangement of the constituent TTF and Ni(dmit), 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).

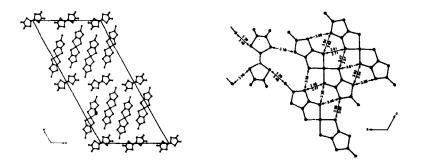
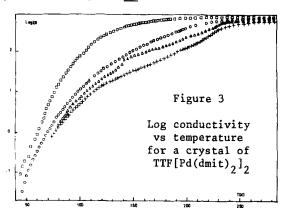


Figure 2. Crystal structure of TTF[Ni(dmi)₂]₂

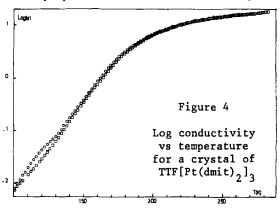
The TTF[Pd(dmit) $_2$] $_2$ complex analogue has the same 1:2 stoichiometry and powder diagrams indicate that this compound is isostructural to the nickel complex. The room temperature conductivity is still higher, \underline{ca} . 700 Ω^{-1} cm $^{-1}$.



The palladium complex exhibits a quasi-metal-like conductivity temperature dependence down to $220 \text{ K} \text{ } (\sigma_{220\text{K}} = 720 \text{ } \Omega^{-1} \text{ cm}^{-1})$ (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;

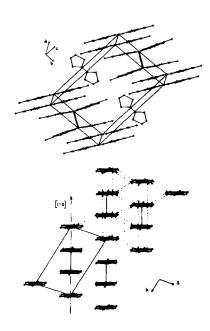


Figure 5
Crystal structure of TTF[Pt(dmit)₂]₃

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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