

Crystal structure and conductivity of the organometallic linear chain system (Et₄N)[Ni(dmit)₂] and related compounds

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CRYSTAL STRUCTURE AND CONDUCTIVITY OF THE ORGANOMETALLIC LINEAR CHAIN SYSTEM(Et₄N)[Ni(DMIT)₂] AND RELATED COMPOUNDS

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ABSTRACT

The crystal structure and conductivity of single crystals of the linear chain system (Et₄N)[Ni(dmit)₂] and a Pd analogue are presented. It appears that the structure is highly one-dimensional and perfectly regular. Nevertheless we find the temperature dependence of the resistivity to be of the form $\ln \sigma \propto -(T_0/T)^{1/2}$, which is typical for 1-D disordered systems. A tentative explanation is given based on the extreme anisotropy of the compounds.

INTRODUCTION

Transition metals coordinated by the organic ligand isotrithione-dithiolato (dmit), provide a suitable acceptor molecule, which can be made to form highly anisotropic (low-dimensional) metals or semiconductors. In the literature examples of these systems are found exhibiting both 1- and 2-dimensional electronic behaviour [1,2]. In this contribution we will focus on two new examples of the series (R₄N)[M(dmit)₂], specifically (Et₄N)[Ni(dmit)₂] and (Et₄N)_{0.5}[Pd(dmit)₂]. Both compounds show the same anomalous temperature dependence of the conductivity, which will be discussed in relation to the crystal structure.

THE SYNTHESIS AND COMPLEX FORMATION OF TETRAALKYLAMMONIUM BIS(ISOTRITHIONE-THIOLATO) METAL CHELATES

The dianionic salts, (NR₄)₂[M(dmit)₂], with R=CH₃, C₂H₅, C₃H₇ or C₄H₉, have been prepared following a synthetic method described in the literature [1,3]. Reaction of sodium and potassium with CS₂ yields the dmit²⁻ anion which is

stabilized as the zinc complex. Further reaction with benzoylchloride and sodium methoxide regenerates the dmit^{2-} ligand and is followed by the addition of the appropriate metal salt.

The $(\text{R}_4\text{N})_1[\text{M}(\text{dmit})_2]$ coordination compounds have been prepared following two different routes: (i) oxidation of $(\text{R}_4\text{N})_2[\text{M}(\text{dmit})_2]$ by iodine (I_2); (ii) auto-oxidation of $(\text{R}_4\text{N})_2[\text{M}(\text{dmit})_2]$ as described by Steimecke and co-workers [3].

The compounds were identified by infrared spectra (position of the C=C vibration) [3], chemical analysis and EPR spectra. The compound $[(\text{C}_2\text{H}_5)_4\text{N}]_{0.5}[\text{Pd}(\text{dmit})_2]$ was synthesized according to the second method with an excess of acetic acid.

THE CRYSTAL STRUCTURE OF TETRAETHYLAMMONIUM BIS(ISOTRITHIONE-DITHIOLATO) NICKELATE (III)

The crystal structure of $(\text{Et}_4\text{N})_1\text{Ni}(\text{dmit})_2$ was determined in order to help to interpret the conduction measurements. It should provide some information about the stacking of the $\text{Ni}(\text{dmit})_2^-$ ions in this compound.

The Ni(III) compound crystallizes in space group $\text{P2}_1/\text{n}$ with parameters $a=7.333(1)$ Å, $b=25.743(3)$ Å, $c=12.798(4)$ Å, $\beta=104.95(2)^\circ$, $Z=4$ and $\text{MW}=581.6$. The structure was solved from the Patterson function followed by the use of the program AUTOFOUR [4] and least-squares refinement. Resulting final $R(R_w)$ values are 4.49(5.36).

The structure contains quasi-planar $[\text{Ni}(\text{dmit})_2^-]$ molecules which are stacked along the a -axis. The planes containing Ni,S1-S5, C1-C3 and Ni,S7-S10, C5-C6, respectively, have an inclination of 7.2° . The average value of the Ni-S bond distances is $2.157(4)$ Å. Short intermolecular contacts between the $[\text{Ni}(\text{dmit})_2^-]$ ions within the chain are expected to give a considerable overlap of the valence orbitals and could therefore give rise to the observed conductivity (table 1; Figures 1 and 2).

TABLE 1

Some relevant distances within the chain

Ni(1) - Ni(2)	4.163	
Ni(1) - Ni(3)	4.243	symmetry operations
S8(1) - S4(2)	3.660	(1) x, y, z
Ni(1) - S2(3)	3.506	(2) $1-x, -y, 1-z$
S5(1) - S8(3)	3.711	(3) $-x, -y, 1-z$

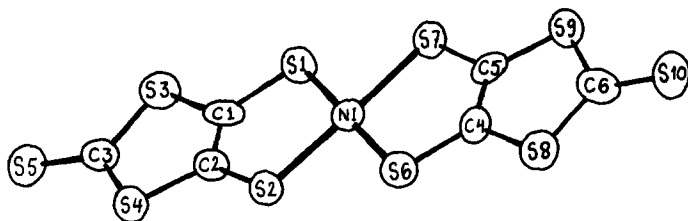


Fig. 1. The $[\text{Ni(III)(dmit)}_2]$ -ion with atomic numbering.

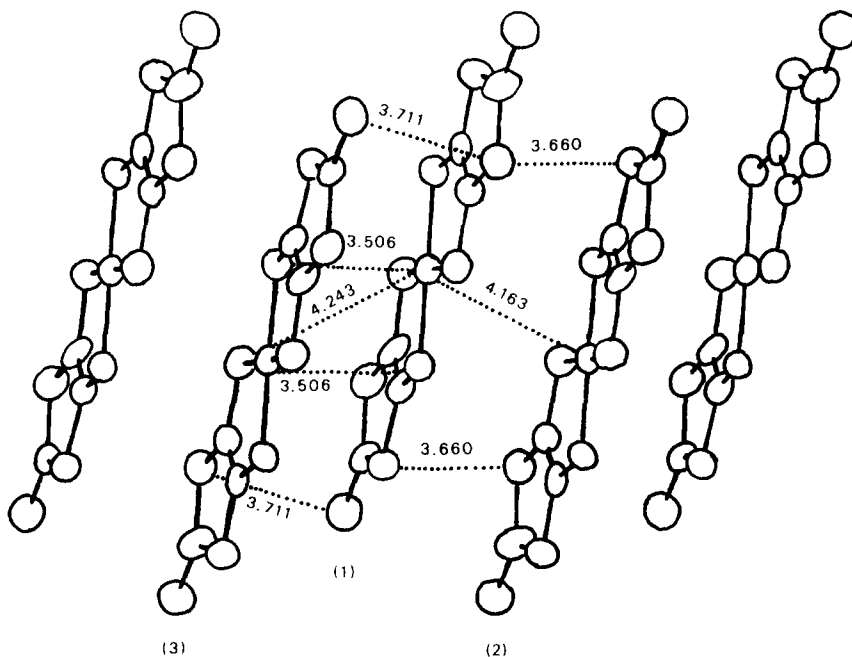


Fig. 2. Stacking of the $[\text{Ni(III)(dmit)}_2]$ -ions along the a -axis.

CONDUCTIVITY AND DISCUSSION

The conductivity of single crystals of $(\text{Et}_4\text{N})[\text{Ni(dmit)}_2]$ and $(\text{Et}_4\text{N})_{0.5}[\text{Pd(dmit)}_2]$ was measured along the stacking axis. A two-probe method was employed and electrical contacts were painted on the sample with silver paint. The same method has been employed by others on a similar type of compound [2]. If the conductivity is interpreted in terms of an activated process, the room temperature activation energies are 0.25 eV for the nickel compound and 0.05 eV

for the palladium compound. However the temperature dependence of the conductivity differs markedly from the usual semiconductor behaviour. Fig. 3 shows the results of these measurements plotted against $T^{-1/2}$. One observes that the $\ln(\sigma) \propto T^{-1/2}$ law holds over seven decades (!) in the conductivity for the nickel compound and over one decade of temperature for the palladium compound.

Such behaviour is often found in one-dimensional compounds, as was first realized by Bloch, Weissman and Varma in 1972 [5], who attributed it to a potential disorder induced on the conducting chain by randomness in the donor system. This randomness causes a localization of the electronic states, which

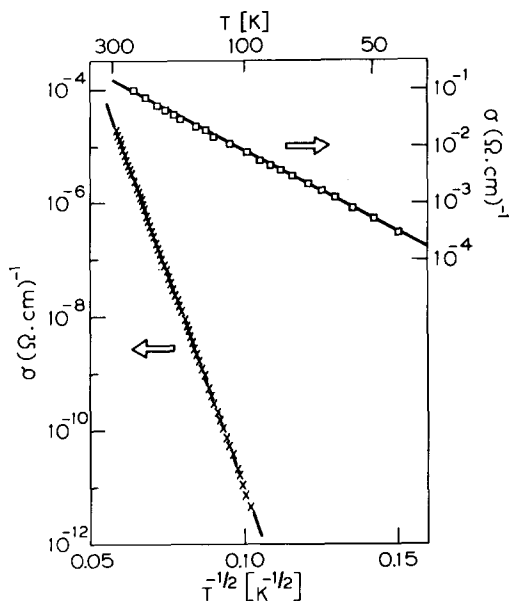


Fig. 3. Conductivity along the stacking axis of $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ (crosses) and $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$ (squares) versus $T^{-1/2}$.

in turn would explain the $T^{-1/2}$ law for the conductivity, which is the 1-D prediction of a general formula for tunneling between localized states derived by Mott [6]. This behaviour has for instance been found in other coordination compounds like KCP [5]. In that case bromium ions occupy the available sites randomly [7], thereby providing a logical source of disorder. The same $T^{-1/2}$ law has recently been derived by Azbel on the basis of other arguments [8].

In $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ however, the room temperature X-ray study and crystal structure indicate that both donors and acceptors form a regular array without any static disorder. Therefore, the application of the above theories seems far off. On the other hand, in one dimension an arbitrary amount of disorder already causes electron localization. Consequently, the higher the electrical anisotropy, the less disorder is needed to create electron localization. It appears that in $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ the stacks are extremely well separated. The smallest interchain S-S distance is of the order of 3.9 Å, much larger than the corresponding Van der Waals radius and much larger than those found in analogous compounds [1,2]. Furthermore, in preliminary measurements we find that $\sigma_{\parallel}:\sigma_{\perp}$ exceeds 100. Therefore, one might expect that a degree of disorder which is too small to manifest itself in X-ray analysis is still capable of producing a disordered electron gas. As possible sources for disorder one may think of lattice defects, chemical impurities, or maybe dynamical disorder produced by thermal vibrations of the $\text{Ni}(\text{dmit})_2$ ions resulting in randomly disordered transfer integrals. It would seem that the same arguments would hold for the palladium compound, for which the crystal structure is not known at present. A very high degree of anisotropy might also explain the low room temperature conductivity of the Ni(III) compound $4 \times 10^{-5} (\Omega \text{ cm})^{-1}$ with respect to the analogous but less anisotropic $(\text{Et}_4\text{N})_{0.5} [\text{Ni}(\text{dmit})_2]$ ($4 \times 10^{-2} (\Omega \text{ cm})^{-1}$), for which the intrachain spacing is very much the same. On the other hand, the large difference in conductivity would also be due to slightly different molecular stacking along the chain axes in both compounds.

Apart from the above considerations, which rely on the 1-dimensional nature of the compounds, we remark that the same $\ln \sigma \propto -(T_0/T)^{\frac{1}{2}}$ law has also been observed in other, widely different physical systems. In granular metal systems (cermets) for instance, many examples have been reported [9]. Quite recently, the same conductivity law was also found for a metal cluster compound [10]. In that case there is no distribution of particle sizes, which was thought to be crucial in the cermet-case. This example, together with the 1-d system discussed in this paper provides us with two examples which, in spite of the lack of apparent disorder, show disorder-like behaviour. This provides a challenging problem in the theory of order/disorder phenomena.

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