

## A New Type of Low-temperature Molecular Metal based on $[\text{Ni}(\text{dmit})_2]$ Anions ( $\text{H}_2\text{dmit} = 4,5\text{-dimercapto-1,3-dithiole-2-thione}$ )

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In contrast to previously studied molecular metal conductors based on metal complex anions, studies of the variation with temperature of the conductivity of  $\text{K}_{0.4}[\text{Ni}(\text{dmit})_2]$  show no metal to semiconductor transition down to 20 K.

The search for new and improved molecular metals is currently one of the prime goals in synthetic chemistry; because of the potential medium to long term applications of this type of material, most known examples involve purely organic molecules in the conduction process but metal complexes have also been shown to behave as molecular metals.<sup>1</sup> Those based on metal complex anions have always undergone a metal to semiconductor transition well above 70 K at atmospheric pressure. We now report a new material some crystals of which show no sign of such a transition down to 20 K.

Previous studies have shown that the  $[\text{Ni}(\text{dmit})_2]^{x-}$  anions with organic donor cations such as tetrathiofulvalene (TTF) yield molecular metals and that  $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ , indeed, behaves as a superconductor [ $T_c = 1.62$  K at 7 kbar (1 bar =  $10^5$  Pa)].<sup>2</sup> In all these materials the organic donor material plays an important role in the conduction process. Non-stoichiometric compounds of  $[\text{Ni}(\text{dmit})_2]$  anions with simple cations such as  $\text{Bu}_4\text{N}^+$  have been reported but these behave as semiconductors.<sup>3</sup>  $[\text{Me}_4\text{N}][\text{Ni}(\text{dmit})_2]_2$  has recently been shown to undergo a metal to semiconductor transition around 100 K possibly connected with the freezing of the rotation of the methyl groups.<sup>4,5</sup> In spite of the transition at atmospheric pressure the compound becomes superconducting at 5 K and 7 kbar.<sup>5</sup> Our previous studies on non-stoichiometric mnt (where mnt is 1,2-dicyanoethylene-1,2-dithiolate) complexes of palladium<sup>6</sup> and platinum<sup>7</sup> have shown that the size of the counter ion is of crucial importance in the design of molecular metals of this type and we are therefore investigating the salts of  $[\text{M}(\text{dmit})_2]$  anions with the group 1 and 2 cations.  $\text{K}_{0.4}[\text{Ni}(\text{dmit})_2]$  was obtained as black poorly formed plates by electrocrystallisation using 0.5 mm diameter platinum wire electrodes at a constant voltage of 1.5 V from acetonitrile solution. The stoichiometry of the material was determined by elemental analysis (Found: S, 63.10; C, 15.39; Ni, 12.0, K, 3.01%. Calc. for  $\text{C}_6\text{S}_{10}\text{K}_{0.4}\text{Ni}$ : S, 68.65; C, 15.42; Ni, 12.57; K, 3.35%). The poor quality of the crystals has so far prevented a structure determination.

Electrical conduction measurements were carried out by d.c. 4-probe measurements using aquadag as the contact material. The room temperature conductivity along the longest axis of the crystals was found to lie between 10 and 230  $\text{S cm}^{-1}$ . The temperature dependence of the conductivity was investigated for numerous crystals and the majority of the crystals showed no evidence of a metal to semiconductor transition. Figure 1 shows the behaviour of three typical crystals. Some crystals showed a steady increase in conductivity

down to 20 K. Others, after the conductivity increased with decreasing temperature down to between 160 and 120 K, showed a small decrease in conductivity below this temperature. However, the fall in conductivity was small compared with that observed for compounds known to undergo a metal to semiconductor transition. For some crystals abrupt falls in conductivity were observed at various temperatures and this type of behaviour in the past has been ascribed to the development of microcracks in the sample.<sup>8</sup> These differences in behaviour from sample to sample could either be due to measurements being made along different crystallographic axes for different crystals or to poor crystal quality.

The behaviour described above is in marked contrast to the behaviour of the previous room temperature of this type based on sulphur donor ligands,  $\text{Li}_{0.8}(\text{H}_3\text{O})_{0.33}[\text{Pt}(\text{mnt})_2] \cdot 2.67 \text{H}_2\text{O}$  which undergoes a metal to semiconductor transitions with  $T_c = 215$  K.<sup>7</sup> The stabilisation of the metallic state to low temperatures in  $\text{K}_{0.4}[\text{Ni}(\text{dmit})_2]$  must arise from the strong intermolecular interactions between the  $[\text{Ni}(\text{dmit})_2]^{x-}$  anions facilitated by the small size of the cations which allow the close approach of the anions in the lattice.

Further studies are in progress and results obtained for other salts of  $[\text{M}(\text{dmit})_2]$  anions (where M is Ni, Pd, or Pt)

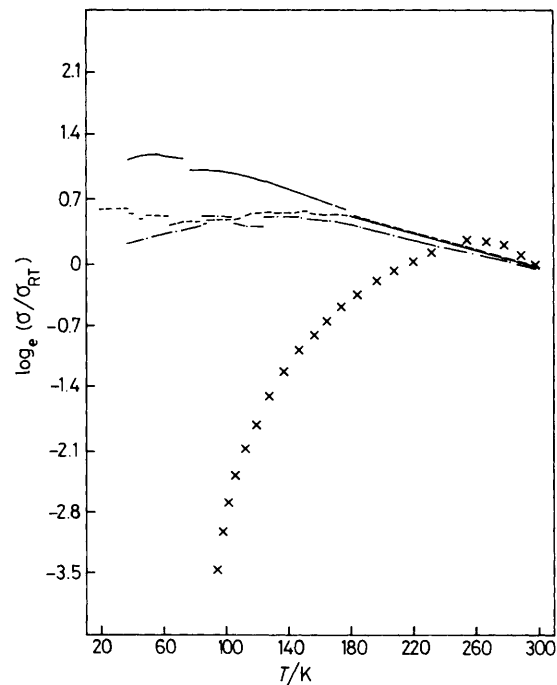
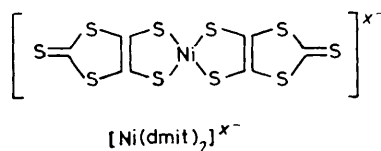


Figure 1. The variation of electrical conductivity as a function of temperature for three crystals of  $\text{K}_{0.4}[\text{Ni}(\text{dmit})_2]$  (---, - · -, —) and  $\text{Li}_{0.8}(\text{H}_3\text{O})_{0.33}[\text{Pt}(\text{mnt})_2] \cdot 2.67\text{H}_2\text{O}$  (× × ×, ref. 7.)

indicate that the size of the cation and the nature of the central metal can radically change the properties of the salts.

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