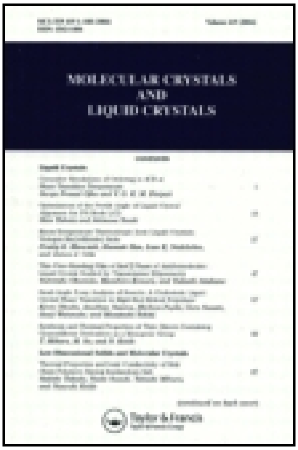

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MeCNQn-TCNQ$_2$, a Low Conductivity Metal above 300 K?

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MeCNQn-$TCNQ_2$, A LOW CONDUCTIVITY METAL ABOVE 300 K?

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Abstract - The 1:2 complex formed between 1-methyl-4-cyanoquinolinium (MeCNQn) and 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) is triclinic with a = 6.533, b = 7.842, c = 15.698 Å, α = 83.31, β = 85.61 and γ = 81.95°. The crystals exhibit a conductivity maximum centred at 300 K with $\sigma(max)$ = 0.1 to 1 S cm^{-1}. Above 300 K the conductivity has a metallic temperature dependence whereas below 200 K it is activated with E_a = 0.06(2) eV. The magnetic susceptibility shows singlet-triplet behaviour with J = 0.013(2) eV.

INTRODUCTION

The electrical and magnetic properties of the title complex were first reported by Kepler et al.[1-2] in 1963. We have reinvestigated the properties of MeCNQn-$TCNQ_2$ to establish the effect of aging. The results obtained from a freshly prepared crystal batch and one prepared at the ICI Corporate Laboratory in the mid 1960s are in close agreement but differ slightly from the published data of Kepler et al..

EXPERIMENTAL

Fine needles of the 1:2 salt were obtained when a hot acetonitrile solution of MeCNQn iodide and neutral TCNQ (1:2 mole ratio) was allowed to cool slowly to ambient temperature. Analysis: calc. C 72.79, H 2.95, N 24.26 %; found, C 72.62, H 3.09, N 24.50 %.

The needle axis conductivity was determined in the temperature range 70 to 350 K using a four-probe technique with silver dag electrodes. With currents of 1 and 100 μA the crystals showed no more than 20 % deviation from ohmic behaviour.

Static susceptibility measurements were carried out, using a Faraday technique, on 30 mg samples placed in a diamagnetic teflon cup and suspended, by aluminium connecting rods, from the head of a CI/Robal microbalance. The Faraday balance was equipped with a Newport magnet with 4" tapered pole pieces and with an Air Poducts Displex refrigerator for variable temperature studies in the range 10 to 300 K. Helium gas was admitted to the apparatus to aid heat-transfer.

RESULTS AND DISCUSSION

The magnetic susceptibility of MeCNQn-$TCNQ_2$ is characteristic of TCNQ salts of the intermediate conductivity class and is described by the equation[1],

$$\chi = \frac{2Ng^2\mu_B^2}{3kT}[1 + \tfrac{1}{3}\exp(J/kT)]^{-1},$$

where J is the singlet-triplet separation, μ_B is the Bohr magneton and N is the number of radical ion pairs. The excitation energy may be obtained, if J is greater than a few kT, from the slope of $\ln(\chi T)$ versus T^{-1} or, alternatively, from $J = 1.61kT_{max}$ where T_{max} is the temperature which corresponds to the susceptibility maximum

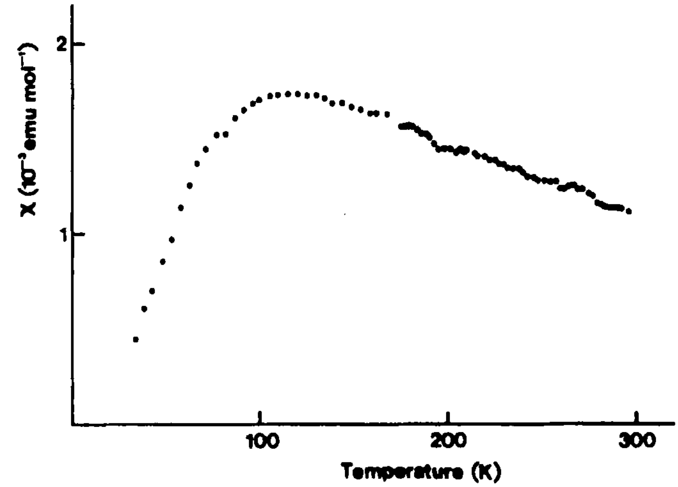

FIGURE 1 Temperature dependence of the molar magnetic susceptibility corrected for core diamagnetism.

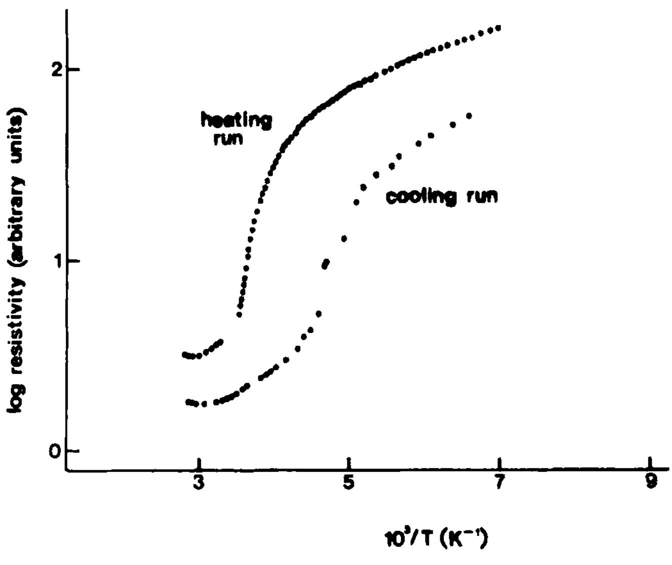

FIGURE 2 Temperature dependence of the resistivity.

(see Figure 1). These methods give J = 0.013(2) eV for the old and new batches of $MeCNQn\text{-}TCNQ_2$ and substitution into the equation above yields a theoretical susceptibility at 300 K of 1.07(3) x 10^{-3} e.m.u. mol^{-1} in close agreement with the experimental value of 1.2(4) x 10^{-3} e.m.u. mol^{-1}. Kepler[1] reported a slightly higher value of J = 0.018 eV.

The electrical properties show some sample dependence but the general variation of the conductivity with temperature is the same for both the old and new crystal batches. The crystals exhibit a maximum in the conductivity centred at 300 K with σ(max) = 0.1 to 1 S cm^{-1}. There is a quasi-metallic temperature dependence above 300 K and, at low temperatures, an exponential dependence with E_a = 0.06(2) eV measured between 70 and 200 K. Connecting these regions the conductivity decreases abruptly, as shown in Figure 2, and hysteresis occurs upon thermal recycling. Kepler et al.[1-2] have reported an activation energy of 0.08 eV consistent with our low-temperature value but do not mention the transition. Metal-to-semiconductor transitions of this type are not uncommon and are often attributed to distortions of the quasi-one-dimensional stacks. In this case, differential scanning calorimetry has not provided evidence of a phase change and the nature of the transition remains unclear.

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REFERENCES

1. R.G.Kepler, J. Chem. Phys., 39, 3528 (1963).

2. W.J.Siemons, P.E.Bierstedt and R.G.Kepler, J. Chem. Phys., 39, 3523 (1963).