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SOLVENT INDUCED TRANSITIONS IN TCNQ SALTS

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Abstract Differential scanning calorimetry (DSC) has revealed transitions close to 229 K and 214 K in TCNQ salts prepared from acetonitrile solution but no transitions in the salts recrystallised from ethyl acetate, ethanol and acetone or mixtures of these solvents. The double transition is characteristic of acetonitrile and may be attributed to the melting point at 229 K and to a solid state transformation at 214 K. It is assumed

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that solvent is trapped in pockets within the crystal lattice. A comparison of the enthalpy data of acetonitrile and the TCNQ salts shows the solvent concentration to be as high as 0.14 moles per mole of the TCNQ salt. The conductivity and magnetic susceptibility show anomalous behaviour close to 229 K.

INTRODUCTION

Many of the solid state properties of TCNQ salts are sample dependent but the purity of the crystals has rarely been questioned. Little is known of the trapped solvent in these salts and its effect on the electrical and magnetic properties although, as long ago as 1974, Flandrois et al. [1,2] reported variable solvent inclusion in their TCNQ salts. They were, however, unable to distinguish between randomly distributed solvent molecules and pockets of solvent trapped by the crystal lattice. Three of their salts also formed well-defined stoichiometric phases with CH_3CN. Subsequent crystallographic studies have shown that in these salts the solvent molecule occupies a hole within the unit cell and forms an integral part of the crystal lattice [3,4]. Many other TCNQ salts are known to form stoichiometric complexes with CH_3CN [3-5], C_6H_6 [6], CH_2Cl_2 [7] and H_2O [8,9]. Upon outgassing the crystals contract and show a marked change in their physical properties [10].

In this paper the discussion is limited to a series of bis-pyridinium TCNQ salts which do not form a well-defined complex with the solvent but which contain isolated pockets of solvent trapped by the crystal lattice. The evidence has

been provided by differential scanning calorimetry. Solvent inclusion is not uncommon in crystals grown from solution [11] and it has been established by electron and optical microscopy that such inclusions can vary in size from several tens of angstroms to several hundreds of microns [12, 13] and take the form of thin continuous channels, lateral layers and small isolated pockets [14,15].

DIFFERENTIAL SCANNING CALORIMETRY

DSC studies were carried out on 15 to 20 mg samples using a Mettler TA3000 Thermal Analysis System. The temperature was increased from 100 K to 400 K at a rate of 5 K per minute and the peaks shown on the DSC trace were integrated using the Mettler TC10 thermal analysis processor. The DSC trace of spectrophotometric grade acetonitrile (Aldrich) shows a distinctive double transition with ΔH = 8.3 kJ mol^{-1} at 229 K and ΔH = 0.80 kJ mol^{-1} at 214 K. The transitions may be attributed to the melting point and a structural modification respectively. The Aldrich Chemical Company gives the melting point of acetonitrile as 225 K [16] which falls between the two values.

TCNQ salts which have been prepared from acetonitrile solution frequently show a DSC transition at 229 K with a weaker transition at 214 K. The enthalpy changes are batch and sample dependent and the larger well-developed crystals usually display higher enthalpies than the microcrystalline samples. When the salts are recrystallised from other solvents (e.g. acetone, ethanol and ethyl acetate) the transitions are not observed.

The DSC results suggest that acetonitrile is trapped in pockets by the crystal lattice. This is supported by the fact that DSC traces obtained at higher temperatures show a series of irreproducible transitions. These may correspond to pockets of solvent bursting free and, indeed, when the samples are thermally recycled in the temperature range 100 to 400 K the enthalpy change at 229 K diminishes. If this interpretation is correct then a comparison of the enthalpy of fusion of acetonitrile with the enthalpy data obtained for the TCNQ salts will provide the concentration of trapped solvent. The results are summarised in Table 1.

ELECTRICAL TRANSITIONS

The solvated TCNQ salts (see Table 1) show anomalous electrical behaviour at the melting point of acetonitrile. The conductivity temperature dependence of 1,4-bis(N-pyridinium methyl)benzene-$TCNQ_4$ and N,N'-bis(p-cyanophenyl)-4,4'-bipyridinium-$TCNQ_4$, determined along the TCNQ stacking axes, are shown in Figures 1 and 2. It is worth noting that the latter shows a pronounced transition and hysteresis whereas the former exhibits only a slight change in slope centred about 229 K. It is assumed that the transitions arise as a result of localised structural distortions as the trapped solvent contracts upon freezing. The different behaviour at the melting point may be explained by considering the TCNQ stacking characteristics. In the N,N'-bis(p-cyanophenyl)-4,4'-bipyridinium salt interplanar spacings of 3.28, 3.36 and 3.00 Å repeat along the TCNQ stacks [17] whereas in the 1,4-bis(N-pyridinium methyl)benzene salt there are altern-

TABLE 1. Transition temperatures and enthalpy data of single crystal samples of the TCNQ salts recrystallised from acetonitrile solution

Salt	T_p/K	ΔH/J g^{-1}	[complex]:[CH_3CN]
N-benzyl-4-(4'-pyridyl)-pyridinium-$TCNQ_2$	224(3)	0.12-0.20	1:0.009 to 1:0.016
N,N'-bis(p-cyanophenyl)-4,4'-bipyridinium-$TCNQ_4$	226(3)	0.05-0.51	1:0.007 to 1:0.072
1,2-bis(N-benzyl-4-pyridinium)ethylene-$TCNQ_5$	226(3)	0.04-0.25	1:0.006 to 1:0.042
1,4-bis(N-pyridinium)butane-$TCNQ_4$	228(3)	0.29-0.45	1:0.036 to 1:0.056
1,4-bis(N-pyridinium methyl)benzene-$TCNQ_4$	228(3)	0.29-1.08	1:0.038 to 1:0.140

All microcrystalline samples gave [complex]:[CH_3CN] > 1:0.001

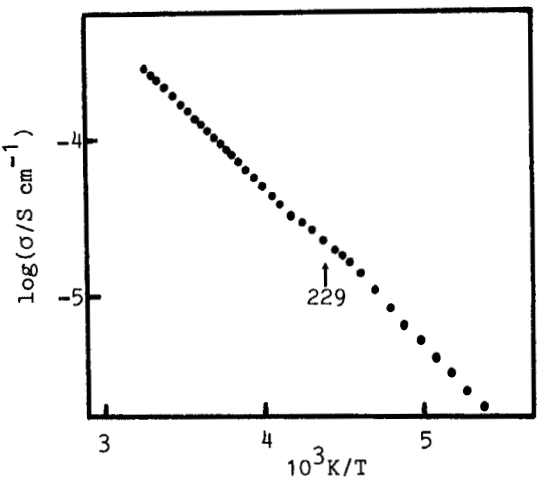

FIGURE 1. Conductivity temperature dependence of 1,4-bis(N-pyridinium methyl)benzene-$TCNQ_4$.

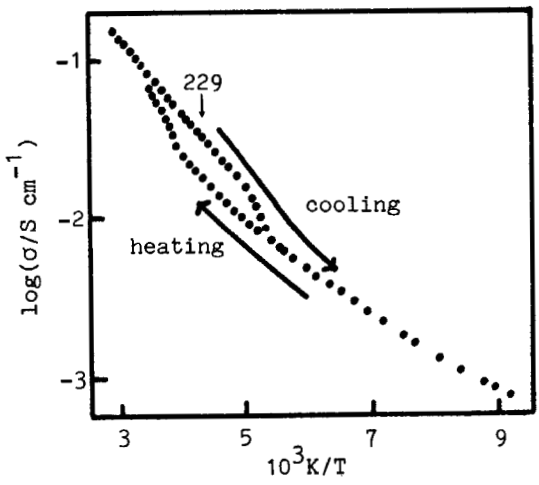

FIGURE 2. Conductivity temperature dependence of N,N'-bis(p-cyanophenyl)-4,4'-bipyridinium-$TCNQ_4$.

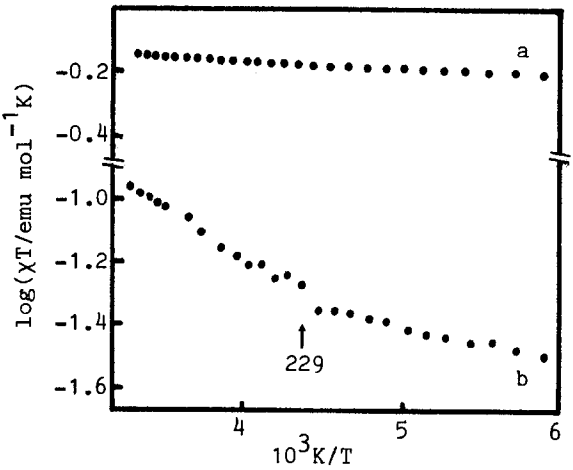

FIGURE 3. Magnetic susceptibility temperature dependence of 1,4-bis(N-pyridinium methyl)benzene-$TCNQ_4$ samples with [salt]:[CH_3CN] ~ 1:0.001 (a) and 1:0.14 (b).

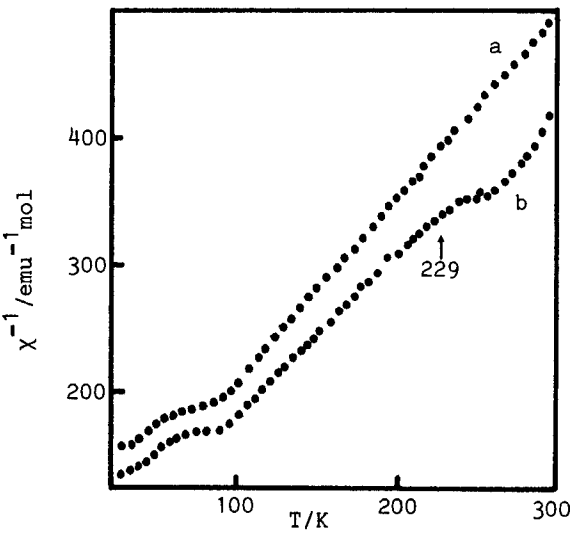

FIGURE 4. Magnetic susceptibility temperature dependence of N,N'-bis(p-cyanophenyl)-4,4'-bipyridinium-TCNQ4 samples with [salt]:[CH_3CN] ~ 1:0.001 (a) and 1:0.072 (b).

ate spacings of 3.22 and 3.40 Å [18]. In this salt the low conductivity of the diadic TCNQ structure is unlikely to be significantly affected by local distortions induced by the solvent freezing.

STATIC SUSCEPTIBILITY

The conductivity transitions are mimicked by the magnetic susceptibility data of Figures 3 and 4. The solvated samples show anomalous behaviour close to 229 K whereas samples with low concentrations of trapped solvent do not undergo these transitions. The properties of the salts are quite different. The magnetic susceptibility of 1,4-bis(N-pyridinium methyl)benzene-$TCNQ_4$ is activated (Figure 3) whereas the susceptibility of N,N'-bis(p-cyanophenyl)-4,4'-bipyridinium-$TCNQ_4$ shows Curie-Weiss behaviour (Figure 4). It varies as $\chi = C/(T + \theta)$ where $C = 0.67$ emu $mol^{-1}K$ from which the effective Bohr magneton number is 2.33 μ_B. The value corresponds to two unpaired spins per stoichiometric unit in agreement with chemical formula. It is of interest that both samples of the N,N'-bis(p-cyanophenyl)-4,4'-bipyridinium salt show a transition at 80 K which may be attributed to a structural modification.

ELECTRON SPIN RESONANCE

ESR studies on the solvated sample of 1,4-bis(N-pyridinium methyl)benzene-$TCNQ_4$ also provided a transition but at 180 K (Figure 5) whereas DSC, conductivity and static suscept-

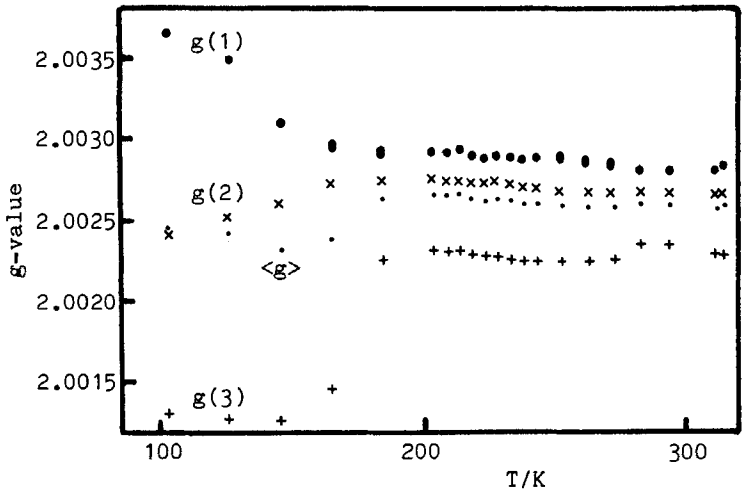

FIGURE 5a. Temperature dependence of the g-value of a 1,4-bis(N-pyridinium methyl)benzene-$TCNQ_4$ sample with [salt]:[CH_3CN] ~ 1:0.14.

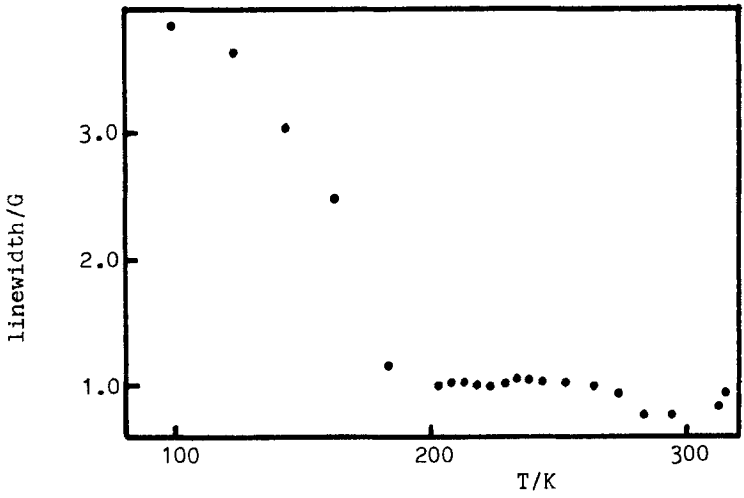

FIGURE 5b. Temperature dependence of the linewidth of a 1,4-bis(N-pyridinium methyl)benzene-$TCNQ_4$ sample with [salt]:[CH_3CN] ~ 1:0.14.

ibility studies on the same crystal batch gave transitions in the range 220 to 240 K. To understand this lower transition temperature it is necessary to carry out ESR studies on the remaining TCNQ salts in Table 1. However, as a preliminary explanation, it may be assumed that at high temperatures ($T > 180$ K) there is a high radical mobility and a large spin-spin exchange interaction which causes the narrow spectral linewidth. The mobility arises because some $TCNQ^-$ is in solution in the solvent pockets. It is assumed that the solutions do not freeze hard enough to inhibit the radical motion and hence the spin-spin exchange until their temperatures are well below the normal melting point of the solvent. The observed transition temperature is ~50 K below the integrated peak temperature obtained from DSC studies.

EPILOG

Throughout the literature many other TCNQ salts have shown unexpected behaviour close to the melting point of the solvent used in the preparation and the transitions have been attributed to surface effects, states in the band gap and to structural changes. An example, relevant to this work, is 1,2-bis(N-ethyl-4-pyridinium)ethane$_2$TCNQ$_9$ which shows an anomalous transition at 250 K but remains metallic to $T <$ 10 K [8]. The DSC trace of a fresh sample has shown a small endothermic transition at 229 K. This and many other transitions may be attributed to the presence of trapped solvent and recrystallisation from a lower melting point liquid may enhance the conductivity to below the usual transition temperature.

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