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FERROMAGNETIC BEHAVIOR OF 1:2 TCNQ/TCNQ$^{\cdot-}$ MIXED SALTS AT ROOM TEMPERATURE

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Abstract Ferromagnetic behavior at room temperature was observed in the tetramethylammonium (NMe_4^+) and cesium (Cs^+) salts of tetracyanoquinodimethane (TCNQ) and its radical anion ($TCNQ^{\cdot-}$) in a molecular ratio of 1:2. The saturation magnetizations and coercive forces are 0.79 emu/mol and ca. 300 Oe for (NMe_4^+•$TCNQ^{\cdot-}$)•1/2TCNQ, and 1.46 emu/mol and ca. 100 Oe for (Cs^+•$TCNQ^{\cdot-}$)• 1/2TCNQ, respectively. In contrast, the 1:1 TCNQ/ $TCNQ^{\cdot-}$ mixed tetraethyammonium (NEt_4^+) salt, (NEt_4^+•$TCNQ^{\cdot-}$)•TCNQ, exhibited no ferromagnetic behavior at room temperature and also at lower temperatures.

INTRODUCTION

Very recently we observed ferromagnetic behavior at room temperature for a 1:2 mixed NMe_4^+ salt of a tetrafluoro-substituted TCNQ ($TCNQF_4$) and its radical anion ($TCNQF_4^{\cdot-}$), ($NMe_4^+ \cdot TCNQF_4^{\cdot-}$)•1/2$TCNQF_4$.[1] As for spin-ordering temperature this observation is quite remarkable, since the highest value (16.1 K) has so far been reported for a tetrakis(dimethylamino)ethylene/fullerene complex.[2] Unfortunately, the saturation magnetization (M_S) (5.72 emu/mol) is very small as compared with that (5,580 emu/mol) of organic ferromagnets with full spin participation.[3] Now, the similar room-temperature ferromagnetic behavior was also recognized in 1:2 TCNQ/$TCNQ^{\cdot-}$ mixed NMe_4^+ and Cs^+ salts, ($NMe_4^+ \cdot TCNQ^{\cdot-}$)•1/2TCNQ and ($Cs^+ \cdot TCNQ^{\cdot-}$)• 1/2TCNQ, whose crystal structures and magnetic properties are described in this paper.

EXPERIMENTAL

When the NMe_4^+ salt of $TCNQ^{\cdot-}$ ($NMe_4^+ \cdot TCNQ^{\cdot-}$)[4] was recrystallized from acetonitrile/ ether in the presence of an equimolar amount of TCNQ, a violet plate crystal (mp 225-226 °C) of ($NMe_4^+ \cdot TCNQ^{\cdot-}$)•1/2TCNQ was obtained. According to the previous literature,[5] the reaction of TCNQ with an excess of CsI in acetonitrile/ methanol gave a ($Cs^+ \cdot TCNQ^{\cdot-}$)• 1/2TCNQ salt, whose single crystal (mp > 300 °C) was obtained by recrystallization from acetonitrile/ether. The similar recrystallization by use of the NEt_4^+ salt of $TCNQ^{\cdot-}$ ($NEt_4^+ \cdot TCNQ^{\cdot-}$) in place of $NMe_4^+ \cdot TCNQ^{\cdot-}$ gave a normal 1:1 TCNQ/$TCNQ^{\cdot-}$ mixed salt, ($NEt_4^+ \cdot TCNQ^{\cdot-}$)•TCNQ (mp 232-233 °C). The satisfactory elemental analyses were obtained. For ($NMe_4^+ \cdot TCNQ^{\cdot-}$)•1/2TCNQ: Anal. calcd. for $C_{22}H_{18}N_7$: C 69.46, H 4.77, N 25.77; found: C 69.52, H 4.81, N 25.79. For ($NEt_4^+ \cdot TCNQ^{\cdot-}$)• TCNQ: Anal. calcd. for $C_{32}H_{28}N_9$: C 71.36, H 5.24, N 23.40; found C 71.42, H 5.22, N 23.51. The X-ray analyses of ($NMe_4^+ \cdot TCNQ^{\cdot-}$)• 1/2TCNQ and ($NEt_4^+ \cdot TCNQ^{\cdot-}$)•TCNQ single crystals were performed on a Rigaku AFC5R diffractometer on purple prisms (($NMe_4^+ \cdot TCNQ^{\cdot-}$)• 1/2TCNQ: 0.20 x 0.10 x 0.10 mm^3; ($NEt_4^+ \cdot TCNQ^{\cdot-}$)•TCNQ: 0.10 x 0.20 x 0.30 mm^3) mounted on a glass rod by the ω-2θ method. For ($NMe_4^+ \cdot TCNQ^{\cdot-}$)• 1/2TCNQ 3283 of a total 3553 collected reflections, and for ($NEt_4^+ \cdot TCNQ^{\cdot-}$)•TCNQ 2175 of a total 2359 collected reflections were observed [$I > 3\sigma(I)$], respectively. The crystal data were as follows. For ($NMe_4^+ \cdot TCNQ^{\cdot-}$)•1/2TCNQ: $C_{22}H_{18}N_7$, M = 380.43, monoclinic, space group $P2_1/n$, a = 7.808(2), b = 9.692(1), c = 27.417(2) Å, β = 94.78(1)°, V = 2067.6(5) $Å^3$, Z = 4, ρ_{calcd} = 1.222 $g \cdot cm^{-3}$, F (000) = 796, λ = 1.54178 Å, T = 300(1) K, $\mu(CuK\alpha)$ = 6.19 cm^{-1}. For ($NEt_4^+ \cdot TCNQ^{\cdot-}$)•TCNQ: $C_{32}H_{28}N_9$, M = 538.63, triclinic, space group

$P1$, a = 7.8427(6) , b = 14.4483(9), c = 7.4934(5) Å, α = 90.190(7), β = 118.195(6), γ = 100.186(6)°, V = 732.9(1) Å^3, Z = 1, ρ_{calcd} = 1.220 g·cm^{-3}, F (000) = 283, λ = 1.54178 Å, T = 300(1) K, $\mu(Cu K\alpha)$ = 6.08 cm^{-1}. The structure was solved by direct methods (SHELX-86) and expanded using Fourier techniques (DIRDIF92). The data were corrected for absorption, Lorentz and polarization effects. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Refinement by full-matrix least-squares calculations converged at R = 0.139 and Rw = 0.103 for (NMe_4^+•$TCNQ^{-\cdot}$)•1/2TCNQ and at R = 0.073 and Rw = 0.079 for (NEt_4^+•$TCNQ^{-\cdot}$)•TCNQ. The ORTEP drawings, and full tables of fractional atomic coordinates and interaction bond distances have been deposited at the Cambridge Crystallographic Data Centre. The electrical conductivity was measured by using four-probe method at room temperature. The electrical contact was achieved with gold paste. The magnetizations were measured at different temperatures and applied fields by using a SQUID magnetometer (MPMS, Quantum Design). The diamagnetic susceptibility (χ_{dia}) was obtained from a slope of a straight line in the magnetization curve or by a Pascal method.

THE CRYSTAL STRUCTURE OF (NMe_4^+•$TCNQ^{-\cdot}$)• 1/2TCNQ

The crystal structure of (NMe_4^+•$TCNQ^{-\cdot}$)•1/2TCNQ is shown in Figure 1. Each column composed of 1:2 TCNQ/$TCNQ^{-\cdot}$ molecules is formed along b axis, and one NMe_4^+ column intervenes between neighboring TCNQ/$TCNQ^{-\cdot}$ columns (see Figure 2). The molecules **A** and **A'** form a tight dimer (the interplanar distance (3.15 Å) is remarkably short as compared with that of a normal π cloud (3.54 Å),[6] the dihedral angle between the planes 2.9°, and the slip distance 0.87 Å), and the dimer makes contact with one molecule **B** molecule by separation of the interplanar distance of 3.22 Å and the slip

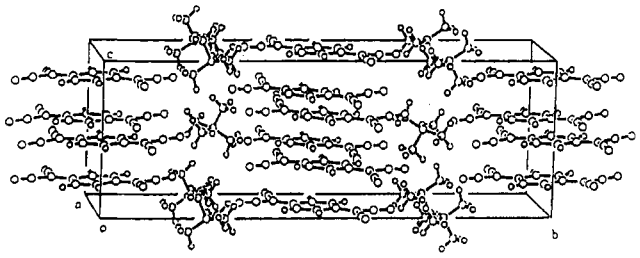


FIGURE 1 The crystal structure of (NMe_4^+•$TCNQ^{-\cdot}$)•1/2TCNQ: the whole view.

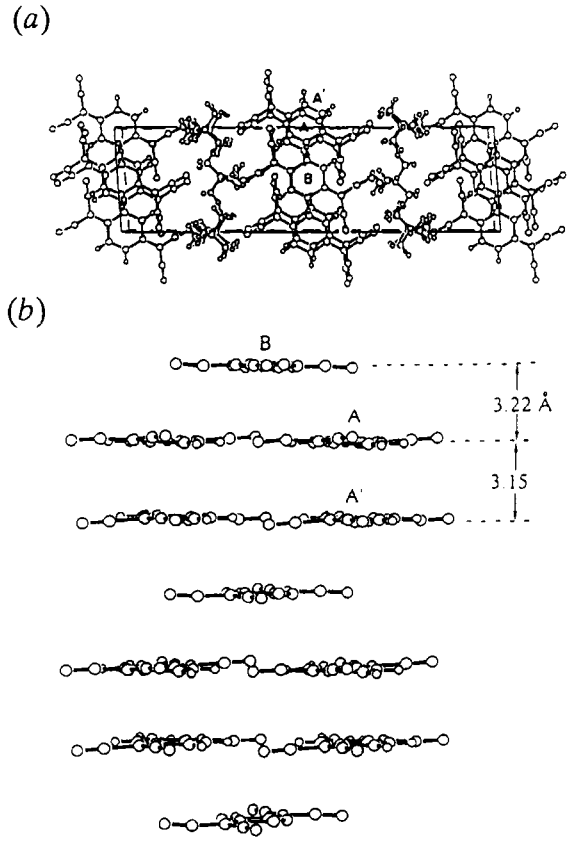
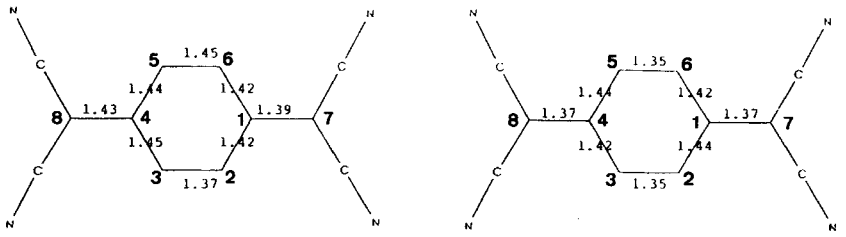


FIGURE 2 The whole packing views projected along (a) *c* and (b) *b* axes for $(NMe_4^+ \cdot TCNQ^{-\cdot}) \cdot 1/2TCNQ$.

distance of 3.68 Å. The main C-C bond distances of **A** (**A'**) and **B** are shown in Figure 3. For **A** (**A'**) the distances are slightly different between C(1)-C(2), C(3)-C(4), C(4)-C(5) and C(1)-C(6) bonds, between C(2)-C(3) and C(5)-C(6) bonds, and between C(1)-C(7) and C(4)-C(8) bonds, respectively, because of the molecular distortion. However, the mean C-C bond distances (1.43, 1.41, and 1.41 Å) are close to the corresponding values of the $TCNQ^{-\cdot}$ molecule for $Na^+ \cdot TCNQ^{-\cdot}$ (1.42, 1.37, and 1.42 Å),[7] regarding **A** (**A'**) as a near $TCNQ^{-\cdot}$ molecule. The quinodimethane skeleton of **B** locates on the crystallographic center of symmetry. Therefore, **B** is almost planar and the distances of C(1)-C(2) and C(4)-C(5) bonds, C(3)-C(4) and C(1)-C(6) bonds, C(2)-C(3) and C(5)-C(6) bonds, and C(1)-C(7) and C(4)-C(8) bonds are equivalent to each other. The mean C-C bond distances (1.43, 1.35 and 1.37 Å) are also almost equal to the corresponding values of TCNQ (1.45, 1.35 and 1.37 Å).[8] Accordingly, **B** is certainly a near TCNQ molecule. It is difficult to determine how much electron transfer from the $TCNQ^{-\cdot}$ dimer



A (A') B

FIGURE 3 The C-C bond distances (Å) of the molecules **A** (**A'**) and **B** for $(NMe_4^+ \cdot TCNQ^{-\cdot}) \cdot 1/2TCNQ$.

to the TCNQ molecule actually occurs from comparison of the C-C bond distnaces between the **A** (**A'**) and **B**, and reference $TCNQ^{-\cdot}$ and TCNQ molecules. Here, it is worthy that the crystal structure of $(NMe_4^+ \cdot TCNQ^{-\cdot}) \cdot 1/2TCNQ$ is compared with that of $(Cs^+ \cdot TCNQ^{-\cdot}) \cdot 1/2TCNQ$,[5] only one exception as an alkali ion/$TCNQ^{-\cdot}$ salt, which usually involves no TCNQ molecule. The Cs^+ (1.67 Å) and NMe_4^+ ions (2.05 Å) have close ionic radii, and are intermediate in size between larger alkylammonium ions with the preferential formation of a 1:1 TCNQ/$TCNQ^{-\cdot}$ mixed salt and smaller alkali ions, where a normal $TCNQ^{-\cdot}$ salt is obtained. It is readily supposed that an intermediate 1:2 TCNQ/$TCNQ^{-\cdot}$ mixed salt can be preferentially produced by use of Cs^+ and NMe_4^+ ions. Also in the crystal structure of $(Cs^+ \cdot TCNQ^{-\cdot}) \cdot 1/2TCNQ$[9] the TCNQ/$TCNQ^{-\cdot}$ molecules stack parallel to *b* axis to form a column, which has a period of charge-separated $TCNQ^{-\cdot}$/TCNQ/$TCNQ^{-\cdot}$ triads. The $TCNQ^{-\cdot}$/$TCNQ^{-\cdot}$ contact has almost the same geometry with that in $(NMe_4^+ \cdot TCNQ^{-\cdot}) \cdot 1/2TCNQ$, but the interplanar distance (3.26 Å) is larger by ca. 0.1 Å. In the TCNQ/$TCNQ^{-\cdot}$ contact the interplanar distance (3.22 Å) is the same with that in $(NMe_4^+ \cdot TCNQ^{-\cdot}) \cdot 1/2TCNQ$, but the geometry is very different, as is shown from a fairly smaller slip distance (2.03 Å) in spite of almost the same slip direction. As a result, one $TCNQ^{-\cdot}$ dimer is arranged with respect to one TCNQ molecule in a different fashion between the NMe_4^+ and Cs^+ salts, giving rise to different electrical conducting and magnetic properties.

THE CRYSTAL STRUCTURE OF $(NEt_4^+ \cdot TCNQ^{-\cdot}) \cdot TCNQ$

Figure 4 shows the crystal structure of $(NEt_4^+ \cdot TCNQ^{-\cdot}) \cdot TCNQ$, where the TCNQ/$TCNQ^{-\cdot}$ in a 1:1 composition and NEt_4^+ layers form alternating columns along *c* axis. This crystal structure is very similar to that of $(NHEt_3^+ \cdot TCNQ^{-\cdot}) \cdot TCNQ$ previously analyzed.[10] In each column the molecules **A** (**A'**) and **B** (**B'**) form a tight dimer, as is obvious from the interplanar distance (3.13 Å), the dihedral angle between

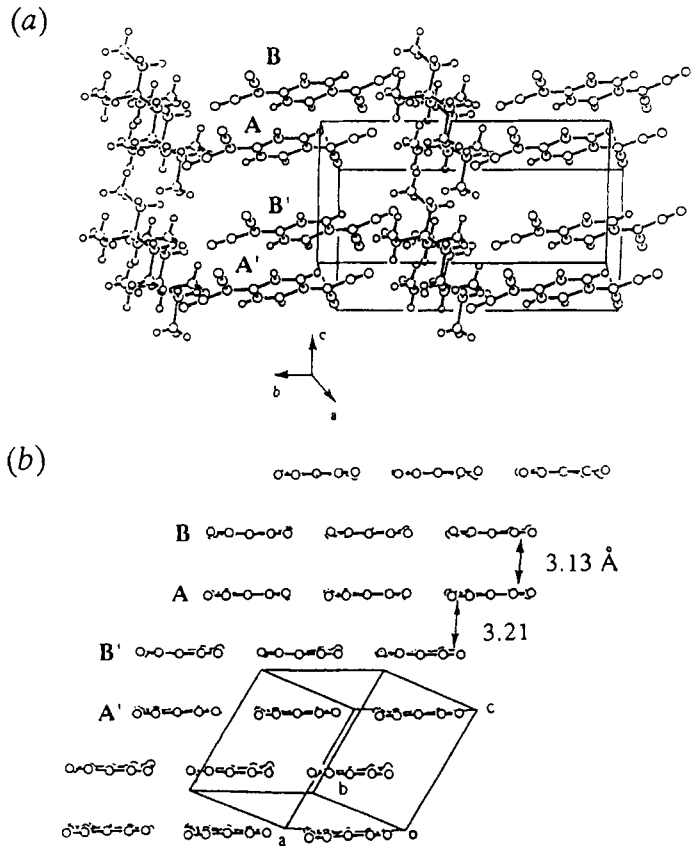
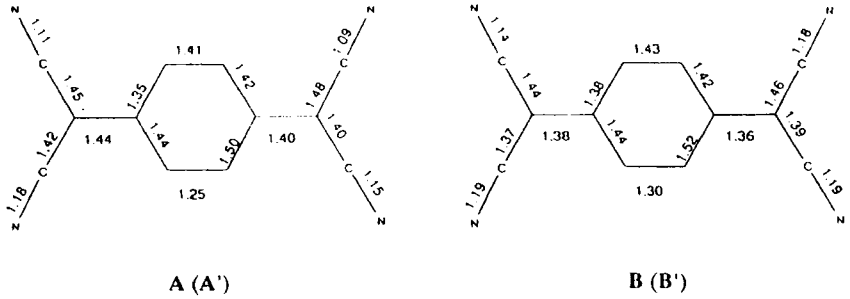


FIGURE 4 The crystal structure of $(NEt_4^+ \cdot TCNQ^{\cdot -}) \cdot TCNQ$: (a) the whole view and (b) the packing view along *a* axis.



A (A') B (B')

FIGURE 5 The bond distances (Å) of the molecules **A** (**A'**) and **B** (**B'**) for $(NEt_4^+ \cdot TCNQ^{\cdot -}) \cdot TCNQ$.

the planes (0.5°), and the sliped distance (2.03 Å). The dimers are separated from each other by the interplanar distance of 3.21 Å and the slip distance of 4.46 Å. The molecules **A** (**A'**) and **B** (**B'**) have almost the same molecular structures from their bond distances as shown in Figure 5. This implies that both molecules **A** (**A'**) and **B** (**B'**) can be assigned to an intermediate of TCNQ and $TCNQ^{-\cdot}$ as a result of whole distribution of an unpaired electron on both TCNQ and $TCNQ^{-\cdot}$ molecules in dimerization.

ELECTRICAL CONDUCTING AND MAGNETIC PROPERTIES OF $(NMe_4^{+}\cdot TCNQ^{-\cdot})\cdot 1/2TCNQ$ AND $(Cs^{+}\cdot TCNQ^{-\cdot})\cdot 1/2TCNQ$

As expected from the crystal structure, $(NMe_4^{+}\cdot TCNQ^{-\cdot})\cdot 1/2TCNQ$ showed not so high electrical conductivity at room temperature (6×10^{-5} S/cm) like $(Cs^{+}\cdot TCNQ^{-\cdot})\cdot 1/2TCNQ$ (2×10^{-3} S/cm).[11] Nevertheless, their magnetic properties gave very remarkable results.

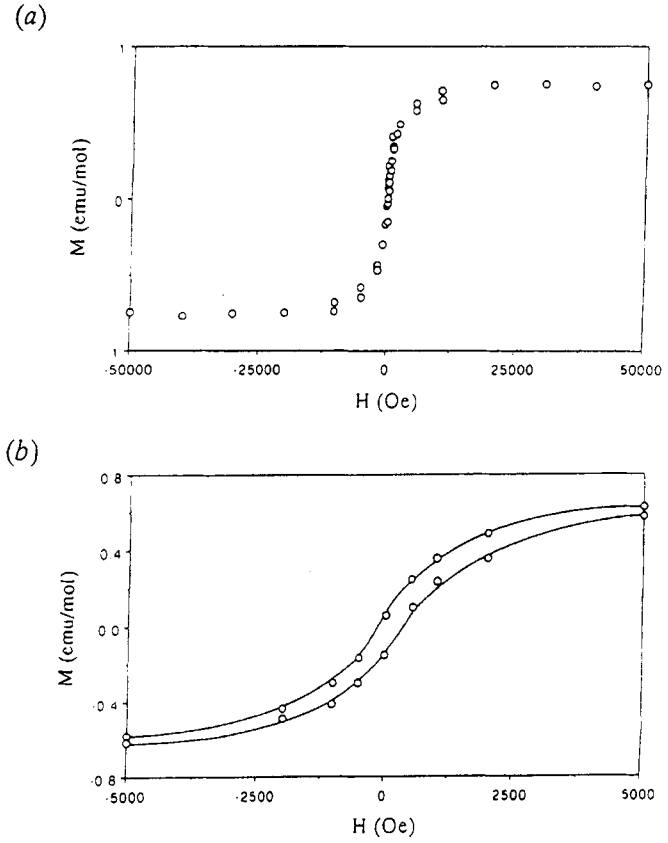


FIGURE 6 The magnetization curves of $(NMe_4^{+}\cdot TCNQ^{-\cdot})\cdot 1/2TCNQ$ in the applied field range of (a) ±50 kOe and (b) ±5 kOe at room temperature.

The magnetization curves of $(NMe_4^+ \bullet TCNQ^{-\cdot})\bullet 1/2TCNQ$ were measured at different temperatures of 300 to 348 K in the applied field (H) range of ±50 kOe by using a SQUID magnetometer. Figure 6 shows a magnetization curve at 300 K, where the magnetization (M) at each H is corrected by subtracting a diamagnetic contribution ((χ_{dia} = -1.56×10^{-3} emu/mol) x H) from the observed value. Obviously, a ferromagnetic behavior can be recognized at room temperature, although the M_S value is extremely small (0.79 emu/mol). The coercive force (H_C) is remarkably large in this case (ca. 300 Oe) in comparison with those in other organic ferromagnets obtained so far. The magnetization curve measurement was also carried out for $(Cs^+ \bullet TCNQ^{-\cdot}) \bullet 1/2TCNQ$ and a ferromagnetic behavior was again observed at room temperature (see Figure 7). The M_S, H_C and χ_{dia} values are 1.46 emu/mol, ca. 100 Oe and -3.17×10^{-4} emu/mol, respectively. For both 1:2 TCNQ/$TCNQ^{-\cdot}$ mixed salts the ferromagnetic behavior remains till 348 K, a upper limit of temperature in our experiment.

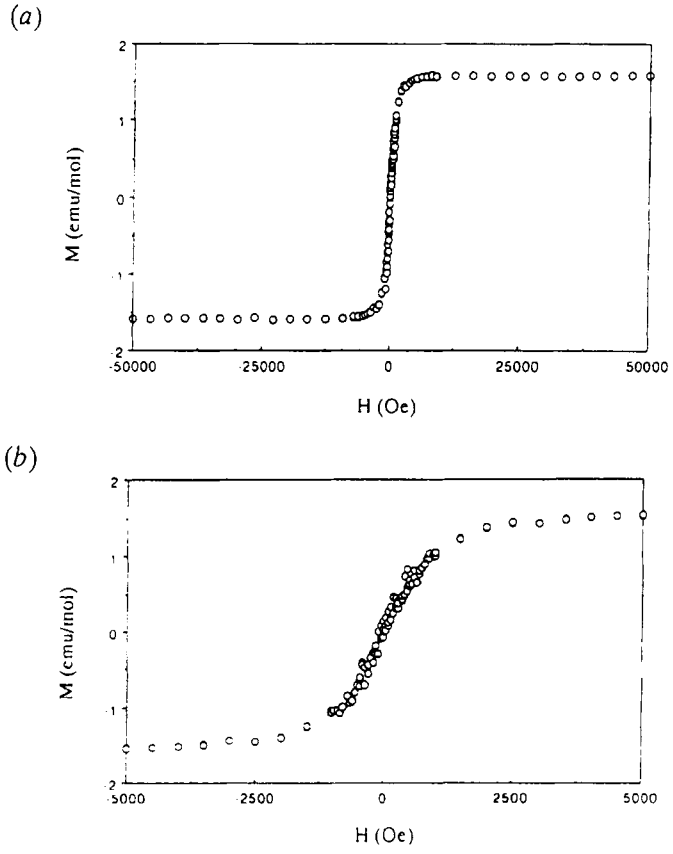


FIGURE 7 The magnetization curves of $(Cs^+ \bullet TCNQ^{-\cdot})\bullet 1/2TCNQ$ in the applied field range of (a) ±50 kOe and (b) ±5 kOe at room temperature.

MAGNETIC PROPERTY OF $(NEt_4^+ \cdot TCNQ^{-\cdot}) \cdot TCNQ$

In contrast to $(NMe_4^+ \cdot TCNQ^{-\cdot}) \cdot 1/2TCNQ$ and $(Cs^+ \cdot TCNQ^{-\cdot}) \cdot 1/2TCNQ$, there was no symptom of ferromagnetic behavior at room temperature and also at lower temperatures for $(NEt_4^+ \cdot TCNQ^{-\cdot}) \cdot TCNQ$. The paramagnetic susceptibility (χ_p) exhibited a temperature dependence as shown in Figure 8. This magnetic behavior can be well interpreted by a one-dimensional Heisenberg model with an exchange integral (J_B/k) of -42 K. Thus, an unpaired electron is equally distributed on both TCNQ and $TCNQ^{-\cdot}$ molecule in close contact with each other. The spins at each pair of TCNQ and $TCNQ^{-\cdot}$ molecules are subject to one-dimensional antiferromagnetic interaction.

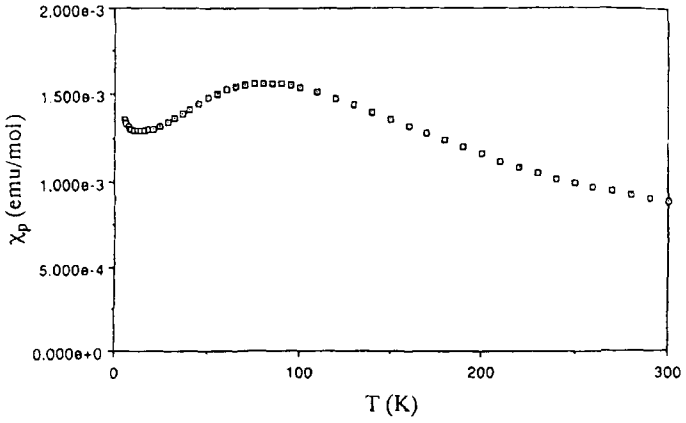


FIGURE 8 The temperature dependence of paramagnetic susceptibility (χ_p) in the temperature range of 5 to 300 K for $(NEt_4^+ \cdot TCNQ^{-\cdot}) \cdot TCNQ$.

SUMMARY

Eventually, room-temperature ferromagnetic behavior was recognized in the three 1:2 TCNQ ($TCNQF_4$)/$TCNQ^{-\cdot}$ ($TCNQF_4^{-\cdot}$) mixed salts. There are the following similarities between them. (1) The composition of TCNQ ($TCNQF_4$) and $TCNQ^{-\cdot}$ ($TCNQF_4^{-\cdot}$) molecules in the mixed salts is 1:2. (2) Apparently, the spin amount of at most 0.1% per formula unit participates, although the value is different from each other. (3) For $(NMe_4^+ \cdot TCNQF_4^{-\cdot}) \cdot 1/2TCNQF_4$ the two crystal forms of plates and needles are present. The room temperature ferromagnetic behavior can only be observed in the needles, whose crystal structure is not yet known, although the crystal structure analysis of the plates has already been accomplished.[1] However, it is supposed that also in the needle crystal the $TCNQF_4/TCNQF_4^{-\cdot}$ molecules stack along one axis to form a column

like the case in (NMe_4^+•$TCNQ^{-\cdot}$)• 1/2TCNQ and (Cs^+•$TCNQ^{-\cdot}$)• 1/2TCNQ, judging from their similar magnetic characteristics. There are two possible explanations concerning the origin of this room temperature ferromagnetic behavior. One could be weak ferromagnetism[12] due to canting of antiferromagnetically interacting, localized spins induced by electron transfer from a $TCNQ^{-\cdot}$ ($TCNQF_4^{-\cdot}$) dimer (donor) to a TCNQ ($TCNQF_4$) molecule (acceptor). The occurrence of electron transfer can be evidenced by the shift of stretching absorptions of the nitrile groups in the TCNQ ($TCNQF_4$) molecules to lower wavenumber region in the IR spectra. In this case the spins are not completely antiparallel, and slightly canted by Dzialoshinsky - Moriya antisymmetric exchange interaction. The other could be itinerant ferromagnetism based on the band structure formation of s/p electrons involved in these solids, as is seen in 3d transition metals and lamthanide metals.[13] The presence of conducting electron is necessary for the operation of this mechanism. The TCNQ/$TCNQ^{-\cdot}$ mixed salts are semiconductors as a whole, so that this mechanism might apparently be not practical, but conceivable, if a conduction site is involved in some part of the solid.

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