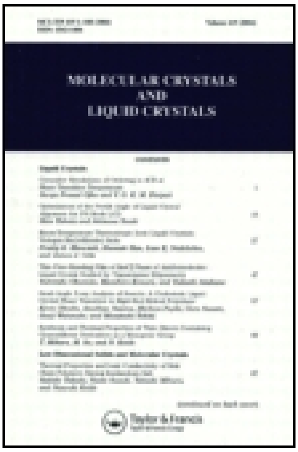

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Crystal Structures and Magnetic Properties of Tetrafluorotetracyanoquinodimethanide Salts

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CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES OF TETRAFLUOROTETRACYANOQUINODIMETHANIDE SALTS

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Abstract The X-ray structure analyses of tetramethylammonium and tetraethylammonium salts of tetrafluorotetracyanoquinodimethanide ($TCNQF_4^{-\bullet}$) ($NMe_4^+\bullet TCNQF_4^{-\bullet}$ and $NEt_4^+\bullet TCNQF_4^{-\bullet}$) were performed. In these crystals the $TCNQF_4^{-\bullet}$ molecules form dimers, which are stacked in a plane-to-plane manner to columns. Recrystallization of $NMe_4^+\bullet TCNQF_4^{-\bullet}$ in the presence of $TCNQF_4$ (or TCNQ) gave a single crystal of $(NMe_4^+\bullet TCNQF_4^{-\bullet})\bullet 1/2TCNQF_4$ (or TCNQ). The crystal is composed of alternating $TCNQF_4$ (or TCNQ)/ $TCNQF_4^{-\bullet}$ and NMe_4^+ ion layers, and the $TCNQF_4$ (or TCNQ)/ $TCNQF_4^{-\bullet}$ layer adopts a unique packing structure, in which each pair of two $TCNQF_4^{-\bullet}$ molecules is arranged in a completely perpendicular manner to each of one $TCNQF_4$ (or TCNQ) molecule. The similar $TCNQF_4$ (or TCNQ)/$TCNQF_4^{-\bullet}$ mixed salt was not obtained in use of $NEt_4^+\bullet TCNQF_4^{-\bullet}$ at all.

INTRODUCTION

Tetracyanoquinodimethane (TCNQ)[1] and its tetrafluoro-substituted derivative ($TCNQF_4$)[2] are well known as common electron acceptors in the formation of charge-transfer complexes. Their radical anions ($TCNQ^{-\bullet}$ and $TCNQF_4^{-\bullet}$) usually form tight pairs even at room temperature in the other alkali metal salts than $Li^+\bullet TCNQF_4^{-\bullet}$,[3] which exhibits weak ferromagnetism at the onset temperature of 12 K.[4] Knowledge of the crystal structure was necessary in order to elucidate the origin of weak ferromagnetism in $Li^+\bullet TCNQF_4^{-\bullet}$. However, in spite of a lot of efforts it is not yet successful to get the single crystal suitable for the X-ray structure analysis. Instead, we have now succeeded in the X-ray structure analysis of its tetramethylammonium and tetraethylammonium salts ($NMe_4^+{\bullet}TCNQF_4^{-\bullet}$ and $NEt_4^+{\bullet}TCNQF_4^{-\bullet}$). In addition, during the recrystallization experiment we have, accidentally got a single crystal with a structural formula of ($NMe_4^+{\bullet}TCNQF_4^{-\bullet}$)•1/2TCNQF4, which has a very unique molecular arrangement of TCNQF4 and $TCNQF_4^{-\bullet}$ molecules within the crystal. The crystal can be obtained in better yield by recrystallization of $NMe_4^+{\bullet}TCNQF_4^{-\bullet}$ in the presence of a half molar amount of TCNQF4. The use of TCNQ in place of TCNQF4 gives a single crystal of ($NMe_4^+{\bullet}TCNQF_4^{-\bullet}$)•1/2TCNQ, which has a similar crystal structure to that of ($NMe_4^+{\bullet}TCNQF_4^{-\bullet}$)•1/2TCNQF4. In this report we discuss the crystal structures and magnetic properties of these $TCNQF_4^{-\bullet}$ salts.

EXPERIMENTAL

The $NMe_4^+{\bullet}TCNQF_4^{-\bullet}$ and $NEt_4^+{\bullet}TCNQF_4^{-\bullet}$ salts were prepared by the reaction of TCNQF4 with an excess of NMe_4I or NEt_4I in refluxing acetonitrile, respectively.[5] Their single crystals were obtained by recrystallization from acetonitrile/ether. The ($NMe_4^+{\bullet}TCNQF_4^{-\bullet}$)• 1/2TCNQF4 (or TCNQ) salt was obtained as its single crystal by recrystallizing $NMe_4^+{\bullet}TCNQF_4^{-\bullet}$ in the presence of a half molar amount of TCNQF4 or TCNQ from acetonitrile/ether. When the similar recrystallization was carried out by using $NEt_4^+{\bullet}TCNQF_4^{-\bullet}$ in place of $NMe_4^+{\bullet}TCNQF_4^{-\bullet}$, the starting $TCNQF_4^{-\bullet}$ salt was only recovered and an ($NEt_4^+{\bullet}TCNQF_4^{-\bullet}$)• 1/2TCNQF4 (or TCNQ) crystal as expected was not isolated. The X-ray crystal analyses were performed on a Rigaku AFC5R diffractometer with graphic monochromated Cu-Kα radiation and 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection were determined from a least-squares fit using the setting angles of 25 carefully centered reflections in the range of $37.77 < 2\theta < 57.25°$ for $NMe_4^+{\bullet}TCNQF_4^{-\bullet}$, $22.96 < 2\theta < 25.11°$ for $NEt_4^+{\bullet}TCNQF_4^{-\bullet}$, $62.36 < 2\theta < 63.95°$ for ($NMe_4^+{\bullet}TCNQF_4^{-\bullet}$)•1/2TCNQF4 and $62.13 < 2\theta < 64.96°$ for ($NMe_4^+{\bullet}TCNQF_4^{-\bullet}$)•1/2TCNQ, respectively.

CRYSTAL STRUCTURES OF $NMe_4^+{\bullet}TCNQF_4^{-\bullet}$ and $NEt_4^+{\bullet}TCNQF_4^{-\bullet}$

Figure 1 shows the bond lengths and bond angles of NMe$_4^+$•TCNQF$_4^{-\bullet}$ and NEt$_4^+$•TCNQF$_4^{-\bullet}$. As is obvious from the bond lengths of both TCNQF$_4^{-\bullet}$ salts,

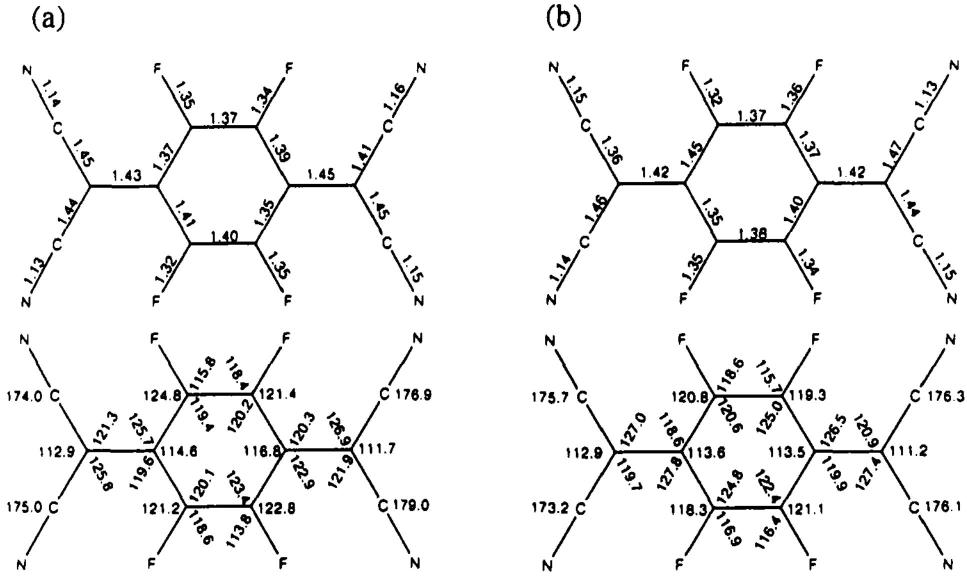

FIGURE 1 The bond lengths (Å) and bond angles (°) for (a) NMe$_4^+$•TCNQF$_4^{-\bullet}$ and (b) NEt$_4^+$•TCNQF$_4^{-\bullet}$.

bond alternation can not be seen in the molecular skeleton of TCNQF$_4^{-\bullet}$. The six-membered ring involving two dicyanomethine groups adopts almost coplanarity: the twist angles between the six-membered ring and dicyanomethine groups are 4.75 and 8.15° for NMe$_4^+$•TCNQF$_4^{-\bullet}$ and 6.55 and 7.82° for NEt$_4^+$•TCNQF$_4^{-\bullet}$, respectively. The crystal structures of the TCNQF$_4^{-\bullet}$ salts projected down the *a* and *b* axes, respectively, are shown in Figures 2 and 3. The two TCNQF$_4^{-\bullet}$ molecules form a dimer with a slightly slipped overlap. The dimers are stacked in parallel to the *a* axis in a plane-to-plane manner to columns. The interplanar distances of alternating TCNQF$_4^{-\bullet}$ molecules are 3.13 and 3.44 Å for NMe$_4^+$•TCNQF$_4^{-\bullet}$, and 3.19 and 3.58 Å for NEt$_4^+$•TCNQF$_4^{-\bullet}$, respectively. Shorter interplanar spacings in a dimer indicate stronger spin interaction, so that the magnitude of interaction is supposed to be stronger in NMe$_4^+$•TCNQF$_4^{-\bullet}$ than in NEt$_4^+$•TCNQF$_4^{-\bullet}$.

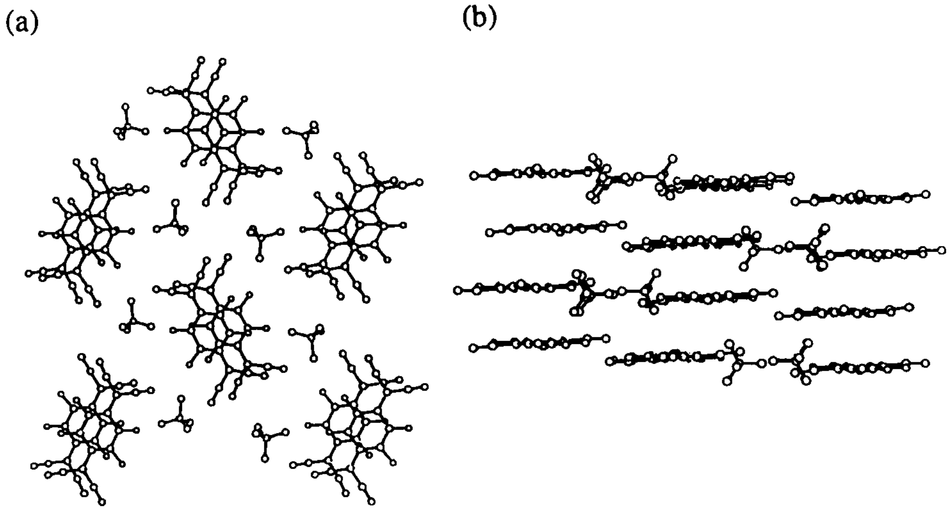

FIGURE 2 The crystal structures of NMe$_4^+$•TCNQF$_4^{-•}$ projected down (a) the *a* and (b) *b* axes.

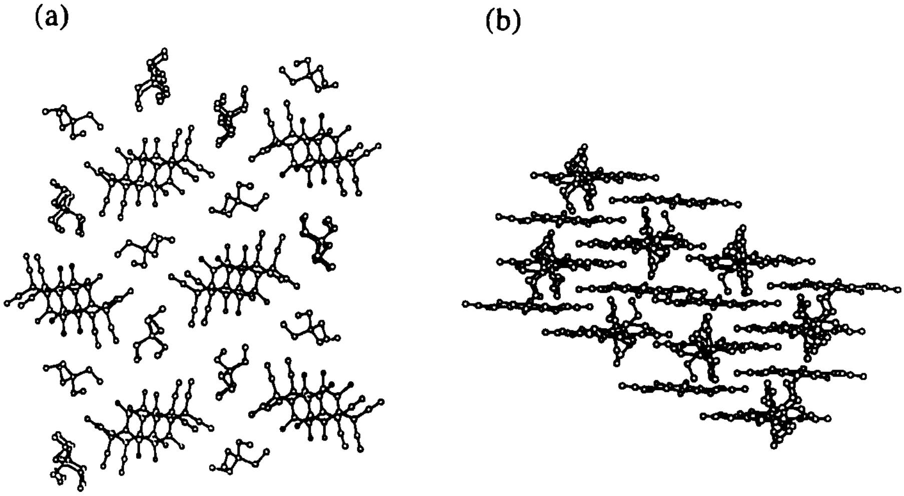

FIGURE 3 The crystal structures of NEt$_4^+$•TCNQF$_4^{-•}$ projected down (a) the *a* and (b) *b* axes.

CRYSTAL STRUCTURES OF (NMe$_4^+$•TCNF$_4^{-•}$)• 1/2TCNQF$_4$ and (NMe$_4^+$•TCNQF$_4^{-•}$)•1/2TCNQ

The crystal structures of $NMe_4^+{\bullet}TCNQF_4^{-\bullet}$ salts contaminated with $TCNQF_4$ or TCNQ are shown in Figure 4. The crystals are composed of alternating $TCNQF_4$ (or TCNQ)/$TCNQF_4^{-\bullet}$ and NMe_4^+ ion layers along the *c* axis. Especially, the $TCNQF_4$ (or TCNQ)/$TCNQF_4^{-\bullet}$ layer adopts a unique packing structure, in which each pair of two $TCNQF_4^{-\bullet}$ molecules (denoted as **A** in Figure 4) is arranged in a completely perpendicular manner to each of one $TCNQF_4$ (or TCNQ) molecule (denoted as **B**).

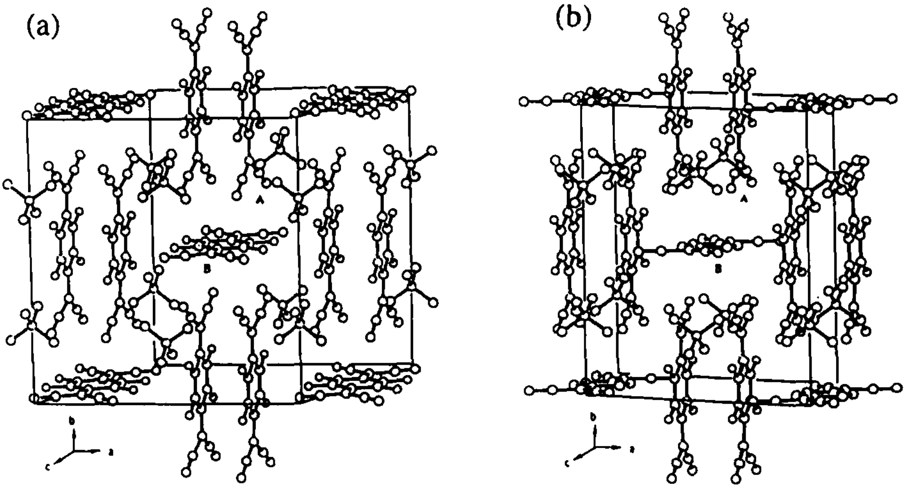

FIGURE 4 The crystal structures of (a) $(NMe_4^+{\bullet}TCNQF_4^{-\bullet}){\bullet}1/2TCNQF_4$ and (b) $(NMe_4^+{\bullet}TCNQF_4^{-\bullet}){\bullet}1/2TCNQ$.

The **A** and **B** molecules can definitely be assigned to $TCNQF_4^{-\bullet}$ and $TCNQF_4$ (or TCNQ), respectively, in view of the bond lengths of the two molecules (Figures 5 and 6). For the **A** molecule bond alternation is very small, suggesting large delocalization of π electrons on the whole molecule. On the other hand, the **B** molecule has significant alternation of single and double carbon-carbon bonds. The **A** molecule is slightly twisted between the six-membered ring and dicyanomethine groups, and the twisted angles are 1.90° for $(NMe_4^+{\bullet}TCNQF_4^{-\bullet}){\bullet}1/2TCNQF_4$ and 4.69° for $(NMe_4^+{\bullet}TCNQF_4^{-\bullet}){\bullet}1/2TCNQ$, respectively. In contrast with this, there is not such a twist in the **B** molecules ($TCNQF_4$ and TCNQ) of both salts. The two neighboring $TCNQF_4^{-\bullet}$ molecules essentially form a tight dimer, judging from the very short contact distance (3.11 Å for $(NMe_4^+{\bullet}TCNQF_4^{-\bullet}){\bullet}1/2TCNQF_4$ and

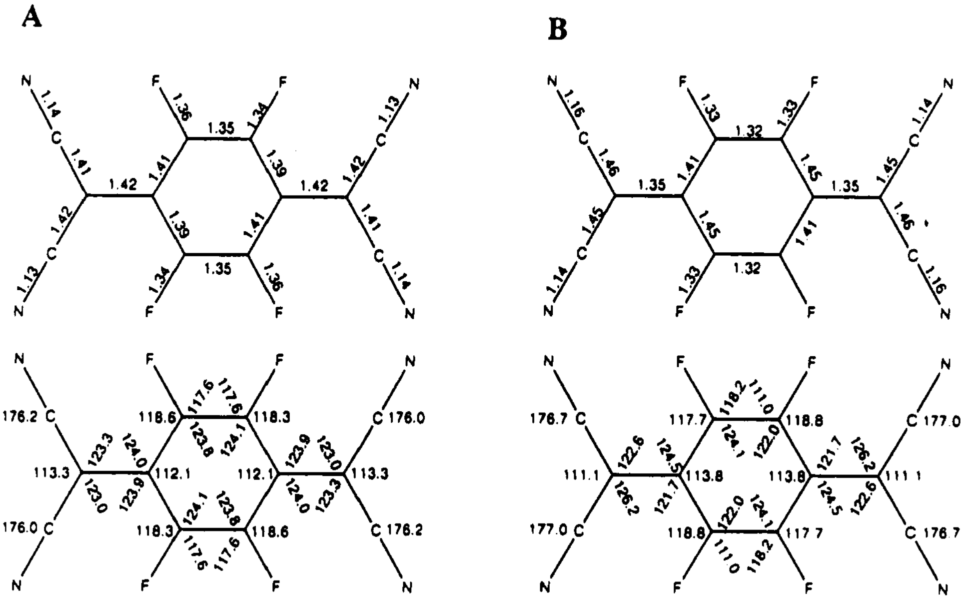

FIGURE 5 The bond lengths (Å) and bond angles (°) of **A** ($TCNQF4^{-\bullet}$) and **B** (TCNQF4) molecules for ($NMe4^{+}\bullet TCNQF4^{-\bullet}$)• 1/2TCNQF4.

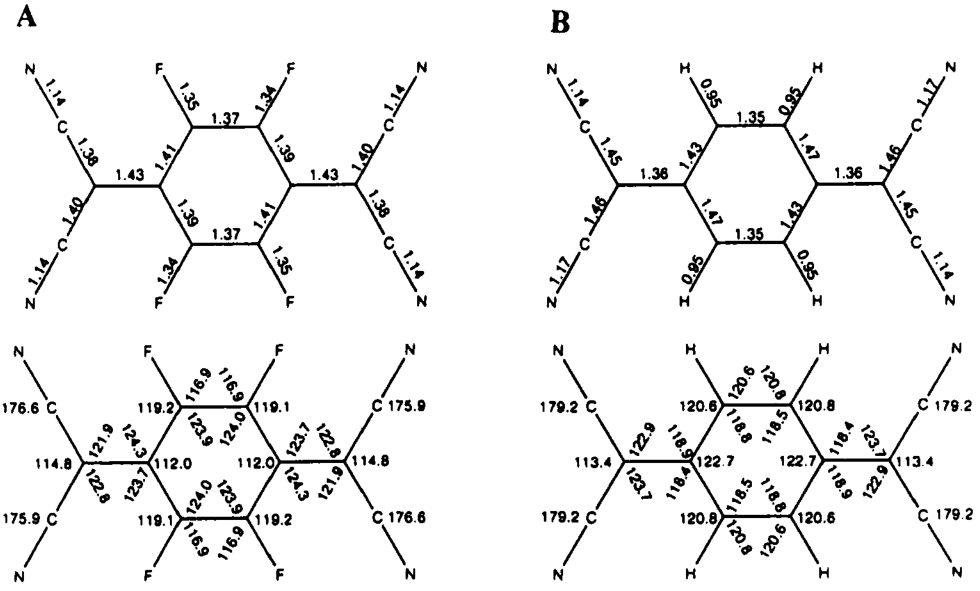

FIGURE 6 The bond lengths (Å) and bond angles (°) of **A** ($TCNQF4^{-\bullet}$) and **B** (TCNQ) molecules for ($NMe4^{+}\bullet TCNQF4^{-\bullet}$)•1/2TCNQ.

3.25 Å for $(\mathrm{NMe4^{+}\bullet TCNQF4^{-\bullet}})\bullet 1/2\mathrm{TCNQ}$ as compared with that of a normal π cloud (3.54 Å). The dimer has two different and strong contacts with the neighboring **B** molecule. Thus, along the *a* axis each of **A** molecules in the dimer contacts with one **B** molecule in such a manner that their molecular planes are completely perpendicular to each other (the dihedral angle: 90.08° for $(\mathrm{NMe4^{+}\bullet TCNQF4^{-\bullet}})\bullet 1/2\mathrm{TCNQF4}$ and 87.71° for $(\mathrm{NMe4^{+}\bullet TCNQF4^{-\bullet}})\bullet 1/2\mathrm{TCNQ}$), and that the difluoroethylene and ethylene bond axes of **B** (TCNQF4) and **B** (TCNQ) molecules pass through the center of the long bisecting axis of **A** molecule, respectively. The closest contact occurs between the difluoroethylene carbons of **A** molecule, and the fluorine atoms in the **B** (TCNQF4) molecule or the hydrogen atoms in the **B** (TCNQ) molecule, and the distances are 3.03 and 3.45 Å for $(\mathrm{NMe4^{+}\bullet TCNQF4^{-\bullet}})\bullet 1/2\mathrm{TCNQF4}$, and 3.00 and 3.31 Å for $(\mathrm{NMe4^{+}\bullet TCNQF4^{-\bullet}})\bullet 1/2\mathrm{TCNQ}$, respectively. On the other hand, along the *b* axis both **A** molecules in the dimer contact together with one **B** molecule, and the molecular planes of **A** and **B** molecules are also completely perpendicular to each other (the dihedral angle: 89.92° for $(\mathrm{NMe4^{+}\bullet TCNQF4^{-\bullet}})\bullet 1/2\mathrm{TCNQF4}$ and 92.29° for $(\mathrm{NMe4^{+}\bullet TCNQF4^{-\bullet}})\bullet 1/2\mathrm{TCNQ}$). In this case the long bisecting axis of **A** molecule passes through one carbon atom of the difluoroethylene or ethylene bond in **B** (TCNQF4) or **B** (TCNQ) molecule. Accordingly, there is a closest contact between the nitrogen atom of cyano group in **A** molecule and the difluoroethylene or ethylene carbons in **B** (TCNQF4) or **B** (TCNQ) molecule, and the distances are 3.51 and 3.80 Å, respectively. In the result a two-dimensional and strong contact network between TCNQF4 (or TCNQ) and $\mathrm{TCNQF4^{-\bullet}}$ molecules is achieved in each TCNQF4 (or TCNQ)/$\mathrm{TCNQF4^{-\bullet}}$ layer. Each $\mathrm{NMe4^{+}}$ ion is located near the midpoint in the cavity surrounded by four cyano groups of four $\mathrm{TCNQF4^{-\bullet}}$ molecules (the distances between the positively-charged nitrogen atom of $\mathrm{NMe4^{+}}$ ion and the negatively-charged nitrogen atoms of cyano groups in $\mathrm{TCNQF4^{-\bullet}}$ molecules are in the range of 4.36 to 4.58 Å) and by four cyano groups of two TCNQF4 (or TCNQ) molecules (4.41 - 5.78 Å). By intervention of the $\mathrm{NMe4^{+}}$ ion layer the two neighboring TCNQF4 /$\mathrm{TCNQF4^{-\bullet}}$ and TCNQ/$\mathrm{TCNQF4^{-\bullet}}$ layers are separated by 9.58 and 9.35 Å in shortest, respectively.

MAGNETIC PROPERTIES OF $\mathrm{NMe4^{+}\bullet TCNQF4^{-\bullet}}$ and $\mathrm{NEt4^{+}\bullet TCNQF4^{-\bullet}}$

Magnetic measurement was performed for the crystalline samples of the $TCNQF_4^{-\bullet}$ salts by using a SQUID magnetometer. Figure 7 shows the temperature dependence of paramagnetic susceptibility ($\chi_p = \chi_{obs} - \chi_{dia}$: χ_{obs} is the magnetic susceptibility

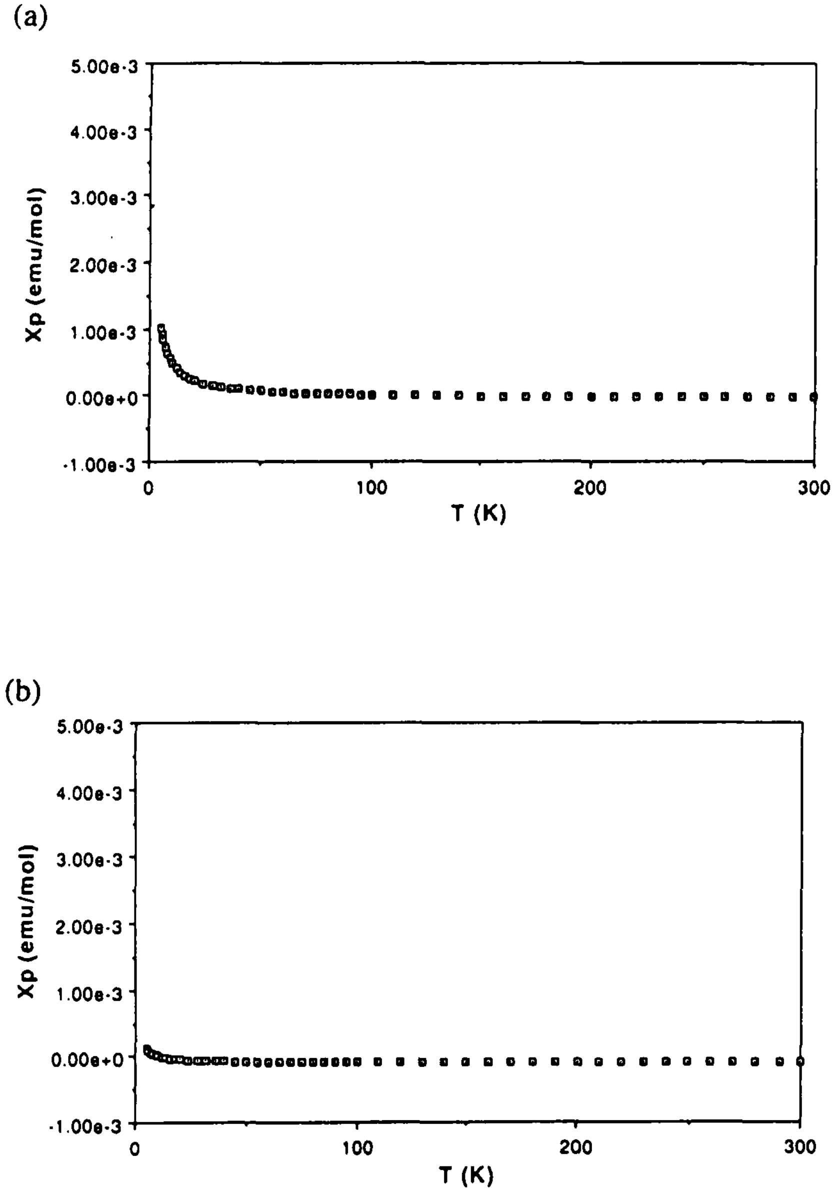

FIGURE 7 The χ_p vs. T plots between 5 and 300 K for (a) $NMe_4^{+}\bullet TCNQF_4^{-\bullet}$ and (b) $NEt_4^{+}\bullet TCNQF_4^{-\bullet}$.

measured under applied magnetic field of 500 Oe and χ_{dia} the diamgnetic susceptibility calculated by Pascal's method) between 5 and 300 K. The χ_p value is almsot zero in the measured temperature range for both salts, indicating disappearance of a net magnetic moment due to the formation of spin pairs. This result can well be explained by the dimer formation of $TCNQF_4^{-\bullet}$ molecules in crystal structures of the salts. At very low temperature the slight increase of χ_p is observed, which indicates the presence of an impurity monoradical involved in the samples.

DISCUSSION

The crystal structures of $NMe_4^+\bullet TCNQF_4^{-\bullet}$ and $NEt_4^+\bullet TCNQF_4^{-\bullet}$ are similar to those of alkali metal salts of $TCNQ^{-\bullet}$ ($M^+\bullet TCNQF_4^{-\bullet}$: M = Rb,[6] Na,[7] K[8]). For both $TCNQF_4^{-\bullet}$ and $TCNQ^{-\bullet}$ salts the radical anion molecules form dimers, which are stacked in a plane-to-plane manner to columns. Nevertheless, the column structures are different between the $TCNQF_4^{-\bullet}$ and $TCNQ^{-\bullet}$ salts. For both NMe_4^+ and NEt_4^+ salts of $TCNQF_4^{-\bullet}$ the columns pass through in parallel to the *a* axis. While, the columns are inclined at an average angle of 74° to the *a* axis for the $TCNQ^{-\bullet}$ salts.

There is no report on the synthesis of the $NMe_4^+\bullet TCNQF_4^{-\bullet}$ salt contaminated with $TCNQF_4$ or TCNQ. Accordingly, this report gives the first instance. The crystal structure is quite unique, in which each of $TCNQF_4^{-\bullet}$ molecules in a dimer formation is two-dimensionally arranged in a completely perpendicular manner to each of one $TCNQF_4$ or TCNQ molecule Such an arrangement can bring much more decrease in Coulomb repulsion between the negative charges of neighboring $TCNQF_4^{-\bullet}$ molecules as well as stabilization due to charge-transfer from a $TCNQF_4^{-\bullet}$ donor to a $TCNQF_4$ or TCNQ acceptor by intervention of $TCNQF_4$ or TCNQ. However, the other molecules than $TCNQF_4$ or TCNQ, for instance, 2,3-dichloro-5,6-dicyano-1,4-benzoquione (DDQ) can't play such a role. Indeed, a crystal of $NMe_4^+\bullet TCNQF_4^{-\bullet}$ including DDQ was not obtained at all. These facts suggest that this crystal structure is strictly governed by the whole size of a molecule included as well as by the kind of functional groups attached in the molecule. In addition, the kind of ammonium ion as a gegencation is responsible for the stabilization of this crystal structure, as is demonstrated by no formation of an $(NEt_4^+\bullet TCNQF_4^{-\bullet})\bullet 1/2TCNQF_4$ (or TCNQ) crystal in the use of NEt_4^+ ion. In comparison of the molecular size between NMe_4^+ and NEt_4^+ ions, the radius of NEt_4^+ ion (3.6 Å) is longer by 0.5 Å than that of NMe_4^+ ion (3.1 Å). This larger molecular size of NEt_4^+ ion results in weak Coulomb interaction between alternating $TCNQF_4$ (or TCNQ)/$TCNQF_4^{-\bullet}$and NEt_4^+ ion layers.

For all crystals of $TCNQF_4^{-\bullet}$ salts investigated in this study the $TCNQF_4^{-\bullet}$ molecules form tight dimers, in which strong antiferromagnetic spin interaction occurs so as to bring loss of a net magnetic moment. This was proven by the magnetic properties of $NMe_4^+\bullet TCNQF_4^{-\bullet}$ and $NEt_4^+\bullet TCNQF_4^{-\bullet}$ crystals. The similar result is also expected for a $(NMe_4^+\bullet TCNQF_4^{-\bullet})\bullet 1/2TCNQF_4$ (or TCNQ) crystal, although the magnetic measurement is now in progress.

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