Organic Radical Crystals Based on a TEMPO–substituted Pyridinium with Radical Anions

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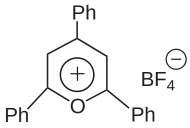
Organic crystals of the TCNQ or $TCNQF_4$ radical anion salts derived from 2,4,6-triphenylpyridinium carrying TEMPO radical were obtained as a couple of different forms and their magnetic properties were found to vary markedly depending on the forms.

It is generally known that the physical properties of a substance, such as conducting or magnetic properties, are dependent conspicuously on the composition or polymorphism[1] of the crystal since the physical properties are decisively affected by the crystal structures of materials.[2] Clarification of the relation between the crystal structure and the magnetic property of a certain spin system is a fundamental research object in the field of molecular-based magnetic materials. In this context, much effort has so far been made to gain insight into the relation by using the crystals of a variety of spin systems, in which the problems of composition or polymorphism are often dealt with.[3] In the course of our search for novel organic spin systems,[4] we have been interested in preparing such hetero spin system that consists of a radical anion[5] and a radical-substituted pyridinium[6] and found that a TEMPO (2,2,5,5-tetramethyl-1-piperidinyloxy)–substituted pyridinium derivative forms a couple of different crystals from the corresponding radical anions to show different magnetic properties at the same time. We wish to report in this paper the structures of the different forms and the magnetic properties derived therefrom.

The tetrafluoroborate salt of 2,4,6-triphenylpyridinium (**3**) was prepared in 17% isolated yield from the corresponding pyrylium tetrafluoroborate **1** by the nucleophilic insertion of 4-amino-TEMPO **2** in a mixed solution of ethanol and dichloromethane.[7] It was apparent from the SQUID measurement that there are no significant intermolecular magnetic interactions (Weiss temperature is almost null) between the spins in the salt **3**. Anion exchange reactions of the tetrafluoroborates **3** with LiTCNQ (lithium 7,7,8,8-tetracyanoquinodimethane) or $LiTCNQF_4$ (lithium 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) in acetonitrile solution gave the corresponding radical anion salts (**4**, **5**) in moderate yields (81–87%).

A couple of crystal forms were obtained when the TCNQ salt **4** was recrystallized from acetonitrile, one with plate shape and the other with rod shape, and both of them could be easily isolated. Weak ferromagenetic interaction obeying the Curie–Weiss law was observed in the spins of the plate-shaped crystal with Weiss temperature of about 0.5 K (Table 1) and it is anticipated from its Curie constant of 0.80 emu·Kmol^{-1} that two weakly interacting $S = 1/2$ spins are present in the crystal.

X-ray analysis of this crystal indicates (for the crystal data, see ESI) that the ratio of cation/anion in the crystal is actually 1:1 and an inspection of the N–O distance of the spin center in the cation as well as the C–C distances of the six-membered ring of the TCNQ molecule suggests the existence of each $S = 1/2$ spin on the respective moieties. No apparent dimerization between the TCNQ molecules is observed to give the isolated spins without singlet formation.



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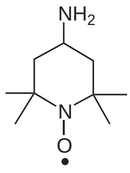

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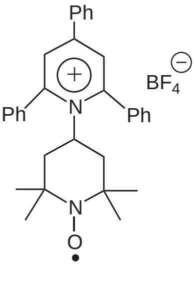

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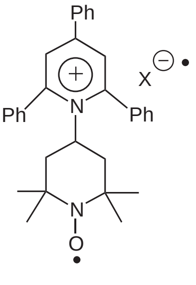

4: X=TCNQ
5: X=$TCNQF_4$

There are short contacts between the oxygen atoms of the NO moiety and a carbon atom in the six-membered ring of the radical anion and between the nitrogen atoms of a couple of cyano groups in the radical anion and a γ-carbon atom in the piperidine ring of the cationic part. Thus, the intermolecular interactions are formed in a three-dimensional manner as shown in Figure 1, which are thought to play significant roles for the intermolecular magnetic interaction observed in this salt.

On the contrary, the ratio of cation-to-anion was found to be 2:3 in the rod-like crystal of salt **4** with the inclusion of $4H_2O$, and the segregated packing feature of the cationic and anionic parts was apparent in the crystal (see SI). No appreciable short contacts can be observed between the radical moieties to give the paramagnetic behavior of the isolated spins even at the cryogenic temperature.[8] The TCNQ radical anions are stacked with three molecules in a unit to form a columnar structure and the observed Curie constant of 0.38 (emu·K/mol) suggests the loss of spins on the radical anions within each three-molecular unit.

Plate-shaped crystals were obtained by the recrystallization of $TCNQF_4$ salt **5** from acetone and the ratio of cation/anion was found to be 1:1 in the crystal. The crystal system is triclinic with the space group of $P - 1$ and mixed stacking of the cations and the anions is apparently observed in the crystal (see SI). The

Table 1. Magnetic data of pyridinium salts[a]

Salts	C/emu·K·mol^{-1}	θ/K	Magnetic interaction
3	0.38	0.00	para
4 (plates)[b]	0.80	0.47	ferro
4 (rods)[c]	0.38	0.00	para
5 (plates)[d]	0.75	0.25	ferro
5 (needles)[d]	0.37	−0.57	antiferro

[a]Fitted by using the Curie–Weiss law. [b]Pyridinium:TCNQ = 1:1. [c]Pyridinium:TCNQ = 2:3 (with $4H_2O$). [d]Pyridinium: $TCNQF_4$ = 1:1.

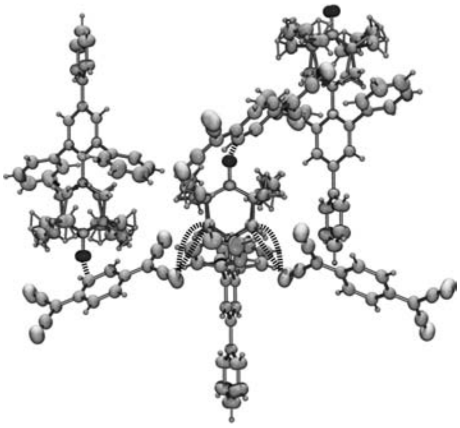

Figure 1. Crystal structure of the plate-shaped crystal of **4**. The broken lines indicate short intermolecular contacts.

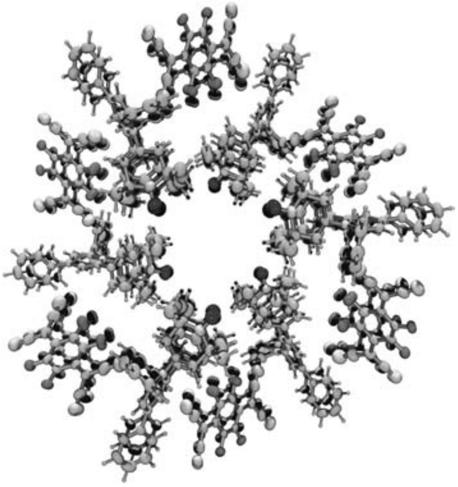

Figure 2. Crystal structure of the needle-shaped crystal of **5**.

TCNQF$_4$ π-systems are inserted between the cationic pyridinium moieties to result in weak ferromagenetic intermolecular interaction obeying the Curie–Weiss law with two weakly interacting $S = 1/2$ spins in the crystal.[5]

On the other hand, another polymorphic form of needle-shaped crystal of TCNQF$_4$ salt **5** was found when it was recrystallized from acetonitrile. Although the cation/anion ratio is also estimated to be 1:1 in the crystal, the packing feature of the molecules is quite different from that of the plate-like crystal, having the space group of $R - 3$ (trigonal). There are fairly large cavities surrounded by the segregated columns of the cations as well as the anions as shown in Figure 2. The dimer structures of TCNQF$_4$ molecules are apparent in the anionic column to cancel the spins on the radical anions by singlet formation and only the spins on the radical moieties are thought to reflect the Curie constant as the result, giving rise to weak antiferromagnetic interaction between the spins.

In summary, a couple of radical anion salts of TEMPO-substituted 2,4,6-triphenylpyridinium have been prepared and found to form crystals with different shapes, in which the difference of the compositions in the pyridinium and the radical anion has been clarified for TCNQ salt **4** while a couple of polymorphic forms has been observed for TCNQF$_4$ salt **5**. Their different packing features as disclosed by the X-ray analysis are thought to give rise to the apparent difference in their magnetic properties, especially the spin-numbers of discrete values.

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