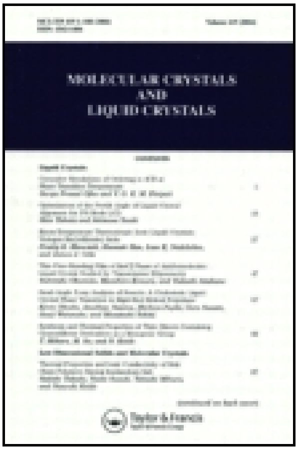

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Magnetic properties of Cs + and (CH 3) 4 N + salts of TCNQ

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MAGNETIC PROPERTIES OF Cs^+ AND $(CH_3)_4N^+$ SALTS OF TCNQ

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$Cs(TCNQ)_{1.5}$ and $[(CH_3)_4N](TCNQ)_{1.5}$ were prepared with using chemicals and solvents purified carefully and were recrystallized under an inert atmosphere to minimize the effect of air. We investigated their magnetic properties and the effect of oxygen on these magnetism. It was found that both paramagnetic susceptibilities (χ_p) of $Cs(TCNQ)_{1.5}$ and $[(CH_3)_4N](TCNQ)_{1.5}$ were very small, especially χ_p of $Cs(TCNQ)_{1.5}$ was remarkably small such as $10 \sim 40 \times 10^{-6}$ emu · mol^{-1} all over the temperature region. After the specimen was exposed to air, χ_p was measured again; for $Cs(TCNQ)_{1.5}$, χ_p increased clearly by about 20×10^{-6} emu · mol^{-1}; however for $[(CH_3)_4N](TCNQ)_{1.5}$, χ_p was not changed. This result suggests that the magnetism of the Cs salt was sensitive to oxygen and that the Me_4N salt is stable to air.

Keywords: TCNQ salt; $[(CH_3)_4N(TCNQ)_{1.5}$; $Cs(TCNQ)_{1.5}$; magnetic properties; molecular conductor

INTRODUCTION

On the history of the development of molecular conductors, TCNQ (teteracyanoquinodimethane) was the epoch-making electron acceptor

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which gave the first organic metal TTF-TCNQ in 1973 [1]. Before the discovery of TTF-TCNQ, many kinds of its salts were prepared and their physical properties were studied. TCNQ takes one electron and forms the radical anion as $TCNQ^{-\cdot}$. Almost all TCNQ salts have 1 : 1 or 1 : 2 stoichiometry as $(M^{+}TCNQ^{-\cdot})$ or $((M^{+}TCNQ^{-\cdot})TCNQ)$. Among the salts, the cesium salt is known to form a exceptional 1 : 1.5 salt as $(Cs^{+}TCNQ^{-\cdot})\cdot 0.5TCNQ)$ and the tetramethylammonium salt was reported recently to have a 1 : 1.5 stoichiometry of $((CH_3)_4N^{+}\cdot TCNQ^{-\cdot})\cdot 0.5TCNQ)$ as well [2,3]. These TCNQ salts show various kinds of magnetism largely deviating from Curie's law. However, the origin of behavior has not been fully understood yet. Therefore, we prepared the crystals of $Cs(TCNQ)_{1.5}$ and $[(CH_3)_4N](TCNQ)_{1.5}$ under an inert atmosphere as pure as possible and reexamined their magnetic properties with a SQUID magnetometer.

In this paper, we report the magnetic properties of $Cs(TCNQ)_{1.5}$ and $[(CH_3)_4N](TCNQ)_{1.5}$ and the effect of oxygen on these magnetism.

EXPERIMENTAL

$CsTCNQ_{1.5}$ and $Me_4NTCNQ_{1.5}$ were synthesized as follows [2,3];

$$1.5TCNQ + CsI \rightarrow Cs(TCNQ)_{1.5}$$

$$TCNQ + LiI \rightarrow LiTCNQ$$

$$LiTCNQ + NMe_4Cl \rightarrow Me_4NTCNQ + LiCl$$

$$Me_4NTCNQ + 0.5TCNQ \rightarrow Me_4NTCNQ_{1.5}.$$

On preparing samples, we used chemicals and anhydrous solvents purified carefully; TCNQ (sublimed 5 times), CsI (recrystallized from MeOH), LiI (Aldrich 99.99% grade), NMe_4Cl (recrystallized from $MeOH/Et_2O$), MeCN (distilled over NaOH), Et_2O (distilled over Na) and MeOH (dried with molecular sieve and distilled). In order to investigate the effect of air, the recrystallization was carried out in an atmosphere of argon by the following method; two round bottom flasks were connected with a three-way glass tube and the remaining end of the tube was joining to a vacuum/argon line; ether and the solution of the sample in acetonitrile were placed in each flask. The atmosphere in the flasks was replaced with argon after freeze-and-thaw cycles for solvents and then, the glass apparatus was placed in the dark. As ether vapor passed through the glass tube and dissolved into acetonitrile gradually, the crystal was growing for two weeks. After that, the filtration of the crystal and all preparations for the magnetic measurements were performed in a glove box where argon gas was flowing, and when the sample was moved from a glove box to the magnetometer, it was kept under inert condition as possible. Magnetic susceptibility and magnetization were measured by use of a Quantum Design MPMS SQUID magnetometer. The paramagnetic susceptibility was obtained by subtracting the core susceptibility (χ_{core}) from the measured susceptibility; χ_{core} was estimated by Pascal's law; $\chi_{\mathrm{core}}(\mathrm{CsTCNQ}_{1.5}) = -216.6 \times 10^{-6}\,\mathrm{emu \cdot mol^{-1}}$; $\chi_{\mathrm{core}}(\mathrm{Me_4NTCNQ}_{1.5}) = -246.2 \times 10^{-6}\,\mathrm{emu \cdot mol^{-1}}$; $\chi(\mathrm{TCNQ}) = -121 \times 10^{-6}\,\mathrm{emu \cdot mol^{-1}}$; $\chi(\mathrm{Cs^+}) = -35.1 \times 10^{-6}\,\mathrm{emu \cdot mol^{-1}}$.

RESULTS AND DISCUSSION

Magnetic Susceptibilities

Figure 1a shows the temperature dependence of paramagnetic susceptibility (χ_p) observed on CsTCNQ$_{1.5}$. The lower curve is χ_p measured just after the recrystallization under an inert atmosphere of argon. As can be seen from this curve, χ_p is remarkably small such as $10 \sim 40 \times 10^{-6}\,\mathrm{emu \cdot mol^{-1}}$ all over the temperature region, while χ_p is a little dependent on temperature. This result suggests that almost all the spins of TCNQ radical anions are forming diamagnetic pairs in the crystal. As temperature is lowered, χ_p decreases gradually down to 200 K, becomes almost constant and then increases below 100 K. The behavior around room temperature is dependent on sample; some samples showed a peak at $280 \sim 290$ K as shown in Figure 1a, while others exhibited the monotonous increase of χ_p without any peak.

The upper curve in Figure 1a shows χ_p observed after the specimen was exposed to air for 20 minutes. As being compared with the lower curve under an atmosphere of Ar, it should be noted that χ_p increased by about $20 \times 10^{-6}\,\mathrm{emu \cdot mol^{-1}}$ over the wide temperature range, while the shape is very similar. This result suggests that air, possibly oxygen, attaches to the surface of the sample and affects χ_p of CsTCNQ$_{1.5}$. A series of the measurements for the specimen exposed to air for 1 min., 5 hrs. and 12 hrs. and further in oxygen for 1 hr were performed. As the results, χ_p for the sample exposed to air for 1 min increased like. Figure 1a. As the sample was exposed to air longer, χ_p increased slightly as the effect seems to saturate; χ_p for the sample in air for 12 hrs. is nearly equal to χ_p exposed to oxygen for 1 hr.

Figure 1b shows $\chi_p$measured on Me$_4$NTCNQ$_{1.5}$ recrystallized under an inert atmosphere and exposed to air by the same way as the Cs salt. As can be seen from this figure, χ_p was not changed for the specimen in air for 20 minutes and even in oxygen. The effect of air could not be observed on the

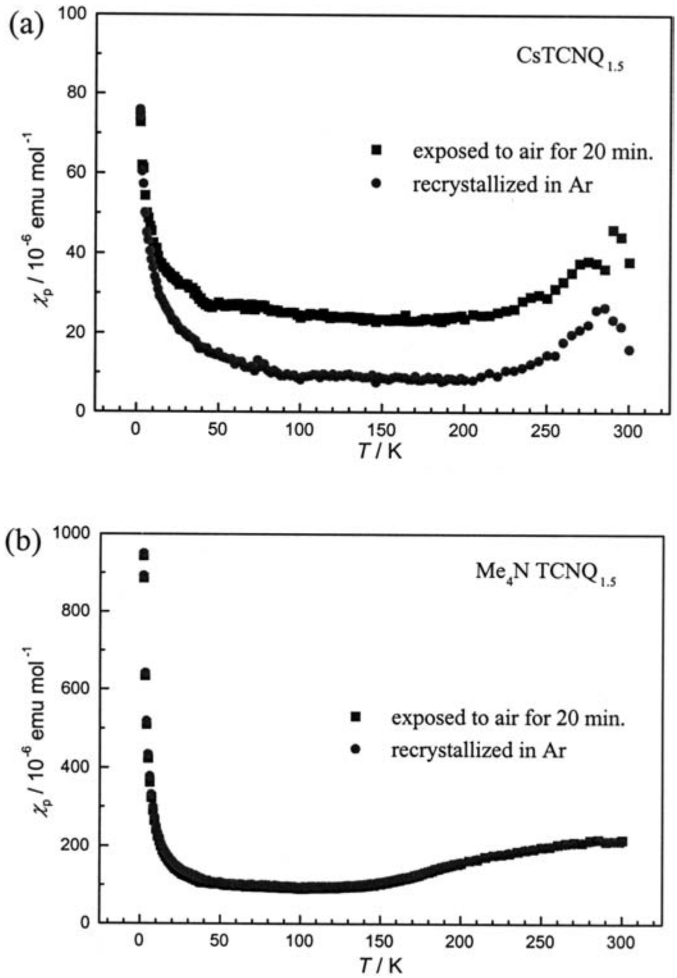

FIGURE 1 The temperature dependence of magnetic susceptibilities of $Me_4NTCNQ_{1.5}$ and $CsTCNQ_{1.5}$.

Me_4N salt. While χ_p was larger than that of the Cs salt, χ_p was rather small such as $100\,emu \cdot mol^{-1}$.

Magnetizations

Figure 2 shows the magnetic field dependence of the magnetization $CsTCNQ_{1.5}$ at 1.85 K. The manetization grows slowly and the hysteretic behavior was not observed at this low temperature on our measurement.

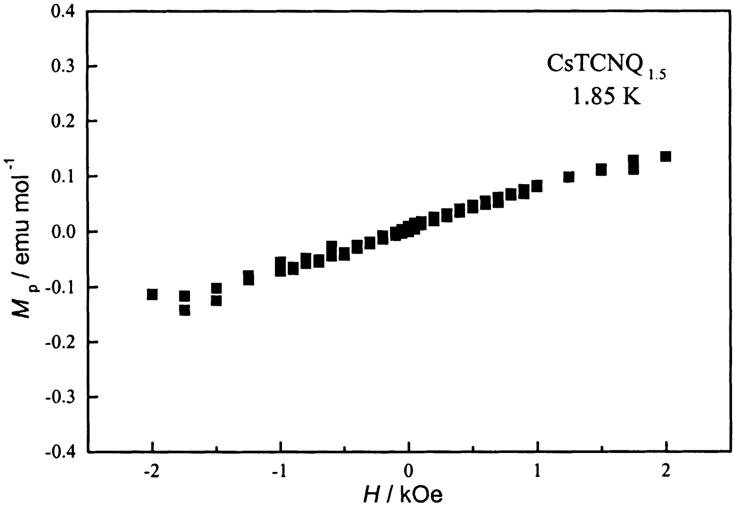

FIGURE 2 The magnetic field dependence of the magnetization of $\mathrm{CsTCNQ}_{1.5}$ in the applied field range ±2 kOe at 1.85 K.

Subsequently, the magnetization was measured at 1.85 K on the sample after exposure to oxygen. The result was the same as Figure 2.

CONCLUSION

We prepared the crystals of $\mathrm{Cs(TCNQ)}_{1.5}$ and $\mathrm{[(CH_3)_4N](TCNQ)}_{1.5}$ under an inert atmosphere as pure as possible and investigated their magnetic properties and the effect of oxygen on these magnetism. It was found that both paramagnetic susceptibilities (χ_p) of the Cs salt and the $\mathrm{Me_4N}$ salt were small, especially that χ_p of the Cs salt was remarkably small such as $10 \sim 40 \times 10^{-6}\,\mathrm{emu \cdot mol^{-1}}$ all over the temperature region. This fact could mean that almost all the spins of TCNQ radical anions are forming diamagnetic pairs. After the specimen was exposed to air, χ_p was measured again; for the Cs salt, χ_p increased clearly by about $20 \times 10^{-6}\,\mathrm{emu \cdot mol^{-1}}$, however for the $\mathrm{Me_4N}$ salt, χ_p was not changed. This result suggests that the magnetism of the Cs salt was sensitive to oxygen and that the $\mathrm{Me_4N}$ salt is stable to air.

The origin of the magnetic behavior of TCNQ salts has not been understood yet. A further study will be needed in order to clarify the mechanism that the magnetic susceptibilities are remarkably small and that oxygen affects the magnetism of TCNQ salts.

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