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Optical and Magnetic Properties of Alkali-(18-Crown-6)-TCNQ Salts

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Synopsis. Absorption spectra, ESR and static susceptibility were measured on TCNQ salts which incorporate Na$^+$- or K$^+$-(18-crown-6) as the cation unit. Results indicate that charge-transfer interaction between TCNQ anions is weak in the Na$^+$ salt, whereas it is very strong in the K$^+$ salt.

Physical processes in TCNQ (7,7,8,8-tetracyanoquinodimethan) salts are usually discussed laying stress only on the interaction between TCNQ molecules. We have recently shown,[1] however, that interaction of TCNQ with the cations is sometimes important in determining the electronic state in the TCNQ chain. Metal-(crown ether)-TCNQ ternary salts[2a—c] are good candidates for studying the effect of the cation-TCNQ interaction. We previously reported anomalous magnetic properties of some alkali-(crown ether)-TCNQ salts.[3] In the present note, we report an example in which a difference in the diameter of alkali cation causes a difference in the shape of the metal-(crown ether) unit, and the latter difference greatly affects the optical and magnetic properties of the TCNQ stacks. Substances studied were 1:1 TCNQ salts with N$^+$- or K$^+$-(18-crown-6) cation units, where 18-crown-6 stands for 1,4,7,10,13,16-hexaoxacyclooctadecane. The experimental procedures were almost the same as before.[3] Absorption spectra and ESR were measured on polycrystalline samples. On the K$^+$ salt, in addition, static magnetic susceptibility was measured. The absorption spectrum of the K$^+$ salt has been outlined.[2a]

Results and Discussion

Absorption Spectra. Absorption spectra of the two salts are shown in Fig. 1. In the spectrum of the Na$^+$ salt, the lowest energy band at 7.5X10^3 cm^{-1} is assigned to the charge-transfer(CT) excitation between TCNQ anions, since many alkali-TCNQ simple salts show CT band in this region.[4,5] Among the three small bands at 11.7, 13.0, and 15.0X10^3 cm^{-1}, the former two and the third are similar respectively to the absorptions of monomer TCNQ$^-$ and TCNQ$^-$ dimer in solution.[6] Therefore, these three bands could be explained by assuming the existence of TCNQ$^-$ monomers embedded at the impurity sites in a dimer-type crystal. However, these bands as a whole may reflect the electronic structure of the TCNQ molecules since the former two bands are too strong to be attributed to the impurity. A large peak at 27.2X10^3 cm^{-1} and a shoulder around 23X10^3 cm^{-1} are ascribed to local excitations in the TCNQ molecules. Energies of this peak and shoulder are almost the same as those respectively of other dimer and monor absorptions in solution.[6] Thus, the Na$^+$ salt is inferred to involve TCNQ columns with a weakly dimerized structure.

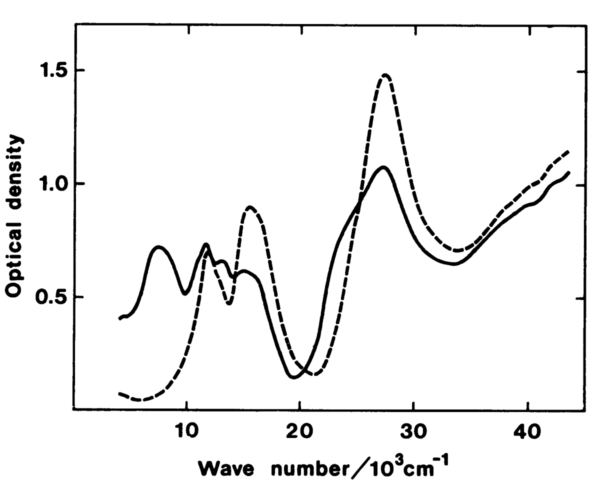

Fig. 1. Absorption spectra of powder samples; Na$^+$-(18-crown-6)- TCNQ$^-$ (——) and K$^+$-(18-crown-6)-TCNQ$^-$ (----).

The absorption spectrum of the K$^+$ salt (Fig. 1) is less complicated. There are three prominent bands at 11.8, 15.5, and 27.3X10^3 cm^{-1}. The first band is located in the energy region of one of the monomer TCNQ$^-$ excitations described before. However, it may be assumed that this band is a CT band associated with the excitation between two TCNQ anions since there is no absorption band in the lower-energy region beyond this band. The CT-band energy of a TCNQ$^-$ dimer is determined mainly by three terms,[4] *i.e.*, on-site Coulomb energy U, configuration-interaction(CI) energy t between ground and CT configurations, and CI-energy t' between CT- and locally-excited configurations. t increases the CT-band energy, whereas t' acts to decrease it. The above energy of the CT band implies that t is very large and, probably at the same time, t' is small in this salt. The crystal structure analyzed by Hirano *et al.*[7] indicates the existence of strong and isolated dimers of TCNQ$^-$ bound by the Coulomb interaction with K$^+$, the vector connecting two TCNQ$^-$ being almost perpendicular to their molecular plane. Thus the above assumptions for the molecular integrals are in harmony with the crystal structure, and the first assumption that the lowest-energy band is the CT band is reasonable. The local-excitation band at 27.3X10^3 cm^{-1} is sharp and has no shoulder on its lower-energy side. This fact is also in agreement with the crystal structure for which the thermal excitation of the monomer-like molecular arrangement seems to be difficult.

Magnetic Properties. The Na$^+$ salt showed a sharp and fairly strong ESR signal at room temperature at a g-value of 2.0029. The spin density was estimated to be 1.4X10^{23} mol^{-1} using purified DPPH as the standard. The temperature variation of the integrated intensity is shown in Fig. 2. While a thermally

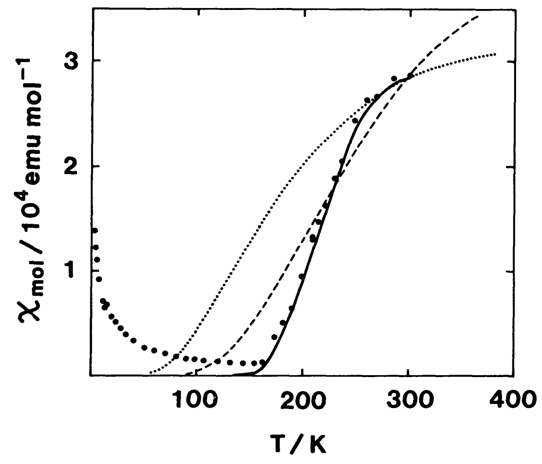

Fig. 2. Temperature dependence of the integrated ESR intensity of Na^+-(18-crown-6)-$TCNQ^-$. Solid line is the result obtained by subtracting the Curie-type contribution. Dashed and dotted lines are respectively the theoretical curves by the singlet-triplet model with $J=0.069$eV and the linear-Ising model with $J=0.038$eV.

activated sharp signal is seen above 160 K, a weak and broad signal which obeys Curie's law is seen below this temperature. The latter signal is considered to come from isolated $TCNQ^-$ at the impurity sites in the crystal.[8] The variation of the thermally activated signal is revealed by subtracting the contribution from the impurity signal. Rise of the solid line thus obtained (Fig. 2) is steeper than the theoretical curves given by the singlet-triplet(ST) model[9] and the linear-Ising(LI) model.[10] The spin density at room temperature corresponds to those of a ST system with $J=0.069$ eV and a LI system with $J=0.038$ eV (Fig. 2). One possible cause of the steep rise of the present result is that the magnetic interaction between TCNQ anions is large in the low-temperature region and becomes weaker as the temperature is raised. This explanation is reasonable since the average distance between molecules increases because of the thermal expansion. The fact that the signal of the thermally activated spins is sharp over the whole temperature range where it is observed means that the magnetic excitons are mobile. These results imply that the dimerization of TCNQ anions is weak in this salt in agreement with the absorption spectrum.

We could not detect an ESR signal for the K^+ salt at room temperature at the maximum sensitivity of our instrument. To confirm that there are no spins, the static magnetic susceptibility was measured. The result $\chi=-2.9_8\times10^{-4}$ emu mol^{-1} agrees well with the diamagnetism estimated by Pascal's law. These observations indicate that the magnetic interaction between TCNQ anions is very strong in this salt, which agrees well with the absorption spectra and the crystal structure.

Shape of the Cation Unit and Property of the Crystal. The marked contrasts observed for the optical and magnetic properties of these two salts imply that their crystal structures are very different. It has been known that the size of the inner space of 18-crown-6 fits to the diameter of K^+ giving a cation unit with symmetric shape, but the diameter of Na^+ is smaller and consequently the shape of the cation unit is distorted.[11] This distortion seems not to favor good packing in the crystal. The structure and properties of TCNQ salts are determined by a critical balance between the Coulomb energy and the CT energy.[12] In the isolated dimer structure of the present K^+ salt,[7] the Coulomb attraction between K^+ and the cyano groups of the TCNQ molecules is inferred to compensate effectively for the repulsion between the TCNQ anions. Stabilization of the singlet ground state is, then, attained by the strong CT interaction.

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