Studies of the Crystallization Processes of *N*-Methylquinolinium TCNQ Ion-radical Salts

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We studied the crystallization processes of the complex ion-radical salt of 7,7,8,8-tetracyanoquinodimethan (TCNQ) and the *N*-methylquinolinium cation. A variety of solvents, rates of crystallization, and concentrations of the solution gave three groups of crystals. The crystals in the first group, which were crystallized as black rods, occluded the solvent molecules in the crystals, and their resistivities were in the range of 2.8—26 Ω cm. Those in the second group were crystallized into the form of fine needles or fine powders. Although the TCNQ-to-cation ratios in the salts varied from 1.6 to 2.2, their electrical resistivities were almost all the same (about 1.0 Ω cm), and these crystals were thought to have a metastable crystal structure. The crystals in the third group were crystallized in the form of triclinic prisms, which belonged to a stable crystal of a high resistivity (1100 Ωcm). The appearance of multiple forms is interpreted on the basis of Ostwald's "Law of Stages" of crystallization and also on the basis of information on the structures of the one-dimensional TCNQ columns of the other complex ion-radical salts of TCNQ.

Molecular compounds based on 7,7,8,8-tetracyanoquinodimethane (TCNQ) have attracted much attention in studying the behavior of electrons in the molecular crystals, because they exhibit a wide range of resistivity, 10^{-3}—10^{11} Ω cm, and also because their physical properties can, in some cases, be regarded as attributes of a one-dimensional conductor.[1] A great effort to synthesize new materials of TCNQ has led to discoveries of various kinds of phase transitions[2–7] and also of the possibility of high-temperature superconductivity.[8] The wide range of the physical properties of the TCNQ compounds is due to their possibility of being crystallized in a variety of forms. There are two limits of crystal structure, between which many variations exist, depending upon the kind and nature of the second component. One structure, which is generally found in compounds called "non-ionic charge-transfer complexes" is characterized by alternating stacks of TCNQ and the second molecule (donor), the mode of the overlap of the two neighboring molecules being nearly direct. The other is a structure in which the TCNQ molecules are stacked plane-to-plane with each other. The latter type of crystal is usually found in the ion-radical salts formed between TCNQ and organic or metallic cations and is believed to contribute to the high conductivity. It has been suggested by various works on the crystallization of the TCNQ molecular compounds that the crystal structure and the physical properties of the compounds are determined not only by the nature of the second component, but also notably by the crystallization processes. This statement may be illustrated by the following four phenomena: (1) The appearance of polymorphic modifications in simple salts of 3,3′-diethylthiacarbocyanium,[9] Rb[10,11] and *N*-methylphenazinium cations.[12] (2) Compounds of different stoichiometries, such as 1:2 salts of various onium cations, 2:3 salts of Cs,[13] morpholinium,[5] trimethylammonium,[14] and *N*-methylquinolinium cations.[15] (3) Unstable crystals, such as morpholinium$_3$(TCNQ)$_4$,[5] *N*-ethylquinolinium(TCNQ)$_2$[15] and methyldiethylcyclohexylammonium(TCNQ)$_2$.[15] (4) The formation of solvent-inclusion compounds such as benzidine·TCNQ(BD·TCNQ).[16,17]

In this paper we wish to report our experimental results on the crystallization of an ion-radical salt formed from the *N*-methylquinolinium (MeQ) cation and TCNQ and show that the MeQ·TCNQ salt can be crystallized either of the above four types of crystals. We will also discuss the effect of the crystallization process on the resulting forms of crystals, considering the unstable nature of the one-dimensional TCNQ columns, and will report that the appearance of multiple forms can be commonly observed in the TCNQ ion-radical salts.

Experimental

Materials. Crude TCNQ was refluxed for several hours with active carbon in acetonitrile; the filtered solution had then been allowed to stand overnight, orange crystals of TCNQ were collected. This procedure was repeated several times.

For the preparation of MeQ(TCNQ)$_x$ salts, *N*-methylquinolinium iodide and a two-molar excess of TCNQ were dissolved and mixed in a boiling solvent. After a suitable period, the crystals were collected, washed with the solvent, and finally washed with ether.

Determination of the Molecular Ratio of TCNQ to the Cation. The accuracy of the elemental analysis of TCNQ was too poor for us to assess the amount of the excess neutral TCNQ molecules in the salt, because the complete combustion of the salt was difficult to achieve. The electronic absorption spectrum was adopted instead. The electronic spectra of TCNQ salts in acetonitrile of high purity were measured with a Cary 14R spectrometer. Acetonitrile was purified by repeated distillations over a small amount of Li(TCNQ). The spectrum was considered to be the overlap of the absorptions of both TCNQ^0 and TCNQ$^-$. The value of the molar extinction coefficient for TCNQ^0 was 68000 l·mol^{-1}·cm^{-1} at the wavelength of 395 nm. The coefficient of TCNQ$^-$ was obtained from the simple salt of MeQ(TCNQ), which exhibited two major maxima, at 420 and 842 nm, with coefficients of 26800 and 51600 l·mol^{-1}·cm^{-1} respectively; the coefficient at 395 nm was 21800 l·mol^{-1}·cm^{-1}. We obtained the molar ratios of TCNQ to the MeQ cation from the following equation, assuming that the TCNQ^0-to-cation ratio is the same as the TCNQ^0-to-TCNQ$^-$ ratio:

$$\mathrm{TCNQ/MeQ} = 1 + (\varepsilon^{-}_{842}/\varepsilon^{0}_{395})(r_2 - r_1)$$

where r_1 and r_2 are the ratios of the optical density at 395 nm to that at 842 nm in the absorption spectra of the simple and complex salts respectively (r_1=0.422) and where ε^{-}_{842} and ε^{0}_{395} are the molar extinction coefficients of $\mathrm{TCNQ^-}$ at 842 nm (51600) and of $\mathrm{TCNQ^0}$ at 395 nm (68000) respectively. In a conventional calculation,[18] a value of r_1 obtained from Li(TCNQ) has been used instead of that from the corresponding simple salt, but there may be no reason for believing that the absorption coefficient of $\mathrm{TCNQ^-}$ is always the same, regardless of the kind of cation component.[19]

Measurements of Electrical Resistivity and Activation Energy. The resistivity data at room temperature were obtained on pressed pellets 13 mm in diameter, and about 5 mm thick, with four-probe electrodes pressed on the pellets with a resistivity-measuring apparatus, Model VR 4 (Kokusai Electric Co., Ltd.). For the activation-energy measurements (from −50 to 50 °C), samples in the form of pressed rods 3 mm in diameter and about 10 mm in length were prepared; on them four-point contacts were made with silver paint.

Measurement of Infrared Absorption Spectra. The infrared absorption spectra were measured using the method of Nujol mull with a Hitachi grating infrared spectrometer, Model 215, in the wave number range between 4000 and 650 $\mathrm{cm^{-1}}$. In case of highly-conducting salts, special care was required in the preparation of a uniform film in order to avoid the scattering of light.

Other Measurements. The measurements of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were made with Shimadzu thermoflex apparatuses, SC-20 and TG-20, in a nitrogen gas atmosphere and at a heating rate of 5 °C/min.

The X-ray diffraction patterns of powder samples were obtained at room temperature with a Philips PW 1051 X-ray diffractometer by the use of a copper-Kα line.

Results and Discussion

Multiple Forms of MeQ·TCNQ Salts and Their Classification. The experimental results of the crystallization of the salts formed from the MeQ cation with TCNQ are shown in Table 1, which also summarizes the relative intensities of the electronic absorptions at 395 and 842 nm of acetonitrile solutions, the cation-to-TCNQ ratio, the crystal forms and the electrical properties at room temperature. The first typical feature of the results is that the molar ratio of the MeQ cation to TCNQ could not be assigned to an integer ratio of 1:2 or 2:3, but varied from 1.6 to 2.2 with the kind of solvent. When acetone was used as the solvent, fine needle crystals ($\mathrm{MeQ(TCNQ)_{1.6}}$) appeared first, and then triclinic prism crystals ($\mathrm{MeQ(TCNQ)_{2.1}}$) were obtained after a day. The second feature is that the apparent form of the crystal varied with the method of preparation; three different forms were recognized, apart from the crystal in the form of fine powders reprecipitated in cold water from a hot dimethylformamide solution (IIc). They were a rod, a fine needle, and a triclinic prism. The electrical resistivity corresponded to the crystal form and not to the content of neutral TCNQ molecules. The crystals in the form of black rods exhibited relatively low resistivities (from 2.8 to 26 Ω cm). The lowest resistivity was found in the fine needle crystal, while the highest was found in the triclinic prism crystal. The reprecipitated fine powders have almost the same resistivity as that of fine needle crystals, so they can be classified into the same group.

At this stage we can classify these crystals into three groups on the basis of both their crystal forms and their resistivities. The first group, I, consists of two compounds with relatively low resistivities which were crystallized in the form of black rods from acetonitrile and nitromethane solutions. The II group includes three types of highly-conducting crystals. The first of them, IIa, was crystallized from dichloromethane, and the second, IIb, from an acetone solution. Both of them were in the form of fine, black needles; they could be formulated as $\mathrm{MeQ(TCNQ)_{2.2}}$ and $\mathrm{MeQ(TCNQ)_{1.6}}$, respectively The last sample of this group, IIc, is $\mathrm{MeQ(TCNQ)_{2.2}}$, which was obtained in the form of a fine powder. We single out as a III group the salt of the highest resistivity, $\mathrm{MeQ(TCNQ)_{2.1}}$, which was crystallized in the form of a triclinic prism. In works by Melby *et al.*[13] and Siemons, Bierstedt, and Kepler,[20] the $\mathrm{MeQ(TCNQ)}_x$ salt synthesized in an acetonitrile solution was regarded as a stoichiometric 1:2 complex. However, it is one of the multiple forms of $\mathrm{MeQ(TCNQ)}_x$ salts, because Frandois *et al.*[15] have reported a crystal of 2:3 stoichiometry from an acetonitrile solution.

Figure 1 shows the infrared spectra of the six crystals obtained. The IR spectra are also divided into three groups which strictly correspond to the above classification based on the crystal forms and resistivities. The optical absorption spectra of the TCNQ ion-radical salts in both infrared and visible regions reflect the structure of the TCNQ columns. Broadenings of the vibrational bands in the infrared range from 2500 to 700 $\mathrm{cm^{-1}}$ are generally observed and may reasonably be related to the electron delocali-

Table 1. Characteristic properties of $\mathrm{MeQ(TCNQ)}_x$ complex salts

Solvent	Electronic spectra r_2 ($\varepsilon_{395}/\varepsilon_{842}$)	Composition (Cation: TCNQ)	Crystal form	Resistivity ρ_{20} (Ω cm)	Activation energy E (eV)	Classification
$\mathrm{CH_3CN}$	1.16	1: 1.6	Rod	2.8	0.07	Ia
$\mathrm{CH_3NO_2}$	1.58	1: 1.9	Fine rod	26	0.13	Ib
$\mathrm{CH_2Cl_2}$	1.95	1: 2.2	Fine needle	1.0	0.05	IIa
$\mathrm{(CH_3)_2CO}$	1.17	1: 1.6	Needle	0.8	0.06	IIb
$\mathrm{H_2O}$[a]	2.04	1: 2.2	Powder	1.0	0.05	IIc
$\mathrm{(CH_3)_2CO}$[b]	1.85	1: 2.1	Triclinic prism	1100	0.20	III

a) Reprecipitated in $\mathrm{H_2O}$. b) See text.

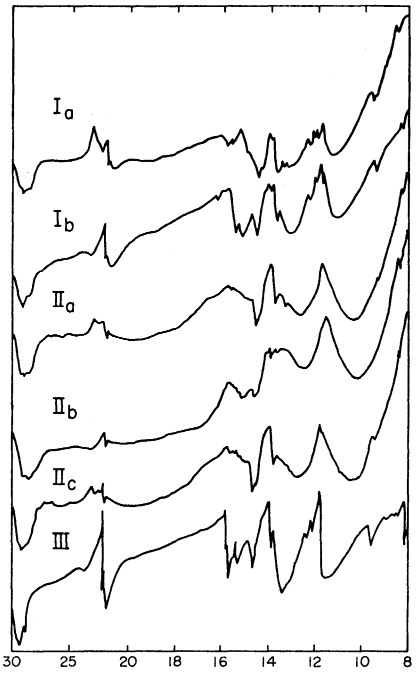

Fig. 1. Infrared absorption spectra of MeQ(TCNQ)$_x$ salts.

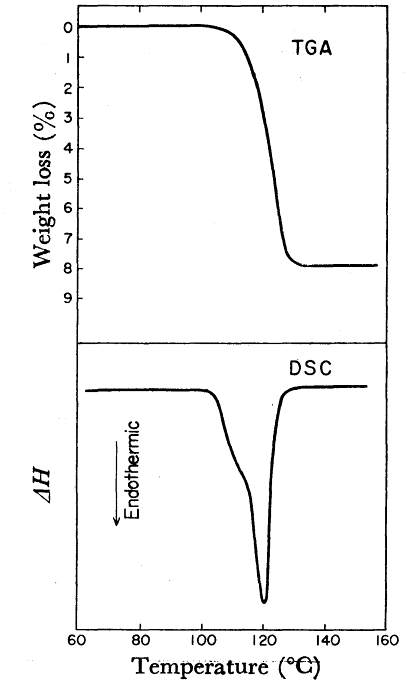

Fig. 2. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves of IIa MeQ(TCNQ)$_{1.6}$(CH$_3$CN).

zation and then to the orderliness of the TCNQ columns. Especially, the bands from 1100 to 1300 cm^{-1} in the spectra of highly-conducting TCNQ complexes are not due to pure intramolecular vibrations, but to some kind of vibronic interaction of conduction electrons with intramolecular TCNQ vibrations.[21]

At first, the spectra will be compared with the spectrum of a thin film of quinolinium(TCNQ)$_2$, Q(TCNQ)$_2$,[22] which exhibits a considerably broader CN stretching band at 2210—2000 cm^{-1}, with sharp lines at 2206 and 2199 cm^{-1}, and strong bands at 1270 and 1050 cm^{-1}, corresponding to, respectively, the CH bending and C–CN stretching modes of the TCNQ molecules.[23,24] The low-resistivity crystal, II, had the pattern most similar to that of Q(TCNQ)$_2$, and the coincidence of the positions and width of the CH bending and C–CN stretching bands was fairly good. The bands of the III crystal were less broad and appeared at a higher-energy side than in the case of either II or Q(TCNQ)$_2$. For example, peaks were found at 1300 cm^{-1} for the CH bending band and at 1130 cm^{-1} for the C–CN stretching band. The IR spectrum of the III-type crystal suggests that there is a different TCNQ column structure, probably with considerable distortions, which will give rise to electron localization and then to an increase in the values of both the resistivity and the activation energy. The I-type crystals, although they had as low resistivity as II, exhibited different patterns. The poor resolution and large broadening of the CN stretching band at about 2210 to 2000 cm^{-1} are similar to those of the low-resistivity crystal, II, but the positions of both the CH bending band (about 1320 cm^{-1}) and the C–CN stretching band (about 1120 cm^{-1}) are more similar to those of the intermediate resistivity compound, III.

The I-Type Crystals, Inclusion Compounds. The thermogravimetric analysis of the MeQ(TCNQ)$_x$ salts revealed that only the crystals classified as I suffered a weight loss. The TGA curves for Ia are shown in Fig. 2. For single crystals of Ia and Ib, the magnitudes of the losses were 8 and 10% in weight respectively, while the temperatures at which the weight started to decrease were 110 and 90 °C respectively. The loss component was trapped in a cell cooled with dry ice and was confirmed by means of the infrared absorption spectrum to be due to the escape of included solvent molecules, namely, acetonitrile for Ia and nitromethane for Ib. The amount of the included solvent was estimated from the magnitude of the loss; it was found that one mole of the solvent molecules was included per mole of the MeQ cation.

Measurements of differential scanning calorimetry (DSC) were made on Ia and Ib; endothermic peaks which exactly corresponded to the TGA curves were thus observed. The result for Ia is also shown in Fig. 2. The magnitudes of the heat associated with the transformation were ΔH=19.1 kcal/mol for Ia and 18.1 kcal/mol for Ib.

It is concluded that the MeQ(TCNQ)$_x$ salts classified as I in the previous section included solvent molecules in the crystal, while the crystals in the other groups did not. The factor determining the type of salt was the kind of solvent used in the preparation, and the included solvents were weakly bound in the host lattice and could leave it easily.

In the case of a BD·TCNQ system,[16,17] which is another example of the formation of inclusion compounds, the main factor determining the type of complex is the solvent used in the preparation. When the molecular volume of the solvent is smaller than 75 cm^3/mol, the BD·TCNQ crystal includes the solvent, while the crystal does not include solvent molecules larger in volume than 80 cm^3/mol. The situation seems to be the same in the case of the MeQ(TCNQ)$_x$ salts. For example, the molecular volumes of the included acetonitrile and nitromethane are 52.2 and 53.7 cm^3/mol respectively, while the solvents not included were dichloromethane and acetone, their molecular volumes being 64.0 and 73.6 cm^3/mol respectively. The heat associated with the evaporation of the solvent molecules from the MeQ·TCNQ system is comparable with that of the solvents from the BD·TCNQ system, which has been reported to be 11.1 kcal/mol. It is striking that the two systems, which differ so sharply in crystal structure, exhibited similar behavior of solvent evaporation. These results suggest that the state of the solvent molecules is essentially the same for both the systems and that the solvent molecules may be situated in a site very weakly affected by the kind of donor or cation molecules.

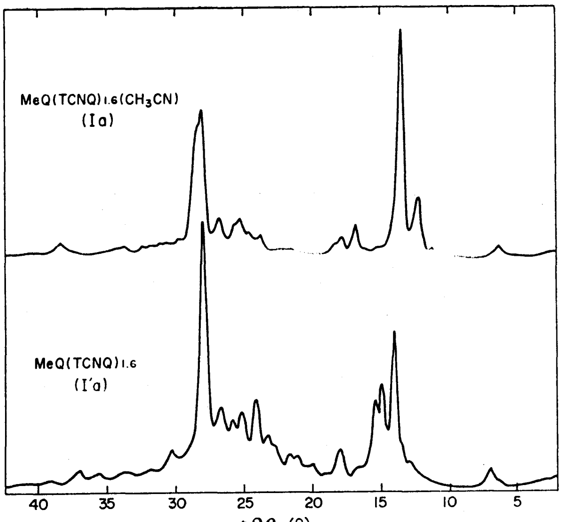

Fig. 3. X-ray diffraction patterns of MeQ(TCNQ)$_x$ salts. Ia: MeQ(TCNQ)$_{1.6}$(CH$_3$CN) and Ia′: MeQ(TCNQ)$_{1.6}$.

The X-ray powder diffraction patterns of the Ia crystal and those treated at 120 °C for 30 min, Ia′, are shown in Fig. 3. The pattern of Ia′ was quite different from that of Ia; that is, the peaks of Ia at 2θ=11.95, 12.87, 12.96, and 27.51° disappeared after heat treatment, resulting in new peaks of Ia′ at 13.50, 14.96, and 27.34°. The resistivities of these salts also changed from 2.8 Ω cm to about 3000 Ω cm. On the other hand, when Ia′ was exposed to the vapor of acetonitrile in a low vacuum (about 100 mmHg) overnight at room temperature, the X-ray pattern became identical with that of Ia and the resistivity was restored to 4.0 Ω cm. Therefore, it is likely that when the solvent molecules leave the crystal, the crystal structure is greatly changed and that, when exposed to the vapor of a suitable solvent, the solvent molecules can easily be included in the crystal, thus restoring the initial structure. These properties are again in accord with the case of the BD·TCNQ system.

When IIa and III were exposed to the vapor of acetonitrile using the same method, the resistivity changed from 1.0 to 2.8 Ω cm for IIa and from 1100 to 5.0 Ω cm for III. From TGA measurements, the contents of acetonitrile molecules of the transformed crystals of IIa and III were determined to be 0.86 mol for the former and 0.90 mol for the latter per mole of the MeQ cation. This fact shows that the formation of the solvent-including salts does not depend on the initial crystal structure; all the crystals can include solvent molecules of a suitable size.

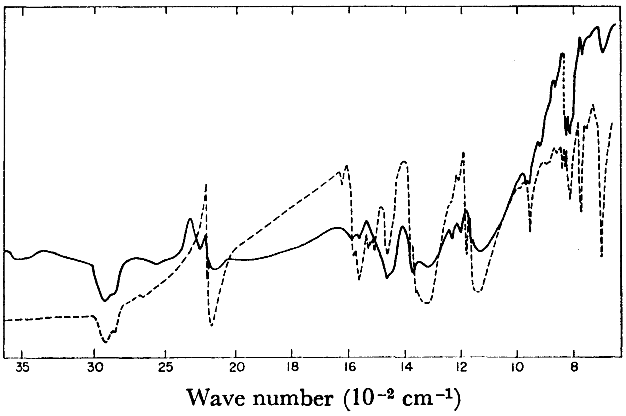

Fig. 4. Infrared absorption spectra of Ia: MeQ(TCNQ)$_{1.6}$(CH$_3$CN) (——) and Ia′: MeQ(TCNQ)$_{1.6}$ (------).

The infrared spectrum of Ia′ is shown in Fig. 4. As with the results of solvent evaporation, the resolution of the spectrum became relatively good and the width of the CN stretching band of TCNQ at 2200 cm^{-1} became narrower than that of Ia. On the contrary, the position of the characteristic bands, the CN stretching, CH bending, and C–CN stretching bands, remained unchanged. From these results, we will make some speculations on the mode of change in the TCNQ column structure, referring to the case of the BD·TCNQ system.[25,26] In a BD·TCNQ(S) crystal (where S stands for a solvent molecule), the BD and TCNQ molecules completely overlap each other to make columns as well as ordinary charge-transfer complexes, while the solvent molecules are situated in the channels between the BD·TCNQ columns and also form parallel columns. It has also been reported that the structure of the BD·TCNQ columns of the inclusion compound is almost the same as that of the solvent-free compound and that the spacings between the column axes of the latter compound are smaller than those of the former. The small change in the IR structure of the MeQ(TCNQ)$_x$(S) crystal suggests little change in the TCNQ column structure, thus excluding the possibility that the solvent molecules are located in the TCNQ columns. They may, thereby, be bound in the channels between the columns, as in the case of the BD·TCNQ system. Crystallographical studies of low-conductive TCNQ ion radical salts with 1:2[24] and 2:3 stoichiometries[27] show that there are relatively large hollows in the columns of the cation, hollows which correspond to the periodic distortions between two TCNQ$^-$'s of the

TCNQ columns. These hollows are thought to be the most probable sites for the solvent molecules. The solvent molecules have only the TCNQ$^-$ in their nearest neighbors; this is in contrast with the cations, which have both TCNQ^0 and TCNQ$^-$. This structure explains the low resistivity of the solvent-including crystals because the higher resistivity of the crystals with a distorted TCNQ column structure is caused by the intermolecular repulsion between the neighboring TCNQ$^-$ molecules. The X-ray powder patterns of Ia and Ia′ also support the above structure. A detailed discussion of the patterns and the mechanism of the transformation will be presented elsewhere.[28]

The resistivity, the infrared spectrum, and the X-ray powder pattern of the transformed crystal, Ia′, were very similar to those of the III-type crystal, irrespective of the content of the excess neutral TCNQ molecule. These facts suggest that the latter crystal has a stable structure of its TCNQ column, the stability being determined by the crystallization process. This will be discussed in the next section.

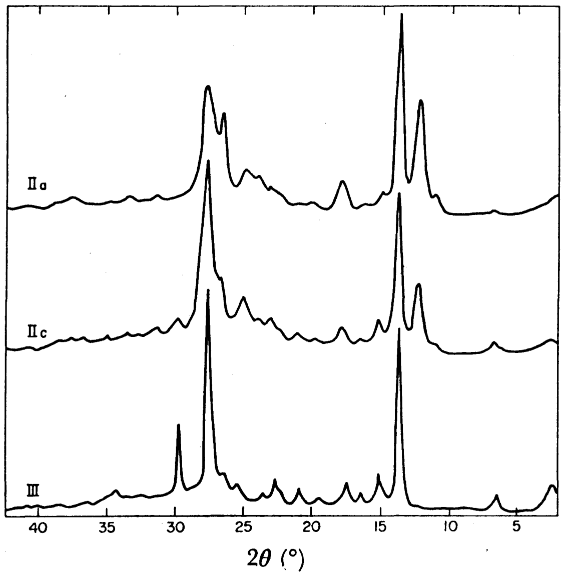

Fig. 5. X-ray diffraction patterns of MeQ(TCNQ)$_x$ salts. IIa: MeQ(TCNQ)$_{2.2}$, IIc: MeQ(TCNQ)$_{2.2}$ and III: MeQ(TCNQ)$_{2.1}$.

The II- and III-Type Crystals, Metastable and Stable Crystals. The X-ray powder patterns of the salts in Groups II and III are shown in Fig. 5. We can distinguish between the patterns of II and III. The IIa and IIc crystals had almost the same patterns, with little difference in the positions of the intense peaks. The pattern for IIa exhibited peaks at 11.8, 13.4, 26.5, and 27.5 degrees, and that for IIc, at 11.8, 13.4, 26.4, and 27.5 degrees. The main peak of III was found at 29.8°, and the peak at 11.8° was absent. Since the stability of the IIb crystal was poor, it was difficult to obtain its X-ray pattern as crystallized, but evidence was found that it may have a structure similar to that of IIa. The three compounds in Group II have, therefore, the same crystal structure, although they differ in both the TCNQ-to-cation ratio and the stability of the resistivity value.[28]

The difference in the crystallization process between II and III was the concentration of the solution. From a concentrated acetone solution (30 mmol/l), the III crystal was obtained one day after the first precipitate, IIb, had been removed by filtration. A dilute solution (13 mmol/l), however, gave only the III crystal in about a day. The IIb crystal was unstable, as has been mentioned above, and it exhibited changes in both resistivity and X-ray pattern at room temperature. For example, the resistivity of IIb was 0.8 Ω cm as crystallized but it increased to about 60 Ωcm after a week. The other crystals in Group II were also unstable or metastable crystals, because they exhibited a significant increase in resistivity at relatively lower temperatures (50—80 °C). The III crystal was thought to be a stable one, although in some cases it displayed a very small change in resistivity at elevated temperatures.

The appearance of the stable and unstable (or metastable) crystals from the same solution has been generalized thermodynamically by Ostwald in his "Law of Stages."[29] According to the law, multiple phases of different stabilities can appear in the order of their relative stabilities from a solution or melt left in a metastable state, because the crystallization takes place with the smallest loss of the free-energy content of the system. For the crystallization of the MeQ(TCNQ)$_x$ salts from a solution, the condition of a higher free-energy content may be established both in the earlier stage of crystallization from an acetone solution (high temperature and high concentration) and when the solubility of the salt is low (when dichloromethane or water was used as the solvent). Therefore, the lower resistivity of the II-type crystals can be explained quite reasonably if we assume them to be crystallized in a metastable state following the Ostwald law. The fact that the infrared spectra of II and III were almost the same as those of Q(TCNQ)$_2$ and *N*-*n*-propylquinolinium(TCNQ)$_2$, NPQ(TCNQ)$_2$, respectively is very helpful in understanding the structure of the TCNQ columns of the metastable and stable crystals.

In Q(TCNQ)$_2$,[30] the TCNQ molecules are stacked with an equal interplanar spacing and with an overlap mode so that one molecule is shifted longitudinally with respect to another by one-fourth the molecular length. A typical example of a distorted TCNQ column structure is NPQ(TCNQ)$_2$,[24] where the interplanar conformations of TCNQ in the column are not identical, but an extended interplanar spacing and a transversally shifted mode of overlap are found periodically.[31] Since we could not obtain any multiple phases or unstable crystals of either Q(TCNQ)$_2$ or NPQ(TCNQ)$_2$, the two structures seem to be representative of the stable TCNQ column structure of *N*-alkyl·Q(TCNQ)$_2$ salts at room temperature. Considering the size of the MeQ cation, it is not impossible that the MeQ(TCNQ)$_x$ salt assumes both types of crystal structures, the Q(TCNQ)$_2$ and NPQ(TCNQ)$_2$ types. The same discussion can apply to the case of the *N*-ethylquinolinium cation; in fact a similar phenomenon has been observed for the *N*-ethyl·Q(TCNQ)$_x$

salt,[15] a study of which is currently being made in our laboratory.

The crystallization rate was a controling factor in the difference between IIb and IIa or IIc. When an acetone solution of MeQ$(TCNQ)_x$ (20 mmol/l) was cooled from 60 to 5 °C at a rate of 0.8 or 0.2 °C/min, the IIb crystal (with a TCNQ-to-cation ratio of 1.6) was obtained. On the other hand, crystals which were obtained from an acetone solution of the same concentration cooled at a rate of 4 °C/min had a TCNQ-to-cation ratio of 2.2 and a low resistivity (about 1 Ω cm), so that they may be thought to be the same as IIa.

A calculation[30] of the stabilization energy of the $(TCNQ)_2^-$ system revealed that the most stable overlap configuration is that found in the Q$(TCNQ)_2$ crystal. The stability of the crystal as a whole is determined not only by the configuration energy of the TCNQ column, but also by the steric factor of the cations.[32] It is likely that a higher rate of crystallization gives rise to a stable configuration of TCNQ, resulting in an unstable structure as a whole. This seems to be the case in the crystallization of IIa or IIc, where the unstable structure may have been frozen with the aid of the steric hindrance of the cation molecules, probably by the rapid quenching of the crystal. This mechanism is supported by the dependence of the content of the neutral TCNQ in the II-type crystals on the crystallization rate. The higher rate prefers the stacking of the TCNQ molecules, defects being left in the column of the cation.

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