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# Synthesis, Electrical Resistivities, and Electronic Reflection Spectra of Alkaline-earth Metal Cation-TCNQ-Crown Ether Complexes

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Two types of alkaline-earth metal cation–TCNQ–crown ether complexes were synthesized: one is the simple salt, expressed as $[M^{2+}(TCNQ^-)_2]_m(\text{crown ether})_n$ and the other is the complex salt expressed as $[M^{2+}(TCNQ^-)_2]_m(TCNQ)_n(\text{crown ether})_i$. The electrical resistivities of the complexes were measured for compacted samples and single crystals. The resistivities of the simple salts were greater than $10^5$ Ω cm, so they are much less conductive than the original TCNQ salts, $M^{2+}(TCNQ^-)_2$. Most of the complex salts were more conductive than the original TCNQ salts, with the resistivities of 4—$10^3$ Ω cm.

The studies on the electrical conductivities of 7,7,8,8-tetracyanoquinodimethan (TCNQ) complexes have clarified that the mixed valent complex is more conductive than the other type complex which does not contain neutral TCNQ.[1] Many metal-cation TCNQ salts have been synthesized. However, most of them are simple salts, expressable as $M^{m+}(TCNQ^-)_m$.[2] Therefore, we can not expect high conductivity.[3] Even if we try to synthesize a complex salt, $M^{m+}(TCNQ^-)_m(TCNQ)_n$, from a solution by the reaction of a simple salt with neutral TCNQ, the simple salt only crystallizes out because of its poor solubility. We noticed that a series of macrocyclic polyethers called crown ethers have a specific property of accepting metal cations into their cavities and thereby of solubilizing many inorganic salts into organic solvents like benzene.[4] We thought that a simple salt solubilized by using crown ether would complex with neutral TCNQ in solution to produce complex salt. In fact, we could obtain several complex salts, as well as simple salts, in the case of alkali-metal cation–TCNQ–crown ether complexes.[5] Comparing the conductivities of the complexes thus obtained with those of the original TCNQ salts, we found comparable conductivities. This fact will be explained as follows. Although the introduction of the crown ether has a negative effect on the conductivity by the steric hindrance, the complex salt formation has a positive effect on the conductivity. Thus, compensation of the two effects resulted in the same order of magnitude of the conductivity in the case of the alkali-metal cation complex. We thought that the former negative effect could be overcome by using the multi-valent cation TCNQ salts. One metal-cation accompanies more than one TCNQ molecule in this case; this may result in a closer distance between TCNQ molecules as compared with the spacing in the alkali-metal cation complex. So we synthesized alkaline-earth metal cation–TCNQ–crown ether complexes, and measured the electrical resistivities of the compacted samples and two single crystals in expectation of achieving highly conductive materials. We also measured the electronic diffuse reflection spectra of the new complexes in order to know the electronic interaction between TCNQ molecules in the solid-state.

## Experimental

*Materials.* Alkaline-earth metal–TCNQ salts were synthesized according to the reported procedures.[6] All the crown ethers were purchased from Nakarai Chemicals, Ltd.

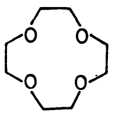
*Synthesis of Cation–TCNQ–Crown Ether Complexes.* Simple salts, $[M^{2+}(TCNQ^-)_2]_m(\text{crown ether})_n$, were synthesized by the reaction of the original $M^{2+}(TCNQ^-)_2$ with a crown ether in methanol. Complex salts, $[M^{2+}(TCNQ^-)_2]_m(TCNQ)_n(\text{crown ether})_i$, were synthesized either by the reaction of a simple salt with neutral TCNQ or by the reaction of $M^{2+}(TCNQ^-)_2$, crown ether and neutral TCNQ in organic solvent. The details of the synthesis were described before.[5]

*Electrical Resistivity Measurements.* Electrical resistivity in the compacted sample was measured by the same procedures as described before.[5] The electrical resistivity of the single crystal was measured by a four probe method, and the temperature was regulated by type-D Cryomini refrigerator (Osaka Sanso Co., Ltd).

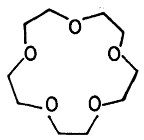
*Electronic Diffuse Reflection Spectra.* Electronic diffuse reflection spectra of the complexes were measured by a Hitachi 340 Recording Spectrophotometer. The sample was smeared onto a filter paper. The reflected light was collected by integrating over a sphere.

## Results and Discussion

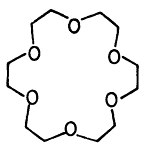
*Isolation of Alkaline-earth Metal Cation–TCNQ–Crown Ether Complexes.* The following crown ethers and TCNQ salts were used for the preparation of the complexes: 12-crown-4, 15-crown-5, 18-crown-6, perhydrobenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecane



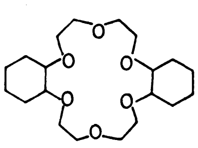
12Cr4



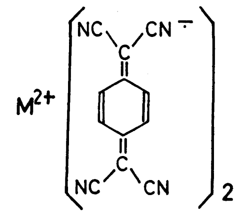
15Cr5



18Cr6



DCH18Cr6



$M^{2+}(TCNQ^-)_2$

$M^{2+} = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}$

(usually called as "dicyclohexy-18-crown-6"), $Mg^{2+}(TCNQ^-)_2 6H_2O$, $Ca^{2+}(TCNQ^-)_2$, $Sr^{2+}(TCNQ^-)_2$, $Ba^{2+}(TCNQ^-)_2$, and $Pb^{2+}(TCNQ^-)_2$ $1.5H_2O$, the molecular structures of which are shown above. In the above figure, the abbreviations of Cr, and DCH mean crown ether, and bis(perhydrobenzo) component, respectively. Thus, DCH18Cr6 denotes "dicyclohexyl-18-crown-6." We have isolated two types of complexes: one is in the simple salts and expressed as $[M^{2+}(TCNQ^-)_2]_m$-(crown ether)$_n$ and the other is in the complex salt and expressed as $[M^{2+}(TCNQ^-)_2]_m$–$(TCNQ)_n$–(crown ether)$_i$. Table 1 summarizes the complexes isolated and their yields, melting points, analytical data, and appearences and colors. As expected, the stoichiometry of the simple salt has a tendency for the crown ether with a cavity comparable to or larger than the cation size to have a one-to-one stoichiometry, while the crown ether with a cavity smaller than the cation size has a two-to-one stoichiometry arising from the cation being sandwiched by crown ethers.[7] The stoichiometries of most of the complex salts are derived from the simple salts plus one molecule of neutral TCNQ. However, the complex salts, including DCH18Cr6, have two molecules of neutral TCNQ. In general, the solubility becomes low when a simple salt complexes with neutral TCNQ. Because the solubilities of DCH18Cr6 complexes are higher than those of the other crown ether complexes, the complex salt of DCH18Cr6 does not crystallize out from the solution until two molecules of neutral TCNQ complex with one simple salt. Some of the magnesium complexes contained water of crystallization. A variety of crystal colors (violet, green, yellow green, or purple) were found in the simple salts; these resulted from the

Table 1. Alkaline-earth metal cation–TCNQ–crown ether complexes

| Complex | Yield$^{a)}$ % | Mp $\theta_m$/°C | Found (Calcd) (%) C | H | N | Description$^{b)}$ |
|---|---|---|---|---|---|---|
| Simple salts | | | | | | |
| $Mg^{2+}(TCNQ^-)_2(15Cr5)_2 2H_2O$ | 11 | 169—170 | 58.74<br>(58.12) | 5.59<br>(5.76) | 12.34<br>(12.32) | violet plate |
| $Mg^{2+}(TCNQ^-)_2(18Cr6)$ | | 239—240 | 62.00<br>(62.04) | 4.57<br>(4.63) | 16.18<br>(16.08) | purple needle |
| $Ca^{2+}(TCNQ^-)_2(12Cr4)_2$ | | 100 | 59.33<br>(59.99) | 4.98<br>(5.03) | 14.07<br>(13.99) | violet needle |
| $Sr^{2+}(TCNQ^-)_2(15Cr5)_2$ | 30 | 242—245 | 56.50<br>(56.43) | 5.21<br>(5.17) | 11.89<br>(11.96) | dark green microcrystal |
| $Ba^{2+}(TCNQ^-)_2(15Cr5)_2$ | 36 | 249—250 | 53.43<br>(53.58) | 5.09<br>(4.91) | 11.42<br>(11.36) | dark green microcrystal |
| $Ba^{2+}(TCNQ^-)_2(18Cr6)$ | 33 | 220—221 | 52.73<br>(53.38) | 4.04<br>(3.98) | 13.70<br>(13.83) | violet plate |
| $Pb^{2+}(TCNQ^-)_2(15Cr5)_2$ | 35 | 265—270 | 50.05<br>(50.04) | 4.59<br>(4.58) | 10.66<br>(10.61) | yellow-green microcrystal |
| Complex salts | | | | | | |
| $Mg^{2+}(TCNQ^-)_2TCNQ(12Cr4)_2$ | 47 | >300 | 62.40<br>(63.13) | 4.45<br>(4.48) | 17.09<br>(16.99) | plate |
| $[Mg^{2+}(TCNQ^-)_2TCNQ]_2(15Cr5)_3 2H_2O$ | | >300 | 62.65<br>(62.16) | 4.40<br>(4.50) | 17.17<br>(17.05) | needle |
| $Ca^{2+}(TCNQ^-)_2TCNQ(12Cr4)_2$ | 21 | 240—245 | 62.09<br>(62.14) | 4.31<br>(4.41) | 17.44<br>(16.72) | microcrystal |
| $Ca^{2+}(TCNQ^-)_2TCNQ(15Cr5)_2$ | 41 | >300 | 61.78<br>(62.14) | 4.65<br>(4.41) | 16.47<br>(16.72) | long thin plate |
| $Ca^{2+}(TCNQ^-)_2TCNQ(18Cr6)$ | 53 | >300 | 61.61<br>(62.87) | 3.98<br>(3.96) | 17.88<br>(18.33) | long thin plate |
| $Ca^{2+}(TCNQ^-)_2(TCNQ)_2(DCH18Cr6)$ | 34 | 234—235 | 66.13<br>(66.44) | 4.35<br>(4.26) | 18.04<br>(18.23) | needle |
| $Sr^{2+}(TCNQ^-)_2TCNQ(15Cr5)_2$ | 59 | 250—257 | 58.92<br>(58.97) | 4.57<br>(4.59) | 14.97<br>(14.73) | needle |
| $Sr^{2+}(TCNQ^-)_2TCNQ(18Cr6)$ | 20 | 195—200 | 59.64<br>(59.77) | 3.51<br>(3.76) | 17.53<br>(17.43) | long thin plate |
| $Ba^{2+}(TCNQ^-)_2TCNQ(12Cr4)_2$ | | 215—216 | 56.01<br>(56.66) | 4.49<br>(4.02) | 15.08<br>(15.25) | plate |
| $Ba^{2+}(TCNQ^-)_2TCNQ(15Cr5)_2$ | 53 | 234—235 | 56.48<br>(56.50) | 4.30<br>(4.40) | 14.34<br>(14.12) | violet needle |
| $Ba^{2+}(TCNQ^-)_2TCNQ(18Cr6)$ | 58 | 261—263 | 56.47<br>(56.84) | 3.62<br>(3.77) | 16.53<br>(16.57) | microcrystal |
| $Ba^{2+}(TCNQ^-)_2(TCNQ)_2(DCH18Cr6)$ | 19 | 235—236 | 60.60<br>(61.57) | 3.81<br>(3.95) | 17.09<br>(16.89) | needle |
| $Pb^{2+}(TCNQ^-)_2TCNQ(15Cr5)_2$ | 58 | 238—240 | 53.38<br>(53.37) | 4.25<br>(4.16) | 13.75<br>(13.34) | purple needle |

a) Unless specified, the yield is less than 10%. b) The colors of most of the complex-salts were black.

Table 2. Electrical resistivities and electronic reflection peak positions of alkaline-earth metal cation–TCNQ–crown ether complexes

| Complex | Resistivity[b] / Ω cm | Reflection peak position/$10^3$ $cm^{-1}$ |
|---|---|---|
| Simple salts | | |
| (1) Violet complex | | |
| $Mg^{2+}(TCNQ^-)_2(15Cr5)_2 2H_2O$ | | 11.1 17.4 24.6 |
| $Mg^{2+}(TCNQ^-)_2(18Cr6)$ | | |
| $Ca^{2+}(TCNQ^-)_2(12Cr4)_2$ | $2.1\times10^5$ | 11.9 17.3 24.2 |
| $Ba^{2+}(TCNQ^-)_2(18Cr6)$ | $9.0\times10^7$ | 11.7 17.0 24.8 |
| (2) Green complex | | |
| $Sr^{2+}(TCNQ^-)_2(15Cr5)_2$ | $7.7\times10^8$ | 8.8 11.7 13.4 29.9 |
| $Ba^{2+}(TCNQ^-)_2(15Cr5)_2$ | $3.7\times10^{10}$ | 8.8 11.7 13.3 29.4 |
| $Pb^{2+}(TCNQ^-)_2(15Cr5)_2$ | $5.8\times10^6$ | 8.8 11.4 13.5 14.7 29.4 |
| Complex salts[a] | | |
| $Mg^{2+}(TCNQ^-)_2TCNQ(12Cr4)_2$ | $4.2\times10^3$ | |
| $[Mg^{2+}(TCNQ^-)_2TCNQ]_2(15Cr5)_3 2H_2O$ | 86, 4[c] | 12.4 17.7 24.7 |
| $Ca^{2+}(TCNQ^-)_2TCNQ(12Cr4)_2$ | 38, 10[c] | 11.7 17.2 25.0 |
| $Ca^{2+}(TCNQ^-)_2TCNQ(15Cr5)_2$ | $4.5\times10^2$ | 11.9 17.3 25.7 |
| $Ca^{2+}(TCNQ^-)_2TCNQ(18Cr6)$ | $1.8\times10^3$ | |
| $Ca^{2+}(TCNQ^-)_2(TCNQ)_2(DCH18Cr6)$ | $1.2\times10^3$ | |
| $Sr^{2+}(TCNQ^-)_2TCNQ(15Cr5)_2$ | $6.5\times10^3$ | 11.8 16.6 25.0 |
| $Sr^{2+}(TCNQ^-)_2TCNQ(18Cr6)$ | $5.1\times10^3$ | 12.0 16.3 25.1 |
| $Ba^{2+}(TCNQ^-)_2TCNQ(12Cr4)_2$ | $6.4\times10^2$ | |
| $Ba^{2+}(TCNQ^-)_2TCNQ(15Cr5)_2$ | $3.5\times10^3$ | 11.7 17.3 25.0 |
| $Ba^{2+}(TCNQ^-)_2TCNQ(18Cr6)$ | $4.5\times10^3$ | 11.8 12.1 17.0 24.4 |
| $Ba^{2+}(TCNQ^-)_2(TCNQ)_2(DCH18Cr6)$ | $5.9\times10^2$ | 11.8 15.2 |
| $Pb^{2+}(TCNQ^-)_2TCNQ(15Cr5)_2$ | $3.2\times10^3$ | |

a) Besides these reflection peaks, all the complex-salts have the reflection bands lower than $7\times10^3$ $cm^{-1}$ ascribable to the charge-transfer transition from $TCNQ^-$ to TCNQ. b) Compacted Sample. c) Single crystal.

Table 3. The resistivities of di-valent metal–TCNQ complexes

| Complex | Resistivities/Ω cm[a] |
|---|---|
| $Mg^{2+}(TCNQ^-)_2 6H_2O$ | $5\times10^3$ |
| $Ca^{2+}(TCNQ^-)_2$ | $1\times10^4$ |
| $Sr^{2+}(TCNQ^-)_2$ | $1\times10^3$ |
| $Ba^{2+}(TCNQ^-)_2$ | $8\times10^5$ |
| $Pb^{2+}(TCNQ^-)_2 1.5H_2O$ | $2\times10^3$ |

a) D. S. Acker, Waynesboro, Va., and D. C. Blomstrom, U. S. Patent 3162641 (1964).

differences of the electronic interaction between the TCNQ anion radicals in the solid state. In other words, we can modify the interaction between TCNQ anion radicals in the solid state by introducing the crown ether. The colors of most of the complex salts were black. The melting points of the complexes thus obtained were much lower than those of the original salts, $M^{2+}(TCNQ^-)_2$, which are higher than 300 °C. This fact will result from the much weaker electrostatic attraction between metal cation and $TCNQ^-$; this results in a much smaller Madelung energy than in the cases of the original salts. Unlike the poor solubilities of the original TCNQ salts in the usual organic solvent, the solubilities of the complexes isolated here were large as expected. Their high solubilities in the organic solvents may be useful for practical applications. These complexes were stable in air for several months.

*Electrical Resistivities.* The electrical resistivities of the simple salts and complex salts were measured for the compressed samples at room temperature. The resistivities of the conductive salts, $Mg^{2+}(TCNQ^-)_2$-$TCNQ(15Cr5)_2 2H_2O$ and $Ca^{2+}(TCNQ^-)_2$ $TCNQ(12Cr4)_2$ were measured for single crystals. Table 2 summarizes the observed results. Table 3 shows the electrical resistivities of the original TCNQ salts, for the sake of comparison. Table 2 shows that the resistivities of the simple salts are greater than $10^5$ Ω cm; these salts are thus much less conductive than the original TCNQ salts (see Table 3). On the other hand, the complex salts are much more conductive than the corresponding simple salts, with the electrical resistivities of 4—$10^3$ Ω cm. Thus, most of the complex salts were more conductive than the original TCNQ salts, which is in line with our expectation. The lowest resistivity (4 Ω cm) was found in $Mg^{2+}(TCNQ^-)_2$ $TCNQ(15Cr5)_2$ $2H_2O$ single crystal at room temperature. The signle crystal of $Ca^{2+}(TCNQ^-)_2$ $TCNQ(12Cr4)_2$ showed a resistivity of 10 Ω cm at room temperature. The temperature dependence of the electrical resistivity of the former single crystal is shown in Fig. 1.8) The change of the temperature dependence of the resistivity at 154 K may be caused by a phase transition. The activation energies were 0.06 eV and 0.02 eV at the higher and lower temperature ranges, respectively. The complex, $Ca^{2+}(TCNQ^-)_2TCNQ$-$(12Cr4)_2$, is expected to incorporate another neutral TCNQ in principle, although we could not isolate such a type of complex from the solution. However, we

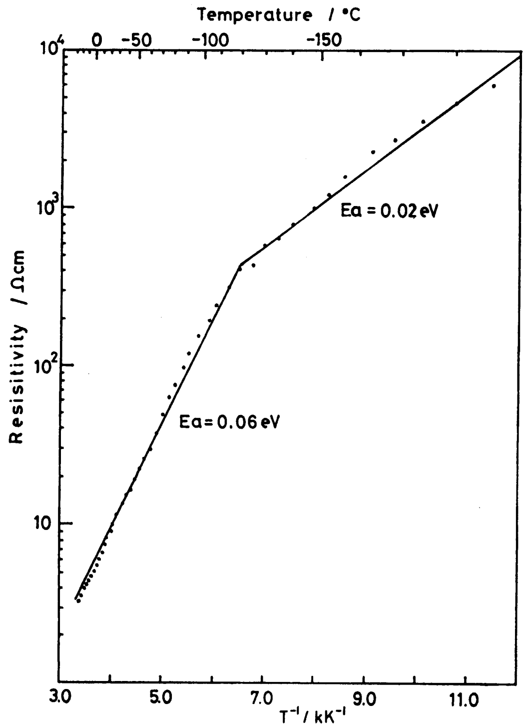


Fig. 1. Temperature dependence of the electrical resistivity of $Mg^{2+}(TCNQ^-)_2$ $TCNQ(15Cr5)_2 2H_2O$ single crystal.

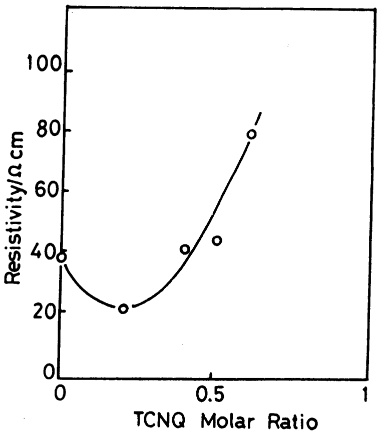


Fig. 2. The plot of the electrical resistivity against the molar fraction of neutral TCNQ added to $Ca^{2+}$-$(TCNQ^-)_2$ $TCNQ(12Cr4)_2$.

found that the complex salt formation occurs by simply grinding $Ca^{2+}(TCNQ^-)_2TCNQ(12Cr4)_2$ with neutral TCNQ in an agate bowl. Figure 2 shows the plot of the electrical resistivity against the molar fraction of neutral TCNQ added to $Ca^{2+}$ $(TCNQ^-)_2$ TCNQ-$(12Cr4)_2$. This complex had a values of 38 Ω cm for the compacted sample at room temperature. As more and more neutral TCNQ was added to this complex, the resistivity of the complex first decreased down to 20 Ω cm and then increased. The increase of the conductivity in the range of less than 0.2 added TCNQ molar fraction indicates that the solid-state complex-salt formation reaction occurs simply by grinding the original salt with neutral TCNQ in an agate bowl. An analogous reaction was also found in alkali-metal cation-TCNQ-crown ether complex.[5] Thus, the solid-state reaction is characteristic of these crown ether complexes: it is not found in the original TCNQ salts. The fact that the above mentioned 12Cr4 complex is a good conductor suggests that the small crown ether may be an important factor in the high conductivity. But the order of the conductivity of the 12Cr4-complex salts does not correspond to the order of the cation size. Thus, we could not simply correlate the conductivities of the complex-salts with the cation size.[9]

Now, let us compare the electrical resistivities of the complexes isolated here with those of the alkali-metal-TCNQ-crown ether complexes. In the case of the alkali-metal cation complexes, simple salts and complex salts had resistivities of the order of $10^8$—$10^{14}$ Ω cm and $10^3$—$10^4$ Ω cm, respectively, On the other hand, in the case of the alkaline-earth metal cation complexes, simple salts and complex salts had resistivities of the order of $10^5$—$10^{10}$ Ω cm and $10^0$—$10^3$ Ω cm, respectively. Thus, the alkaline-earth metal cation complexes are much more conductive than the alkali-metal cation complexes both in the simple and complex salts, which is in line with our expectation.

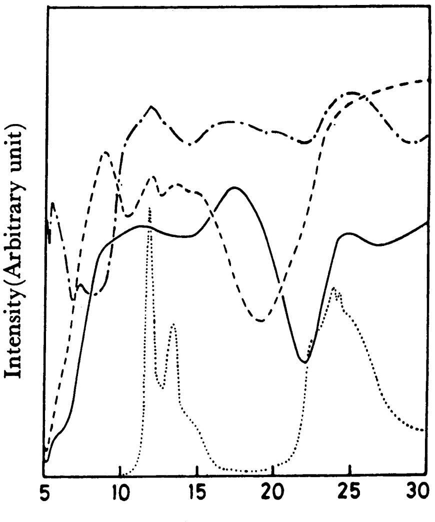


Fig. 3. Diffuse reflection spectra of the alkaline-earth metal cation-TCNQ-crown ether complexes.
——: $Ca^{2+}(TCNQ^-)_2(12Cr4)_2$, ------: $Ba^{2+}(TCNQ^-)_2$-$(15Cr5)_2$, —·—: $Ca^{2+}(TCNQ^-)_2TCNQ(12Cr4)_2$, ······: $K^+TCNQ^-$ in acetonitrile solution.

*Electronic Diffuse Reflection Spectra.* Electronic diffuse reflection spectra of the complexes were measured at room temperature.[10] Figure 3 shows the spectra of $Ca^{2+}(TCNQ^-)_2(12Cr4)_2$, $Ba^{2+}(TCNQ^-)_2(15Cr5)_2$, and $Ca^{2+}(TCNQ^-)_2$ $TCNQ(12Cr4)_2$ as typical examples. This figure also shows the absorption spectra of $K^+$-$TCNQ^-$ in acetonitrile solution for the sake of comparison.

All the violet complexes showed two broad absorption peaks at less than $20\times10^3$ $cm^{-1}$, like $Ca^{2+}(TCNQ^-)_2$-$(12Cr4)_2$. Although the crystallographic study and polarized absorption measurements are needed for the assignments of these absorption bands, the most probable assignment of the lowest energy band is the charge-transfer (CT) transition between TCNQ anion radicals, and that of the next band is the local excitation band within $TCNQ^-$.[11] Thus, a TCNQ dimer structure is suggested from the spectra. On the other hand, all the green complexes have the characteristic profiles at $8—15\times10^3$ $cm^{-1}$ like $Ba^{2+}(TCNQ^-)_2(15Cr5)_2$. In view of the similarity of the spectrum of the green complex to that of $K^+TCNQ^-$ in solution, one possibility is that the $TCNQ^-$ is isolated in the crystal.[12] All the complex salts gave almost the same reflection spectra as $Ca^{2+}(TCNQ^-)_2TCNQ(12Cr4)_2$. The absorption band at less than $7\times10^3$ $cm^{-1}$ is ascribed to the CT transition from TCNQ anion radical to neutral TCNQ. Table 2 shows the absorption peak positions of the isolated simple and complex salts. Some relation exists between the colors of the simple salts and their resistivities: violet complexes were more conductive than the green ones in the simple salts. If $TCNQ^-$ is isolated in the green complex as discussed above, its poor conductivity can be explained by the small overlap of the $\pi$-electron could between adjacent TCNQ molecules.

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## References

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8) Because of the fragility of $Ca^{2+}(TCNQ^-)_2TCNQ$-$(12Cr4)_2$ single crystal, we could not measure the temperature dependence of its resistivity.

9) The resistivity of $Na^+TCNQ^-TCNQ(12Cr4)_2$ was found to be $1.5\times10^3$ $\Omega$ cm.

10) Uncorrected spectra.

11) J. Tanaka, M. Tanaka, T. Kawai, T. Takabe, and O. Maki, *Bull. Chem. Soc. Jpn.*, **49**, 2358 (1976).

12) The reflection spectrum of the green complex may be due to the isolated $TCNQ^-$ in the crystal, shifted about $3\times10^3$ $cm^{-1}$ to the lower energy side by the crystal field. Another possibility is that the band at $8.85\times10^3$ $cm^{-1}$ is the CT transition between $TCNQ^-$ molecules and that the bands at $10—15\times10^3$ $cm^{-1}$ correspond to the isolated $TCNQ^-$.