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The Syntheses, Electrical Resistivities, and Electronic Absorption Spectra of Cation–TCNQ–Crown Ether Complexes

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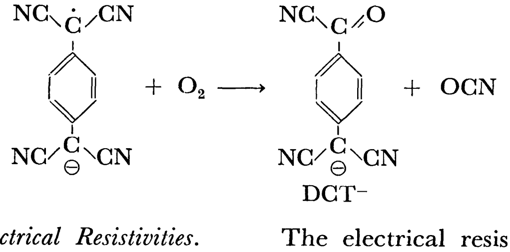
Crown ether complexes with alkali-metal–, ammonium–, and barium–TCNQ salts were isolated. Their electrical resistivities and electronic absorption spectra were measured. The simple salts, (crown ether)$_m$(M$^+$-TCNQ$^-$)$_n$, were almost all insulators with resistivities greater than $10^7\,\Omega$ cm. However, the complex salts, (Crown ether)$_m$(M$^+$TCNQ$^-$)$_n$(TCNQ), were much more conductive than simple salts with resistivities of 10^2—$10^4\,\Omega$ cm. Three types of electronic-absorption spectra were observed for the simple salts. The simple salts with charge-transfer absorption bands were much more conductive than those without charge-transfer absorption bands.

Since tetracyanoquinodimethane (TCNQ) has been synthesized,[1)] much attention has been paid to the high electrical conductivities and characteristic magnetic, optical, and structural properties of TCNQ complexes.[2)] It has been clarified that a structure with segregated stacks of donor and acceptor molecules in the crystal greatly influences the physical properties. The modification of the crystal structure might, therefore, induce interesting properties. In order to confirm this, we chose to study metal-cation– and ammonium–TCNQ salts and have tried to surround the cation with crown ethers.[3)] Surrounding the cation with crown ethers will weaken the interaction between the cation and TCNQ anion radicals,[4)] leading to a change in the physical properties. We have isolated the complexes of alkali-metal–, ammonium–, and barium–TCNQ salts with crown ethers and cryptand, and have measured their electrical resistivities and electronic-absorption spectra.[5)]

Results and Discussion

Isolation of Alkali-Metal–, Ammonium–, and Barium–TCNQ–Crown Ether Complexes. The following crown ethers, cryptand, and TCNQ salts were used for the preparation of the complexes: 12-crown-4 (**1**), 15-crown-5 (**2**), 18-crown-6 (**3**), dibenzo-18-crown-6 (**4**), dicyclohexyl-18-crown-6 (**5**), dibenzo-24-crown-8 (**6**), cryptand [2,2,2] (**7**), Li$^+$TCNQ$^-$ (**8**), Na$^+$TCNQ$^-$ (**9**), K$^+$TCNQ$^-$ (**10**), Rb$^+$TCNQ$^-$ (**11**), Cs$^+$TCNQ$^-$ (**12**), NH$_4^+$TCNQ$^-$ (**13**), and Ba^{2+}(TCNQ$^-$)$_2$ (**14**). We have isolated two types of complexes *i.e.*, simple salts, expressed as (crown ether)$_m$(M$^+$TCNQ$^-$)$_n$, and complex salts, expressed as (crown ether)$_m$ (M$^+$-TCNQ$^-$)$_n$(TCNQ).[6)] Table 1 lists the complexes isolated and their yields, melting points, stoichiometries, and analytical data, with some remarks. Most of the complexes were obtained as crystals. A variety of crystal colors were found for simple salts. As expected, the stoichiometry of a 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 sandwiched by crown ethers.[4)] In spite of the above tendency, however, several exceptions to these rules exist for simple salts; 18-crown-6 and substituted 18-crown-6 make complexes of different stoichiometries with the same cation, as has been shown for Rb-cation complexes with **3**, **4**, and **5**, and Cs-cation complexes with **3**, **4**, and **5**. Most of the complex salts have the stoichiometry to be expected from those of simple salts. However, there are some exceptions, such as **2–11–15**, **3–12–15**, and **4–12–15**. In the case of the system with 15-crown-5 and Cs$^+$TCNQ$^-$, we could not isolate the simple salt, while the complex salt could be isolated easily. In this connection, we could isolate the complex salts of sodium and potassium cations, *i.e.*, **2–10–15**, **3–9–15**, **3–10–15**, and **4–10–15**, while the corresponding original complex salts, Na$^+$-TCNQ$^-$TCNQ and K$^+$TCNQ$^-$TCNQ, have not been obtained thus far. Besides the complexes in Table 1, we tried to obtain the following simple salts and complex salts: **2–13**, **6–13**, **4–14**, **2–9–15**, **4–9–15**, **7–9–15**, **3–10–15**, **7–10–15**, **4–11–15**, **7–11–15**, **7–12–15**, **2–13–15**, **6–13–15**, and **4–14–15**. However, the existence of these salts could not be verified.

The simple salts of purple, violet, and blue colors and all the complex salts were found to be stable in the air for several months. However, the greenish yellow, yellow, and green complexes were unstable, and the surfaces of the solids became brown in the air or in an oxygen atmosphere for several hours. They were stable in a vacuum or in an argon atmosphere. The change in the diffuse reflectance spectra of these complexes with time in the air showed the gradual disappearence of the absorption band in the near-infrared region and the appearence of the absorption band at 480 nm. The 480 nm band may be due to the α,α-dicyano-*p*-(cyanocarbonyl)-α-toluenide anion (DCT$^-$) produced by the following reaction:[7)]



Electrical Resistivities. The electrical resistivities of the simple salts and complex salts measured with compressed samples are shown in Table 2. Table 3 shows the reported electrical resistivities, together with our measurements of the original TCNQ salts

Table 1. Cation-TCNQ-crown ether complexes

Complex	Yield/%[a]	Mp/°C[b]	Stoichiometry[c]	Found (Calcd) (%)			Remark
				C	H	N	
Simple salts							
1-8			1 : 1	61.15 (62.02)	5.21 (5.20)	14.33 (14.46)	Black plates
1-9	48	183—185	2 : 1	57.94 (58.02)	6.21 (6.26)	9.51 (9.67)	Blue needles
2-9	19	150	1 : 1	58.86 (59.06)	5.36 (5.41)	12.35 (12.52)	Purple hexahedral
3-9		151—153	1 : 1	57.04 (58.65)	5.53 (5.74)	11.40 (11.40)	Blue needles
4-9	57	214—216	1 : 1	65.45 (65.41)	4.78 (4.80)	9.60 (9.54)	Yellow green plates
5-9	18	173—174	1 : 1	64.07 (64.09)	6.82 (6.72)	9.26 (9.34)	Purple plates
7-9	60	160—161	1 : 1	59.69 (59.69)	6.63 (6.68)	13.90 (13.92)	Yellow powder
2-10	46	210	2 : 1	56.17 (56.20)	6.65 (6.48)	8.29 (8.19)	Purple hexahedral
3-10	58	203—205	1 : 1	56.50 (56.79)	5.57 (5.56)	11.30 (11.04)	Purple needles
4-10	65	202—204	1 : 1	63.71 (63.67)	4.65 (4.68)	9.19 (9.28)	Yellow green plates
5-10		189—192	1 : 1	62.13 (62.42)	6.30 (6.55)	9.88 (9.10)	Violet plates
7-10	56	137	1 : 1	58.21 (58.14)	6.50 (6.51)	13.58 (13.56)	Blue hexahedral
2-11	58	202—203	2 : 1	52.62 (52.64)	6.14 (6.07)	7.68 (7.67)	Purple hexahedral
3-11	64	208—210	2 : 1	51.87 (52.04)	5.15 (5.09)	10.08 (10.11)	Violet needles
4-11	38	173—177	1 : 1	61.57 (61.81)	5.07 (5.19)	5.69 (5.54)	Green needles
5-11	39	190—192	1 : 1	58.01 (58.05)	6.18 (6.09)	8.30 (8.46)	Purple plates
6-11	43	106—108	1 : 1	58.07 (58.58)	4.84 (4.92)	7.81 (7.59)	Yellow green plates
7-11	43	146—148	1 : 1	53.97 (54.09)	6.05 (6.05)	12.60 (12.62)	Violet hexahedral
3-12	30	198—200	3 : 2	49.07 (49.12)	5.54 (5.50)	7.67 (7.64)	Yellow plates
4-12	42	156	2 : 1	59.33 (59.04)	5.04 (4.95)	5.57 (5.30)	Green needles
6-12	54	137—138	1 : 1	55.11 (55.04)	4.59 (4.62)	7.06 (7.13)	Yellow green plates
7-12	62	151—153	1 : 1	50.55 (50.50)	5.66 (5.65)	11.68 (11.78)	Violet hexahedral
2-13	36	140—142	2 : 1	57.82 (57.99)	7.46 (7.30)	10.57 (10.57)	Violet needles
3-13	15	170—172	1 : 1	59.01 (59.25)	6.41 (6.63)	14.16 (14.39)	Purple needles
4-13	60	168—170	2 : 1	65.91 (66.23)	5.77 (5.99)	7.64 (7.43)	Green needles
5-13	12	156—157	1 : 1	64.60 (64.63)	7.55 (7.46)	11.58 (11.78)	Blue hexahedral
2-14		253—255	2 : 1	53.43 (53.58)	5.09 (4.91)	11.42 (11.36)	Yellow green plates
3-14		249—251	1 : 1	52.73 (52.38)	4.04 (3.98)	13.70 (13.83)	Purple needles
Complex salts							
3-9-15	37		1 : 1 : 1	61.94 (62.15)	4.47 (4.64)	15.96 (16.11)	Black needles
2-10-15			2 : 1 : 1	59.49 (59.51)	5.42 (5.45)	12.41 (12.62)	Black needles

Table 1. (Continued)

Complex	Yield/%[a]	Mp/°C[b]	Stoichiometry[c]	Found (Calcd) (%) C	H	N	Remark
Complex salts							
4-10-15	36	224—225	1 : 1 : 1	65.18 (65.42)	3.92 (3.99)	13.91 (13.87)	Black hexahedral
2-11-15[d]		260	2 : 1 : 1	56.45 56.45 (56.56)	5.17 5.19 (5.18)	12.01 11.91 (11.99)	Black needles
3-11-15[d]	59	235	1 : 1 : 1	56.91 56.95 (57.03)	4.23 4.21 (4.25)	14.98 14.73 (14.78)	Black plates
2-12-15			2 : 1 : 1	53.99 (53.83)	4.83 (4.93)	11.68 (11.41)	Black hexahedral
3-12-15	58		1 : 1 : 1	53.56 (53.67)	3.93 (4.00)	14.00 (13.91)	Black needles
4-12-15		173—174	4 : 2 : 1	59.59 (60.05)	4.81 (4.69)	7.08 (7.24)	Black needles
3-13-15	20	160—162	1 : 1 : 1	62.39 (62.60)	5.23 (5.25)	18.20 (18.25)	Black hexahedral
4-13-15		162—164	2 : 1 : 1	67.98 (67.17)	4.63 (4.61)	15.93 (16.02)	Black needles
5-13-15	10	167	1 : 1 : 1	66.05 (66.15)	6.01 (6.06)	15.96 (15.78)	Black hexahedral
2-14-15		245—247	2 : 1 : 1	57.71 (57.99)	7.53 (7.30)	10.60 (10.57)	Black needles
3-14-15		287—289	1 : 1 : 1	56.47 (56.84)	3.62 (3.77)	16.53 (16.57)	Black powder

a) Unless specified, the yield is less than 10%. b) Unless specified, the melting point is higher than 300 °C. c) Crown ether: $M^{n+}(TCNQ^-)_n$ for simple salts. Crown ether: $M^{n+}(TCNQ^-)_n$: TCNQ for complex salts. d) The upper analytical data were obtained for the samples using the one-step method, and the lower ones, for the samples using two-step method. The other analytical data were obtained for the samples with the one-step method.

for the sake of comparison. Table 2 shows that the electrical resistivities of the simple salts are greater than 10^7 Ωcm. On the other hand, the complex salts are much more conductive than the corresponding simple salts, having electrical resistivities of 10^2—10^1 Ωcm. When we compare the values of Table 2 with those of Table 3, it is clear that simple salts are much less conductive than the corresponding original TCNQ salts. On the other hand, the electrical resistivities of the complex salts are of almost the same order as those of the original TCNQ salts. It is noteworthy that **3–9–15** and **3–13–15** are much more conductive than **9** and **13** respectively. Considering the fact that the complex salt can be easily produced for cation–TCNQ-crown ether complexes, these complexes may be expected to be good candidates for highly conductive organic materials.

We have found that a close correlation exists between the colors of the simple salts and their electrical resistivities. All the yellow or greenish-yellow complexes[8] have electrical resistivities greater than 10^{14} Ωcm.[9] On the other hand, blue, purple, violet, or green complexes[10] are much more conductive than the yellow or greenish-yellow complexes with the electrical resistivities of 10^7—10^{11} Ωcm. This is probably because of the difference in the strength of the interaction between adjacent TCNQ anion radicals in the crystal. The TCNQ anion radicals in the yellow or greenish-yellow crystals are almost completely isolated from each other. On the other hand, the overlap of the π-molecular orbitals of the neighboring TCNQ anion radicals occurs to some extent in the other simple salts.

We have also found evidence of complex-salt formation by only grinding a mixture of a simple salt and neutral TCNQ in an agate bowl. Figure 1 shows the plot of the electrical resistivities of the mixture against the initial neutral TCNQ molar fraction in **3–10** and **15** mixtures. The electrical resistivity drops about four orders of magnitude at the TCNQ molar fraction of *ca.* 0.7. The attained minimum electrical resistivities are one order of magnitude greater than in the pure complex salt, thus showing the complex-salt formation.

Electronic Absorption Measurements. The electronic absorption spectra were measured by the nujol-mull method. Figure 2 shows the electronic absorption spectra of **10** in an acetonitrile solution and in nujol mull. The absorption band at 7×10^3 cm^{-1} for the nujol-mull spectrum is ascribed to the charge-transfer (CT) transition between TCNQ anion radicals.[11] Table 2 summarizes the absorption-peak positions of the cation–TCNQ-crown ether complexes. Three types of absorption spectra were observed for the simple salts: Type A, purple, violet, or blue complexes with two absorption bands with comparable intensities below 20×10^3 cm^{-1}; Type B, yellow or greenish-yellow complexes with a sharp absorption peak around 12×10^3

Table 2. Electrical resistivities and electronic-absorption peak positions of cation-TCNQ-crown ether complexes

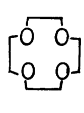
Complex	Resistivities	Absorption peak positions		
	Ω cm	10^3 cm^{-1}		
Simple salts				
Type A				
1-9	6.6×10^{8}	7.0	14.3	
2-9	1.3×10^{10}	9.3	14.3	
5-9		11.2	14.9	
2-10	8.5×10^{11}	9.6	15.2	
3-10	6.7×10^{9}	11.7	15.2	
5-10		10.8	14.8	
7-10	1.3×10^{10}	8.3	14.7	
2-11	1.3×10^{9}	10.5	14.6	
3-11	6.9×10^{9}	11.6	14.9	
5-11	2.8×10^{11}	10.4	14.8	
7-11	7.4×10^{9}	8.3	14.8	
7-12	2.4×10^{10}	8.1	14.7	
2-13	4.0×10^{8}	10.6	14.7	
3-13	2.3×10^{9}	11.8	14.9	
Type B				
4-9	$>10^{14}$	11.0	13.0	
7-9	$>10^{14}$	11.8	13.2	
4-10	$>10^{14}$	11.6	13.2	
6-11		11.3	12.9	14.5
3-12	$>10^{14}$	11.8	13.4	
6-12	$>10^{14}$	11.6	13.2	
Type C				
4-11	2.0×10^{9}	7.1	11.5	13.3
4-12	1.1×10^{11}	7.1	11.4	12.8
4-13	6.6×10^{7}	7.7	11.6	13.9
2-14		8.8	11.8	
Complex salts[a]				
3- 9-15	1.9×10^{3}	9.9	11.4	14.7
2-10-15		10.4		
4-10-15	4.4×10^{3}	9.9	11.4	
2-11-15	1.5×10^{4}	10.2	16.4	
3-11-15	1.2×10^{4}	10.6		
2-12-15		9.6	11.1	16.1
3-12-15	2.8×10^{3}	10.6		
3-13-15	4.6×10^{2}	10.8		
5-13-15		11.4	13.2	
2-14-15		11.2	15.2	

a) Besides these absorption peaks, all the complex salts have the absorption bands below 5×10^3 cm^{-1}.

Table 3. Electrical resistivities of cation-TCNQ salts[a]

Complex	Resistivities/Ω cm
8	2×10^{5}
9	3×10^{4}
10	5×10^{3}
11	2.8×10^{3} [b]
12	3×10^{4}
13	3×10^{4} [b]

a) D. S. Acker, Wayneshoro, Va., and D. C. Blomstrom, US Patent 3162641 (1964). b) Our measurements.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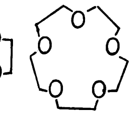
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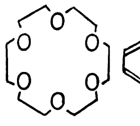
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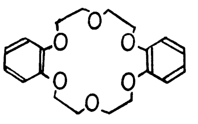
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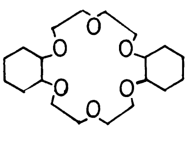
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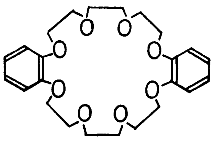
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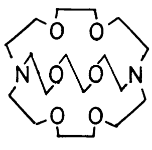
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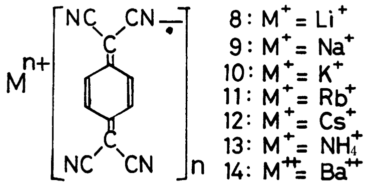
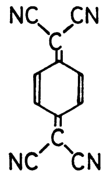


8,9,10,11,12,13,14



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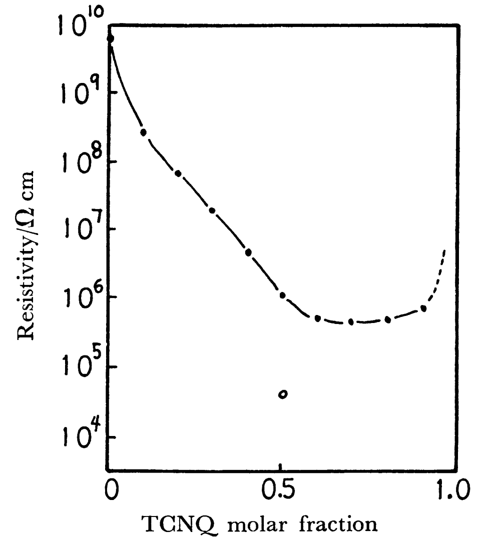

Fig. 1. The plot of the electrical resistivities of the mixture of **3–10** and **15** against initial neutral TCNQ molar fraction. Open circle denotes the electrical resistivity of the complex salt **3–10–15**.

cm^{-1} and no or weak absorption below 12×10^3 cm^{-1}, and Type C, green complexes with a sharp absorption peak around 12×10^3 cm^{-1} and a relatively strong absorption peak below 12×10^3 cm^{-1}. All the complex salts have a characteristic absorption below 5×10^3 cm^{-1}. Figures 3, 4, and 5 show the electronic absorption spectra of several simple salts of Types A, B, and C respectively as typical examples. Figure 6 shows the electronic absorption spectra of three complex salts.

Although crystallographic study and the polarized absorption spectra are needed for the assignment of the absorption bands, the most probable assignment for the Type A complex is that the lowest-energy

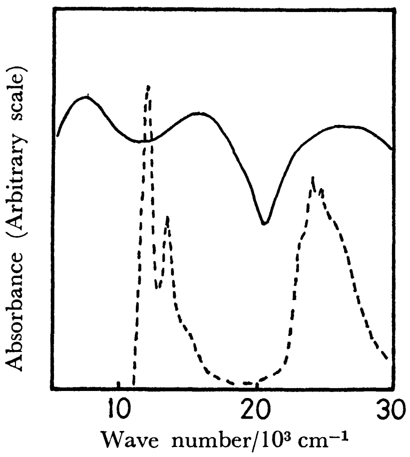

Fig. 2. The electronic absorption spectra of **10** in acetonitrile solution and in nujol mull.
---- in acetonitrile; —— in nujol mull.

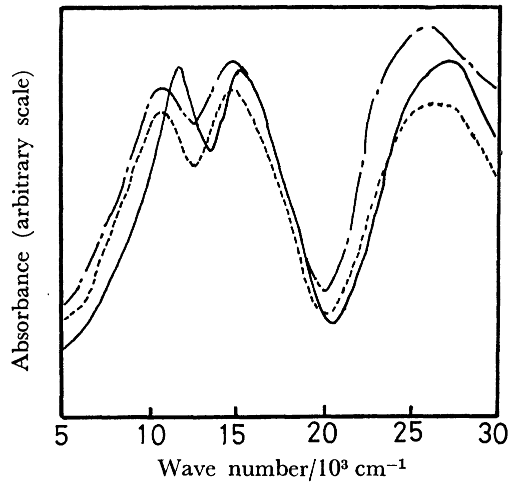

Fig. 3. The electronic absorption spectra of type A complexes in nujol mull.
—— **3-10**; ---- **2-11**; ——— **2-13**.

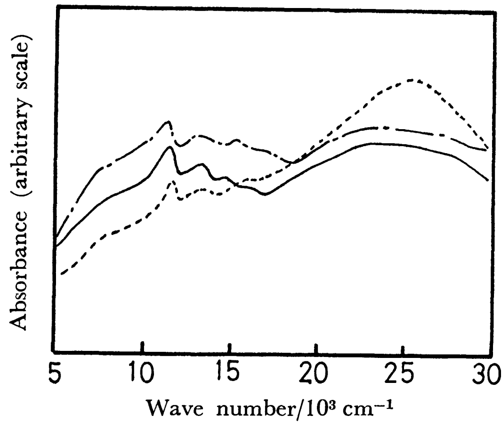

Fig. 4. The electronic absorption spectra of type B complexes in nujol mull.
—— **4-10**; ——— **6-11**; ---- **7-9**.

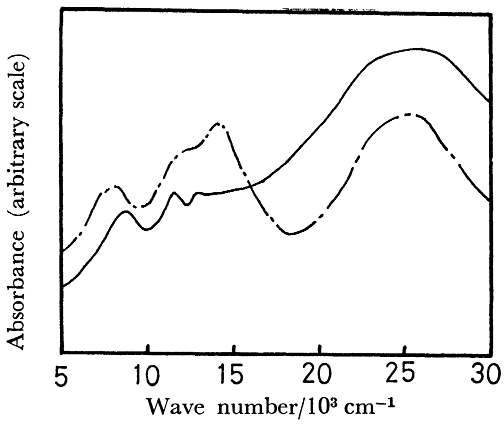

Fig. 5. The electronic absorption spectra of type C complexes in nujol mull.
—— **2-14**; ——— **4-13**.

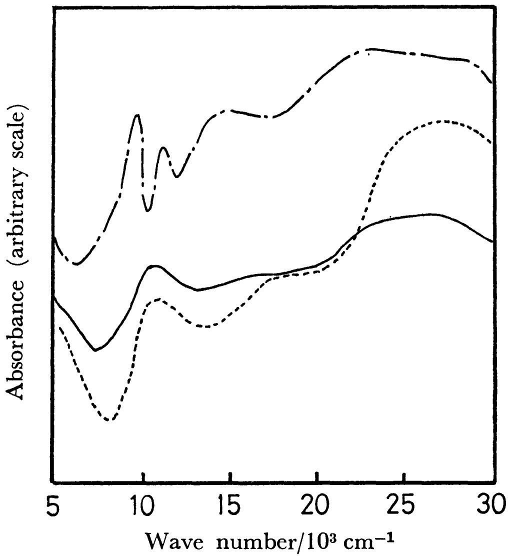

Fig. 6. The electronic absorption spectra of the complex salts in nujol mull.
——— **3-9-15**; —— **3-11-15**; ---- **3-13-15**.

band is due to the charge-transfer transition between TCNQ anion radicals, and the second band, to the local excitation within TCNQ anion radical. It is interesting to note that the absorption-peak positions of the lowest-energy band of the Type A complexes vary from complex to complex, ranging from 7.0×10^3 cm^{-1} to 11.8×10^3 cm^{-1}. If these bands are ascribed to the charge-transfer absorption, this fact will reflect the difference in the strength of the interaction between TCNQ anion radicals in Type A complexes. More exactly, the peak position of this band is affected by the crown ethers in the following order: 12-crown-4 complexes (7.0×10^3 cm^{-1})<cryptand [2,2,2]-complexes ($8.1—8.3\times10^3$ cm^{-1})<15-crown-5-complexes ($9.3—10.6\times10^3$ cm^{-1})<dicyclohexyl-18-crown-6-complexes ($10.4—11.2\times10^3$ cm^{-1})<18-crown-6-complexes ($11.6—11.8\times10^3$ cm^{-1}). In the 15-crown-5-complexes, an increase in the cation size results in a shift of the peak position to the higher-energy region, *i.e.*, 9.3×10^3 cm^{-1} for $\mathrm{Na^+TCNQ^-}$ ($R_{\mathrm{Na^+}}=1.90$ Å)< 9.6×10^3 cm^{-1} for $\mathrm{K^+TCNQ^-}$ ($R_{\mathrm{K^+}}=2.66$ Å)<10.5×10^3 cm^{-1} for $\mathrm{Rb^+TCNQ^-}$ ($R_{\mathrm{Rb^+}}=2.96$ Å)<10.6×10^3 cm^{-1} for $\mathrm{NH_4^+TCNQ^-}$ ($R_{\mathrm{NH_4^+}}=2.84$ Å) Here, $R_{\mathrm{M^+}}$ indicates the ionic diameter of the $\mathrm{M^+}$ cation. Contrary to this, a reverse order was found for the dicyclohexyl-18-crown-6-complexes, *i.e.*, 11.2×10^3 cm^{-1} for Na$^+$TCNQ$^-$ > 10.8×10^3 cm^{-1} for K$^+$TCNQ$^-$ > 10.4×10^3 cm^{-1} for NH$_4^+$TCNQ$^-$. Although these clear correlations between the peak positions of the CT-bands and the molecular structures of the complexes are noteworthy, we can not discuss these characteristics any more without crystallographic data.

Type B complexes have almost the same absorption peaks, which resemble the absorption spectrum of TCNQ anion radical in shape and peak position (see Fig. 2). This fact suggests that TCNQ anion radicals are isolated in the Type B complexes. The unstable properties of these complexes in the air or in the oxygen atmosphere described before may also arise from the isolated structure of the TCNQ anion radical in the crystal.

The absorption spectra of the Type C complexes show an intermediate character between those of the Types A and B complexes, having a charge-transfer band and an isolated TCNQ$^-$ band.

All the complex salts have absorption bands below 5×10^3 cm^{-1}, as is evident from Fig. 6. These absorptions are to be ascribed to the charge-transfer transition from the TCNQ anion radical to neutral TCNQ.[11]

Correspondence between the Electrical Resistivities of the Complexes and Their Electronic Absorption Spectra. It has been clarified that the semi-conducting and, in some cases, metallic properties of several TCNQ complexes arise from the crystal structure with one-dimensional TCNQ columns, thereby having a large overlap of the π-electron clouds between adjacent TCNQ molecules.[2] The electronic absorption spectra of such complexes showed charge-transfer absorption bands between the adjacent TCNQ anion radicals[11] in the infrared region, reflecting the strong electronic interaction between TCNQ molecules.

We have found that simple salts may be divided into two groups from the viewpoint of the electrical resistivity, *i.e.*, the relatively conducting Types A and C complexes, and the insulating Type B complexes. Types A and C complexes have charge-transfer absorption bands showing an overlap of the π-electron clouds between TCNQ anion radicals. Thus, an electron can move through the overlap of the π-electron clouds in these complexes. On the other hand, the TCNQ anion radical is considered to be isolated in the Type B complexes, judging from their electronic absorption spectra. Thus, the π-electron on a TCNQ$^-$ can hardly move to the neighboring TCNQ, resulting in the insulating properties of Type B complexes.

The complex salts were much more conductive than simple salts. The observation of the charge-transfer absorption bands also shows a large overlap of the π-electron clouds between adjacent TCNQ molecules. Moreover, the Coulomb repulsion between the mobile electrons is much more reduced in the complex salt, resulting in much higher conductivities than in simple salts.

Experimental

Materials. All the crown ethers and cryptand were purchased from Nakarai Chemicals, Ltd. TCNQ and its cation salts were synthesized according to the literature.[12]

Isolation of Simple Salts. Most of the simple salts, (crown ether)$_m$(M$^+$TCNQ$^-$)$_n$, were isolated as follows. A cation-TCNQ salt and crown ether (1.2—2 molar ratio)[13] were dissolved in hot methanol and refluxed for 15 min with stirring, after which the hot solution was filtered. The filtrate was allowed to stand at room temperature, and then it was cooled at 0 °C for several hours. Crystals thus precipitated were collected, washed with a small amount of methanol, and dried in a vacuum. When crystals did not come out, the solution was cooled to −15 °C, or to 0 °C after being concentrated. In addition to the above general techniques, we used the following procedures if necessary: (i) In the case of cryptand [2,2,2], we used acetone as a solvent instead of methanol. (ii) After collecting the complexes of dibenzo-18-crown-6 and dibenzo-24-crown-8, they were washed first with benzene and then with methanol. (iii) Because the solubility of dibenzo-18-crown-6 and dibenzo-24-crown-8 is smaller than that of the other crown ethers, we used much more solvent. (iv) When the starting materials were recovered, we used more crown ether and less solvent the next time.

Isolation of Complex Salts. Complex salts, (crown ether)$_m$(M$^+$TCNQ$^-$)$_n$(TCNQ), were isolated by either a one-step method or a two-step method. In the one-step method, methanol containing cation-TCNQ salt and crown ether was mixed with an acetonitrile solution of neutral TCNQ (0.5—1.0 molar ratio),[14] after which the solution was refluxed with stirring for 15 min. The hot solution was filtered, allowed to stand at room temperature, and then cooled to 0 °C. The crystals thus precipitated were collected, washed with a small amount of methanol, and dried in a vacuum. In the two-step method, simple salt was first synthesized, and then the methanol solution of the simple salt was mixed with an acetonitrile solution of neutral TCNQ (0.5—1.0 molar ratio).[14] The solution was refluxed with stirring for 15 min, after which the hot solution was filtered. The filtrate was allowed to stand at room temperature and then cooled to 0 °C. The crystals thus precipitated were collected, washed with a small amount of methanol, and dried in a vacuum. In addition to the above techniques, we used the following procedures if necessary: (i) Crystallization should be done as slowly as possible. (ii) When neutral TCNQ came out initially, the crystallized TCNQ was filtered off, and then the solution was cooled again. (iii) When neutral TCNQ and complex salt came out together, we used either of two methods: (a) we separated the two materials by the use of spatula, or (b) if we could not separate them by the use of a spatula, we used more solvent and added either simple salt or crown ether and original TCNQ salt (M$^+$TCNQ$^-$). (iv) When complex salt and simple salt came out together, we added more solvent, or we added more solvent and a small amount of TCNQ.

Typical examples are shown below.

Preparation of 18-Crown-6–K$^+$TCNQ$^-$, ***(3—10)****.* K$^+$TCNQ$^-$ (150 mg) and 18-crown-6 (175 mg) were added to methanol (120 ml), after which solution was refluxed for 15 min. The hot solution was filtered, allowed to stand at room temperature, and then cooled to 0 °C overnight. The crystals were collected, washed with a small amount of methanol, and dried in a vacuum.

Preparation of Dibenzo-18-crown-6–Na$^+$TCNQ$^-$, ***(4—9)****.* Na$^+$TCNQ$^-$ (100 mg) and dibenzo-18-crown-6 (165 mg) were added to methanol (200 ml), after which the solution was refluxed for 15 min. The hot solution was filtered, allowed to stand at room temperature, and then cooled to 0 °C overnight. The crystals were collected, washed with a large amount of benzene and a small amount of methanol, and dried in a vacuum.

*Preparation of Cryptand [2,2,2]-Rb^+TCNQ^-, (**7—11**).* Rb^+TCNQ^- (150 mg) and cryptand [2,2,2] (190 mg) were added to acetone (120 ml), after which the solution was refluxed for 15 min. The homogeneous solution was concentrated to about 30 ml by rotary evaporator and then filtered. The solution was allowed to stand at room temperature and then cooled to −15 °C overnight. The crystals were collected, washed with a small amount of acetone, and dried in a vacuum.

*Preparation of (18-Crown-6)$_2$(Cs^+TCNQ^-) (TCNQ), (**3—12—15**).* Cs^+TCNQ^- (200 mg) and 18-crown-6 (300 mg) were added to methanol (160 ml), after which the solution was mixed with an acetonitrile solution (40 ml) of TCNQ (120 mg). The solution was refluxed for 15 min, and the hot solution was filtered. The solution was allowed to stand at room temperature and then cooled to 0 °C overnight. The crystals were collected, washed with a small amount of acetonitrile and methanol, and dried in a vacuum.

*Preparation of (18-Crown-6)$_2$(Rb^+TCNQ^-) (TCNQ), (**3—11—15**).* Rb^+TCNQ^-(18-crown-6)$_2$ (111 mg) in 80 ml of methanol was mixed with an acetonitrile solution (20 ml) of TCNQ (50 mg). The procedures were the same as in the preparation of **3—12—15**.

Measurement of Electrical Resistivity. A sample (150 mg) ground in an agate bowl was compressed at 2.2 t/cm^2 to obtain a pellet with a diameter of 13 mm and a thickness of about 0.8—0.9 mm. Silver paste was painted onto both surfaces of the pellet as electrodes, and the electrode area was measured by tracing the electrode shape on a section paper. The electrode area was usually about 50 mm^2. Copper wires were then attached to the electrodes by means of the silver paste. The electrical current was measured by means of Takeda-Riken TR-8651 Electrometer.

Electronic-absorption Measurements. The electronic-absorption spectra were measured by means of a Hitachi ESP-3T spectrometer. The nujol mull sample was sandwiched between the plates of two quartz cells.

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9) The largest limit of the electrical resistivity in our measurement is $10^{14}\ \Omega$ cm.

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