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The Synthesis and Electrical Resistivities of Complexes of Cation–TCNQ–Salts with Crown Ethers, Cryptands, and 1,13-Di(8-quinolyl)-1,4,7,10,13-pentaoxatridecane

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Cation–TCNQ complexes with crown ethers, cryptands, and 1,13-di(8-quinolyl)-1,4,7,10,13-pentaoxatridecane were isolated. The cations include alkali-metal, and alkyl- and arylammonium ions. Nine types of complexes were isolated. These complexes are classified into two groups: complexes containing neutral TCNQ, and the complexes not containing neutral TCNQ. The electrical resistivities of the compaction samples were mainly measured at room temperature. The complexes containing neutral TCNQ were much more conductive than the other type of complexes; they exhibit resistivities of 8.2—10^3 Ω cm. The complexes of 1,13-di(8-quinolyl)-1,4,7,10,13-pentaoxatridecane contained methanol when we synthesized them from methanol solution.

We previously reported the synthesis and electrical resistivities of many alkali-metal and alkaline-earth-metal cation–TCNQ–crown ether complexes.[1–4] By using crown ether, we could isolate the complex salts, $[M^{n+}(TCNQ^-)_n]_m(TCNQ)_i(\text{crown ether})_j$, which contain neutral TCNQ, as well as simple salts, $[M^{n+}(TCNQ^-)_n]_m(\text{crown ether})_i$. A comparison of the electrical conductivities of the crown ether–TCNQ complexes with those of the original TCNQ salts, $M^{n+}(TCNQ^-)_n$, shows that simple salts are much less conductive than the original TCNQ salts.[1,2] On the other hand, complex salts including the alkali-metal cation are about 10 times more conductive than the corresponding original TCNQ salts, M^+TCNQ^-.[1,2] In the case of the complex salts including alkaline-earth-metal cations, however, most of them were much more conductive than the original TCNQ salts, $M^{2+}(TCNQ^-)_2$. The fact that the conductivities of the complex salts including alkaline-earth-metal cations were higher than those of the alkali-metal cations was explained by the closer distance between TCNQ molecules in the former complexes.[3]

1,13-Di(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (usually called simply "Kryptofix-5") is an acylic polyether with two quinolyl groups at both ends of the molecule, and it has a property of coordinating metal cations by means of its five oxygens and two nitrogens.[5] The electrical conductivities of TCNQ–"Kryptofix-5" complexes are interesting in connection with famous good conductor, quinolinium–TCNQ complex.[6] We have now isolated several alkali-metal cation–TCNQ–"Kryptofix-5"-complexes.

Crown ethers are known to include ammonium ions.[7] We have previously reported several ammonium–TCNQ–crown ether complexes.[1,2] We have now synthesized alkyl- and arylammonium–TCNQ–crown ether complexes in order to see the effect of the substituent groups on the electrical conductivities.

We measured the electrical resistivities of the several types of new complexes mentioned above with the compaction samples, mainly at room temperature. We also measured the diffuse-reflection spectra of the new complexes in order to ascertain the electronic interaction between TCNQ molecules.

Experimental

Materials. The crown ethers, cryptands, and 1,13-di(8-quinolyl)-1,4,7,10,13-pentaoxatridecane were purchased from Tokyo Kasei Kogyo Co. Ltd.

Synthesis of the Complexes. The following four methods were employed for the synthesis of the complexes.

Method 1: Most of the complexes not containing neutral TCNQ (Types A, B, and H in Fig. 1) were obtained by the reactions of cation TCNQ salts with crown ethers. The details have been presented previously.[2]

Method 2: Most of the complexes containing neutral TCNQ (Types C and I in Fig. 1) were obtained by the reactions of cation-TCNQ salts, neutral TCNQ, and crown ether. The details have been presented previously.[2]

Method 3: The quinolinium-type "Kryptofix-5" complexes (Types D, E, and F in Fig. 1) were obtained by this method. This method is subdivided into four subtypes: (*3-1*) "Kryptofix-5" and 2,3,5,6-tetramethyl-1,4-benzenediol (1:2.1 molar ratio) were dissolved in acetonitrile. To this solution we then added an acetonitrile solution of TCNQ (3—4 molar ratio); this mixtures was then refluxed for 10 min, and the hot solution was filtered. After the solution had been kept at 0 °C for a few hours, the precipitate was filtered, washed with a small amount of acetonitrile and diethyl ether, and dried in a vacuum. (*3-2*) "Kryptofix-5" was dissolved in dioxane, and the solution was heated to 60 °C. To the solution we then added an equimolar amount of aqueous hydrogen iodide, and the "Kryptofix-5"-hydroiodide precipitated was collected quickly. (When the filtration was done too slowly, we obtained a reddish brown oil.) In this case, the solvent was distilled out completely, and then hexane was added to the oil which remained; we thus obtained the powder of "Kryptofix-5"-hydroiodide. The hydroiodide was then dissolved in a small amount of water, and an aqueous solution of Li^+TCNQ^- (2.1 molar ratio) was added through a filter paper. The precipitate was collected, washed with water, and dried in a vacuum. (*3-3*) To the acetonitrile solution of the complex obtained by Procedure (*3-1*) or Procedure (*3-2*), we added acetonitrile solutions of alkali metal TCNQ salt (equimolar amount) and TCNQ (1—3 molar ratio). The solution was heated for 10 min, and the hot solution was filtered. The filtrate was allowed to stand at room temperature and then kept 0 °C for several hours. The precipitate was collected, washed with a small amount of acetonitrile, and dried in a vacuum. (*3-4*) The complexes obtained by Method 1 or Method 2 were dissolved in acetonitrile, and 2,3,5,6-tetramethyl-1,4-benzenediol (2.1 molar fraction) was added. The solution was heated to dissolve the reactants, and then an acetonitrile solution of TCNQ (3—4 molar ratio) was added. After the solution had been refluxed for 10 min, the hot solution was filtered. The filtrate was allowed to stand at room temperature and then kept at 0 °C for several hours. The precipitate was collected, washed with a small amount of acetonitrile, and dried in a vacuum.

Method 4: Ammonium–TCNQ–crown ether complexes (Type G in Fig. 1) were obtained by the same procedures as in Method 1. In this case, however, we obtained complexes containing neutral TCNQ. The solvents we used were methanol in the case of the methylammonium complex and 2-propanol in the cases of the other complexes.

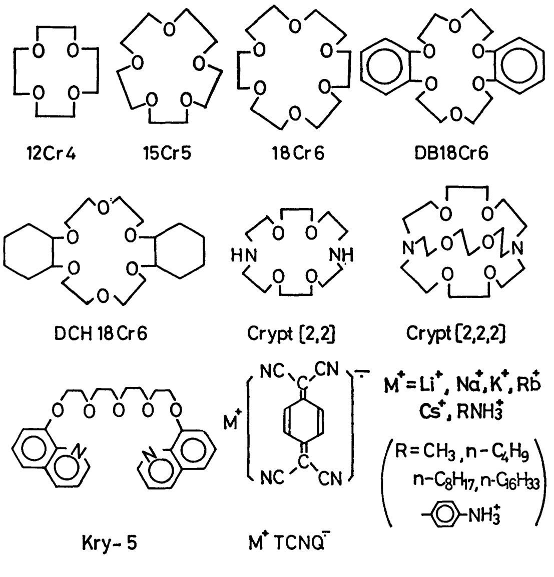
Measurements of the Electrical Resistivities. The room-temperature resistivities of the complexes were measured by the procedures described before.[2)] The temperature dependence of the resistivity was measured by means of a type-D cryomini refrigerator (Osaka Sanso Co., Ltd).

Measurements of Diffuse Reflection Spectra. The diffuse reflection spectra of the complexes were measured by means of a Hitachi 340 recording spectrophotometer, with an integrating sphere attached.

Differential Thermal Analysis and Thermogravimetry. Differential thermal analysis was done by the use of a Dainiseikosha SSC 560 apparatus, and thermogravimetry, by the use of a Rigaku Thermoflex.

Results and Discussion

Isolation of the Complexes. The following crown ethers, cryptands, acyclic polyether, and cation-TCNQ salts were used for the preparation of the complexes: 12-crown-4, 15-crown-5, 18-crown-6, dibenzo-18-crown-6, "dicyclohexyl-18-crown-6"[8)], cryptand[2.2], cryptand[2.2.2], "Kryptofix-5"[9)], Na^+TCNQ^-, K^+-$TCNQ^-$, Rb^+TCNQ^-, Cs^+TCNQ^-, $CH_3NH_3^+TCNQ^-$, n-$C_4H_9NH_3^+TCNQ^-$, n-$C_8H_{17}NH_3^+TCNQ^-$, n-$C_{16}H_{33}$-$NH_3^+TCNQ^-$, and *p*-phenylenediammonium TCNQ; their structures are shown below. In this figure, Cr, DB, DCH, Crypt, and Kry-5 indicate crown ether, dibenzo and perhydrodibenzo groups, crystand, and "Kryptofix-5" respectively. We have isolated nine kinds of complexes; they are designated as Types A, B, C, D, E, F, G, H, and I.[10)] Figure 1 shows the structures of these complexes. All the complexes are stable and have a good solubility in many organic solvents; this may be useful for their practical application. Table 1 lists the complexes isolated and their yields, melting points, analytical data, synthetic methods, appearances, and resistivities.



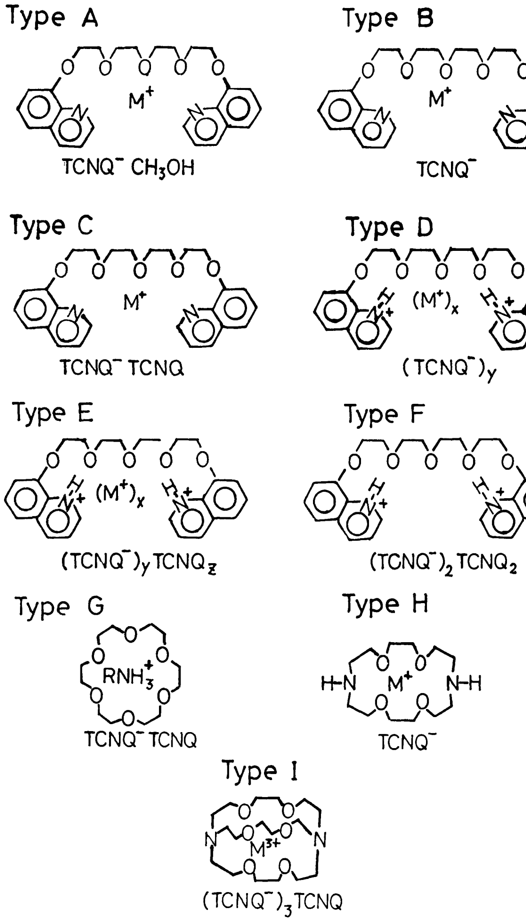


Fig. 1. Nine kinds of complexes isolated.

Cation–TCNQ–"Kryptofix-5" Complexes: Types A, B, C, D, E, and F are included in these complexes. The complexes, of Types C, D, E, and F contain neutral TCNQ, while those of the Types A and B do not contain neutral TCNQ.

The complexes of Types A and B were isolated by means of procedures described before.[2)] It is noteworthy that the complex of Type A contained one molecule of methanol when we crystallized it from a methanol solution. However, when we used other solvents, such as ethyl acetate or ethanol, we obtained solvent-free complexes (Type B). The colors of the complexes of Type A were yellow green. On the other hand, the colors of the complexes of Type B were purple. When the Type-A complexes were heated under vacuum, the corresponding complexes of Type B were obtained, hence giving rise to the color change. In order to see the conversion from Type A to Type B, we performed differential thermal analyses and thermogravimetries of Type-A complexes;

TABLE 1. CATION-TCNQ-CROWN ETHER COMPLEXES AND THEIR RESISTIVITIES

Complexes	Method	Yields/%	Mp θ_m/°C	Found(Calcd)(%)			Appearances	Resistivities/Ω cm[a]
				C	H	N		
Type A								
Kry-5 $Na^+TCNQ^-CH_3OH$	1	10	119—121	66.43 (66.19)	5.03 (5.12)	12.13 (11.87)	dark green microcrystal	
Kry-5 $K^+TCNQ^-CH_3OH$	1	10	113—114	64.90 (64.72)	4.81 (5.01)	11.69 (11.61)	yellow green microcrystal	1.1×10^8
Kry-5 $Rb^+TCNQ^-CH_3OH$	1	69	134—135	60.87 (60.82)	4.59 (4.71)	11.05 (10.91)	yellow green microcrystal	1.8×10^{10}
Kry-5 $Cs^+TCNQ^-CH_3OH$	1	70	102—104	57.46 (57.29)	4.30 (4.44)	10.36 (10.27)	yellow green microcrystal	1.7×10^8
Type B								
Kry-5 Na^+TCNQ^-	1	38	116—118	67.22 (67.55)	4.76 (4.77)	12.39 (12.44)	green cube	1.2×10^8
Kry-5 K^+TCNQ^-	1	10	138—139	66.18 (65.98)	4.86 (4.66)	12.19 (12.15)	purple hexahedral	1.5×10^{10}
Kry-5 Rb^+TCNQ^-	1	62	140—141	61.92 (61.82)	4.37 (4.37)	11.48 (11.39)	purple hexahedral	2.5×10^{10}
Kry-5 Cs^+TCNQ^-	1	28	108—110	58.35 (58.09)	4.32 (4.11)	10.75 (10.70)	purple hexahedral	6.0×10^9
Type C								
Kry-5 K^+TCNQ^-TCNQ	2	13	159—162	67.60 (67.03)	4.00 (4.05)	15.59 (15.63)	black powder	34
Kry-5 $(Rb^+TCNQ^-)_x$-$(TCNQ)_y$[b]	2	31	154—157				black powder	32
Kry-5 $(Cs^+TCNQ^-)_x$-$(TCNQ)_y$[b]	2	34	160—163				black powder	63
Type D								
Kry-5-2H+ $Na^+(TCNQ^-)_3$	3-3, 3-4	64	147—148	68.65 (68.55)	3.85 (3.90)	17.89 (18.06)	black powder	
Type E								
Kry-5-2H+ $K^+(TCNQ^-)_3$-TCNQ	3-3, 3-4	53	152—154	68.18 (68.04)	3.89 (3.55)	19.23 (19.30)	black powder	10.0
Kry-5-2H+$(Rb^+)_x$-$(TCNQ^-)_yTCNQ_z$[b]	3-3, 3-4	46	140—142				black powder	8.8
Kry-5-2H+$(Cs^+)_x$-$(TCNQ^-)_yTCNQ_z$[b]	3-3, 3-4	57	145—147				black powder	8.2
Type F								
Kry-5-2H+ $(TCNQ^-)_2$-$(TCNQ)_2$	3-1, 3-2	44	167—171	69.59 (70.11)	3.73 (3.67)	19.40 (19.90)	black powder	22
Kry-5-H+ $TCNQ^-TCNQ$	3-1, 3-2	24	155—157	69.41 (69.97)	4.40 (4.36)	16.99 (16.35)	black powder	27
Type G								
(15Cr5)$(CH_3NH_3^+)$-$TCNQ^-TCNQ$	4	27	151	63.71 (63.63)	4.89 (5.19)	19.20 (19.09)	black plate	9.2×10^2
(18Cr6)$(CH_3NH_3^+)$-$TCNQ^-TCNQ$	4	69	165	63.29 (63.06)	5.68 (5.43)	17.94 (17.89)	black plate	7.3×10^3
(DB18Cr6)$(CH_3NH_3^+)$-$TCNQ^-TCNQ$	4	58	169—170	67.34 (67.49)	4.69 (4.78)	15.77 (15.74)	black plate	4.5×10^2
(DCH18Cr6)$(CH_3NH_3^+)$-$TCNQ^-TCNQ$	4	19	152—153	66.76 (66.49)	6.22 (6.20)	15.94 (15.94)	black plate	1.5×10^2
(18Cr6)$(n\text{-}C_4H_9NH_3^+)$-$TCNQ^-TCNQ$	4	32	130	64.78 (64.32)	5.70 (5.94)	17.56 (17.57)	black plate	46
(18Cr6)$(n\text{-}C_8H_{17}NH_3^+)$-$TCNQ^-TCNQ$	4	15	127	65.97 (65.81)	6.71 (6.03)	15.68 (15.70)	black powder	1.1×10^7
(18Cr6)$(n\text{-}C_{16}H_{33}NH_3^+)$-$TCNQ^-TCNQ$	4	7	127—133	66.84 (68.25)	7.62 (7.49)	13.60 (13.77)	black powder	
$(15Cr5)_2(^+H_3NC_6H_4NH_3^+)$-$(TCNQ^-)_2TCNQ_2$	4	16	138	65.16 (65.00)	4.73 (4.87)	18.97 (18.44)	black microcrystal	
$(18Cr6)_2(^+H_3NC_6H_4NH_3^+)$-$(TCNQ^-)_2TCNQ_2$	4	32	205	64.29 (64.36)	5.12 (5.12)	17.33 (17.32)	black microcrystal	7.2×10^2
$(DB18Cr6)_2(^+H_3NC_6H_4NH_3^+)$-$(TCNQ^-)_2TCNQ_2$	4	31	165—170	68.68 (68.52)	4.15 (4.53)	16.55 (15.30)	black microcrystal	1.3×10^2

Table 1. (Continued)

Complexes	Method	Yields/%	Mp θ_m/°C	Found(Calcd)(%) C	H	N	Appearances	Resistivities/Ω cm[a)]
$(DCH18Cr6)_2(^+H_3NC_6H_4NH_3^+)$-$(TCNQ^-)_2TCNQ_2$	4	24	145	66.90 (67.53)	5.72 (5.91)	16.41 (15.08)	black microcrystal	3.9×10²
Type H								
crypt[2.2]Na^+TCNQ^-	1	7	170—171	58.87 (58.90)	6.27 (6.13)	17.06 (17.18)	dark blue hexagonal	
crypt[2.2]K^+TCNQ^-	1	39	184—185	57.22 (57.02)	6.20 (5.94)	16.65 (16.63)	dark blue hexagonal	
crypt[2.2]Rb^+TCNQ^-	1	3	145—146	52.20 (52.22)	5.47 (5.44)	15.34 (15.23)	dark blue needle	
Type G								
crypt[2.2.2]$Ce^{3+}(TCNQ^-)_3$-TCNQ[c)]	2	27	186—188	60.83 (59.45)	5.14 (3.93)	17.63 (18.91)	black powder	1.5×10³
crypt[2.2.2]$Sm^{3+}(TCNQ^-)_3$-TCNQ[c)]	2	33	194—196	61.95 (59.01)	4.72 (3.90)	18.83 (18.76)	black powder	68

a) Pressed pellt sample. b) We could not obtain the complex with a stoichiometric composition. c) We could not obtain a good analytical agreement.

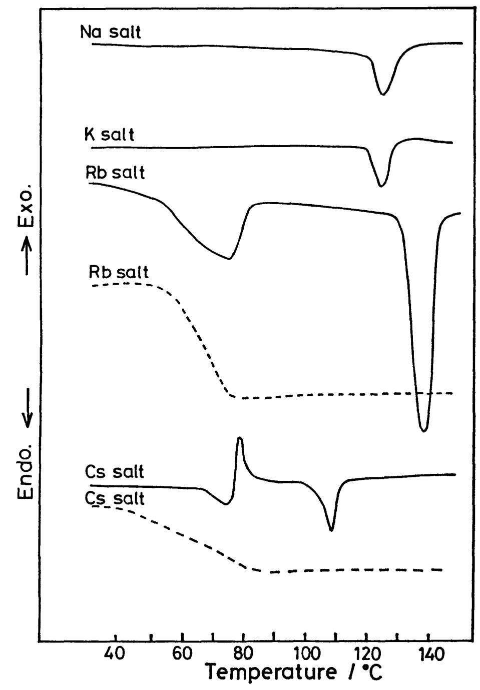


Fig. 2. Differential thermal analysis and thermogravimetry of the methanol-containing "Kryptofix-5" complexes.

——: Differential thermal analysis, ······: thermogravimetry.

the results are shown in Fig. 2. The sodium and potassium complexes in Type A showed only one endothermic signal at their melting points, and the weight losses were not observed. On the other hand, the rubidium and cesium complexes of Type A showed two endothermic signals. The lower-temperature signals were accompanied by weight losses. The higher-temperature signals correspond to the melting points. Thus, methanol is bound more tightly in the sodium and potassium complexes than in the rubidium and cesium complexes in Type A.

The Type-C complexes were isolated by means of procedures described before.[2)] Unfortunately, except for the potassium complex, they did not give the stoichiometric compositions.

The Type-D and Type-F complexes were obtained principally by two methods: by the reaction of "Kryptofix-5", 2,3,5,6-tetramethyl-1,4-benzenediol, and neutral TCNQ, and by the reaction of "Kryptofix-5"-dihydroiodide and Li^+TCNQ^-. We obtained metal containing (Type D) and metal-free (Type F) complexes with quinolinium structures. The Type-F complexes and sodium and potassium complexes of Types D and E gave stoichiometric compositions. However, the rubidium and cesium complexes in Type D gave nonstoichiometric compositions. The complexes in Types C, D, and F were black.

Substituted Ammonium–TCNQ–Crown Ether Complexes: The complexes of Type G are included in these complexes. Several alkyl- and arylammonium–TCNQ salts were obtained by the reactions of the corresponding ammonium iodides with Li^+TCNQ^-. Their reactions with crown ether in methanol gave Type-G complexes. To our surprise, all the complexes contained neutral TCNQ, whereas we did not add neutral TCNQ to the reaction system. The reason for this remains to be clarified.

Miscellaneous Complexes: The complexes of Types H and I were obtained by means of procedures described before.[2)] The Type-I complexes containing Ce^{3+} and Sm^{3+} did not give good analytical agreements.

Electrical Resistivities of the Complexes. We measured the electrical resistivities of the complexes isolated with the compaction samples, mainly at room temperature; the results are shown in Table 1.

Cation–TCNQ–"Kryptofix-5" Complexes: The complexes of Types A, B, and D, none of which contain neutral TCNQ, were poor conductors and exhibited resistivities of 10^8—10^{10} Ω cm. On the other hand, the complexes of Types C, E, and F, which contain neutral TCNQ, were much more conductive than the former type of complexes and exhibited resistivities of the order of $10^1\ \Omega$ cm. The resistivities of the complexes of Types E and F were less than $10\ \Omega$ cm. The best conductor was found in the Type-E complexes possessing Cs ions, which exhibited $8.2\ \Omega$ cm. Unfortunately, we could not obtain these complexes as single crystals. The temperature dependence of the resistivities of Kry-5-$2H^+(Rb^+)_x(TCNQ^-)_y(TCNQ)_z$ and Kry-5-$2H^+(Cs^+)_x(TCNQ^-)_y(TCNQ)_z$ measured between 125 K and 250 K showed semiconducting properties; the activation energies were 0.05 eV and 0.06 eV respectively.[11)]

Substituted Ammonium–TCNQ–Crown Ether Complexes: The resistivities of most of the substituted ammonium–TCNQ–crown ether complexes were 10^2—$10^3\ \Omega$ cm. However, (18-crown-6)$C_8H_{17}NH^+_3TCNQ^-TCNQ$ showed a very low conductivity. When we see the effect of the alkyl groups on the electrical resistivities, we find that (18-crown-6)$C_4H_9NH_3^+TCNQ^-TCNQ$ is more conductive than (18-crown-6)$CH_3NH_3^+TCNQ^-$-TCNQ and (18-crown-6)$C_8H_{17}NH_3^+TCNQ^-TCNQ$.

Miscellaneous Complexes: As has been described in the Introduction, multivalent cation–TCNQ–crown ether complexes can be expected to be highly conductive materials. In line with this, $Sm^{3+}(TCNQ^-)_3$-TCNQ crypt[2.2.2] was a relatively good conductor ($68\ \Omega$ cm); it was *ca.* 300 times more conductive than the original salts, $Sm^{3+}(TCNQ^-)_3$ ($2\times10^4\ \Omega$ cm).[6)]

Electronic Diffuse Reflection Spectra of the Complexes. We measured the electronic diffuse reflection spectra of the complexes isolated in order to ascertain the electronic interaction between TCNQ molecules in the solid state.[12)]

Type-A and Type-B Complexes: As has been discussed above, we obtained methanol-containing complexes (Type A) and methanol-free complexes (Type B). Figure 3 shows the diffuse reflection spectra of both types of complexes. (Kry-5)$K^+TCNQ^-CH_3OH$ and (Kry-5)K^+TCNQ^- were chosen as typical examples in this figure, together with the absorption spectrum of K^+TCNQ^- in an acetonitrile solution. The reflection spectrum of the methanol-containing complex has a characteristic vibrational structure, which resembles the absorption spectrum of K^+TCNQ^- in an acetonitrile solution. This fact suggests that $TCNQ^-$ is isolated in this complex. On the other hand, the methanol-free complex showed two broad absorption bands in the near-IR region. The lower-energy band may have mainly the charge-transfer character between TCNQ anion radicals, while the higher-energy band has mainly the local excitation character within TCNQ anion radicals, like many TCNQ salts.[13)]

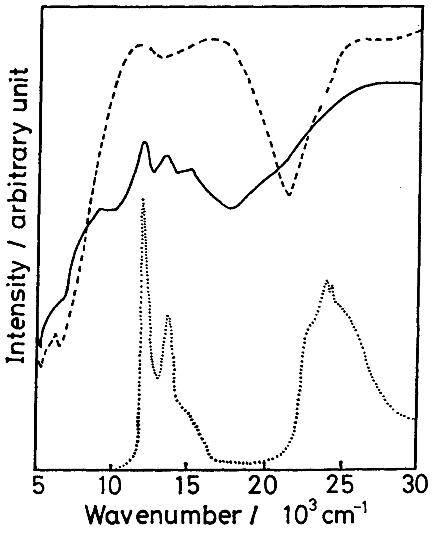


Fig. 3. Electronic diffuse reflection spectra and electronic absorption spectrum of the complexes.
----: Kry-5 K^+TCNQ^-, ——: Kry-5 K^+TCNQ^--CH_3OH, ······: K^+TCNQ^- in acetonitrile solution.

Type-C, E, F, G, and I Complexes: All the complexes containing neutral TCNQ have absorption bands below 7×10^3 cm^{-1}; this may be ascribable to the charge-transfer transition from the TCNQ anion radical to neutral TCNQ.

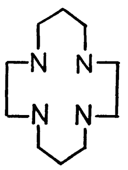
Correspondence between the Electrical Resistivities of the Complexes and Their Electronic Reflection Spectra. As has been discussed above, the complexes containing neutral TCNQ (Types C, E, F, G, and I) are much more conductive than those not containing neutral TCNQ (Types A, B, D, and H). All the complexes of the first type have absorption bands below 7×10^3 cm^{-1}, originating from the charge-transfer transition from $TCNQ^-$ to TCNQ. This fact shows that $TCNQ^-$ and TCNQ are located close together in the complex. Since electrons flow through TCNQ molecules under an electric field, the reduced Coulomb repulsion force between mobile electrons[14)] because of the existence of neutral TCNQ gives rise to relatively high conductivities for the former type of complex.

Many complexes of the latter type (Types B, D, and H) have two absorption bands at the near-infrared region (charge-transfer transition between $TCNQ^-$ molecules); this fact suggests the dimer structure of $TCNQ^-$ molecules. In this case, it is well known that a band-gap is formed;[14)] this results in the poor conductivity, in line with the experimental observations.

The absorption spectra of the Type-A complexes showed that $TCNQ^-$ is isolated in the complexes; this fact gives rise to the poor conductivities of Type-A complexes.

Summary of the Electrical Resistivities of a Series of Cation–TCNQ–Crown Ether Complexes

Comparison of the Electrical Resistivities. We previously synthesized about 100 kinds of cation–TCNQ–crown ether complexes and measured their electrical resistivities, mainly with the compaction samples at room temperature.[1–4)] The cations we used were alkali-metal ions, alkaline-earth-metal ions, alkyl- and arylammonium ions, and transition-metal ions. We classified the complexes into two groups: the complexes containing neutral TCNQ, and the complexes not containing neutral TCNQ. The former type of complexes were semiconductors and were much more conductive than the latter type of complexes; most of the latter type of complexes were insulators. We



"Cyclam"

used not only crown ethers, cryptands, and "Kryptofix-5," but also 1,5,8,12-tetraazacyclotetradecane (usually called "cyclam"), since the latter compounds can include many transition-metal ions.[15]

As a summary of our work, we compared the electrical resistivities of the cation–TCNQ–crown ether complexes with the original TCNQ complexes; this is shown schematically in Fig. 4. The upper half of this figure shows the resistivity range of the cation–TCNQ–crown ether complexes, classified by the cations. We have shown only the resistivity ranges of the complexes containing neutral TCNQ, since they are relatively good conductors. The lower half of Fig. 4 shows the resistivity ranges of the original TCNQ complexes, also classified by the cations.

Roughly speaking, many of the alkali-metal–TCNQ–crown ether complexes are about 10 times more conductive than the original alkali-metal–TCNQ complexes. It is interesting to note that the alkali-metal–TCNQ–"Kryptofix-5" complexes are from about 1000 to about 10000 times more conductive than the alkali-metal–TCNQ complexes. All the alkaline earth metal–TCNQ–crown ether complexes are more conductive (up to 1000 times) than the alkaline earth metal–TCNQ complexes.[6] Many of the ammonium–TCNQ–crown ether complexes are about 10 to 100 times more conductive than the corresponding original TCNQ complexes.[6] Thus, most of the cation–TCNQ–crown ether complexes are more conductive than the corresponding original TCNQ complexes. However, we could not find any significant improvement in the conductivities of transition metal–TCNQ–"cyclam" complexes[4] as compared with transition metal–TCNQ complexes.[6] The most striking difference in the chemical properties of the cation–TCNQ–crown ether complexes from the original TCNQ complexes is that the former complexes are very soluble to the organic solvents, whereas the solubilities of the latter complexes are very low. This fact may be useful for the practical application of the cation–TCNQ–crown ether complexes.

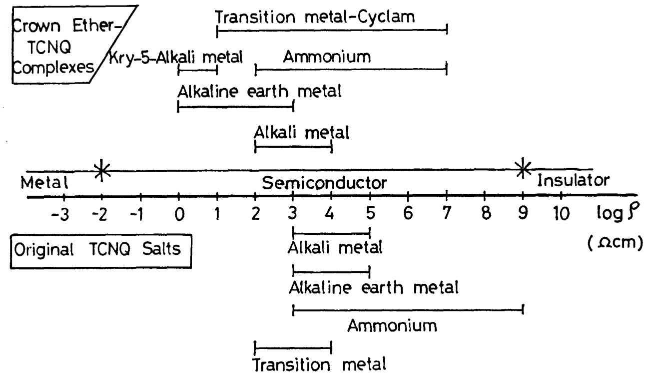


Fig. 4. Comparison of the electrical resistivities of cation–TCNQ–crown ether complexes with those of the corresponding cation–TCNQ complexes.

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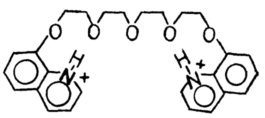
8) Formal name: perhydrodibenzo[*b*,*k*][1,4,7,10,13,16]-hexaoxacyclooctadecin.

9) Formal name: 1,13-di(8-quinolyl)-1,4,7,10,13-pentaoxatridecane.

10) In Type-G complexes, we used not only 18-crown-6, as is shown in Fig. 1, but also 15-crown-5, dibenzo-18-crown-6, and "dicyclohexyl-18-crown-6".

11) Kry-5-2H$^+$ denotes the following diprotonated "Kryptofix-5".



12) Uncorrected spectra.

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