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Preparation and Electrical Conductivity of Some Simple and Complex Salts Formed between *N,N*-Dialkyl-1,3-dichalcogenacycloalkan-2-iminium and TCNQ$^{\overline{\cdot}}$

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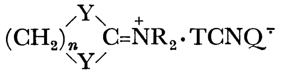
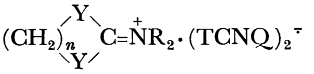
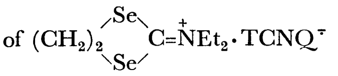
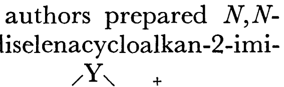
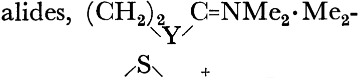
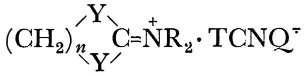
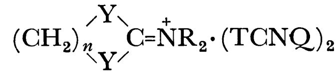
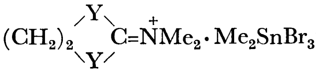
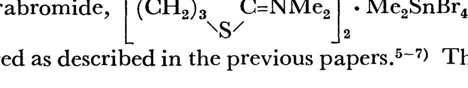
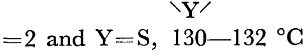
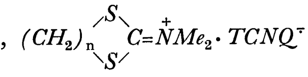
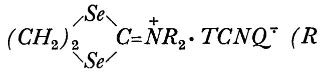
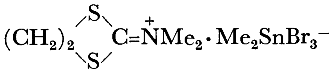
Four simple salts and six complex salts of TCNQ$^{\overline{\cdot}}$ radical anion with *N,N*-dialkyl-1,3-dichalcogenacycloalkan-2-iminium cations,  $(CH_2)_n{<}^{Y}_{Y}{>}C{=}\overset{+}{N}R_2\cdot TCNQ^{\overline{\cdot}}$ and  $(CH_2)_n{<}^{Y}_{Y}{>}C{=}\overset{+}{N}R_2\cdot(TCNQ)_2^{\overline{\cdot}}$ (n=2 or 3, Y=S or Se, R=Me or Et) were prepared. The electrical resistivity of  $(CH_2)_2{<}^{Se}_{Se}{>}C{=}\overset{+}{N}Et_2\cdot TCNQ^{\overline{\cdot}}$ (1.1×10^4 ohm cm) was more than 10 times lower than other three simple salts ($(6.1-8.7)\times10^5$ ohm cm). Electronic absorption spectra and magnetic susceptibilities suggest that the latter three involve dimeric $(TCNQ)_2{}^{2-}$, while in the former the interaction between two TCNQ$^{\overline{\cdot}}$ radical anions is weak in the solid state. All the complex salts with compaction samples exhibited the resistivity of 2.4—4.0 ohm cm with very low activation energies (0.018—0.087 eV). Electronic spectra and magnetic susceptibilities show that the interaction between two TCNQ$^{\overline{\cdot}}$ radical anions decreases owing to the implication of neutral TCNQ.

There has been reported the preparation of various salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) radical anion with inorganic and organic cations which show a wide range of electrical conductivities, largely depending on the properties of the counter cations. Some of those are known as best electrically conductive organic salts, such as quinolinium-$(TCNQ)_2^{\overline{\cdot}}$ [1] and *N*-methylphenazinium-TCNQ$^{\overline{\cdot}}$.[2] Charge-transfer complexes between TCNQ and tetrathiafulvalene or its derivatives also were reported to display high electrical conductivities.[3] The cationic moieties of these electrically conductive organic salts or complexes generally not only adopt a planar structure but also involve hetero atoms with large polarizability. Garito and Heeger have mentioned the importance of these two factors for obtaining organic complexes with high electrical conductivities.[4]

Some time ago, one of the authors prepared *N,N*-dimethyl-1,3-dithia- and 1,3-diselenacycloalkan-2-iminium dimethyltin(IV) halides,  $(CH_2)_2{<}^{Y}_{Y}{>}C{=}\overset{+}{N}Me_2\cdot Me_2SnBr_3^-$ (Y=S and Se) and  $[(CH_2)_3{<}^{S}_{S}{>}C{=}\overset{+}{N}Me_2]_2\cdot Me_2SnBr_4^{2-}$.[5-7] The iminium cations of these salts adopt a planar Y_2CN moiety[6] involving largely polarizable hetero atoms. This fact prompted us to prepare TCNQ$^{\overline{\cdot}}$ radical anion salts of these iminium cations. This paper reports the synthesis and the electrical conductivity of several simple and complex salts of TCNQ$^{\overline{\cdot}}$ with the iminium cations,  $(CH_2)_n{<}^{Y}_{Y}{>}C{=}\overset{+}{N}R_2\cdot TCNQ^{\overline{\cdot}}$ and  $(CH_2)_n{<}^{Y}_{Y}{>}C{=}\overset{+}{N}R_2\cdot(TCNQ)_2^{\overline{\cdot}}$ (n=2, 3; Y=S, Se; R=Me, Et; but not all combinations). Electronic spectra and magnetic properties of these salts also are described in terms of interaction between the TCNQ$^{\overline{\cdot}}$ radical anions.

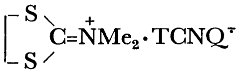
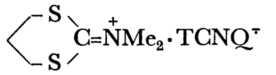
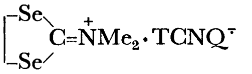
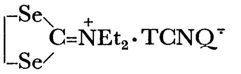
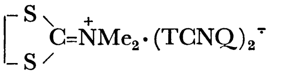
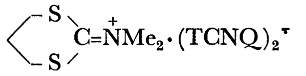
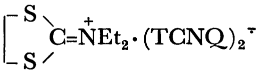
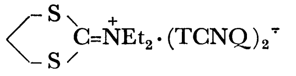
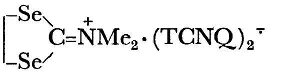
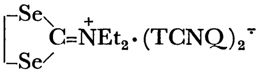
Experimental

Materials. *N,N*-Dimethyl-1,3-dithia- and 1,3-diselenacyclopentan-2-iminium dimethyltin(IV) tribromide,  $(CH_2)_2{<}^{Y}_{Y}{>}C{=}\overset{+}{N}Me_2\cdot Me_2SnBr_3^-$ (Y=S, Se), and bis(*N,N*-dimethyl-1,3-dithiacyclohexan-2-iminium) dimethyltin(IV) tetrabromide,  $\left[(CH_2)_3{<}^{S}_{S}{>}C{=}\overset{+}{N}Me_2\right]_2\cdot Me_2SnBr_4^{2-}$ were prepared as described in the previous papers.[5-7] The corresponding *N,N*-diethyliminium compounds,  $(CH_2)_n{<}^{Y}_{Y}{>}C{=}\overset{+}{N}Et_2\cdot Me_2SnBr_3^-$, mp 97—99 °C for n=2 and Y=S, 130—132 °C for n=3 and Y=S, and 122—124 °C for n=2 and Y=Se, were similarly synthesized by reaction of bis(diethyldithiocarbamato or diethyldiselenocarbamato)dimethyltin(IV), $Me_2Sn(Y_2CNEt_2)_2$ (Y=S, Se), with 1,2-dibromoethane or 1,3-dibromopropane.

N,N-*Dialkyl-1,3-dichalcogenacycloalkan-2-iminium-TCNQ Simple Salts,*  $(CH_2)_n{<}^{S}_{S}{>}C{=}\overset{+}{N}Me_2\cdot TCNQ^{\overline{\cdot}}$ (n=2 (**1**), 3 (**2**)) *and*  $(CH_2)_2{<}^{Se}_{Se}{>}C{=}\overset{+}{N}R_2\cdot TCNQ^{\overline{\cdot}}$ *(R=Me (**3**), Et (**4**)).* To a solution of $Li^+TCNQ^{\overline{\cdot}}$ (2.8 mmol) in boiling ethanol (40 cm^3) was added a hot ethanol (20 cm^3) solution of  $(CH_2)_2{<}^{S}_{S}{>}C{=}\overset{+}{N}Me_2\cdot Me_2SnBr_3^-$ (2.8 mmol). The mixture was allowed to stand at room temperature, giving purple plates of **1**, which were recrystallized from ethanol, 71% yield. Other three simple salts were similarly prepared by reactions of TCNQ$^{\overline{\cdot}}$ with the appropriate iminium cations in ethanol, 60—77% yields.

N,N-*Dimethyl-1,3-dithiacycloalkan-2-iminium-TCNQ Complex Salts,*  $(CH_2)_n{<}^{S}_{S}{>}C{=}\overset{+}{N}Me_2\cdot(TCNQ)_2^{\overline{\cdot}}$ (n=2 (**5**), 3 (**6**)). To a boiling acetonitrile (50 cm^3) solution of **1** obtained above (2.0 mmol) was added neutral TCNQ (2.0 mmol) in boiling

TABLE 1. PROPERTIES AND ANALYTICAL DATA OF THE $\mathrm{TCNQ}^{\bar{\cdot}}$ SALTS

No.	Compound		Mp (dec) °C	Found (%) C	Found (%) H	Found (%) N	Calcd (%) C	Calcd (%) H	Calcd (%) N
1	 $\overset{+}{C}=NMe_2\cdot TCNQ^{\bar{\cdot}}$	Purple plates	220—223	57.99	3.87	20.05	57.93	4.01	19.87
2	 $\overset{+}{C}=NMe_2\cdot TCNQ^{\bar{\cdot}}$	Purple plates	205—209	59.06	4.21	19.09	58.98	4.41	19.11
3	 $\overset{+}{C}=NMe_2\cdot TCNQ^{\bar{\cdot}}$	Purple plates	237—239	45.71	2.94	15.75	45.74	3.17	15.70
4	 $\overset{+}{C}=NEt_2\cdot TCNQ^{\bar{\cdot}}$	Dark-blue plates	172—175	47.80	3.58	14.76	48.11	3.83	14.77
5	 $\overset{+}{C}=NMe_2\cdot (TCNQ)_2^{\bar{\cdot}}$	Black needles	245—250	62.55	3.00	22.79	62.56	3.27	22.65
6	 $\overset{+}{C}=NMe_2\cdot (TCNQ)_2^{\bar{\cdot}}$	Black needles	227—244	62.67	3.14	22.05	63.13	3.54	22.09
7	 $\overset{+}{C}=NEt_2\cdot (TCNQ)_2^{\bar{\cdot}}$	Black needles	240—243	63.80	3.59	21.51	63.68	3.79	21.56
8	 $\overset{+}{C}=NEt_2\cdot (TCNQ)_2^{\bar{\cdot}}$	Black needles	217—227	63.98	3.78	21.14	64.18	4.05	21.06
9	 $\overset{+}{C}=NMe_2\cdot (TCNQ)_2^{\bar{\cdot}}$	Black needles	278—280	53.35	2.71	19.28	53.55	2.79	19.38
10	 $\overset{+}{C}=NEt_2\cdot (TCNQ)_2^{\bar{\cdot}}$	Black needles	198—200	55.00	3.17	18.30	54.88	3.27	18.58

acetonitrile ($30\ cm^3$). After filtration, the mixture was allowed to stand in a refrigerator overnight to afford black needles of **5**, 88% yield. Complex salt **6** was similarly prepared by reaction of **2** with TCNQ at the mole ratio of 1: 1 in acetonitrile, 85% yield.

N,N-*Diethyl-1,3-dithiacycloalkan-2-iminium-TCNQ Complex Salts,* $(CH_2)_n\overset{S}{\underset{S}{\langle}}\overset{+}{C}=NEt_2\cdot(TCNQ)_2^{\bar{\cdot}}$ *(n=2 (7), 3 (8)).*

To a boiling ethanol ($30\ cm^3$) solution of $Li^+TCNQ^{\bar{\cdot}}$ (2.2 mmol) was added $(CH_2)_2\overset{S}{\underset{S}{\langle}}\overset{+}{C}=NEt_2\cdot Me_2SnBr_3^-$ (2.2 mmol) in hot ethanol ($20\ cm^3$). The mixture was allowed to stand in a refrigerator overnight to give black needles of **7**, which were recrystallized from acetonitrile, 62% yield based on $Li^+TCNQ^{\bar{\cdot}}$. A similar reaction of $(CH_2)_3\overset{S}{\underset{S}{\langle}}\overset{+}{C}=NEt_2$ with $TCNQ^{\bar{\cdot}}$ at the mole ratio of 1: 1 in ethanol afforded **8**, 60% yield based on $TCNQ^{\bar{\cdot}}$.

N,N-*Dialkyl-1,3-diselenacyclopentan-2-iminium-TCNQ Complex Salts,* $(CH_2)_2\overset{Se}{\underset{Se}{\langle}}\overset{+}{C}=NR_2\cdot(TCNQ)_2^{\bar{\cdot}}$ *(R=Me (9), Et (10)).*

These complex salts were prepared by reaction of the appropriate simple salt, **3** or **4** with TCNQ in acetonitrile by the procedure described in **5** and **6**.

Elemental analyses and properties of the simple and complex salts obtained are listed in Table 1.

Physical Measurements. Electrical resistivities were measured by two-probe method in the 20—90 °C range; current measurements were performed with a TOA DEMPA KOGYO PM-18 micro volt-ammeter or a TAKEDA RIKEN-TR-6355 multimeter, and voltage measurements with a NATIONAL VP-653B pen-recorder calibrated by the use of the multimeter. A compaction sample, 20 mm in diameter and about 1 mm thick, for the measurement was prepared by pressing at $270\ kg/cm^2$, followed by vacuum-evaporating gold metal as electrodes. The resistivities of some complex salts were also measured by four-probe method; the values obtained were very close to those by two-probe method (see Table 2).

Electronic absorption spectra were recorded in Nujol mulls and in acetonitrile (10^{-5} M) on a HITACHI EPS-03 spectrophotometer (3850—16700 cm^{-1}) and a HITACHI 124 spectrophotometer (12500—40000 cm^{-1}). Infrared spectra were measured in hexachlorobutadiene mulls on a HITACHI 215 grating infrared spectrophotometer. Magnetic susceptibilities were measured for micro-crystalline materials by the Gouy method at room temperature.

Results and Discussion

Synthesis. *N,N*-Diethyl-1,3-dithiacycloalkan-2-iminium cations reacted with $TCNQ^{\bar{\cdot}}$ to give the complex salts, **7** and **8**, whereas the reaction of the remaining iminium cations with $TCNQ^{\bar{\cdot}}$ afforded the simple salts, **1**—**4**, irrespective of the mole ratio of the reactants. These simple salts further reacted with an equimolar amount of neutral TCNQ to yield the complex salts, **5**, **6**, **9**, and **10**. All the $TCNQ^{\bar{\cdot}}$ salts obtained here are stable to air in the solid state.

Electrical Properties. Figures 1 and 2 show the electrical resistivity (ρ) of the simple and the complex salts at various temperatures, respectively. The ρ values

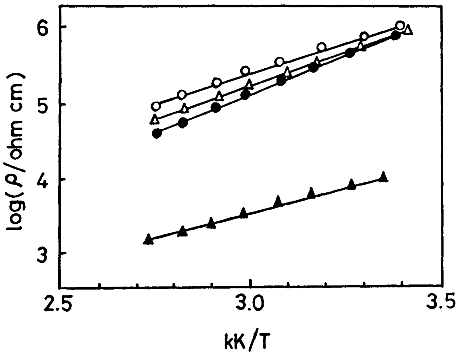


Fig. 1. Temperature dependence of the resistivity of the TCNQ$^{\cdot-}$simple salts; **1** (○), **2** (△), **3** (●), and **4** (▲).

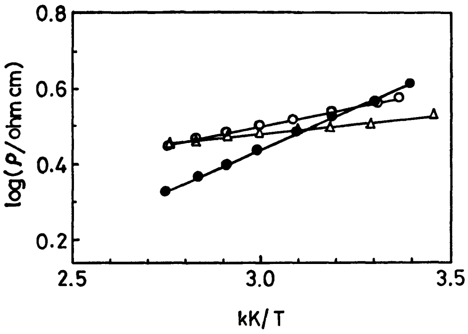


Fig. 2. Temperature dependence of the resistivity of the TCNQ$^{\cdot-}$ complex salts; **5** (○), **7** (△), and **9** (●).

TABLE 2. ELECTRICAL RESISTIVITY AND ACTIVATION ENERGY OF THE TCNQ$^{\cdot-}$ SALTS

Compound	$\rho_{25\,°C}$[a)] / ohm cm	E_a / eV
Simple salt		
1	8.7×10^5	0.30
2	6.8×10^5	0.34
3	6.1×10^5	0.37
4	1.1×10^4	0.27
Complex salt		
5	3.8	0.041
6	3.5	0.076
7	3.3	0.018
8	2.9(2.6)	0.060
9	4.0(3.4)	0.087
10	2.4	0.046

a) The values in parentheses were obtained by four-probe method.

at 25 °C and the activation energies (E_a) calculated from the equation $\rho=\rho_0\exp(E_a/kT)$ are summarized in Table 2. It is noted that the ρ value of **4** was more than 10 times lower than those of the other simple salts, although the E_a values of the four simple salts were in the same order of magnitude.

The electrical resistivity of TCNQ$^{\cdot-}$ complex salts is known to markedly depend on the nature of counter cations. The ρ values of the present complex salts are relatively small compared with those of many TCNQ$^{\cdot-}$ complex salts reported so far,[1)] but larger by one order of magnitude than that of the highest conductive complex salt with a compaction sample, quinolinium-(TCNQ)$_2^{\cdot-}$ (0.5 ohm cm).[1)] The E_a values of the complex salts obtained here also are small, in particular that of **7** (0.018 eV) is compared with the activation energy of quinolinium-(TCNQ)$_2^{\cdot-}$ (0.013 eV).[1)]

Electronic Spectra and Magnetic Properties. An acetonitrile solution of **1** exhibited absorption bands around 12000 and 24000 cm^{-1}. Essentially the same spectra were observed for **2**—**4** in the same solvent, irrespective of the counter iminium cations. The appearance of these spectra also closely resembles that of K$^+$TCNQ$^{\cdot-}$[8)] and Et$_3$NH$^+$TCNQ$^{\cdot-}$[1)] in acetonitrile, where they are known to dissociate into monomeric TCNQ$^{\cdot-}$ and K$^+$ or Et$_3$NH$^+$.

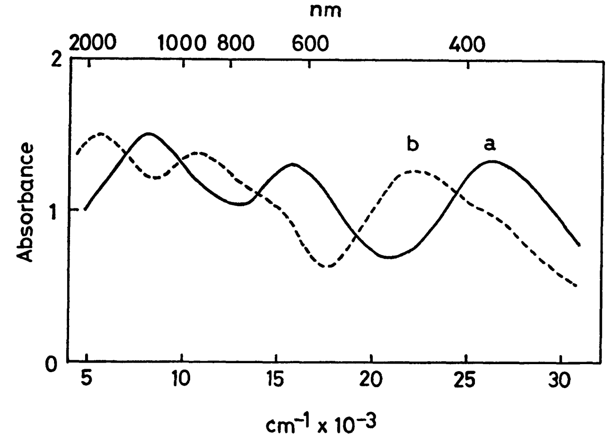


Fig. 3. Absorption spectra of **1** (a) and **4** (b) in Nujol mulls.

Figure 3 illustrates the electronic absorption spectra of two representative simple salts, **1** and **4**, in the solid state. Compound **1** exhibits three absorption maxima, whose wave numbers (see Table 3) are close to those observed in the reflectance spectra of several TCNQ$^{\cdot-}$ simple salts such as with Li$^+$, NH$_4^+$, and MePh$_3$P$^+$ (around 9000, 16000, and 27000 cm^{-1}) reported previously; the lowest energy band has been assigned to the charge-transfer (CT) transition between TCNQ$^{\cdot-}$ radical anions,[8,9)] and the two remaining bands to the (TCNQ)$_2^{2-}$ dimer.[8)] The band around 16000 cm^{-1} has also been suggested to be characteristic of the dimer type electron configuration of TCNQ$^{\cdot-}$ crystals.[9)] It is therefore suggested that **1** consists of the iminium cation and dimeric (TCNQ)$_2^{2-}$ anion in the solid state. The existence of (TCNQ)$_2^{2-}$ is also evidenced from the fact that **1** exhibited a diamagnetic susceptibility of -1.7×10^{-4} emu mol^{-1} at 25 °C, which is in good agreement with the value calculated from Pascal's constants (-1.697×10^{-4} emu mol^{-1}). This diamagnetism indicates that two TCNQ$^{\cdot-}$ radical anions may be coupled completely with each other. The same conclusion can be drawn for **2** and **3** on the basis of similarity of their electronic spectra to that of **1**, although the highest energy band of **3** was found at a little low frequency, as shown in Table 3.

The spectrum of **4** in the solid state showed three absorption maxima at 5600, 10800, and 22200 cm^{-1}.

TABLE 3. ABSORPTION MAXIMA OF THE ELECTRONIC SPECTRA OF THE TCNQ$^{\cdot-}$ SALTS IN NUJOL MULLS

Compound	$\mathrm{cm}^{-1} \times 10^{-3}$ a)				
1	8.3			15.9	26.3
2	8.3			15.6	27.0
3	8.1			15.2	24.4
4	5.6	10.8		(15)	22.2 (27)
5		10.0	11.4	17	26.7
6		9.9	11.4	17	26.7
7		10.0	11.4	17	27.0
8		9.9	11.2	17	27.0
9		9.9	11.4	17	26.7
10		9.9	11.2	17	27.0

a) Shoulders in parentheses.

The lowest energy band may tentatively be assigned to the CT transition between TCNQ$^{\cdot-}$ radical anions, although the wave number is considerably lower than that of **1**—**3** (Fig. 3 and Table 3). On the other hand, the 10800 and 22200 cm^{-1} bands, which are assignable to locally-excited transitions of the TCNQ$^{\cdot-}$ moiety, LE$_1$ and LE$_2$ respectively,⁹⁾ showed no appreciable blue shift compared with the corresponding bands arising from monomeric TCNQ$^{\cdot-}$ in acetonitrile. Thus, the absorption spectrum has not revealed the electronic state of TCNQ$^{\cdot-}$ in solid **4**. It is, however, noted that the magnetic susceptibility of **4** in the solid state was 1.5×10^{-4} emu mol^{-1} at 25 °C. Such a paramagnetism which is unusual in various simple salts, may be correlated with somewhat higher electrical conductivity of **4** than **1**—**3**.

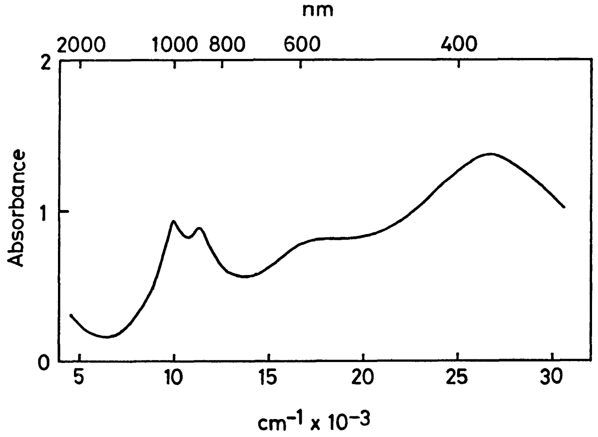


Fig. 4. Absorption spectra of **5** in Nujol mulls.

Complex salt **5** in acetonitrile gave a similar spectrum in appearance to some TCNQ$^{\cdot-}$ complex salts, such as with Et$_3$NH^{+}¹⁾ and MePh$_3$P^{+},⁸⁾ in the same solvent. The solid state spectrum of **5** is illustrated in Fig. 4, which shows three absorption bands around 10000, 17000, and 27000 cm^{-1}. The latter two frequencies are close to those of the two high energy bands observed in solid **1**—**3** (Table 3). The intense absorption around 27000 cm^{-1} may be contributed from both the LE$_2$ state of TCNQ$^{\cdot-}$ and the excited state of neutral TCNQ.⁹⁾ The band around 10000 cm^{-1} is due to the TCNQ$^{\cdot-}$ monomer, as previously described in the reflectance spectra of some TCNQ$^{\cdot-}$ complex salts.⁸⁾ More quantitatively, this band is assigned to a transition to the LE$_1$ state of TCNQ$^{\cdot-}$ or the coupled transition of the LE$_1$ state of TCNQ$^{\cdot-}$ and the CT state between TCNQ$^{\cdot-}$.⁹⁾ The presence of monomeric TCNQ$^{\cdot-}$ does not contradict the fact that **5** exhibited a large paramagnetic susceptibility of 6.5×10^{-4} emu mol^{-1} at 25 °C. This magnitude of the paramagnetism is commonly found in many TCNQ$^{\cdot-}$ complex salts.¹⁰⁾ Other complex salts **6**—**10** exhibited essentially the same spectra as **5** in the solid state. In addition, all the complex salts displayed a very broad band ranging from 3400 to 2700 cm^{-1}, which was never seen in the spectra of the simple salts. This band is assignable to the charge-transfer transition between TCNQ$^{\cdot-}$ and TCNQ.⁸⁾ It may therefore be concluded that the interaction between two TCNQ$^{\cdot-}$ radical anions in the solid complex salts decreases owing to the implication of neutral TCNQ.

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