Bull. Chem. Soc. Jpn., 53, 1247—1251 (1980)

Synthesis and Electrical Properties of TCNQ Radical Anion Salts with *N,N'*-Ethylenedi(1,3-dithiolan-2-iminium) Dication and Related Dications

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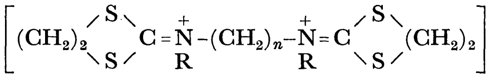
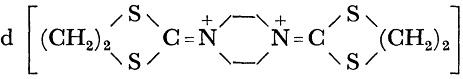
(Received September 27, 1979)

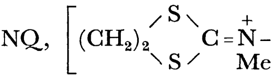
Simple and complex salts of the TCNQ$^{\overline{\cdot}}$ radical anion with *N,N'*-ethylenedi(1,3-dithiolan-2-iminium) dication and related dications,

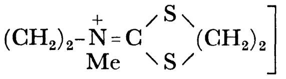


$\left[(CH_2)_2\langle S_2\rangle C=\overset{+}{N}R-(CH_2)_n-\overset{+}{N}R=C\langle S_2\rangle(CH_2)_2\right]$ (TCNQ)$_m^{2\overline{\cdot}}$ (R=H, Me; n=2, 6; m=2, 3, or 4) and



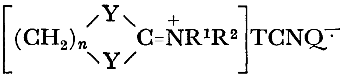
$\left[(CH_2)_2\langle S_2\rangle C=\overset{+}{N}(CH_2CH_2)_2\overset{+}{N}=C\langle S_2\rangle(CH_2)_2\right]$ (TCNQ)$_m^{2\overline{\cdot}}$ (m=2, 3) were synthesized. All the salts as compacted samples display semiconducting behaviors in the 77—300 K range. Electrical resistivities of the simple salts are in the range of 1.8×10^5—9.8×10^7 Ω cm at 25 °C. Electronic absorption spectra and magnetic susceptibilities suggest that the simple salts in the solid state involve (TCNQ)$_2^{2-}$ dimer. The 1 : 3 complex salt of *N,N'*-dimethyl-*N,N'*-ethylenedi(1,3-dithiolan-2-iminium) with TCNQ,





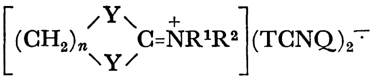
$\left[(CH_2)_2\langle S_2\rangle C=\overset{+}{N}Me-(CH_2)_2-\overset{+}{N}Me=C\langle S_2\rangle(CH_2)_2\right]$ (TCNQ)$_3^{2\overline{\cdot}}$, exhibits a lower electrical resistivity (3.4 Ω cm) than other four complex salts (2.4×10—2.5×10^3 Ω cm). Electronic absorption spectra and magnetic susceptibilities of the both 1 : 3 and 1 : 4 complex salts are interpreted in terms of the interaction between the TCNQ moieties.

According to the molecular requirements for obtaining highly conducting 7,7,8,8-tetracyanoquinodimethane (TCNQ) salts, for example, planar structure and high polarizability of the cation moiety, one of the authors recently prepared some simple and complex salts formed between *N,N*-dialkyl-1,3-dichalcogenacycloalkan-2-iminium cations and TCNQ$^{\overline{\cdot}}$ radical anion;



$\left[(CH_2)_n\langle Y_2\rangle C=\overset{+}{N}R^1R^2\right]$TCNQ$^{\overline{\cdot}}$

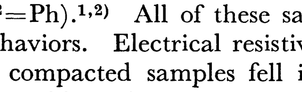
and



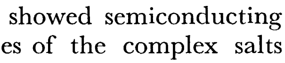
$\left[(CH_2)_n\langle Y_2\rangle C=\overset{+}{N}R^1R^2\right]$(TCNQ)$_2^{\overline{\cdot}}$

(n=2 or 3; Y=S or Se; $R^1=R^2$=Me, Et, n-Pr, n-Bu, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, and Ph; R^1=Me and R^2=Ph).[1,2] All of these salts showed semiconducting behaviors. Electrical resistivities of the complex salts as compacted samples fell in the 2.4—90 Ω cm range at 25 °C with activation energies of 0.018—0.12 eV, whereas the simple salts exhibited the electrical resistivities of 4.4×10^3—1.3×10^9 Ω cm with activation energies of 0.16—1.3 eV.

Thus, the iminium cations may be useful as cation sources in the synthesis of electrical conducting organic crystals. In this study, we have taken up di(1,3-dithiolan-2-iminium) dications, **A** and **B**, as the cation moieties of TCNQ$^{\overline{\cdot}}$ salts.



A



B

R= H, Me; n=2, 6

These dications are expected to have potential possibility of the formation of unusual stoichiometric TCNQ$^{\overline{\cdot}}$ salts with interesting electrical and magnetic properties. In fact, the stoichiometries of diquarternized 1,2-di(4-pyridyl)ethane and 1,2-di(4-pyridyl)-ethylene salts with TCNQ are 1:3,[3] 1:4,[4] 1:5,[5] and 2:5,[6] and the 1:4 complex salt of 1,2-bis(1-ethylpyridinim-4-yl)ethylene dication with the TCNQ$^{\overline{\cdot}}$ radical anion exhibit a metallic behavior below room temperature.[7]

This paper reports the preparation and electrical resistivity of some simple and complex salts of TCNQ$^{\overline{\cdot}}$ with the iminium dications. Electronic absorption spectra and magnetic susceptibilities of these salts are discussed in terms of the interaction between the TCNQ moieties.

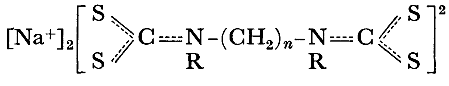
Experimental

Disodium polymethylenebis(dithiocarbamate) (**1a**—**d**) were prepared as described in the literature.[8] Bis(triethylammonium) 1,4-piperazinebis(carbodithioate) (**2**) were obtained similarly by the reaction of piperazine in ethanol with triethylamine, followed by the addition of carbondisulfide.

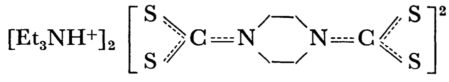
N,N'-*Ethylene-*, N,N'-*Dimethyl-*N,N'-*ethylene-*, N,N'-*Hexamethylene-*, N,N'-*Dimethyl-*N,N'-*hexamethylenedi(1,3-dithiolan-2-iminium) and* N,N'-*Bis(1,3-dithiolan-2-ylidene)piperazine-1,4-diium Salts (**3a**—**d** and **4**).* To a suspension of **1a** (3.0 g, 12 mmol) in ethanol (20 ml) was added large excess 1,2-dibromoethane (5.1 g). The mixture was refluxed for 6 h, during which time white color of the suspension turned to yellow. A floating solid material in the suspension was collected by filtration and recrystallized from water to give white needles of *N,N'*-ethylenedi(1,3-dithiolan-2-iminium) dibromide (**3a**) in a 40% yield; mp 210—212 °C. Found: C, 22.26; H, 3.35; N, 6.60%. Calcd for $C_8H_{14}N_2S_4Br_2$: C, 22.54; H, 3.32; N, 6.57%. Similarly four other iminium dications were obtained as hexafluorophosphate or tetraphenylborate in 40—55% yields by the reaction of **1b**—**d** or **2** with excess 1,2-dibromoethane in ethanol, followed by the addition of ammonium hexafluorophosphate or sodium tetraphenylborate. *N,N'*-Dimethyl-*N,N'*-ethylenedi(1,3-dithiolan-2-iminium) bis(hexafluorophosphate) (**3b**), mp 280—281 °C. Found: C, 20.26; H, 3.05; N, 4.68%. Calcd for $C_{10}H_{18}N_2S_4P_2F_{12}$: C, 20.55; H, 3.10; N, 4.79%. *N,N'*-Hexamethylenedi(1,3-dithiolan-2-iminium) bis(hexafluorophosphate) (**3c**), mp 198—200 °C. Found: C, 23.27; H, 3.58; N, 4.63%. Calcd for $C_{12}H_{22}N_2S_4P_2F_{12}$: C, 23.53; H, 3.62; N, 4.57%. *N,N'*-Dimethyl-*N,N'*-hexamethylenedi(1,3-dithiolan-2-iminium) bis(hexafluorophosphate) (**3d**), mp 225—227 °C. Found: C, 26.03; H, 4.02; N, 4.25%. Calcd for $C_{14}H_{26}N_2S_4P_2F_{12}$: C, 26.25; H, 4.09; N, 4.37%. *N,N'*-Bis(1,3-dithiolan-2-ylidene)piperazine-1,4-diium bis(tetraphenylborate) (**4**), mp 260—262 °C. Found: C, 74.10; H, 6.13; N, 3.23%. Calcd for $C_{58}H_{56}N_2S_4B_2$: C, 74.83; H, 6.06; N, 3.01%.

*N,N'-Ethylene-, N,N'-Dimethyl-N,N'-ethylene-, N,N'-Hexamethylene-, N,N'-Dimethyl-N,N'-hexamethylenedi(1,3-dithiolan-2-iminium) and N,N'-Bis(1,3-dithiolan-2-ylidene)piperazine-1,4-diium-TCNQ Simple Salts (**5**—**9**).* To a boiling ethanol (20 ml) solution of $Li^+TCNQ^{\cdot-}$ (0.50 g, 2.4 mmol) was added a hot aqueous (10 ml) solution of **3a** (0.50 g, 1.2 mmol). The mixture was allowed to stand in a refrigerator overnight. The resulting precipitate was recrystallized from acetonitrile to give **5** in a 71% yield. Other four simple salts **6**—**9** were prepared similarly by the equimolar reaction of $TCNQ^{\cdot-}$ in ethanol with the appropriate iminium dications in an acetonitrile/ethanol mixture (2:1 v/v), 67—85% yields.

*N,N'-Ethylene-, N,N'-Dimethyl-N,N'-ethylene-, N,N'-Haxamethylene-, N,N'-Dimethyl-N,N'-hexamethylenedi(1,3-dithiolan-2-iminium) and N,N'-Bis(1,3-dithiolan-2-ylidene)piperazine-1,4-diium-TCNQ Complex Salts (**10**—**14**).* To a boiling acetonitrile (50 ml) solution of the simple salt **5** (0.53 g, 0.78 mmol) was added two equivalent amounts of neutral TCNQ (0.32 g, 1.6 mmol) in boiling acetonitrile (25 ml). The mixture was allowed to stand at room temperature to afford **10** in a 75% yield. Similarly other complex salts **11**—**14** were prepared by the reactions of **6**—**9** with neutral TCNQ at the mole ratio of 1:2 in acetonitrile, respectively, 64—71% yields.



1a: R=H; n=2
1b: R=Me; n=2
1c: R=H; n=6
1d: R=Me; n=6



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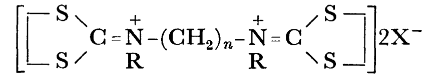

3a: R=H; n=2; X=Br
3b: R=Me; n=2; X=PF_6
3c: R=H; n=6; X=PF_6
3d: R=Me; n=6; X=PF_6

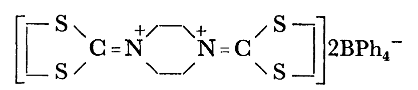

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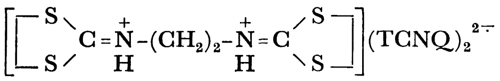
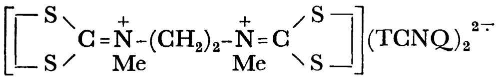
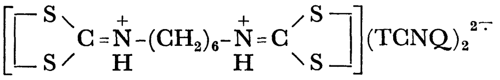
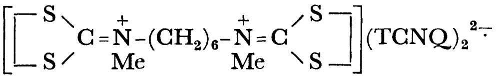
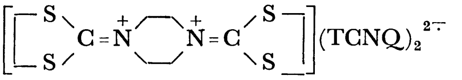
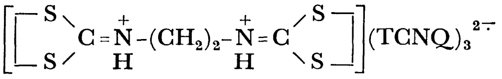
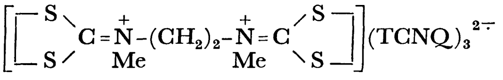
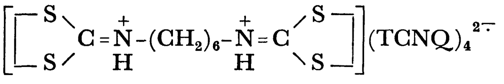
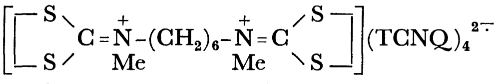
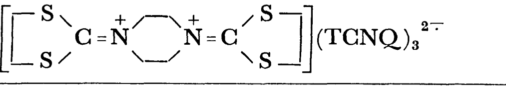
TABLE 1. ANALYTICAL DATA AND PROPERTIES OF THE $TCNQ^{\cdot-}$ SALTS

No.	Salt	Color	Mp(dec.) / °C	%C Found (Calcd)	%H Found (Calcd)	%N Found (Calcd)	$\mathrm{TCNQ}^{a)}$ / $\mathrm{TCNQ}^{\cdot-}$
5		Violet microcrystals	195—197	57.21 (56.96)	3.45 (3.29)	20.43 (20.76)	
6		Dark-violet needles	228—230	56.99 (56.64)	3.56 (3.92)	19.46 (19.43)	
7		Dark-violet needles	155—157	58.93 (59.16)	4.08 (4.14)	19.30 (19.16)	
8		Dark-violet needles	177—181	59.16 (60.12)	4.33 (4.52)	18.06 (18.46)	
9		Violet needles	250—252	57.81 (58.28)	3.75 (3.67)	21.09 (20.79)	
10		Black microcrystals	215—216	60.28 (60.05)	2.76 (3.18)	22.90 (22.84)	0.48
11		Black microcrystals	292—294	61.12 (60.92)	3.09 (3.33)	21.69 (21.62)	0.49
12		Black microcrystals	231—233	63.54 (63.25)	3.32 (3.36)	22.01 (22.13)	0.95
13		Black cubes	255—259	63.60 (63.78)	3.44 (3.63)	21.49 (21.60)	0.94
14		Black microcrystals	275—277	60.80 (61.05)	3.22 (3.12)	21.43 (21.67)	0.48

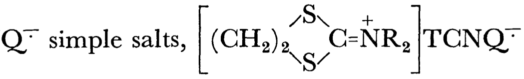
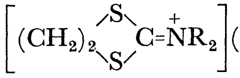
a) See text.

Physical Measurements. Electrical resistivities were measured as described previously,[1)] in the 286—370 K range (for **5**—**9** and **12**) or using a OXFORD CF 104 cryostat equipped with digital temperature controller DTC-2 in the 77—300 K range (for **10**, **11**, **13**, and **14**). Electronic spectra were recorded on a HITACHI 340 spectrophotometer (3900—16700 cm^{-1}) and a UNION GIKEN SM 401 spectrophotometer (11100—50000 cm^{-1}). Infrared spectra were measured on a HITACHI 215 infrared spectrophotometer. Magnetic susceptibilities were measured for microcrystalline materials by a SHIMADZU MB-11 magnetic balance in the range of 77—300 K.

Results and Discussion

Synthesis and Characterization. Five *N*,*N'*-polymethylenedi(1,3-dithiolan-2-iminium) dications reacted with TCNQ$^{\overline{\cdot}}$ radical anion to give simple salts **5**—**9** with the composition of 1:2. Simple salts **5**, **6**, and **9** further reacted with neutral TCNQ in acetonitrile to afford the 1:3 complex salt, irrespective of the mole ratio of the reactants. On the other hand, the reactions of simple salts **7** and **8** with neutral TCNQ yield the 1:4 complex salts. This variation in compositions of the complex salts may reflect the distance between two cation sites in a given iminium dication.

The ratios of the TCNQ$^{\overline{\cdot}}$ radical anion to neutral TCNQ in these complex salts (Table 1) were determined by the absorbances at 395 and 842 nm in acetonitrile,[9)] where the absorbance at 395 nm is a sum of those for the TCNQ$^{\overline{\cdot}}$ radical anion and neutral TCNQ and the absorbance at 842 nm is due to only the TCNQ$^{\overline{\cdot}}$ radical anion.

Electrical Properties. Temperature dependence of electrical resistivities for the simple and complex salts are illustrated in Fig. 1. The electrical resistivities (ρ) of simple and complex salts at 25 °C and the activation energies (E_a) calculated from the Arrhenius plots based on the equation, $\rho=\rho_0\exp(E_a/kT)$, are listed in Table 2, where ρ_0 is the constant value and k is the Boltzmann's constant. All the simple and complex salts showed typical semiconducting behaviors in the temperature range measured. The ρ values of simple salts **5**—**9** are in the same range as those of *N*,*N*-dialkyl-1,3-dithiolan-2-iminium-TCNQ$^{\overline{\cdot}}$ simple salts,  $\left[(\mathrm{CH_2})_2\begin{smallmatrix}\mathrm{S}\\ \\ \mathrm{S}\end{smallmatrix}\mathrm{C{=}\overset{+}{N}R_2}\right]\mathrm{TCNQ}^{\overline{\cdot}}$ (R= Me, *n*-Pr, *n*-C_6H_{13}; $2.2\times10^5-1.3\times10^7\,\Omega$ cm).[1,2)] The ρ values shown in Table 2 indicate that the substitution of methyl group on the iminium nitrogen is more or less effective for obtaining organic salts with low electrical resistivities (compare **6**, **8**, **11**, and **13** with **5**, **7**, **10**, and **12**, respectively). On the other hand, the ρ values do not seem to be rationalized in terms of the methylene chain lengths (for instance, compare **12** and **13** with **10** and **11**, respectively), though more methylene groups between the two cation sites in a given iminium dications is possible to result in lowering planarity of the iminium dications. It should be noted that complex salt **11** exhibits a small ρ value, which is compared with those of *N*,*N*-dimethyl- and *N*,*N*-diethyl-1,3-dithiolan-2-iminium–TCNQ$^{\overline{\cdot}}$ complex salts,  $\left[(\mathrm{CH_2})_2\begin{smallmatrix}\mathrm{S}\\ \\ \mathrm{S}\end{smallmatrix}\mathrm{C{=}\overset{+}{N}R_2}\right](\mathrm{TCNQ})_2^{\overline{\cdot}}$ (3.8 and 3.3 Ω cm for R=Me and Et, respectively).[1)] The resistivity, however, is larger by one order of magnitude than that of the highest conducting complex salt, quinolinium(TCNQ)$_2^{\overline{\cdot}}$ (0.5 Ωcm as compacted sample).[10)]

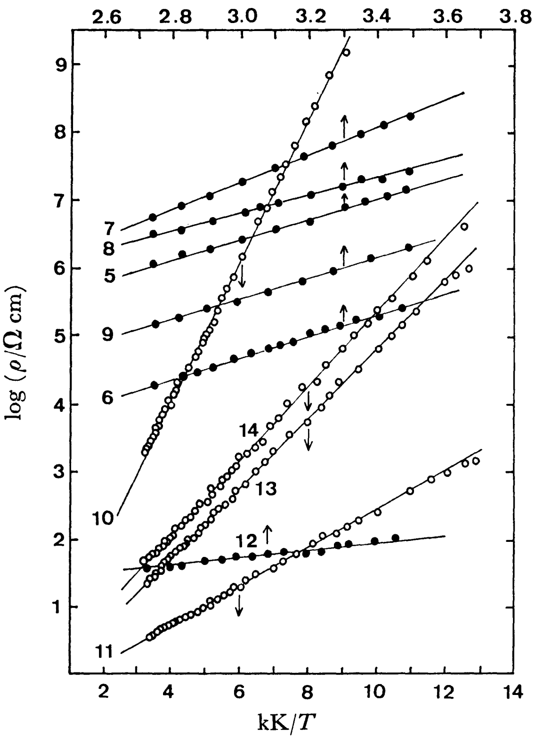


Fig. 1. Temperature dependence of the resistivity of the TCNQ$^{\overline{\cdot}}$ salts.

Table 2. Electrical resistivity (ρ) and activation energy (E_a) of the TCNQ$^{\overline{\cdot}}$ salts

Salt	$\rho_{25\,°\mathrm{C}}$ / Ω cm	E_a / eV
Simple salt		
5	8.9×10^6	0.30
6	1.8×10^5	0.32
7	9.8×10^7	0.40
8	1.9×10^7	0.26
9	1.3×10^6	0.30
Complex salt		
10	2.5×10^3	0.21
11	3.4	0.058
12	9.2×10	0.12
13	2.4×10	0.10
14	5.3×10	0.11

Electronic Spectra and Magnetic Properties. Figure 2 illustrates the electronic absorption spectra of **6**, **11**, and **13** in the solid state. Simple salt **6** exhibits three absorption bands in the range of 4000—32000 cm^{-1}, of which the lowest energy band is assigned to the charge-transfer (CT) transition between the TCNQ$^{\overline{\cdot}}$ radical anions and the remaining two bands to the (TCNQ)$_2^{2-}$ dimer.[11)] The presence of the (TCNQ)$_2^{2-}$ dimer in **6** is supported also from its diamagnetic property in the solid state at room temperature (χ_M=

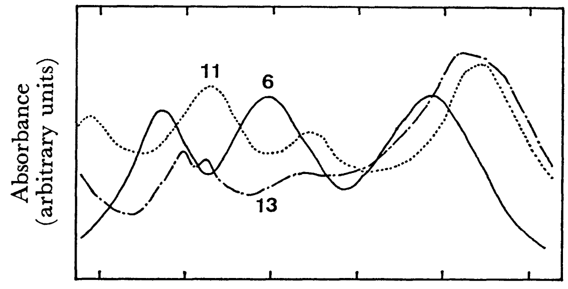


Fig. 2. Electronic absorption spectra of **6**, **11**, and **13** in Nujol mulls.

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

Salt	Wave number/10^3 cm^{-1} a)				
Simple salt					
5			8.3	15.1	24.7
6			8.5	14.5	24.4
7			9.0	15.0	25.2
8			8.3	15.3	25.5
9			8.9	14.9	24.5
Complex salt					
10	4.6		10.8	16.1	26.3
11	4.4		11.4	17.2	27.2
12		10.0	11.5	(17.0)	26.7
13		9.9	11.4	(16.7)	25.8
14	4.7		11.0	17.2	26.8

a) Shoulders in parentheses.

-3.0×10^{-4} emu mol^{-1}). Other four simple salts **5**, **7**, **8**, and **9** in the solid state showed electronic absorption spectra similar to that of **6**, as listed in Table 3. They also exhibited diamagentic properties at room temperature, which suggest that two TCNQ$^{\bar{\cdot}}$ radical anions are coupled completely with each other, resulting in the formation of the $(\mathrm{TCNQ})_2^{2-}$ dimer pair in solid **5**, **7**, **8**, and **9**.

The spectrum of **11** showed four absorption maxima in the 4000—32000 cm^{-1} range, of which the lowest energy band may be due to the CT transition between the TCNQ$^{\bar{\cdot}}$ radical anion and neutral TCNQ,[11] whereas the spectral appearance of the remaining three bands roughly resembles that of simple salt **6**, suggesting that the TCNQ$^{\bar{\cdot}}$ radical anions more or less interact with each other regardless of the additional TCNQ in neutral form. This is consistent with the diamagnetic property of **11** at room temperature ($\chi_M=-1.2\times10^{-4}$ emu mol^{-1}). In addition, the spectral features of **11** are very similar to those of $(\mathrm{Cs}^+)_2(\mathrm{TCNQ})_3^{2\bar{\cdot}}$,[11] $(\mathrm{morpholinium}^+)_2(\mathrm{TCNQ})_3^{2\bar{\cdot}}$,[11] and $\left[(\mathrm{CH_2})_2\langle\mathrm{S}\rangle_{\mathrm{S}}\overset{+}{\mathrm{C}}{=}\mathrm{N}(n\text{-}\mathrm{C_{10}H_{21}})_2\right]_2(\mathrm{TCNQ})_3^{2\bar{\cdot}}$.[2] Complex salt **11** is, therefore, suggested to have a stacking of TCNQ moieties similar to these 2:3 complex salts, where exists the unit consisting of two TCNQ$^{\bar{\cdot}}$ radical anions and one neutral TCNQ. The same conclusion can be drawn for **10** and **14** on the basis of their electronic spectra similar to that of **11** and diamagnetisms at room temperature.

The 1:4 complex salt **13** exhibits a spectrum similar to those of the 1:2 complex salts of *N*,*N*-dialkyl-1,3-dithiolan-2-iminium cations, $\left[(\mathrm{CH_2})_2\langle\mathrm{S}\rangle_{\mathrm{S}}\mathrm{C}{=}\overset{+}{\mathrm{N}}\mathrm{R_2}\right]$-$(\mathrm{TCNQ})_2^{\bar{\cdot}}$ (R= *n*-Pr, *n*-Bu, and Ph);[2] the intense absorption around 26000 cm^{-1} may be contributed from both the LE$_2$ state of the TCNQ$^{\bar{\cdot}}$ radical anion and the excited state of neutral TCNQ.[11] The band around 10000 cm^{-1} may be assigned to a transition to the LE$_1$ state[11] of the TCNQ$^{\bar{\cdot}}$ radical anion. The presence of monomeric TCNQ$^{\bar{\cdot}}$ is consistent with the fact that **13** showed a paramagnetism at room temperature ($\chi_M=6.6\times10^{-4}$ emu mol^{-1}). Another 1:4 complex salt **12** also exhibited essentially the same spectrum as **13** in the solid satte (Table 3). In addition, **12** and **13** showed a very broad band ranging from 4000 to 2500 cm^{-1}, which was never seen in the spectra of simple salts **5**—**9**. This band is assigned to the CT transition between TCNQ$^{\bar{\cdot}}$ and neutral TCNQ.[11]

Temperature dependence of the paramagnetic terms (χ_P) for complex salts **11** and **13** are illustrated in Fig. 3. The susceptibilities were obtained by subtracting the diamagnetic term calculated from Pascal's constants from the observed molar susceptibilities χ_M. Complex salt **11** obeys the Curie-Weiss' law. On the other hand, **13** shows a maximum near 160 K and its paramagnetic susceptibility increases as the temperature increases above 190 K. This behavior may indicate that the interaction between the unpaired electrons is changing irregularly with temperature. Whether the interaction is due to antiferromagnetic interaction, or the singlet-triplet equilibrium which

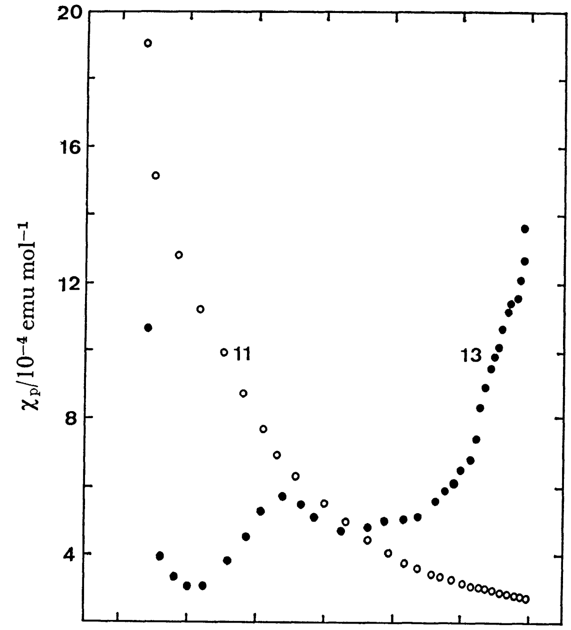


Fig. 3. Temperature dependence of paramagnetic susceptibilities of **11** and **13**.

has been reported in intermediate conductive 1:2 complex salts such as $\mathrm{Et_3\overset{+}{N}H(TCNQ)_2}^{\cdot-}$,12) is not clear in the present work. However, it is noted that the degree of the localization of the unpaired electrons (or spins) may be somewhat larger in **13** than **11**. This assumption may be correlated with the fact that **13** has a larger ρ value by one order of magnitude than **11**.

The authors wish to express their thanks to the Central Research Institute, Matsushita Electric Industrial Co., Ltd. for supplying a sample of TCNQ. They also would like to thank Professor Jiro Shiokawa of Osaka University for giving them the opportunity to use a magnetic balance. This work was carried out with a Grant-in-Aid for Scientific Research No. 347066 from the Ministry of Education, Science and Culture.

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