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3,5-DIAMINO-1,2-DITHIOLIUM TCNQ RADICAL ANION SALTS. PREPARATION AND ELECTRICAL PROPERTIES

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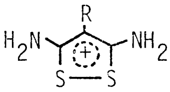
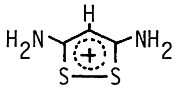
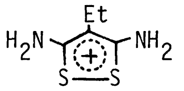
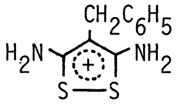
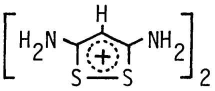
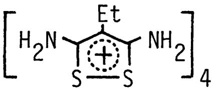
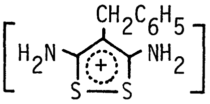
Some simple and complex salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) radical anion with 3,5-diamino-1,2-dithiolium cations,  (R = H, Et, and $CH_2C_6H_5$), were prepared. The complex salts as polycrystalline samples exhibit the resistivity of 3.0-9.8 Ω cm with very low activation energies (0.023-0.075 eV). Electronic spectra and magnetic properties of these salts are discussed.

In the search of highly conducting TCNQ salts, interest has been focused so far on the 1,3-dithiol system as counter moieties.$^{1)}$ One of the authors recently prepared some simple and complex salts of 1,3-dithiolium cations and its selenium analogues (*i.e.*, N,N-dialkyl-1,3-dichalcogenacycloalkan-2-iminium cations) with $TCNQ^{\bar{\cdot}}$ radical anion, the latter of which showed the resistivity of 2.4-4.0 Ω cm at 25°C as compaction samples.$^{2)}$ 1,2-Dithiolium cations also are expected to provide a series of highly conducting $TCNQ^{\bar{\cdot}}$ radical anion salts owing to their extensive electronic delocalization.$^{3)}$ There has, however, been reported only a communication on the 1,2-dithiolium-$TCNQ^{\bar{\cdot}}$ salts.$^{4)}$ Thus, we attempted to prepare $TCNQ^{\bar{\cdot}}$ radical anion salts of 1,2-dithiolium cation. This paper reports the synthesis and electrical properties of simple and complex salts of $TCNQ^{\bar{\cdot}}$ radical anion with 3,5-diamino-1,2-dithiolium cation and some 4-alkyl analogues.

3,5-Diamino-1,2-dithiolium iodide, and its 4-ethyl and 4-benzyl derivatives, were prepared by slightly modifying the literature method.$^{5)}$ To a hot aqueous solution (15 ml) of 3,5-diamino-1,2-dithiolium iodide (0.63 g, 2.4 mmol) was added a solution of $Li^+TCNQ^{\bar{\cdot}}$ (0.51 g, 2.4 mmol) in boiling ethanol (35 ml). The mixture was allowed to stand at room temperature for 4 h. The resulting precipitate was recrystallized from acetonitrile to give simple salt **1** (Table 1), in a 54% yield. Other simple salts **2** and **3** were similarly prepared by the equimolar reaction of the appropriate 1,2-dithiolium iodide in water with $TCNQ^{\bar{\cdot}}$ radical anion in ethanol, 47 and 56% yields, respectively. Simple salts **1**-**3** further reacted with neutral TCNQ in acetonitrile to afford complex salts. To a boiling acetonitrile solution (25 ml) of neutral TCNQ (0.31 g, 1.5 mmol) was added simple salt **1** obtained above (0.51 g, 1.5 mmol) in acetonitrile/ethanol mixture (2:1 v/v). The solution was allowed to stand in a refrigerator overnight to afford a precipitate, which was recrystallized from acetonitrile to give the 2:3 complex salt **4** in a 52% yield. The 4:7 and 1:2 complex salts, **5** and **6**, were similarly prepared by the reactions of **2** and **3** with neutral TCNQ at the mole ratio of 1:1 in acetonitrile, 65 and 60% yields, respectively. The composition of complex salts was confirmed not only by elemental analysis but also from the $TCNQ/TCNQ^{\bar{\cdot}}$ ratio obtained from electronic spectra in acetonitrile (see Table 1). Similar unique stoichiometries have been found in substituted pyridinium-$TCNQ^{\bar{\cdot}}$ complex salts.$^{6)}$

Table 1. Analytical data and properties of 1,2-dithiolium TCNQ$^{\cdot-}$ salts

No.	Salt	Color	mp / °C	%C Found (Calcd)	%H Found (Calcd)	%N Found (Calcd)	TCNQ / TCNQ$^{\cdot-}$ [a)]
1	 TCNQ$^{\cdot-}$	Dark-violet needles	190-191	53.11 (53.40)	2.56 (2.69)	24.87 (24.91)	
2	 TCNQ$^{\cdot-}$	Dark-violet needles	182-184	55.64 (55.87)	3.67 (3.59)	23.18 (23.00)	
3	 TCNQ$^{\cdot-}$	Dark-violet needles	232-234	61.60 (61.81)	3.45 (3.54)	19.55 (19.66)	
4	 (TCNQ)$_3^{2\cdot-}$	Black microcrystals	225-227 (dec)	57.17 (57.39)	2.41 (2.52)	25.18 (25.50)	0.51
5	 (TCNQ)$_7^{4\cdot-}$ b)	Black plates	205-208 (dec)	60.07 (60.22)	2.94 (3.11)	24.44 (24.31)	0.74
6	 (TCNQ)$_2^{\cdot-}$	Black microcrystals	250-253 (dec)	64.38 (64.65)	3.11 (3.03)	22.05 (22.17)	0.98

a) Calculated from the absorbances at 395 and 842 nm in acetonitrile.

b) Calcd. as 1:2 salt: C, 61.15; H, 3.01; N, 24.59%.

Electrical resistivities, electronic absorption spectra, and magnetic susceptibilities were measured as described previously.[7)]

The electrical resistivity (ρ) of the simple and complex salts at 25°C and the activation energy (E_a) calculated by the equation, $\rho = \rho_0 \exp(E_a/kT)$, are listed in Table 2. All the salts show typical semiconducting behaviors in the temperature range measured (293-370 K for simple salts and 77-300 K for complex salts). The conductivity of complex salts are about 10^3 times larger than the corresponding simple salts. It should be noted that the 4:7 complex salt **5** exhibits a small ρ value, although the resistivity is larger by one order of magnitude than that of the highest conducting complex salt, (quinolinium)$^+$-(TCNQ)$_2^{\cdot-}$ (0.5 Ω cm as polycrystalline sample).[8)]

Table 2. Electrical resistivity (ρ), activation energy (E_a), and magnetic susceptibility (χ_M) of 1,2-dithiolium TCNQ$^{\cdot-}$ salts

Salt	$\rho_{25°C}$ / Ω cm	E_a / eV	χ_M [a)] / emu mol^{-1}
Simple salt			
1	4.4×10^3	0.27	-1.4×10^{-4}
2	1.7×10^3	0.15	-1.7×10^{-4}
3	1.0×10^4	0.29	-1.9×10^{-4}
Complex salt			
4	9.8	0.054	1.3×10^{-4}
5	3.0	0.023	1.5×10^{-3}
6	6.5	0.075	9.6×10^{-4}

a) Measured at room temperature.

Figure 1 illustrates the electronic absorption spectra of **1**, **4**, and **5** in the solid state. Simple salt **1** displays three absorption maxima at 5900, 15500, and 23800 cm^{-1}. Similar spectra were observed in other simple salts 2 and 3. The spectral patterns of 1-3 closely resemble those of several simple salts which have been reported to involve dimeric $(TCNQ)_2^{2-}$.[2)] The existence of the $(TCNQ)_2^{2-}$ dimer in 1-3 is suggested also from their diamagnetic properties at room temperature (Table 2).

The spectrum of the 2:3 complex salt 4 shows five absorption bands at 5900, 10000, 11500, and 24000 cm^{-1}. Except for the weak absorption at 5900 cm^{-1}, the appearance of the spectrum does not resemble those of some 2:3 complex salts such as $(Cs^+)_2$-$(TCNQ)_3^{2\bar{\cdot}}$ [9)] and $(molpholinium^+)_2$-$(TCNQ)_3^{2\bar{\cdot}}$,[9)] but several 1:2 complex salts such as $(MePh_3P)^+(TCNQ)_2^{\bar{\cdot}}$ [9)] and $(N\text{-propylquinolinium})^+(TCNQ)_2^{\bar{\cdot}}$.[9)] While the lowest energy band at 5900 cm^{-1} may tentatively be assigned to the charge-transfer (CT) transition between $TCNQ^{\bar{\cdot}}$ radical anions, the CT interaction is assumed to be extremely weak. This assumption is consistent with the fact that 4 exhibits a small paramagnetism at room temperature (Table 2).

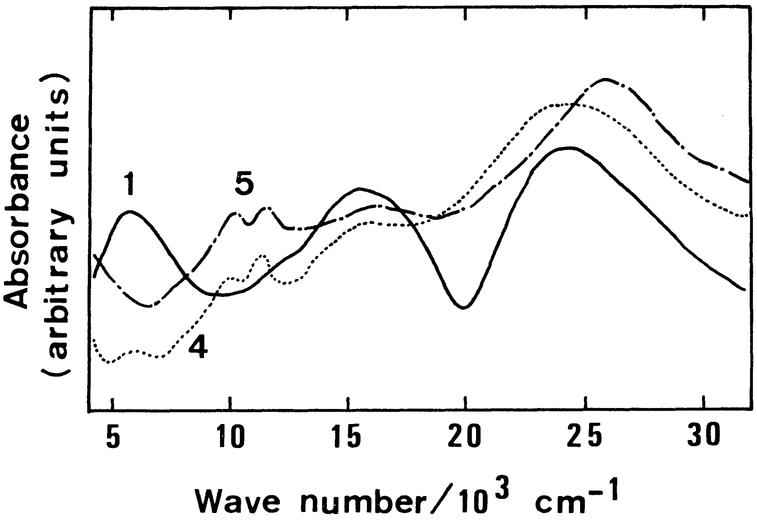


Fig. 1. Electronic absorption spectra of 1, 4, and 5 in Nujol mulls.

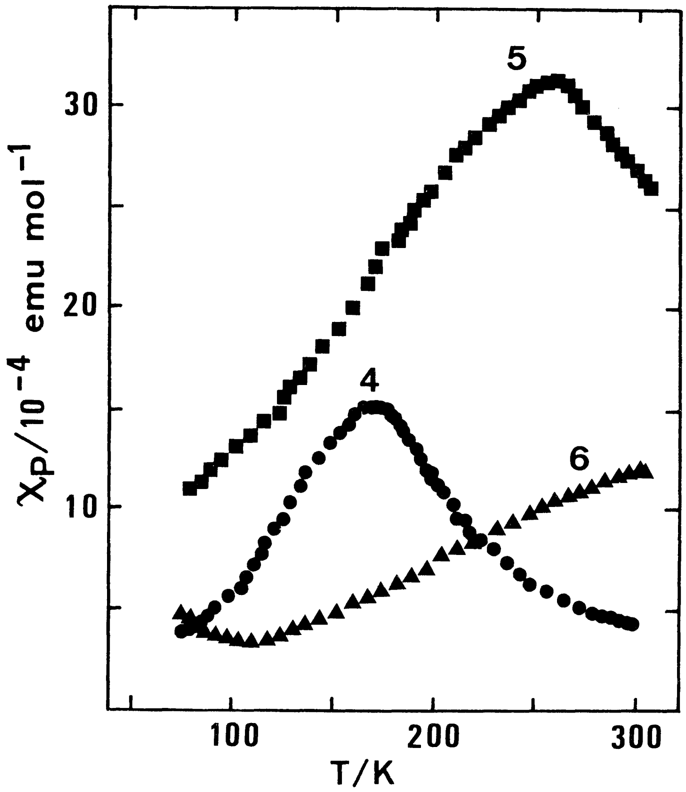


Fig. 2. Temperature dependence of the paramagnetic susceptibility of 4, 5, and 6.

The 4:7 complex salt 5 exhibits four absorption bands at 10200, 11500, 16100, and 26040 cm^{-1}. The spectrum is very similar to those of the 1:2 complex salts of N,N-dialkyl-1,3-dithiolan-2-iminium cations with $TCNQ^{\bar{\cdot}}$ radical anion (λ_{max}: *ca.* 10000, 11000, 17000, and 26000 cm^{-1}),[2)] where exist monomeric $TCNQ^{\bar{\cdot}}$ radical anions. The presence of $TCNQ^{\bar{\cdot}}$ monomer in solid 5 is suggested from a large paramagnetism of 5 at room temperature (Table 2). The 1:2 complex salt 6 also exhibited essentially the same spectrum as 5 in the solid state. Furthermore, infrared spectra of all the complex salts showed a CT band between $TCNQ^{\bar{\cdot}}$ radical anion and neutral TCNQ in the 3500-2700 cm^{-1} range.

Temperature dependence of the paramagnetic susceptibilities (χ_p) for complex salts 4-6 is illustrated in Fig. 2. The susceptibilities were obtained by subtracting the diamagnetic term estimated from Pascal's law from their observed molar susceptibilities (χ_M). Both complex salts 4 and 5 show a maximum χ_p value around 175 and 260 K, respectively, and above these temperatures obeyed the Curie-Weiss law. These temperature dependences of paramagnetic terms may be explained by a singlet-triplet model which has been applied for several 1:2 complex salts such as $(Et_3NH)^+$-$(TCNQ)_2^{\overline{\cdot}}$.[10] In this model, χ_p is given by;

$$\chi_p = \frac{2Ng^2\mu_B^2}{kT[3 + \exp(J/kT)]}$$

where N is the number of spin-coupled pairs, J is the singlet-triplet energy separation, and g is a g-factor in the triplet state. By using this model, we have estimated a pair of the N and J values;[10] N = 1/2 x (the number of $TCNQ^{\overline{\cdot}}$ radical anions), J = 0.030 eV for 4 and J = 0.017 eV for 5. The difference in the J value between 4 and 5 may be correlated with the fact that 5 is more conductive than 4, although slightly. On the other hand, the paramagnetic susceptibility of the 1:2 complex salt 6 increases monotonically as the temperature increases in the 100-300 K range. This magnetic behavior also may be interpreted by a singlet-triplet model, but the detail explanation has to await the susceptibility measurements in much more extended temperature range.

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References

1) For example, "Synthesis and Properties of Low-Dimensional Materials," ed by J. S. Miller and A. J. Epstein, *Ann. N. Y. Acad. Sci.*, 313, (1978).
2) S. Araki, H. Ishida, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 51, 407 (1978); S. Araki and T. Tanaka, *ibid.*, 51, 1311 (1978).
3) H. Prinzbach and E. Futterer, "Advances in Heterocyclic Chemistry," ed by A. R. Katritzky and A. J. Boulton, Academic Press, New York (1966), vol. 7, P. 39.
4) G. L. Coustumer, J. Amzil, and Y. Mollier, *J. Chem. Soc., Chem. Commun.*, 1979, 353.
5) K. A. Jensen, H. R. Baccaro, and O. Buchardt, *Acta Chem. Scand.*, 17, 163 (1963).
6) M. Murakami and S. Yoshimura, *Chem. Lett.*, 1977, 929.
7) Y. Yumoto, R. Nishioka, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, submitted for publication.
8) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, 84, 3374 (1962).
9) Y. Iida, *Bull. Chem. Soc. Jpn.*, 42, 71, 637 (1969); J. Tanaka, M. Tanaka, T. Kawai, T. Takabe, and O. Maki, *ibid.*, 49, 2358 (1976).
10) R. G. Kepler, *J. Chem. Phys.*, 39, 3528 (1963); I. F. Shchegolev, *Phys. Status Solidi A*, 12, 9 (1972).

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