2796 © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 2796—2799 (1980) [Vol. 53, No. 10

Electrical and Optical Properties of the 5,6:11,12-Bis(epidithio)naphthacene–Bromine System (TTT-Br_n). Formation of Organic Mixed-valence Compounds (TTT)(TTT^+)Br^- and (TTT^+)(TTT^{2+})(Br^-)$_3$

Yoshio MATSUNAGA* and Kazuhiro TAKAYANAGI
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received April 10, 1980)

The electrical resistivity of the 5,6: 11,12-bis(epidithio)naphthacene–bromine system (TTT–Br_n) was examined over the composition range from $n=0.3$ to 2.0 using polycrystalline compactions. The room-temperature resistivity shows a minimum of about 7 Ω cm near $n=0.5$, suggesting the formation of a mixed-valence compound, (TTT)(TTT^+)Br^-. The resistivity increases monotonously with n. No anomaly was found at the composition of (TTT^+)Br^-. The formation of another mixed-valence compound, the ideal composition of which may be expressed by the formula (TTT^+)(TTT^{2+})(Br^-)$_3$, is indicated by an abrupt change of the resistivity from 100 to 4000 Ω cm around $n=1.5$. This change is accompanied by an increase of the activation energy for semiconduction by a factor of almost two and also by the change of sign in the variation of the Seebeck coefficient with the temperature from positive to negative. A further increase of the resistivity by a factor of ten was observed between $n=1.5$ and 2.0. The electronic and vibrational spectra support the coexistence of the TTT molecule and the TTT^+ ion near $n=0.5$ and that of the TTT^+ and TTT^{2+} ions near $n=1.5$.

The term "mixed-valence" has been adopted for the description of the inorganic systems containing an element in two different states of oxidation. Such systems are of great interest as their properties are frequently far from the sum of the properties of the two metal ions taken separately. The appearance of electronic conduction much higher than those in the compounds containing either valence state alone, as is exemplified by magnetite, $Fe^{II}Fe^{III}{}_2O_4$, is one of the striking features of many mixed-valence compounds. A large number of organic compounds, which contain both the molecules and the radical ions, have been prepared in the last two decades. Some of them are highly conducting. Tetrathiafulvalene–tetracyano-*p*-quinodimethane (TTF–TCNQ), complex TCNQ salts, and so-called iodine complexes are notable examples. In contrast to a great variety of valence in inorganic compounds, all the organic compounds so far studied consist of the formally neutral molecules and the monopositive or mononegative radical ions. In this work, we searched for the first example of the organic mixed-valence compounds where the mean valence would be higher than one. 5,6 : 11,12-Bis(epidithio)naphthacene (TTT) seemed to be the best molecular species for our purpose as a number of the stable TTT^+ salts and also fairly stable TTT^{2+} salts are known from the work of Marschalk and Niederhauser.[1] The counter ions which they used to prepare both TTT^+ and TTT^{2+} salts are Cl^-, Br^-, NO_3^-, and SO_4^{2-}. We selected the bromides as the most promising component compounds.

The mixed-valence compounds of TTT with the mean valence of less than one have been studied by several workers. One of the present authors reported the preparation of the *o*-chloranil and *o*-bromanil complexes of a 3 : 1 mole ratio.[2,3] In their electronic spectra, there are strong absorption bands assignable to the TTT^+ ion. In addition, a broad electronic absorption band having a maximum around 2500 cm^{-1} is indicative of an interaction between the TTT molecule and the TTT^+ ion. The compactions exhibit resistivities of the order of one Ω cm at room temperature. The bis(1,2-ethylenedithiolato)nickel(II) complex prepared by Interrante *et al.* is another example.[4] As the complex has the empirical formula $TTT_{1.2}(NiS_4C_4H_4)$ and there is complete charge transfer from TTT to $NiS_4C_4H_4$, on the average each of the TTT molecules bears a formal charge of +5/6. The dc resistivity along the c-axis direction of the single crystal has been reported to be about 0.03 Ω cm at 25 °C. The extensively-studied iodine complex TTT–$I_{1.5}$ is also a kind of mixed-valence compound.[5–7] Because of the formation of polyiodide ions, the mean valence is less than one even if more iodine is added.[8] The single crystal resistivities measured along the needle axes in both the TTT–$I_{1.5}$ and TTT–$I_{2.7}$ phases are known to be metallic in the temperature range from 200 to 300 K. Therefore, it seemed very likely that low-resistivity mixed-valence compounds can be found with the TTT–Br_n system.

Experimental

Materials. TTT was synthesized following the method reported by Marschalk and Stumm and recrystallized three times from trichlorobenzene.[9] The dibromide was prepared by the oxidation of powdered TTT suspended in trichlorobenzene with bromine.[1] The samples with n values less than two were prepared by grinding the weighed $TTT^{2+}(Br^-)_2$ and TTT in an agate mortar in the presence of a small amount of benzene; the powders were then dried at 100 °C. The compositions were determined by microanalysis.

Measurements. The electrical resistivities and Seebeck coefficients of polycrystalline compactions were recorded as functions of the temperature from −100 to 100 °C by the procedures employed in our previous work.[8] The electronic and vibrational spectra were measured both as potassium bromide disks by means of a Beckman DK 2A spectrophotometer and a JASCO IR-G spectrophotometer respectively.

Results and Discussion

Electrical Properties. The temperature depend-

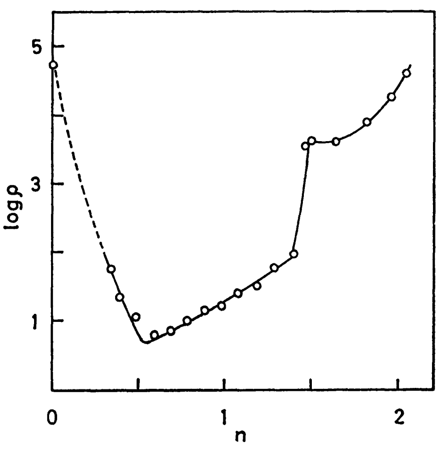

Fig. 1. Electrical resistivity at 25 °C plotted against the bromine content (n Br atoms/TTT molecule).

ence of the resistivity, ρ, of the polycrystalline compactions follows the typical semiconductor behavior: $\rho = \rho_0 \exp(E_a/kT)$. In Fig. 1, the logarithm of resistivity at 25 °C is plotted against n. The drastic decrease of the resistivity compared to those at $n=0$ and 2 is clearly due to the oxidation-reduction between the TTT molecule and the TTT^{2+} ion. The solid-state and solution spectra of the mono- and dibromides are distinctly different from each other,[10)] so there is no doubt about the existence of TTT^+Br^- and $TTT^{2+}(Br^-)_2$. The specimens with n values between one and two must formally consist of the TTT^+ and TTT^{2+} ions and bromide ions; those with n values less than one must consist of the TTT molecules, the TTT^+ ions, and bromide ions. As the resistivity is sensitive to the composition change, its measurement provides a simple means of detecting the possible mixed-valence compounds. An anomaly appearing in these two composition ranges can be assigned to such a compound. A minimum resistivity of about 7 Ω cm found near $n=0.5$ is indicative of the formation of the compound $(TTT)_2Br$. The formation of this mixed-valence compound is not unexpected. Very recently, Ritvay-Emandity *et al.* have concluded that the chloride precipitated upon mixing the methanol solutions of TTT^+ acetate and potassium chloride has the composition of $(TTT)_2Cl$.[11)] In addition, a closely-related 5,6:11,12-(epidiseleno)naphthacene (TSeT) has been known to form the chloride of the same ratio, $(TSeT)_2Cl$.[12)]

The electrical resistivity increases monotonously up to 100 Ω cm by $n=1.4$. No indication of a well-established compound TTT^+Br^- is found in the resistivity-composition isotherm. For this compound, Perez-Albuerne *et al.* have reported a resistivity of 50 Ω cm at 25 °C.[13)] Our value at this composition is 18 Ω cm. Between $n=1.4$ and 1.5, the resistivity increases by a factor of forty. Such a behavior may arise from the formation of a nonstoichiometric compound, the lower limit of the existence region being located at $n=1.4$. The sharp edge appearing in this figure suggests that the ideal composition of this phase is $(TTT)_2Br_3$. This is the kind of compound we looked for in this system. The additional carriers introduced by the incorporation of extra TTT^+ ions into this ideal compound account for the marked decrease of the resistivity in this narrow composition range. Above $n=1.5$, the resistivity increases again and reaches about 4×10^4 Ω cm at $n=2$.

The formation of the latter mixed-valence compound is strongly supported by the variation in the activation energy for semiconduction in its existence region. The activation energy is approximately constant below $n=1$, the value being 0.115 eV. This value is in good agreement with 0.11 eV reported by Perez-Albuerne *et al.* for TTT^+Br^-. The energy increases gradually to 0.13 eV by $n=1.4$ and then abruptly to 0.21 eV by $n=1.5$. Above this composition, it remains at this value.

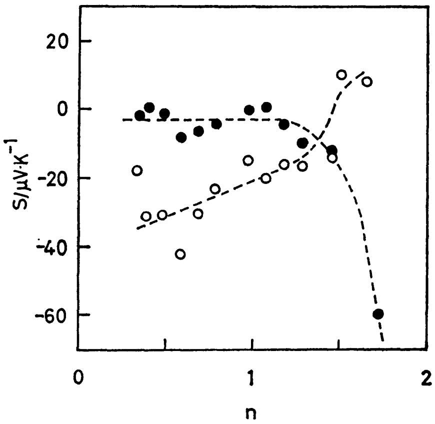

Fig. 2. Seebeck coefficients at −90 °C (○) and at 60 °C (●) plotted against the bromine content.

The whole composition range is also divided into two by the sign and temperature dependence of the Seebeck coefficient. When n is less than one, the coefficient is −20 to −30 μV K^{-1} at low temperatures and increases monotonously to about 0 μV K^{-1} at high temperatures. The direction of the temperature variation is reversed above $n=1.5$. A small positive value found below 0 °C is nearly independent of the temperature. The coefficient becomes negative above 0 °C and shows a large decrease by the further raising of the temperature. In Fig. 2, the behavior is exemplified by the values at −90 °C shown by open circles and by those at 60 °C shown by shaded circles. Thus, the existence of the mixed-valence compound, $(TTT)_2Br_3$, is manifested by the anomalous changes observed with all the electrical quantities examined.

Optical Properties. The electronic spectra of the TTT^+ and TTT^{2+} salts in both the solid and dissolved states have been examined by one of the present authors.[10)] The monomeric TTT^+ ion in alcohol exhibits three weak bands at 8.0, 9.5, and 10.7×10^3 cm^{-1}, and a strong band at 17.3×10^3 cm^{-1}, followed by weaker ones at 18.7 and 21.5×10^3 cm^{-1}. The three in the near-infrared region may be ascribed to the vibrational structure of the first electronic transition.[14)] The solid-state spectrum resembles the solution spectrum. By means of the transmission measurements through potassium bromide disks, we observed absorption maxima at 7.5, 9.2, 18.0, and 21.2×10^3 cm^{-1}. Except for the lowest-energy transition, these wavenumbers are in good agreement with those obtained earlier by the diffuse reflectance method; namely, 6.3, 9.5, and 18.0×10^3 cm^{-1} and a shoulder located at 21×10^3 cm^{-1}.[10] The bands appearing in the near-infrared region are very much widened and intensified in the solid state, compared to the bands in the dissolved state. This is the region where we expect the absorption associated with the interaction between the TTT$^+$ ions. This expectation is consistent with the fact that the intensity ratio between the band in this region and that in the visible region depends markedly on the kind of the counter ion.[10] Furthermore, Kamaras and Grüner have recently demonstrated that an intense absorption emerges at 5.6×10^3 cm^{-1} upon cooling the methanol solution of TTT$^+$ acetate.[15] They attributed the new absorption to the dimer ion, (TTT$^+$)$_2$.

The spectrum of the brown-colored TTT^{2+}(Br$^-$)$_2$ is rather similar to the above-mentioned in the visible region; that is, the maxima are located at about 18 and 21×10^3 cm^{-1}. No absorption appears in the infrared region. When the salt is dissolved in dilute acid, the bands become sharper and are shifted to 20.7 and 23.6×10^3 cm^{-1} respectively. In addition, a shoulder is found at 22.7×10^3 cm^{-1}.

The mixed-valence compound, (TTT)$_2$Br, exhibits a spectrum close to that of TTT$^+$Br$^-$. However, the bands at 7.5 and 9.2×10^3 cm^{-1} are weakened compared to those in the visible region and an extra band seems to exist below 5×10^3 cm^{-1}. This new transition may be indicative of an interaction between the TTT molecule and the TTT$^+$ ion. The spectrum at the composition of (TTT)$_2$Br$_3$ looks like a superposition of those of TTT$^+$Br$^-$ and TTT^{2+}(Br$^-$)$_2$. No sign of the interaction between the TTT$^+$ and TTT^{2+} ions could be seen in the electronic spectrum.

TABLE 1. WAVENUMBERS OF THE VIBRATIONAL BANDS IN THE SPECTRA OF TTT$^+$Br$^-$, (TTT)$_2$Br$_3$, AND TTT^{2+}(Br$^-$)$_2$
(Relative intensity: vs=very strong, s=strong, m=medium, w=weak, br=broad, sh=shoulder)

TTT$^+$Br$^-$	(TTT)$_2$Br$_3$	TTT^{2+}(Br$^-$)$_2$
1601 s	1603 s	1601 s
1550 br	1550 br	
	1473 m	1473 s
1465 s		
	1452 vs	1451 vs
1430 m		
	1390 m	1390 m
1365 s	1370 w	
	1325 s	1324 s
1312 s	1319 s	
	1305 s	1305 s
1289 vs	1290 s	
1277 vs	1280 m	
1250 s	1250 br	1249 w
1162 m	1165 m	1163 s
1129 m	1131 s	
	1110 sh	1110 br
1056 s	1060 m	
998 s	1000 s	
970 s	970 sh	
	946 w	947 w
	780 s	778 s
750 br	750 m	

Perez-Albuerne *et al.* have noted that the vibrational spectra clearly show the difference between neutral TTT and the TTT$^+$ salts.[13] More recently, Ritvay-Emandity *et al.* have observed that the spectrum of (TTT)$_2$Cl consists of bands corresponding to both the TTT molecule and TTT$^+$ ion.[11] Our mixed-valence compound, (TTT)$_2$Br, shows a spectrum which is also a superposition of those of TTT and TTT$^+$Br$^-$. As the former spectrum is much simpler than the latter, the spectrum of (TTT)$_2$Br is dominated by the contribution from the cation. Nevertheless, the presence of both TTT and TTT$^+$ ion is apparent from the relative intensities, which are markedly different from those in the spectrum of TTT$^+$Br$^-$. In Table 1, the bands found in the second mixed-valence compound, (TTT)$_2$Br$_3$, are listed together with those found in TTT$^+$Br$^-$ and TTT^{2+}(Br$^-$)$_2$. Our wavenumbers for TTT$^+$Br$^-$ are mostly in good agreement with those reported by Ritvay-Emandity *et al.*[11] The existence of the TTT$^+$ ion in this compound can be confirmed by the bands appearing at 1290, 1280, 1131, 1000, and 750 cm^{-1}. The bands assignable to the TTT^{2+} ion are also abundantly observed in this mixed-valence compound. Apparently, the bands located at 1473, 1452, 1390, 1325, and 780 cm^{-1} arise from the TTT^{2+} ion. These observations indicate that the lifetime of a definite valence state on the TTT molecule is longer than the vibrational period. An entirely different situation has been reported for some other organic mixed-valence compounds prepared by us. For example, in the spectrum of cobalticinium(3,3′,5,5′-tetrachloro-*p*-diphenoquinone)$_2$ neither the vibrational pattern due to the quinone molecule nor that due to the semiquinone anion has been found.[16] A single broad carbonyl stretching band is located at 1610 cm^{-1}; this is intermediate between that in the quinone, 1640 cm^{-1}, and that in the semiquinone salt, 1530 cm^{-1}. Similarly, the vibrational spectrum of (phenothiazine)$_2$Br is different from either that of the neutral molecule or that of its cation.[17] There is a pattern characteristic of the phenothiazine molecule bearing the charge of $+1/2$. In other words, the constituent molecules in these examples are equivalent to each other on the time scale of infrared spectroscopy. It may be added that the electrical resistivities of these two compounds are of the order of 10 or 100 Ω cm and are intermediate between the resistivity of (TTT)$_2$Br and that of (TTT)$_2$Br$_3$.

The authors wish to express their thanks to Dr. Kohji Fukushi for the recording of the laser Raman spectra of some specimens in order to check for polybromide bands. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 234028).

References

1) C. Marschalk and J. P. Niederhauser, *Bull. Soc. Chim. Fr.*, **1952**, 151.

2) Y. Matsunaga. *J. Chem. Phys.*, **42**, 2248 (1965).

3) Y. Okamoto, S. Shah, and Y. Matsunaga, *J. Chem. Phys.*, **43**, 1904 (1965).

4) L. V. Interrante, J. W. Bray, H. R. Hart, Jr., J. S. Kasper, P. A. Piacente, and G. D. Watkins, *J. Am. Chem. Soc.*, **99**, 3523 (1977).

5) L. I. Buravov, G. I. Zvereva, V. F. Kaminskii, L. P. Rosenberg, M. L. Khidekel, R. P. Shibaeva, I. F. Shchegolev, and E. B. Yagubskii, *J. Chem. Soc., Chem. Commun.*, **1976**, 720.

6) L. C. Isett and E. A. Perez-Albuerne, *Solid State Commun.*, **21**, 433 (1977).

7) K. Kamaras, K. Ritvay-Emandity, G. Mihaly, and G. Grüner, *Solid State Commun.*, **24**, 93 (1977).

8) T. Inabe and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **51**, 2813 (1978).

9) C. Marschalk and C. Stumm, *Bull. Soc. Chim. Fr.*, **1948**, 418.

10) Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **45**, 770 (1972).

11) K. Ritvay-Emandity, K. Kamaras, and G. Grüner, *Chem. Phys. Lett.*, Submitted for publication (personal communication).

12) L. I. Buravov, A. I. Kotov, M. L. Khidekel, I. F. Shchegolev, and E. B. Yagubskii, *Izv. Akad. Nauk, Ser. Khim.*, **1976**, 475.

13) E. A. Perez-Albuerne, H. Johnson, Jr., and D. J. Trevoy, *J. Chem. Phys.*, **55**, 1547 (1971).

14) A. I. Kiss, M. Kertesz, P. Carsky, and H. Wedel, *Tetrahedron*, **35**, 515 (1979).

15) K. Kamaras and G. Grüner, *Solid State Commun.*, **30**, 277 (1979).

16) Y. Matsunaga and Y. Narita, *Bull. Chem. Soc. Jpn.*, **45**, 408 (1972).

17) S. Doi and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **48**, 3747 (1975).