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Electronic States of Crystalline Cation Radical Salts. Simple Salt of Phenothiazine$^{+\cdot}$Br$^-$ and Complex Salt of (Phenothiazine)$_2^{+\cdot}$Br$^-$

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Synopsis. Phenothiazine forms not only simple cation radical salt of Phenothiazine$^{+\cdot}$ Br$^-$ but also complex salt of (Phenothiazine)$_2^{+\cdot}$ Br$^-$. In this paper, less-than-half occupied Hubbard model was applied to the complex salt in order to explain its crystal electronic state.

The prominent magnetic, electrical, and optical properties of solid ion radical salts have been the subject of many theoretical and experimental investigations over the past seventeen years.[1] In such solid ion radical salts, the planar ion radical molecules are known to form, in themselves, a segregated stacking into columns so as to make a large overlap between their half-occupied molecular orbitals. In this case, any individual radical molecule interacts through charge transfer most strongly with two other neighboring radicals, and the electronic and magnetic properties of the solid salt differ distinctly from those of ion radical monomer. Moreover, in some cases, we can obtain complex ion radical salts, which include not only ion radical molecule but also its parent neutral molecule.[1–4] The optical and magnetic properties of crystalline complex ion radical salts are very interesting in comparison with those of the corresponding simple salts. In the present paper, we shall examine the electronic state of complex cation radical salt, (Phenothiazine)$_2^{+\cdot}$ Br$^-$, together with that of simple salt, Phenothiazine$^{+\cdot}$ Br$^-$.

Phenothiazine (PT) is a strong electron donating molecule and forms chemically stable cation radical salts with various diamagnetic counter anions. A simple cation radical salt of PT$^{+\cdot}$ Br$^-$ is a kind of such compounds. The electronic spectrum of solid PT$^{+\cdot}$ Br$^-$ shows a strong low-energy band at 12900 cm^{-1} and high-energy bands at 20500, 23000, and 28600 cm^{-1}.[2–5] The high-energy bands are known to come from the monomer absorptions of phenothiazine cation radical in solution, while the low-energy band at 12900 cm^{-1} is characteristic of the solid salt and was assigned to the charge-transfer transition between cation radicals.[3–5] The magnetic susceptibility of this salt was found to be almost diamagnetic, indicating that strong antiferromagnetic spin exchange interaction acts between adjacent cation radicals. According to Sato *et al.*,[6] the change in the paramagnetic susceptibility with temperature was found to fit well the curve calculated from regular one-dimensional Ising model, for which the spin-exchange coupling parameter, J, was taken to be 970 cm^{-1}. In order to understand those optical and magnetic properties, a regular one-dimensional half-occupied Hubbard model is applied to the segregated stack of phenothiazine cation radicals in simple cation radical salt of PT$^{+\cdot}$ Br$^-$. This model is a simplification of the real crystal and is described by two parameters I and T.[5] T is the transfer matrix element of an unpaired electron which describes hopping between adjacent molecular sites, while I is the on-site Coulomb repulsion between two electrons with up and down spins on the same molecule. Then, T favors electron delocalization through band formation, whereas I favors localization due to electron-electron repulsions. On the basis of this model, we can explain the reason why the intermolecular charge-transfer absorption appears in the solid-state spectrum of PT$^{+\cdot}$ Br$^-$. The peak energy of the charge-transfer absorption corresponds to $\omega=I$, and if the electron transfer matrix element, T, is not zero, the absorption has observable intensity.[5,7] As for the magnetic property of this system, Takahashi showed that, in the case of $I\gg|T|$, the half-occupied Hubbard model becomes equivalent to the following effective Hamiltonian,[8]

$$\mathscr{H}_{\mathrm{eff}} = \frac{4T^2}{I}\sum_i\left(\boldsymbol{S}_i\cdot\boldsymbol{S}_{i+1}-\frac{1}{4}\right)+0\left(\frac{T^3}{I^2}\right), \tag{1}$$

where $\boldsymbol{S}_i$, $(S=1/2)$, is the spin operator of an electron at the i-th site. In other words, if the value of I is much larger than $|T|$, we can neglect such higher terms as $0(T^3/I^2)$, and the one-dimensional half-occupied Hubbard model is reduced to one-dimensional Heisenberg antiferromagnetic model with exchange interaction, $J=2T^2/I$. In this respect, our application of Hubbard model receives strong support from the fact that in PT$^{+\cdot}$ Br$^-$ there acts antiferromagnetic spin exchange interaction between adjacent PT$^{+\cdot}$ cation radicals.[6] Rigorously speaking, the J value of Heisenberg model should correspond to $2T^2/I$. However, since only the J value estimated with linear Ising model is available, we approximately use the estimated $J=970$ cm^{-1} value as $J\approx 2T^2/I$. If we use the $I=$ 12900 cm^{-1} value obtained spectroscopically, the T value was determined as $T\approx -2500$ cm^{-1} for the one-dimensional system of PT$^{+\cdot}$ cation radicals in simple PT$^{+\cdot}$ Br$^-$ salt.

Next, we consider the crystal electronic state of complex cation radical salt of (PT)$_2^{+\cdot}$ Br$^-$. The existence of this complex salt was earlier suggested by Matsunaga and Shono and by the present author,[2,3] and was later confirmed by Doi and Matsunaga.[4] In the electronic spectrum of the solid complex salt, the charge-transfer absorption due to the transition between cation radicals appears at 12600 cm^{-1}. In addition, a broad absorption is observed at 5200 cm^{-1}, which was assigned to the electronic transition from neutral phenothiazine to its cation radical.[4] In the complex salt, it appears that the positive charge is equally shared by the two molecules of phenothiazine and that phenothiazine molecules form, in themselves, a segregated stacking into infinite one-dimensional columns. Then, we can apply regular one-dimensional less-than-half occupied Hubbard model to the segregated stack of phenothiazine molecules.

Shiba[9] and Klein and Seitz[10] have shown that the magnetic susceptibility of a uniform stack of lessthan-half occupied molecules (average number of unpaired electrons per site is ρ) is related to the susceptibility of a uniform stack of half-occupied molecules ($\rho=1$) in simple ion radical salt. It is assumed that the values of I and T in less-than-half occupied Hubbard model are common to those in half-occupied system, respectively. If the value of I is much larger than that of $|T|$, the less-than-half occupied one-dimensional Hubbard model becomes identical to an antiferromagnetic Heisenberg chain with exchange interaction,[11]

$$J=\frac{2T^2\rho}{I}\left(1-\frac{\sin 2\pi\rho}{2\pi\rho}\right). \tag{2}$$

In fact, if we take $\rho=1$ in Eq. 2 for half-occupied Hubbard model, we simply obtain $J=2T^2/I$, which is identical with the J value of simple ion radical salt in Eq. 1. For the complex cation radical salt of $(\mathrm{PT})_2{}^{+\cdot}$ Br^-, we can choose $\rho=1/2$, $I=12900\ \mathrm{cm}^{-1}$ and $T\approx-2500\ \mathrm{cm}^{-1}$ because of the assumption that the I and T values of the complex salt are almost the same as those corresponding to the simple salt of $\mathrm{PT}^{+\cdot}$ Br^-. Then, using Eq. 2, the J value of the complex salt of $(\mathrm{PT})_2{}^{+\cdot}$ Br^- was estimated to be $485\ \mathrm{cm}^{-1}$. Temperature dependence of the magnetic susceptibility, χ, of the complex salt can be given by Bonner and Fisher's theoretical equation with $J=485\ \mathrm{cm}^{-1}$.[12] More practically, as an excellent fit to their equation, Torrance proposed an analytical expression of χ *versus* temperature and J.[11] If we compare the $J=970\ \mathrm{cm}^{-1}$ value of the simple salt with the $J=485\ \mathrm{cm}^{-1}$ value of the complex salt, we note marked decrease of the J value in the complex salt. This will give more paramagnetism to the susceptibility of the complex salt. The strong dependence of J on ρ means that the antiferromagnetic spin exchange interaction between unpaired electrons is caused mostly by the charge-transfer interaction between unpaired electrons and that less density of unpaired electron in the complex salt gives smaller J value, compared to the J value in the simple salt.

As for the optical property of the complex salt, $(\mathrm{PT})_2{}^{+\cdot}$ Br^-, the above-mentioned Hubbard model can also explain the observed charge-transfer absorption due to the transition between cation radicals. This absorption is observed at $12600\ \mathrm{cm}^{-1}$, which is close to the $12900\ \mathrm{cm}^{-1}$ value of the simple salt. Theoretically speaking,[7] the regular one-dimensional less-than-half occupied Hubbard model leads to the charge-transfer absorption spectrum of $\mathrm{Re}\,\sigma_{\mathrm{xx}}(\omega)\propto\mathrm{Re}\,\sigma^+(\omega)+\mathrm{Re}\,\sigma^-(\omega)$;

$$\mathrm{Re}\,\sigma^{\pm}(\omega)=\frac{e^2}{4}\,\frac{I^2\rho\left(1-\frac{1}{2}\rho\right)}{\omega^2\sqrt{\omega^2-2I^2\rho\left(1-\frac{1}{2}\rho\right)}}\times\sqrt{4T^2-\left\{-(\rho-1)I\pm\sqrt{\omega^2-2I^2\rho\left(1-\frac{1}{2}\rho\right)}\right\}^2}, \tag{3}$$

where we neglected the term of Fermi distribution function. For the simple salt of $\mathrm{PT}^{+\cdot}$ Br^- with $\rho=1$ and $I=12900\ \mathrm{cm}^{-1}$, the charge-transfer absorption, $\mathrm{Re}\,\sigma_{\mathrm{xx}}(\omega)$, has a divergent peak at $\omega=I$; this spectroscopic feature was mentioned previously. For the complex salt of $(\mathrm{PT})_2{}^{+\cdot}$ Br^-, however, if we put $\rho=1/2$, $I=12900\ \mathrm{cm}^{-1}$ and $T\approx-2500\ \mathrm{cm}^{-1}$, the absorption peak of $\mathrm{Re}\,\sigma_{\mathrm{xx}}(\omega)$ will take place around $\omega=\sqrt{4T^2+2IT+I^2}=11300\ \mathrm{cm}^{-1}$. Therefore, the charge-transfer absorption of the complex salt will show red-shift in comparison with that of the simple salt. The experimental peak energy, $12600\ \mathrm{cm}^{-1}$, of the complex salt shows a little red-shift compared to the $12900\ \mathrm{cm}^{-1}$ value of the simple salt, but this magnitude of the red-shift is not so large as that predicted theoretically. One of the reasons for this is that the I value of the complex salt may be a little larger than that of the simple salt and that the role of counter anion of Br^- in the complex salt may be less effective to decrease on-site Coulomb repulsion than in the simple salt, because average number of Br^- anions per one site of phenothiazine in the complex salt is just half of that in the simple salt.

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