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Optical and Magnetic Properties of Solid Anion Radical Salts Derived from Halogen-Substituted *p*-Benzoquinones

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Crystalline anion radical salts derived from halogen-substituted *p*-benzoquinones are known to show charge-transfer transition between anion radicals in the low-energy region and to possess antiferromagnetic spin exchange interaction between the anion radicals. Using Hubbard Hamiltonian, the optical and magnetic properties of Na^+ *p*-Chloranil$^{\bar{\cdot}}$ were explained in terms of a dimer model, while those of K^+ *p*-Chloranil$^{\bar{\cdot}}$ and K^+ *p*-Bromanil$^{\bar{\cdot}}$, in terms of an infinite non-alternant linear chain model.

The prominent magnetic, electrical and optical properties of a number of solid ion radical salts have been the subject of many theoretical and experimental investigations over the past fifteen years.[1–5] In such 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.[5–8] In one case, ion radical molecules stack predominantly in a pair-by-pair manner, so that the crystal system can be practically confined to a dimer of ion radicals. Another case is that ion radical molecules stack into infinite non-alternant one-dimensional column. In both cases, since any individual radical molecule interacts through charge-transfer most strongly with other neighboring radicals, the electronic spectrum of the solid salt differs distinctly from the monomer spectrum of the radical ion in solution but shows a charge-transfer transition between ion radicals in the low-energy region.[3–5] In the present paper, we apply half-filled Hubbard Hamiltonian to the dimer and the non-alternant one-dimensional system of ion radical molecules and investigate the optical and magnetic properties of certain crystalline anion radical salts derived from *p*-chloranil, *p*-bromanil and 2,5-dibromo-3,6-dichloro-*p*-benzoquinone (*p*-QBr_2Cl_2).

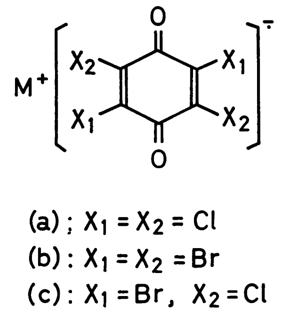

Fig. 1. The anion radical salts derived from (a) *p*-chloranil, (b) *p*-bromanil, and (c) 2,5-dibromo-3,6-dichloro-*p*-benzoquinone (*p*-QBr_2Cl_2). M^+ represents an alkali metal cation such as sodium or potassium cation.

Na^+ *p*-Chloranil$^{\bar{\cdot}}$

Several years ago,[4] we measured the diffuse reflection spectrum of this solid salt, together with the absorption spectrum of the *p*-chloranil anion radical in acetone solution. The monomer spectrum of the *p*-chloranil anion radical consists of absorption bands at 22200 cm^{-1}, 26700, and 30300. These absorptions were assigned to the $^2B_{3g}\rightarrow{}^2B_{1u}$, $^2B_{3g}\rightarrow{}^2A_u$, and $^2B_{3g}\rightarrow{}^2B_{1u}$ transitions, respectively.[4] On the other hand, the solid-state spectrum of Na^+*p*-Chloranil$^{\bar{\cdot}}$ salt shows a strong low-energy absorption at 11600 cm^{-1}, a high-energy band at 26500 and a shoulder beyond 30000. The high-energy band at 26500 cm^{-1} was assigned to the shifted band of the $^2B_{3g}\rightarrow{}^2B_{1u}$ transition at 22200 for the anion radical monomer, while the strong low-energy band at 11600 cm^{-1} characteristic of the solid salt, to the charge-transfer transition between *p*-chloranil anion radicals in the solid state.[4]

The magnetic property of solid Na^+*p*-Chloranil$^{\bar{\cdot}}$ salt was examined by Sugano and Kuroda.[9] The temperature dependence of the observed static magnetic susceptibility could be well explained in terms of a dimer model of the *p*-chloranil anion radicals. The paramagnetism comes from triplet excited state lying $\delta=1130\ cm^{-1}$ above the ground singlet state.

In order to understand the above experimental results in more detail, we consider the optical and magnetic properties of the dimer model of ion radicals in terms of Hubbard Hamiltonian, which is written by[10,11]

$$\mathscr{H} = \sum_{\sigma} T(C_{1\sigma}{}^{+}C_{2\sigma}+C_{2\sigma}{}^{+}C_{1\sigma}) + I(n_{1\uparrow}n_{1\downarrow}+n_{2\uparrow}n_{2\downarrow}), \tag{1}$$

where $n_{i\sigma}=C_{i\sigma}{}^{+}C_{i\sigma}$, and $C_{i\sigma}{}^{+}$ and $C_{i\sigma}$, ($i=1$ or 2), are the creation and annihilation operators of an electron with σ-spin at the i-th site, respectively, and where T (<0) is the transfer matrix element between ion radicals in a dimer, and the repulsive potential, I, appears only when two electrons are at the same site. If we only take the half-occupied molecular orbital of ion radical for each site, there are six bases of the wave functions for the dimer. After solving the eigenvalue problem, we obtain, for the triplet state, $c=C_{1\uparrow}{}^{+}C_{2\uparrow}{}^{+}|0>$, $d=C_{1\downarrow}{}^{+}C_{2\downarrow}{}^{+}|0>$, and $a^{+}=2^{-1/2}\times\{C_{1\uparrow}{}^{+}C_{2\downarrow}{}^{+}+C_{1\downarrow}{}^{+}C_{2\uparrow}{}^{+}\}|0>$ with energy zero, while we obtain, for the singlet states, $(1+(E_{\pm}/2T)^2)^{-1/2}\times(a^{-}+(E_{\pm}/2T)b^{+})$ with energy $E_{\pm}=I/2\pm\{(I/2)^2+(2T)^2\}^{1/2}$, and b^{-} with energy I. Here, $a^{-}=2^{-1/2}\times\{C_{1\uparrow}{}^{+}C_{2\downarrow}{}^{+}-C_{1\downarrow}{}^{+}C_{2\uparrow}{}^{+}\}|0>$, $b^{\pm}=2^{-1/2}\{C_{1\uparrow}{}^{+}C_{1\downarrow}{}^{+}\pm C_{2\uparrow}{}^{+}C_{2\downarrow}{}^{+}\}|0>$, and $|0>$ indicates the state of the dimer without any unpaired electron. The charge-transfer absorption of the dimer corresponds to the optical transition from the ground singlet state of $(1+(E_{-}/2T)^2)^{-1/2}(a^{-}+(E_{-}/2T)b^{+})$ to the excited charge-transfer singlet state, b^{-}. Therefore, in the dimer model of ion radicals, the energy of the charge-transfer absorption, $h\nu_{\mathrm{CT}}$, and the singlet-triplet energy separation, δ, are given by[12]

$$h\nu_{\mathrm{CT}} = \left\{\left(\frac{1}{2}I\right)^2 + (2T)^2\right\}^{1/2} + \frac{1}{2}I, \tag{2}$$

$$\delta = \left\{\left(\frac{1}{2}I\right)^2 + (2T)^2\right\}^{1/2} - \frac{1}{2}I. \tag{3}$$

This model was then applied to the above experimental results of the solid Na$^+$*p*-Chloranil$^{\cdot-}$ anion radical salt. By putting the observed values of $h\nu_{\mathrm{CT}} = 11600\ \mathrm{cm}^{-1}$ and $\delta = 1130\ \mathrm{cm}^{-1}$ into Eqs. 2 and 3, we obtain $I = h\nu_{\mathrm{CT}} - \delta = 10470\ \mathrm{cm}^{-1}$ and $T = -1800\ \mathrm{cm}^{-1}$, respectively. The $I = 10470\ \mathrm{cm}^{-1}$ value thus estimated for the Na$^+$ *p*-Chloranil$^{\cdot-}$ salt corresponds to the effective Coulomb repulsion energy in the solid salt. The repulsion energy is screened in the presence of neighboring sodium cations roughly by a factor of $(1-\alpha/r^3)$, where α is the polarizability of the cation and r is the effective distance between *p*-chloranil anion radical and neighboring cation.[13,14] In fact, in addition to the dimer formation in crystal, the *p*-chloranil anion radicals are known to dimerize even in ethanol solution,[15] where the screening appears to be less effective than in the solid state. The charge-transfer absorption of the dimer in ethanol solution is found at 14900 cm^{-1}, suggesting the I value much larger than the $I = 10470$ cm^{-1} value of the dimer in the solid Na$^+$*p*-Chloranil$^{\cdot-}$ salt.

Another interesting fact is that the charge-transfer band of solid Na$^+$*p*-Chloranil$^{\cdot-}$ salt at 11600 cm^{-1} is much influenced by applying a pressure; the peak position exhibits a red-shift with 58 cm^{-1} per kbar.[15] As is shown in Eq. 2, if the applied pressure only causes an increase in the transfer matrix element, $|T|$, the charge-transfer band peak will show a blue-shift under high pressure. The main reason for the observed red-shift is then attributable to the decrease of the I value, because the factor $(1-\alpha/r^3)$ will be decreased with the decrease of the distance between *p*-chloranil anion radical and neighboring sodium cation by applying pressure.

K$^+$ *p*-Chloranil$^{\cdot-}$ and K$^+$ *p*-Bromanil$^{\cdot-}$

The crystal structure analysis of K$^+$*p*-Chloranil$^{\cdot-}$ salt was made by Konno *et al.*[8] Although there are several polymorphs, in the structure of the orthorhombic α-form the *p*-chloranil anion radicals are stacked with equal intervals, forming non-alternant one-dimensional columns parallel to the c-axis, the interplanar spacing being 3.47 Å. The K$^+$ ion lies at the center of a rectangle formed by four oxygen atoms of the *p*-chloranil anion radicals related by c translation.

Earlier, we measured the solid-state spectrum of K$^+$*p*-Chloranil$^{\cdot-}$ salt,[4] which shows a weak low-energy band at 11800 cm^{-1}, a strong high-energy band at 23300 and a shoulder around 30000. The latter two high-energy absorptions were assigned to the $^2\mathrm{B}_{3\mathrm{g}} \rightarrow {}^2\mathrm{B}_{1\mathrm{u}}$ transitions at 22200 cm^{-1} and at 30300, respectively, of the monomer spectrum, while the low-energy band at 11800 cm^{-1}, to the charge-transfer transition between the anion radicals along the one-dimensional column in the solid state. It was further noted that the spectroscopic features of the solid K$^+$*p*-Chloranil$^{\cdot-}$ salt was rather similar to the monomer spectrum of the *p*-chloranil anion radical. On the other hand, although there is a phase transition around 210—260 K,[16] the temperature dependence of the observed magnetic susceptibility of the K$^+$*p*-Chloranil$^{\cdot-}$ salt in the region above the transition temperature was well explained in terms of an antiferromagnetic linear Ising model with exchange interaction of 113 cm^{-1}.[9]

In previous papers,[17—20] we examined the optical and magnetic properties for a system of non-alternant one-dimensional stacks of ion radicals in terms of Hubbard Hamiltonian, which can be written by

$$\mathscr{H} = \sum_{i,j,\sigma} T_{ij} C_{i\sigma}^{+} C_{j\sigma} + I \sum_{i} n_{i\uparrow} n_{i\downarrow}, \tag{4}$$

where $T_{ij}(<0)$ is the transfer matrix element between the i-th and j-th sites. For non-alternant one-dimensional column of ion radicals, we consider the half-occupied molecular orbital of the unpaired electron as one site of ion radical molecule, and only take into account the transfer matrix element between the nearest neighbor sites. Hereafter, it is simply denoted by $T(<0)$. We consider a paramagnetic state for our system, and further assume a δ-function for each elementary transition in which the spin and the wave vector of an electron are conserved. The intermolecular charge-transfer absorption, $\sigma(\omega)$, is given by[17]

$$\sigma(\omega) \propto \frac{e^2}{4} \frac{I^2}{\omega^2\sqrt{\omega^2 - I^2}} \sqrt{4T^2 - \omega^2 + I^2}. \tag{5}$$

A schematic representation of the absorption line shape has been given in Fig. 1 of Ref. 17. The theoretical charge-transfer absorption has a sharp divergent peak at $\omega = I$, and has a band width of $\sqrt{I^2 + 4T^2} - I$ in the region $\omega > I$. On the other hand, we examine the magnetic properties of the same system. In a region of small $|T|$ limit, the Hubbard model leads to a non-alternant one-dimensional antiferromagnet with an exchange interaction $J \approx 2T^2/I$ for our case.[14] Therefore, if we combine the experimental data on the peak energy of the observed charge-transfer absorption and the exchange interaction parameter derived from the magnetic susceptibility measurement, we can uniquely determine the magnitudes of I and T for our system.

We apply this approach to the system of non-alternant one-dimensional column of the K$^+$*p*-Chloranil$^{\cdot-}$ salt. The observed peak energy of the charge-transfer absorption, 11800 cm^{-1}, thus corresponds to $I = 11800\ \mathrm{cm}^{-1}$. As for the antiferromagnetic exchange interaction, rigorously speaking, the J value of Heisenberg model should correspond to $2T^2/I$, but only the J value estimated with Ising model is available at the present time. Therefore, we approximately use the estimated $J = 113\ \mathrm{cm}^{-1}$ value as $J \approx 2T^2/I$. By putting the $I = 11800\ \mathrm{cm}^{-1}$ value into this relation, we obtain $T = -820\ \mathrm{cm}^{-1}$ for the one-dimensional system of the potassium salt. The $|T|$ value thus estimated is found to be much smaller than the $|T| = 1800\ \mathrm{cm}^{-1}$ value of the Na$^+$*p*-Chloranil$^{\cdot-}$ salt, indicating weak intermolecular interaction between the *p*-chloranil anion radicals in the potassium salt. This is supported by the fact that the intermolecular distance between the anion radicals in the potassium salt is as large as 3.47 Å and also by the spectroscopic features that the high-energy bands at 23300 cm^{-1} and 30000 of the potassium salt show no appreciable shifts in comparison with those of the monomer spectrum of the *p*-chloranil anion radical.

Next, we examine the case of solid K$^+$*p*-Bromanil$^{\dot{-}}$ salt, whose situation is found to be very similar to that of K$^+$*p*-Chloranil$^{\dot{-}}$. The solid-state spectrum of the K$^+$*p*-Bromanil$^{\dot{-}}$ salt shows a very weak charge-transfer band at 10900 cm^{-1}, a weak shoulder at 17500 and a strong high-energy band at 23000.4) For this salt, the observed magnetic susceptibility data were analyzed with linear Ising model, and the antiferromagnetic spin exchange parameter, J, was estimated to be 97 cm^{-1}.9) Therefore, in a way similar to that of K$^+$*p*-Chloranil$^{\dot{-}}$, the values of $I=10900$ cm^{-1} and $T=-730$ cm^{-1} were estimated for the one-dimensional system of the K$^+$*p*-Bromanil$^{\dot{-}}$ salt. Again, the $|T|$ value is found to be as small as that of the K$^+$*p*-Chloranil$^{\dot{-}}$ salt. Although there is no crystal structure data for purposes of reference, the intermolecular interaction between the *p*-bromanil anion radicals is certainly weak in the K$^+$*p*-Bromanil$^{\dot{-}}$ salt.

Na$^+$ *p*-QBr$_2$Cl$_2^{\dot{-}}$ and K$^+$ *p*-QBr$_2$Cl$_2^{\dot{-}}$

The solid-state spectrum of Na$^+$*p*-QBr$_2$Cl$_2^{\dot{-}}$ salt is quite different from the monomer spectrum of the *p*-QBr$_2$Cl$_2$ anion radical but shows a strong low-energy charge-transfer absorption at 12200 cm^{-1} and a high-energy band at 26300.4) The latter band was assigned to the shifted band of the monomer absorption at 22100 cm^{-1}. Earlier, we measured the temperature dependence of the magnetic susceptibility of the Na$^+$ *p*-QBr$_2$Cl$_2^{\dot{-}}$ salt.21) Although no rigorous agreement between the observed and theoretical temperature dependences was obtained either by the singlet-triplet model or by the linear Ising model, the singlet-triplet energy separation, $\delta=970$ cm^{-1}, was estimated by the dimer model, while the antiferromagnetic exchange parameter, $J=810$ cm^{-1}, was estimated by the linear Ising model.21) Although no crystal structure data are available at the present time, we may explain the electronic state of this solid salt in terms of either the dimer model or the non-alternant one-dimensional system of the anion radicals. In the case of the dimer model, we again took an approach similar to that of Na$^+$*p*-Chloranil$^{\dot{-}}$, and the values of $I=11200$ cm^{-1} and $T=-1730$ cm^{-1} were thus estimated for the Na$^+$*p*-QBr$_2$Cl$_2^{\dot{-}}$ salt. If the non-alternant one-dimensional model was applied, the values of I and T were found to be 12200 cm^{-1} and -2200 cm^{-1}, respectively.

On the other hand, the solid-state spectrum of K$^+$ *p*-QBr$_2$Cl$_2^{\dot{-}}$ salt is rather similar to the monomer spectrum of the *p*-QBr$_2$Cl$_2$ anion radical and has a very weak charge-transfer absorption at 11500 cm^{-1}.4) As for the magnetic properties, although no rigorous agreement between the observed and theoretical magnetic susceptibilities was again obtained, the singlet-triplet energy separation, $\delta=153$ cm^{-1}, was estimated by the dimer model, while $J=97$ cm^{-1} was estimated by the linear Ising model.21) These optical and magnetic data lead to $I=11300$ cm^{-1} and $T=-710$ cm^{-1} for the dimer model or to $I=11500$ cm^{-1} and $T=-750$ cm^{-1} for the non-alternant one-dimensional model.

In either of the models, the magnitude of the transfer matrix element of the K$^+$ *p*-QBr$_2$Cl$_2^{\dot{-}}$ salt was found to be much smaller than that of the Na$^+$*p*-QBr$_2$Cl$_2^{\dot{-}}$ salt. This means that the *p*-QBr$_2$Cl$_2$ anion radicals in the sodium salt stack, in themselves, very closely, while the intermolecular interaction between the anion radicals is very weak in the potassium salt. Detailed crystal structure analyses of the Na$^+$*p*-QBr$_2$Cl$_2^{\dot{-}}$ and K$^+$*p*-QBr$_2$Cl$_2^{\dot{-}}$ salts are now required to confirm the above situation and also to determine by which model (dimer model or non-alternant one-dimensional model) the *p*-QBr$_2$Cl$_2$ anion radicals are stacked in those solid salts.

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