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Electronic Absorption Spectra and Electronic Structures of Some Würster's Blue Salts

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Electronic absorption spectra were measured at various temperatures for Würster's blue iodide, bromide, and chloride. The charge-transfer bands were found to be strongly dependent upon temperature. Concerning the iodide, the temperature dependency can be explained quantitatively, or at least semiquantitatively, by the aid of the linear Ising model in relation to the local ordering of the electron spins of Würster's blue cation radicals. This model gives the exchange energy of 99 ± 23 cm^{-1} for the iodide. For the bromide and the chloride, the dimer model was successfully applied to the analysis of the temperature dependence of the charge-transfer bands, giving singlet-triplet energy separations of 248 ± 30 cm^{-1} and 255 ± 30 cm^{-1} for the bromide and the chloride, respectively. The electronic structure and the intermolecular interaction were discussed for these radical salts, their electronic absorption spectra being compared with one another.

The Würster's blue radical salts are interesting research subjects because of their peculiar physicochemical properties.[1-12] For example, Würster's blue perchlorate (WBP) exhibits an unusual temperature dependency in the intensity of its electronic absorption spectrum. In previous papers[11,12] we studied this phenomenon, paying special attention to the phase transition mechanism and concluded that the dimerization mechanism of the phase transition is appropriate to solid WBP and that the disproportionation mechanism proposed by Kommandeur *et al.*[7-10] may be disregarded.

In the present paper, the temperature dependence of electronic absorption spectra was measured for the other Würster's blue salts: Würster's blue iodide (WBI), Würster's blue bromide (WBB), and Würster's blue chloride (WBC). The X-ray crystal analysis study of WBI was performed by de Boer *et al.*[13] According to their result, WBI takes a crystal structure in which the Würster's blue cations pack face-to-face to form regular columns parallel to the *b*-axis. The magnetic susceptibility of WBI was found to be well explained in the temperature range of 77—300°K by the aid of the linear Ising model.[14,15] From this it is revealed that the phase transition observed for WBP may not occur WBI in this temperature range. In view of this, we have undertaken to measure the temperature dependence of the electronic absorption spectra of WBI, WBB, and WBC and to compare the results with those for WBP.

Experimental

WBI and WBB were prepared by the method described in the literature.[16] WBC was prepared by oxidizing *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine in methanol with chlorine gas.

A Cary recording spectrophotometer model 14 M was used for the measurement of the electronic absorption spectra of solid samples. Solid, thin films used for the

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absorption measurements were prepared by coating powdered samples on quartz plates by a stainless steel spatula.[11)]

Absorption measurements at low temperatures were made by using glass Dewar vessels containing liquid helium or liquid nitrogen as a refrigerant, the temperature being measured by a thermocouple of (Au–Co) and Cu.

Results and Discussion

The Temperature Dependence of the Charge-Transfer Band of WBI. According to the X-ray crystal analysis data, WBI takes the crystal structure in which WB cations are located face-to-face forming one-dimensional columns.[13)] Since the overlap between the π-electron orbitals of the neighboring cations is expected to be largest in the direction parallel to the columns, the one-dimensional model is applicable to the study of the charge-transfer (abbreviated hereafter to CT) interaction in solid WBI.

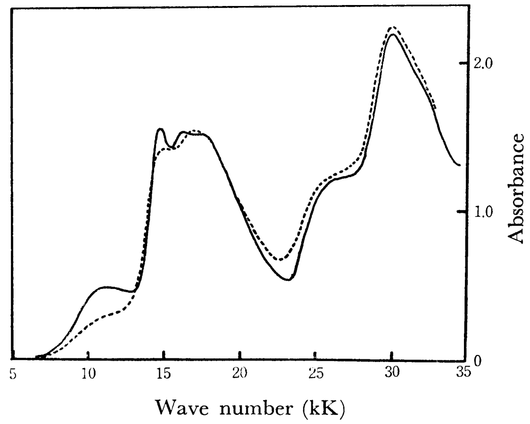

Fig. 1. The electronic absorption spectrum of the solid WBI.
---- at 260°K, ——— at 40°K

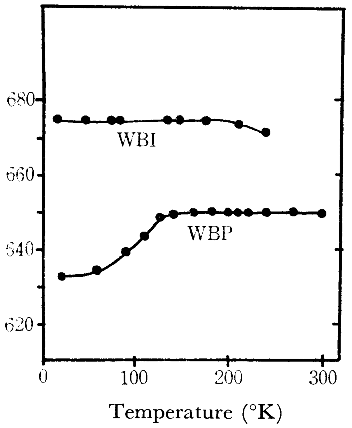

Fig. 2. Temperature dependence of the peak position of the first vibronic band for WBI and WBP.

The electronic absorption spectra of WBI measured at 260°K and at 40°K are shown in Fig. 1. First, let us consider the 600 mμ band due to the $^2B_{1u}\leftarrow{}^2B_{3g}$ transition of the WB cation. The peak position of this band is almost independent of temperature, though the vibrational structure becomes sharp with the decreasing temperature. The temperature dependence of the first vibronic band position observed for WBI is shown in Fig. 2, together with that for WBP. The peak position is almost constant for WBI in the temperature range of 40—260°K, while it varies greatly for WBP below the phase transition point. This suggests that the phase transition does not occur for WBI in this temperature range.

The 900 mμ band observed for solid WBI can safely be regarded as the CT band due to electron transfer between the half-occupied orbitals of the WB cation radicals. Its intensity greatly depends on temperature and increases with the decreasing temperature, as seen in Fig. 3. Since WBI shows no phase transition as mentioned above, it is not probable that solid WBI takes the dimer model which can be successfully applied to WBP. Therefore, we have undertaken to interpret the temperature dependency of the CT band of WBI by the aid of the one-dimensional Ising model, taking only the two neighboring WB cations in a chain.

The CT transition corresponding to the electron

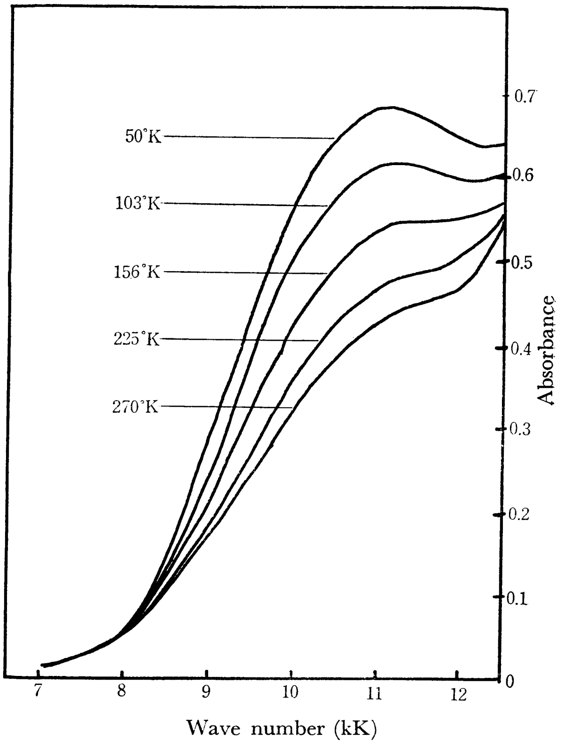

Fig. 3. The temperature dependence of the CT band of solid WBI.

transfer between the half-occupied orbitals of the two WB cation radicals is allowed, when the unpaired electron spins on these two orbitals are antiparallel with each other in the ground state ($S_1^z S_2^z = -1/4$). When they are parallel ($S_1^z S_2^z = 1/4$), however, the transition is forbidden. This rule comes from the facts that the two spins must be antiparallel in the CT state from Pauli's principle and that the electron does not change its spin in the optical transition. We define the normalized intensity of the CT band, I_{CT}, in such a way as it takes 1 and 0 for the allowed and forbidden transitions, respectively; it is expressed with regard to the spin of the ground state as follows:

$$I_{\mathrm{CT}} = -2S_1^z S_2^z + \frac{1}{2} \tag{1}$$

The above consideration can be generalized for a regular linear chain as follows:

$$I_{\mathrm{CT}} = -2\langle S_i^z S_{i+1}^z \rangle + \frac{1}{2} \tag{2}$$

where $\langle\ \rangle$ represents the statistical average for the system. Now let us write the Ising Hamiltonian of the system by the aid of the exchange energy, J, as follows:[17]

$$\boldsymbol{H} = 2J\sum_i S_i^z S_{i+1}^z \tag{3}$$

The solution of this Hamiltonian is well known, and $\langle S_i^z S_{i+1}^z \rangle$ is given as follows:

$$\langle S_i^z S_{i+1}^z \rangle = -\frac{1}{4}\tanh\frac{J}{2kT} \tag{4}$$

Accordingly, the following equation can be obtained from Eqs. (2) and (4):

$$I_{\mathrm{CT}} = \frac{1}{2}\left(\tanh\frac{J}{2kT} + 1\right) \tag{5}$$

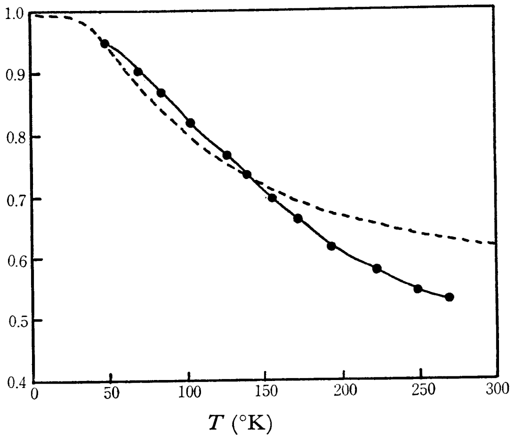

Fig. 4. The temperature dependence of the normalized intensity of the CT band.
----- theoretical curve by the linear Ising model
——— experimental curve

Figure 4 shows the temperature dependence of the normalized intensity of the CT band.[*1]

We can obtain J from the temperature, T_1, at which I_{CT} equals 3/4, namely, $\tanh J/2kT_1 = 1/2$. From Fig. 4, T_1 may be taken to be 130±30°K; J is evaluated to be $99\pm23\ \mathrm{cm}^{-1}$. The theoretical curve for $J = 99\ \mathrm{cm}^{-1}$ is also shown in Fig. 4 for the purpose of comparison. The discrepancy between the theoretical and observed curves becomes predominant at higher temperatures. There may be two reasons for this discrepancy: 1) the J value and the transition probability may be dependent upon the temperature through the intermolecular distance, and 2) the Ising model may be applied inadequately. At any rate, it may be said that the calculated I_{CT} values are at least semiquantitatively

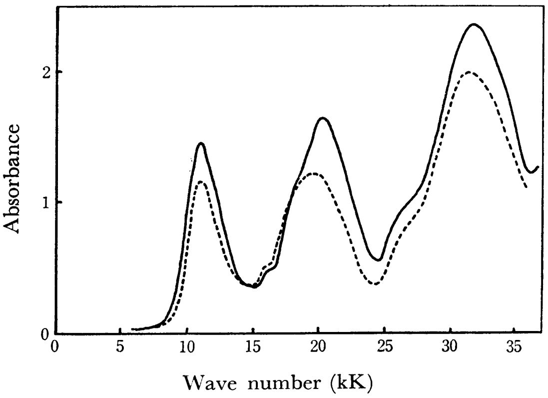

Fig. 5(a). The absorption spectra of WBC and WBB.
——— WBC ---- WBB

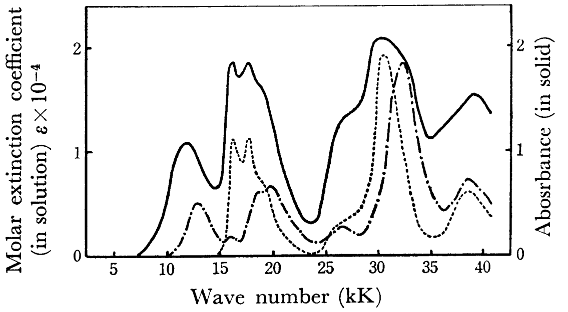

Fig. 5(b). The absorption spectra of WPB in solid and solution.
——— solid at 48°K, ---- ethanol solution at 295°K, —·— ethanol solution at 110°K

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[*1] The CT band intensity was obtained by integrating the area below the respective absorption curve over the frequency region lower than $11300\ \mathrm{cm}^{-1}$. Since, in our experiment, the lowest temperature was 50°K, the intensity at 0°K was estimated approximately by extrapolation.

Table 1. The peak positions (cm^{-1}) of the absorption bands of various Würster's blue salts

		CT	1st LE	3 rd LE
Solution	WBP monomer	—	17000	30700
	WBP dimer	12900	19800	32300
Solid	WBP (high temp.)	11700	16500	30000
	WBP (low temp.)		17000	30800
	WBI (77°K)	11300	17000	30000
	WBB (77°K)	11200	19600	31600
	WBC (77°K)	11100	20500	31900

coincident with the observed values at lower temperatures. The *J* value obtained by this method agrees with that obtained from the magnetic susceptibility (83 cm^{-1}) measurements within the expermental error.[14] This seems to mean that our explanation on the temperature dependence of the CT band intensity is essentially correct for solid WBI.

The Absorption Spectra of Solid WBB and WBC. The absorption spectra of solid WBB and WBC were measured at ~77°K; the results are shown in Fig. 5(a). In Fig. 5(b) the absorption spectra of solid WBP and the free WB cation in solution are shown for the purpose of comparison. As is clearly seen in Fig. 5, the absorption spectra of solid WBB, WBC, and WBP are different from one another in their peak positions and in their shapes. In Table 1, the peak positions in the absorption spectra of the solid Würster's blue salts under consideration are shown, together with those for WBP in solution. In this table, the first and third locally excited (LE) bands correspond, respectively, to the ~600 mμ and ~330 mμ ones of the WB cation radical monomer. Approximate values are taken for the peak positions of the first local excitation bands of WBP and WBI, since it is difficult to obtain their values definitely because of the vibrational structure. As is seen in Table 1, the first LE band shifts to higher frequencies in the order of WBP (high-temperature form)<WBI<WBP (low-temperature form)<WBB<WBC. The same tendency was observed for the third LE band. Furthermore, the ratio of the intensity of the CT band to that of the first or the third LE band also increases in the above order. This means that the ~600 mμ and ~330 mμ bands of the monomer are increasingly perturbed by the intermolecular interaction in the above order. That is to say, the strong interaction between the WB cation radicals is not only the source of the CT band but also has an influence on the intramolecular excitation band. In this connection, it may be noticed that the vibrational structures characteristic of the first absorption band of the WB cation radical disappear in solid WBB and WBC and that their band shapes resemble the spectra of the dimer in solution as seen in Fig. 5.

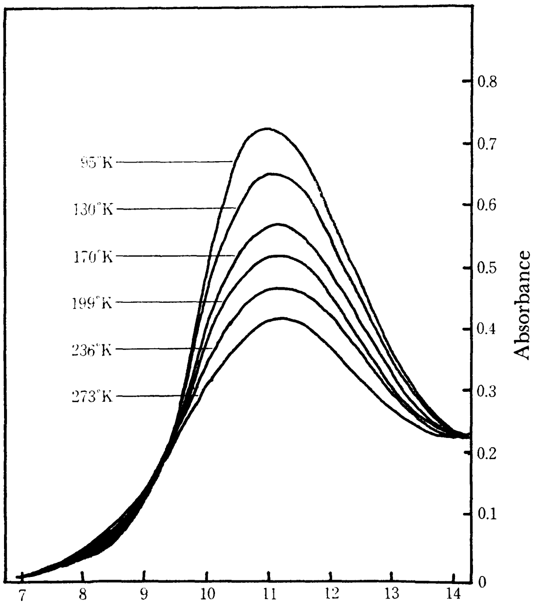

Fig. 6(a). The temperature dependence of the CT band of solid WBC.

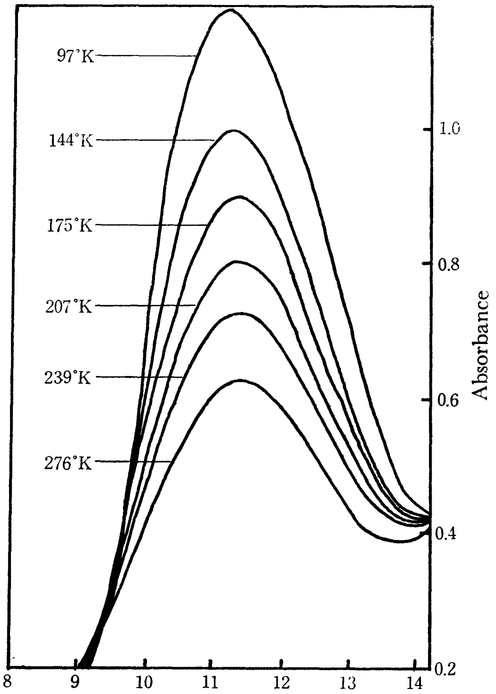

Fig. 6(b). The temperature dependence of the CT band of solid WBB.

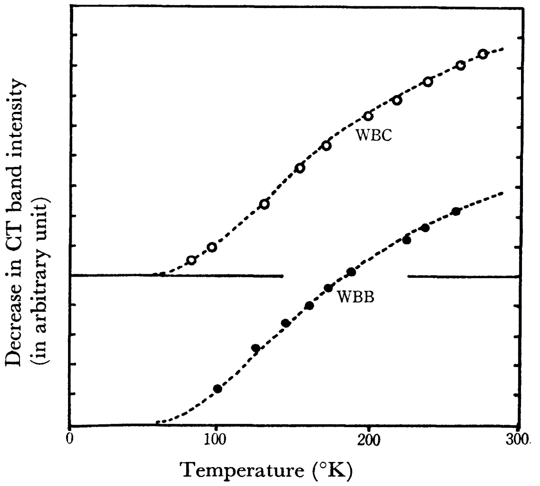

Fig. 7. Temperature dependence of the CT band intensity for WBC and WBB. The circles represent the observed values and the broken lines the theoretical ones.

The temperature dependence of the CT band was measured for WBB and WBC; we found an increase in its intensity with the decreasing temperature. Since this tendency observed for WBB and WBC is similar to that for WBP in the low-temperature phase, it may be expected that the temperature dependence of the CT band observed for the former salts can be explained by the dimer model which was successfully applied to the latter.[11] According to this model, the decrease in the CT band intensity turns out to be proportional to the population on the thermally accessible triplet exciton state caused by the exchange interaction between the two radical monomers. Actually, we applied the analytical method described in a previous paper[11] to the experimental data given in Fig. 6 and evaluated the singlet-triplet separation, J', as $248 \pm 30\ \text{cm}^{-1}$ and $255 \pm 30\ \text{cm}^{-1}$ for WBB and WBC, respectively. The theoretically expected temperature dependence of the CT band, calculated by the aid of the evaluated singlet-triplet separation, is shown in Fig. 7 for WBC and WBB. In this figure the observed values are also plotted for the purpose of comparison. We can find good agreement between the theoretical and experimental values for both WBC and WBB.

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