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Diffuse Reflection Spectra of Some Würster Salts

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Nine Würster salts derived from *p*-phenylenediamine, benzidine, and their *N*-methyl derivatives were examined for diffuse reflection spectra and classified into three groups, namely, those showing a strong charge-transfer band similar to that in the solution's dimer spectrum, those showing a strong α-band characteristic of the monomer and a relatively weak charge-transfer band, and, finally, those showing a spectrum which bears no resemblance to either the monomer or dimer spectrum. The mode of intermolecular interaction in these cation-radical salts was speculated upon on the basis of the spectra and the magnetic susceptibilities.

Prior to about 1960 the chief emphasis in studies of solid ion-radical salts was on measuring the magnetic susceptibilities of Würster salts, cation-radical salts obtained by the one-electron oxidation of aromatic diamines.[1-4] However, since the appearance of a series of TCNQ anion-radical salts, which are more stable and easily obtainable in the form of single crystals, studies of the electron spin resonance and the electrical conductivity have been among the most fruitful of pursuits.[5-8] The application of these physical methods has

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1) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **65**, 1747 (1943).

2) G. K. Hughes and N. S. Hush, *J. Proc. Roy. Soc. N. S. W.*, **81**, 48 (1947).

3) W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962).

4) K. Okumura, *J. Phys. Soc. Japan*, **18**, 69 (1963).

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6) D. D. Thomas, H. Keller and H. M. McConnell, *ibid.*, **39**, 2321 (1963).

7) W. J. Siemons, P. E. Bierstedt and R. G. Kepler, *ibid.*, **39**, 3523 (1963).

8) R. G. Kepler, *ibid.*, **39**, 3528 (1963).

thus far revealed that intermolecular interactions in such solids are often more-than-by-pairs. The electronic spectrum, which has been traditionally the most popular tool for elucidating the electronic structures of molecules and solids, should be able to produce some information concerning the interactions in solid ion-radical salts. It is the purpose of this paper, the first of our attempts along this line, to report the results of our electronic spectrum measurements of nine solid Würster salts and to make a tentative classification of the salts on the basis of their optical and magnetic properties.

The cation-radicals in solution have been known to be in monomer-dimer equilibria.⁹⁾ For example, the cation radical derived from *p*-phenylenediamine shows a visible spectrum comprising the α, β, and γ-bands, a doublet at 20.4 and 21.1, a broad shoulder at 27.6, and a strong band at 30.5 kK, when the concentration is low.¹⁰⁾ If the solution is more concentrated or cooled, a new broad band appears at 16.4 kK. This band has been ascribed to the charge-transfer absorption in the dimer by Hausser and Murrell.¹¹⁾ According to their theory, the cation-radicals in a dimer are stacked face-to-face and the spin exchange interaction leads to a singlet ground state and an excited triplet state. Then, we must take into consideration the fact that intermolecular charge-transfer may make a significant contribution to stabilizing the ground singlet state of the dimer. The low-energy absorption characteristic of the dimer arises from a transition from the thus-stabilized ground state to an excited singlet state expressed by an antisymmetric combination of the wave-functions for charge-transfer structures, R-R^{++}.

Both the present cation-radicals and TCNQ anion-radicals are platelike, and, to the best of our knowledge, they are stacked in the solid salts flat upon one another to form parallel chains.⁶,¹²⁻¹⁵⁾ Any individual radical may interact most strongly with one or two other radicals. In the former case, the interaction is predominantly pair-by-pair; therefore, we may speculate that the solid-state spectrum will be close to the solution's dimer spectrum. If the singlet-triplet excitation energy, to which both the spin exchange and charge-transfer interactions contribute, is rather small, the triplet state may become thermally accessible and paramagnetism may be observed. Secondly, when a radical interacts equally strongly with two neighbors, the following two extreme cases may be conceived. With a weak interaction, the solid-state spectrum may bear some resemblance to the monomer spectrum and paramagnetism of close to 100% free radicals may be exhibited. If any charge-transfer absorption is observable, the paramagnetism may decrease accordingly. On the other hand, if the more-than-by-pairs interaction is strong enough, the salt may be considered to be a linear antiferromagnet. Here again, the charge-transfer interaction may contribute to the stabilization of the state where spins are antiparallel. Therefore, the spectrum may have no similarity to either the monomer or dimer spectrum and the susceptibility may be low or even negative. These speculations clearly represent oversimplified cases; however, we have found that they are well followed in the Würster salts.

Experimental

Materials. The following Würster salts were prepared according to the methods of Michaelis and Granick¹⁾ and of Hughes and Hush²⁾; *p*-phenylenediamine bromide,¹⁾ *N,N*-dimethyl-*p*-phenylenediamine (Würster's red) bromide,¹⁾ Würster's red ferrocyanide,²⁾ *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (Würster's blue) perchlorate,¹⁾ Würster's blue ferrocyanide,²⁾ Würster's blue iodide prepared in aqueous methanol (high-susceptibility form),²⁾ Würster's blue iodide prepared in methanol - ether (low-susceptibility form),²⁾ benzidine bromide,²⁾ and *N,N,N',N'*-tetramethylbenzidine bromide.²⁾ They were assumed to exhibit the magnetic behavior reported in the references.

Measurements. The solid bromide was diluted with potassium bromide in a ratio of about 1 : 200 by grinding it to obtain a reasonable reflectance. The spectra were recorded as the difference in reflectance between the mixture and pure potassium bromide in the range from 4.0 to 30.8 kK by a Beckman DK-2A spectroreflectometer, and were then plotted using the Kubelka-Munk function $f(R)=(1-R)^2/2R$, where R is the reflectance. To avoid anion-exchange between the salt and the diluent, the iodide was ground with potassium iodide, and the perchlorate and ferrocyanide, with naphthalene. (With the last diluent, the measurements are reliable only in the range from 10 to 25 kK because of absorption due to the hydrocarbon.)

Results and Discussion

***p*-Phenylenediamine Bromide (Fig. 1, Curve a).** The low-energy band in the solid-state spectrum is found at 12.7 kK, which is much lower than the 16.4 kK value for the charge-transfer band in the dimer spectrum and also the 20.4 and 21.1 kK values for the α-band in the monomer spectrum. Although no information is available on the crystal structure, we suppose that the intermolecular interaction in this salt is

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9) K. Uemura, S. Nakayama, Y. Seo, K. Suzuki and Y. Ooshika, This Bulletin, **39**, 1348 (1966).

10) Y. Iida and Y. Matsunaga, *ibid.*, **41**, 2535 (1968).

11) K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

12) C. J. Fritchie, Jr., and P. Arthur, Jr., *Acta Cryst.*, **21**, 139 (1966).

13) C. J. Fritchie, Jr. *ibid.*, **20**, 892 (1966).

14) J. Tanaka, T. Sakabe, M. Mizuno and C. Tanaka, Paper presented at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966.

15) M. Mizuno, T. Sakabe and J. Tanaka, Paper presented at the Symposium on Molecular Structure, Osaka, October, 1966.

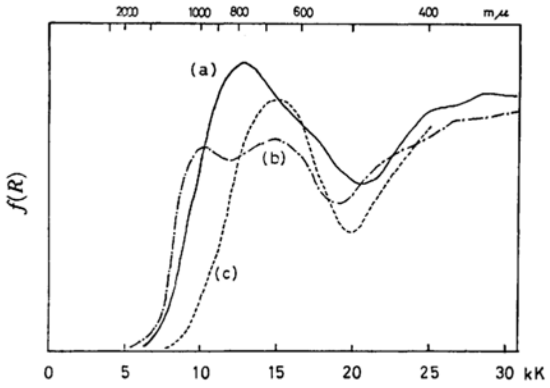

Fig. 1. Diffuse reflection spectra of *p*-phenylenediamine bromide (curve a), Würster's red bromide (curve b) and Würster's red ferrocyanide (curve c).

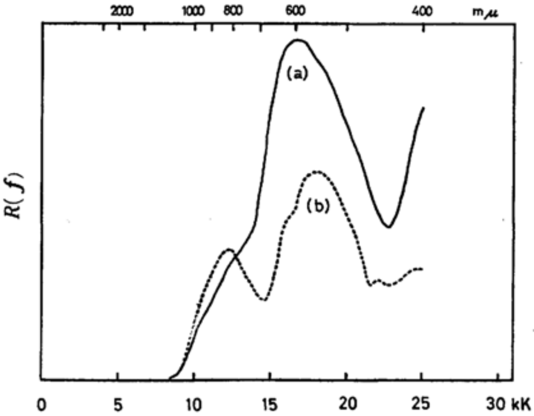

Fig. 2. Diffuse reflection spectra of Würster's blue perchlorate (curve a) and ferrocyanide (curve b).

strong and more-than-by-pairs. The magnetic susceptibility reported by Michaelis and Granick is $-(109\pm10)\times10^{-6}$ emu/mol, which is in agreement with the estimated diamagnetic term, $-(98\pm16)\times10^{-6}$.[1]

Würster's Red Bromide (Fig. 1, Curve b). The solid-state spectrum has absorptions at 10.4 and 14.8 kK. The charge-transfer band in the dimer is located at 14.7 kK, and the α-band in the monomer, at 18.0 and 19.4 kK.[10,16] Again, the spectrum is different from either the dimer or monomer spectrum and extends to the lower-energy region. The crystal structure has been examined by Tanaka *et al.*[14] The cation-radicals are equally spaced in a linear chain at the remarkably short distance of 3.135 Å. These pieces of evidence indicate that the intermolecular interaction here is more-than-by-pairs and is strong. The salt is diamagnetic, the reported values being -102×10^{-6} by Michaelis and Granick[1] and -130×10^{-6} emu/mol by Hughes and Hush.[2] This is in accordance with our conclusion. Tanaka *et al.* have reported that the low-energy absorption is polarized out of the molecular plane, presumably in the direction to connect the centers of neighboring molecules.[14]

Würster's Red Ferrocyanide (Fig. 1, Curve c). Unlike the dark-green bromide, this salt shows only one broad absorption in the low-energy region, at 14.8 kK. This energy is in good agreement with the 14.7 kK value for the charge-transfer band in the solution's dimer spectrum.[16] According to the measurements by Hughes and Hush, this salt is paramagnetic; $+1098\times10^{-6}$ emu/mol at 293°K.[2] A cation-radical in this salt appears to interact predominantly with one neighbor, but merely weakly.

Würster's Blue Perchlorate (Fig. 2, Curve a). The crystal is known to be orthorhombic and to be built up from linear chains of equivalent cation-radicals at room temperature. A phase change into the monoclinic form occurs at 186°K, and the radicals pair up to form dimers. The singlet-triplet energy separation in the latter phase has been estimated as 0.246 kK.[6] Thus, the salt at room temperature has been considered to be a normal paramagnet. In accordance with this view, the strong band at 16.7 kK in the solid-state spectrum corresponds well with the α-band in the monomer spectrum, 16.4 and 17.8 kK.[10] However, the presence of a shoulder around 12 kK must be noted. This is the place where the charge-transfer band appears in the solution's dimer spectrum[16] and also in the solid-state spectrum at low temperatures.[17] The paramagnetic susceptibility above the transition temperature has been reported to be consistent with a Curie-Weiss law; however, the observed paramagnetism is often short of the expected 100% free radical value. For example, Duffy has found it to be 94% and Okumura, as low as 81%.[3,4] It is difficult to see how these deviations from 100% free radicals are related with the weak charge-transfer absorption in the solid-state spectrum. At any rate, both the optical and magnetic pieces of evidence clearly indicate that the interaction in Würster's blue perchlorate is weak at room temperature.

Würster's Blue Ferrocyanide (Fig. 2, Curve b). Although the main bands, located at 16.4 and 18.2 kK, again correspond well with the α-band in the monomer spectrum, the charge-transfer band at 12.3 kK is clearly recorded. The susceptibility reported by Hughes and Hush is as high as $+1031\times10^{-6}$ emu/mol at 291°K,

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16) K. Suzuki, Y. Ooshika, Y. Seo, K. Uemura and S. Nakayama, Paper presented at the Symposium on Molecular Structure, Nagoya, October, 1965.

17) T. Sakata and S. Nagakura, *Technical Report of ISSP*, Ser. A, No. 244, March, (1967), published by the Institute for Solid State Physics, the University of Tokyo.

which is only a little bit lower than the $+1114\times 10^{-6}$ emu/mol value for the perchlorate.²⁾ As is indicated by the strong charge-transfer absorption and lower susceptibility, the cation-radicals in the ferrocyanide must interact with each other slightly more strongly than those in the perchlorate; otherwise, the situations in these two substances seem to be very much alike.

Würster's Blue Iodide (Fig. 3, Curves a and b). Judging from the spectrum and the susceptibility (as high as $+1004\times 10^{-6}$ emu/mol at 289°K),²⁾ the high-susceptibility form is similar to the perchlorate and ferrocyanide discussed above. The charge-transfer band at 11.4 kK and the band at 25.8 kK are very much intensified in the low-susceptibility form, for which a value of $+51\times 10^{-6}$ emu/mol at 289°K has been found by Hughes and Hush.²⁾ On the other hand, the α-band at 16.4 kK and the γ-band at 30.6 kK almost disappear. This feature is the one expected for the dimer spectrum.¹⁶⁾ Therefore, it is likely that the cation-radicals pair up strongly in the low-susceptibility form. However, the possibility that the sample for the high-susceptibility form is contaminated with a small amount of the low-susceptibility form, or *vice versa*, can not be excluded.

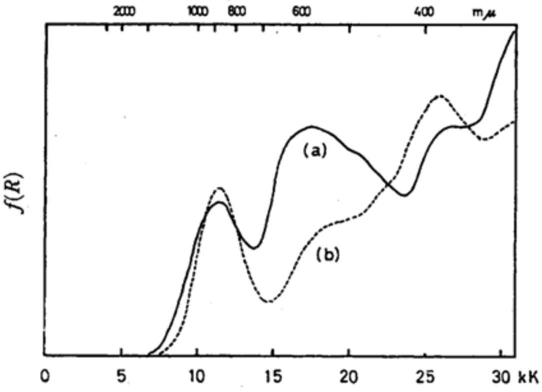

Fig. 3. Diffuse reflection spectrum of Würster's blue iodide, high-susceptibility form (curve a) and low-susceptibility form (curve b).

Mizuno *et al.* have studied the crystal structure of a dark-green Würster's blue bromide recrystallized from methanol.¹⁵⁾ The perpendicular separation between the molecular planes has been found to be as great as 3.515 Å. It is interesting to note that the spectrum reported by them is similar to that of the high-susceptibility form of the iodide.

Benzidine Bromide (Fig. 4, Curve a). The monomer spectrum comprises bands at 11.6 and 13.1, and shoulder at 14.3, and a strong band with some vibrational structures around 21.6 kK, while at low temperatures these absorptions are diminished and new bands appear at 12.4, 16.4, and 27.8 kK.¹⁸⁾ They have been assigned to the dimer. Unfortunately, the lower-energy region, in which we are most interested, could not be examined because of absorption due to the solvent. Consequently, there are not enough data for comparison and we cannot choose between a pair-by-pair and a more-than-by-pairs charge-transfer interaction as the cause of the absorption at 6.7 kK in the solid-state spectrum. The salt is known to be diamagnetic (-123×10^{-6} emu/mol);²⁾ therefore, the interaction is certainly strong.

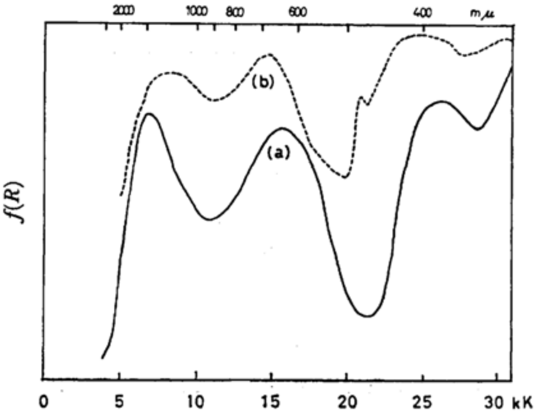

Fig. 4. Diffuse reflection spectra of benzidine bromide (curve a) and *N,N,N',N'*-tetramethylbenzidine bromide (curve b).

***N,N,N',N'*-Tetramethylbenzidine Bromide (Fig. 4, Curve b).** The solution study by Takemoto *et al.*, although valuable as an example of monomer-dimer equilibrium, does not provide us with a complete dimer spectrum for comparison.¹⁹⁾ The solid-state spectrum is very much like that of the afore-mentioned benzidine bromide except for the shift of the low-energy absorption to 8.0 kK. The salt has a susceptibility of -173×10^{-6} emu/mol.²⁾

General Remarks. Summarizing the above-mentioned results, we may note that the Würster salts can tentatively be classified into the following three groups:

(I) The paramagnetic Würster's red ferrocyanide and the low-susceptibility form of Würster's blue iodide are in this group. The solid-state spectrum has a strong low-energy absorption near the place where the charge-transfer band is located in the solution's dimer spectrum. The intermolecular interaction seems to be predominantly pair-by-pair. A possible candidate for this group is the monoclinic form of Würster's blue perchlorate provided that the measurements are made well

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18) H. Matsusaka and K. Suzuki, Paper presented at the 19 th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966.

19) K. Takemoto, H. Matsusaka, S. Nakayama, K. Suzuki and Y. Ooshika, This Bulletin, **41**, 764 (1968).

below the transition temperature. The diamagnetic benzidine and tetramethylbenzidine bromides may be classified into this group or the third group.

(II) The group is represented by Würster's blue perchlorate, ferrocyanide, and iodide (the high-susceptibility form). All of them are highly paramagnetic, containing over 80% free radicals. In addition to a strong absorption corresponding to the α-band in the monomer spectrum, a relatively weak low-energy absorption, almost corresponding to the charge-transfer band in the dimer spectrum, is observed in the solid-state spectrum. The intermolecular interaction is supposed to be perfectly symmetric, but so weak that the absorption process is confined to a region no wider than a single pair.

(III) The *p*-phenylenediamine and Würster's red bromides belong to this group; both are diamagnetic. The solid-state spectrum bears no resemblance to either the monomer or dimer spectrum and extends to a lower-energy region. A strong, more-than-by-pairs interaction is expected to cause such behavior.

Now we have to say a few words why we took only the extremes into consideration for the more-than-by-pairs interaction. The intermediate case may be observed only when the temperature of the measurement is comparable with the interaction. This condition may be fulfilled by Würster's blue perchlorate near the transition temperature. However, carrying out the measurements at room temperature, we can scarcely ever meet with such an intermediate case.

Discussing paramagnetic excitons in solid free radicals, McConnell and Lynden-Bell have speculated that, as linear chains of $S=1/2$ atoms or molecules are unstable with respect to distortions that produce an alternation in the distances between the interacting units, one individual radical can interact equally strongly with two others only at temperatures large compared to the exchange interaction.(20) The Würster salts in the second group apparently fit this speculation; however, we must remark that the very presence of a third group violates their speculation.

The mode of interaction depends naturally on the stacking of the cation-radicals, which is in turn affected not only by the size and shape of the cation itself, but also by those of the counter ion. Understandably, methyl substitution on the cation and a counter ion as bulky as ferrocyanide are unfavorable factors for a strong intermolecular interaction.

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20) H. M. McConnell and R. Lynden-Bell, *J. Chem. Phys.*, **36**, 2393 (1962).