Magnetic Study of *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine (Wurster's Blue) Tetrafluoroborate Cation Radical

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Wurster's Blue cation radical, which is composed of TMPD cation and BF_4 anion moieties, was prepared and its magnetic properties were examined. The cation radical shows similar magnetic behavior to that of the TMPD–ClO_4 cation radical, but there is a slight perturbation when changing the counteranions from perchlorate to tetrafluoroborate. A phase transition takes place at 190.5 K, which is attributable to a dimerization involving a small molecular displacement in the crystal lattice. These phenomena are discussed using the magnetic susceptibility data, thermal study, and ESR observations due to triplet exciton. The magnetic data are described by comparison with Wurster's Blue perchlorate cation radical.

The phase transition of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) perchlorate has been studied extensively. The cation radical called Wurster's Blue perchlorate experiences the first-order phase transition at about 190 K, as was ascertained from magnetic susceptibilities,[1-2] heat capacity,[3] electron spin resonance,[4] nuclear magnetic resonance,[5] and crystal structure determinations.[6] The nature of the phase transition was discussed previously.[7] Some of the anion radicals composed of tetracyanoquinodimethane (TCNQ)[8] and several kinds of neutral radicals[9] also exhibit magnetic phase transition; the former undergo first-order transitions and the latter second-order. On the other hand, Wurster's Blue iodide (TMPD-I) is paramagnetic from room temperature till liquid nitrogen temperature and no phase transition has been observed in this temperature range.[10] In the case of donor and acceptor complexes of TMPD, there exist both diamagnetic and paramagnetic species. For instance, the complex compounds of TMPD with chloranil and bromanil are almost diamagnetic, while TMPD–iodanil compound is weakly paramagnetic.[11] TCNQ salt with TMPD, which is also one of the donor and acceptor complexes, shows a weak paramagnetism; there is a thermally accessible triplet state lying above a singlet ground state with an energy separation $\Delta E=$ 0.075 eV.[12] Thus, the magnetic properties of the cation radical of TMPD vary with counteranions.

Hunig has pointed out a two-step redox system for the stable radical ions of nitrogen-containing aromatic molecules.[13] According to the fundamental work of Michaelis, the three oxidation levels are called "reduced form," "semiquinone," and "oxidized form."[14] Among these oxidation levels "semiquinone" has one unpaired electron in each molecule. Hunig isolated the above-mentioned three types of compounds with a careful choice of counteranions (perchlorate or tetrafluoroborate).[15] Thus, it might be an interesting problem to see the influence of tetrafluoroborate anion moiety upon magnetic interactions between unpaired electrons of TMPD cation moiety. After a successful attempt to prepare Wurster's Blue tetrafluoroborate, its magnetic properties were made clear and discussions on the magnetic phase transition were made in comparison with Wurster's Blue perchlorate.

Experimental

A detailed description of the apparatus and experimental techniques used in this experiment was published previously.[16] Only a brief comment will be given here. The diamagnetic contribution was calculated from Pascal's constants to be -153×10^{-6} emu/mol, on the assumption that diamagnetism of BF_4^- is -32×10^{-6} emu/mol. This contribution is a little larger than that of TMPD–ClO_4 obtained by Michaelis *et al.*,[17] -138×10^{-6} emu/mol, in spite of the minor difference between the presumed diamagnetic susceptibilities of BF_4^- and ClO_4^- anion moieties. As a paramagnetic susceptibility standard, we used the 4-methyl derivative of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TANOL), which conforms to the Curie law from room temperature down to 1.8 K.[18] The differential scanning calorimeter was a conventional one, Perkin-Elmer DSC-1. We made a temperature calibration using hexane and chloroform.

Samples were prepared following the procedure of Michaelis and Granick,[17] with a slight modification as required. One gram of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, prepared by the method of Cox *et al.*,[19] was dissolved in a mixed solution of 18 ml water and 24 ml methanol containing 9 g of sodium tetrafluoroborate. It was cooled to -10 °C, then 32 ml of 0.252 mol kg^{-1} aqueous bromine solution was added dropwise. The crystals were filtered, washed several times with small portions of ice-cold methanol, then abundantly with dry ether. The yield of TMPD–BF_4 melting at 126—127 °C (dec) after recrystallization from methanol was 0.8 g (52%). The crystals have a brownish purple metallic luster. Chemical analysis gave 6.64% (H), 47.85% (C), and 11.12% (N), which is to be compared with calculated values of $C_{10}H_{16}N_2BF_4$: 6.42 % (H), 47.82% (C), and 11.16% (N).

Results

Figure 1 shows the magnetic susceptibility versus temperature curve, in which one can recognize a sharp peak around 190 K. Upon lowering the temperature, the susceptibility drops steeply and then decreases gradually. This behavior is quite similar to that of TMPD–ClO_4 salt. In order to compare the magnetic behavior between Wurster's Blue tetrafluoroborate and perchlorate salts we also carried out a susceptibility measurement on the perchlorate salt as shown in Fig. 2, although many investigations have already been published.[1-2] It should be noted here that some of the differences are found in the maximum value of magnetic

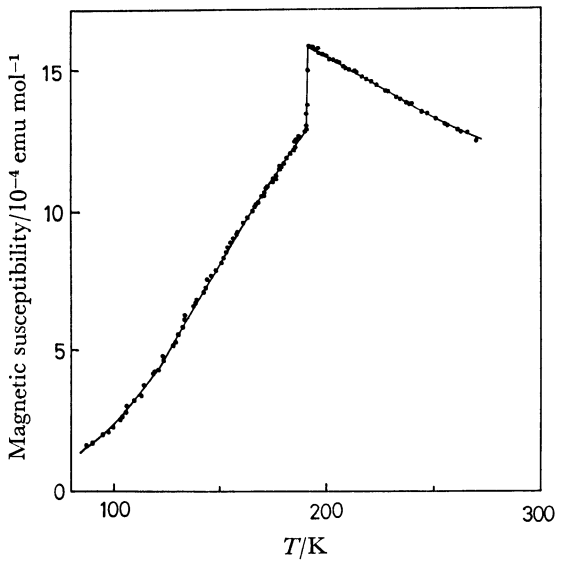

Fig. 1. Magnetic susceptibility *versus* temperature curve of TMPD–BF_4 cation radical.

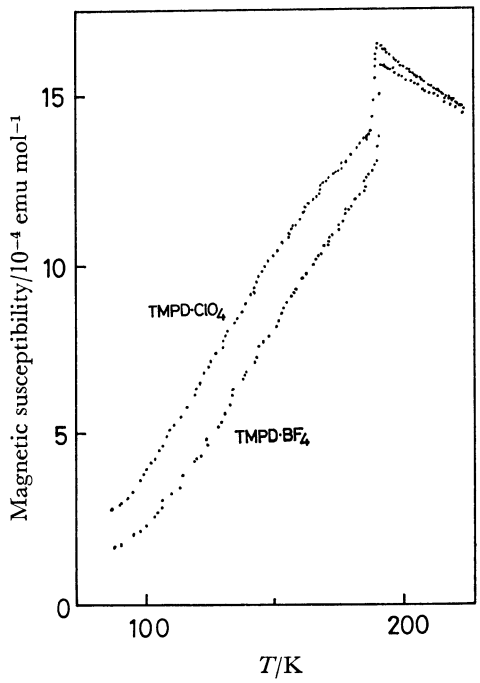

Fig. 2. Magnetic susceptibility *versus* temperature curves of TMPD–BF_4 and –ClO_4 cation radicals below the transition temperatures.

TABLE 1. MAGNETIC SUSCEPTIBILITY RESULTS AND TRANSITION TEMPERATURE

	χ_{max} [a]	T_{max}/K	$\Delta\chi_{tr}$ [a]	χ_{77} [a]	T_{tr}/K	
TMPD–BF_4	16.0	191	3.1	0.82	190.5 [b]	Present work
TMPD–ClO_4	16.8	190	2.8	2.00	190	Present work
	15.8	186	0.8		186	Duffy[1]
	14.5	189	1.4		189	Okumura[2]

a) $\times 10^{-4}$ emu/mol. b) The transition temperature was determined from thermal studies.

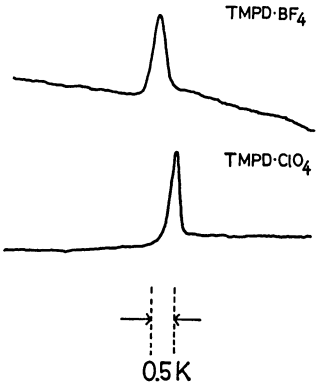

Fig. 3. Differential scanning calorimetry. The temperature was gradually elevated from right to left. The temperature difference was calibrated by the melting points of hexane and chloroform.

susceptibility (χ_{max}), in the temperature where the susceptibility takes its maximum value (T_{max}), and in the temperature dependence of the susceptibility below T_{max}. The former two characteristics are summarized in Table 1 and the latter is depicted in Fig. 2.

According to the thermal study using the differential scanning calorimeter (DSC), endothermic or exthothermic behavior was observed with TMPD–BF_4 at a slightly higher temperature than with TMPD–ClO_4. The temperature difference was found to be 0.5 K, as

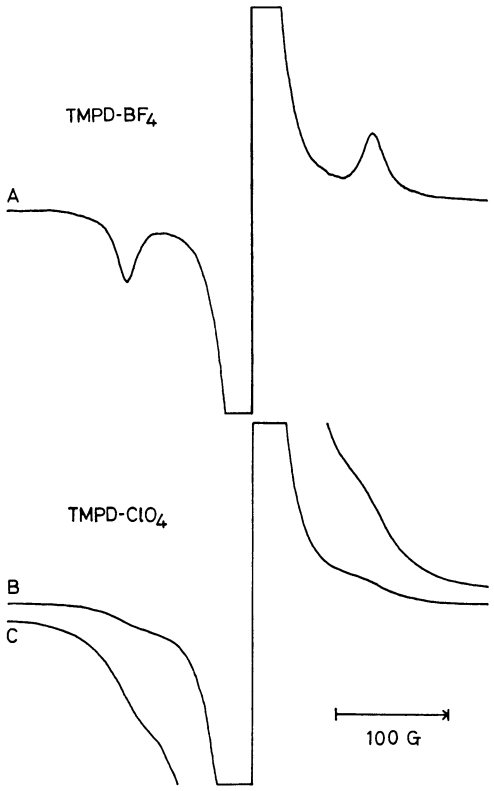

Fig. 4. Polycrystalline ESR spectra at 77 K. The triplet excitons can be clearly observed in TMPD–BF_4 (A), while the fine structure in TMPD–ClO_4 is exchange-narrowed because of the fast motion of triplet excitons (B and C). The field modulation was 1 G in A and B and 10 G in C.

shown in Fig. 3. The abscissa is a temperature scale, but only the difference between the peaks was calibrated using the standard materials described in the experimental section.

Electron spin resonance was observed at room temperature and at liquid nitrogen temperature in order to obtain information on the phase transition. The polycrystalline spectrum at 77 K is given in Fig. 4. This is characteristic of triplet exciton spectrum of polycrystalline samples.[20] A single crystal study of this exciton in TMPD-ClO_4 has been reported elsewhere.[4] The powder pattern of TMPD-ClO_4 at 77 K is also drawn in Fig. 4 for comparison. The ESR data are tabulated in Table 2.

Table 2. ESR results and zero field splitting parameters

	g-value[a]	Linewidth/G[a]	E/G	D/G
TMPD-BF_4	2.00325	2.64	73.0	0
TMPD-ClO_4	2.00325	2.68	75.7[b]	0[b]

a) At room temperature. b) Ref. 4.

Discussion

The magnetic behavior of Wurster's Blue tetrafluoroborate and that of perchlorate salts above the transition temperature are identical, as seen from Tables 1 and 2. The ESR g-values and linewidths at room temperature show the same experimental values. The magnetic susceptibility also shows the same temperature variation, as far as we could determine, although Duffy[1] and Okumura[2] have published smaller values in TMPD-ClO_4. These facts indicate that the crystal structure of TMPD-BF_4 may have the same molecular packing of TMPD cations as that of TMPD-ClO_4 salt along the a-axis.[6]

The magnetic susceptibilities of TMPD-BF_4 and -ClO_4 salts start to deviate from each other in the vicinity of the transition temperature and then exhibit sharp decreases at 191 and 190 K, respectively. The decreases ($\Delta\chi_{tr}$) at these temperatures are steeper than those published previously for TMPD-ClO_4 salt (see Table 1). The discontinuity comes from cooperative phenomena of a first-order nature, as suggested in TMPD-ClO_4, so that the above fact may be concerned with the degree of purification of the crystals. In fact, Okumura reported 81% radical contribution due to a deterioration of the crystal. On the other hand, Duffy observed 94% radical concentration calculated from the Curie constant. However, both their room temperature susceptibilities show nearly the same value, 10.5×10^{-4} emu/mol.

TMPD-BF_4 salt also experiences a magnetic phase transition accompanied by a crystal distortion. The proposed model in TMPD-ClO_4 salt is that there is a strongly alternating antiferromagnet and a regular antiferromagnet in the low and high temperature phases, respectively.[21] This is caused by a dimerization of TMPD cation molecules in the crystal. This may be also true in TMPD-BF_4 and can be ascertained partly from the low temperature ESR study which indicates the presence of triplet excitons.

The transition temperature of TMPD-ClO_4 salt has been reported by many investigators: 186 K (Duffy),[1] 189 K (Okumura),[2] and 189.9 K (Chihara *et al.*).[3] In our study a good agreement with a precise heat capacity measurement by Chihara *et al.* was obtained in TMPD-ClO_4. However, the DSC study gave 0.5 K difference between the transition temperatures of BF_4 and ClO_4 salts, so that we concluded that the transition temperature of TMPD-BF_4 is 190.5 K in spite of the susceptibility maximum at 191 K. This is partly because we believe the experimental errors in the heat capacity and DSC measurements are smaller than those in the susceptibility measurement. The error found in the susceptibility is at most 0.5 K.

The magnetic susceptibilities below the transition temperature are different, as is shown in Fig. 2. This means that, although both of the cation radicals have dimerized structures which form a strongly alternating antiferromagnet, the triplet exciton density in TMPD-BF_4 is much smaller at a given temperature than that of TMPD-ClO_4. This fact suggests that the observation of triplet exciton spectra of TMPD-BF_4 may be possible at a higher temperature region, because one can observe fine-structure due to triplet entities in ESR measurements at a relatively low triplet density.[22] In fact, we were able to observe clearly the fine-structure of triplet excitons in TMPD-BF_4 at 77 K, while in the case of TMPD-ClO_4 the spectrum at 77 K shown in Fig. 4 was an exchange-narrowed one with a feeble indication of triplet excitons around the strong absorption. At 77 K the exchange interactions between triplet excitons are not small enough to be neglected in the case of TMPD-ClO_4 salt. McConnell *et al.*[4] noted that they have seen clear exciton paramagnetic resonance spectra in polycrystalline samples of TMPD-ClO_4 at 50 K. The spectra in Fig. 4 can be accounted for by the spin Hamiltonian:

$$\mathcal{H} = DS_z^2 + E(S_x^2 - S_y^2),$$

where S_x, S_y, and S_z are the components of spins in the direction of the principal fine structure axes, and D and E are zero-field splitting parameters. The spectral analysis implies the vanishing of D as in the case of TMPD-ClO_4 salt.[4] The spectral separation between the two side-absorptions was 219.1 G, leading to $|E|=73.0$ G for TMPD-BF_4, while $|E|=75.7$ G for TMPD-ClO_4. These facts give microscopic evidence for a dimerization of TMPD cations below the transition temperature. In order to obtain the principal coordinates of dipolar interactions, however, more detailed experiments using single crystals must be performed.

A comparison of the ionic radii of BF_4^- and ClO_4^- suggests that tetrafluoroborate anions have a smaller ionic radius. However, the conjecture that both of the crystals have the same structure in the high temperature region is reasonable if we take into account that there are no significant differences in the magnetic properties. On the contrary, in the low temperature phase, the smaller anion moiety makes it easier for the TMPD cations to get nearer. Therefore, the presumption that the molecular displacement of TMPD cations

of BF_4 salt at the transition temperature may be larger explains the larger $\Delta\chi_{tr}$ and smaller susceptibility values, that is, the larger antiferromagnetic interactions at or below T_{tr}. In this context, the triplet interaction parameters, D and E, are also dependent on the distance between the dimerized molecules. Since D and E are inversely proportional to the third power of distance, the shorter the distance between TMPD cations, the larger the D and E values. However, BF_4 salt has a smaller E value, 73.0 G, than that of 75.7 G for ClO_4 salt. This is because the D and E values also depend on the molecular symmetry around the pairing axis. The most perfect vanishing of the D value is also explainable by the molecular conformation.[4)]

In conclusion, the cation radical TMPD–BF_4 experiences a phase transition of the first-order at 190.5 K. This transition may be accompanied by a dimerization of TMPD cation molecules, as proposed in the case of TMPD–ClO_4 salt. The magnetic susceptibility measurements, thermal calorimetry, and ESR observations support these conclusions. Observation of the triplet excitons at the low temperature phase supports the strongly alternating antiferromagnetic interaction. The magnetic properties of the two cation radicals, TMPD–BF_4 and –ClO_4, are almost identical. The few discrepancies might be due to the ionic radii of the anions, BF_4^- and ClO_4^- and this influence should be clarified by X-ray crystal analysis.

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