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

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(Received May 24, 1990)

One of the Wurster's blue cation radicals, which is composed of the *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine cation and iodine anion moieties, was prepared and its magnetic susceptibility measured from 2.6 to 300 K. The cation radical underwent no phase transition within this temperature range in striking contrast with the first-order phase transition observed in perchlorate and tetrafluoroborate salts, regardless of similar crystallographic structures. In addition, the temperature dependence of the magnetic susceptibility could be well-reproduced by a dimer model: a thermally accessible triplet state lying above a singlet ground state with an energy separation of $\Delta E/k$=229 K. This behavior is controversial regarding the crystallographic determination. The unusual magnetic properties of the iodide salt were discussed, together with the crystal structure, ESR and visible absorption data, in comparison with those of the other salts.

Wurster's blue cation radicals containing *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) have attracted much attention since the crystals display interesting magnetic properties, ranging from very weak to strong paramagnetism; in particular, the TMPD perchlorate (-ClO_4) and tetrafluoroborate (-BF_4) salts undergo phase transitions. The first-order phase transitions at about 190 K were ascertained from various magnetic measurements such as magnetic susceptibility,[1-3] heat capacity,[3,4] electron spin resonance (ESR),[3,5] nuclear magnetic resonance (NMR),[6,7] and crystal structure determination.[8] In the case of the donor and acceptor complexes of TMPD, as well, there exist both very weakly and strongly paramagnetic species.[9] Thus, the magnetic properties of the cation radicals of TMPD vary with the counteranions; it thus seems interesting to determine in which respect the structures of the two types of compound differ.

Measurements of the magnetic susceptibility of TMPD iodide (-I) as a function of the temperature within the range from 2.6 to 300 K are reported here, and the characteristics of the magnetic interaction in this compound are contrasted with those of TMPD-ClO_4 and TMPD-BF_4. It has been briefly stated that TMPD-I is paramagnetic from room temperature until liquid-nitrogen temperature and that no phase transition has been observed within this temperature range.[10] However, there have been no detailed quantitative analyses or discussions reported. A crystallographic analysis has revealed that the cation radicals are stacked equidistantly to form a one-dimensional array, like that of TMPD-ClO_4.[10] Nevertheless, we have observed an essentially different magnetic susceptibility and ESR line width.

Experimental

A detailed description of the apparatus and experimental techniques used in this experiment was published previously.[11] Only a brief comment is given here. The diamagnetic contribution was calculated from Pascal's constants to be -171×10^{-6} emu mol^{-1},[a] based upon the assumption that the diamagnetism of I^- is -50.6×10^{-6} emu mol^{-1}. Those for TMPD-ClO_4 and TMPD-BF_4 are described in the literature.[3] As a paramagnetic susceptibility standard we used 4-methyl-4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl, which conforms to Curie's law from room temperature down to 1.8 K.[12]

Visible spectra were obtained by means of a polycrystalline KBr method using a Shimadzu UV and visible spectrometer (type UV MPS-50L).

Samples were prepared following the procedure of Michaelis and Granick,[13] with a slight modification as required. TMPD 1 g, freshly prepared by the method of Cox et al.,[14] was dissolved in a mixed solution of 18 ml water and 28 ml methanol containing 14 g of potassium iodide. After cooling it down to −10 °C, 32 ml of a 0.252 mol kg^{-1} aqueous bromine solution was added dropwise. The crystals were filtered off, washed several times with small portions of ice-cold methanol, then abundantly with dry ether. The yield of TMPD-I melting 147—148 °C (decomp) after recrystallization from methanol was 1.1 g (62%). The crystals had a brownish-purple metallic luster. Chemical analysis gave 5.38% (H), 41.03% (C), 9.53% (N), and 43.31% (I), which are compared with the calculated values of $C_{10}H_{16}N_2I$: 5.54% (H), 41.25% (C), 9.62% (N), and 43.59% (I). The crystal structure of TMPD-I used in this experiment was examined using a JEOL X-ray diffractometer (type JDX-8F). The X-ray diffraction patterns of the powdered TMPD-ClO_4 and TMPD-I at room temperature were almost the same and showed only a slight shift of each absorption angle, depending on the different lattice constants reported in the literature.[8,10]

Results

The magnetic susceptibility gradually increased upon decreasing the temperature, reaching a broad maximum at 143 K. Below this temperature it dropped and then rose again around 10 K. The weak paramagnetism observed at such low temperatures is usually caused by an isolated paramagnetic species, a

a) In SI unit multiply $4\pi\times10^{-6}$.

so-called "impurity", which may be due to a crystal imperfection in pairwise interactions between the TMPD cation moieties (discussed later). This minor contribution was deliberately subtracted in order to deduce any intrinsic magnetic interactions in the crystal. Figure 1 shows a very good Curie behavior for the "impurity" susceptibility from 2.6 up to 9 K. This paramagnetism was expressed as

$$\chi_{imp} = 57.14 \times 10^{-4}/T \quad (1)$$

in units of emu mol^{-1}. This amount corresponds to a 1.5% impurity, compared with molar Curie paramagnetism. The observed paramagnetic susceptibility was corrected with this equation and is shown in Fig. 2. The same procedure was employed regarding the observed magnetic susceptibilities of TMPD-ClO_4 and TMPD-BF_4 in order to disclose any intrinsic magnetic interactions in the crystals. The characteristics in those magnetic susceptibilities are summarized in Table 1.

The X-band ESR spectra of powdered TMPD-I indicated neither a phase transition between 77 and 300 K nor fine structures at 77 K. The most characteristic is the line width of TMPD-I. It amounted to 6.20 mT at 300 K. This value is very large compared to 0.268 mT of TMPD-ClO_4. The line width became narrow (3.12 mT) at 77 K. The ESR results are summarized in Table 2.

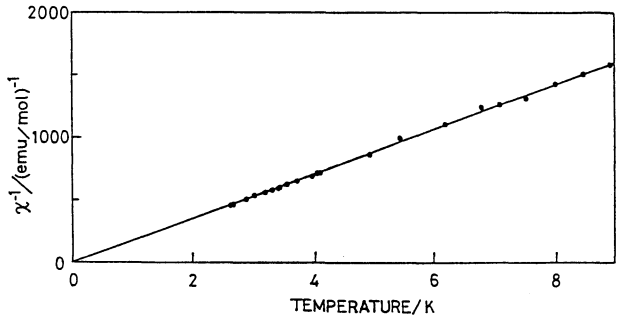

Fig. 1. Inverse of the magnetic susceptibility of TMPD-I in the very low temperature region. The linear relation represents the Curie behavior expressed by the Eq. 1.

Table 1. Magnetic Susceptibility Results

	χ_{max}[a]	T_{max}/K	T_{tr}/K	$\Delta E/k$/K	J/k/K	
TMPD-I	13.2	143	—	229	114.5	This work
TMPD-ClO_4	16.8	190	190	347[c]	56[b]	Ref. 3 and
					217[c]	This work
TMPD-BF_4	16.0	190.5	190.5	403[c]	56[b]	Ref. 3 and
					252[c]	This work

a) $\times 10^{-4}$ emu mol^{-1}. b) In the high temperature phase. c) In the low temperature phase.

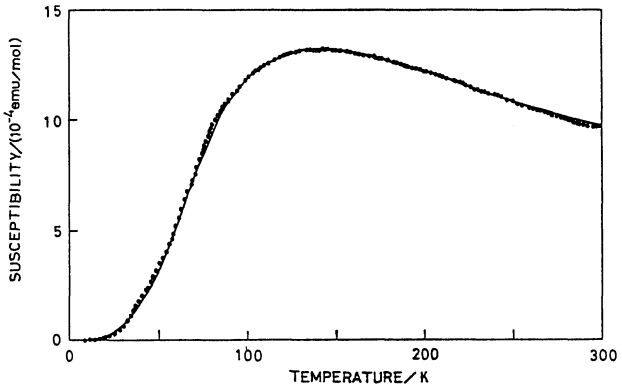

Fig. 2. Temperature dependence of the magnetic susceptibility of TMPD-I. This was plotted after the correction of the paramagnetic "impurity" determined in the very low temperature region. The solid line represents a dimer model with J/k=114.5 K ($\Delta E/k$=229 K).

Discussion

Crystal Structures. According to de Boer's crystallographic analyses,[8,10] crystals of TMPD-I have orthorhombic symmetry, with a=5.919, b=9.855, c=9.901 Å, space group *Pnnm*, and Z=2. Our samples belong to this morphology, as stated in the experimental section. The TMPD cation radicals lie equidistantly along the a-axis and the magnetic interaction between them is the strongest in this direction. Crystals of TMPD-ClO_4 also have orthorhombic symmetry, with a=5.956, b=10.229, c=10.187 Å, space group *Pnnm*, and Z=2 at room temperature. At 110 K, however, the crystals have monoclinic symmetry, with a=11.655, b=10.147, c=20.130 Å, β=92.57°, space group $B2_1/d$, and Z=8. The a and c axes are almost doubled in length compared with those of the orthorhombic modification. Besides, the TMPD cation radicals are spaced alternately along the a-axis in the monoclinic low-temperature phase, whereas they are arranged with equal spacings in the orthorhombic room-temperature phase. Two neighboring TMPD molecules with some short distances are shown in Fig. 3 for TMPD-I, TMPD-ClO_4(RT), and TMPD-ClO_4(LT). It is noteworthy to point out that the

Table 2. ESR Results

	g-Value[a]	Line Width/mT[a]	E/mT	D/mT	
TMPD-I	2.00286	6.20 (3.12)[b]	—	—	This work
TMPD-ClO_4	2.00325	0.268	7.57	0	Ref. 3, 5
TMPD-BF_4	2.00325	0.264	7.30	0	Ref. 3

a) At room temperature. b) At 77 K.

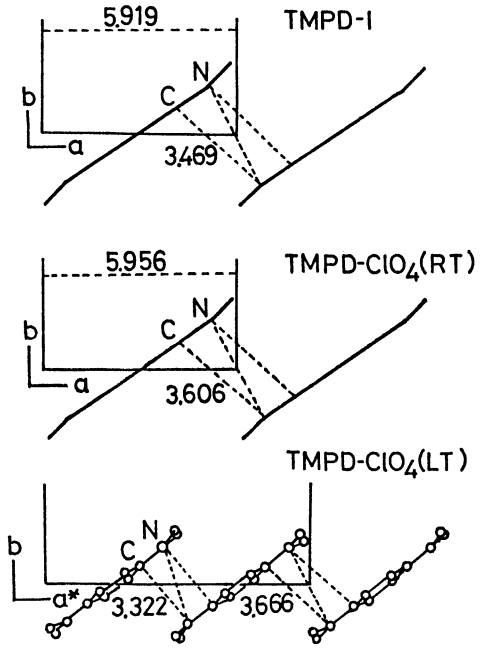

Fig. 3. Comparison of the nearest-neighbor interactions between the TMPD cation radicals in TMPD-I, TMPD-ClO_4(RT), and TMPD-ClO_4(LT) determined from the X-ray analyses.

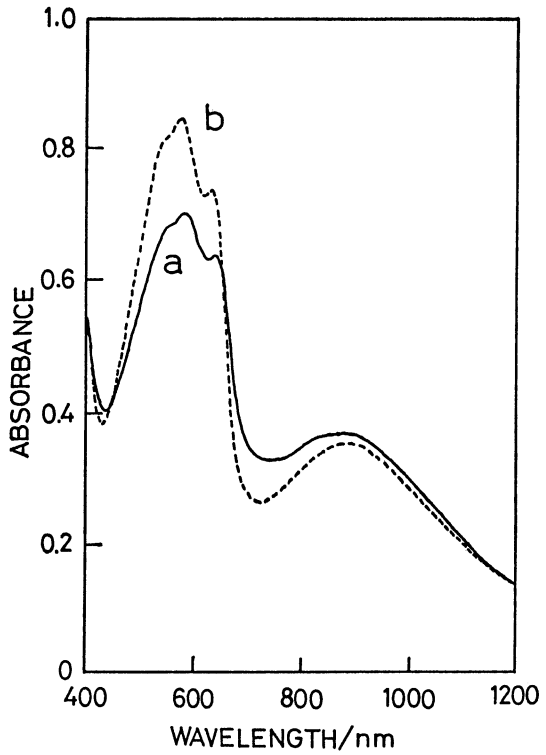

Fig. 4. Visible absorption spectra of polycrystalline TMPD-I (a) and TMPD-ClO_4(b) in KBr at room temperature.

magnetic interaction between the TMPD cation radicals in TMPD-I is supposed to be of quite similar type as that in TMPD-ClO_4(RT) and to be much stronger. Judging from the distances of those radical pairs, the magnetic interaction in TMPD-ClO_4(LT) would be the strongest of all. Regarding this crystallographic discussion, controversy has arisen concerning the regular stacking of the TMPD cation radicals in TMPD-I since alternating structures, like TMPD-ClO_4(LT), have been concluded due to the following precise magnetic susceptibility analysis.

Visible Spectra. Polycrystalline absorption spectra are compared in Fig. 4. The absorption maxima are 547, 580, 637, 882 nm for TMPD-I and 545, 576, 632, 895 nm for TMPD-ClO_4. Those spectra are almost identical, except for the charge-transfer bands in the 800—1000 nm region. The charge-transfer interaction seems to be slightly stronger in TMPD-I. The electronic spectra of several TMPD salts in single crystals and spectral changes due to the phase transition have been investigated.[15-17] The temperature-dependent absorption spectra have revealed a drastic change in the 500—700 nm bands in the low-temperature phase,[16] whereas the reflection spectra of single crystals of TMPD-ClO_4 have shown a marked blue-shift of the absorption peaks in the low-temperature phase.[17] Therefore, the fact that these two absorption spectra are similar to each other may suggest, like the X-ray diffraction experiments, that the crystal structure of TMPD-I is something like that of TMPD-ClO_4; the regular stacking of the TMPD cation radicals is consistent with the crystal structure determinations.

One Dimensional Magnetic Interactions and a Dimer Model. A regular or an alternating one-dimensional array of exchange-coupled plate-like molecules, stacked face-to-face, leads to an exchange interaction problem expressed by the following linear Heisenberg model:[18,19]

$$\mathcal{H} = \sum_{j=1}^{N/2} \{2J(1+\delta)S_{2j}S_{2j+1} + 2J(1-\delta)S_{2j}S_{2j-1}\}. \quad (2)$$

Here, δ is an alternating parameter. When $\delta \approx 0$, each spin interacts strongly with two adjacent spins. On the other hand, when $\delta \approx 1$ each spin interacts strongly with only one other spin, in which the two spins form a triplet state.

The magnetic susceptibility shown in Fig. 2 exhibits no discontinuity, indicating no phase transition in this temperature range. Quantitative analysis suggests $\delta \approx 1$ in Eq. 2 for TMPD-I. In Fig. 2 the solid line is drawn as a theoretical magnetic susceptibility based on a perfect dimer model ($\delta=1$), in which the exchange parameter is taken to be $J/k=114.5$ K. Quantitative agreement is excellent, strongly suggesting a dimer model of ground singlet-excited triplet states with an energy separation of $\Delta E/k=229$ K.

On the other hand, quantitative magnetic susceptibility analyses disclosed that TMPD-ClO_4 and TMPD-BF_4 in the high-temperature phase exhibit magnetic interactions $\delta=0$ and small J/k values.

Bonner and Fisher's regular chain model[20] predicts J/k=56 K. In the low-temperature phase, however, magnetic interactions of δ=1 and very large J/k values become dominant, being due to a crystallographic phase transition as has been revealed by X-ray analyses. This indicates a reasonable consistency between the magnetic susceptibilities and the crystal structures. The low-temperature susceptibilities of TMPD-ClO_4 and TMPD-BF_4 were corrected very carefully in terms of isolated paramagnetic "impurity" and fitted by a dimer model (δ=1), giving $\Delta E/k$=347 and 403 K, respectively. Both the experimental and theoretical magnetic susceptibilities are compared in Fig. 5. It is somehow reasonable that the exchange interaction parameters or singlet-triplet energy separations have been found to become large correspondingly to the molecular distances between the adjacent cation radicals for TMPD-ClO_4 (HT), TMPD-I, and TMPD-ClO_4 (LT). It is strange, however, that there is an almost perfect δ=1 behavior in the TMPD-I case, which seems contradictory to the molecular stacking structure of the TMPD cation radicals.

ESR Line width and *g*-Values. The ESR linewidth of TMPD-I was anomalous because it amounted to 6.20 mT at room temperature, compared to 0.268 mT (TMPD-ClO_4) or 0.264 mT (TMPD-BF_4). The line width of about 0.3 mT seems to indicate an exchange narrowed case; at the room temperature phase, however, both TMPD-ClO_4 and TMPD-BF_4 possess smaller J values than does TMPD-I, so that the narrowness in the ESR line width seems to be due to an exchange narrowing of the dipolar interaction for Wannier spin excitons (δ=0).[19] On the other hand, even the larger J value is reduced by a factor $1-\delta$ in Frenkel excitons (δ=1).[19] This seeems to be the case regarding TMPD-I, where δ=1 is suggested from the magnetic susceptibility.

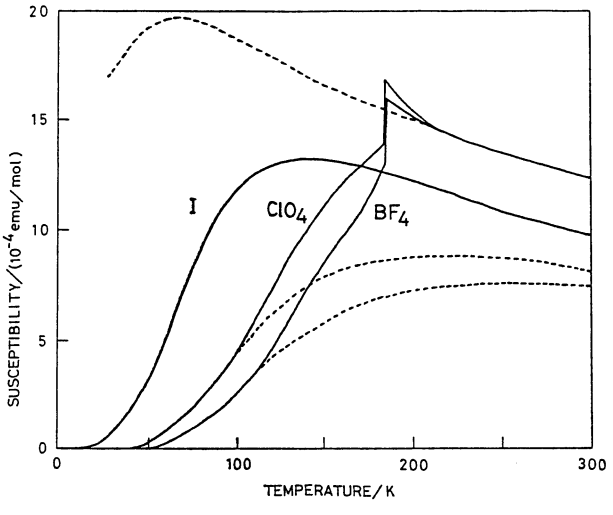

Fig. 5. Comparison of the magnetic susceptibilities of TMPD-I, TMPD-ClO_4, and TMPD-BF_4. The solid lines represent the experimental data and the dotted lines the theoretical predictions. For TMPD-I the experimental curve almost coincides with a theoretical dimer model. In the high temperature phases of TMPD-ClO_4 and TMPD-BF_4 the dotted line comes from Bonner and Fisher's regular chain prediction and in the low temperature phases the dotted lines come from the low temperature susceptibilities fitted by theoretical dimer models.

Broad ESR lines have also been reported in some semiconductive polymers doped by I_2, where a relaxation mechanism involving a spin-orbit coupling in the iodine atoms is responsible.[21] Though line broadening due to spin-orbit coupling may be one of the reasons in TMPD-I, those semiconductive compounds have a remarkably large conductivity, like 3.7×10^{1} or 4×10^{-1} S cm^{-1}.[21] As a matter of fact, even an I_2-doped polymer with 2.6×10^{-5} S cm^{-1} showed only 0.787 mT, whereas a heavily doped one with 3.7×10^{1} S cm^{-1} showed 69.9 mT. In such conductive materials the unpaired electron has much chance to stay attached to the iodine atoms. Thus, the spin-orbit coupling of the iodine atoms works more towards spin relaxation. The TMPD-I solid can safely be treated as tightly bound electrons, and the exchange problem along each chain reduces to that of the linear Heisenberg model as expressed by Eq. 2.

Little contribution of the spin-orbit coupling in TMPD-I is also evidenced by the *g*-values. The *g*-values become large when the spin-orbit coupling is effective, as revealed by the iodine-doped polymers, where the *g*-values increase along with increasing conductivity.[21] TMPD-I showed an even more smaller *g*-value than the least I_2-doped polymer with a conductivity of 2.6×10^{-5} and a line width of 0.787 mT. We, therefore, believe that the broad line width of TMPD-I is caused by the Frenkel spin excitons (δ=1), as is suggested from the magnetic study.

At the low-temperature phase of TMPD-ClO_4 or TMPD-BF_4, fine structures were observed at considerably lower temperatures than the transition temperatures. We could not see these symptons at 77 K, probably because of the still high triplet density at this temperature.[22]

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