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Magnetic Susceptibilities of Ionic Electron-Donor-Acceptor Complexes

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In previous papers, we discussed the magnetic properties of ionic electron-donor-acceptor complexes formed between aromatic diamines and tetracyano-*p*-quinodimethane[1,2] and benzoquinone derivatives.[3] Their magnetic susceptibilities showed large deviations from the Curie law and were explained by the linear chain model of the interacting unpaired electrons on radical ions. We report here the magnetic susceptibilities of the ionic complexes of tetracyanoethylene (TCNE) with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) and *N,N′*-diphenyl-*p*-phenylenediamine (DPPD).

Tetracyanoethylene is known to be very reactive with aromatic amines.[4] Actually, of the seven amines tested, only the above two were found to give stable solid complexes. The complex of TMPD·TCNE (1 : 1) was precipitated as dark brown microcrystals by mixing cooled solutions (−10°C) of TMPD and TCNE in dichloromethane. The dark violet crystals of DPPD·TCNE (1 : 1) were prepared in a similar manner at −18°C. The complex of TMPD·TCNE turned reddish brown when it was kept in air for two days. The complex of DPPD·TCNE was found to be more stable.

The infrared absorption spectra of these solid complexes indicate that they are essentially of ionic type in their ground states. In the complex of DPPD·TCNE, for example, the $C\equiv N$ stretching vibration was found at 2150 and 2110 cm^{-1}, while in neutral TCNE[5] it was reported to appear at 2270 and 2240 cm^{-1}. The C–C–C bending and wagging vibrations, observed respectively at 576 and 552 cm^{-1} in neutral TCNE,[5] were found at 510 and 480 cm^{-1} in the complex. These shifts observed upon complex formation are in line with those reported in the change from neutral TCNE to TCNE anion.[6]

The susceptibilities of these complexes were measured with freshly prepared samples by the Faraday method. Their observed molar magnetic susceptibilities are shown in Fig. 1 as a function of temperature. In the higher temperature region, the susceptibility decreased with decrease in temperature. The behavior is similar to that given previously,[1-3] and may be explained in terms of the singlet-triplet model or the linear Ising model. In the former model, the

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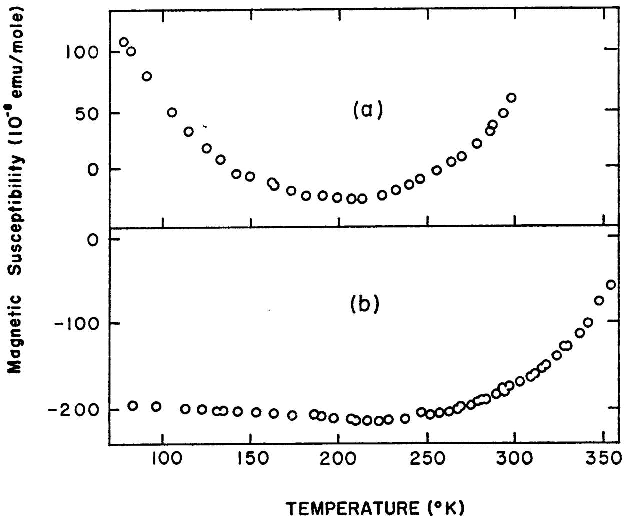

Fig. 1. Temperature dependence of the observed magnetic susceptibilities of (a) TMPD·TCNE and (b) DPPD·TCNE.

susceptibility is expressed by

$$\chi_p = (2Ng^2\beta^2/kT)[3+\exp(\delta/kT)]^{-1} \qquad (1)$$

where δ is the singlet-triplet separation and N the Avogadro number, and in the latter by

$$\chi_p = (Ng^2\beta^2/2kT)\exp(-J/kT) \qquad (2)$$

where J is the interaction energy of the unpaired electrons. If $\delta, J \gg kT$, these expressions are reduced to

$$\chi_p = C\exp(-E/kT)/T. \qquad (3)$$

The intrinsic paramagnetic susceptibilities χ_p of these complexes were obtained after corrections had been made for the diamagnetic part ($\chi_d = -116 \times 10^{-6}$ for TMPD·TCNE and $\chi_d = -214 \times 10^{-6}$ for DPPD·TCNE) and for the impurity paramagnetism by the procedure described previously.[3] The plots of $\ln(\chi_p T)$ against $1/kT$ gave straight lines. The activation energy E was obtained to be 0.17 eV for TMPD·TCNE and 0.28 eV for DPPD·TCNE. However, the E values thus obtained do not explain the observed susceptibilities. In other words, they yield a very large value for N when substituted into parameter δ or J of the above equations together with χ_p obtained at a certain high temperature. Thus, it is very likely that the parameter δ or J decreases linearly with increase in temperature. On this assumption, the δ-values estimated at various temperatures from Eq. (1) with the obtained χ_p's and with $N = 6 \times 10^{23}$, were plotted against temperature in Fig. 2. The plots yielded straight lines of the form $\delta = \delta_0 + \alpha T$. The values of δ_0 and α obtained from the analysis of Fig. 2 are given in Table 1, where the values for the complexes of chloranil and bromanil[3] are also shown for comparison.

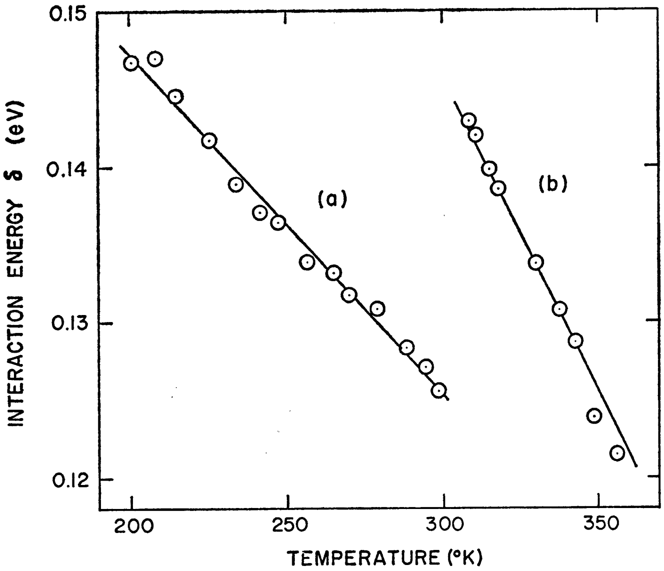

Fig. 2. Variations of the singlet-triplet energy separation δ with temperature for (a) TMPD·TCNE and (b) DPPD·TCNE.

Table 1. Temperature variation of interaction energy

	E (eV)	δ_0 (eV)	$\delta_{300°K}$ (eV)	α (eV/deg)
TMPD·TCNE	0.17	0.16	0.13	-1.9×10^{-4}
DPPD·TCNE	0.28	0.27	0.15	-4.0×10^{-4}
TMPD·*p*-CA	0.34	0.34	0.17	-6.0×10^{-4}
TMPD·*p*-BA	0.21	0.21	0.15	-1.8×10^{-4}
PD·*p*-CA	0.18	0.18	0.15	-0.8×10^{-4}
PD·*p*-BA	0.24	0.24	0.15	-4.4×10^{-4}

In the analysis, the value of δ_0 was expected to agree closely with E. The close agreement can be seen in Table 1. The negative value of α indicates that the interaction between unpaired electrons becomes weaker with the rise of temperature. The value of δ or J is determined by the combination of the exchange interaction of unpaired electrons and the charge-transfer resonance effect.[3] These effects are dependent directly upon the intermolecular spacings. Thus, it is not surprising that the value of $|\alpha|$ thus obtained coincides in order of magnitude with the expansion coefficients of the usual organic compouds. It should be noted that the unit cell dimension of anthracene:*s*-trinitrobenzene complex is known to change by about 2 percent between room temperature and -100°C in the direction of molecular stacking,[7] that is, the average linear expansion coefficient of the complex is also of the order of 10^{-4}.

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