Spin Correlation in Metal-Chelate-TCNQ Radical Salts

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We have been interested in the paramagnetism of anion radical salts of 7,7,8,8-tetracyano-*p*-quinodimethan (TCNQ), and our study has been extended to the salts with metal-chelates. We synthesized a new kind of organo-metallic radical salts by the reaction between octahedral tris-dipyridyl (dip) metal-chelate compounds and TCNQ, and examined paramagnetic behavior of the salts as a function of temperature in the temperature region from 77 to 300°K, by a Faraday-type magnetic balance. The experimental procedure was the same as described in a previous paper.[1]

Preparation. Fe(dip)$_3$(TCNQ)$_2\cdot$3H$_2$O (reddish black crystals), Ni(dip)$_3$(TCNQ)$_2\cdot$3H$_2$O (greenish black crystals) and Cu(dip)$_3$(TCNQ)$_3$Cl$\cdot$4H$_2$O (black powder) were obtained by the reactions of Fe(dip)$_3$Cl$_2\cdot$7H$_2$O, Ni(dip)$_3$Cl$_2\cdot$6H$_2$O, and of Cu(dip)$_3$Cl$_2\cdot$7H$_2$O with Li$\cdot$TCNQ in methanol, respectively.

Results and Discussion

Fe(dip)$_3^{2+}$(TCNQ$^{\overline{\cdot}}$)$_2\cdot$3H$_2$O. The magnetic susceptibility decreased with decreasing temperature, although a small rise was observed in the lower temperature region. The curve (a) in Fig. 1 shows the temperature dependence of the paramagnetic susceptibility observed, after the correction was made for molecular diamagnetism of dipyridyl, TCNQ and H$_2$O, using the values determined experimentally and Pascal's constants. The curve (b) shows the susceptibility for Fe(dip)$_3$Cl$_2\cdot$7H$_2$O, after diamagnetism due to dipyridyl, Cl$^-$ and H$_2$O was subtracted from the observed susceptibility. The corrected value showed a small paramagnetism of unknown character. The difference between (a) and (b), the curve (c), means the paramagnetic susceptibility resulted from the salt formation with TCNQ. If it is assumed that the rise in the lower temperature region originated from impurities, and that the susceptibility of impurities obeys Curie law as expressed by the curve (d), the difference between (c) and (d) could be attributed to the paramagnetism for TCNQ radicals in the salt, which is indicated by black circles in Fig. 1. The impurities would be TCNQ radicals which are improperly located in a lattice, as suggested by Kepler for other TCNQ salts.[2]

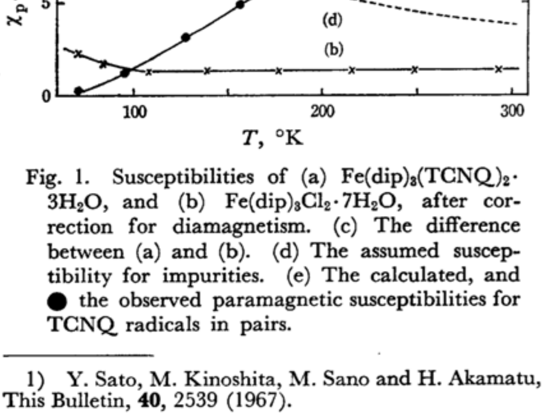

Fig. 1. Susceptibilities of (a) Fe(dip)$_3$(TCNQ)$_2\cdot$3H$_2$O, and (b) Fe(dip)$_3$Cl$_2\cdot$7H$_2$O, after correction for diamagnetism. (c) The difference between (a) and (b). (d) The assumed susceptibility for impurities. (e) The calculated, and ● the observed paramagnetic susceptibilities for TCNQ radicals in pairs.

According to the recent development in theoretical treatments of paramagnetism for organic free radicals, the paramagnetism can be reasonably interpreted in terms of an exchange-coupled linear chain model.[3-5] For the case, in which spin correlation exists only in a pair of free radicals and gives rise to a ground singlet state and a thermally accessible triplet state (a singlet-triplet model), the paramagnetic susceptibility is expressed by

$$\chi_p = (2N'g^2\beta^2/\boldsymbol{k}T)\cdot[3+\exp(\delta/\boldsymbol{k}T)]^{-1},$$

where δ is the singlet-triplet energy separation, and N' is the number of spin pairs.

As can be seen in Fig. 1, the estimated susceptibility for TCNQ radicals finds a good fit to the value calculated from the singlet-triplet model, the curve (e), for which δ was taken to be 0.047 eV, and N', 5.17×10^{23}. The result reveals that the majority of anion radicals of TCNQ are pairing in the salt.

Ni(dip)$_3^{2+}$(TCNQ$^{\overline{\cdot}}$)$_2\cdot$3H$_2$O. The susceptibilities for this TCNQ salt and Ni(dip)$_3^{2+}$Cl$_2^-\cdot$6H$_2$O were both paramagnetic at room temperature, and increased with decreasing temperature. Figure 2 shows an appreciable amount of difference between

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[1] Y. Sato, M. Kinoshita, M. Sano and H. Akamatu, This Bulletin, **40**, 2539 (1967).

[2] R. G. Kepler, *J. Chem. Phys.*, **39**, 3528 (1963).

[3] R. M. Lynden-Bell and H. M. McConnell, *ibid.*, **37**, 794 (1962).

[4] A. S. Edelstein, *ibid.*, **40**, 488 (1964).

[5] Z. G. Soos, *ibid.*, **43**, 1121 (1965).

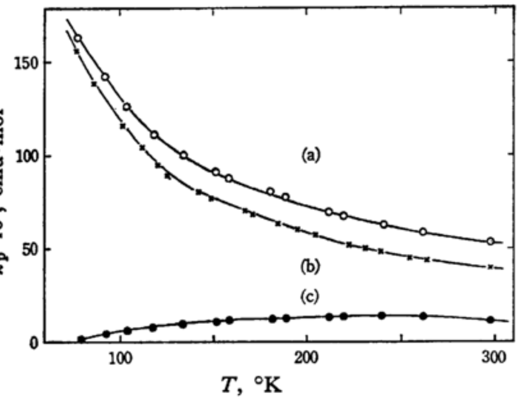

Fig. 2. Paramagnetic susceptibilities of (a) $\mathrm{Ni(dip)_3(TCNQ)_2\cdot 3H_2O}$, and (b) $\mathrm{Ni(dip)_3Cl_2\cdot 6H_2O}$. (c) The calculated, and ● the observed paramagnetic susceptibilities for TCNQ radicals in pairs.

the susceptibility values for these compounds. TCNQ radicals in the salt are thus found to contribute considerably to the observed paramagnetism. The temperature dependence of the susceptibility for the radicals in pairs could be explained on the basis of the singlet-triplet model for $\delta = 0.04$ eV, and $N' = 5.45\times 10^{23}$.

This result indicates that the paramagnetism for the TCNQ salt could be explained without considering superexchange interaction between d-electrons in $\mathrm{Ni(dip)_3{}^{2+}}$ and π-electrons in TCNQ radicals, and that spin correlation exists only in a pair of TCNQ anion radicals.

$\mathbf{Cu(dip)_3{}^{2+}(TCNQ^{\dot{-}})(TCNQ)_2Cl^-\cdot 4H_2O}$. The paramagnetic susceptibility changed anomalously with the change in temperature. The susceptibility for TCNQ radicals, which was estimated tentatively from the difference between the value for the salt and that for $\mathrm{Cu(dip)_3{}^{2+}Cl_2^{-}\cdot 7H_2O}$ is shown by the curve (c) in Fig. 3. It was nearly independent of temperature above 130°K, but it increased steeply in the temperature region below 130°K. The steep rise could not be fitted either to the values estimated by Curie law or by the Curie-Weiss law with a negative Weiss temperature. The electrical resistivity for this TCNQ salt was found to be as low as 270 Ω·cm at room temperature.

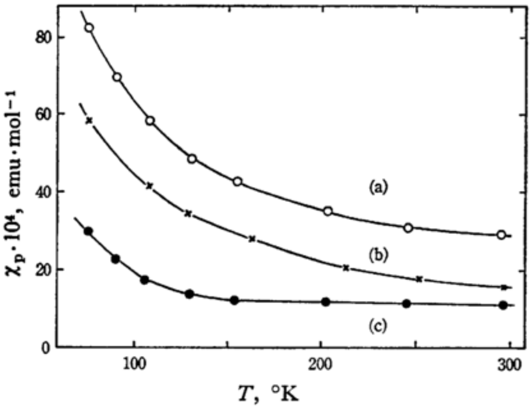

Fig. 3. Paramagnetic susceptibilities of (a) $\mathrm{Cu(dip)_3(TCNQ)_3Cl\cdot 4H_2O}$, and (b) $\mathrm{Cu(dip)_3Cl_2\cdot 7H_2O}$. (c) The difference between (a) and (b).

$\mathbf{Ba^{2+}(TCNQ^{\dot{-}})_2\cdot 2H_2O}$, $\mathbf{Ni^{2+}(TCNQ^{\dot{-}})_2\cdot 3H_2O}$, $\mathbf{Fe^{2+}(TCNQ^{\dot{-}})_2\cdot 3H_2O}$, and $\mathbf{Cu^{+}(TCNQ^{\dot{-}})(TCNQ)}$. The reciprocal values of paramagnetic susceptibility for the former three salts were plotted against temperature, as shown in Fig. 4, after correction was made for their molecular diamagnetism. The paramagnetism of the nickel and ferrous salts was found to obey Curie law, and the value of the susceptibility agreed with the value expected on the basis of the cation alone. The same result has been reported by Kepler.2)

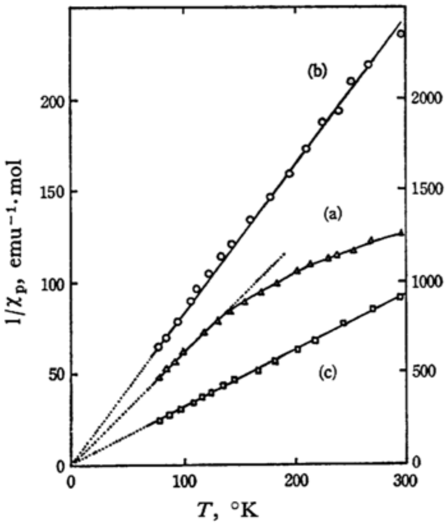

Fig. 4. Inverse paramagnetic susceptibilities of (a) $\mathrm{Ba(TCNQ)_2\cdot 2H_2O}$, (b) $\mathrm{Ni(TCNQ)_2\cdot 3H_2O}$, and (c) $\mathrm{Fe(TCNQ)_2\cdot 3H_2O}$. The scale for (a) is shown on right, while for (b) and (c) on left.

The plots for the barium salt, on the other hand, deviate from a straight line. $\mathrm{Ba^{2+}}$ itself is diamagnetic, so that the paramagnetism observed could be associated entirely with TCNQ radicals, and the deviation exhibits a strong spin exchange interaction between radicals. The temperature dependence of the susceptibility for the spin-paired radicals was explained by the singlet triplet model for which δ was taken to be 0.080 eV, and N', 4.77×10^{23}.

The product from metathesis of cupric sulfate with Li·TCNQ in methanol was found to have the composition of $\mathrm{Cu(TCNQ)_2}$ by an elementary analysis. The inclusion of neutral TCNQ and its 1 : 1 ratio to TCNQ anion in the salt were determined by the measurement of an infrared absorption spectrum, which revealed that an electron transfer occurred from a TCNQ anion to $\mathrm{Cu^{2+}}$, forming a diamagnetic $\mathrm{Cu^{+}}$. The paramagnetic susceptibility of the salt was low, 1.90×10^{-4} emu/mol at room temperature, and was independent of temperature.

Conclusion

The paramagnetic susceptibility for the TCNQ salts studied here, except for the copper salts, could be explained by a simple summation of the susceptibility value for the cation and that for anion radicals of TCNQ. The majority of the radicals in a salt are pairing in the sense of their spin exchange interaction, and the paramagnetism for the radicals in pairs is explained quantitatively on the basis of the singlet-triplet model. The singlet-triplet energy separation for the paired radicals in the metal-chelate-TCNQ salts is smaller than that in the simple metal-TCNQ salts.