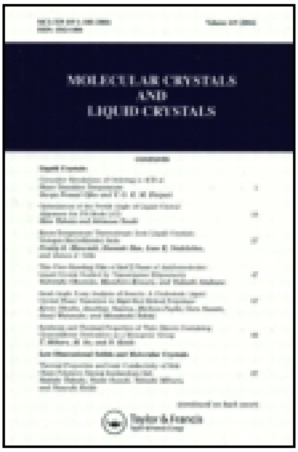

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Anomalous Magnetic Property of Crystalline m-phenylenebis-(galvinoxyl) Biradical. An Evidence for the Strong Ferromagnetic Intermolecular Interaction in Biradical Crystal

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ANOMALOUS MAGNETIC PROPERTY OF CRYSTALLINE m-PHENYLENEBIS-(GALVINOXYL) BIRADICAL. AN EVIDENCE FOR THE STRONG FERROMAGNETIC INTERMOLECULAR INTERACTION IN BIRADICAL CRYSTAL

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Abstract Magnetic susceptibility (χ_M) has been measured for the m-phenylenebis(galvinoxyl) biradical 1. χ_M follows the Curie-Weiss law with a Curie constant of C=0.60 K·emu/mol and a Weiss constant of θ=1 K in the temperature region 280-160 K, indicating two noninteracting spin 1/2 particles. χ_M deviates from Curie-Weiss law and $\chi_M T$ increases below 160 K to reach a broad maximum ($\chi_M T$= 1.83 K·emu/mol) at 72 K. The value of $\chi_M T$ at 72 K (1.83 K·emu/mol) is much higher than that (1.00 K·emu/mol) expected for a triplet (S=1) molecule and is indicative of a strong ferromagnetic interaction between biradical molecules. The anomaly of the susceptibility below 160 K is probably due to a first-order phase transition, because the susceptibility shows the phenomena of thermal hysteresis.

INTRODUCTION

Paramagnetic susceptibility measurements of most crystalline aromatic free radicals usually give negative Weiss constants. In such a case, their susceptibilities (χ_M) exhibit broad maxima at a low temperature, indicating that the spins on adjacent free radicals in the crystal lattice couple antiferromagnetically with each other. McConnell[1] pointed out the possibility of a ferromagnetic exchange interaction favoring parallel (total) spin angular momentum on neighboring molecules in odd-alternant radicals which have large positive and negative atomic π-spin densities. The unpaired electron distribution on galvinoxyl really corresponds to this case as calculated by the McLachlan Molecular Orbital method.[2] In fact, a positive Weiss constant (θ=11 K) was observed for galvinoxyl radical solids, and interpreted in terms of both the overlap of $2p_z$ π-orbitals inferred from the molecular packing and the spin densities.[3-5]

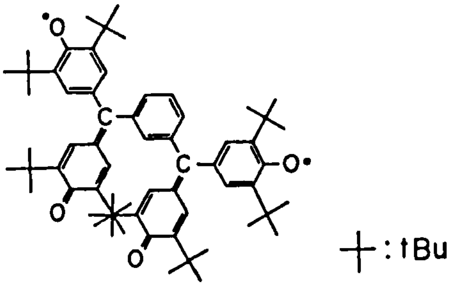

FIGURE 1 Molecular structure of m-phenylenebis(galvinoxyl) biradical 1.

The magnetic property of galvinoxyl is very interesting, because of the possibility of ferromagnetism at low temperature. However, the galvinoxyl radical shows a first-order phase transition at 85 K, accompanied by a pairing of the magnetic spins, and the susceptivility at low temperature (T<85K) was found to be diamagnetic (weak paramagnetic).$^{3,6-8}$ Recently, several examples of organic free radical crystals which indicate ferromagnetic intermolecular interactions at low temperatures have been reported.$^{8-16}$ However, the ferromagnetic behavior reported happens at liquid helium temperature region, indicating weak ferromagnetic interaction between the radical molecules.

Generally, the phenoxyl derivatives have large positive and negative atomic π-spin densities in the molecule, and we can expect ferromagnetic intermolecular interaction between the radical molecules from the theory of McConnell.^{1} However, the examples of the crystalline phenoxyl derivatives of which detailed magnetic properties have been studied are very limited.$^{3,17-21}$ In the present work, we prepared the crystalline m-phenylenebis(galvinoxyl) biradical 1 having two galvinoxyl groups in a molecule (see Fig. 1), and studied the magnetic susceptibility of the biradical 1.

EXPERIMENTAL

The synthesis of m-bis[bis(3,5-di-butyl-4-hydroxyphenyl)methyl]benzene (mp 223-224°C) was reported previously.^{22,23} The m-phenylenebis(galvinoxyl) biradical 1-A was prepared by the oxidation of the above phenol precursor in a mixture of diethyl ether and an aqueous alkaline $K_3Fe(CN)_6$ solution under a nitrogen atmosphere, with the temperature kept between 0 and 5°C, following the method of Müller and Ley.^{24} A brown solid having greenish metallic luster was isolated from the diethyl ether solution. The biradical 1-B was prepared by the oxidation of the phenol precursor with PbO_2 in 2-methyltetrahydrofuran (2-MeTHF) solvent under a nitrogen atmosphere, with the temperature kept between 0 and 5°C. The

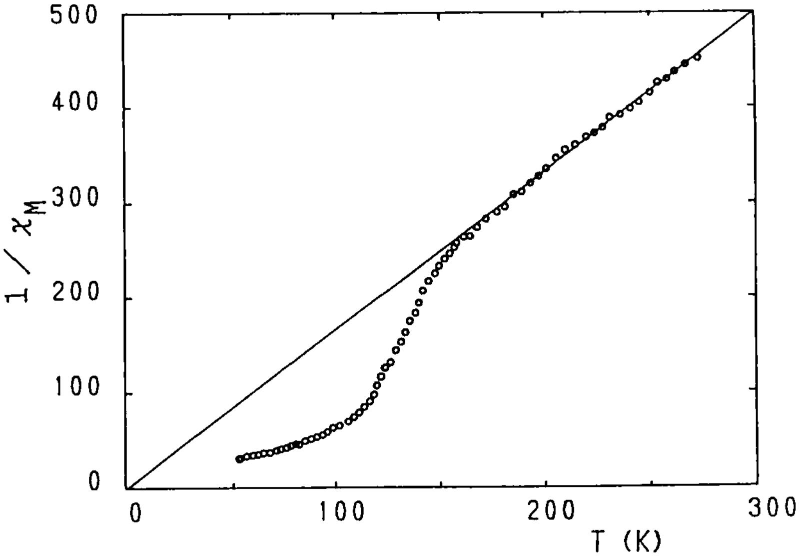

FIGURE 2 Inverse molar susceptibility of m-phenylenebis-(galvinoxyl) biradical 1-A vs temperature.

results of the iodometric titration indicated the existence of 1.7-1.8 moles of unpaired electrons per mole of the biradical samples.[24]

The susceptibility measurements from 54 to 280 K were carried out with a Shimadzu type MB-2 magnetic torsion balance, equipped with a low temperature cryostat.

RESULTS AND DISCUSSION

The inverse molar susceptibility of the m-phenylenebis(galvinoxyl) biradical 1-A, prepared by the oxidation with an aqueous alkaline $K_3Fe(CN)_6$ solution in diethyl ether, are shown in Fig. 2 as a function of the temperature. The data have been corrected for the diamagnetic contribution of χ_{dia}=-0.595 x 10^{-3}emu/mol, calculated by Pascal's method. The susceptibility of the biradical 1-A follows a Curie-Weiss law, with a Curie constant of 0.60 K·emu/mol and a Weiss constant of 1 K in the temperature range 280-160 K. A plot of $\chi_M T$ vs T (see Fig. 3) clearly shows that the value of product $\chi_M T$ (0.60 K·emu/mol) is much smaller than that of 1.00 K·emu/mol for pure triplet (S=1) particles, and is rather close to that of 0.752 K·emu/mol, corresponding to the high temperature limit ($|2J_{intra}|<<kT$) of the singlet-triplet equili-

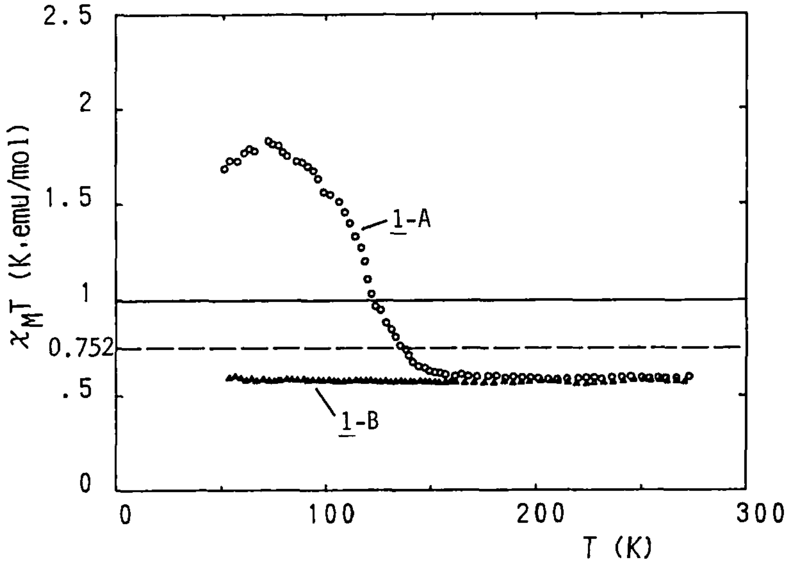

FIGURE 3 Plots of the product $\chi_M T$ vs T for the biradicals 1-A (○) and 1-B (△). Solid and broken lines represent the Curie laws with Curie constants of 1.00 and 0.752 K·emu/mol, respectively.

brium (ST) model, i.e., two noninteracting spin 1/2 particles. The difference between the observed and calculated Curie constants is due to both diamagnetic and monoradical impurities in the individual samples. Radical concentration of the biradical calculated from the above Curie constant, assuming noninteracting spin 1/2 particles, is 80%, being consistent with that (85-90%) obtained chemically by iodometric titration.

However, χ_M of the biradical 1-A deviates from Curie-Weiss law, and $\chi_M T$ increases below 160 K to reach a broad maximum ($\chi_M T$=1.83 K·emu /mol) at 72 K, as shown in Fig. 3. The value of $\chi_M T$ at 72 K is much higher than that (1.00 K·emu/mol) expected for a triplet (S=1) molecule and is indicative of a strong ferromagnetic intermolecular interaction between biradical molecules.

Further, it was found that the magnetic susceptibility of the biradical 1-A between 160-54 K depends remarkably on the thermal history of the specimen. For instance, at 77 K, the value of $\chi_M T$ increases gradually with time from 0.65 K·emu/mol at t=0 to 1.68 K·emu /mol at t=11 hrs, as shown in Fig. 4. When the temperature is lowered

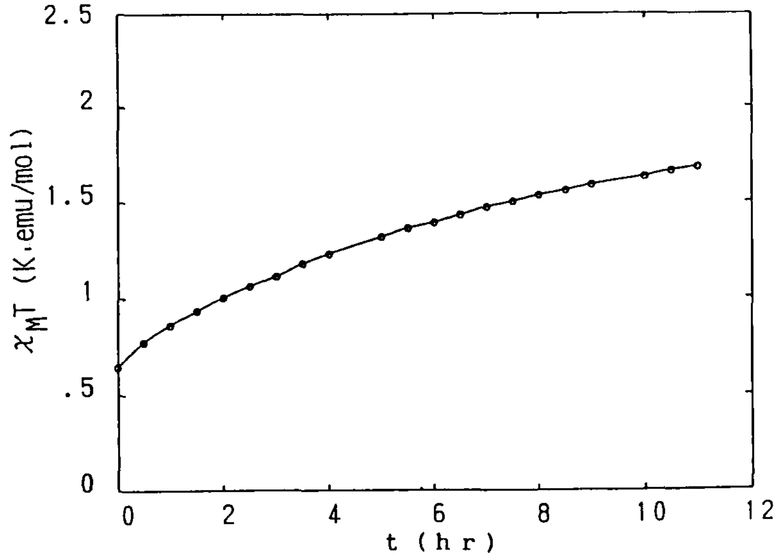

FIGURE 4 Plots of the product $\chi_M T$ vs time for the biradical 1-A at 77 K.

from 77 K, $\chi_M T$ remains constant (approx. 1.68 K•emu/mol) between 77-54 K, as shown in Fig. 5 (Run I). As the temperature is heated above 54 K, $\chi_M T$ value increases gradually and reaches a broad maximum at about T= 72 K. The temperature dependence of χ_M shows clearly the phenomena of thermal hysteresis. Similar measurements were performed for the same specimen of 1-A differing in the thermal history. As keeping the specimen for 4 hrs at 77 K, $\chi_M T$ increases with time from 0.65 K•emu/mol to 1.24 K•emu/mol, as shown in Fig. 5 (Run II). χ_M shows similar temperature dependence to that of Run I with subsequent heating after the sample was cooled down to 54 K from 77 K. Therefore, the anomaly of the susceptibility below 160 K will be due to a first-order phase transition.

On the other hand, quite different magnetic behavior has been observed for the biradical 1-B, prepared by the oxidation with PbO_2 in 2-MeTHF. The susceptibility of the biradical 1-B follows the Curie-Weiss law with a Curie constant of C=0.58 K•emu/mol and a Weiss constant of θ=1 K in the temperature range 280-54 K. As is clear from the results shown in Fig. 3, the anomaly in the magnetic susceptibility observed for the biradical 1-A was disappeared in the biradical 1-B. The value of Curie constant obtained for the biradical 1-B agrees well with that

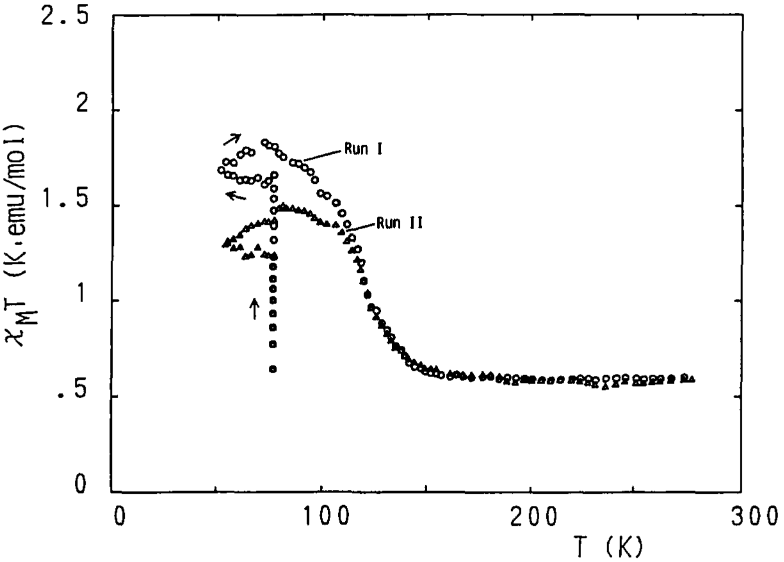

FIGURE 5 Plots of the product $\chi_M T$ vs T for the biradical 1-A, showing thermal hysteresis. Runs I and II indicate the experiments differing in thermal history on the same specimen.

(C=0.60 K·emu/mol) obtained for the biradical 1-A in the temperature range 280-160 K. Further, the result obtained for the biradical 1-B indicates that the intra- and inter-molecular exchange interactions in the biradical 1-B are weaker than the thermal excitation, i.e., $|2J_{intra}|$ and $|2J_{inter}|$<<54 K.

As described above, anomalous magnetic property has been observed for the biradical 1-A. In order to ascertain the anomalous magnetic susceptibility observed for the biradical 1-A, several samples of both the biradical 1-A and 1-B were synthesized independently, and the susceptibility measurements were performed repeatedly. Anomalous magnetic susceptibility was only observed for the biradical 1-A, and not for the biradical 1-B, indicating that the anomaly in the susceptibility is intrinsic property to the biradical 1-A. Quite different magnetic properties have been observed for the specimens of the biradicals 1-A and 1-B prepared by using different oxidizing agents and solvents. Therefore, in order to clarify the effect of the paramagnetic impurity which may arise from $K_3Fe(CN)_6$ used as oxidizing agent, the following experiments were performed. The specimen of biradical 1-A which shows anomalous magnetic property was dissolved into 2-MeTHF solvent, and the solvent was evaporated under vacuum for 3 hrs. The susceptibility of the specimen of 1-A follows the Curie-Weiss law with C=0.55 K·emu/mol and θ=5 K between 280-54 K, and the anomaly in the susceptibility disappeared. The result indicates that the anomaly in the susceptibility is not due to the paramagnetic impurities such as Fe(II) and Fe(III) ions arising from $K_3Fe(CN)_6$. The disappearance of the anomalous magnetic behavior in the biradical 1-A may relate to the 2-MeTHF molecules remaining in powder crystal of the biradical 1.

ESR spectra of m- and p-phenylenebis(galvinoxyl) biradicals 1 and 2 have been reported in previous papers.[22,23] The biradicals 1 and 2 show nine line hyperfine splittings (a_m^H=0.69 G) due to the equivalent eight meta-ring protons in the two galvinoxyl rings in 2-MeTHF solution. The spectra were ascribed to a biradical whose exchange energy, J_{intra}, is larger than the proton coupling constant, a_m^H ($|J_{intra}| \gg a_m^H$; a_m^H=0.69 G for 1 and 2). When the solution containing the biradicals 1 and 2 is frozen into a rigid glass (77 K), one can observe some dipolar splittings due to typical triplet state (see Figs. 2 and 3 in ref. 23). In both the biradicals 1 and 2, the zero-field splitting parameters (D and E) and the g-tensor values have been estimated to be $|D|$=26.1 G, $|E|$=1.1 G, g_{xx}=2.0039, g_{yy}=2.0056 and g_{zz}=2.0038 for 1, and $|D|$=20.0 G, $|E|$=1.1 G, g_{xx}=2.0045, g_{yy}=2.0049 and g_{zz}=2.0043 for 2. The ESR absorptions which indicate the existence of high spin state (S>1) in the biradical 1 were not observed.

As described above, the biradical 1-A shows large magnetic susceptibility at low temperature between 90 and 54 K. For instance, the value of the product $\chi_M T$ is 1.83 K·emu/mol (Run I) at 72 K. Such a large value of $\chi_M T$ in the biradical 1-A is well interpreted by assuming the ferromagnetically coupled structure at low temperature. Ferromagnetic intramolecular exchange interaction ($2J_{intra}$) in biradical 1-A is thought to be not so strong, because $|J_{intra}| \ll 54$ K in the biradical 1-B. Consequently, the strong ferromagnetic interaction observed for the biradical 1-A will be due to the intermolecular one. The value of $\chi_M T$ at 72 K (1.83 K·emu/mol) seems to correspond approximately to the value for S=5/2 or sextet. It appears that the ferromagnetic interaction extends over at least five biradical molecules on an average in the crystal. As it is clear from the results shown in Figs. 4 and 5, the spin multiplicity in the biradical 1-A will increase from S=5/2, by keeping the specimen for longer hours at 77 K.

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