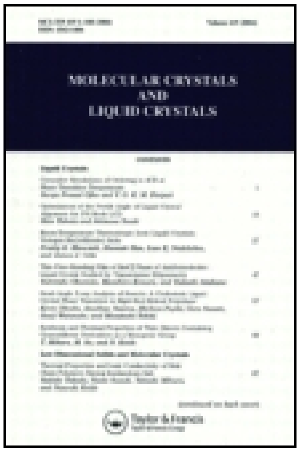

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MAGNETIC PROPERTIES OF PURELY ORGANIC RADICAL MAGNETS, *N*-(ARYLTHIO)-2,4,6-TRIARYLPHENYLAMINYLS: SUSCEPTIBILITY AND HEAT CAPACITY MEASUREMENTS

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Abstract The magnetic properties of *N*-[(dichlorophenyl)thio]-2,4,6-tris(chlorophenyl)phenylaminyl radical crystals are reported. The stable radical crystals of *N*-[(2,4-dichlorophenyl)thio]-2,4,6-tris(4-chlorophenyl)phenylaminyl (**1**) and *N*-[(2,4-dichlorophenyl)thio]-2,4,6-tris(3-chlorophenyl)phenylaminyl (**2**) have shown one-dimensional ferromagnetic behavior which have described using the Bonner-Fisher model with the large ferromagnetic exchange interaction of $J/k_B = 14.0$ K and $J/k_B = 5.7$ K, respectively. In addition to these ferromagnetic compounds, *N*-[(3,5-dichlorophenyl)thio]-2,4,6-tris(4-chlorophenyl)phenylaminyl (**3**) has also shown the ferromagnetic intermolecular exchange interaction of $J/k_B = 1.8$ K. For these crystals, we have carried out low-temperature susceptibility and heat capacity measurements below 2 K. Radical **1** has shown a magnetic phase transition at 0.4 K. The susceptibility in the ordered state, however, shows spin-flip transition, indicating antiferromagnetic long range ordering. For the ordered state, the interchain interactions are also estimated to be $J'/k_B = 0.02$ K and $J''/k_B = -0.01$ K. In order to clarify the electronic structures, ab-initio molecular orbital calculations of their substituted radicals are carried out. The correlation between the magnetic interactions and the electronic structures is discussed.

INTRODUCTION

As promising candidates for organic molecule-based magnets, a variety of stable radical species have been investigated.[1] The requirement of the large spin-polarization for the ferromagnetic intermolecular exchange[2] is easily realized for the free radicals with localized spin-structures as nitroxide and nitronyl nitroxide radicals. Their intermolecular ferromagnetic exchange interactions are, however, small in magnitude due to the localization of the unpaired electron. Recently, the ferromagnetic exchange interactions have also been found for the stable radicals with delocalized spin structures such as thioaminyl radicals[3,4] and thiooxoverdazyl radicals.[5] Both species have shown large ferromagnetic interactions compared to the nitroxide and nitronyl nitroxide radicals with the localized spin structure.

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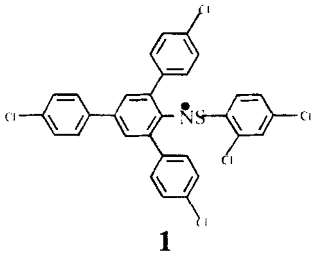
In this paper, the magnetic properties of the following three ferromagnetic *N*-[(dichlorophenyl)thio]-2,4,6-tris(chlorophenyl)phenylaminyl radical crystals **1-3** are reported. Temperature dependence of the molar paramagnetic susceptibility of these radical crystals from 1.7 K to 300 K are well interpreted by the one-dimensional ferromagnetic Heisenberg model. The low-temperature susceptibility and heat capacity of the polycrystalline samples of **1** and **2** are examined in the temperature region 50 mK - 2.0 K. Ab-initio MO calculations are also carried out for **1**. The correlation between the magnetic exchange interaction and the electronic structures also discussed based on the MO calculations.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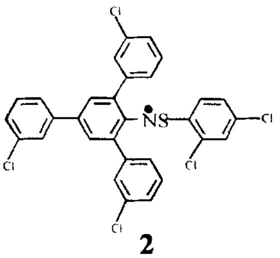
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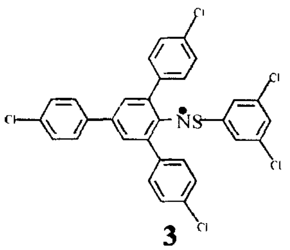
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EXPERIMENTAL

The free radicals, **1** - **3**, were synthesized by the procedures which we have already reported.[3] The temperature and magnetic field dependences of dc-susceptibility were measured by a SQUID magnetometer. The low-temperature ac-susceptibility and heat capacity measurements below 2 K were carried out for **1** and **2**. The ac-susceptibility was measured by the Hartshorn bridge method at 200 Hz. For the low-temperature experiments, we have cooled the sample using a $^3He/^4He$ dilution refrigerator. For all measurements polycrystalline samples were used.

RESULTS AND DISCUSSION

(i) Magnetic Behavior in the High-Temperature Region 1.7 K - 300 K

The magnetic behavior of **1** and **2** in the temperature region 1.7 K - 300 K were already reported in our previous paper.[4] The temperature dependence of molar susceptibility (χ_{mol}) of **1** was well fitted to the regular one-dimensional Heisenberg model ($H = -2J\Sigma S_i \cdot S_j$) with ferromagnetic exchange interaction of $J/k_B = 14.0$ K as shown in Figure 1(a). It should be noted that the magnitude of the exchange interaction is very large compared to those of nitroxide or nitronyl nitroxide radicals. This large exchange inter-action may come from the delocalized spin structure of the thioaminyl radical. Like **1**, the temperature dependence of χ_{mol} of **2** was also interpreted in terms of the one-dimensional Heisenberg model with J/k_B = 5.7 K (see Figure 1(b)). In this paper, we will add *N*-[(3,5-dichlorophenyl)-thio]-2,4,6-tris(4-chlorophenyl)phenylaminyl **3** as another example of the thioaminyl radical crystals with one-dimensional ferromagnetic intermolecular exchange interaction of J/k_B = 1.8 K (Figure 1(c)).

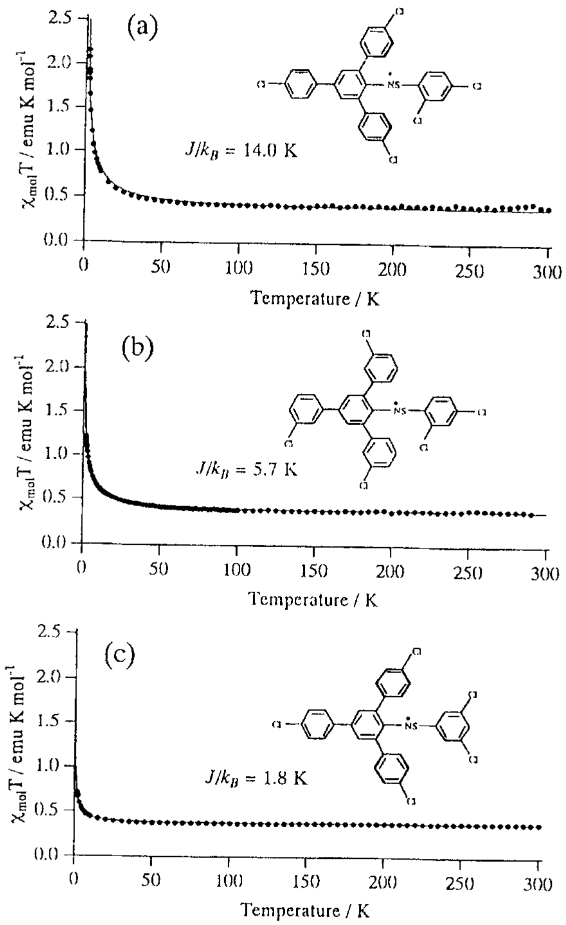

FIGURE 1. Temperature dependence of $\chi_{mol}T$ of **1-3** from 1.7 K to 300 K.

(ii) Low Temperature Magnetic Properties and Phase Transitions

Low temperature magnetic behaviors were investigated for the polycrystalline samples of **1** and **2**. For the sample **2**, only a broad maximum was observed at 0.1 K in the ac-susceptibility measurements and we could not observe a sharp peak in the heat capacity measurement above 50 mK. We therefore focus our discussion on the results of **1**. The ac-susceptibility of the polycrystalline powder sample of **1** shows a sharp peak around T_N = 0.45 K as shown in Figure 2(a). This transition temperature corresponds to the λ-type anomaly observed at T_N = 0.40 K in the zero-field heat capacity measurements, shown in

Figure 2(b). The small disagreement in the transition temperature T_N between the ac-susceptibility and the heat capacity measurements may be ascribable to the thermal contact problem in the low-temperature susceptibility measurements. Figure 2(c) shows the entropy change calculated from the heat capacity change. In the spin 1/2 system, the entropy change arising from the phase transition toward the ordered phase should be Rln2 = 0.693R. In this system, such a entropy change below T_N is ca. 0.2R. This means that ca. 70 % of the entropy change has been already consumed by the short range ferromagnetic ordering of spins in the temperature range above T_N. This is a characteristic nature in the one-dimensional spin system, showing the strong low-dimensionality in the present system.

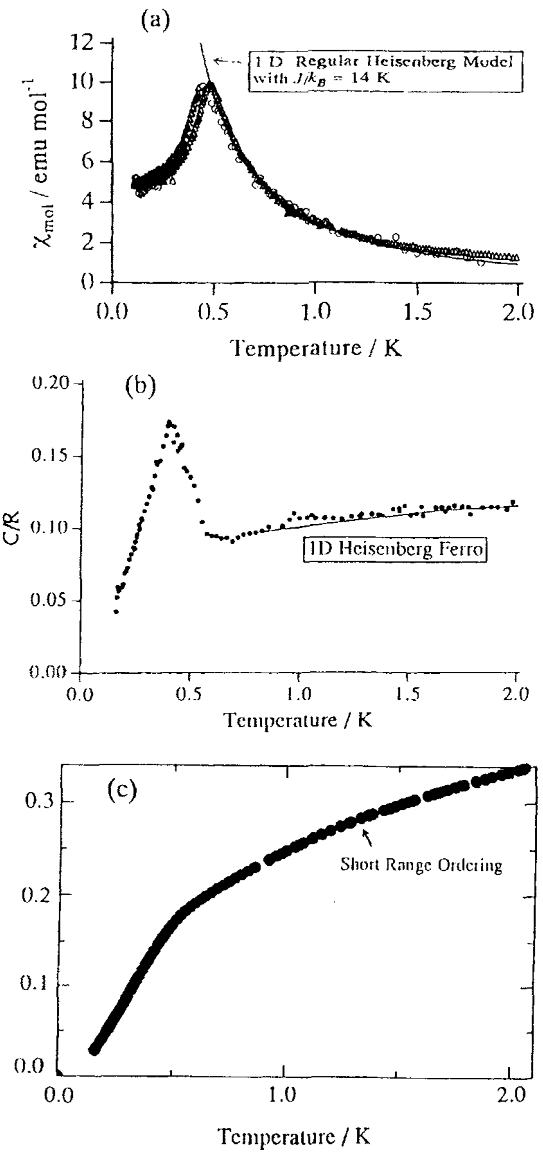

FIGURE 2. Temperature dependence of ac-magnetic susceptibilities (a), heat capacity (b) and magnetic entropy (c) in low-temperature region (50 mK - 2.0 K).

In order to check the ordered phase in more details, we examined the field dependence of the susceptibility. Figure 3 shows the typical field dependence observed at 300 mK. The peak originated from the spin flop transition characteristic of the antiferro-magnet or

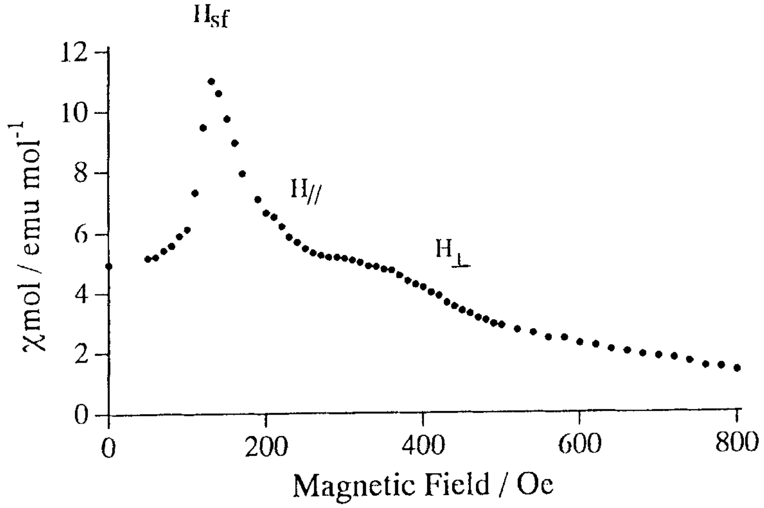

FIGURE 3. ac-Susceptibilities as a function of the external field.

metamagnet was observed at ca. 150 Oe. Since the present sample is the polycrystalline powder, the observed total χ_{ac} is the sum over all the susceptibility $\chi_{ac}(\theta,\phi)$ in which the external field is along to the spatial direction (θ,ϕ). In such a case, we can obtain the values of $H_{//}$ and $H_{\perp}$ as indicated in Figure 3. $H_{//}$, $H_{\perp}$ and the spin flop field H_{sf} are given using the interchain antiferromagnetic exchange field H_{ex} and the anisotropic field H_A as follows.

$$H_{//} = 2H_{ex} + H_A, \qquad H_{\perp} = 2H_{ex} - H_A, \qquad H_{sf} = \sqrt{H_A(2H_{ex}-H_A)}. \tag{1}$$

In a mean field theory, the staggered susceptibility is given by

$$\chi_s = \frac{\chi_0}{1 - (|J'/k_B| + |J''/k_B|)\chi_0} \tag{2}$$

where χ_0 is the reduced susceptibility $k_B\chi/\mu^2$ calculated by one-dimensional Heisenberg model.[6] From equation (1), we obtain

$$H_{ex} = 165 \text{ Oe} \quad \text{and} \quad H_A = 100 \text{ Oe}, \tag{3}$$

The interchain interactions can be also estimated from equation (2) using the above experimentally determined values and $\chi_0 = 36.2$ at T_N=0.4 K which is calculated by the one-dimensional Heisenberg model.[7] The estimated interchain exchanges are given by

$$J'/k_B = 0.02 \text{ K} \quad \text{(ferromagnetic)}, \tag{4}$$

and

$$J''/k_B = -0.01 \text{ K} \quad \text{(antiferromagnetic)}. \tag{5}$$

Since the intrachain ferromagnetic exchange J/k_B is 14.0 K, the coupling ratio J'/J is

0.0014 and J''/J is -0.0007, which characterize the strong one-dimensionality of the present system. In conclusion, the ordered state can be described as the ferromagnetic plane system interacting antiferromagnetically between planes since the exchanges J and J' is positive and only J'' is negative.

(iii) Electronic Structure of Molecule **1**

In order to clarify the electronic structure of **1** and the origin of the ferromagnetic intermolecular exchanges, we have carried out ab-initio molecular orbital calculations based on the density-functional theory (DFT) using Gaussian 94. We used the STO 6-31G basis set and UHF Becke3LYP hybrid method. Since there was no available molecular structure data for this molecule, we first determined the reasonable molecular structure using the MM2 method which had a minimized steric hindrance. Then, we carried out the ab-initio MO calculations. The obtained one-electron molecular orbital energies are shown in Figure 4. This figure shows the unoccupied β-SOMO is closely located on the α-LUMO. This situation is one of the conditions required for the ferromagnetic intermolecular exchange interaction. Although this molecule has the spin-structure in which the unpaired electron delocalize onto the phenyl rings adjacent to the NS site, this result means that the thioaminyl radical site (-N-S-) has a still enough spin-polarization effect. The large polarized spin-structure favors the ferromagnetic interaction when the large orbital overlap between α-SOMO and α-LUMO on the phenyl rings of the neighboring molecules is realized. This finding is consistent with the observation of the ferromagnetic intermolecular exchange interaction in **1**-**3**.

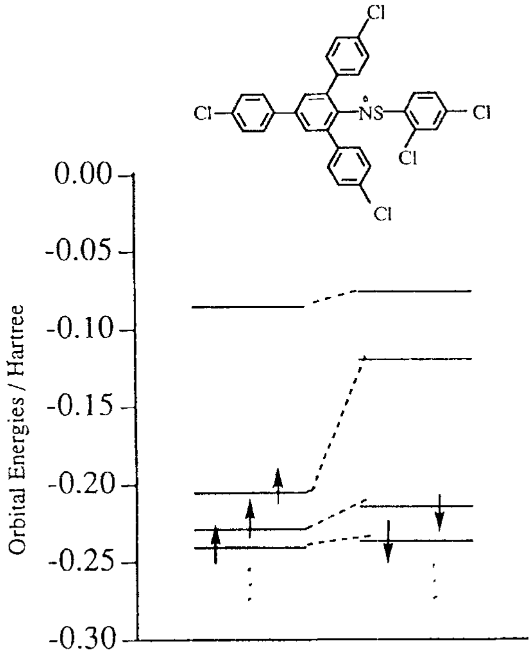

FIGURE 4. Location of the one-electron molecular orbitals obtained from the UHF ab-initio MO calculation using DFT method.

CONCLUSIONS

The present results show that the large ferromagnetic intermolecular exchange interaction has been realized in the purely organic thioaminyl radicals crystals with delocalized spin-structures. Although the dimensionality of the magnetic interaction is low (one-dimensional) in the present systems **1-3**, this finding may open a way for purely radical magnets with higher *Tc*. The present results strongly suggests that the stable radical species with slightly delocalized spin structure such as thioaminyl radicals are one of the promising candidates for the high *Tc* molecular-based magnets. In addition, it should be noted that the thioaminyl radical crystal **1** is one of ideal model systems for the low-dimensional magnets since this system has very low inter-intra chain coupling ratio of $J'/J=0.0014$ and $J''/J=-0.0007$ and $g \cong 2.00$ (small spin-orbit coupling).

ACKNOWLEDGMENT

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