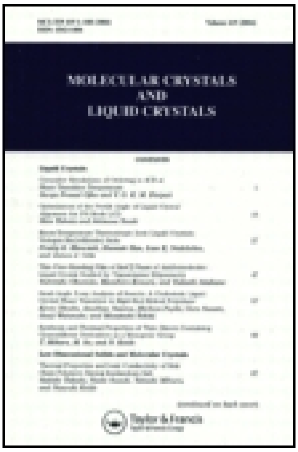

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# Ferromagnetic Behavior of a Purely Organic Magnetic Material. N-(Arylthio)-2,4,6-Triarylphenylaminyl Radical Crystals

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# FERROMAGNETIC BEHAVIOR OF A PURELY ORGANIC MAGNETIC MATERIAL. *N*-(ARYLTHIO)-2,4,6-TRIARYLPHENYLAMINYL RADICAL CRYSTALS

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Abstract The magnetic behavior of stable free radical crystals of *N*-(arylthio)-2,4,6-triarylphenylaminyl are described as studied by the magnetic susceptibility and ESR measurements. The temperature dependence of the magnetic susceptibility and the ESR spectrum were examined from 1.7 K to room temperature. When the temperature is decreased from 298 to 2 K, the line width of the ESR spectrum increases enormously below 5 K in the case of *N*-[(2,4-dichlorophenyl)thio]-2,4,6-tris(3-chlorophenyl)phenylaminyl radical crystals, **1**. The susceptibility measurements of **1** show the intermolecular ferromagnetic (FM) interaction among the radical spins. The product $\chi_{mol}T$ increases with lowering of the temperature. The Weiss constant, $\Theta$, obtained for the Curie-Weiss law, is +5.7 K, indicating ferromagnetic intermolecular interaction among the spins. The magnitude of the FM interaction is fairly large, compared with those of other purely organic ferromagnets.

## INTRODUCTION

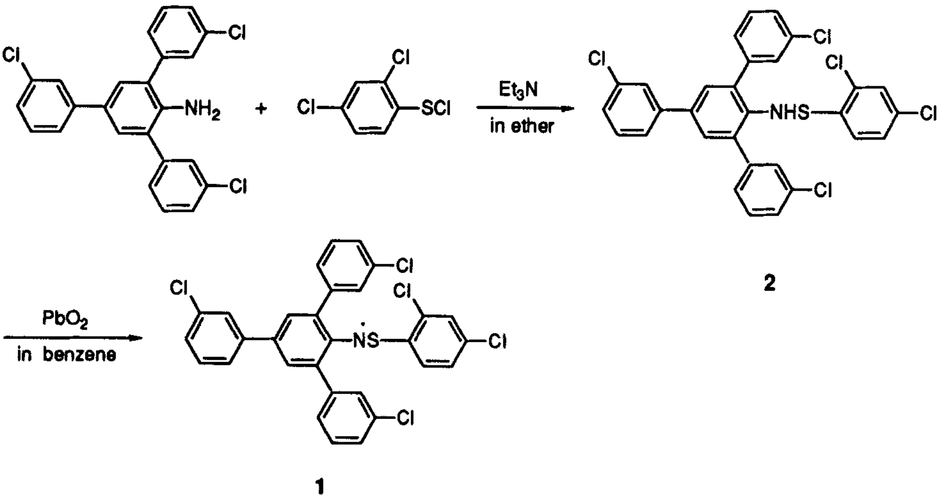
Purely organic crystalline ferromagnts and ferrimagnets are one of the most important targets in the field of molecular based magnetism. Quite recently, purely organic ferromagnets have been reported[1-5]. The number of the reports is, however, still limited and almost were nitronyl nitroxide and nitroxide radicals in which the spin is localized in the $\rangle$N-O function. Among the organic crystals showing ferromagnetic (FM) behavior, the only exception is 3-(4-chlorophenyl)-1,5-dimethyl-6-thiooxoverdazyl radical,[6] which has a delocalized spin structure. The magnetic properties of the radical crystals with a delocalized spin structure are, therefore, quite interesting in the field of the molecular magnetism.

We have recently found that *N*-(arylthio)-2,4,6-triphenylphenyl-aminyl radicals, a new class of stable radicals, can be isolated as pure radical crystals.[7] In this radical, the unpaired $\pi$-electron in SOMO is extensively delocalized over the whole molecule. Thus, the ca.60% amount of the unpaired electron resides on the nitrogen (40%) and sulfer (20%). The remainder is delocalized on the five phenyl rings via the $\pi$ conjugation. Recently, we have discovered that *N*-(anylthio)-2,4,6-triphenylphenylaminyls show a quasi one-dimensional alternating chain behavior with a fairly large antiferromagnetic (AFM) interaction.[8] We have continued our magnetic studies for structurally related *N*-(arylthio)-2,4,6-triarylphenylaminyl radicals and found that *N*-[(2,4-dichlorophenyl)thio]-2,4,6-tris(3-chlorophenyl)phenylaminyl radical, **1**, shows a ferromagnetic behavior in the radical crystals. In this paper we report the ferromagnetic behavior of **1** as studied by magnetic susceptibility and ESR measurements.

## EXPERIMENTAL

### (i) Synthesis of the Stable Radical 1

The synthesis of the stable *N*-[(2,4-dichlorophenyl)thio]-2,4,6-tris(3-chlorophenyl)phenylaminyl radical **1** was performed according to scheme 1.[9] To a stirred solution of 4.13 mmol of 2,4,6-tris(3-chlorophenyl)aniline and 10.8 mmol of triethylamine in 150 $cm^3$ of dry ether was added dropwise a solution of 6.2 mmol of 2,4-dichlorobenzenesulfenyl-chloride in 30 $cm^3$ of dry ether at 0 °C. After being stirred for 2h at 0 °C, the reaction mixture was filtered, and evaporated, and the residure was colum chromatographed on alumina with 1:4 benzene-hexane. Crystallization from ethanol gave precursor **2** in 56% yield as light brown fine prisms with mp 124-126 °C. Precursor **2** (200mg) was dissolved in 20 $cm^3$ of benzene with stirring. After 2.0 g of $K_2CO_3$ was added, 2.0 g of $PbO_2$ was added over 2 min, and the resulting colored mixture was stirred for additional 0.5 min. After filtration, the solvent was removed by freeze-drying. The resultant crystalline powder was crystallized from hexane to give **1** in 48 % yield dark green fine needles with mp 120-121 °C.



Scheme 1

(ii) **Magnetic Susceptibility and ESR Measurements**

The stable radical **1** used for the susceptibility and ESR measurements were purified by repeated recrystalizations from hexane. After the recrystalizations, the sample was dried for 5 h in vacuum. The polycrystalline sample was used for the magnetic susceptibility and ESR measurements. The magnetic susceptibility was measured in the temperature range 1.7 - 298 K with a SQUID magnetometer (Quantum-Design

MPMS2). The diamagnetic component was subtracted by the estimation based on the Pascal's sum rule of the atomic contributions and structural corrections. The ESR spectra were measured in the temperature range 2.0 - 298 K with a Bruker ESP300 spectrometer equipped with a helium-flow type's variable temperature controller (Oxford ESR910).

## RESULTS AND DISCUSSION

### (A) Magnetic Susceptibility

The temperature dependence of the molar susceptibility ($\chi mol$) of the polycrystalline sample of **1** is shown in Figure 1. All of the susceptibility data have been corrected for the diamagnetic contribution of $\chi dia = -3.30 \times 10^{-4}$ emu/mol. The reciprocal susceptibility is also shown in the same figure. The solid curve in Figure 1 represents the susceptibility calculated for the Curie-Weiss

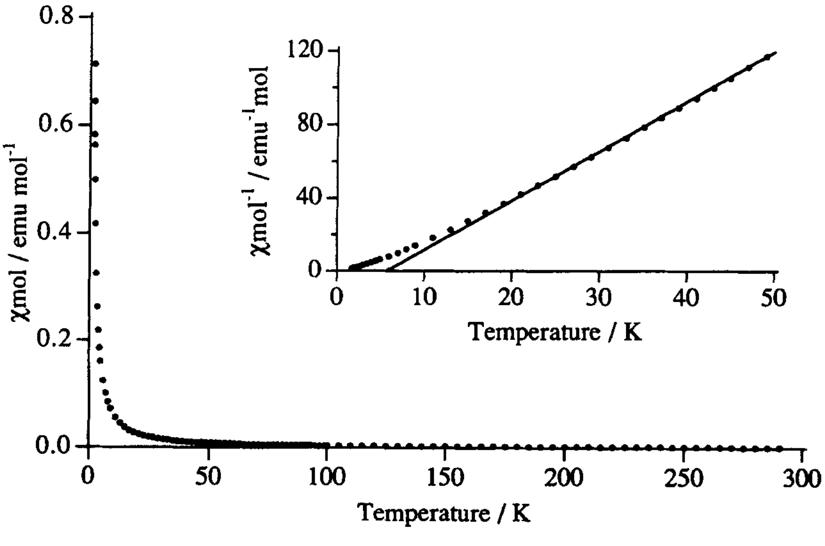


FIGURE 1 Temperature dependence of the molar susceptibility $\chi_{mol}$ of the polycrystals of **1**

law of S = 1/2, with a Curie constant (C) of 0.378 emu K/mol ($g$ = 2.0068) and a positive Weiss constant of $\Theta$ = +5.7 K, indicating ferromagnetic intermolecular interactions among the electron spins.

Figure 2 shows plots of $\chi_{mol}T$ as a function of the temperature. The $\chi_{mol}T$ values exhibit a significant increase below 10 K. The high-temperature value (0.380 emu K/mol at 290 K) is close to the theoretical value (0.376) for the noninteracting S= 1/2 system of free spin $g$-value (2.0023), showing that the origin of the magnetism is certainly due to the purely organic radical.

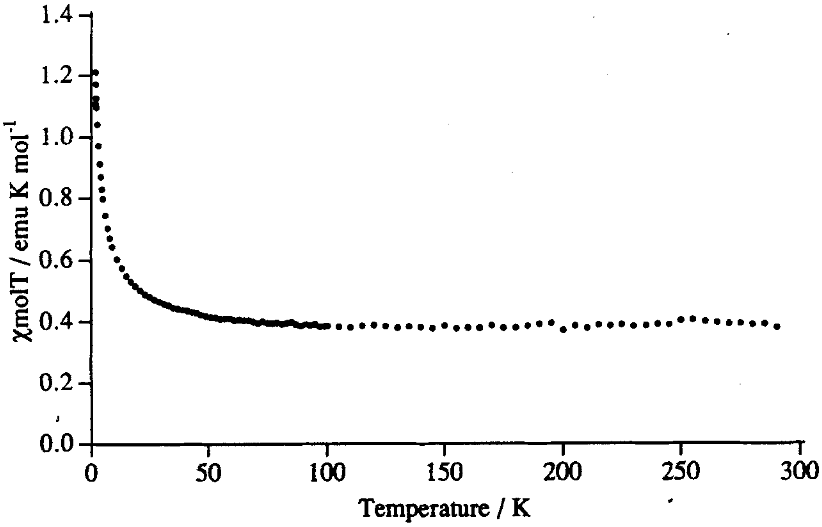


FIGURE 2 Temperature dependence of $\chi_{molT}$ of the polycrystals of **1**

The external magnetic field dependence of the magnetization measured at 2 - 10 K is shown in Figure 3. The solid curves represent the magnetization calculated using the theoretical Brillouin functions for S= 1/2 - 5 states constructed from S = 1/2 species (therefore, the saturated magnetization is ca. 5500 emu G/mol). It is obvious from Figure 3 that the magnetization grows slowly and the slopes of the curves in the low-field region become steeper with the decreasing temperatures. The effective spin value reaches to S=3.5 at 2 K. Thus, the operation of FM interaction in the crystal of **1** is confirmed by the magnetization measurements.

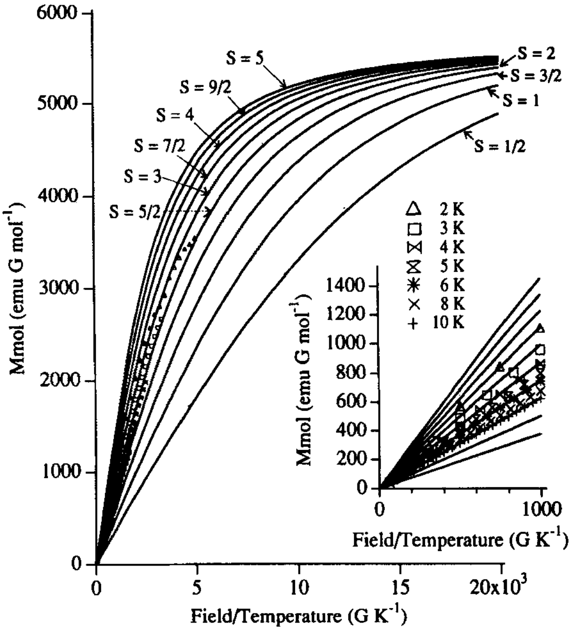


FIGURE 3 Magnetization isotherms of **1** at several temperatures

### (B) **Temperature Dependence of ESR Spectra**

At room temperature, the ESR spectrum for the polycrystalline sample of **1** shows a symmetrical single narrow line without any structure arising from the anisotropy of *g* tensor and from the hyperfine splitting of the nitrogen atom. This means that any splitting coming from the anisotropy has been completely smeared out in this crystal as a result of the intermolecular exchange interaction. The averaged *g* values has been determined to be 2.0068 at room temperature. The temperature dependence of the cw-ESR spectra are shown in Figure 4. As the temperature is decreased, the line-width increases and the asymmetry of the line shape increases especially below 5 K. This asymmetrical line broadening might be arising from the appearance of the magnetostatic mode (Walker mode) or a intensity became enormously strong. These finding may be understood for the critical phenomena near at the bulk phase transition at low temperature. In order to check whether this material becomes a ferromagnet or not, further low temperature measurements of the magnetic susceptibility are in progress.

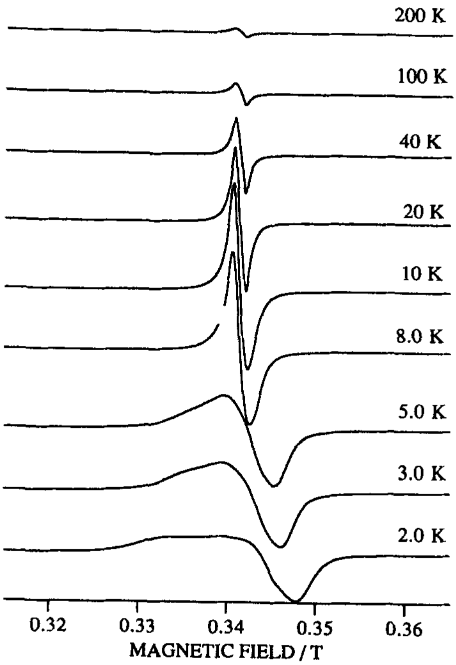


FIGURE 4 Temperature dependence of the ESR spectrum for the polycrystals of 1

## CONCLUSIONS

We have discovered a new example of the ferromagnetic molecular crystal of a novel stable radical with the delocalized unpaired $\pi$ electron in the molecule. The magnitude of the FM interaction is fairly large. The phenomena of ESR line-broadening was observed, which might comes from the appearance of the Walker mode resulting from the FM interaction in the crystal. In order to check whether the phase transition toward a ferromagnet occurs or not, the lower temperature measurements of the magnetic susceptibility are in progress. The X-ray structural analysis is also planed.

## ACKNOWLEDGMENTS

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