Magnetic Phase Transition between Ferromagnetic High-Temperature Phase and Antiferromagnetic Low-Temperature Phase in 5-Carboxy-2-thienyl Nitronyl Nitroxide

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From the measurements of the temperature dependence of magnetization, a magnetic phase transition at 145 K with a thermal hysteresis is found for an organic radical 5-carboxy-2-thienyl nitronyl nitroxide. Ferromagnetic intermolecular interaction is observed in the high-temperature phase while antiferromagnetic interaction is obtained for the low-temperature phase.

Of a huge number of stable organic molecular crystals composed of neutral radicals and/or radical ions, the compounds which exhibit magnetic phase transitions of the first order have little been reported so far. The radical cation salt *N,N,N',N'*-tetramethyl-1,4-phenylenediamine perchlorate $(TMPD)^{\bullet+}ClO_4^-$ shows the first-order magnetic phase transition at 190 K,[1] while the radical anion salts, triphenylmethylphosphonium 7,7,8,8-tetracyanoquinodimethane $[(C_6H_5)_3PCH_3]^+(TCNQ)^{\bullet-}$, rubidium tetracyanoquinodimethane $Rb^+(TCNQ)^{\bullet-}$, and potassium 2,3,5,6-tetrachloro-4-oxido-1-phenoxyl (known as potassium chloranil $K^+(CA)^{\bullet-}$), exhibit the first-order phase transitions at 315 K, 381 K, and 260 K, respectively.[2–4] The magnetic phase transition at 305 K is recently reported for the neutral radical 1,3,5-trithia-2,4,6-triazapentalenyl TTTA.[5] The phase transitions in all the compounds mentioned above take place between high-temperature (HT) and low-temperature (LT) phases associated both with antiferromagnetic (AFM) intermolecular interactions.

The magnetic phase transition observed in the neutral radical 4-[[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]methyl]-2,6-bis(1,1-dimethylethyl)phenoxyl (known as galvinoxyl) is unique in the sense that the HT phase shows ferromagnetic (FM) intermolecular interaction whereas the LT phase has AFM interaction.[6]

We have found from the measurements of magnetization that the neutral radical 2-(5-carboxy-2-thienyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (5-carboxy-2-thienyl nitronyl nitroxide for a trivial name and abbreviated as 2-CATNN, see Figure 1) exhibits a phase transition at 145 K between the FM HT phase and AFM LT phase reminiscent of galvinoxyl. In this letter, we present the temperature dependence of paramagnetic susceptibility χ_p of 2-CATNN and discuss nature of the magnetic phase transition.

The radical 2-CATNN was prepared according to the procedure reported,[7] purified through column chromatography, and recrystallized from a methanol–ether solution (mp ≅ 175 °C dec). The magnetic susceptibility was measured by using a Quantum Design MPMS SQUID (superconducting quantum interference device) magnetometer[8] over the temperature range from 1.8 K to 300 K at the magnetic field 0.1 T. The diamagnetic susceptibility was subtracted from the susceptibility measured by assuming that the intrinsic contribution of χ_p is negligible at low temperatures and the extrinsic term of crystal defects and/or chemical impurities follow the Curie–Weiss law.

Figure 1 shows the temperature dependence of the product of paramagnetic susceptibility and temperature, χ_pT, of 2-CATNN. Upon increasing temperature from 1.8 K, χ_pT increases gradually up to about 140 K and suddenly at 145 K, while it decreases abruptly at 135 K as the temperature decreases from that higher than 150 K. That is to say, there is a discontinuous change in magnetic property associated with a considerable thermal hysteresis. This behavior is reminiscent of a first-order phase transition. Preliminary measurements of heat capacity of 2-CATNN revealed a sharp peak and a discontinuous change at 145 K, which are characteristic of a first-order phase transition.[9] The hysteresis behavior was also observed in the temperature dependence of g factor and linewidth of electron spin resonance spectra.

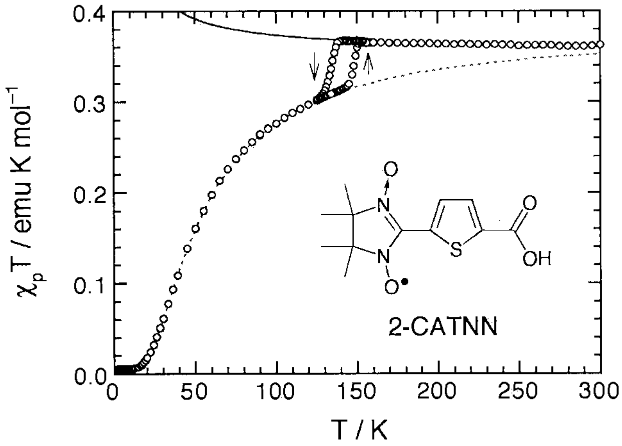

Figure 1. Temperature dependence of χ_pT of 2-CATNN. Open circles show experimental data. Solid and broken lines represent theoretical curves calculated for the high- and low-temperature phases, respectively (see the text). The arrows indicate the data collected in the cooling (down) and warming (up) processes.

In the HT phase, χ_pT decreases as the temperature increases, suggesting FM intermolecular interaction. We have estimated an exchange coupling constant *J/k* by fitting the experimental data to the one-dimensional (1-d) FM Heisenberg model,[10] although the data are available only above 135 K as shown by the solid line in Figure 1. The *J/k* value thus obtained is 2.6 ± 0.2 K and is comparable to that observed in nitronyl nitroxide radicals exhibiting FM intermolecular interactions.[11]

In the LT phase, χ_pT decreases monotonously down to 0.0056 emu K mol^{-1}, which corresponds to 1.5% crystal defects and/or chemical impurities, as the temperature decreases. By considering the extrinsic contribution mentioned above, the experimental data are well reproduced in terms of the singlet–triplet (S–T) dimer model[12] with $J/k = -48 \pm 2$ K as represented by the broken line in Figure 1. The absolute value of the coupling constant obtained for the LT phase of 2-CATNN is significantly large for nitronyl nitroxide radicals and is comparable to that observed in 2-imidazolyl nitronyl nitroxide 2-IMNN (J/k = –86 K)[13] and *N*-methyl-*p*-pyridiniumyl nitronyl nitroxide iodide $(p\text{-MPYNN})^{\bullet+}I^-$ (J/k = –74 K),[14] which show the largest AFM exchange coupling constants for nitronyl nitroxide derivatives so far reported.

The magnetic phase transition in 2-CATNN shown above therefore takes place between the FM and AFM phases. To the best of our knowledge, this is the second example of the phase transition from the FM HT phase to the AFM LT phase. The width of the thermal hysteresis, ΔT, observed in 2-CATNN is 15 ± 2 K. This value is remarkably large for the phase transition where the change in susceptibility is not so large as that observed in galvinoxyl[6a] and $K^+(CA)^{\bullet-}$.[4a] It is worth noting that $(TMPD)^{\bullet+}ClO_4^-$, in which magnitude of the change in susceptibility at the phase transition is similar to that observed in 2-CATNN, does not exhibit evidence for thermal hysteresis.[15]

The exchange coupling constants J/k in the HT and LT phases, the transition temperature T_t, and the width of the thermal hysteresis ΔT, observed in 2-CATNN are summarized in Table 1, together with those obtained for galvinoxyl.[16] The FM and AFM interactions in galvinoxyl are about five times as large as those obtained for 2-CATNN. This suggests that the 2-CATNN molecules would stack not on top but side-by-side to the neighboring molecules as found for 4-carboxyphenyl nitronyl nitroxide,[17] while the galvinoxyl molecules form regular stacks.[18]

Table 1. The exchange coupling constants J/k in the high- and low-temperature (HT and LT) phases, the transition temperature T_t, and the width of the thermal hysteresis ΔT of 2-CATNN and galvinoxyl

	J/k/K		T_t/K	ΔT/K
	HT phase (1-d Heisenberg)	LT phase (S–T dimer)		
2-CATNN	2.6 ± 0.2	–48 ± 2	145	15 ± 2
Galvinoxyl	13 ± 1	–230 ± 20	85	5 ± 1

The phase transition observed in 2-CATNN appears to be accompanied with a structural transformation although the crystal structures in the HT and LT phases are not known yet, because the temperature dependence of $\chi_p T$ is interpreted in terms of 1-d FM Heisenberg model in the HT phase and is well reproduced by the S–T dimer model in the LT phase. That is to say, the 2-CATNN molecules make regular stacks in the HT phase and the molecular stacks transforms to dimeric molecular arrangements in the LT phase.

The structural transformation from the regular stacks to the dimeric arrangements is reminiscent of the spin-Peierls transition.[19] However, this would not be the case for 2-CATNN. The spin-Peierls transition is essentially second order and magnetic susceptibility changes continuously at the phase transition. The phase transition observed in 2-CATNN is therefore unlikely to be the spin-Peierls transition.

For the first-order phase transition in organic radical crystals having regular stacks in the HT phase and dimeric arrangements in the LT phase, several mechanisms were proposed in terms of lattice-distortion mediated interaction between triplet excitons in high density[20] and a charge polarization instability with a lattice distortion.[21] To discuss further the origins of the phase transition in 2-CATNN, X-ray crystal structure analyses, which provide information about charge distributions in the molecules and lattice distortions in both phases, are currently in progress.

In summary, we have shown that the organic radical 2-CATNN exhibits the magnetic phase transition at 145 K between the ferromagnetic high-temperature phase with the coupling constant J/k = 2.6 ± 0.2 K and the antiferromagnetic low-temperature phase with J/k = –48 ± 2 K.

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