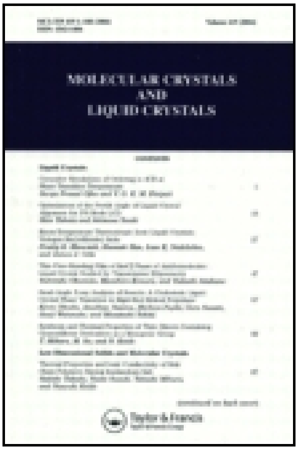

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Several Kinds of Aminoxyl Radicals and their Metal Ion Complexes

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Several Kinds of Aminoxyl Radicals and their Metal Ion Complexes

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Recent results of magnetization, magnetic susceptibility and muon spin rotation/relaxation (μSR) measurements of some organic neutral radicals based on aminoxyl and their anion radical complexes with alkali and transition metal cations are reported. Ferromagnetic intermolecular interactions, coexistent with antiferromagnetic ones, in several carboxyaryl nitronyl nitroxide radicals are affected by inserting alkali metal ions, while the incorporation of transition metal ions result in complex behavior suggesting in part ferromagnetic interactions. Temperature dependence of spontaneous magnetization of TANOL suberate in the ordered state, obtained through the results of μSR measurements, is characteristic of a two-dimensional magnetic lattice, consistent with that of magnetic susceptibility above the ordering temperature.

Keywords: molecular magnetism; aminoxyl radicals; ion radical complexes

INTRODUCTION

Aminoxyl (nitroxide) radical is a stable open-shell molecular compound and is therefore suitable for studying magnetic properties of molecular materials in various states; neutral and ionic, with and without other atoms and molecules[1]. One of our current interests is the effects of magnetic metal ions, placed between aminoxyl radical molecules, on the magnetism in such metal-organic complexes that consist of both components. From this point of view, we have recently been investigating alkali metal and transition metal complexes of aminoxyl radicals having a carboxylatoaryl or sulfonatoaryl moiety as a functional group for metal coordination[2]. Since the alkali metal ions are non-magnetic while the transition metal ions are often magnetic, it is interesting to compare magnetic behavior of these two kinds of metal complexes with that of uncoordinated aminoxyl radicals to discuss the effects of metal ions on the magnetism. Another interest is the magnetic order in organic radicals. To elucidate magnetic behavior below transition temperatures, we have been studying muon spin rotation/relaxation (μSR) of several kinds of aminoxyl radicals and found the phase transitions to magnetically ordered states[3]. The μSR techniques provide information on magnetic dimensionality by analyzing the temperature dependence of the μSR oscillation frequency which is proportional to the spontaneous magnetization.

In this paper, we first present magnetic behavior of lithium, sodium, and potassium complexes of 2-carboxyfuryl and *p*-carboxymethoxyphenyl nitronyl nitroxide (2-CAFNN and *p*-CAMOPNN, see Fig. 1). Next, the magnetic properties of manganese(II), cobalt(II) and copper(II) complexes of 2-CAFNN and *p*-CAMOPNN are reported. Finally, magnetic dimensionality of bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidinyl) suberate (TANOL suberate, see Fig.1) is described on the basis of μSR and susceptibility.

EXPERIMENTAL

All the organic radicals studied here were prepared according to the reported method[4,5], purified by column chromatography if it is necessary, and recrystallized from a benzene, chloroform or methanol solution. The alkali metal complexes were prepared by combining methanol solutions of radicals with alkali metal hydroxide in methanol. The transition metal complexes were obtained by reacting the radicals in methanol with transition metal sulfate or chloride in a methanol or aqueous solution.

Magnetization isotherms up to 5.5~7 T at 1.8~10 K and magnetic susceptibility χ at 0.1~0.5 T and 1.8~300 K of a polycrystalline sample were measured by using Quantum Design MPMS SQUID magnetometers. Paramagnetic susceptibility χ_p was obtained by subtracting the diamagnetic contribution, which was estimated from the χ *vs.* $1/T$ plot at high temperatures.

Low-temperature μSR measurements for polycrystalline pellet samples were carried out at the ISIS muon facility of the Rutherford Appleton Laboratory (UK) by using a dilution refrigerator. Details of the experiments and theoretical analyses were described elsewhere[3].

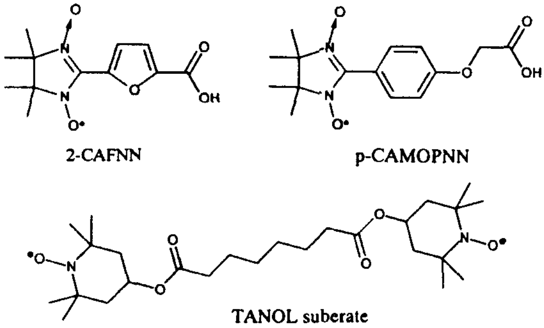

FIGURE 1 Molecular structures of the organic radicals.

RESULTS AND DISCUSSION

Magnetism in alkali metal complexes of nitronyl nitroxide radicals

Carboxylato and sulfonato groups have the potential to coordinate metal cations. We have therefore synthesized carboxylatoaryl and sufonatoaryl nitronyl nitroxide to study the effects of magnetic and non-magnetic counter ions on the magnetism of ionic organic molecular compounds.

Figure 2 shows temperature dependence of the product of paramagnetic susceptibility and temperature, $\chi_p T$, of lithium, sodium and potassium complexes of 2-carboxylatofuryl nitronyl nitroxide (here we abbreviate it also as 2-CAFNN for convenience) together with that of the uncoordinated compound 2-CAFNN. As previously shown, the temperature dependence of

χ_pT of 2-CAFNN is interpreted in terms of the coexistence of ferromagnetic (FM) and antiferromagnetic (AFM) intermolecular interactions[6].

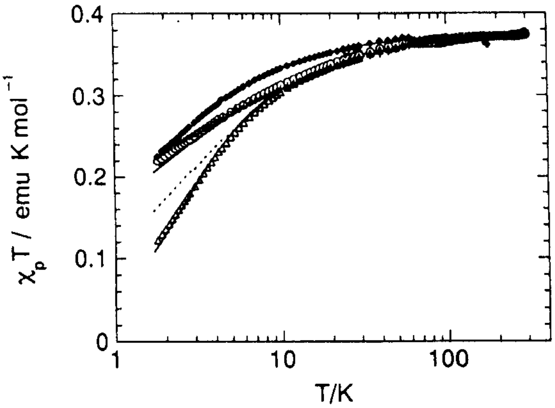

FIGURE 2 Temperature dependence of χ_pT of Li (+), Na (Δ) and K (♦) complexes of 2-CAFNN (o).

Incorporation of sodium and potassium cations into 2-CAFNN results in a reduction of FM interaction. The temperature dependence of χ_pT of Na(2-CAFNN) is well reproduced by the one-dimensional (1-d) AFM Heisenberg model with an exchange coupling constant J/k = -1.7 K as represented by a solid line in Fig. 2. The temperature dependence of χ_pT of K(2-CAFNN) follows the Curie-Weiss law $\chi_p = C/(T - \theta)$ with the Weiss constant $\theta = -1.24$ K down to 1.8 K as shown in Fig. 2. These results indicate that sodium and potassium cations interrupt the intermolecular exchange pathways in 2-CAFNN in such a way that the FM interaction is unfavorable. In contrast, lithium cations involved in the exchange pathways in 2-CAFNN do not affect significantly the magnetic behavior. The temperature dependence of χ_pT of Li(2-CAFNN) is very close to that of 2-CAFNN. The close similarity between the temperature dependence of χ_pT of both compounds suggests that there is a coexistence of FM and AFM intermolecular interactions in Li(2-CAFNN) as well as in 2-CAFNN. The effects of alkali metal cations on the magentism in 2-CAFNN are thus not simple but rather complicated.

Complicated effects of alkali metal cations on the magnetism are also observed in the alkali metal complexes of *p*-carboxylatomethoxyphenyl nitronyl nitroxide (abbereviated also as *p*-CAMOPNN) in a different way from that found for 2-CAFNN. Figure 3 shows the temperature dependence of χ_pT of lithium, sodium and potassium complexes of *p*-CAMOPNN. In the case of *p*-CAMOPNN, the lithium cations do not change magnetic behavior remarkably as well as observed in Li(2-CAFNN). The temperature dependence of χ_pT of the uncoordinated radical *p*-CAMOPNN is explained in terms of the coexistence of FM and AFM interactions[6]. The potassium cations incorporated into *p*-CAMOPNN interrupt the FM interaction. As represented by the solid line in Fig. 3, the temperature dependence of χ_pT of K(*p*-CAMOPNN) follows the Curie-Weiss law with θ = -1.82 K over the whole temperature range, thereby indicating an almost complete reduction of FM interaction.

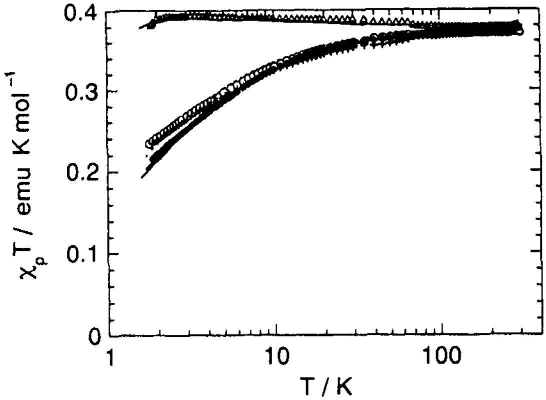

FIGURE 3 Temperature dependence of χ_pT of Li (+), Na (Δ) and K (◆) complexes of *p*-CAMOPNN (o).

The effects of sodium cations on the exchange pathways of *p*-CAMOPNN are distinguished from those of the other alkali metal cations mentioned above. The sodium ions enhance considerably the FM intermolecular interaction. The temperature dependence of χ_pT of Na(*p*-CAMOPNN is reproduced by the model in which 1-d FM Heisenberg chains are couplec antiferromagnetically. The best fit values for intra- and interchain exchange coupling constants of Na(*p*-CAMOPNN) are J/k =1.80 K and J'/k = -0.41 K, respectively, while those obtained for *p*-CAMOPNN are J/k = 0.22 K and J'/k = -0.7 K[6]. To discuss further, it is necessary to investigate the crystal structures of these alkali metal complexes.

Magnetism in transition metal complexes of nitronyl nitroxide radicals

Incorporation of transition metal cations such as manganese(II), cobalt(II) and copper(II) into the organic radical crystals might yield remarkable changes in magnetism, because these ions have magnetic moments inherently[7]. Figures 4 and 5 show the temperature dependence of $\chi_p T$ of Mn^{II}, Co^{II} and Cu^{II} complexes of 2-CAFNN and *p*-CAMOPNN, respectively. Upon lowering the temperature, the $\chi_p T$ value decreases in all the complexes, indicating predominant AFM interactions. At high temperaturs, the $\chi_p T$ values of Mn(2-CAFNN)$_2$ approaches to 5.125 emu K mol^{-1} expected for uncorrelated spins of S = 5/2 (Mn^{II}) and two S = 1/2 (2-CAFNN) by assuming a spin-only magnetic moment on Mn^{II}. The experimental data follows the Curie-Weiss law with θ = -2.3 K above 7 K, whereas the data deviate towards values which are larger than those calculated by using the Curie-Weiss law. The deviation towards larger values implies a coexistence of a minor FM interaction with a major AFM interaction, as mentioned in the preceding section. The $\chi_p T$ values of Mn(*p*-CAMOPNN)$_2$ approaches to 7.9 emu K mol^{-1}, which exceeds the value expected for uncorrelated spins. It is worth noting that FM coupling between metal and organic spins yields $\chi_p T$ = 7.93 emu K mol^{-1}, which is close to the values observed at high temperatures.

Co(2-CAFNN)$_2$ as well as Co(*p*-CAMOPNN)$_2$ show more complicated behavior. At 300 K a $\chi_p T$ value 3.1 emu K mol^{-1} is observed in both complexes, much higher than 2.625 emu K mol^{-1} expected for uncorrelated spins of S = 3/2 (Co^{II}) and two S = 1/2. However, this does not readily mean FM interaction, because the Co^{II} ion would not be spin-only but has orbital contributions. The g factor of Co^{II} is anisotropic and $g_X \cong 4$ and $g_Z \cong 2$. By asumming g_{av} = 3.5, $\chi_p T$ = 6.4 emu K mol^{-1}. A plataeu observed at 10~30 K is reminiscent of the multi-spin system with a combination of FM and

AFM interactions[8]. It should be noted that Cu(2-CAFNN) and Cu(*p*-CAMOPNN) exhibit AFM couplings leaving $S = 1/2$ at low temperatures..

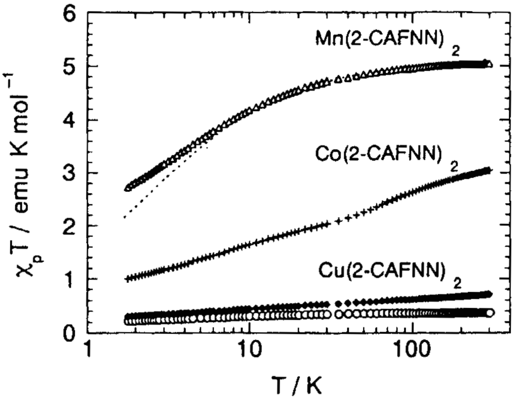

FIGURE 4 Temperature dependence of χ_pT of Mn (Δ), Co (+) and Cu (◆) complexes of 2-CAFNN (o).

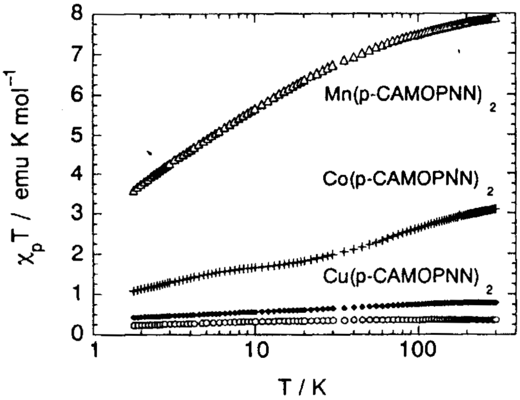

FIGURE 5 Temperature dependence of χ_pT of Mn (Δ), Co (+) and Cu (◆) complexes of *p*-CAMOPNN (o).

Two-dimensional magnetism in TANOL suberate

TANOL suberate is known to be a metamagnet below 0.38 K[9,10]. The two radical moieties at each terminal of one diradical molecule (see Fig. 1) make separately sheet-like arrangements in which the magnetic moments are almost localized[11]. The neutron scattering experiments confirmed that the magnetic moments lie in the planes of the sheets and the directions of magnetic moments, aligning parallel to each other in a sheet, are antiparallel to those in the adjacent sheets[10]; that is, FM interaction in the sheets and AFM interaction between the sheets through the suberate moiety of the diradical. Although the temperature dependence of paramagnetic susceptibility of TANOL suberate was analyzed by the model assuming 1-d FM interaction associated with interchain interactions[9], it is apparent that the magnetic dimensionality of this diradical is likely 2-d.

Since the μSR technique gives information on magnetic dimensionality by analyzing the temperature dependence of the spontaneous magnetization, we have examined μSR spectra in the vicinity of the magnetic transition temperature 0.38 K. Clear oscillations of the muon spin polarization are observed below 0.395 K in our samples. The temperature dependence of the μSR oscillation frequency ν at zero applied field is shown in Fig. 6. The frequency follows the equation $\nu(T) = \nu(0)\ (1 - T/T_C)^{\beta}$ where $\nu(0) = 3.38$ MHz, $\beta = 0.22$ and $T_C = 0.40$ K. Since ν is proportional to the internal magnetic field B around the muon spin embedded in the sample, it is a measure of spontaneous magnetization. The critical exponent β obtained from the temperature dependence of spontaneous magnetization reflects magnetic dimensionality[12]. For the 2-d XY magnets, $\beta \cong 0.23$ is predicted[13], while $\beta \cong 0.36$ is suggested for the 3-d Heisenberg model[12]. In fact, many 2-d spin systems give a critical exponent between 0.22 and 0.26 experimentally[13]. Our results that $\beta = 0.22$ therefore clearly indicate 2-d magnetism in TANOL suberate.

The 2-d behavior is also found in the temperature dependence of $\chi_p T$ of TANOL suberate in the paramagnetic state, as shown in Fig. 7. Experimental data are well described with the 2-d FM square lattice model with intralayer coupling $J/k = 0.67$ K as represented by the solid line in Fig. 7, whereas both the 1-d FM Heisenberg model (dotted line) and the 3-d mean-field model, that is, the Curie-Weiss law (dash-dotted line) fail to fit below about 5 K. Addition of very weak interlayer AFM interaction J'/k = -0.02 K to the intralayer FM interaction improves the fit at low temeratures. It is therefore quite likely that TANOL suberate is a 2-d magnet with very weak interlayer interaction.

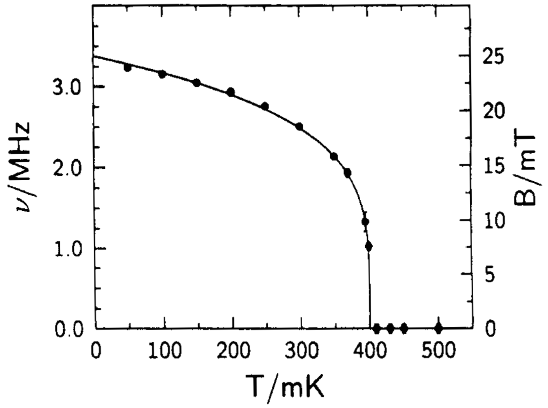

FIGURE 6 Temperature dependence of μSR oscillation frequency ν and internal magnetic field B of TANOL suberate at zero field.

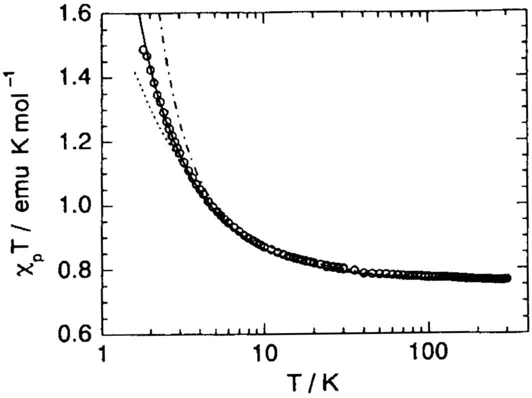

FIGURE 7 Temperature dependence of $\chi_p T$ of TANOL suberate. Dotted, solid and dash-dotted lines represent the data calculated by 1-d, 2-d and 3-d models, respectively.

Acknowledgments

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References

[1] See for example, Proceedings of the preceding Conferences on Molecule-Based Magnets; edited by J.S. Miller and A.J. Epstein, *Mol. Cryst. Liq. Cryst.*, **271–274** (1995) and edited by K. Itoh, J.S. Miller and T. Takui, *Mol. Cryst. Liq. Cryst.*, **305–306** (1997).

[2] T. Sugano and P. Day, *Synth. Metals,*to be published.

[3] S.J. Blundell, P.A. Pattenden, F.L. Pratt, K.H. Chow, W. Hayes and T. Sugano, *Hyperfine Interact.*, **104,** 251 (1997) and references cited therein.

[4] E.F. Ullman, J.H. Osiecki, D.G.B. Boocock and R. Darcy, *J. Am. Chem. Soc.*, **94,** 7049 (1972).

[5] H. Lemaire, A. Rassat and P. Rey, *Bull. Soc. Chim. France,* 886 (1968).

[6] T. Sugano, S.J. Blundell, F.L. Pratt, W. Hayes, H. Uekusa, Y. Ohashi, M. Kurmoo and P. Day, *Mol. Cryst. Liq. Cryst.*, **305,** 435 (1997).

[7] N.C. Schiødt, F.F. de Biani, A. Caneschi and D. Gatteschi, *Inorg. Chim. Acta,* **248,** 139 (1996).

[8] A. Rassat and R. Chiarelli, *Magnetic Molecular Materials* (Kluwer Academic Publishers, Dordrecht, 1991), p. 191.

[9] G. Chouteau and Cl. Veyret-Jeandey, *J. de Phys.*, **47,** 1441 (1981).

[10] A. Benoit, J. Flouquet, B. Gillon and J. Schweizer, *J. Mag. Mag. Mat.*, **31–34,** 1155 (1983).

[11] A. Capiomont, *Acta Cryst. B,* **28,** 2298 (1972).

[12] L.J. de Jongh and A.R. Miedema, *Adv. Phys.*, **23,** 1 (1974).

[13] S.T. Bramwell and P.C.W. Holdsworth, *J. Phys., Condens. Matter,* **5,** L53 (1993).