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Organic heterospin-composite systems based on supramolecular crystal engineering

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Abstract

In this study, a novel crystal engineering approach to organic ferrimagnetics is proposed. As a supramolecular heterospin system, we have designed and synthesized a ternary coordination compound of an anionic nitronyl nitroxide biradical and crown–ether derivatives with a closed-shell or an open-shell substituent. The intra-molecular exchange interaction of the anionic biradical in its sodium salt has been determined to be antiferromagnetic from ESR spectra and magnetic susceptibility measurements. The intra-molecular interaction of the anionic biradical, however, has been found to be ferromagnetic in a salt with the closed-shell Na⁺-crown–ether. A peculiar nonmagnetic (diamagnetic) ground state has been found in a salt of the anionic biradical with the open-shell Na⁺-crown–ether derivative of nitronyl nitroxide radical. According to our previous prediction based on a theoretical model, the occurrence of the nonmagnetic ground state is attributed to a spin frustration effect inherent in organic molecular assemblages. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Organic ferrimagnet; Nitronyl nitroxide; Magnetic susceptibility; Charged biradical; Electron spin resonance; Supramolecular crystal engineering

1. Introduction

The first purely organic crystalline ferromagnet was discovered 10 years ago [1]. Extensive studies have been done on organic molecule-based ferromagnets and other molecular functionality magnetism in recent years [2]. Organic molecule-based magnetism and magnetism have been the focus of current topics in an interdisciplinary area of physics, chemistry, and materials science [2]. Together with organic ferromagnetic substances based on purely ferromagnetic inter-molecular interactions, ferrimagnets have been attracting attention as one of the facile approaches to organic magnets after Buchachenko's proposal for organic ferrimagnetics in 1979 [3]. Genuinely organic ferrimagnets composed of discrete, two kinds of organic open-shell molecules, however, have not been documented yet and they are a challenging issue in materials science.

Ferrimagnetic spin ordering is conventionally regarded as an antiferromagnetic ordering of different spin quantum numbers, e.g., $S = 1$ and $S = 1/2$, giving net and bulk magnetization. This classical picture has been initiated by Néel in his mean field theory [4]. Recently, we have reported theoretical calculations on the ferrimagnetic spin alignment in organic molecule-based assemblages in terms of a spin Hamiltonian [5,6]

$$H = \sum_{i=1}^N [-2J_1 \mathbf{S}_{b1,i} \cdot \mathbf{S}_{b2,i} - 2J_2 (\mathbf{S}_{b2,i} \cdot \mathbf{S}_{m,i} + \mathbf{S}_{m,i} \cdot \mathbf{S}_{b2,i+1}) - 2J'_2 (\mathbf{S}_{b1,i} \cdot \mathbf{S}_{m,i} + \mathbf{S}_{m,i} \cdot \mathbf{S}_{b1,i+1})] \quad (1)$$

The Hamiltonian mimics a one-dimensional molecular assemblage of biradicals with two unpaired electrons $S_{b1} = S_{b2} = 1/2$ and monoradicals with $S_m = 1/2$, as schematically shown in Fig. 1. The biradical spins S_{b1} and S_{b2} are coupled with a neighboring monoradical spin S_m by the antiferromagnetic exchange interactions $J_2 < 0$ and $J'_2 < 0$. In organic open-shell molecules, the spin density is distributed over many atomic sites within the molecule. The intra-molecular exchange interactions

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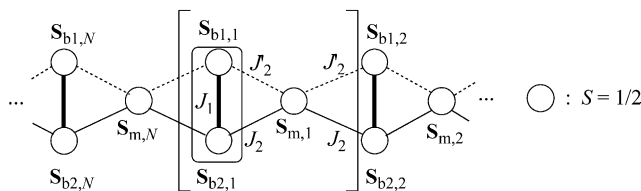


Fig. 1. Schematic representation of the Heisenberg spin Hamiltonian of the generalized ferrimagnetic chain. The circles indicate the $S = 1/2$ spin operators. The lines denote the intra- and inter-molecular interactions J_1 , J_2 , and J_2' .

in stable $S > 1/2$ molecules are not so strong as compared with inter-molecular interactions. In order to consider these features, twofold inter-molecular interactions J_2 and J_2' are introduced in the Hamiltonian [5–9]. The multicentered inter-molecular interactions and the intra-molecular magnetic degree of freedom of spins have been overlooked in traditional magnets composed of transition metal ions with onecentered, intraatomic strong exchange interactions.

When the intra-molecular exchange interaction J_1 of the biradical is ferromagnetic $J_1 > 0$, the molecular assemblage yields a ferrimagnetic ground state with the total spin $S_T = N/2$ (N : the number of repeating units) [5]. Thus, superficially there is no peculiarity in organic molecule-based ferrimagnetic systems. Only a spin contraction of the biradical spin, $\langle (S_{b1} + S_{b2})^2 \rangle < 2$, has been found to occur in the ground state of the biradical-monoradical alternating chain (Fig. 1) [5]. The spin contraction indicates that an $S_b \equiv S_{b1} + S_{b2} = 1$ is not a good quantum number in describing magnetic properties of a ground state triplet biradical embedded in the exchange-coupled heterospin systems.

On the other hand, when the intra-molecular interaction is antiferromagnetic $J_1 < 0$, the alternating molecular chain has been found to have three kinds of ground states; two with seemingly ferrimagnetic spin alignments of the total spin $S_T = N/2$ and one with a spinless (diamagnetic) state [6]. The energy preference of the three states depends on the relative ratios of the intra- and the inter-molecular interactions J_1 , J_2 , and J_2' [6]. In nonquantum terms, biradicals with a singlet ($S = 0$) ground state would seemingly have no contribution to the magnetization at low temperatures, $k_B T < |J_1|$. An $S_b = 0$ is not a good quantum number as well, when a ground state singlet biradical is embedded in the exchange-coupled molecular assemblages. The exotic ground states result from quantum spin frustration inherent in antiparallel couplings in a triangular motif [6], as depicted in Fig. 1.

As a model system for the exotic ferrimagnetism, a ternary organic complex salt has been designed in this study, which is composed of a phenoxide biradical $\mathbf{1}^-$ (Fig. 2), a Na^+ ion, and a crown-ether derivative of nitronyl nitroxide $\mathbf{2a}$ [10]. In the complex salt, cation-

anion Coulombic interactions and the complexation ability of crown-ethers are introduced as a driving force of self-aggregation of the two kinds of open-shell components [11,12]. The neutral precursor of the anion $\mathbf{1}^-$ with a phenol substituent is known to have a triplet ($S = 1$) ground state with a singlet–triplet energy gap of $\Delta E/k_B \sim 10$ K [13]. A conversion of the ground state spin multiplicity from a triplet into a singlet on ionization has been found in the potassium salt of $\mathbf{1}^-$ [14]. The ground state spin multiplicity of the anionic biradical $\mathbf{1}^-$ is thoroughly examined both for a simple salt of $\text{Na}^+\mathbf{1}^-$, and a complex salt composed of $\mathbf{1}^-$ and a closed-shell crown-ether derivative $\mathbf{2b}$, abbreviated as $[\text{Na2b}]^+\mathbf{1}^-$, in frozen solutions and solid states. Possible occurrence of the exotic ferrimagnetic spin alignment in the complex salt $[\text{Na2a}]^+\mathbf{1}^-$ is discussed from magnetic susceptibility measurements.

2. Experimental

The monoradical $\mathbf{2a}$ was synthesized according to the reported method [10]. The ternary coordination compounds $[\text{Na2a}]^+\mathbf{1}^-$ and $[\text{Na2b}]^+\mathbf{1}^-$ were prepared by treating the neutral phenol biradical [13] with sodium *tert*-butoxide or sodium hydride and the crown-ether derivatives $\mathbf{2a}$ and $\mathbf{2b}$ in acetonitrile or tetrahydrofuran solutions under argon atmosphere. Single crystals of $\text{Na}^+\mathbf{1}^-$ and $[\text{Na2a}]^+\mathbf{1}^-$ were obtained by recrystallization from hexane/acetone and diethyl ether/acetone solutions, respectively.

The X-ray diffraction measurements were made on a Rigaku Mercury CCD diffractometer at 173 K with graphite monochromated Mo $K\alpha$ radiation up to $2\theta_{\text{max}} = 55^\circ$. The crystal structure was solved by direct methods and succeeding Fourier syntheses followed by the full-matrix least-squares refinement with the anisotropic approximation for non-hydrogen atoms. Positions of the hydrogen atoms were calculated and included in the final refinement. All the calculations were made using the program package *teXsan* by Molecular Structure Corporation.

The ESR spectra were recorded in toluene solutions with the concentration of 1×10^{-4} mol dm^{-3} using a Bruker X-band spectrometer ESP300 in the temperature range of 3–30 K. The solutions were degassed by a freeze-pump-thaw cycle and sealed in vacuo.

The static paramagnetic susceptibility was measured for randomly oriented polycrystals and diluted samples (10.8%) in PVC (polyvinyl chloride) films by use of a Quantum Design SQUID magnetometer MPMS-XL with an applied field of 0.1 T in the temperature range of 1.9–300 K.

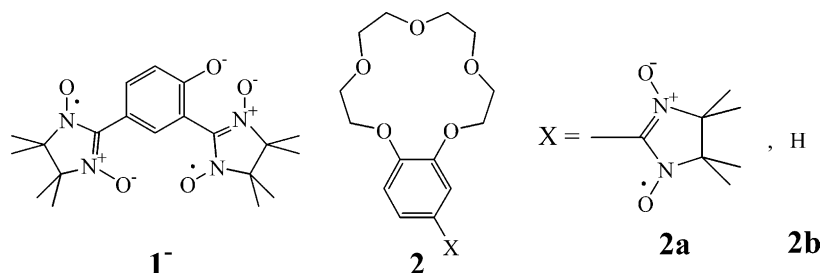


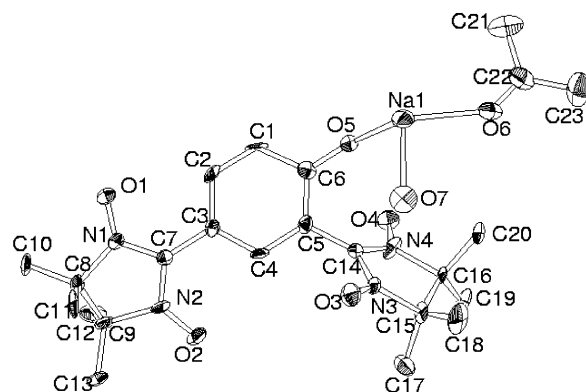
Fig. 2. Building block molecules for supramolecular composite systems.

3. Results and discussion

3.1. Crystal structure and magnetic properties of Na^+1^-

3.1.1. X-ray crystal structure

The crystallographic data for the salt Na^+1^- are listed in Table 1. The molecular structure is shown in Fig. 3 with the atom numbering. The crystal contains one mole of acetone and water molecules as crystal solvents. The oxygen atoms, O6 and O7, of the solvent molecules and the phenoxide oxygen, O5, are coordinated to the sodium ion. The bond lengths between the sodium and the oxygen atoms fall within a typical range of sodium phenoxide derivatives [15]. It is found from differential Fourier syntheses that one or two more oxygen atoms of water are coordinated to the sodium ion [16]. They are, however, disordered, rendering a somewhat unsatisfactory convergence. The residual of $R=0.113$ is attributed to the disorder. The dihedral angles between the best-fit planes of the phenyl ring and the ONCNO groups of the anion 1^- are 20° along C3–C7 and 64° along C5–C14. The dihedral angle of 64° is quite large as compared with those of the neutral phenol precursor [13]. The electrostatic repulsion between the

Fig. 3. Molecular structure of Na^+1^- with 50% thermal ellipsoids.

oxygen of the ONCNO group (O4) and the phenoxide oxygen (O5) probably gives rise to the large dihedral angle, which is likely to weaken the intra-molecular exchange interaction through the π -conjugation in 1^- as compared with those of the neutral precursor [17].

3.1.2. ESR spectra in frozen solutions

The molecular ground state of the anionic biradical 1^- is examined by ESR spectra in diluted glassy solutions of toluene, in which inter-molecular exchange interactions are negligible. In order to avoid saturation effects, the power of the microwave applied in the measurements was kept such that the signal intensity was proportional to the square root of the microwave power. The lineshape of forbidden spectra with $\Delta m_S = \pm 2$ remained unchanged in the whole range of temperature examined. Thus, the peak-to-peak height of the forbidden transitions is measured as signal intensity I_{ESR} . The temperature dependence of the signal intensity is displayed as a function of temperature in Fig. 4. The observed temperature dependence of intensity was analyzed assuming the thermal equilibrium between the singlet ($S=0$) and the triplet ($S=1$) states,

$$I_{\text{ESR}} = \frac{1}{T} \times \frac{1}{3 + \exp(-\Delta E/k_{\text{B}}T)} \quad (2)$$

where k_{B} is Boltzmann constant and ΔE denotes the singlet–triplet energy gap in the biradical molecule,

$$\Delta E = E(S=0) - E(S=1) \quad (3)$$

Table 1
Crystallographic data of the salt Na^+1^-

Formula	$\text{C}_{23}\text{H}_{35}\text{N}_4\text{NaO}_7$ ($\text{C}_{20}\text{H}_{27}\text{N}_4\text{NaO}_5 \cdot \text{C}_3\text{H}_6\text{O} \cdot \text{H}_2\text{O}$)
Formula weight	502.54
Crystal dimensions (mm)	$0.3 \times 0.3 \times 0.1$
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a (Å)	7.540(4)
b (Å)	10.817(6)
c (Å)	32.08(2)
V (Å ³)	2616(2)
Z	4
T (K)	173
μ (Mo K α) (cm ⁻¹)	1.03
No. of unique reflections	3377
R_1^a	0.113
R_w, R_w^a	0.239, 0.234

^a The function minimized is $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. The residuals are defined as $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R = \sum (F_o^2 - F_c^2) / \sum F_o^2$, $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

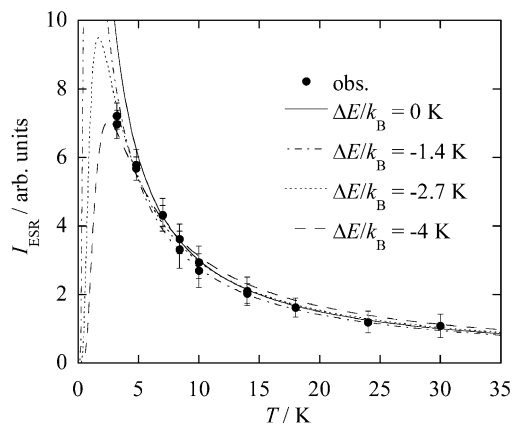


Fig. 4. Temperature dependence of the intensity I_{ESR} for the forbidden ESR transitions from the frozen toluene solution of $\text{Na}^+\mathbf{1}^-$. The circles denote the observed peak-to-peak heights. The solid, dash-dotted, dotted, and short-dashed lines represent the calculated intensity using Eq. (2) with the singlet–triplet energy gap of $\Delta E/k_{\text{B}} = 0, -1.4, -2.7,$ and 4.0 K, respectively.

The observed temperature dependence for the biradical salt $\text{Na}^+\mathbf{1}^-$ was reproduced by assuming the singlet ground state with $\Delta E/k_{\text{B}} = -2.7 \pm 1.3$ K. The molecular ground state of the anionic biradical $\mathbf{1}^-$ in the salt $\text{Na}^+\mathbf{1}^-$ is found to change from triplet into singlet on ionization. The conversion of the ground state spin multiplicity on ionization has been confirmed for both the potassium [14] and the sodium salts.

3.1.3. Magnetic susceptibility in a solid state

The temperature dependence of paramagnetic susceptibility χ_{p} for the randomly oriented polycrystalline samples of the salt $\text{Na}^+\mathbf{1}^-$ is shown in Fig. 5 in the $\chi_{\text{p}}T$ vs. T plots. The $\chi_{\text{p}}T$ value of $0.75 \text{ emu K mol}^{-1}$ at 300 K is consistent with 2 moles of $S = 1/2$ spins with the g -factor of $g = 2.0$. The product $\chi_{\text{p}}T$ exhibits a monotonic decrease on lowering the temperature, indicating that the dominant interaction in the anionic biradical $\mathbf{1}^-$ in the salt is antiferromagnetic. An estimate of the intra-

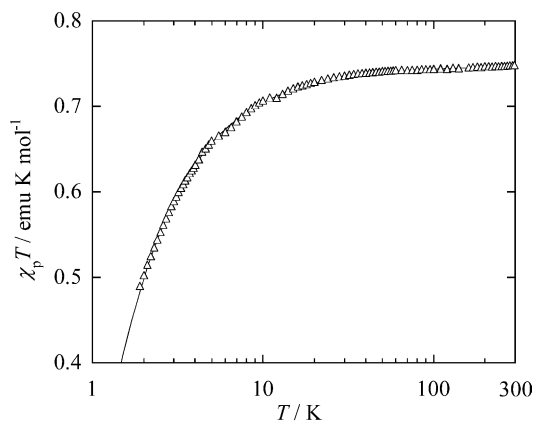


Fig. 5. Magnetic susceptibility χ_{p} of the powder samples of $\text{Na}^+\mathbf{1}^-$ in the $\chi_{\text{p}}T$ vs. T plots. The solid line is calculated from Eq. (4) with the parameters $\Delta E/k_{\text{B}} = -2.2$ K, $\theta = 0$, $\alpha = 0.99$, and $g = 2.007$.

and inter-molecular exchange interactions is acquired using the modified Bleaney–Bowers model [18]

$$\chi_{\text{p}} = \frac{2\alpha N_{\text{A}} g^2 \mu_{\text{B}}^2}{k_{\text{B}}(T - \theta)} \times \frac{1}{3 + \exp(-\Delta E/k_{\text{B}})} \quad (4)$$

In Eq. (4), the intra-molecular singlet–triplet energy gap is denoted by ΔE as defined in Eq. (3). The parameter θ represents the inter-molecular interactions in the mean-field approximation. The purity of the sample is designated by α . N_{A} is Avogadro constant. The observed $\chi_{\text{p}}T$ is reproduced, as depicted by the solid curve in Fig. 5, by Eq. (4) with $\Delta E/k_{\text{B}} = -2.2 \pm 0.2$ K, $\alpha = 0.99$, and the g -factor of $g = 2.007$ taken from the observed isotropic ESR spectra in a solution. The inter-molecular interaction is vanishing, $\theta = 0$. Nonzero θ values did not improve the fitting. An apparent discrimination is not allowed between inter- and intra-molecular interactions from the susceptibility measurements in the solid state. The energy gap ΔE from the susceptibility is, however, consistent with that from the ESR experiments in the frozen solution described above, confirming the energy preference of the singlet ($S = 0$) state for the anionic biradical $\mathbf{1}^-$.

3.2. Magnetic properties of the crown-ether-based salt $[\text{Na}2\mathbf{b}]^+\mathbf{1}^-$

The magnetic susceptibility χ_{p} of the complex salt of $[\text{Na}2\mathbf{b}]^+\mathbf{1}^-$, composed of the closed-shell complex cation $[\text{Na}2\mathbf{b}]^+$ and the anionic biradical $\mathbf{1}^-$, is measured both in a neat crystalline state and in a diluted solid state in order to examine the ground state spin multiplicity of $\mathbf{1}^-$ after complexation. The temperature dependence of the product $\chi_{\text{p}}T$ for the neat microcrystals is shown in Fig. 6. The $\chi_{\text{p}}T$ value increases gradually from $0.75 \text{ emu K mol}^{-1}$ at 300 K as the temperature is lowered and rapidly decreases below 10 K. The observed temperature dependence of $\chi_{\text{p}}T$ indicates that the ground state of the anionic biradical in the complex salt $[\text{Na}2\mathbf{b}]^+\mathbf{1}^-$ is triplet ($S = 1$). The curve in Fig. 6 designates our best-fit in terms of the singlet–triplet equilibrium model of Eq. (4) with the parameters $\Delta E/k_{\text{B}} = 6.5 \pm 0.5$ K, $\theta = -1.4 \pm 0.1$ K, $g = 2.007$, and $\alpha = 0.99$. Since the amplitude of the parameter θ is close to $\Delta E/k_{\text{B}}$, the parameters obtained from the mean-field approximation give only a measure of the intra- and the inter-molecular interactions. It is, however, found that the ground state triplet, i.e., the intra-molecular ferromagnetic interaction, in the biradical molecule is recovered, which has been lost in the simple sodium phenolate salt $\text{Na}^+\mathbf{1}^-$.

Further proof of the triplet ground state for the biradical in the complex salt $[\text{Na}2\mathbf{b}]^+\mathbf{1}^-$ is given by susceptibility measurements on diluted samples (10.8%)

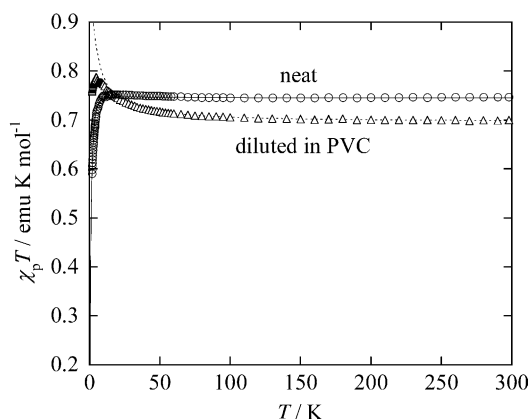


Fig. 6. Magnetic susceptibility χ_p of the complex salt $[\text{Na2b}]^+1^-$ in the $\chi_p T$ vs. T plots. The circles represent the $\chi_p T$ values of the neat crystalline samples. The solid line is calculated from Eq. (4) with the parameters $\Delta E/k_B = 6.5$ K, $\theta = -1.4$ K, $\alpha = 0.99$, and $g = 2.007$. The triangles denote the $\chi_p T$ values of the diluted samples in the PVC film. The dashed line calculated with $\Delta E/k_B = 6.5$ K, $\theta = 0$, $g = 2.007$, and $\alpha = 0.93$.

in the PVC films, in which inter-molecular interactions should be diminished. The $\chi_p T$ values of the PVC film increase more steeply on lowering the temperature and the maximum in $\chi_p T$ appears at a lower temperature than those of the neat crystals. The observed temperature dependence of $\chi_p T$ values down to 10 K is reproduced by the model of Eq. (4) with the parameters $\Delta E/k_B = 6.5 \pm 0.5$ K, $\theta = 0$, $g = 2.007$, and $\alpha = 0.93$. Although the temperature dependence of the $\chi_p T$ values around the maximum has not been reproduced by Eq. (4) with any nonzero $\theta < 0$, the appearance of the maximum indicates that the inter-molecular interactions are not completely suppressed in the diluted samples (10.8%) of the PVC film, which is probably due to incomplete dispersion of the molecules in the polymer. The triplet ground state with the energy gap of $\Delta E/k_B = 6.5$ K is, however, confirmed from the susceptibility measurements of the diluted samples. The energy preference of the ground state spin multiplicity for the anionic biradical 1^- is sensitive to the environment such as the counter cations and the medium.

3.3. Magnetic properties of the crown-ether-based salt $[\text{Na2a}]^+1^-$

From a preliminary X-ray crystal structure analysis, the complex salt $[\text{Na2a}]^+1^-$, in which both the cationic and the anionic components have unpaired electrons, is found to belong to the triclinic system with space group $P\bar{1}$, $a = 11.36$ Å, $b = 12.20$ Å, $c = 16.64$ Å, $\alpha = 78.00^\circ$, $\beta = 83.86^\circ$, $\gamma = 85.80^\circ$ and $Z = 2$.

The temperature dependence of magnetic susceptibility of $[\text{Na2a}]^+1^-$ is shown in Fig. 7. The $\chi_p T$ value of 1.04 emu K mol $^{-1}$ at 300 K is smaller than that

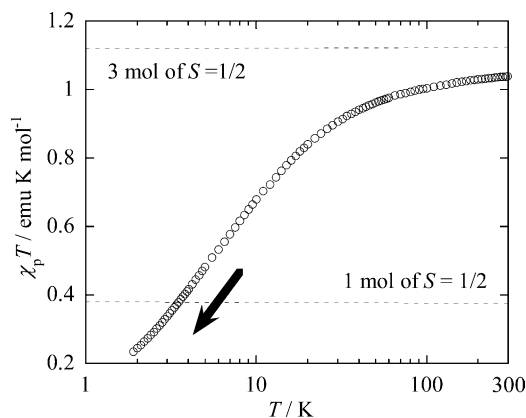


Fig. 7. Magnetic susceptibility χ_p of the complex salt $[\text{Na2a}]^+1^-$ in the $\chi_p T$ vs. T plots. The horizontal lines denote the $\chi_p T$ values for 1 and 3 moles of noninteracting $S = 1/2$ spins with $g = 2.0$.

expected for 3 moles of $S = 1/2$ spins with the g -factor of 2.0. This finding indicates that the intra- or inter-molecular exchange interaction of $[\text{Na2a}]^+1^-$ in the crystalline solid state is not negligible as compared with the thermal energy $k_B T$ of 300 K. The $\chi_p T$ value decreases on lowering the temperature, indicating that antiferromagnetic interactions predominate in the solid state. It should be noted that the $\chi_p T$ value is lower than 0.375 emu K mol $^{-1}$ at low temperatures. Crossing the $\chi_p T$ value expected for 1 mole of $S = 1/2$ spin on lowering the temperature clearly indicates the occurrence of the nonmagnetic (diamagnetic) ground state for $[\text{Na2a}]^+1^-$.

In nonquantum terms, where we neglect the frustration effects inherent in the multicentered nature of the Hamiltonian in Fig. 1, the alternating aggregation of biradicals and monoradicals with three $S = 1/2$ spins in a repeating unit never affords any nonmagnetic ground state. In this context, if the intra-molecular interaction J_1 in the complex $[\text{Na2a}]^+1^-$ is antiferromagnetic and the alternating molecular aggregation of the cationic monoradical $[\text{Na2a}]^+$ and 1^- is made in the crystal, the nonmagnetic ground state found in the susceptibility measurement is attributable to one of the exotic ground spin states, which have been predicted in the theoretical model (Fig. 1) of the generalized ferrimagnetic spin assemblage [6]. Another possible explanation of the nonmagnetic ground state is found for the ferromagnetic intra-molecular interaction J_1 in $[\text{Na2a}]^+1^-$: if J_1 is ferromagnetic, the alternating molecular chains have ordinary ferrimagnetic short-range ordering and an antiferromagnetic coupling between the chains should afford the nonmagnetic ground state. The crystal structure analysis of $[\text{Na2a}]^+1^-$ gives a clue and is in progress in order to determine the alternating molecular packing of the anionic biradical and the monoradical molecules.

4. Conclusion

The ESR spectra of the frozen solutions and the magnetic susceptibility on both the neat crystals and the diluted samples have shown that the ground state spin multiplicity of the anionic biradical $\mathbf{1}^-$ is sensitive to the chemical environment. As a novel supramolecular crystal engineering approach for designing two-component assemblages of open-shell molecules, the complex salt $[\mathbf{Na2a}]^+\mathbf{1}^-$ has been synthesized. From the magnetic susceptibility of $[\mathbf{Na2a}]^+\mathbf{1}^-$ in the crystalline solid state, the possible occurrence of an exotic spinless ground state has been demonstrated. The occurrence of the spinless ground state arises from the internal magnetic degree of freedom in the organic biradical and the multicentered inter-molecular interactions, both of which are neglected in conventional atom-based magnetism. The internal magnetic degree of freedom and the multicentered nature are essential in organic molecular-based magnetism.

5. Supplementary material

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre. Any request to the CCDC for this material should quote the full literature citation and the deposition number CCDC No.: 194331. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk/>).

Acknowledgements

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