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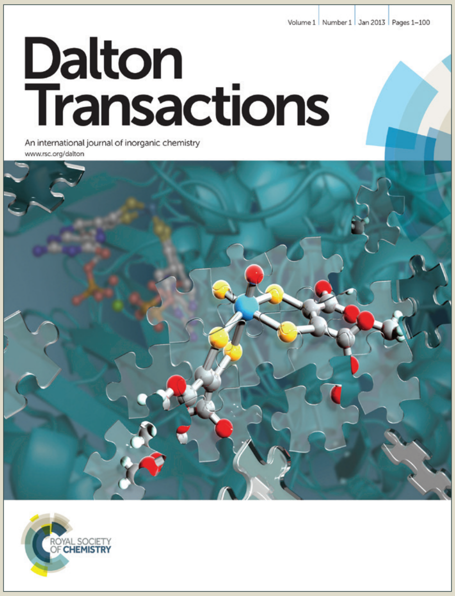

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Ferromagnetic Ordering in the Organic Radical Cation Salt BBDTA•Au(CN)$_2$ at 8.2 K

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Wataru Fujita[a]

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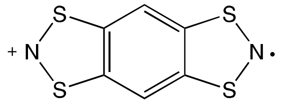
An organic radical cation salt, BBDTA•Au(CN)$_2$, with a slipped π-stacking columnar structure and intercolumnar short contacts, shows ferromagnetic ordering at 8.2 K, the highest reported temperature among the BBDTA$^+$ cation salts.

Organic radicals with sulfur-nitrogen heterocyclic rings, the so-called heterocyclic thiazyl radicals, play an important role in the development of molecule-based functional materials.[1] In particular, heterocyclic thiazyl radical derivatives are magnetically ordered materials based on organic molecules with spontaneous magnetization. In 1996, Rawson et al. reported canted antiferromagnetism with spontaneous magnetization below 36 K in the heterocyclic thiazyl radical β-*p*-NCC$_6$H$_4$CNSSN•.[2] This discovery was surprising to researchers studying organic magnets, because until then ferromagnetic transition temperatures in organic radical magnets were below 1 K,[3] except for the charge transfer complex C$_{60}$•TDAE.[4] Subsequently, bulk ferromagnetic ordering below 7.0 K in the radical cation salt γ-BBDTA•GaCl$_4$, which is a monocation salt of benzo[1,2-d:4,5-d']bis[1,3,2]dithiazole (BBDTA, Scheme 1), was found in 2002.[5] The transition temperature was above the temperature of liquid helium (4.2 K), which is rare for magnetic materials. In 2008, Oakley et al. reported bis-1,2,3-diselenazolyl radical derivatives with ferromagnetism below 17 K and canted antiferromagnetism below 27 K.[6] Furthermore, heterocyclic thiazyl radicals show magnetic bistability, photo-induced phase change, unique pressure dependence, electric conductivity, and negative resistance phenomena.[7]



Scheme 1 Structural formula of BBDTA$^+$ cation.

This report focuses on the radical cation salt of BBDTA$^+$. The BBDTA$^+$ radical was first reported by Wolmershäuser et al. in 1988 as the cation salt BBDTA•FeCl$_4$•CH$_3$CN,[8] in which BBTDA$^+$ forms a face-to-face dimerized structure and has an antiferromagnetic phase transition originating from the counter anion Fe(III)Cl$_4^-$ (S = 5/2) at 6.6 K. In a previous report, the crystal structure and magnetic

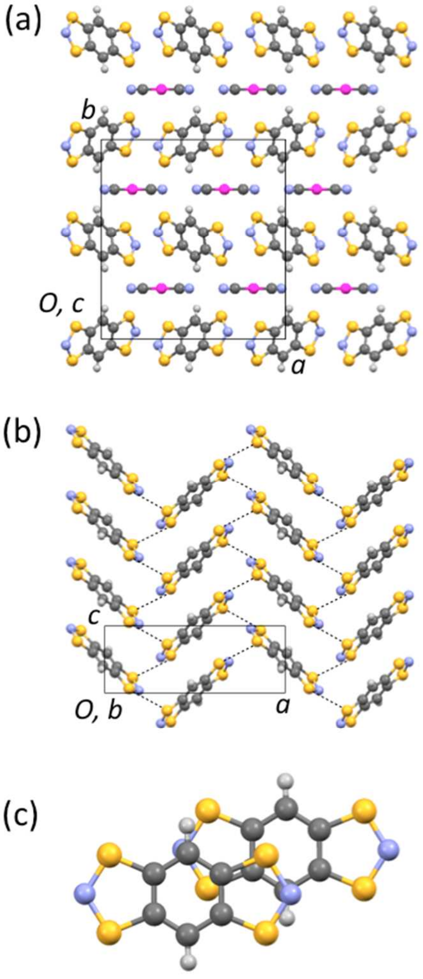


Fig. 1 Crystal structure of BBDTA•Au(CN)$_2$. (a) View along the *c* axis. (b) Molecular alignment of BBDTA$^+$ in the organic cation layer. (c) Relative orientation of BBDTA$^+$ cations in the regular alignment.

properties of BBDTA$^+$ cation radical salts were systematically investigated with various anions, mainly halogens or halogenometallate ions, to determine the antiferromagnetic ordering, metamagnetic phase transition, and spin-Peierls transition.[9] Additionally, ferrimagnetic states in salts with paramagnetic halogenometallate ions were realized.[10]

The observed diversity in the magnetic behavior of BBDTA$^+$ cation salts originates from the various molecular alignments of BBDTA$^+$ cations in the crystalline states, which may be governed by effects such as Coulomb interactions between ions, interatomic S•••N and/or S•••S contacts between neighboring radical cations, and halogen bonds between radical cations and counter anions.

In this study, the preparation, crystal structure, and magnetic properties were determined for BBDTA•Au(CN)$_2$, a radical cation salt with dicyanoaurate ions, which are linear with no halogen atoms. BBDTA•Au(CN)$_2$ shows the highest ferromagnetic ordering temperature of the reported BBDTA$^+$ cation salts. The origin of ferromagnetic interactions between BBDTA$^+$ cations in the salt, estimated from molecular orbital calculations based on atomic coordinates obtained from the crystal data, is also discussed.

BBDTA•Au(CN)$_2$ was prepared by the slow diffusion of BBDTA•FeCl$_4$[8,11] and tetra-*n*-butylammonium dicyanoaurate in dry acetonitrile in a test tube at room temperature. Black needle-like crystals were formed after 1 day. The salt was stable in air and insoluble in organic solvents such as acetone, acetonitrile, toluene, and dichloromethane. In BBDTA$^+$ salts, polymorphs are often found. For instance, there are three polymorphs in the GaCl$_4$ salt, namely, two diamagnetic phases and one ferromagnetic phase.[5] In this case, BBDTA•Au(CN)$_2$ has only a single phase.

BBDTA•Au(CN)$_2$ crystallized in the orthorhombic *Pnma* space group, wherein half unit of the cation and one unit of the anion were crystallographically asymmetric. The crystal structure of BBDTA•Au(CN)$_2$ comprised stacks of alternating BBDTA$^+$-assembled layers and diamagnetic Au(CN)$_2^-$-assembled layers along the *b*-axis, as shown in Fig. 1a. Figure 1b depicts the molecular alignment of the radical cations in the BBDTA$^+$ layer in the *ac*-plane. BBDTA$^+$ cations formed a columnar structure with a regular alignment along the *c*-axis. The cations did not directly eclipse the molecular planes but were slipped, as shown in Fig. 1c. This may be due to electric repulsions between the cationic charges. There were no short intermolecular contacts between the cations in the column. In this situation, it is thought that the overlaps of the magnetic orbitals in neighboring cations may be small. Meanwhile, interatomic S•••S distance of 3.566(3) Å was present between the columns, which are represented by broken lines, as shown in Fig. 1b. This is shorter than the distance of the van der Waals contact between sulfur atoms, ca. 3.6 Å. In this salt, BBDTA$^+$ cations construct a magnetic network of one-dimensional regular chains along the *c*-axis and interchain magnetic interactions via interatomic S•••S contacts in the BBDTA$^+$-assembled layer.

BBDTA•Au(CN)$_2$ has a different type of molecular alignment of BBDTA$^+$ cations from those of BBDTA$^+$ salts with halogenometallate anions.[9,10] There are many short interatomic S•••Au, S•••C (cyano group) and S•••N (cyano group) contacts between BBDTA$^+$ and Au(CN)$_2^-$. Such short contacts between BBDTA$^+$ and Au(CN)$_2^-$, coulombic interactions molecular packing and so on, may play an important role for the molecular alignment of BBDTA$^+$ cations in the BBDTA$^+$ layer.

DC magnetic measurements of BBDTA•Au(CN)$_2$ were carried out at 500 Oe using a SQUID magnetometer; the results are shown in Fig. 2. BBDTA•Au(CN)$_2$ was adopted as the molar unit. The diamagnetic susceptibility was estimated to be $\chi_{\mathrm{dia}} = -0.000409$ emu mol^{-1} by assuming that the magnetic properties of this material obey the Curie-Weiss law[12] at high temperatures. Figure 2a shows the $\chi_{\mathrm{p}}T$ vs. T plot for this material. The $\chi_{\mathrm{p}}T$ value at 300 K was 0.422 emu K mol^{-1}, which is larger than the theoretical value of 0.375 emu K mol^{-1},[12] estimated by assuming that no magnetic interactions exist between 1 mol of $S = 1/2$ ($g = 2.00$) spins. This discrepancy indicates that intermolecular ferromagnetic interactions between the radical cations are present. The g value of a powdered sample BBDTA•Au(CN)$_2$ was estimated to be 2.0083 from ESR spectroscopy. Data in the range 250–300 K were fit according to the Curie-Weiss law, with $C = 0.125g^2S(S+1) = 0.378$ emu K mol^{-1} (fixed) and $\theta = +14.5$ K, where C and θ are the Curie and Weiss constants, respectively. As the temperature decreased from 300 K, $\chi_{\mathrm{p}}T$ increased. Below 10 K, $\chi_{\mathrm{p}}T$ rapidly increased and became 13.2 emu mol^{-1} at 7 K.

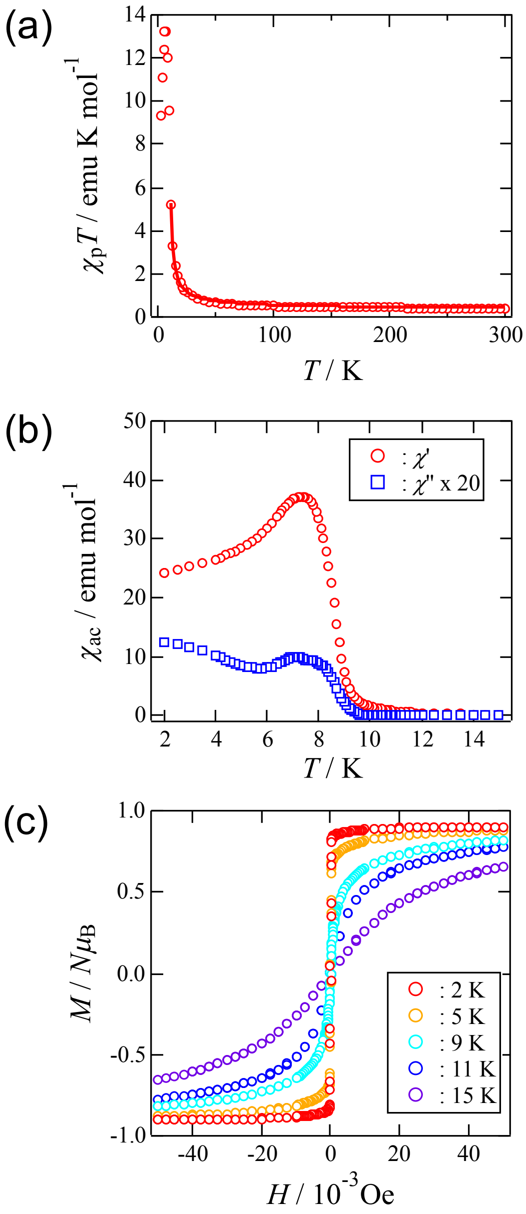


Fig. 2 Magnetic properties of BBDTA•Au(CN)$_2$. (a) $\chi_{\mathrm{p}}T$ vs. T plot. (b) χ_{ac} vs. T plots for the real (χ_{ac}') and imaginary (χ_{ac}'') parts of the magnetic susceptibility. (c) M–H curves at varying temperatures.

The magnetic behavior of this material can be interpreted in terms of the ferromagnetic regular chain model using the Hamiltonian in eq 1, where J_{intra} is the intrachain magnetic coupling constant between neighboring magnetic molecules i and j,

$$H = -2J_{\text{intra}} \sum S_i \cdot S_j \quad (1).$$

The analytical expression for the paramagnetic susceptibility $\chi_{1\text{D}}$ of the S = 1/2 1D Heisenberg ferromagnetic chain model[13] is given as,

$$\chi_{1\text{D}} = \frac{C}{T}\left(\frac{1+a_1 \cdot K + a_2 \cdot K^2 + a_3 \cdot K^3 + a_4 \cdot K^4 + a_5 \cdot K^5}{1+a_6 \cdot K + a_7 \cdot K^2 + a_8 \cdot K^3 + a_9 \cdot K^4}\right)^{2/3} \quad (2),$$

where C (the Curie constant) = $Ng^2\mu_B^2/(4k_B)$, $K = J_{\text{intra}}/(2k_BT)$, a_1 = 5.797991, a_2 = 16.902653, a_3 = 29.376885, a_4 = 29.832959, a_5 = 14.036918, a_6 = 2.7979916, a_7 = 7.0086780, a_8 = 8.6538644, a_9 = 4.5743114. N, g, μ_B, and k_B are the Avogadro's number, the coordination number, the g factor, the Bohr magneton, and the Boltzmann constant, respectively.

The interlayer magnetic interaction J_{inter} in the paramagnetic susceptibility, χ_p, of **1** then can be deduced by using a simple mean field approximation: [14]

$$\chi_p = \frac{\chi_{1\text{D}}}{1-\left(\frac{2zJ_{\text{inter}}}{g^2\mu_B^2 N}\right)\chi_{1\text{D}}} \quad (3),$$

where z is the coordination number. The solid curve in Fig. 2(a) is the best fit with g = 2.0083 (fixed), J_{intra}/k_B = +46 K, and zJ_{inter}/k_B = +1.2 K.

In order to investigate the low-temperature magnetic behavior of this material, AC magnetic susceptibility measurements were carried out. Figure 2b shows the temperature dependence of real χ_{ac}' and imaginary χ_{ac}'' parts of the AC susceptibility under an AC field strength of 5 Oe (100 Hz) and DC field strength of 0 Oe. χ_{ac}' reached a peak at 7.5 K and χ_{ac}'' also increased in the same range, but was consistently zero above 10 K. This suggests the appearance of a ferromagnetic domain below 10 K.[15] Figure 2c shows the M–H curve of this material at various temperatures. Above 10 K, the magnetization value increased gradually with an increase in the magnetic field. The magnetization curve increased more rapidly under lower temperatures. At 2 K, the magnetization value was almost saturated at 300 Oe. The value of magnetization at 50,000 Oe was 0.900 $N\mu_B$, which is close to the theoretical value for the ferromagnetic ordered state of 1 mol of S = 1/2 spin species.[12] Thus, the low-temperature magnetic data indicate ferromagnetic ordering around 10 K. A negligibly small hysteresis loop with a width less than 10 Oe was observed, indicating that the obtained material is a soft magnet.

The temperature dependence of the heat capacity C_p of BBDTA•Au(CN)$_2$ was studied for the needle-like crystals over the temperature range 2–100 K; the results are depicted in Fig. 3. The heat capacity exhibits an anomaly at 8.2 K, supporting the occurrence of magnetic ordering at the peak temperature. The total magnetic entropy was evaluated to be 4.63 J K^{-1} mol^{-1} by integrating the C_p/T values with respect to T. This value is 80.4 % of the expected value of the magnetic entropy for 1 mol of S = 1/2 spins (Rln 2 = 5.76 J K^{-1} mol^{-1}).[16]

The exchange coupling constants of intermolecular ferromagnetic interactions in assorted organic radical magnetic materials and BBDTA•Au(CN)$_2$ are summarized in Table 1. The material used in this study has stronger ferromagnetic interactions than those of other reported organic radical magnetic materials. The ferromagnetic interaction in this material is about twice as large as that of the highest organic ferromagnet. Additionally, its ferromagnetic ordering temperature is relatively high due to the simple molecular structure of BBDTA$^+$ and lack of bulky substitution groups on the periphery of the π-conjugated system, which aids the formation of short intermolecular distances. However, many neutral sulfur-nitrogen radicals with no substitution groups form dimers with large intermolecular π-overlaps and have a diamagnetic ground state. In BBDTA$^+$, intermolecular columbic repulsions arising from the positive charges on the radical cations may prevent large intermolecular π-overlaps.

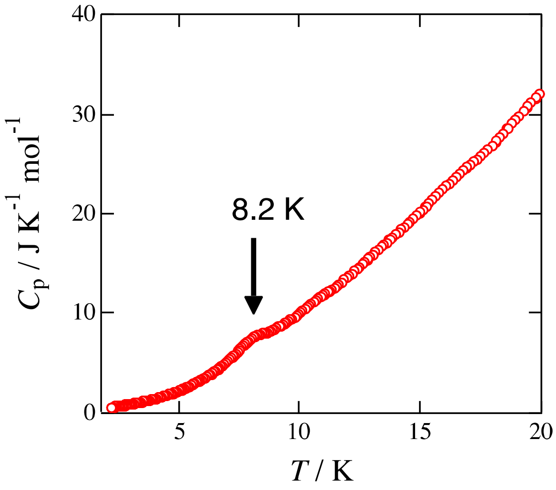


Fig. 3 Temperature dependence of heat capacity C_p for BBDTA•Au(CN)$_2$.

Table 1. Magnetic parameters and magnetic ground states of assorted organic radicals with intermolecular ferromagnetic interactions.

Radicals	Jk_B^{-1}/K	T_c/K	Ground State	Ref.
Galvinoxyl	+4.4	81[a]	Diamagnet	17
β-*p*-NPNN	+4.3	0.65	Ferromagnet	18
2,6-DFPImNN	+66	–	Paramagnet[b]	19
C_{60}•TDAE	~ 0[c]	16.1	Ferromagnet	4
$(NH_4)_2$•tdapO_2•I	+24	–	Paramagnet[c]	20
$C_6H_4N_3S_4$	+8.9	5[d]	Metamagnet	21
$C_7H_5ClN_3Se_4$	+22.9[c]	17	Ferromagnet	6
γ-BBDTA•$GaCl_4$	+16.5	7.0	Ferromagnet	5
BBDTA•InI_4	+12.8	11.3[d]	Metamagnet	10
BBDTA•Au(CN)$_2$	+46, +1.2	8.2	Ferromagnet	This work

[a]Paramagnetic-to-diamagnetic phase transition, [b]Down to 2 K, [c]Weiss Constant, [d]Metamagnetic phase transition.

In conclusion, this report detailed the synthesis and crystal structure of the organic radical cation BBDTA•Au(CN)$_2$ and compared its magnetic properties with those of other organic radical magnetic materials. Ferromagnetic ordering was observed at 8.2 K, which is the highest reported ferromagnetic ordering temperature of any BBDTA$^+$ cation salt. This material also showed the largest ferromagnetic interaction of the reported organic ferromagnets. The results also show that to construct a ferromagnet with a higher transition temperature, it is necessary to enhance the intra- and interchain magnetic interactions. Controlling the molecular alignment through a combination of organic radical cations, appropriate anions, and/or substitution of sulfur atoms in the sulfur-nitrogen radicals to heavier atoms[6,22] such as selenium or tellurium may beneficially alter the transition temperature.

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Notes and references

[a] Department of Information and Biological Sciences, Graduate School of Natural Sciences, Nagoya City University. Yamanohata 1, Mizuho-cho, Mizuho-ku, Nagoya 467-8501, Japan. E-mail: fujitaw@nsc.nagoya-cu.ac.jp; Tel: 81-52-872-5856.

† Electronic Supplementary Information (ESI) available: crystal structure analyses, molecular orbital calculations, magnetic measurements and analyses, heat capacity measurements. CCDC1017180. See DOI: 10.1039/c000000x/

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