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# Observation of an unusual hysteretic magnetic transition in a heteroleptic nickel-bis-1,2-dithiolene compound

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## ABSTRACT

A heteroleptic nickel-bis-1,2-dithiolene ion-pair complex, [BzQI][Ni(dmit)(mnt)] (where BzQI<sup>+</sup> = 1-(ben-zyl)quinolinium; dmit<sup>2-</sup> = 2-thioxo-1,3-dithiole-4,5-dithiolate, mnt<sup>2-</sup> = maleonitriledithiolate), was synthesized and characterized structurally, which exhibited novel magnetic bistability. The compound crystallized in triclinic system with space group P-1. The anions and cations form alternating layered alignments, and the anionic layer is built by the irregularly heteroleptic [Ni(dmit)(mnt)]<sup>-</sup> chains, where the neighboring anions are connected via lateral-to-lateral S...S contacts of dmit<sup>2-</sup> ligands. The temperature dependences of magnetic susceptibility follow the S =  $\frac{1}{2}$  Heisenberg alternating linear-chain model in high-temperature phase and Curie–Weiss law in low-temperature phase.

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Molecular materials with magnetic bistability have aroused a great deal of attention owing to their potential applications in magneto-thermal switching, information storage, and other molecular electronic devices [1–3]. Up to date, various molecules with magnetic bistability, in which the most well-known example is transition metal spin–crossover (SC) complexes [4–9], including charge transfer (CT) complexes [10,11], valence ordering compounds [12,13], and pure organic radical compounds [14–16], have been developed.

As conducting and magnetic materials as well nonlinear optical materials, metal-bis-1, 2-dithiolene ion–pair complexes have been actively studied for a long time [17–21]. Experimental and theoretical investigations disclosed that the unusual physical properties in such ion–pair complexes result from the intermolecular interactions of metal-bis-1,2-dithiolate anions, which are strongly affected by the structural features of both dithiolene ligand and countercation [22–28]. It is favorable for metal-bis-1,2-dithiolate anions, owing to the planar structure and delocalized negative charge. Especially, for the sulfur-rich dithiolene, such as 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit<sup>2–</sup>), the lateral-to-lateral and head to tail S...S contacts as well cofacial stacking between metal-bis-1,2-dithiolene anions generally align the anions in the form of ladders or layers.

In our previous studies, the flexible A-shaped benzylpyridinium derivatives  $(BzPy^+)$  were chosen as the countercation of  $S = \frac{1}{2}$   $[Ni(mnt)_2]^-$  anion  $(mnt^{2-} = maleonitriledithiolate)$ , and a series of

spin-Peierls-type ion–pair complexes [BzPy][Ni(mnt)<sub>2</sub>] were synthesized, in which the spin-Peierls-type magnetic transition temperature can be finely tuned via systematically modifying the nature of substituents in the benzylpyridinium derivative [29]. Furthermore, replacement of the anion mnt<sup>2–</sup> in [BzPy][Ni(mnt)<sub>2</sub>] with sulfurrich dmit<sup>2–</sup> produced one-dimensional (1-D) laddered spin-Peierls compounds [27] and two-dimensional (2-D) bi-layered magnetic bistability compounds [28].

To investigate the effect of the structural feature of dithiolene ligand on the stacking structure of metal-bis-1,2-dithiolene anions and magnetic property of the corresponding ion-pair complex, we are focusing on the study of correlation of the structure and magnetic behavior for the heteroleptic metal-bis-1,2-dithiolene spin systems of [BzPy][Ni(dmit)(mnt)]. Herein we report the crystal structure and magnetic property of a heteroleptic nickel-bis-1,2-dithiolene complex, [BzQl][Ni(dmit)(mnt)] (1), which exhibits an unusual thermal hysteresis loop in the temperature dependent magnetic susceptibility.

Compound 1-benzylquinolinium bromide ([BzQI]Br) was prepared using a similar process for preparation of [BzPy]Br [30] and  $(n-Bu_4N)[Ni(dmit)(mnt)]$  were synthesized following the published procedure [31]. Complex **1** was prepared by means of a metathetical reaction [32].

Heteroleptic nickel-bis-1,2-dithiolene complex **1** crystallizes in the triclinic space group P-1 [33]. As shown in Fig. 1a, its asymmetric unit contains one  $[Ni(dmit)(mnt)]^-$  anion and one BzQl<sup>+</sup> cation. The  $[Ni(dmit)(mnt)]^-$  anion adopts a planar geometry with a dihedral angle of 6.4° between the mean molecular planes of dmit<sup>2–</sup> and mnt<sup>2–</sup> ligands. The Ni–S bond distances range from 2.152 to 2.174 Å, and the S–Ni–S bite angles are 92.74(5)° and 92.94(5)°,

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**Fig. 1.** (a) ORTEP drawing with 30% thermal ellipsoids probability and (b) packing diagram showing the alternating layered structures of anions and cations as well as the anionic layer built from the anionic chains for **1**.

both of which are comparable to those in reported  $(n-Bu_4N)$ [Ni(dmit) (mnt)] [31]. The BzQl<sup>+</sup> cation exhibits a non-planar conformation with normal bond lengths and bond angles. The characteristic dihedral angles are 46.9° and 67.7° between the referred plane N3–C17–C18 and phenyl ring as well as quinolyl ring; 83.9° between the quinolyl and the phenyl fragments. Two mean molecule planes of dithiolene ligands in the anion moiety are approximately parallel to quinolyl ring in the cation moiety with a dihedral angle of 7.9° between dmit<sup>2–</sup> ligand and quinolyl ring versus 2.6° between mnt<sup>2–</sup> ligand and quinolyl ring.

As displayed in Fig. 1b, the anions and cations form an alternating anion and cation layered arrangements and the molecular layers are parallel to the crystallographic (101) plane. It is noted that the magnetic anion layer is consisted of the anionic anti-parallel chains, which are connected via the lateral-to-lateral S...S contacts of dmit<sup>2-</sup> ligands between neighboring anions with  $d_{S3...S3\#1} = 3.666$  Å and  $d_{S4...S4\#2} = 3.429 \text{ Å}$  (symmetric codes #1 = 1 - x, -y, 2 - z and #2 = 1 - x, -y, 1 - z) anions along the crystallographic c-axis direction. This situation is similar to the homoleptic  $[Ni(dmit)_2]^-$  complexes [27,28]. On the other hand, it is noticeable that there exist nonclassical C-H...S and C-H...N hydrogen-bonding interactions between the anions and cations, for instance, the shorter S...H and N...H distances, d<sub>C17-H17A...S7#3</sub>=2.936, d<sub>C22-H22...S7#4</sub>=2.870, d<sub>C20-H20...S1#5</sub>=2.996,  $d_{C17-H17B...N1\#6} = 2.467$ ,  $d_{C8-H8...N1\#6} = 2.736$ ,  $d_{C9-H9...N2\#6} = 2.704$ and  $d_{C10-H10...N2\#7} = 2.598$  Å, and the symmetric codes #3 = -x, 1 = -xy, 1-z; #4=x, y, z; #5=x, 1+y, z; #6=1+x, y, -1+z and #7=-x, 2-y, 1-z, are observed in the crystal of **1**, respectively.

The purity of the polycrystalline sample was checked by powder X-ray diffraction technique besides elemental analysis, the simulated and experimental diffraction patterns are displayed in Fig. 2 and indicated that the sample of **1** has high phase purity.

The plots of magnetic susceptibility versus temperature measured in the temperature range of 2-300 K under an applied field of 1000 Oe is shown in Fig. 3, where  $\chi_m$  represents the mole magnetic susceptibility with one [Ni(dmit)(mnt)]<sup>-</sup> ion per molecular formula and the diamagnetism correction for **1** was not made. The magnetic behavior of **1** features in: (1) the temperature dependent magnetic susceptibility shows typical characteristics of low-dimensional antiferromagnetic spin system in temperature range of 40-300 K. It is worthy of note that two maximums of magnetic susceptibility occur around 85 and 65 K whereas the minimum of magnetic susceptibility between two maximums is localized at ~70 K upon cooling; the magnetic susceptibility plots upon cooling and heating do not coincide with each other in the temperature 60–140 K, which gives rise to an unusual shaped thermal hysteresis loop (the inset of Fig. 3a) and indicates the occurrence of a magnetic transition below 70 K. (2) The Curie–Weiss type magnetic susceptibility nature appears in the low temperature below 40 K. Even if the homoleptic nickel-bis-1,2-dithiolene  $[Ni(mnt)_2]^-$  and  $[Ni(dmit)_2]^-$  ion-pair complexes have been comprehensively studied so far, the heteroleptic [Ni(dmit)(mnt)]<sup>-</sup> complexes have very rarely been investigated in the field of magnetochemistry. To the best of our knowledge, this is the first report of [Ni(dmit)(mnt)]<sup>-</sup> complex with magnetic bistability.

In the nickel-bis-1,2-dithiolene crystals, the magnetic exchange interaction may be transmitted through long nonbonded contacts involving sulfur atoms. As noted in the crystal description, the magnetic  $[Ni(dmit)(mnt)]^-$  anions form inequivalent distanced 1-D chains via short lateral-to-lateral S...S contacts between the neighboring dmit<sup>2-</sup> ligands, therefore, it is reasonable that an alternating-exchange S =  $\frac{1}{2}$  Heisenberg linear-chain model was chosen for the fits of the magnetic susceptibility in high-temperature phase. The spin Hamiltonian for the Heisenberg alternating linear chain may be written as

$$\hat{H} = -2J \sum_{i=1}^{n/2} \left[ \hat{S}_{2j-1} \hat{S}_{2j} + \alpha \hat{S}_{2j} \hat{S}_{2j+1} \right]$$
(1)

where J is the exchange constant between a spin and its left neighbor and  $\alpha$ J is the exchange constant between a spin and its right neighbor. For an antiferromagnetic exchange system (J<0 and 0 $\leq \alpha \leq 1$ ), extremely, when  $\alpha = 0$  the alternating linear-chain model is simplified to the dimer model with pairwise interactions and when  $\alpha = 1$  the alternating linear-chain model to the regular linear-chain model [34].



Fig. 2. Powder X-ray diffraction patterns of 1 (upper line: simulation and bottom: experimental patterns).



**Fig. 3.** (a) Temperature dependent magnetic susceptibility and inset showing the thermal hysteresis loop (b) fits of magnetic susceptibility in low- and high-temperature regimes (solid squares: experimental data and lines: fits).

Based on the above-mentioned spin Hamiltonian, the molar magnetic susceptibility as a function of temperature for an alternating-exchange  $S = \frac{1}{2}$  Heisenberg linear chain which is deduced from the cluster approach [34] can be expressed as

$$\chi_{chain} = \frac{Ng^2 \mu_B^2}{k_B T} \cdot \frac{A + Bx + cx^2}{1 + Dx + Ex^2 + Fx^3}$$
(2)

where  $x = |J|/k_BT$ . Eq. (2) with the two sets of parameters A–F is valid for  $k_BT/|J| \ge 0.5$  and  $J \le 0$ . If the magnetic susceptibility contributions from the paramagnetic impurity, diamagnetism of atoms core of molecules and the temperature-independent paramagnetism are further considered and the experimental molar magnetic susceptibility is given in Eq. (3),

$$\chi_m = P^* \chi_{chain} + (1 - P) \frac{C}{T - \theta} + \chi_0 \tag{3}$$

Where the second term represents the Curie–Weiss type paramagnetic susceptibility contributed from the magnetic impurity and 1-P is the molar fraction of magnetic impurity, C and  $\theta$  are Curie and Weiss constants, respectively. The parameter  $\chi_0$  represents the summations of diamagnetism contributed from the atoms core of molecules and the temperature-independent van Vleck-type paramagnetic susceptibility originating from the coupling of the ground and excited states through a magnetic field [35]. The best fit of the magnetic susceptibility data of **1** in the temperature range of 70– 300 K (in the cooling model) yielded the parameters  $\alpha = 0.119(3)$ being held, C=0.386(6) emu K mol<sup>-1</sup>, J/k<sub>B</sub>=69.3(13) K and P=0.97(2) with the g-factor value of 2.093(2) as well as the parameters  $\theta$  and  $\chi_0$  were taken from the magnetic susceptibility fits in the low-temperature region (see next section). Since **1** exhibits the historical dependence of the magnetic susceptibility around magnetic transition temperature, the magnetic susceptibility data in the range of 70–300 K (in the elevating temperature mode) were also fitted using Eqs. (2) and (3) with the same values for the parameters C, P,  $\alpha$ ,  $\theta$  and  $\chi_0$  obtained in the cooling model, to give J/k<sub>B</sub> = 70.9(1) K with the g-factor value of 2.087(2) that are quite similar to those gained from the fits in the cooling model.

In the low-temperature region below 40 K, the temperature dependence of magnetic susceptibility of **1** was fitted to Eq. (4),

$$\chi_m = \frac{C}{T - \theta} + \chi_0 \tag{4}$$

where the symbols of C,  $\theta$  and  $\chi_0$  have normal meanings. The best fits for the magnetic susceptibility of **1** in the temperature range of 2– 35 K gave rise to C=3.78(3)×10<sup>-2</sup> emu Kmol<sup>-1</sup>,  $\theta$ =-1.20(3) K and  $\chi_0$ =3.5(2)×10<sup>-4</sup> emu mol<sup>-1</sup>, respectively.

In summary, a heteroleptic nickel-bis-1,2-dithiolene ion-pair complex [BzQI][Ni(dmit)(mnt)] was synthesized and characterized structurally, which exhibited novel magnetic bistability. In comparison with the homoleptic [Ni(dmit)<sub>2</sub>]<sup>-</sup> and [Ni(mnt)<sub>2</sub>]<sup>-</sup> compounds, the stacking pattern of the heteroleptic [Ni(dmit)(mnt)]<sup>-</sup> ions is similar to the homoleptic [Ni(dmit)<sub>2</sub>]<sup>-</sup>, namely, the neighboring anions are connected via lateral-to-lateral S...S contacts of dmit<sup>2-</sup> ligands. This work shed a light on the design and preparation of new magnetic bistability materials. The further and systematical exploration in this context is in progress.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.inoche.2011.09.023.

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- [32] Preparation of 1: 637 mg (1 mmol) of (n-Bu<sub>4</sub>N)[Ni(dmit)(mnt)]<sub>2</sub> was reacted with 330 mg (1.1 mmol) of [BzQ]]Br in 10 mL MeCN for 2 h. The dark-green precipitate was filtered off, and washed with water. The crude product was recrystallized in acetone to give dark-green crystals. Yield: ~60%. Anal. Calc. For C<sub>23</sub>H<sub>14</sub>N<sub>3</sub>NiS<sub>7</sub>: C, 44.88; N, 6.82; H, 2.29%. Found: C, 44.55; N, 6.78; H, 2.68%. IR spectrum (KBr disc, cm<sup>-1</sup>): 1343 for v<sub>C-C</sub> and 1064 for v<sub>C-S</sub> of dmit<sup>-</sup>; 2205 for v<sub>C=N</sub> of mnt<sup>2-</sup>; 3087 for v<sub>C-H</sub>
- [33] Crystal data of 1 (CCDC no. 825094): C23H14N3NiS7, Mw = 615.50, triclinic system, space group P-1, a=8.8939(13) Å, b=11.7079(16) Å, c=12.8073(18) Å,  $\alpha$ =83.591(2)°  $\beta$ =78.000(2)°  $\gamma$ =73.645(2)° V=1249.7(3) Å3, Z=2; Dc=1.636 g cm<sup>-3</sup>,  $\mu$ =1.381 mm-1; F(000)=626, data collect  $\theta$  range=1.63-27.46° index range of  $-11 \le h \le 11$ ,  $-15 \le k \le 14$ ,  $-16 \le 16$ ; reflections measured =11063, unique reflections =5608 [Rint=0.0700] and observed reflections =3491 [I>20(1)]; R1=0.0865, wR2=0.1259 for all reflections, S=0.933; residual peak/hole =1.455/-0.607 eÅ<sup>-3</sup>. Single crystal diffraction data were collected on a Bruker-SMART CCD diffractometer with graphite monochromatic Mo K $\alpha$  radiation at 190(2) K. The structure were solved by direct methods and refined on F2 using full matrix least-squares methods with SHELXTL version 97. Anisotropic thermal parameters were refined for non-H atoms, and H atoms were theoretically added and riding on the parent atoms.
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