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# Unusual magnetic property associated with a structural phase transition within a new ion-pair complex

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## Abstract

A novel ion-pair complex, [BrbzPyNH<sub>2</sub>][Ni(mnt)<sub>2</sub>], where [BrbzPyNH<sub>2</sub>]<sup>+</sup> = 1-(4'-bromobenzyl)-4-aminopyridinium and  $mnt^{2-}$  = maleonitriledithiolate, forms a completely segregated uniform stacking column with the Ni…Ni distance 3.952 Å and undergoes a magnetic phase transition from paramagnetism in the high-temperature (HT) phase to diamagnetism in the low-temperature (LT) phase at around 105 K.

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1D molecular-based materials are currently of extensive interest owing to their multifarious physical properties such as spin-Peierls transition, valence-ordering, spin-charge separation states, charge-density-wave states and spin-density-wave states [1].

The study on Ni(mnt)<sub>2</sub> complexes as building blocks for new molecular magnets has attracted much attention because they show novel magnetic properties [2]. Especially, the discovering in 1996 of the ferromagnetic complex containing Ni(mnt)<sub>2</sub><sup>-</sup> ion, NH<sub>4</sub> · Ni(mnt)<sub>2</sub> · H<sub>2</sub>O, strongly stimulated this field [3]. Recently, in the course of our project to design 1D molecular-based magnets, we have developed a new class of complexes [RbzPy]<sup>+</sup>[M(mnt)<sub>2</sub>]<sup>-</sup> ([RbzPy]<sup>+</sup> = benzylpyridinium derivative), and found that these ion-pair complexes exhibit versatile magnetic properties [4]: Our continuing re-

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search with  $[M(mnt)_2]^-$  complexes is to find more suitable multifunctional organic cations to tune the crystal stacking structure of  $[M(mnt)_2]$  anion, and establish a relationship between the magnetic interactions and the stacking pattern of anions or cations. Herein, we report the crystal structure and magnetic property of a novel 1D molecular magnets  $[1-(4'-bromobenzyl)-4-aminopy-ridinium][Ni(mnt)_2]$  (1) which exhibits a switching from paramagnetism to diamagnetism at around 105 K. To the best of our knowledge, the uniformly spaced 1D Ni(III) chain exhibiting magnetic switching is very rare for the  $M(mnt)_2^-$  complexes.

 $[1-(4'-bromobenzyl)-4-aminopyridinium]_2[Ni(mnt)_2]$  was prepared by the direct combination of 1:2:2 molequivalent of NiCl<sub>2</sub> · 6H<sub>2</sub>O, Na<sub>2</sub>mnt and 1-(4'-bromobenzyl)-4-aminopyridinium)pyridinium bromide in water by a similar mothod described in the literature [5]. The resulting red precipitate product (1.0 mmol) was solved in 20 ml MeCN, then a MeCN solution (10 ml) of I<sub>2</sub> (0.59 mmol) was slowly added, the mixture was stirred for 1 h, and then 100 ml *i*-PrOH was added.

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1035



Fig. 1. ORTEP plot (30% probability ellipsoids) showing the molecule structure of complex 1. Selected bond distances (Å) and angles (°): Ni(1)–S(1) 2.1455(12), Ni(1)–S(2) 2.1351(12), Ni(1)–S(3) 2.1396(12), Ni(1)–S(4) 2.1402(12), S(1)–Ni(1)–S(2) 92.47(5), S(1)–Ni(1)–S(4) 89.23(5), S(3)–Ni(1)–S(4) 92.23(5), S(2)–Ni(1)–S(3) 86.02(5).

After the mixture was allowed to stand overnight, 510 mg dark microcrystals produced were filtered off, washed with *i*-PrOH and Et<sub>2</sub>O and dried in a vacuum [6].

An ORTEP drawing of 1 with non-hydrogen atomic labeling in an asymmetric unit is shown in Fig. 1 [7]. The Ni (III) ion in the  $[Ni(mnt)_2]^-$  anion is coordinated by four sulfur atoms of two mnt<sup>2-</sup> ligands, and exhibits square planar coordination geometry. The average S– Ni–S bond angle within the five-membered ring is 90.0°, and the average Ni–S bond distance is 2.14 Å, these values are in agreement with those of found in other  $[Ni(mnt)_2]^-$  complexes [8]. In the  $[BrbzPyNH_2]^+$ moiety, the dihedral angles of the C(14)–C(15)–N(5) reference plane are 100.4° for benzene ring, 83.7° for pyridine ring, respectively.

The most notable structural feature of 1 is that the anions and cations posses the stacking pattern with well-separated column along the direction of c-axis (Fig. 2). Within an anion column, the nearest  $Ni \cdots Ni$ distance is 3.952 Å, the nearest  $S \cdots S$  and  $Ni \cdots S$  contacts have 3.773 and 3.712 Å, respectively. Therefore, the Ni(III) ions within a  $[Ni(mnt)_2]^-$  anionic column form a 1D-uniformly spaced chain via intermolecular Ni $\cdots$ S, S $\cdots$ S, Ni $\cdots$ Ni or  $\pi \cdots \pi$  interactions. Within a column of  $[BrbzPyNH_2]^+$  cation, the adjacent cations stack into chair-type conformation and form 1D chains via  $p-\pi$  interactions between Br atom and benzene rings. The closest Ni···Ni separation between anion chains is 13.532 Å, which is significantly longer than that of Ni...Ni separation within a chain (3.952 Å). From the point of view of the structure, 1 is an ideal 1D magnetic chain system.

The plot of  $\chi_m T$  versus T for the complex is shown in Fig. 3 with  $\chi_m$  being the magnetic susceptibility per nickel atom corrected by the diamagnetic contribution. For the complex 1, the overall magnetic behavior corresponds to an antiferromagnetically coupled system. The value of  $\chi_m T$  at 300 K is 0.135 emu K mol<sup>-1</sup>, a value which is significantly lower than the expected for magnetically isolated Ni(III) ion $(0.375 \text{ emu K mol}^{-1})$ . Upon cooling down of the sample,  $\chi_m T$  smoothly increases and reaches a value of  $0.268 \text{ emu K mol}^{-1}$  at 130 K. This behavior is indicative of weak ferromagnetic coupling between Ni(III) ions in the 1D magnetic chain. It is interesting that the complex 1 exhibits a switching from paramagnetic to diamagnetic around 105 K which may be estimated from the  $d(\chi_m T)/dT$  vs. T plot (the inset of Fig. 3). The magnetic susceptibility abrupt decrease at 105 K is associated with the pack structure changing of 1 from uniform spin clusters to dimmers between neighboring spin carries, which is often found in the similar systems [4b,4e,4f]. The feature that the value of  $\chi_m T$  at room temperature is significantly lower than



Fig. 2. The packing diagram of a unit cell for complex 1 as viewed along *c*-axis.



Fig. 3. The plot of  $\chi_m T$  versus T for complex 1 (inset:  $d(\chi_m T)/dT$  versus T).



Fig. 4. DSC plot for 1 showing the phase transition at 111.3 K.

 $0.375 \text{ emu K mol}^{-1}$  deserves and needs to be studied further.

The power-compensated DSC trace for 1 from 100 to 293 K at a warming rate of 20 K min<sup>-1</sup> is displayed in Fig. 4. An abruptly endothermic peak in the DSC trace is observed. The phase transition temperature determined from thermal analysis is 111.3 K, very close to the value measured from magnetic susceptibility measurements. The endothermic enthalpy change ( $\Delta H$ ) of 401.7 J mol<sup>-1</sup> can be estimated from the peak area. The result of thermal analysis of 1 confirms that the magnetic phase transition observed is first order [9].

In conclusion, this work describes the synthesis, crystal structure and magnetism of a new ion-pair complex containing Ni(mnt)<sub>2</sub><sup>-</sup> anion. The X-ray structural characterization shows Ni(mnt)<sub>2</sub><sup>-</sup> anions of the complex form completely segregated uniform stacking columns with the Ni···Ni distance 3.952 Å in the Ni(mnt)<sub>2</sub><sup>-</sup> stacking column by intermolecular Ni···S, S···S, Ni···Ni or  $\pi \cdot \cdot \pi$  interactions. The measurement of the temperature dependence of the magnetic susceptibility and DSC reveal the title complex undergoes a magnetic transition from paramagnetism to diamagnetism. Future study on magnetic properties of the title complex is in progress.

# Supplementary material

Supplementary crystallographic data are available from the Cambridge Crystallographic Data Centre, CCDC No. 238997. 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; deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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- [6] Yield: 84%. Anal. Calc. for C<sub>20</sub>H<sub>12</sub>BrN<sub>6</sub>NiS<sub>4</sub>: C, 39.82; H, 2.00; N, 13.93. Found: C, 39.90; H, 2.05; N, 13.81%. IR (KBr, cm<sup>-1</sup>): 3381.7s, 1650.9vs, 2205.2s, 1453.9s.
- [7] The diffraction data for crystal of 1 were collected at 293 K on a Siemens SMART CCD area detector using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystallographic data of 1 are: C<sub>20</sub>H<sub>12</sub>BrN<sub>6</sub>NiS<sub>4</sub>, *Fw* = 603.22, monoclinic, space group *P*2<sub>1</sub>*c*, a = 11.988(3) Å, b = 26.662(6) Å, c = 7.560(2) Å,  $\alpha = 102.43(4)^\circ$ , V = 2359.6(9) Å<sup>3</sup>, Z = 4,  $D_c = 1.698$  Mg/m<sup>3</sup>,  $\mu = 2.891$ , *F*(000) = 1698, crystal size =  $0.20 \times 0.35 \times 0.40$  mm<sup>3</sup>. A total of 12,495 reflections ( $1.90 \le \theta \ge 26.00^\circ$ ) were used for structural elucidation ( $R_{int} = 0.044$  [ $I > 2\sigma(I)$ ]). The final  $R_1$  and  $wR_2$  were 0.0409 and 0.1048, respectively. The structure was solved by the direct method and refined by the full-matrix least-squares against  $F^2$  using a SHELXTL software package.
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