

# Synthesis, crystal structure and magnetic property of a new 1D molecular material [1-(4'-chlorobenzyl)–4-aminopyridinium](+) bis(maleonitriledithiolato)nickel(–)

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## Abstract

A new ion-pair complex, [1-(4'-chlorobenzyl)–4-aminopyridinium](+)bis(maleonitrile-dithiolato)nickel(–), [ClbzPyNH<sub>2</sub>][Ni(mnt)<sub>2</sub>] (**1**), has been prepared and characterized. X-ray single crystal structure conforms that the Ni(mnt)<sub>2</sub><sup>–</sup> anions and [ClbzPyNH<sub>2</sub>]<sup>+</sup> cations of **1** form completely segregated uniform stacking columns with the Ni...Ni distance 3.944 Å in the Ni(mnt)<sub>2</sub><sup>–</sup> stacking column. The temperature dependence of the magnetic susceptibility reveals that **1** undergoes a magnetic transition, and exhibits ferromagnetic interaction in the high-temperature phase and spin gap system in the low-temperature phase.

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## 1. Introduction

Transition metal complexes of 1,2-dithiolenes are currently of extensive interest owing to their application as potentially building blocks in molecular-based materials showing magnetic, superconducting, and optical properties [1–3]. The complexes containing [M(mnt)<sub>2</sub>]<sup>–</sup> (mnt<sup>2–</sup> = maleonitriledithiolate, M = Ni(III) or Pt(III)) ions) have attracted much attention because they show novel magnetic properties [4–11]. Especially, the discovery 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, in 1996, strongly stimulated the study on Ni(mnt)<sub>2</sub> complexes as building blocks for new molecular magnets [12]. One of the current interests in our laboratory has been developed 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 such as ferromagnetic ordering at low temperature [13], magnetic transition from ferromagnetic coupling to diamagnetism [14], meta-magnetism [15] and spin-Peierls-like transitions [16–18]. In these ion-pair complexes, the prominent structural feature is that the Ni(mnt)<sub>2</sub><sup>–</sup> ions and [RbzPy]<sup>+</sup> cations stack into well-segregated columns in the solid state. In our continuing research with [M(mnt)<sub>2</sub>]<sup>–</sup> complexes, we have focused on the following two strategies. One is to find more suitable multifunctional organic cations to tune the crystal stacking structure of [M(mnt)<sub>2</sub>]<sup>–</sup> anion with a view to obtaining ideal molecular magnets. The second strategy is to 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 material [1-(4'-chlorobenzyl)–4-aminopyridinium][Ni(mnt)<sub>2</sub>](**1**)

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showing a magnetic transition at around 86.5 K. To the best of our knowledge, the uniformly spaced 1D chain exhibiting magnetic transition is very rare for the Ni(mnt)<sub>2</sub> complexes.

## 2. Experimental

### 2.1. Materials and methods

All chemicals and solvents were of reagent grade and were used without further purification. 1-(4'-chlorobenzyl)-4-aminopyridinium bromide and disodium maleonitriledithiolate (Na<sub>2</sub>mnt) were synthesized following the published procedures [19,20]. [1-(4'-chlorobenzyl)-4-aminopyridinium]<sub>2</sub>[Ni(mnt)<sub>2</sub>] was prepared by the direct combination of 1:2:2 mol equivalent of NiCl<sub>2</sub>·6H<sub>2</sub>O, Na<sub>2</sub>mnt and 1-(4'-chlorobenzyl)-4-aminopyridinium bromide in water by a similar method described in the literature [20]. Elemental analyses were run on a Model 240 Perkin-Elmer CHN instrument. IR spectra were recorded on an IF66 V FT-IR (400–4000 cm<sup>-1</sup> region) spectrophotometer in KBr pellets. Magnetic susceptibility data on crushed single crystals of **1** were collected over the temperature range 2–300 K using a Quantum Design MPMS-5S super-conducting quantum interference device (SQUID) magnetometer, and the experimental data were corrected for diamagnetism of the constituent atoms estimated from Pascal's constants.

### 2.2. Synthesis of [1-(4'-chlorobenzyl)-4-aminopyridinium]<sub>2</sub>[Ni(mnt)<sub>2</sub>]

[1-(4'-Chlorobenzyl)-4-amino pyridinium]<sub>2</sub>[Ni(mnt)<sub>2</sub>] (778 mg, 1.0 mmol) was solved in 20 cm<sup>3</sup> MeCN, then a MeCN solution (10 cm<sup>3</sup>) of I<sub>2</sub> (150 mg, 0.59 mmol) was slowly added, the mixture was stirred for 1 h, and then 50 cm<sup>3</sup> *i*-PrOH was added. After the mixture was allowed to stand overnight, 546 mg dark microcrystals produced were filtered off, washed with *i*-PrOH and Et<sub>2</sub>O and dried in a vacuum. Yield: 86%. Found (calcd.) for C<sub>20</sub>H<sub>12</sub>ClN<sub>6</sub>NiS<sub>4</sub>: C, 42.72 (42.99); H, 2.25 (2.16); N, 14.85 (15.04)%. IR (cm<sup>-1</sup>): 3381.3 m, 1651.2 s, 2205.7 s, and 1453.3 s.

### 2.3. X-ray structure determination

Single crystals suitable for X-ray structure analyses were obtained by evaporating solution of **1** in mixtures of MeCN and *i*-PrOH (1:1v/v). A single crystal with dimension 0.3 × 0.2 × 0.2 mm<sup>3</sup> for **1** was used for structural determination at 293 K on a Siemens SMART CCD area detector equipped with graphite-monochromated MoK $\alpha$  radiation. All computations were carried out via a PC-586 computer using the SHELXTL-PC program package [21]. Number of measured, unique,

Table 1  
Crystallographic data for **1**

Formula	C <sub>20</sub> H <sub>12</sub> ClN <sub>6</sub> NiS <sub>4</sub>
<i>M</i>	558.76
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	12.000(2)
<i>b</i> (Å)	26.544(3)
<i>c</i> (Å)	7.504(1)
$\beta$ (°)	102.10(2)
<i>V</i> (Å <sup>3</sup> )	2337.2(5)
<i>Z</i>	4
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	1.588
<i>F</i> (000)	1132
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.016
<i>R<sub>1</sub></i> , <i>wR<sub>2</sub></i> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0550, 0.1008
(all data)	0.1037, 0.1129
(Δρ) <sub>max</sub> , (Δρ) <sub>min</sub> (eÅ <sup>-3</sup> )	0.984, -0.920

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

Table 2  
Selected bond parameters and intermolecular contacts for **1**

<i>Bond distances</i> (Å)	
Ni(1)–S(1)	2.1352(12)
Ni(1)–S(2)	2.1501(13)
Ni(1)–S(3)	2.1457(12)
Ni(1)–S(4)	2.1330(12)
<i>Bond angles</i> (°)	
S(1)–Ni(1)–S(2)	92.40(5)
S(1)–Ni(1)–S(4)	86.53(5)
S(3)–Ni(1)–S(4)	92.00(5)
S(2)–Ni(1)–S(3)	89.02(5)
<i>Intrachain distances</i> (Å)	
Ni...Ni (nearest separation)	3.944
Ni...S	3.680
S...S	3.767
<i>Interchain distances</i> (Å)	
Ni...Ni (nearest separation)	13.530

and observed reflections [*I* > 2σ(*I*)] are 12497, 4581, and 2955 (*R*<sub>int</sub> = 0.038). The structure was solved by direct method by using SHELXS 97 and refined on *F*<sup>2</sup> by full-matrix least-squares methods. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained to ride on the respective carbon atoms with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of their parent atom. Crystal data are summarized in Table 1. Selected bond lengths, bond angles and some short stacking contacts are listed in Table 2.

## 3. Results and discussion

### 3.1. Crystal structures

[ClbzPyNH<sub>2</sub>][Ni(mnt)<sub>2</sub>](1) crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* at room temperature. An

ORTEP drawing of **1** with non-hydrogen atomic labeling in an asymmetric unit is shown in Fig. 1. The Ni(III) ion in the  $[\text{Ni}(\text{mnt})_2]^-$  anion is coordinated by four sulfur atoms of two  $\text{mnt}^{2-}$  ligands, and exhibits square planar coordination geometry. The average S–Ni–S bond angle within the five-membered ring is  $90.0^\circ$ , and the average Ni–S bond distance is  $2.15 \text{ \AA}$ ; these values are in agreement with those found in other  $[\text{Ni}(\text{mnt})_2]^-$  complexes [22]. In the  $[\text{ClbzPyNH}_2]^+$  moiety, the dihedral angles of the C(14)–C(15)–N(5) reference plane are  $103.1^\circ$  for benzene ring, and  $96.5^\circ$  for pyridine ring.

The most notable structural feature of **1** is that the anions and cations possess the stacking pattern with well-separated column along the direction of *c*-axis (Fig. 2). Within an anion column, the nearest Ni...Ni distance is  $3.944 \text{ \AA}$ , the nearest S...S and Ni...S contacts have  $3.767$  and  $3.68 \text{ \AA}$ , respectively. Therefore, the Ni(III) ions within a  $[\text{Ni}(\text{mnt})_2]^-$  anionic column form a 1D uniformly spaced chain via intermolecular Ni...S, S...S, Ni...Ni or  $\pi$ ... $\pi$  interactions (Fig. 3). Within a column of  $[\text{ClbzPyNH}_2]^+$  cations, the adjacent cations stack into chair-type conformation (Fig. 4) and form 1D chains via p- $\pi$  interactions between Cl atom and benzene rings. Similar phenomena have been found in halogen-benzene derivatives in solid state [23–25]. The closest Ni...Ni separation between anion chains is  $13.530 \text{ \AA}$ , which is significantly longer than that of Ni...Ni separation within a chain ( $3.944 \text{ \AA}$ ). Therefore, **1** is an ideal 1D magnetic chain system from the point of view of the structure.

### 3.2. Magnetic properties

The temperature dependence of the magnetic susceptibility for **1** was measured under an applied field of  $1000 \text{ Oe}$  in temperature range  $2\text{--}300 \text{ K}$ . The plots of  $\chi_m$  versus  $T$  and  $\chi_m T$  versus  $T$  for these complexes are shown in Figs. 2, 5 and 6 with  $\chi_m$  is 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. On increasing the temperature back to the original temperature, the same  $\chi_m T$  curve is obtained without hysteresis effect being detected.

The value of  $\chi_m T$  at  $300 \text{ K}$  is  $0.299 \text{ cm}^3 \text{ K mol}^{-1}$ , a value which is somewhat lower than the expected for magnetically isolated Ni(III) ion ( $0.375 \text{ cm}^3 \text{ K mol}^{-1}$ ). Upon cooling down the sample,  $\chi_m T$  smoothly increases and reaches a value of  $0.447 \text{ cm}^3 \text{ K mol}^{-1}$  at  $100 \text{ K}$ . This behavior is indicative of weak ferromagnetic coupling between Ni(III) ions in the 1D magnetic chain. The high-temperature region ( $T > 95 \text{ K}$ ) can be well fitted by the equation  $\chi_m = C/(T - \theta) + \text{TIP}$  with the fitting parameters being  $C = 0.421 \text{ cm}^3 \text{ K mol}^{-1}$ ,  $\theta = 2.70 \text{ K}$ , and  $\text{TIP} = 5.0 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$  (Fig. 6).

As the sample **1** was continuously cooled, the  $\chi_m T$  value first slightly decreases; around  $95 \text{ K}$ , the abrupt drops of the value of  $\chi_m T$  from  $0.444$  to  $0.094 \text{ cm}^3 \text{ K mol}^{-1}$  within  $9.5 \text{ K}$  indicates that **1** exhibits the characteristics of a spin gap system. The transition temperature,  $86.5 \text{ K}$ , may be estimated from the  $d(\chi_m T)/dT$  versus  $T$  plot (the inset of Fig. 5). The magnetic susceptibility of **1** may be estimated by the

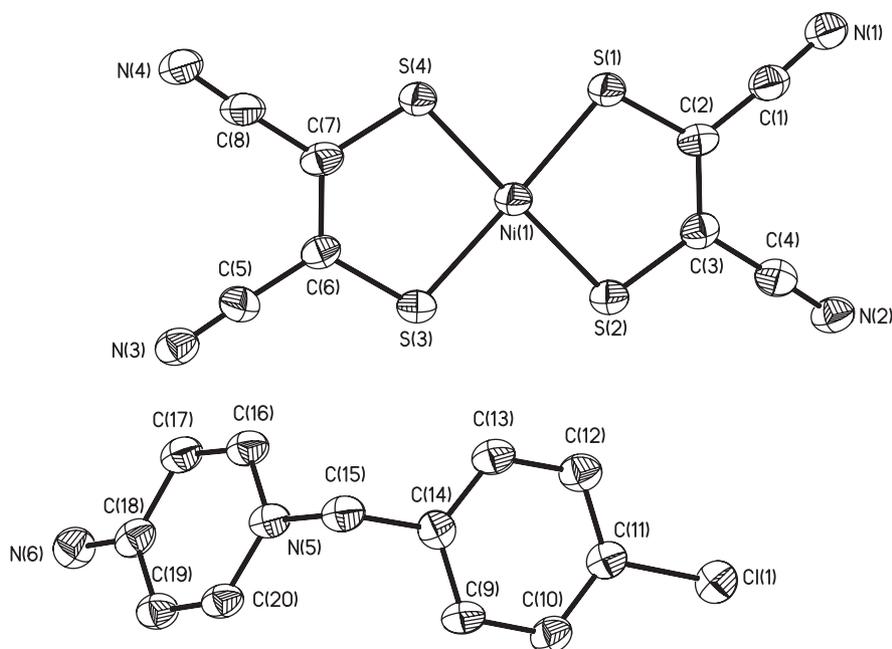


Fig. 1. ORTEP plot (30% probability ellipsoids) showing the molecule structure of complex **1**.

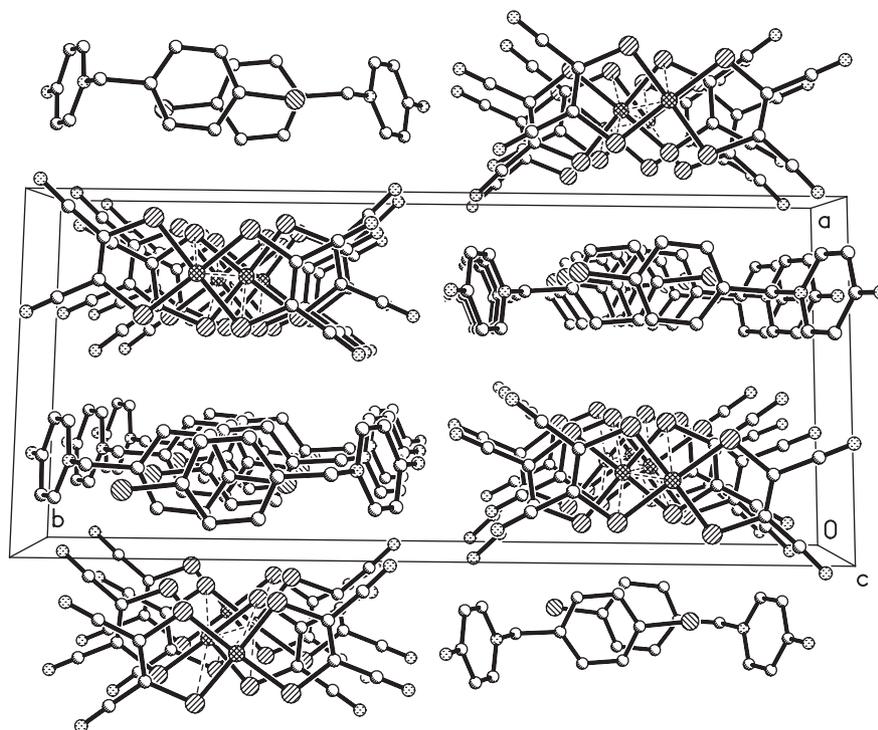


Fig. 2. The packing diagram of a unit cell for complex **1** as viewed along *c*-axis.

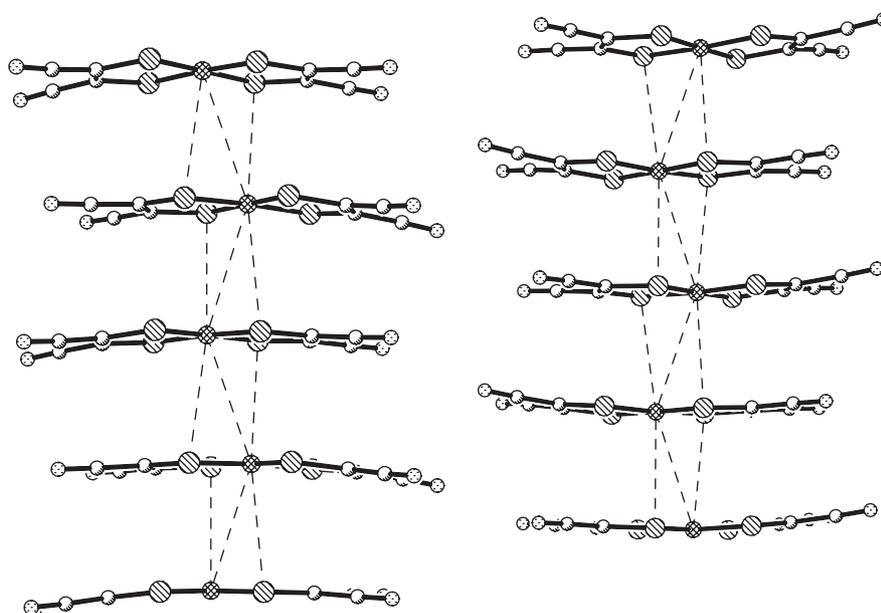
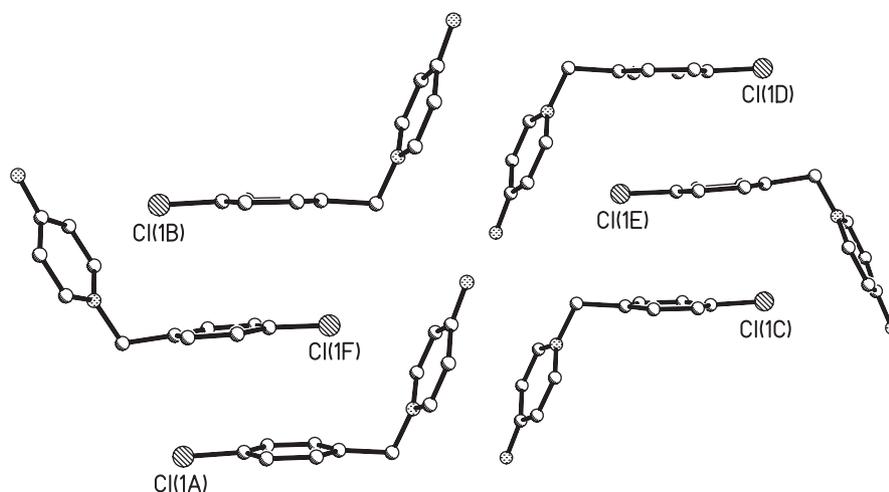
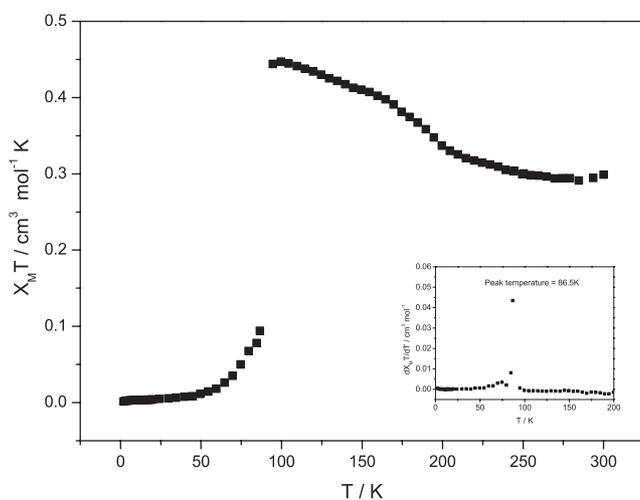
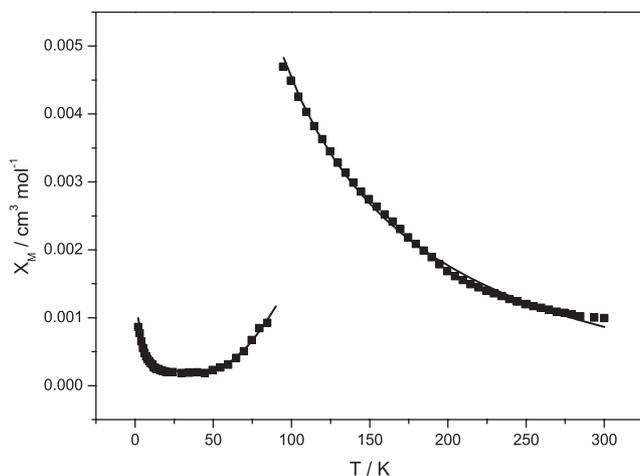


Fig. 3. Side view of the anions stack of complex **1** showing the uniform space linear-chain of  $[\text{Ni}(\text{mnt})_2]^-$ .

formula  $\chi_m = [\alpha \exp(-\Delta/k_B T)]/T + C/T + \chi_0$ , where  $\alpha$  is a constant value corresponding to the dispersion of excitation energy,  $\Delta$  is the magnitude of the spin gap,  $\chi_0$  contributes from the core diamagnetism and the possible Van Vleck paramagnetism, and the other symbols have their usual meaning [26]. The best fit curve (2–86.5 K) for **1** are shown in Fig. 6, and the corresponding

parameters are given as follows:  $\alpha = 7.55$ ,  $\Delta/k_B = 398.70$ ,  $\chi_0 = -1.5 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ ,  $C = 1.69 \times 10^{-3} \text{ cm}^3 \text{ K mol}^{-1}$ , and  $R = 1.8 \times 10^{-9}$  ( $R$  is defined as  $\Sigma(\chi_m^{\text{calcd}} - \chi_m^{\text{obsd}})^2 / (\chi_m^{\text{obsd}})^2$ ). The values of the parameter  $2\Delta/k_B T_c$  ( $T_c$  is the transition temperature) are estimated to be 9.22 for **1** on the basis of the above results, which is higher than the ideal value of 3.53 derived from the BCS

Fig. 4. Side view of the cations stack of complex **1**Fig. 5. The plot of  $\chi_m T$  versus  $T$  for complex **1** (inset:  $d(\chi_m T)/dT$  versus  $T$ ).Fig. 6. Plot of  $\chi_m$  versus  $T$  for **1**. The solid line are reproduced from the theoretic calculations and detailed fitting procedure described in the text.

formula in a weak coupling regime. This result thus means that the short-range magnetic correlations within a chain are not fully developed and intrinsic magneto elastic instability of a 1D system cannot be considered as a driving force for this transition; namely, the transition is not a pure spin-Peierls transition [18]. The origins of the phase transition for **1** are attributed to cooperative interactions of Ni...S bonding, inter-plane repulsion of the  $[\text{Ni}(\text{mnt})_2]^-$  anions [27],  $\pi \cdots \pi$  stacking interactions between of adjacent cations, spin–lattice interaction [28] and spin–spin coupled interaction between nearest-neighbor anions [29].

This work describes the synthesis, crystal structure and magnetism of a new ion-pair complex containing  $\text{Ni}(\text{mnt})_2^-$  anion. The X-ray structural characterization shows  $\text{Ni}(\text{mnt})_2^-$  anions of the complex form completely segregated uniform stacking columns with the Ni...Ni distance 3.944 Å in the  $\text{Ni}(\text{mnt})_2^-$  stacking column by intermolecular Ni...S, S...S, Ni...Ni or  $\pi \cdots \pi$  interactions. The measurement of the temperature dependence of the magnetic susceptibility reveals that the title complex undergoes a magnetic transition, and exists ferromagnetic interaction in the high-temperature phase and spin gap system in the low-temperature phase.

#### 4. Supplementary materials

Supplementary crystallographic data are available from the Cambridge Crystallographic Data Center, CCDC No. 239015. 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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