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# Syntheses, spectra, crystal structures and magnetic properties of molecular solids based on the $M(mnt)_2^-$ ion (M = Ni, Pt)

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# Abstract

Two new ion-pair complexes [1-(4'-nitrobenzyl)-4-aminopyridinium]-bis(maleonitriledithiolato)nickel ([NO<sub>2</sub>BzPyNH<sub>2</sub>][Ni(mnt)<sub>2</sub>]) (1) and [1-(4'-nitrobenzyl)-4-aminopyridinium]-bis(maleonitriledithiolato)platinum ([NO<sub>2</sub>BzPyNH<sub>2</sub>][Pt(mnt)<sub>2</sub>]) (2) have been prepared and characterized by elemental analyses, IR, electronic and MS spectra, single crystal X-ray diffraction and magnetic susceptibility. 1 and 2 crystallize in the monoclinic space group  $P_{21}/c$ , a = 12.331(3) Å, b = 26.937(6) Å, c = 7.322(2) Å, V = 2349.0(10) Å<sup>3</sup>, Z = 4 for 1, and a = 10.600(3) Å, b = 8.376(2) Å, c = 27.089(7) Å, V = 2362.2(11) Å<sup>3</sup>, Z = 4 for 2. The Ni(III) ions of 1 form a 1D zigzag chain within a Ni(mnt)<sub>2</sub><sup>-</sup> column, while 2 is a dimer. Magnetic susceptibility and DSC measurements for 1 in the temperature range 2.0–300 K show the occurrence of an unusual magnetic phase transition around 160 K, and an antiferromagnetic interaction in the high-temperature phase (HT) and a spin gap in the low-temperature phase (LT), while 2 is diamagnetic. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Maleonitriledithiolate; 1-(4'-Nitrobenzyl)-4-aminopyridinium; Nickel (III) complex; Platinum (III) complex; Crystal structures; Magnetic properties

# 1. Introduction

Metal complexes of bis-dithiolenes have been widely investigated due to their application as building blocks in molecular-based materials showing magnetic, superconducting and optical properties [1–3]. The complexes containing  $[M(mnt)_2]^-(mnt^{2-} = maleonitriledithiolate,$ M = Ni(III) or Pt(III) ions) have attracted much interestbecause they show novel magnetic properties [4–11].Especially the discovery in 1996 of the ferromagneticcomplex containing the Ni(mnt)<sub>2</sub><sup>-</sup> ion, NH<sub>4</sub> · Ni(mnt)<sub>2</sub> ·H<sub>2</sub>O, strongly stimulated the study on Ni(mnt)<sub>2</sub> complexes as building blocks for new molecular magnets [12]. One of the interesting works in our laboratory is to develop a new class of ion-pair complexes  $[RbzPy]^+$ - $[M(mnt)_2]^-$  ( $[RbzPy]^+$  = benzylpyridinium derivative, M = Ni, Pt). We have found that the prominent feature of these ion-pair complexes is that the  $Ni(mnt)_2^{-}$  anions and  $[RbzPy]^+$  cations stack into well-segregated columns in the solid state, and they exhibit versatile magnetic properties such as ferromagnetic ordering at low temperature [13], magnetic transitions from ferromagnetic coupling to diamagnetism [14], meta-magnetism [15] and spin-Peierls-like transitions [16–18]. In the continuing research with  $[M(mnt)_2]^-$  complexes, we have focused on finding more suitable multifunctional organic cations to tune the crystal stacking structure of the  $[M(mnt)_2]^$ anion with a view to obtaining ideal molecular magnets. Herein, we report the syntheses, spectra, crystal structures and magnetic properties of two novel 1D molecular

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solids [1-(4'-nitrobenzyl)-4-aminopyridinium]-bis(maleonitriledithiolato)nickel([NO<sub>2</sub>BzPyNH<sub>2</sub>][Ni(mnt)<sub>2</sub>]) (1)and [4-aminopyridinium]-bis(maleonitriledithiolato)platinum ([NO<sub>2</sub>BzPyNH<sub>2</sub>][Pt(mnt)<sub>2</sub>])(2). To the best ofour knowledge, a uniform chain exhibiting an unusualmagnetic transition is very rare in the Ni(mnt)<sub>2</sub>complexes.

# 2. Experimental

#### 2.1. General materials and techniques

The starting materials, 1-(4'-nitrobenzyl)-4-aminopyridinium bromide ([NO<sub>2</sub>BzPyNH<sub>2</sub>]Br), and disodium maleonitriledithiolate (Na<sub>2</sub>mnt) were synthesized following the literature procedures [19,20]. A similar method for preparing [Bu<sub>4</sub>N]<sub>2</sub>[Ni(mnt)<sub>2</sub>] was utilized to prepare [NO<sub>2</sub>BzPyNH<sub>2</sub>]<sub>2</sub>[Ni(mnt)<sub>2</sub>] and [NO<sub>2</sub>BzPy-NH<sub>2</sub>]<sub>2</sub>[Pt(mnt)<sub>2</sub>] [20].

Elemental analyses were run on a Model 240 Perkin-Elmer C H N instrument. IR spectra were recorded on an IF66V FT-IR (400-4000 cm<sup>-1</sup> region) spectrophotometer in KBr pellets. Electronic spectra were recorded on a Shimadzu UV-3100 spectrophotometer. All solution concentrations were ca.  $10^{-5}$  mol dm<sup>-3</sup> in CH<sub>3</sub>CN. The electrospray-mass spectra [ESI-MS] were determined on a Finnigan LCQ mass spectrograph, sample concentration ca. 1.0 mmol dm<sup>-3</sup>. DSC was carried out with a Perkin-Elmer calorimeter. Thermal analyses of crushed polycrystalline samples for 1 placed in an aluminum crucible were performed on warming (rate of 20 K mol<sup>-1</sup>) from 98 to 293 K. Magnetic susceptibility data on crushed polycrystalline samples of 1 and 2 were collected over the temperature range of 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. Syntheses of complexes

# 2.2.1. $[NO_2BzPyNH_2]_2[Ni(mnt)_2]$ (1)

 $[NO_2BzPyNH_2]_2[Ni(mnt)_2]$  (0.800 g, 1.0 mmol) was dissolved in 30 cm<sup>3</sup> MeCN, then a MeCN solution (10 cm<sup>3</sup>) of I<sub>2</sub> (0.150 g, 0.59 mmol) was slowly added, the mixture was stirred for 1 h, and then 100 cm<sup>3</sup> CH<sub>3</sub>OH was added. After the mixture was allowed to stand overnight, 0.508 g dark microcrystals produced were filtered off, washed with CH<sub>3</sub>OH and Et<sub>2</sub>O, and dried in a vacuum. Yield: 89.3%. *Anal.* Calc. for C<sub>20</sub>H<sub>12</sub>NiN<sub>7</sub>S<sub>4</sub>O<sub>2</sub>: C, 42.19; H, 2.12; N, 17.22. Found: C, 42.12; H, 2.23; N, 17.16%. IR (cm<sup>-1</sup>): 3380.4s, 3073.1w, 2207.1s, 1651.3s, 1606.6m, 1565.4m, 1536.6s, 1518.6m, 1454.2s, 1346.1s.

Single crystals suitable for X-ray structure analysis were obtained by evaporating a solution of 1 in a mixed solution of MeCN and *i*-PrOH (1:2 v/v).

#### 2.2.2. $[NO_2BzPyNH_2][Pt(mnt)_2]$ (2)

The procedure for preparing **2** was similar to that for **1**. Yield: 87.5%. *Anal.* Calc. for  $C_{20}H_{12}PtN_7S_4O_2$ : C, 34.04; H, 1.71; N, 13.89. Found: C, 34.12; H, 1.84; N, 13.76%. IR (cm<sup>-1</sup>): 3371.9s, 3070.4w, 2205.9s, 1648.2s, 1604.8m, 1564.4m, 1535.2s, 1508.5m, 1449.8s, 1332.8m.

Single crystals suitable for X-ray structure analysis were obtained by evaporating a solution of 2 in a mixed solution of MeCN and *i*-BuOH (1:2 v/v).

#### 2.3. Single-crystal X-ray structure determination

Measurements of the studied complexes 1 and 2 were performed on a Smart APEX CCD area detector using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda =$ 0.71073 Å) by the  $\omega$  scan mode within the angular range 1.87° <  $\theta$  < 26.0° for 1 and 1.96° <  $\theta$  < 25.0° for 2. Space group, lattice parameters and other relevant information are listed in Table 1. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares, employing Bruker's SHELXTL [21]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were placed in calculated positions, assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic U value of the attached atom, and allowed to ride on their respective parent atoms.

# 3. Results and discussion

# 3.1. Descriptions of the structures

#### 3.1.1. X-ray structure of 1

Complex 1 crystallizes in the monoclinic space group  $P2_1/c$  at room temperature. Selected bond distances, bond angles and intermolecular Ni...Ni, Ni...S and  $S \cdots S$  distances are summarized in Table 2. An ORTEP drawing of 1 with non-hydrogen atomic labelling in an asymmetric unit is shown in Fig. 1. 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 CN groups are slightly tipped out of the plane, and the deviations from the plane are -0.4477 Å for N(1), -0.4875 Å for N(2), -0.1285 Å for N(3) and -0.2619 Å for N(4). The average S-Ni-S bond angle within the five-membered ring is 90.0(5)°, and the average Ni-S bond distance is 2.139(1) Å, these values are in agreement with those found in other  $[Ni(mnt)_2]^-$  complexes [22]. The cation  $[NO_2BzPyNH_2]^+$ , adopts a conformation in which the benzene and pyridine rings are almost perpendicular to the reference plane C(14)-C(15)-N(5) (dihedral angles

Table 1 Crystal data and structure refinements for 1 and 2

Compound	1	2		
Temperature	293 (2)	293 (2)		
Empirical formula	$C_{20}H_{12}NiN_7S_4O_2$	$C_{20}H_{12}PtN_7S_4O_2$		
Formula weight	569.32	705.70		
Wavelength	0.71073	0.71073		
Space group	$P2_{1}/c$	$P2_1/c$		
Crystal system	monoclinic	monoclinic		
Unit cell dimensions				
<i>a</i> (Å)	12.331(3)	10.600(3)		
b (Å)	26.937(6)	8.376(2)		
c (Å)	7.322(2)	27.089(7)		
$\beta$ (°)	105.02(1)	100.84(1)		
Volume (Å <sup>3</sup> ), Z	2349.0(10), 4	2362.2(11), 4		
$D_{\rm calc} ({\rm g/cm}^3)$	1.610	1.984		
Absorption coefficient (mm <sup>-1</sup> )	1.216	6.328		
<i>F</i> (000)	1156	1356		
Crystal size (mm <sup>3</sup> )	$0.35 \times 0.30 \times 0.20$	$0.40 \times 0.35 \times 0.25$		
Absorption correction	empirical (SHELXA)	empirical (SHELXA)		
Maximum and minimum transmission	0.78 and 0.66	0.21 and 0.09		
$\theta$ Range for data collection (°)	1.87-26.00	1.96-25.00		
Limiting indices	$-15 \leqslant h \leqslant 15$ ,	$-9 \leqslant h \leqslant 12$ ,		
	$-33 \leqslant k \leqslant 21$ ,	$-\leqslant k\leqslant 9,$		
	$-8 \leqslant l \leqslant 8$	$-32 \leqslant l \leqslant 21$		
Reflections collected	12474	11200		
Independent reflections	4604	4142		
R <sub>int</sub>	0.084	0.047		
Refinement method	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$		
Goodness-of-fit on $F^2$	1.016	1.014		
Final <i>R</i> indices $[I > 2\sigma (I)]$	$R_1 = 0.0545, wR_2 = 0.1104$	$R_1 = 0.0335, wR_2 = 0.0678$		
Final <i>R</i> indices (all data)	$R_1 = 0.0973, wR_2 = 0.1195$	$R_1 = 0.0431, wR_2 = 0.0699$		
Largest difference in peak and hole (e $Å^{-3}$ )	0.34 and -0.47	1.07 and -0.81		

Table 2

Selected bond j	parameters	and	intermolecular	contacts	for	1	and 2
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Compound	1		2
Bond distances $(\mathring{A})$			
Ni(1)–S(1)	2.134(1)	Pt(1)-S(1)	2.264(2)
Ni(1)-S(2)	2.146(1)	Pt(1)-S(2)	2.253(2)
Ni(1)-S(3)	2.141(1)	Pt(1)-S(3)	2.257(2)
Ni(1)-S(4)	2.136(1)	Pt(1)-S(4)	2.255(2)
S(1)-C(2)	1.716(4)	S(1)-C(2)	1.716(6)
S(2) - C(3)	1.715(4)	S(2) - C(3)	1.699(6)
S(3)–C(6)	1.706(4)	S(3)-C(6)	1.716(6)
S(4)–C(7)	1.702(4)	S(4)–C(7)	1.714(5)
Bond angles (°)			
S(1)-Ni(1)-S(2)	92.50(5)	S(1) - Pt(1) - S(2)	89.88(6)
S(1)-Ni(1)-S(4)	86.63(5)	S(1) - Pt(1) - S(4)	90.71(5)
S(3)–Ni(1)–S(4)	92.23(5)	S(3) - Pt(1) - S(4)	89.95(5)
S(2)–Ni(1)–S(3)	88.60(5)	S(2)-Pt(1)-S(3)	89.46(6)
Intrachain distances (Å)			
NiNi (nearest separation)	3.855	PtPt (nearest separation)	3.511
Ni···S	3.644	Pt···S	4.066
S····S	3.725	$\mathbf{S} \cdot \cdot \cdot \mathbf{S}$	3.488

of 90.4° and 91.0°, respectively). The phenyl ring and the pyridine ring make a dihedral angle of  $112.5^{\circ}$ . The plane defined by S(1)S(2)Ni(1)S(3)S(4) with the phenyl and pyridine rings make dihedral angles of  $17.2^{\circ}$  and  $113.8^{\circ}$ , respectively. The most notable structural feature

of **1** is that the anions and cations possess a stacking pattern with well-separated columns along the direction of the *c*-axis (Fig. 2). Within an anionic column, the nearest Ni $\cdots$ Ni distance is 3.855 Å, and the nearest S $\cdots$ S and Ni $\cdots$ S contacts are 3.725 and 3.664 Å, respectively.



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



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

Therefore, the Ni(III) ions within a [Ni(mnt)<sub>2</sub>]<sup>-</sup> anionic column form a 1D uniformly spaced chain through intermolecular Ni $\cdots$ S, S $\cdots$ S, Ni $\cdots$ Ni or  $\pi \cdots \pi$  interactions (Fig. 3(a)). The adjacent cations stack into a column via a boat-type conformation (Fig. 3(b)). The contact distances between the nitrogen atom of the  $NO_2$  group and neighboring phenyl rings are 3.562 and 3.799 Å, respectively. So the cations form a 1D chain via  $\pi$ - $\pi$  interactions between the NO<sub>2</sub> group and benzene rings. The closest Ni ··· Ni separation between anionic chains is 12.604 Å, which is significantly longer than that of the Ni···Ni separation within a chain (3.855 Å). Therefore, **1** is an ideal 1D uniform magnetic chain system from the point of view of the structure. There are three intermolecular hydrogen bonds between the anions and cations in the crystal structure of 1 (Table 3).



Fig. 3. (a) Side view of the anions stack of 1 showing the uniform space linear-chain of  $[Ni(mnt)_2]^-$ . (b) Side view of the cations stack of 1.

#### 3.1.2. X-ray structure of 2

The coordination geometry of the  $[Pt(mnt)_2]$  anion is essentially identical to that described above for 1, while the stacking pattern of the [Pt(mnt)<sub>2</sub>] anion and [NO<sub>2</sub>Bz-PyNH<sub>2</sub>] cation in 2 is significantly different from that of 1. Selected bond distances, bond angles and intermolecular  $Pt \cdots Pt$ ,  $Pt \cdots S$  and  $S \cdots S$  distances are summarized in Table 2. The cation is situated above the plane of the  $[Pt(mnt)_2]$  anion (Fig. 4(a)) in which the dihedral angles between the S(1)S(2)Pt(1)S(3)S(4) plane and phenyl and pyridine rings are 84.8° and 135.6°, respectively. The reference plane defined by C(14)-C(15)-N(5) and the aromatic rings make dihedral angles of 37.4° for the phenyl ring and 115.8 for pyridine ring. The  $Pt(mnt)_2^-$  anions of 2 form a dimer with a  $Pt\cdots Pt$  distance 3.511 Å and a S $\cdots$ S distance 3.488 Å, which is significantly different from that of 1. Obviously, the short contacts of  $M \cdots M$ ,  $S \cdots S$  and  $\pi - \pi$  interactions in 2 are smaller than those of 1, therefore it is possible that the

Table 3 Hydrogen bonds for **1** and **2** (Å and °)

$D-H\cdots A$	d(D-H)	$d(\mathbf{H} \cdot \cdot \cdot \mathbf{A})$	$d(\mathbf{D}\cdots\mathbf{A})$	∠(DHA)
Complex 1				
$N(6)-H(6A)\cdots N(4)#1$	0.86	2.56	3.132(6)	125.0
$N(6)-H(6A)\cdots N(1)#2$	0.86	2.62	3.323(6)	140.0
$N(6)-H(6A)\cdots N(2)#3$	0.86	2.43	3.059(6)	131.0
Complex 2				
$N(6)-H(6A)\cdots N(1)#4$	0.86	2.49	3.273(8)	153.0
$N(6)-H(6A)\cdots N(3)#5$	0.86	2.55	3.207(8)	134.0
$C(15)-H(15A)\cdots N(4)\#6$	0.97	2.55	3.397(8)	146.0
C(16)-H(16A)···O(1)#7	0.93	2.52	3.275(8)	138.0
$C(19)-H(19A)\cdots N(2)#8$	0.93	2.56	3.310(8)	138.0

Symmetry transformations used to generate equivalent atoms: #1 = -x + 1, -y, -z + 1; #2 = x - 1, -y + 1/2, z - 1/2; #3 = -x + 1, y - 1/2, -z + 1/2; #4 = -x + 1, -y, -z + 2; #5 = -x, y - 1/2, -z + 3/2; #6 = x, y + 1, z; #7 = -x + 1, -y + 1, -z + 2; #8 = x, -y + 1/2, z - 1/2.



Fig. 4. (a) ORTEP plot (30% probability ellipsoids) showing the molecule structure of **2**. (b) The packing diagram of a unit cell for **2** as viewed along the *b*-axis.

interaction between  $M(mnt)_2^-$  anions in 2 may be stronger than that in 1, and 2 forms a dimer structure (Fig. 4(b)). It is worth noting that five intermolecular hydrogen bonds between anions and cations were observed in the crystal structure of 2, as listed in Table 3. The anion-anion, anion-cation and cation-cation contacts may play important roles in crystal packing and the stabilization of 2.

#### 3.2. Infrared spectra

The infrared spectra of the two complexes 1 and 2 are very much consistent with the structural data presented

above. The bands at 3380.4(s) and 1651.3(s) cm<sup>-1</sup> for **1**, and 3371.9 and 1648.2 cm<sup>-1</sup> for **2** are attributable to N–H stretching and bending of the amino group. The bands at 3073.1 and 3070.4 cm<sup>-1</sup> are due to the stretching vibration frequencies of C–H in the aromatic ring. The complexes **1** and **2** show one strong band at 2207.1 and 2205.9 cm<sup>-1</sup>, respectively, which are CN stretching bands. The v(C=N) and v(C=C) bands for the pyridine ring and phenyl ring are located at 1606.6, 1565.4 and 1518.6 cm<sup>-1</sup> for **1**, and 1604.8, 1564.4, and 1508.5 cm<sup>-1</sup> for **2**. The v(C=C) band of mnt<sup>2–</sup> is at 1452.2 cm<sup>-1</sup> for **1** and 1449.8 cm<sup>-1</sup> for **2**. The v(NO<sub>2</sub>) bands of complexes **1** and **2** are presented at 1536.6, 1346.1 cm<sup>-1</sup> and 1535.2, 1332.8 cm<sup>-1</sup>.

# 3.3. Electronic absorption spectra and electrospray mass spectra

The UV–Vis absorption spectra of 1 and 2 were measured in CH<sub>3</sub>CN solvent in the region of 230–1200 nm (Table 4). All bands are attributed to the anionic portions of these compounds. The characteristic bands of 1 at 859.6, 473.0, 374.0 and 271.0 nm, are assigned as  $L(\pi) \rightarrow M$ ,  $L(\sigma) \rightarrow M$ ,  $L^* \rightarrow L$  and  $L(\sigma) \rightarrow M$ , respectively, which is basically similar to those of  $[(n-C_4H_9)_4N][Ni(mnt)_2]$  [23]. The bands of 2 are similar to those of 1. The negative-ion and positive-ion ESI-MS spectra of 1 and 2 in MeCN solution show that the mass spectrum is dominated by the 230.2 peak, which is due to  $[NO_2BzPyNH_2]^+$ , the peaks at 340.3 and 476.3 are assigned to  $[Ni(mnt)_2 + H]^-$  and  $[Pt(mnt)_2 + H]^-$ , respectively.

#### 3.4. Magnetic properties

The temperature dependence of the magnetic susceptibility for **1** and **2** is measured under an applied field of 1000 Oe in the temperature range 2–300 K. The plot of  $\chi_m$  versus *T* for **1** is shown in Fig. 5, where  $\chi_m$  is the magnetic susceptibility per nickel atom corrected by the diamagnetic contribution. For the complex **1**, the

Table 4 The main UV–Vis spectra (CH<sub>3</sub>CN) of 1 and 2

Complex	$\lambda$ (nm)	$\epsilon (mol^{-1}dm^3cm^{-1}10^3)$
1	1178.0	0.33
	859.6	0.76
	629.0	0.18
	473.0	0.34
	374.0	7.68
	271.0	133.47
2	1180.0	0.27
	850.0	4.91
	629.0	0.35
	455.0	3.27
	333.6	10.70
	273.0	147.66



Fig. 5. Plots of  $\chi_m$  vs. *T* for 1 (inset: plots of  $d(\chi_m T)/dT$  vs. *T*). The solid line are reproduced from the theoretical calculations and detailed fitting procedure described in the text.

overall magnetic behaviors correspond to a paramagnetic system with an antiferromagnetic coupling interaction. As the temperature decreases, the value of  $\chi_{\rm m}T$  slightly decreases from 0.391 emu K mol<sup>-1</sup> at 300 K (the value is somewhat higher than that expected for magnetically isolated Ni(III) ions) to  $0.187 \text{ emu K mol}^{-1}$  at 160 K for 1. In the LT phase, as the samples are continuously cooled, the magnetic susceptibilities decrease exponentially (Fig. 5), indicating that 1 exhibits the characteristics of a spin gap system [24]. On increasing of temperature back to the original one, the same  $\chi_m - T$  curves are obtained without hysteresis effect. These findings indicate that complex 1 undergoes a reversible phase transition. The phase transition temperature is evaluated as the temperature at the maximum of the  $d(\chi_m T)/dT$  derivative, that is  $\sim 160$  K for 1 (inset of Fig. 5).

The spin-gapped system has attracted extensive interest recently [25–28], but it is very rare for Ni(III) complexes [18]. The magnetic susceptibilities of **1** may be estimated by the formula:

$$\chi_{\rm m} = \alpha \exp\left(-\frac{\varDelta}{k_{\rm b}T}\right) \left(\frac{1}{T}\right) + \frac{C}{T} + \chi_0, \tag{1}$$

where  $\alpha$  is a constant value corresponding to the dispersion of the 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 meanings [29]. The best fit curves are shown in Fig. 5, and the corresponding parameters are given as follows:  $\alpha = 1.28$ ,  $\Delta/k_b = 494.97$  K,  $\chi_0 = -5.3 \times 10^{-4}$  emu mol<sup>-1</sup>,  $C = 3.7 \times 10^{-3}$  emu K mol<sup>-1</sup> and  $R = 2.2 \times 10^{-5}$  (*R* is defined as  $\Sigma(\chi_m^{calcd} - \chi_m^{obsd})^2/(\chi_m^{obsd})^2$ ). The value of the parameter  $2\Delta/k_bT_c$  (*T*<sub>c</sub> is the transition temperature) is estimated to be 7.84 on the basis of the above results, which is higher than the ideal value of 3.53 derived from the BCS formula in a weak coupling regime. These results suggest 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; that is, the transition is not a pure spin-Peierls transition [18]. The origins of the phase transition for 1 is attributed to cooperative interactions of Ni · · · S bonding, interplane repulsion of the [Ni(mnt)<sub>2</sub>]<sup>-</sup> anions,  $\pi \cdots \pi$  stacking interactions between of adjacent cations, spin-lattice interactions and spin-spin coupled interaction between nearest-neighbor anions [30–32].

Complex 2 is expected to be diamagnetic on account of the dimerized structure.

# 3.5. Thermodynamic properties

To obtain additional information about the thermodynamic properties of the observed phase transition of 1, DSC measurements on 1 were performed. The power-compensated DSC traces for 1 from 98 to 293 K at a warming rate of 20 K min<sup>-1</sup> are displayed in Fig. 6. For 1, an abruptly endothermic peak in the



Fig. 6. DSC plot for 1.

DSC trace is observed, and the phase transition temperature determined from thermal analysis is 166.4 K, close to the value measured from magnetic susceptibility measurements. The endothermic enthalpy change ( $\Delta H =$ 385.43 J mol<sup>-1</sup>) was estimated from the peak area. Therefore, the result of thermal analysis of 1 further confirms that the magnetic phase transition observed is first-order [33,34]. According to the equation  $\Delta S =$  $\Delta H/T_c$  and  $\Delta H$  estimated above, the estimated entropy change from DSC experiments is 2.31 J mol<sup>-1</sup>, which is much less than the magnetic transition entropy (5.76 J mol<sup>-1</sup> K) calculated according to  $\Delta S = R \ln$ [( $2S_{\rm HT} + 1$ )/( $2S_{\rm LT} + 1$ ), This is expected from the short-range order effects between nearest-neighbor spins in the HT phase [35].

# 4. Conclusion

Here, we have reported the syntheses, spectra, crystal structures and magnetic properties of two new ion-pair complexes containing the  $M(mnt)_2^-$  anion (M = Ni,Pt). The Ni(mnt)<sub>2</sub><sup>-</sup> anions and cations of complex 1 form completely segregated stacking columns, and the Ni(III) ions of 1 forms a 1D zigzag chain with an interatomic Ni $\cdot$ ·Ni distance of 3.855 Å within a Ni(mnt)<sub>2</sub>column, while 2 is dimer. The measurement of the temperature dependence of the magnetic susceptibilities reveal that 1 undergoes a magnetic transition around 160 K and exhibits antiferromagnetic interactions in the high-temperature phase and spin gap systems in the low-temperature phase, while 2 is diamagnetic. The phase transition is first order for 1 as determined by DSC analyses. The different magnetic properties of 1 and 2 are associated with the different packing pattern of the  $M(mnt)_2^-$  anion in these two complexes.

# 5. Supplementary materials

The crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC-242502 and 252467. Copies of the data 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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