# Two Spin-Peierls-like Compounds Exhibiting Divergent Structural Features, Lattice Compression, and Expansion in the Low- Temperature Phase

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Two quasi-one-dimensional (quasi-1D) compounds,  $[4'-CH_3Bz-4-RPy][Ni(mnt)_2]$  (mnt<sup>2-</sup> = maleonitriledithiolate), where 4'-CH<sub>3</sub>Bz-4-RPy<sup>+</sup> = 1-(4'-methylbenzyl)pyridinium (denoted as compound 1) and 1-(4'methylbenzyl)-4-aminopyridinium (denoted as compound 2), show a spin-Peierls-like transition with  $T_{\rm C} \approx$ 182 K for 1 and  $T_{\rm C} \approx 155$  K for 2. The enthalpy changes for the transition are estimated to be  $\Delta H = 316.6$  $J \cdot mol^{-1}$  for 1 and 1082.1  $J \cdot mol^{-1}$  for 2. From fits to the magnetic susceptibility, the magnetic exchange constants in the gapless state are calculated to be J = 166(2) K with g = 2.020(23) for 1 versus J = 42(0)K with g = 2.056(5) for 2. In the high-temperature (HT) phase, 1 and 2 are isostructural and crystallize in the monoclinic space group  $P2_1/c$ . The nonmagnetic cations and paramagnetic anions form segregated columns with regular anionic and cationic stacks. In the low-temperature (LT) phase, the crystals of the two compounds undergo a transformation to the triclinic space group P-1, and both anionic and cationic stacks dimerize. In the transformation from the HT to LT phases, the two compounds exhibit divergent structural features, with lattice compression for 1 but lattice expansion for 2, due to intermolecular slippage. Combined with our previous studies, it is also noted that the transition temperature,  $T_{\rm C}$ , is qualitatively related to the cell volume in the HT phase for the series of compounds [1-(4'-R-benzylpyridinium][Ni(mnt)<sub>2</sub>] (where R represents the substituent). When there is a single substituent in the para position of benzene, giving a larger cell volume, the transition temperature increases.

# Introduction

Functional molecular materials with switching properties and memory transduction are of considerable interest due to their potential technological applications.<sup>1</sup>

As one of this group of functional molecular materials, spin transition compounds display switchable stable/metastable spin states in response to external stimuli such as temperature, pressure, or light. In this rapidly emerging field, spin-crossover compounds that exhibit crossover between high-spin (HS) and low-spin (LS) states are promising examples of technologically useful materials.<sup>2</sup> In addition, spin transition phenomena can probably occur in a charge/electron transfer compound, since the spin transition is associated with the process of charge/ electron transfer between different magnetic centers.<sup>3–7</sup> This also applies to mixed-valence compounds (where the transition arises from charge/valence ordering)<sup>8,9</sup> and quasi-1D quantum magnetic chain compounds, where the strong spin-lattice interaction leads to the spin system displaying a wide range of ground states at low temperature, such as the spin-Peierls state,<sup>10</sup> spin density wave (SDW) state,<sup>11</sup> and so on.

In our previous studies, a series of quasi-1D quantum magnetic chain systems have been built using the bis(maleoni-triledithiolato)nickelate monoanion ( $[Ni(mnt)_2]^-$ ) as the basic magnetic architecture and the benzylpyridinium derivative as

### **SCHEME 1**



the countercation (Scheme 1).<sup>13,14</sup> [Ni(mnt)<sub>2</sub>]<sup>-</sup> is a half spin moiety (S = 1/2) with planar geometry and an extended electronic structure that favors the formation of stacks via intermolecular  $\pi \cdots \pi$  interactions.<sup>12</sup> Thus, it is often observed that both anions and cations form segregated stacks in the crystal structure of such compounds, with each magnetic stack of anions surrounded by four nonmagnetic stacks of organic cations. From the viewpoint of the crystal structure, the compound is an ideal quasi-1D magnetic system with S = 1/2. Theoretically, it is possible for a spin-Peierls (SP) transition to occur in an antiferromagnetically (AFM) coupled S = 1/2 Heisenberg or *XY* magnetic chain when magnetoelastic coupling induces a progressive lattice dimerization.<sup>15</sup> In fact, a spin-Peierls-like transition is observed in these quasi-1D quantum magnetic systems, with the following features: (1) the magnetic chain is

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uniform above the transition and dimerization occurs below the transition; (2) applied pressure strongly promotes the transition, while nonmagnetic doping suppresses the transition;  $^{16,17}$  (3) the pretransitional structural fluctuation (which is a common phenomenon existing in the quasi-1D conductors or magnets and originates from electron-phonon or magnetoelastic coupling interactions) appears in the temperature dependent oscillation photographs.<sup>17,18</sup> As a result, the transition is very similar to the spin-Peierls transition. However, a sharp  $\lambda$ -shaped thermal anomaly, a typical thermodynamic feature of a first-order transition, is observed in the heat capacity measurements in some cases.<sup>13c,17,18</sup> In order to understand these issues further and extend our research, this work reports the use of (4'-methylbenzyl)pyridinium derivatives as the countercation of [Ni(mnt)<sub>2</sub>]<sup>-</sup> to prepare two new compounds, which exhibit spin-Peierls-like transition features.

## **Experimental Section**

The starting materials Na<sub>2</sub>mnt,<sup>19</sup> [4'-CH<sub>3</sub>Bz-4-RPy]Br and [4'-CH<sub>3</sub>Bz-4-RPy]<sub>2</sub>[Ni(mnt)<sub>2</sub>]<sup>13</sup> were synthesized according to literature procedures. Please refer to Scheme 1,  $R_1 = CH_3$ ,  $R_2 = R = H$ ;  $R_1 = CH_3$ ,  $R_2 = R = NH_2$  for compounds 1 and 2, respectively.

**Preparation of [4'-CH<sub>3</sub>BzPy][Ni(mnt)<sub>2</sub>] (1).** An acetonitrile (MeCN) solution (10 cm<sup>3</sup>) of I<sub>2</sub> (150 mg, 0.59 mmol) was slowly added to a MeCN solution (20 cm<sup>3</sup>) of [4'-CH<sub>3</sub>BzPy]<sub>2</sub>[Ni(mnt)<sub>2</sub>] (710 mg, 1.0 mmol). Then, the mixture was stirred for 15 min and then allowed to stand overnight after methanol (MeOH) (90 cm<sup>3</sup>) was added. Brown microcrystals (400 mg) were precipitated and filtered off, washed with MeOH, and dried in a vacuum. Yield: 76.5%. Anal. Calcd for C<sub>21</sub>H<sub>14</sub>N<sub>5</sub>NiS<sub>4</sub>: C, 48.20; H, 2.70; N, 13.38%. Found: C, 48.15; H, 2.65; N, 13.34%. IR spectrum (cm<sup>-1</sup>):  $\nu$ (CN), 2205s;  $\nu$ (C=C) of mnt<sup>2–</sup>, 1458m.

**Preparation of**  $[4'-CH_3Bz-4-NH_2Py][Ni(mnt)_2]$  (2). The procedure for preparing compound 2 is similar to that for 1. Yield: 78.0%. Anal. Calcd for C<sub>21</sub>H<sub>15</sub>N<sub>6</sub>NiS<sub>4</sub>: C, 46.85; H, 2.81; N, 15.61%. Found: C, 46.80; H, 2.79; N, 15.60%. IR spectrum (cm<sup>-1</sup>):  $\nu$ (CN), 2205s;  $\nu$ (C=C) of mnt<sup>2-</sup>, 1456m.

Single crystals of **1** and **2** suitable for X-ray analysis were obtained by evaporating solutions of the corresponding compounds in MeCN.

**Physical Measurements.** Elemental analyses for C, H, and N were performed with a Perkin-Elmer 240 analytical instrument. IR spectra (KBr pellets) were obtained in the 4000–400 cm<sup>-1</sup> region using a IFS66 V FT-IR spectrophotometer. Differential scanning calorimetry (DSC) experiments were performed with a Perkin-Elmer calorimeter; polycrystalline samples were placed in an aluminum crucible and measurements carried out during warming (at a rate of 20 K min<sup>-1</sup>) over the temperature range –170 to 20 °C (103–293 K). Magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL superconducting quantum interference device (SQUID) magnetometer over the range 2–300 K, and diamagnetic correction for each compound was performed utilizing Pascal's constants  $2.35 \times 10^{-4}$  and  $2.42 \times 10^{-4}$  emu•mol<sup>-1</sup> for **1** and **2**, respectively.<sup>20</sup>

**X-ray Single Crystallography.** Crystallographic data for **1** and **2** were collected using a Smart CCD area detection diffractometer with Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation from a graphite monochromator at 293 K (HT) and 123 K (LT), respectively. Structures were solved by the direct method using the SHELXL-97 software package.<sup>21</sup> The non-hydrogen atoms were refined anisotropically using the full-matrix least-squares

TABLE 1: Crystallographic Data for 1 and 2 at 298 and 123  $K^a$ 

compound	1		2	
mol. formula	$C_{21}H_{14}N_5NiS_4$		C21H15N6NiS4	
temperature	293 K	123 K	293 K	123 K
CCDC no.	612873	635758	612874	635759
mol. mass	523.32	523.32	538.34	538.34
space group	$P2_1/c$	P-1	$P2_1/c$	P-1
a/Å	12.123(4)	7.239(3)	12.137(3)	7.311(3)
b/Å	26.446(8)	12.109(5)	26.690(7)	12.252(5)
c/Å	7.389(2)	26.347(11)	7.526(2)	28.680(11)
α/deg	90.00	88.629(6)	90.00	91.557(4)
$\beta/\text{deg}$	103.168(4)	86.360(6)	103.896(5)	92.682(4)
γ/deg	90.00	76.992(4)	90.00	104.625(6)
V/Å <sup>3</sup> /Z	2306.7(12)/4	2245.6(16)/4	2366.6(11)/4	2481.0(17)/4
$\mu/\text{mm}^{-1}$	1.222	1.255	1.194	1.139
λ/Å	0.71073	0.71073	0.71073	0.71073
$\rho/g \cdot cm^{-3}$	1.507	1.548	1.511	1.441
$R_1$	0.0500	0.0520	0.0561	0.0717
$wR_2$	0.0980	0.1157	0.1426	0.1821
${}^{a}R_{1} = \sum_{x}   R_{1} ^{2}$	$F_{\rm o} $ – $ F_{\rm c}  /\Sigma$	$ F_{o} $ and $wR$	$_{2} = \{\Sigma[w(F$	$F_{\rm o}^2 - F_{\rm c}^2)^2]/$

method on  $F^2$ . All H atoms were placed at calculated positions (C-H = 0.930 Å for benzene, 0.970 Å for methylene, and 0.860 Å for  $-NH_2$ ) and refined riding on the parent atoms with U(H) = 1.2Ueq (bonded C or N atoms). Details of the crystal parameters, data collection, and refinements for crystals 1 and 2 at 293 and 123 K are summarized in Table 1. It is noteworthy that the diffuse scattering around the phase transition that is probably driven by magnetoelastic interactions<sup>13c,18</sup> influences the inaccuracy of the diffraction data of 1 and 2, and leads to the parameters,  $wR_2$  and  $R_1$ , being somewhat higher than those in the high-temperature phase.

# **Results and Discussion**

**Crystal Structures of 1 and 2.** In the HT phase, the crystals of **1** and **2** belong to the monoclinic system with space group  $P2_1/c$ . These are isostructural with the reported [4'-RBzPy][N-i(mnt)<sub>2</sub>] compounds (in which the single substituent is located at the para position of benzene in the cation). The asymmetric units in the unit cell of **1** (**2**) comprise one [Ni(mnt)<sub>2</sub>]<sup>-</sup> together with one 4'-CH<sub>3</sub>BzPy<sup>+</sup> (4'-CH<sub>3</sub>Bz-4-NH<sub>2</sub>Py<sup>+</sup>), as shown in Figure 1a (Figure 1b). The NiS<sub>4</sub> core in the [Ni(mnt)<sub>2</sub>]<sup>-</sup> anion exhibits a slightly distorted square planar geometry. The Ni–S bond lengths, ranging from 2.1338(9) to 2.1436(9) Å in **1** (2.1347(11) to 2.1477(10) Å in **2**), and the S–Ni–S bite angles of 92.21(4) and 92.58(4)° in **1** (92.27(4) and 92.41(4)° in **2**) are in agreement with the values reported for other [Ni(mnt)<sub>2</sub>]<sup>-</sup> compounds.<sup>13</sup>

As expected, the anions and cations in the crystals of 1 and 2 form completely segregated stacks along the *c*-axis direction (as displayed in Figure 2 for 1 and Figure S1 in the Supporting Information for 2). Both cationic and anionic stacks are regular, similar to other reported compounds in the series [4'-RBzPy][N $i(mnt)_2$ ]. The nearest Ni····Ni distance is 3.865 Å for 1 versus 3.947 Å for 2 within an anionic stack, and the centroid-tocentroid separation is 4.488 Å for 1 versus 4.296 Å for 2 within a cationic stack. Other significant interatomic contacts within an anionic or a cationic stack are illustrated in Figure 3, Figure 4, and Figure S3 in the Supporting Information, and summarized in Table 2. It is worth noting that only weak van de Waals forces exist between the adjacent anionic and cationic stacks in 1, while strong H-bonding interactions from the NH2 groups of the cation to the CN groups of the mnt<sup>2-</sup> ligands as well as CN··· $\pi$ interactions between the CN group and the pyridine ring are



Figure 1. Molecular structures with atomic labels for (a) 1 and (b) 2 at 293 K (H atoms omitted for clarity).



Figure 2. Packing diagram of 1 showing the segregated cationic and anionic stacks at 293 K.



Figure 3. Illustrations showing the shortest distances for (a) Ni $\cdots$ Ni, Ni $\cdots$ S, and S $\cdots$ S within an anionic stack and (b) the C atom of the methyl group to the centroid of aromatic rings within a cationic stack in the crystal of 1 (H atoms omitted for clarity).

present in 2 (as shown in Figure 4). The corresponding geometric parameters are listed in Tables 2 and 3.

From the HT to LT phases, the space group of the crystal changes from  $P2_1/c$  to P-1 for both 1 and 2, with the asymmetric unit containing either one pair of anion and cation or two pairs of anions and cations. Although the molecular structures in the LT and HT phases for each compound are almost identical, distinct differences were observed between their stacking structures.

For 1, the phase transition results in a nonuniform lattice compression due to dimerization of both cationic and anionic



**Figure 4.** Strong H-bonding and  $CN \cdots \pi$  interactions between the pyridine moiety of the cation and the CN groups of the mnt<sup>2–</sup> ligands in **2** (H atoms omitted for clarity).

TABLE 2:	Significant	Interatomic	Separations	in	the
Crystals of	1 and 2				

distance/Å	1 (293 K)	<b>1</b> (123 K)	<b>2</b> (293 K)	<b>2</b> (123 K)
b1 <sup>a</sup>	3.865	3.795	3.947	3.964
b1′	3.865	3.656	3.947	3.896
b2	3.620	3.584	3.700	3.702
b2′	3.620	3.589	3.700	3.548
b3	3.710	3.675	3.794	3.799
b3′	3.710	3.507	3.794	3.708
a1	4.488	4.304	4.296	4.353
a1′	4.488	4.516	4.296	4.332
a2	3.742	3.612	3.805	3.524
a2′	3.742	3.718	3.805	3.922
a3	3.698	3.680	3.912	3.813
a3′	3.698	3.565	3.912	3.623
a4	3.879	4.017	3.641	3.756
a4′	3.879	3.801	3.641	4.034
c1			3.416	3.477
c1′			3.416	4.192

<sup>*a*</sup> b1, b2, b3, a1, a2, a3, a4, and c1 represent the distances between Ni $\cdots$ Ni, Ni $\cdots$ S, S $\cdots$ S, the centroid-to-centroid distance between the benzene rings, the C atom-to-centroid of benzene ring, the C atom-to-centroid of the pyridine ring, and the N atom-to-centroid of the pyridine ring, respectively (see Figures 4 and 5 and Figure S3 in the Supporting Information).

stacks and the intermolecular slippage. The features of the transition are the following: (1) the cell volume reduces from 2306.7(12) Å<sup>3</sup> at 293 K to 2245.6(16) Å<sup>3</sup> at 123 K; (2) the adjacent anions shrink unevenly along the longer molecular axis direction giving alternating Ni···Ni distances in an anionic stack (3.656 and 3.795 Å); (3) the distortion within a cationic stack is reflected in the centroid-to-centroid separations between adjacent benzene rings (from 4.488 Å in the HT phase to 4.304 and 4.516 Å in the LT phase). Other typical distances which reflect the intermolecular slippage in the HT and LT phases are listed in Table 2.

In the transition from the HT to LT phase of compound **2**, the lattice is compressed along the direction of the anionic and

TABLE 3: H-Bond Lengths (Å) and Angles (deg) in the Crystal of 2 at 293 and 123  $K^{\alpha}$ 

D-H····A	d(D-H)	<i>d</i> (H•••A)	$angle(D-H \cdots A)$	$d(D{\boldsymbol{\cdots}}A)$
		293 K		
$N(6) - H(6A) \cdots N(1) 1^{b}$	0.86	2.47	129.6	3.086(6)
$N(6) - H(6B) \cdots N(3)1^{c}$	0.86	2.48	126.5	3.073(6)
		123 K		
$N(12) - H(12B) \cdots N(3)^{2b}$	0.86	2.57	124.8	3.140(6)
$N(12) - H(12A) \cdots N(4)^{2c}$	0.86	2.52	141.3	3.233(6)
$N(10) - H(10B) \cdots N(6)^{2d}$	0.86	2.63	143.7	3.361(7)

<sup>*a*</sup> Symmetry codes: b = -x + 1, y + 1/2, -z + 1/2; c = -x + 1, -y + 1, -z. Symmetry codes: c = -x, -y + 1, -z + 2; c = x - 1, y - 1, z; d = -x, -y + 1, -z + 1.

cationic stacks due to the dimerization of the stacks (to give rise to the alternating adjacent Ni ···· Ni distances of 3.896 and 3.964 Å), which is similar to that which occurs in 1, with expansion along the longer and shorter molecular axes of the planar anion. Such lattice expansions give rise to the cell volume increase from 2366.6(11) Å<sup>3</sup> at 293 K to 2481.0(17) Å<sup>3</sup> at 123 K. To the best of our knowledge, it is a rare case that the lattice increases upon cooling.<sup>22</sup> As illustrated in Figures 3 and 4 and Tables 2 and 3, it has been found that the separations of the C atom in the methyl group to the centroid of pyridine, the centroid-to-centroid separations between the adjacent benzenes in the cationic stack, as well as the separations of the N atom in the CN group to the centroid of pyridine between the anionic and cationic stacks become longer in the LT phase as a result of the slippages of the anions and cations along the longer and shorter molecular axes of the planar anion.

Magnetic Susceptibilities of 1 and 2. The variable temperature molar magnetic susceptibilities of 1 and 2 were investigated over the temperature range 2–300 K. Upon cooling from 300 to 2 K, a spin-Peierls-like transition occurred at around 182 K for 1 and 155 K for 2. On raising the temperature back to room temperature, no sizable hysteresis was detected for either compound. In the HT phase, the overall magnetic behaviors of 1 and 2 correspond to an antiferromagnetically coupled system. The value of  $\chi_m T$  at 300 K is 0.275 emu·K·mol<sup>-1</sup> for 1 versus 0.333 emu·K·mol<sup>-1</sup> for 2, less than the 0.375 emu·K·mol<sup>-1</sup> for a spin-only value with S = 1/2 per formula unit. Below the transition, the magnetic susceptibility drops steeply and a small paramagnetic-like tail is observed in the low-temperature region for the  $\chi_m$  values of 1 and 2.

A comparison of the magnetic features for two compounds reveals the following two significant differences: (1) the transition temperature of **2** is lower than that of **1**; (2) below the transition temperature, the magnetic susceptibility of **2** changes much more rapidly and attains a nonmagnetic state, whereas the magnetic susceptibility of **1** decreases progressively, which is the characteristic of a spin-Peierls transition due to the dimerized state possessing a continuum of excited states.<sup>15</sup>

To estimate the magnetic coupling interaction in the HT phase, we fitted the temperature dependent magnetic susceptibilities of **1** (in the range 187–300 K) and **2** (in the range 156–300 K) utilizing a simple Curie–Weiss equation, to obtain the Curie–Weiss parameters  $C = 0.575(26) \text{ emu} \cdot \text{mol}^{-1}$  with  $\theta = -290(23)$  K and  $C = 0.371(4) \text{ emu} \cdot \text{mol}^{-1}$  with  $\theta = -10(2)$  K for **1** and **2**, respectively. The theoretical plot of the temperature dependence of the magnetic susceptibility well matches the experimental data for **2** (please refer to Figure S4 in the Supporting Information), while the Curie constant for **1** is not reasonable. On the other hand, the phenomenology of the magnetic transitions in **1** and **2** closely resembles that of a spin-Peierls transition in a quasi–1D spin system and, from the

structural viewpoint, the magnetic chain is regular. On the other hand, it was found that the single crystal magnetic susceptibilities are almost independent of the magnetic field direction for other members in this series of spin-Peierls-like compounds.<sup>13c</sup> Therefore, we have further analyzed their magnetic behavior in the HT phase using the regular antiferromagnetic Heisenberg model for a linear chain with  $S = 1/2.^{23}$  The temperature dependences of the magnetic susceptibility in the range 187–300 K for **1** and 156–300 K for **2** are simulated using eq 1:

$$\chi_{\rm m} = \frac{Ng^2 \mu_{\rm B}^2}{4k_{\rm B}T} \cdot \frac{1 + \sum_{i=1}^5 N_i X^{-i}}{1 + \sum_{i=1}^6 D_i X^{-i}}$$
(1)

where  $X = k_{\rm B}T/||J||$ , where J is the magnetic exchange constant of the neighboring spins in a magnetic chain, and the coefficients of  $N_i$  and  $D_i$  in the power series. The best fit yielded  $J/k_{\rm B} =$ 166(2) K with a g-factor of 2.020(23) for **1** and  $J/k_{\rm B} =$  42 (0) K with a g-factor of 2.056(5) for **2** (Figure 5). The fitted g-factors are close to the experimental values from EPR measurements.<sup>24</sup>

In the low-temperature phase, an opening of the spin gap was observed. Accordingly, we simulated the magnetic susceptibilities of both 1 (temperature range 2–123 K) and 2 (2–141 K) using eq  $2^{23,25}$ 

$$\chi_{\rm m} = \frac{\alpha}{T^{\gamma_0}} \exp(-\Delta/k_{\rm B}T) + \frac{C}{T}$$
(2)

where  $\alpha$  is a constant corresponding to the dispersion of the excitation energy,  $\Delta/k_{\rm B}$  is the magnitude of the spin gap,  $\gamma_0$  is a constant ( $\gamma_0 = 0.5$ ), and the *C/T* term represents the contribution from magnetic impurities. Simulation gave the results  $\alpha = 1.68(18)$ ,  $\Delta/k_{\rm B} = 933(17)$  K, and  $C = 0.52(1) \times 10^{-3}$  emu·mol<sup>-1</sup> for **1** and  $\alpha = 54(166)$ ,  $\Delta/k_{\rm B} = 1474(442)$  K, and  $C = 1.36(2) \times 10^{-3}$  emu·mol<sup>-1</sup> for **2**. Obviously, the fitted results for **2** appear to be unreasonable.

Thermodynamic Properties. DSC measurements on 1 and 2 were performed, and the thermogramms for a warming rate of 20 K  $\cdot$  min<sup>-1</sup> are depicted in Figure 6, in which 2 shows a more abrupt endothermic peak around its transition temperature. The peak temperatures  $T_{\text{max}}$  (~182 K for 1 and 154 K for 2) are close to the results from the magnetic susceptibility measurements. The endothermic enthalpy changes ( $\Delta H$ ), which were calculated from the integrated peak areas, are estimated to be 316.6  $J \cdot mol^{-1}$  for **1** and 1082.1  $J \cdot mol^{-1}$  for **2**, confirming that the transitions are first-order.<sup>26-29</sup> Compared with 1, compound 2 shows a larger endothermic enthalpy change. This observation is probably related to the strong H-bonding interactions in 2, and the larger enthalpy change is essential contribution of lattice degrees of freedom in the transition of 2. Combined with our previous studies, the qualitative relationship between the transition enthalpy and the magnetic susceptibility below the transition temperature has been noted; namely, a larger enthalpy change corresponds to the sharp drop of magnetic susceptibility, while a smaller one matches the progressive decrease of magnetic susceptibility in the LT phase. The latter case is similar to a spin-Peierls transition (where the transition enthalpy is zero). On the basis of the above analysis, it is further assumed that the magnetic gap in the dimerized state follows



Figure 5. Plots of  $\chi_m(T)$  vs T for compounds 1 and 2 (open circles, experimental data; solid lines, fits; for details, see the text).



**Figure 6.** DSC curves for compounds 1 and 2 showing  $T_{\text{peak}}$  and  $\Delta H$  of the phase transition.



Figure 7. The linear relationship between  $T_{\rm C}$  and cell volume for two series of spin-Peierls-like compounds.

the usual temperature dependence of the BCS energy gap in the case of the transition with smaller enthalpy change.<sup>15</sup>

Relationship between the Substituent Group and the Transition Temperature. Over the last half decade, we have investigated the crystal structure and magnetic properties of a series of [Ni(mnt)<sub>2</sub>]<sup>-</sup> compounds using different benzylpyridinium derivatives as the counter cations, and observed the presence of a spin-Peierls-like transition in many cases. It is interesting that the transition temperature  $T_{\rm C}$  can be tuned by modifying the substituents on the aromatic rings. For two series of compounds with a single substituent in the para position of benzene, the variation of  $T_{\rm C}$  seems to be independent of the electronic effect of the substituent. The compounds in question, abbreviated as [4'-RBzPy][Ni(mnt)<sub>2</sub>], are isostructural and crystallize in monoclinic space group  $P2_1/c$  in the HT phase (see inset of Figure 7).<sup>13</sup> For example, the electron affinity of the substituents should follow the order NO<sub>2</sub>, CN > F > Cl >Br > I, whereas the variation of  $T_C$  in the corresponding compounds does not show this simple order. On the other hand,

NO<sub>2</sub> and CH<sub>3</sub> show different effects of electron donating and withdrawing, but the two corresponding compounds show a similar transition temperature. As shown in Figure 7, the variation of  $T_{\rm C}$  looks to be dependent on the size of the substituent group, since the spin-Peierls-like transition temperature rises with the cell volume of the crystal, which increases with the atomic size as well as atomic numbers of the substituent located in the para position of the benzene ring. The effect of the size of the substituent group on  $T_{\rm C}$  is probably related to the so-called "chemical pressure" effect.<sup>30</sup>

### **Conclusion and Remarks**

In conclusion, we have shown that two molecular compounds (1 and 2) assemble into novel spin transition systems, via  $\pi - \pi$ stacking between the planar molecular groups  $[Ni(mnt)_2]^-$ . For 1 and 2, the spin transition is associated with a structural transition. However, both the structural and magnetic aspects of the transition are distinct from each other. From the HT phase to the LT phase, a lattice compression is observed for 1 but a lattice expansion for 2. Below the transition temperature and upon further cooling, the magnetic susceptibility progressively decreases for 1 (the progressive decrease of the magnetic susceptibility is probably related to the dimerized state possessing a temperature dependence of the BCS energy gap), whereas it drops sharply for 2. Combined with our previous studies, we find that the variation of the transition temperature,  $T_{\rm C}$ , increases with the cell volume in the HT phase for two series of compounds with a single substituent in the para position of benzene [4'-RBzPy][Ni(mnt)<sub>2</sub>] (see Figure 7).

Theoretically, the relationship between the transition temperature  $T_{\rm C}$  and applied pressure P, at thermal equilibrium, is given by the Clapeyron equation,  $dP/dT_{\rm C} = \Delta S/\Delta V = \Delta H/(T_{\rm C} \cdot \Delta V)$ , where  $\Delta H$ ,  $\Delta S$ , and  $\Delta V$  represent the enthalpy, entropy, and volume changes between the HT and LT phases,

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respectively. In the case of lattice compression in the LT phase,  $T_{\rm C}$  is actually observed to shift to higher temperature under pressure.<sup>16</sup> For **2**, the cell volume increases in the LT phase, and as a consequence, a new issue is opening, which is whether  $T_{\rm C}$  does or does not decrease with *P*. We are exploring collaboration for the study of the magnetic susceptibility under pressure.

**Supporting Information Available:** Crystallographic data (excluding structure factors) for the structures of 1 and 2 at 293 and 123 K and figures showing the packing diagram of 2, the interactions between the pyridine moieties of the cation in 2, the nearest distances in anionic and cationic stacks, magnetic susceptibility vs *T* plots for 1 and 2, and a  $\chi_m$  vs *T* plot for 2. This material is available free of charge via the Internet at http:// pubs.acs.org.

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