

Peculiar Magnetic Transition Behaviour Around 208 K in One-dimensional Nickel(III) Chain Complex [1-(4'-Vinylbenzyl)pyridinium][Ni(mnt)₂] (mnt²⁻ = Maleonitriledithiolate)

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A new ion-pair complex, [VBzPy][Ni(mnt)₂], where [VBzPy]⁺ = 1-(4'-vinylbenzyl)pyridinium and mnt²⁻ = maleonitriledithiolate, has been synthesized. The cations and anions stack into completely separated columns and Ni(III) ions form a uniformly spaced one-dimensional (1-D) zigzag chain within a [Ni(mnt)₂]⁻ column in solid state. Magnetic susceptibility and DSC measurements revealed that there exists a first-order phase transition at approximately 208 K.

Transition-metal complexes of maleonitriledithiolate (mnt) have drawn great attention in the field of chemistry and physics because of their specific electrical, magnetic, and optical properties.¹⁻⁴ Recently, we have reported a series of complexes formed by [M(mnt)₂]⁻ and benzylpyridinium derivatives.^{5,6} One of interesting features of them is that the constituent planar anions [Ni(mnt)₂]⁻ form completely segregated stacking column and further result in an uniform or alternately spaced 1-D magnetic chain of spin *S* = 1/2 through the intermolecular *d*_{z²} or π orbital interactions. In addition, the stacking structure of these complexes can be tuned by systemically varying of the substituents on aryl ring of the cations, and further lead to versatile magnetic exchange properties. To extend our research and understand these novel magnetic properties, we should investigate the relationship between the magnetic interactions and the stacking pattern of anions and cations systemically. Herein, we report a new ion-pair complex [1-(4'-vinylbenzyl)pyridinium][Ni(mnt)₂] (**1**) showing a peculiar transition around 208 K. To our best knowledge, the transition temperature higher than 200 K is very rare in the [M(mnt)₂]⁻ complexes.

[VBzPy]₂[Ni(mnt)₂] was prepared by the direct combination of 1:2:2 mol equiv. of NiCl₂·6H₂O, Na₂mnt and [VBzPy]Br in H₂O. Oxidation of [VBzPy]₂[Ni(mnt)₂] with I₂ in MeCN furnished complex **1** in 78% yield. Single crystals suitable for X-ray structure analyses were obtained by evaporating the MeCN solution of **1**.

Complex **1** crystallizes in the monoclinic space group *P*2₁/*c* at room temperature.⁷ The coordination geometry of the nickel atom in the [Ni(mnt)₂]⁻ exhibits square planar with four sulfur atoms. The average S–Ni–S bond angle within the five-membered ring is 92.29(8)°. The average Ni–S bond distance is 2.141(2) Å, which is in agreement with those found in other mnt complexes.^{5,6} In the cation, the terminal methylene of vinyl group is disordered between two positions about 1.63 Å apart, and one of which is modeled at 50% occupancy. The benzene ring and pyridine ring are twisted to the reference plane defined by N5–C14–C15 with the dihedral angles 93.2° for benzene ring and 85.7° for pyridine ring, respectively. As might be anticipated, in complex **1**, anions and cations form completely segregated stacking column along the direction of *c* axis (Figure 1). As

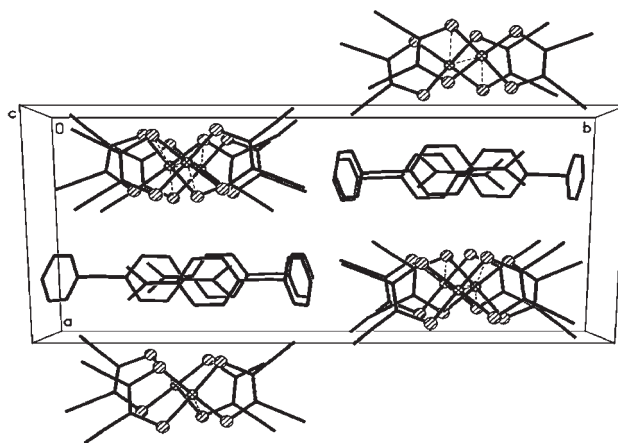


Figure 1. Structure of the anions and cations of the complex viewed along the *c* axis.

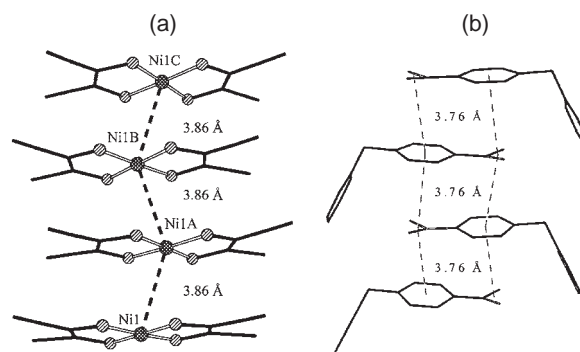


Figure 2. (a) one-dimensional (1-D) zigzag chain of Ni(III) ions. (b) π – π interactions between vinyl groups and benzene rings.

illustrated in Figure 2, within a column of [VBzPy]⁺, the neighboring benzene rings are almost parallel to each other with the dihedral angle of 6.0°. The distance of the center of the disordered vinyl group and the center of the neighboring benzene ring is 3.76 Å. Obviously, the cations form 1-D chain through π – π interactions between vinyl groups and benzene rings; Within an anion column, Ni(III) ions form a uniformly spaced 1-D zigzag chain and the nearest Ni...Ni, Ni...S, and S...S distances are 3.86, 3.65, 3.72 Å, respectively. The closest Ni...Ni separation between anion chains is 11.95 Å, which is significantly longer than that within a chain. Therefore, from viewpoint of crystal structure, the [Ni(mnt)₂]⁻ anion column can be considered as 1-D magnetic chain.

The variable-temperature magnetic properties of **1** have been investigated at 2 kOe in the temperature range 2–300 K

(Figure 3). The overall magnetic behavior of **1** corresponds to an antiferromagnetic system. The value of $\chi_m T$ at 300 K is $0.308 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$, significantly less than the value of $0.375 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ expected for one spin-only Ni(III) ion with $S = 1/2$ per formula unit. With decreasing temperature, the $\chi_m T$ value first decreases slightly till reaching $0.243 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ at 208 K. Then $\chi_m T$ drops more sharply below this temperature. On increase of the temperature back to the original temperature, the same curve is obtained, and no hysteresis is detected. Obviously, **1** undergoes a phase transition at approximately 208 K. To obtain more information about this transition, DSC measurements of **1** were performed in the temperature range of 170–240 K at a warming rate of $20 \text{ K}\cdot\text{min}^{-1}$. There is an abrupt endothermic peak in the DSC trace, which indicates the phase transition is of first order. The endothermic enthalpy change (ΔH) is $559.4 \text{ J}\cdot\text{mol}^{-1}$. The phase transition temperature observed from DSC trace is 208.1 K, in agreement with the value measured from magnetic susceptibility measurements.

In the low-temperature phase, **1** exhibits the characteristics of a spin gap system, so the magnetic susceptibility may be estimated by the eq 1:

$$\chi_m = \frac{\alpha}{T} \exp\left(-\frac{\Delta}{k_B T}\right) + \frac{C}{T} + \chi_0 \quad (1)$$

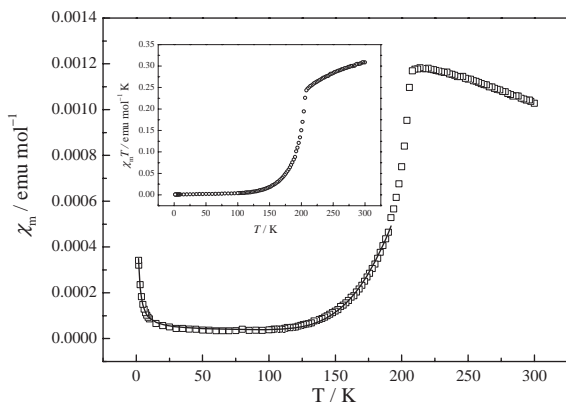


Figure 3. The plot of χ_m vs T for **1**. The solid line represents the best fit; inset: $\chi_m T$ vs T for **1**.

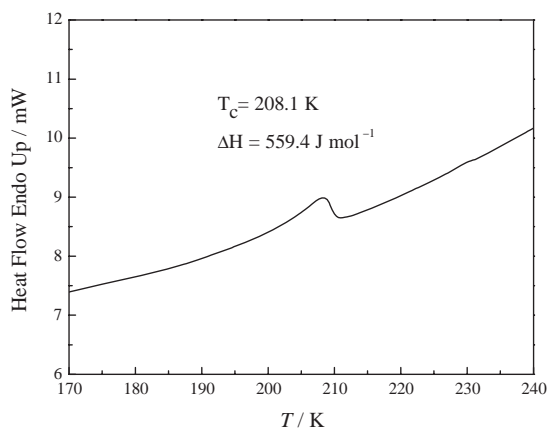


Figure 4. DSC plot for **1** showing the phase transition at 208.1 K.

Where α is a constant value corresponding to the dispersion of excitation energy, Δ is the magnitude of the spin gap, χ_0 is the constant term caused by the core diamagnetism and the possible Van Vleck paramagnetism, and other symbols have their usual meaning.^{6,8} The best fit curve in the temperature range 2–200 K is displayed in Figure 3, and the corresponding parameters are given as following: $\alpha = 114 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$, $\Delta/k_B = 1337 \text{ K}$, $C = 5.7 \times 10^{-4} \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$, $R = \sum(\chi_m^{\text{obs}} - \chi_m^{\text{calc}})^2 / \sum(\chi_m^{\text{obs}})^2 = 5.38 \times 10^{-11}$. The value of the parameter, $2\Delta/k_B T_c$ (T_c is the transition temperature 208 K), is 14.18 and more removed from the ideal value of 3.53 derived using the BCS formula in a weak coupling regime. This exceptionally large value means that the short-range magnetic correlations within the chain are not fully developed and intrinsic magnetoelastic instability of a 1-D system cannot be considered as a driving force for the transition; namely, the transition is not a conventional spin-Peierls transition.⁶ The phase transition results from cooperative interactions of π - π stacking interactions between the adjacent cations, Ni...S bonding, interplane repulsion of anions,⁹ spin-spin coupled interaction between nearest neighbor anions,¹⁰ and spin lattice interactions.^{11,12}

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- 7 Crystallographic data of **1** are: $\text{C}_{22}\text{H}_{14}\text{N}_5\text{NiS}_4$, monoclinic, $P2_1/c$, fw 535.33, $a = 12.168(3)$, $b = 27.046(7)$, $c = 7.354(2)$ Å, $\beta = 103.00(1)^\circ$, $V = 2358.1(11)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.508 \text{ g cm}^{-3}$, $T = 293 \text{ K}$, $R = 0.076$ [$I > 2\sigma(I)$], and 4066 independent reflections. Deposited in No. CCDC-260369.
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