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A New Quasi-1D Spin System with Spin Transition Exhibiting Novel CN···π Interactions

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A new molecular tecton with a flexible conformation, 1-methylethyldeneaminopyridinium, was synthesized, and its corresponding compound with [Ni(mnt)$_2$]$^-$ exhibits novel CN···π interactions and spin transition.

The generatation of functional materials utilizing crystal-oriented syntheses via noncovalent interactions (such as hydrogen-bonding and cation$-\pi$ and $\pi-\pi$ stacking interactions between suitable molecules or ions) has attracted considerable attention.[1,2] Because of the important role in biochemical processes such as transporting and binding amino acids and nucleotides, research of a relatively new anion binding motif, the anion$-\pi$ interaction, has become a challenge in supramolecular chemistry.[3−6]

The molecular tectons of [M(mnt)$_2$]$^-$ (M = Ni, Pd, and Pt; mnt^{2-} = maleonitriledithiolate) possess a planar configuration with an extended electronic structure, which promotes the formation of stacks via intermolecular $\pi-\pi$ interactions. In our previous studies, these systems were chosen as the magnetic architectures to construct a series of quasi-1D magnets with spin transition,[7,8] which have potential applications in spintronic devices.[9,10] The theoretical investigation of the [Ni(mnt)$_2$]$^-$ spin system further demonstrates that the magnetic coupling feature is very sensitive to the overlap pattern of the nearest-neighboring [M(mnt)$_2$]$^-$ molecules in a stack.[11] Therefore, a slight change in the overlap pattern, probably induced by temperature/pressure change or disorder−order transformation,[12] can trigger a spin transition. As a result, it is possible to achieve a spin-transition system through softening of the crystal phase based on the [M(mnt)$_2$]$^-$ magnetic architecture,[13] which requires the countercation to have a flexible conformation. We have synthesized such a cation, 1-methylethyldeneaminopyridinium (abbreviated as $C_3H_6{=}NPy^+$, in which two moieties of the molecule, $C_3H_6{=}N$ and Py, can rotate freely around the N$-$N$_{Py}$ single bond), and the corresponding compound [$C_3H_6{=}NPy$][Ni(mnt)$_2$] (**1**) exhibits a spin transition. It is also interesting to note that a novel CN···π interaction is observed in this molecular system.

The starting materials for the preparation of **1**, hydroxylamine-*O*-sulfonic acid,[14,15] [N$-$NH$_2$Py]I,[16] Na$_2$mnt,[17] and [N$-$NH$_2$Py]$_2$[Ni(mnt)$_2$][18] were synthesized according to literature procedures. In the process of [N$-$NH$_2$Py]$_2$[Ni(mnt)$_2$] oxidation, [N$-$NH$_2$Py]$^+$ reacts with solvent acetone to form [C_3H_6-NPy]$^+$.

The variable-temperature magnetic properties of **1** were investigated over the range 2−350 K (Figure 1). The value of $\chi_m T$ at 350 K is 0.249 emu·K·mol^{-1}, significantly less

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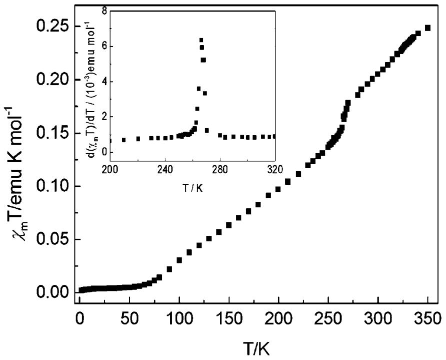

Figure 1. Plot of $\chi_m(T)$ vs T for **1** (inset: plot of $d(\chi_m T)/dT$ vs T in which a peak appears at 266.2 K).

than the value of 0.375 emu·K·mol^{-1} expected for a spin-only system with $S = {}^1/_2$. Upon cooling, the $\chi_m T$ value first decreases gradually and reaches 0.178 emu·K·mol^{-1} at 270 K and then drops sharply and reaches 0.149 emu·K·mol^{-1} at 260 K. Below this temperature, the $\chi_m T$ value decreases gradually again and reaches 0.005 emu·K·mol^{-1} at 50 K. The sudden drop at 270 K indicates a transition occurring (the spin−lattice interactions might be one of the main driving forces for the transition),[18] and the transition temperature is determined as 266.2 K with the peak temperature in the plot of $d(\chi_m T)/dT$ vs T. No sizable hysteresis is detected while the temperature is increased back to room temperature.

X-ray single-crystal structure[19] determinations reveal that **1** crystallizes in the monoclinic space group $P2_1/n$ in both high-temperature (HT) and low-temperature (LT) phases, and an asymmetric unit comprises one $[Ni(mnt)_2]^-$, together with one $[C_3H_6{=}NPy]^+$, as shown in Figure 2a. In an anionic moiety, the Ni−S bond lengths and S−Ni−S angles in a chelate ring are normal in both HT and LT phases, which is in agreement with those in the reported $[Ni(mnt)_2]^-$ compounds.[12,18] As anticipated, anions and cations form segregated stacks along the *a*-axis direction, as illustrated in Figure 3. The other novel characteristic is CN···π interactions between CN of the mnt^{2-} ligand and the pyridine ring (cf. Figure 2b), and the shorter interatomic contacts are 3.380, 3.481, and 3.681 Å in the HT phase versus 3.466, 3.469, and 3.667 Å in the LT phase for N2···C10A, N2···C11A, and N2···C12A (symmetric code A = 2 − *x*, 1 − *y*, 1 − *z*). The N···centroid distances in the HT and LT phases are 3.438 and 3.408 Å, respectively, which are comparable with the results in the literature.[20] Generally, the anion−π interaction is found between an electron-deficient π-electron system of aromatic compounds and an anion, in which case the contributions from electrostatic interactions and anion-induced polarization are energetically favorable.[4] To understand further the origin of CN···π interaction, the charge distributions in **1** were calculated under the theoretical framework of density functional theory (DFT) at the UBPW91/LANL2DZ level,[21] the entire molecular structure of **1** was taken directly from the X-ray crystallographic structure at 298 K, and the convergence criterion of the self-consistent field was 10^{-8}. The calculation results indicate that the partial charges δ on N2, C10A, C11A, and C12A are −0.0477, +0.0959, +0.1366, and +0.1159 electrons, respectively. Thus, CN···π interaction is primarily attributed to electrostatic attraction.

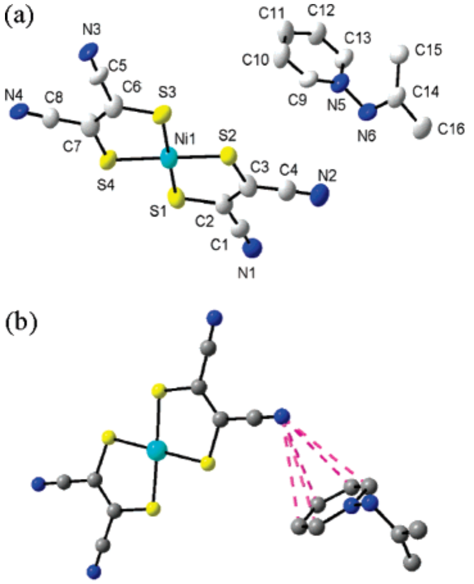

Figure 2. (a) Asymmetric unit of **1** (H atoms are omitted for clarity). (b) Interaction between the pyridine ring and CN at 298 K.

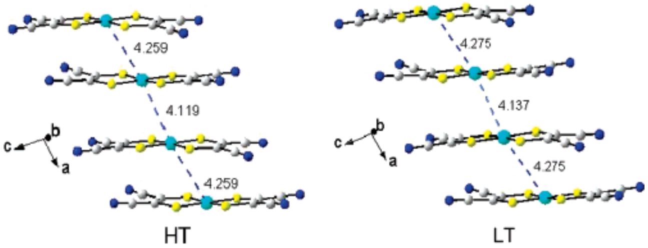

Figure 3. Side view of the 1D anion chain for **1** in the HT and LT phases.

Three distinctions are observed in crystal structures between HT and LT phases. The first one concerns the nonuniform expansion and slippage of the anion stacks, as shown in Figure 3. The nearest-neighboring Ni···Ni distances rise from 4.119 and 4.259 Å in the HT phase to 4.137 and 4.275 Å in the LT phase, which results in a slight increase of the cell parameters *a*, *b*, and *V*. Although such a phenomenon has been reported in some inorganic materials,[22] to our best knowledge, it is the first example in dithiolene complexes where the unit cell volume of the crystal rises

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(19) Crystal data of **1** at 298(2) K: $C_{16}H_{11}N_6NiS_4$, $M_r = 474.26$, monoclinic, space group $P2_1/n$, $a = 7.883(2)$ Å, $b = 17.777(3)$ Å, $c = 14.967(3)$ Å, $\beta = 99.931(4)°$, $V = 2065.9(7)$ Å^3, $Z = 4$, $\rho = 1.525$ g·cm^{-3}, $\mu = 1.357$ cm^{-1}, $F(000) = 964$, GOF = 1.081. Of 4056 total reflections collected, 3260 were unique ($R_{int} = 0.0395$). R1 (wR2) = 0.0578 (0.1363) for 234 parameters and 4056 reflections [$I > 2\sigma(I)$]. Crystal data of **1** at 253(2) K: $C_{16}H_{11}N_6NiS_4$, $M_r = 474.26$, monoclinic, space group $P2_1/n$, $a = 7.910(7)$ Å, $b = 17.789(14)$ Å, $c = 14.957(12)$ Å, $\beta = 100.004(13)°$, $V = 2073.0(3)$ Å^3, $Z = 4$, $\rho = 1.520$ g·cm^{-3}, $\mu = 1.352$ cm^{-1}, $F(000) = 964$, GOF = 1.104. Of 4061 total reflections collected, 3178 were unique ($R_{int} = 0.0395$). R1 (wR2) = 0.0592 (0.1495) for 246 parameters and 4061 reflections [$I > 2\sigma(I)$].

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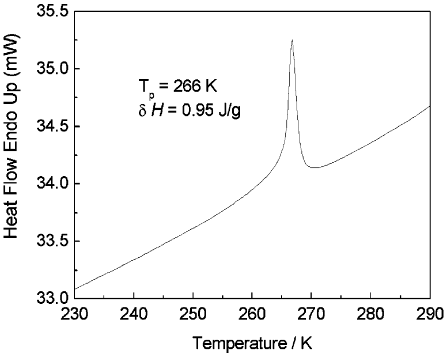

Figure 4. DSC curve of **1** showing T_{peak} and δH of the phase transitions.

slightly in the lower temperature structure, associated with a looser stacking. The second distinction is that the N···centroid distance decreases by 0.03 Å from the HT phase to the LT phase, which means that the CN···π interactions become stronger in the LT phase. The third distinction involves the change in the dihedral angle between the methylethyl plane and the pyridine ring (from 80.7° in the HT phase to 95.2° in the LT phase), thereby providing further evidence that the spin transition is coupled with the counterionic conformation change.

Differential scanning calorimetry (DSC) measurements on **1** were performed to further explore the thermodynamic properties of the spin transition. The power-compensated DSC traces at a warming rate of 20 K·min^{-1} are displayed in Figure 4. An abrupt endothermic peak at the transition temperature ($T_{\mathrm{peak}} = 266$ K and $\Delta H \approx 451.0$ J·mol^{-1}) is observed, which is in good agreement with the result from the magnetic susceptibility measurement. The existence of a nonzero enthalpy change validates the first-order transition.[23,24] It is deduced that the entropy difference of the phase transition is approximately 1.70 J·mol^{-1}·K^{-1} according to $\Delta S = \Delta H/T_{\mathrm{C}}$ and the ethalpy estimated above. The magnetic entropy can be calculated from $R \ln[(2S_{\mathrm{HT}} + 1)/(2S_{\mathrm{LT}} + 1)] = R \ln 2 \approx 5.76$ J·mol^{-1}·K^{-1}, where $R = 8.31441$ J·mol^{-1}·K^{-1} is the gas constant.[25] The estimated entropy change from DSC measurement is equal to ~29.5% of the magnetic entropy alone, which is expected because of the short-range order effects between the nearest-neighboring spins in the HT phase.[26]

In summary, $[\mathrm{M(mnt)_2}]^-$ monoanions (M = Ni, Pd, and Pt) are effective tectons of supramolecular electrical and/or magnetic materials[27−29] because of their unique solid-state properties, such as their ability to undergo spin transitions. We have obtained a new spin-transition system by combining a countercation with a flexible conformation and the $[\mathrm{Ni(mnt)_2}]^-$ monoanion. In the solid state, a rare noncovalent interaction is observed between the neutral CN group and a deficient π system (Py$^+$), which may be responsive to the nonuniform expansion and slippage of the anion stacks that lead to a slight increase of the cell volume in the lower temperature structure.

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Supporting Information Available: Crystallographic CIF files for **1** in HT and LT phases, full synthetic details for **1**, selected bond distances and angles, packing diagram, models of overlapping of $[\mathrm{Ni(mnt)_2}]^-$ anions, and the charge distributions in **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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