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Alkyl side chain on the 1-methylimidazolium ring of countercation modulating thermal and magnetic properties of metal-dithiolene complexes

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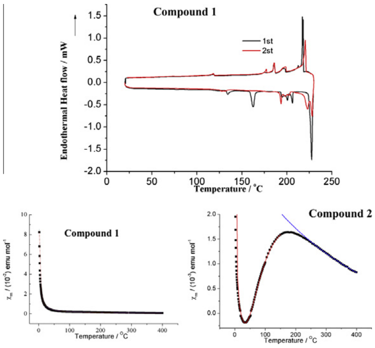
HIGHLIGHTS

- Multi-step solid to solid state phase transition was observed for **1**.
- **1** exhibits weak paramagnetism and **2** shows spin gap in the low-temperature phase.
- The cations and anions formed mixed column along the crystallographic *a*-axis direction in the crystal of **1**.

GRAPHICAL ABSTRACT

Multi-step solid to solid state phase transition was observed for **1** by DSC. **1** exhibits weak paramagnetism over the temperature range of 2–400 K and **2** shows spin gap in the low-temperature phase.



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ABSTRACT

Two low-dimensional ion-pair compounds [1,5-bis(1-methylimidazolium)pentane][Ni(mnt)$_2$]$_2$ (**1**) and [1,9-bis(1-methylimidazolium)nonane][Ni(mnt)$_2$]$_2$ (**2**) (mnt^{2-} = maleonitriledithiolate) were designed and synthesized. The cations and anions formed mixed column along the crystallographic *a*-axis direction in the crystal of **1·0.5DMF**. Two compounds display different thermal and magnetic behaviors. Multi-step solid to solid state phase transition was observed for **1** by DSC. **1** exhibits weak paramagnetism over the temperature range of 2–400 K and **2** shows spin gap in the low-temperature phase. Thus by changing of the alky chain length of the counter-cation allows the modulation thermal and magnetic behaviors for such system.

Introduction

Recently, there has been much interest in one-dimensional (1D) electron system, or quantum wires, because they have many characteristic physical properties, such as spin-Peierls (SP) transition in Heisenberg chain [1], spin-density-wave (SDW) and charge-density-wave (CDW) state in organic conductors [2], and slow relaxation of magnetization in several ferro- or ferrimagnetic compounds [3]. The SP transition occurs when a system of uniform antiferromagnetic (AFM) Heisenberg linear chains undergoes a transformation to a system of dimerized or alternating AFM linear chains. This

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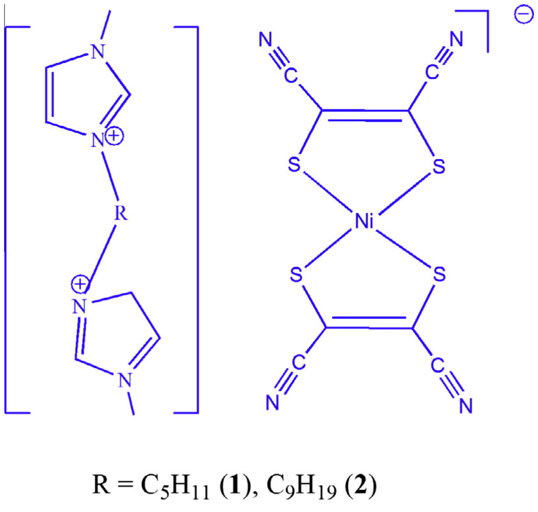
dimerization is mainly caused by the spin-phonon coupling between the 1D spin system and the three-dimension (3D) phonon system. The SP transition has been found in several inorganic compounds [4] and dithiazolyl radicals [5], which is promoted by the SP dimerization of the magnetic chains [6].

Our research interests focus on the assembly of SP-type transition system which have been based on the molecular architecture of bis-(maleonitriledithio)metalate monoanions ($[M(mnt)_2]^-$ and M = Ni, Pd, or Pt) [7]. A SP-type transition observed in our studies is usually trigged by structure phase transition. Thus, to achieve such types of SP-type transition molecular solids, a critical issue is design a suitable counter-cation which can strongly affect the packing mode of anions and inducing phase transition. Recently, we introduce the rod-like flexible mono-cation into the $Ni(mnt)_2]^-$ spin system, and founded crystal to liquid crystal phase transition can induce SP-type transition [8]. In order to further explore the correlation among the structural features of the counter cation, arranging pattern of the anions stack column as well as the features of SP-type transition, we expand the types of cations. In this paper, we designed the bis-N-alkylimidazolium-type dication. Compared with Λ-shaped benzylpyridinium derivatives, this typed dication has more flexible —CH_2— single bond which allows two 1-methylimidazolium head to rotate easier, and the size and polarity of cation is easily regulated by changing the alkyl chain. According to the above-mentioned research results, $[1,5\text{-bis}(1\text{-methylimidazolium})\text{pentane}]^{2+}$ and $[1,9\text{-bis}(1\text{-methylimidazolium})\text{nonane}]^{2+}$ dication was brought in the $[Ni(mnt)_2]^-$ spin system to yield two ion-pair compounds (ref. Scheme 1, where R = C_5H_{11} and C_9H_{19}, corresponding to compounds **1** and **2**, respectively) and the crystal structure, thermal and magnetic properties were studies for two compounds.

Experimental section

Chemicals and materials

All reagents and chemicals were purchased from commercial sources and used without further purification. Disodium maleonitriledithiolate (Na_2mnt) was prepared following the published procedure [9], 1,5-bis(1-methylimidazolium)pentane dibromide, 1,9-bis(1-methylimidazolium)nonane dibromide, $[1,5\text{-bis}(1\text{-methylimidazolium})\text{pentane}][Ni(mnt)_2]$ and $[1,9\text{-bis}(1\text{-methylimidazolium})\text{nonane}][Ni(mnt)_2]$ were synthesized according to the similar procedure described in the literature [8].



R = C_5H_{11} (**1**), C_9H_{19} (**2**)

Scheme 1. Illustration for the molecular structures of **1** and **2**.

Synthesis of compound 1 and 2

$[1,5\text{-bis}(1\text{-methylimidazolium})\text{pentane}][Ni(mnt)_2]_2$ (1) A MeOH solution (10 cm^3) of I_2 (0.80 mmol) was slowly added to the mixture of MeOH (25 cm^3) and $[1,5\text{-bis}(1\text{-methylimidazolium})\text{pentane}][Ni(mnt)_2]$ (1.0 mmol), after stirred for 25 min, the mixture was allowed standing overnight. The black precipitate formed and were filtered off, washed with MeOH and dried at 100 °C in vacuum. Yield: ~36%.

A similar procedure was used for preparation of 2 and the final product of each compound was dried at 80 °C under vacuum for microanalysis.

The single crystals of **1** suitable for X-ray structure analyses were obtained by evaporation of the solutions of **1** in DMF at room temperature for 5–7 days. The single crystals suitable for X-ray analysis were failed to be obtained for **2**, as a consequence, their crystal structure data are unavailable at present.

Chemical characterization and physical measurements

Elemental analyses (C, H and N) were performed with an Elementar Vario EL III analytical instrument. Rom temperature IR spectra of compound $[1,5\text{-bis}(1\text{-methylimidazolium})\text{pentane}][Ni(mnt)_2]$ was recorded on a Bruker Vector 22 Fourier Transform Infrared Spectrometer (170SX) (KBr disc). Powder X-ray diffraction (PXRD) measurements were performed on Bruker D8 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Magnetic susceptibility data for polycrystalline samples were measured over a temperature range of 1.8–400 K using a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer. Differential scanning calorimetry (DSC) experiments were carried out on a Pyris 1 power-compensation differential scanning calorimeter with the heating and cooling rate of 10 K/min.

X-ray single crystallography

Selected crystals were centered on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire 3 CCD detector and a mirror monochromated Mo Kα radiation ($\lambda = 0.71073$). The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlis [10]. Structures were solved by the direct method using the SHELXL-97 software package [11]. The non-hydrogen atoms were refined anisotropically using the full-matrix least-squares method on F^2. DMF molecule is disordered with two possible sites, and the occupied factor for each site was refined. All H atoms were placed at calculated positions and refined riding on the parent atoms with U(H) = 1.2Ueq for aromatic carbon atoms and Uiso(H) = 1.5Ueq(C) for methyl groups. Details of the crystal parameters, data collection, and refinements for crystals **1·0.5DMF** at 296 K are summarized in Table 1.

Results and discussion

Crystal structure of 1·0.5DMF

Crystal of **1·0.5DMF** at 296 K belongs to triclinic system with space group *P*-1, the asymmetric unit in the unit cell of **1·0.5DMF** comprise two $[Ni(mnt)_2]^-$ anions, one dication and one half of DMF molecule. The molecular structure of **1·0.5DMF** is illustrated in Fig. 1a. The NiS_4 core in the $[Ni(mnt)_2]^-$ anion exhibits approximated planar geometry; the bond lengths and angles in $[Ni(mnt)_2]^-$ anions listed in Table 2 are in good agreement with the reported compounds [8,12]. The dication is composed of a hydrocarbon chains and two 1-methylimidazolium head cores,