



Two molecular metals with one-dimensional non-uniform magnetic chain of bis(maleonitriledithiolate)nickel(III) monoanion: Syntheses, structures and magnetic properties

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ABSTRACT

Two new molecular metals, [2FBz-2NH₂Py][Ni(mnt)₂] (**1**) and [4FBz-2NH₂Py][Ni(mnt)₂] (**2**) ([2FBz-2NH₂Py]⁺ = 1-(2'-fluobenzyl)-2-aminopyridinium, [4FBz-2NH₂Py]⁺ = 1-(4'-fluobenzyl)-2-aminopyridinium, mnt²⁻ = maleonitriledithiolate), have been prepared and characterized by elemental analyses, IR, MS spectra, single crystal X-ray diffraction. The Ni(III) ions of **1** and **2** form a 1D zigzag non-uniform magnetic chain within a [Ni(mnt)₂]⁻ column through Ni···Ni, Ni···S, Ni···C, S···C, N···C or π···π interactions both at 293 and 150 K (the crystal structure of **2** at 293 K has been briefly reported earlier, here the crystal structure at 150 K and magnetic susceptibility are investigated). Upon the temperature is lowered, the non-uniform chain has been compressed with the shortness of Ni···Ni distance. Variable temperature magnetic susceptibility measurements agree very well with the 1D non-uniform chain structures, and **1** exhibits a spin-gap transition around 260 K with Δ/k_B = 1160.0 K, while **2** shows two spin-gap transitions around 235.7 K (Δ/k_B = 867.8 K) and 10.4 K (Δ/k_B = 19.1 K), respectively.

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1. Introduction

Hybrid organic–inorganic salts have attracted considerable attention due to their novel physical properties such as non-linear optical behavior, magnetic and electrical properties [1–5]. The properties of these salts depend strongly on not only the molecular structure of the building units but also on the arrangement of the structural units in the crystal lattice [6–8]. In the past few years, the ongoing study of low-dimensional magnetic lattices has led us to study a series of salts of formula A_n[M(mnt)₂] (mnt = maleonitriledithiolate; n = 1 or 2) where A is an organic cation, usually NH₄⁺, ethylpyridinium and substituted benzyl pyridinium or triphenylphosphonium, and M is Ni, Pd, Pt or Cu ion. A wide variety of these salts, especially with bis(maleonitriledithiolate)Ni(III) anion are known [9–14]. The use of these cations with their variety of size and shape produces 1D chain within the lattice, resulting in a variety of magnetic behaviors such as ferromagnetic ordering at low temperature, magnetic transition from ferromagnetic coupling to

diamagnetism, meta-magnetism, spin-Peierls-like transitions, and spin gap transitions [9–22]. The magnetic properties of these salts are dominated by non-covalent interactions between the [Ni(mnt)₂]⁻ anions. The change in location of the substituent on the aromatic ring changes both the dihedral angle between aromatic rings and the hydrogen bonding capabilities. Substantial efforts have been committed to looking for more suitable organic counter-cations to tune the crystal stacking structure of [Ni(mnt)₂]⁻ ions with a view to obtaining ideal molecular magnets. Recently, we have synthesized and characterized two molecular solids containing substituted 2-aminopyridinium, [Bz-2NH₂Py][Ni(mnt)₂] and [2-NpCH₂-2NH₂Py][Ni(mnt)₂] ([Bz-2NH₂Py]⁺ = 1-benzyl-2-aminopyridinium and [2-NpCH₂-2NH₂Py]⁺ = 1-(2'-naphthylmethylene)-2-aminopyridinium), and found that the Ni(III) ions of them form a 1D zigzag magnetic chain through Ni···N or π···π interactions, while the overlapping fashions of the [Ni(mnt)₂]⁻ anions and their magnetic behaviors are different when the 2-aminopyridine ring has been fixed and the phenyl ring has been changed into the naphthyl ring [23]. The presence of fluorine in organic compounds can enhance the stability against oxidation and modify the structure due to its high electro-negativity, relatively small size, and very low polarizability, etc. [24,25]. With a view to extending our study, in this article, we have used two cations containing fluorine

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Table 1
Crystal data and structure refinements for **1** and **2**.

Compound	1 (293 K)	1 (150 K)	2 (293 K) [24]	2 (150 K)
Chemical formula	C ₂₀ H ₁₂ NiN ₆ S ₄ F	C ₂₀ H ₁₂ NiN ₆ S ₄ F	C ₂₀ H ₁₂ NiN ₆ S ₄ F	C ₂₀ H ₁₂ NiN ₆ S ₄ F
Formula weight	542.31	542.31	542.31	542.31
Temperature (K)	291(2)	291(2)	293(2)	150(2)
Space group	C2/c	C2/c	P2 ₁ /n	P2 ₁ /c
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Unit cell dimensions				
<i>a</i> (Å)	24.616(3)	24.515(3)	7.577(1)	7.412(1)
<i>b</i> (Å)	12.590(1)	12.463(2)	12.788(2)	12.820(1)
<i>c</i> (Å)	15.216(2)	15.044(2)	23.542(3)	23.712(2)
β (°)	96.23(1)	95.08(2)	99.26(1)	98.24(1)
Volume (Å ³), <i>Z</i>	4687.8(9), 8	4578.1(10), 8	2251.4(5), 4	2229.8(3), 4
Density (calculated) (g/cm ³)	1.537	1.574	1.600	1.615
Absorption coefficient (mm ⁻¹)	1.212	1.242	1.262	1.274
<i>F</i> (000)	2200	2200	1100	1100
Crystal size (mm ³)	0.12 × 0.18 × 0.23	0.11 × 0.13 × 0.18	0.25 × 0.28 × 0.43	0.11 × 0.16 × 0.22
Max. and min. transmission	0.768 and 0.868	0.807 and 0.876	0.725 and 0.665	0.788 and 0.868
θ range for data collection (°)	1.66–25.50	1.67–25.50	1.75–25.00	1.81–25.49
Limiting indices	–29 ≤ <i>h</i> ≤ 27 –15 ≤ <i>k</i> ≤ 14 –18 ≤ <i>l</i> ≤ 18	–29 ≤ <i>h</i> ≤ 29 –15 ≤ <i>k</i> ≤ 15 –18 ≤ <i>l</i> ≤ 17	–8 ≤ <i>h</i> ≤ 8 –11 ≤ <i>k</i> ≤ 15 –27 ≤ <i>l</i> ≤ 27	–8 ≤ <i>h</i> ≤ 8 –15 ≤ <i>k</i> ≤ 15 –28 ≤ <i>l</i> ≤ 28
Reflections collected	17291	16524	10979	16305
Independent reflections	4363	4273	3944	4141
<i>R</i> _(int.)	0.038	0.034	0.043	0.047
Goodness-of-fit on <i>F</i> ²	1.027	1.029	1.019	1.032
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0421, <i>wR</i> ₂ = 0.1149	<i>R</i> ₁ = 0.0250, <i>wR</i> ₂ = 0.0697	<i>R</i> ₁ = 0.0377, <i>wR</i> ₂ = 0.0945	<i>R</i> ₁ = 0.0273, <i>wR</i> ₂ = 0.0718
Final <i>R</i> indices (all data)	<i>R</i> ₁ = 0.0529, <i>wR</i> ₂ = 0.1232	<i>R</i> ₁ = 0.0298, <i>wR</i> ₂ = 0.0727	<i>R</i> ₁ = 0.0480, <i>wR</i> ₂ = 0.0983	<i>R</i> ₁ = 0.0312, <i>wR</i> ₂ = 0.0742
Residual [e Å ⁻³]	0.613 and –0.649	0.269 and –0.355	0.448 and –0.300	0.406 and –0.295

$$R_1 = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}, wR_2 = \frac{[\sum w(|F_o|^2 - |F_c|^2)^2]}{\sum w(|F_o|^2)^2}]^{1/2}.$$

substituent, [2FBz-2NH₂Py]⁺ and [4FBz-2NH₂Py]⁺, as counterion of [Ni(mnt)₂]⁻ anion to synthesize [2FBz-2NH₂Py][Ni(mnt)₂] (**1**) and [4FBz-2NH₂Py][Ni(mnt)₂] (**2**), and examine their crystal structures at the room temperature and 150 K, along with their magnetic properties. Especially, so far as we know, it is unusual that the molecular solid containing [Ni(mnt)₂]⁻ anion exhibits two spin-gap transitions upon the temperature is lowered.

2. Experimental

2.1. Materials and methods

2-Aminopyridine, 2-fluobenzyl bromide, 4-fluobenzyl bromide, nickel(II) chloride were purchased from commercial sources and used as received. Disodium maleonitriledithiolate (Na₂mnt), 1-(2'-fluobenzyl)-2-aminopyridinium bromide ([2FBz-2NH₂Py]Br) and 1-(4'-fluobenzyl)-2-aminopyridinium bromide ([4FBz-2NH₂Py]Br) were synthesized following the literature procedures [26,27]. Elemental analyses for C, H and N were run on a Model 240 Perkin-Elmer instrument. IR spectra were recorded as KBr pellets on an IF66V FT-IR spectrophotometer (4000–400 cm⁻¹), and referenced to polystyrene. Electrospray mass spectra [ESI-MS] were determined on a Finnigan LCO mass spectrometer. Magnetic data on crushed polycrystalline samples of **1** and **2** were collected in 2–300 K temperature using a Quantum Design MPMS SQUID magnetometer. The temperature-dependent magnetic data were obtained at a magnetic field of *H* = 2 kOe.

2.2. Syntheses of **1** and **2**

[2FBz-2NH₂Py][Ni(mnt)₂] (**1**) and [4FBz-2NH₂Py][Ni(mnt)₂] (**2**) were prepared following the literature method [28]. Yield of **1**: 80.2%. Anal. Calc. for C₂₀H₁₂FN₆NiS₄: C, 44.29; H, 2.23; N, 15.50. Found: C, 44.24; H, 2.32; N, 15.37%. IR (cm⁻¹): 3376m, 3223m, 3088w, 3063w, 2213m, 1668s, 1588m, 1524m, 1492m, 1459m, 1239m, 1162m, 1096w, 1027w, 851w, 756m. Yield of

2: 83.5%. Anal. Calc. for C₂₀H₁₂FN₆NiS₄: C, 44.29; H, 2.23; N, 15.50. Found: C, 44.20; H, 2.35; N, 15.42%. IR (cm⁻¹): 3372m, 3226w, 3098w, 3071w, 2973w, 2919w, 2848w, 2206m, 1652m, 1625m, 1581m, 1509m, 1460w, 1417w, 1222w, 1156m, 765m, 498m. The black block-shaped crystals suitable for X-ray structure analyses and other measurements were obtained by evaporating the solution of **1** in CH₃OH/*i*-PrOH (1:1, v/v) and **2** in CH₃CN/*i*-PrOH (1:1, v/v).

2.3. X-ray crystallography

Suitable size crystals of **1** and **2** were selected, attached to a glass fiber, and mounted on a Smart APEX CCD system with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) using φ and ω scans for data collection at 291 and 150 K, respectively. Cell parameters were determined using SMART software and refined using SAINTplus [29]. Data reduction and absorption corrections were made via SADABS [29]. The structures were solved via direct methods using SHELXS97 [27] and refined via least squares using SHELXL97 [27]. Hydrogen atoms bonded to carbon atoms were placed in calculated positions and refined as a riding model with fixed isotropic values. The positions of H atoms bonded to nitrogen atoms were refined with anisotropic thermal parameters. Details of the data collection parameters and crystallographic information for **1** and **2** are provided in Table 1.

3. Results and discussion

3.1. Infrared spectra and electrospray mass spectra

Bands at 3376, 3223 cm⁻¹ for **1** and 3372, 3226 cm⁻¹ for **2** are due to the stretching vibration frequencies of N–H in the NH₂ group. The bands at 3088, 3063 cm⁻¹ for **1** and 3098, 3071 cm⁻¹ for **2** are due to the stretching vibration frequencies of C–H in the aromatic ring. The strong band at 2213 cm⁻¹ for **1** and 2206 cm⁻¹ for **2** is the CN stretching band. Bands at 1668, 1588, 1524, 1492 cm⁻¹

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