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Molecular spin ladders self-assembly from $[Ni(dmit)_2]^-$ building blocks: Syntheses, structures and magnetic properties

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Abstract

Two ion-pair compounds, consisting of 1-(4′-R-benzyl)pyridinium ($[RBzPy]^+$, R = NO_2 (**1**) and Br (**2**)) and $[Ni(dmit)_2]^-$ ($dmit^{2-}$ = 2-thioxo-1,3-dithion-4,5-dithiolato), have been synthesized and structurally characterized. The anions of $[Ni(dmit)_2]^-$ stack into dimers, which further construct into two-leg ladder through terminal S···S interactions in **1**, lateral S···S interactions in **2**. The weak H-bonding interactions of C–H···S were observed in **2**, while only weak van de Waals interactions between anion and cations in **1**. The magnetic susceptibilities measured in 2–300 K indicate AFM exchange interaction domination both two compounds. A peculiar magnetic transition at ~100 K was observed in **1**. An AFM ordering below ~11 K was found in **2**, and the best fit to magnetic susceptibility above 45 K in this compound, using a dimer model with $s = 1/2$, give rise to $\Delta/k_B = 36.1$ K, $zJ = -0.91$ K, $C = 3.2 \times 10^{-3}$ emu K mol^{-1} and $\chi_0 = -4.0 \times 10^{-6}$ emu mol^{-1} with g of 2.0 fixed.

Keywords: Bis(2-thioxo-1,3-dithion-4,5-dithiolato)nickelate compound; Crystal structure; Magnetic property; Spin ladder

1. Introduction

Recently, a great deal of research has been reported on conductivity and magnetic property of different types of bis-dithiolate metal complexes [1].

In our previous research, using benzylpyridinium derivatives ($[RBzPy]^+$) as the counter-cation of $[M(mnt)_2]^-$ (M = Ni, Pd and Pt), a series of ion-pair compounds with segregated columnar stacks of cations and anions have been prepared [2–6]. The quasi-one-dimensional magnetic nature of these compounds was attributed to intermolecular π-orbital interactions within the anionic columns. Furthermore, for some compounds, spin-Peierls-like transition was observed [1a,4,5a]. More presently, we are devoted to our research interesting on the molecular magnets self-assembly from $[Ni(dmit)_2]^-$ ion due to its molecular and electronic structure resemble $[Ni(mnt)_2]^-$ ion, which is expected to obtain new series of molecular magnets with peculiar magnetic phase transition via incorporating the benzylpyridinium derivatives into $[Ni(dmit)_2]^-$ spin system. Herein, we report syntheses, crystal structures, and magnetic properties of two compounds consisting of $[Ni(dmit)_2]^-$ and benzylpyridinium derivatives.

2. Experiments

2.1. Physical measurements

Elemental analyses were performed with a Perkin–Elmer 240 analytical instrument. Magnetic susceptibility

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data on polycrystalline sample were collected in 2–300 K using a MagLab system 2000 magnetometer.

2.2. Syntheses of $[NO_2BzPy][Ni(dmit)_2]$ (1) and $[BrBzPy][Ni(dmit)_2]$ (2)

1 and **2** were prepared according to the procedure described in [7], elemental *Anal.* Calc. for $C_{18}H_{11}N_2NiO_2S_{10}$: C, 32.4; H, 1.66; N, 4.20. Found: C, 31.9; H, 1.70; N, 4.18% for **1**, and *Anal.* Calc. for $C_{18}H_{11}BrNNiS_{10}$: C, 30.9; H, 1.58; N, 2.00. Found: C, 30.7; H, 1.68; N, 1.96% for **2**.

The single crystals suitable for X-ray analysis were obtained by dispersing Et_2O into MeCN solution of **1** for one week.

2.3. X-ray crystallography

Diffraction data of **1** was collected at 293 K on a CAD4 with Mo Kα radiation. The structure of **1** was solved by direct method and refined on F^2 by full-matrix least-squares method using the SHELXTL program package [8]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their calculated positions and refined following the riding model. Crystal data for **1**: $C_{18}H_{11}N_2NiO_2S_{10}$, $M = 666.60$, triclinic, space group $P\bar{1}$, $a = 9.3500(19)$ Å, $b = 11.780(2)$ Å, $c = 11.860(2)$ Å, $\alpha = 80.16(3)°$, $\beta = 89.52(3)°$, $\gamma = 76.04(3)°$, $V = 1248.3(4)$ Å^3, $Z = 2$, $D_{calc} = 1.773$ g cm^{-3}, $\mu = 1.635$ mm^{-1}, final R, $R_w = 0.0450$, 0.1034. 3601 observed

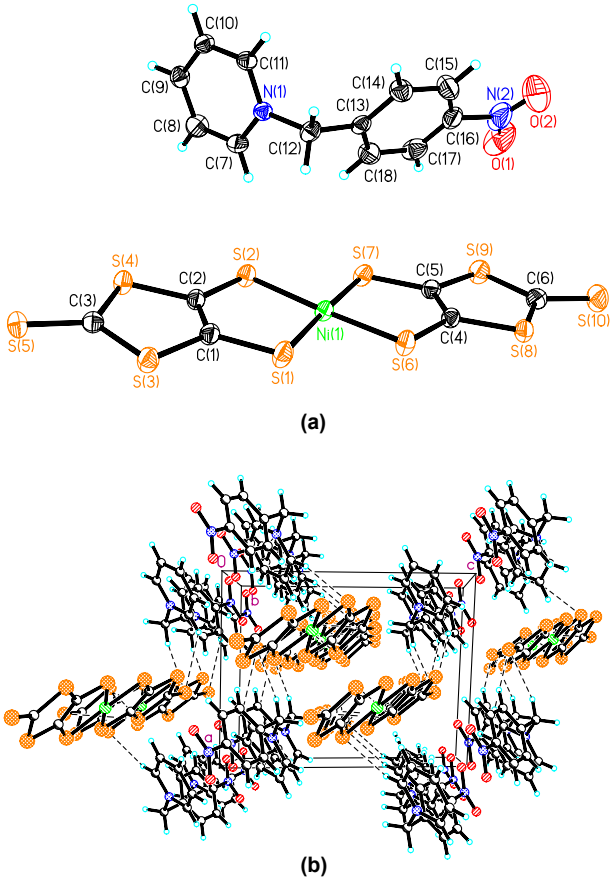

Fig. 1. (a) ORTEP drawing of **1** with 30% possibility ellipsoids and (b) the packing structure projected along *c*-axis.

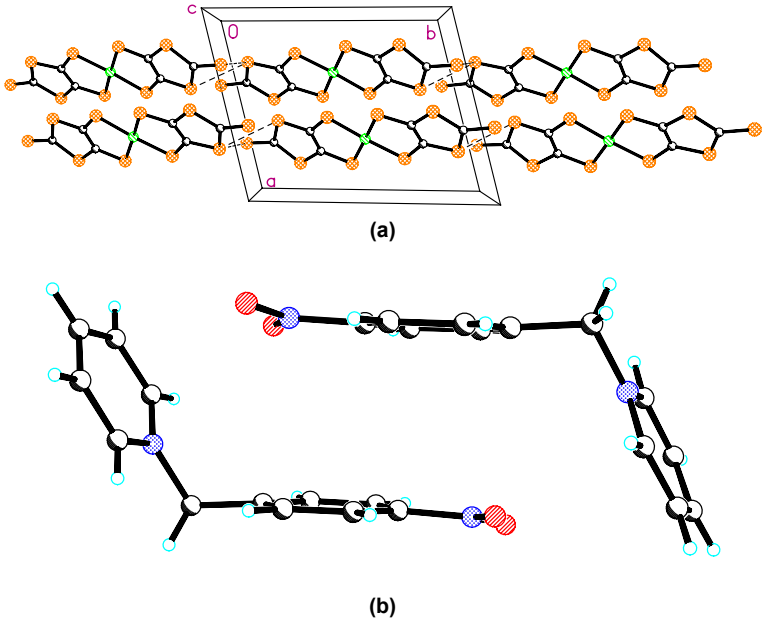

Fig. 2. (a) Spin ladder (the direction of ladder leg is parallel to *b*-axis) (b) dimer of cation in **1**.