Solid State Sciences 11 (2009) 1216–1221

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Effect of counter cationic geometry on stacking structures and magnetic properties of $[Ni(mnt)_2]^-$ complexes

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ARTICLE INFO

Article history:
Received 19 January 2009
Received in revised form
9 March 2009
Accepted 19 March 2009
Available online 31 March 2009

Keywords:
Bis(maleonitriledithiolato)nickelate monoanion
Crystal structure
H-bonding interaction
Magnetic property

ABSTRACT

The crystal structures and magnetic properties of two new ion-pair complexes, $[N\text{-}NH_2Py][Ni(mnt)_2]$ (**1**) and $[N\text{-}NH_2Ql][Ni(mnt)_2]$ (**2**) ($N\text{-}NH_2Py^+$ = 1-aminopyridinium, $N\text{-}NH_2Ql^+$ = 1-aminoquinolinium; mnt^{2-} = maleonitriledithiolate) have been investigated. The differences of the molecular topology and size of the counter cation result in distinct anionic and cationic stacking patterns in the crystals, namely, in the crystal of **1** the anions (A) and cations (C) alternate to stack into a mixed column in the fashion of …AACCAACC…, and the neighboring columns are connected together via intermolecular H-bonding interactions as well as van der Waals forces; while, in the crystal of **2**, the anions and cations alternate to form a mixed columnar stack in the manner of …ACAC…, and the adjacent columns are held together via weak van der Waals forces. Investigations of variable-temperature magnetic susceptibility indicated that **1** is a spin gap system but its magnetic behavior does not follow the Bleaney–Bowers spin dimer model; **2** shows a magnetic feature of linear decrease of $\chi_m T$ value upon cooling, and this kind of magnetic behavior is probably related to the presence of temperature independent paramagnetism.

1. Introduction

Considerable efforts have been directed towards the utilization of crystal-oriented syntheses via non-covalent interactions, such as H-bonding and π···π stacking interactions between suitable molecules or ions to produce functional materials. The use of bis(dithiolato)metalate complexes as building units in the construction of such molecule based materials has received extensive attention due to their potential applications in the areas of near-infrared (near-IR) dyes [1,2], conducting [3,4], magnetic [5,6] or nonlinear optical materials [7,8]. The planar $[M(mnt)_2]^-$ anions (mnt^{2-} = maleonitriledithiolate; M = Ni or Pt) possess $S = 1/2$ spin and are favorable to form face-to-face stack via the intermolecular M···M, M···S, S···S and π···π interactions, the molecular materials constructed from such molecular architectures exhibit versatile magnetic properties, for instance, ferromagnetic ordering, magnetic field induced antiferromagnetic to ferromagnetic transition, and spin-Peierls-like transitions [9–11].

In our previous studies, the pyridinium derivatives were employed as the counter cation of $[Ni(mnt)_2]^-$ molecular architectures to achieve a series of quasi-one-dimensional (quasi-1D) spin systems, some of which exhibit novel spin-Peierls-like transition [12,13] without sizable hysteric loop, a crucial characteristic for potential molecular device. It is noteworthy that the existence of hysteric loop seems to be related to the intermolecular cooperativity in a spin transition system [14,15], and this motivates us to introduce a counteraction as a potential H-bonding donor to the spin system of $[Ni(mnt)_2]^-$. On the other hand, the topology and size of counter cation in $[Ni(mnt)_2]^-$ complexes strongly influence the $[Ni(mnt)_2]^-$ stacking pattern, which impose directly effect on the magnetic properties of the complexes. To deepen understanding of the magnetostructural relationship in $[Ni(mnt)_2]^-$ complexes, we herein report the structures and magnetic properties of two new complexes, $[N\text{-}NH_2Py][Ni(mnt)_2]$ (**1**) and $[N\text{-}NH_2Ql][Ni(mnt)_2]$ (**2**) (for the molecular structures of $N\text{-}NH_2Py^+$ and $N\text{-}NH_2Ql^+$ see Scheme 1).

2. Experimental

2.1. Chemicals and reagents

All reagents and chemicals were purchased from commercial sources and used without further purification.

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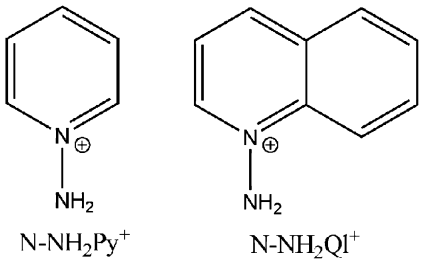
doi:10.1016/j.solidstatesciences.2009.03.013



Scheme 1. The cationic structures of N-NH_2Py^+ and N-NH_2Ql^+.

Table 1
Crystallographic and refinement data for **1** and **2**.

Complex	**1**	**2**
Molecular formula	$C_{13}H_7N_6NiS_4$	$C_{17}H_9N_6NiS_4$
CCDC numbers	643587	643589
Molecular mass	434.200	484.25
Space group	$P2_1/n$	$P2_1/n$
a/Å	15.620(4)	7.799(2)
b/Å	6.8484(18)	6.1944(19)
c/Å	17.388(5)	19.905(6)
α/°	90.000	90.00
β/°	115.719(4)	99.405(5)
γ/°	90.000	90.00
V/Å^3, Z	1675.7(8), 4	948.6(5), 2
μ/mm^{-1}	1.664	1.479
ρ/g cm^{-3}	1.721	1.695
R_1	0.0556	0.0467
wR_2	0.1136	0.1333

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

2.2. Physical measurements

Elemental analyses were performed on an Elementar Vario EL III analytic instrument. IR spectra were recorded on a Bruker Vector 22 Fourier Transform Infrared Spectrometer (170SX) (KBr disc). Magnetic susceptibility data on polycrystalline sample were collected over the temperature range of 2–350 K using a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer.

2.3. Preparations for **1** and **2**

The starting materials Na_2mnt, [N-NH_2Py]I and [N-NH_2Ql]I were synthesized following the literature procedures [16,17]. A similar method to prepare $[Bu_4N]_2[Ni(mnt)_2]$ [18] was employed to synthesize [N-NH_2Py]$_2$[Ni(mnt)$_2$] and [N-NH_2Ql]$_2$[Ni(mnt)$_2$].

*[N-NH_2Py][Ni(mnt)$_2$] (**1**).* A MeCN solution (10 cm^3) of I_2 (150 mg, 0.59 mmol) was slowly added to a MeCN solution (20 cm^3) of [N-NH_2Py]$_2$[Ni(mnt)$_2$] (530 mg, 1.0 mmol) with stirring for 15 min. After MeOH (90 cm^3) was added, the mixture was allowed to stand overnight, and 350 mg of black microcrystalline sample was filtered off, washed with MeOH, and dried in a vacuum. Yield: 80.6%. Anal. Calcd for $C_{13}H_7N_6NiS_4$: C, 35.96; H, 1.63; N, 19.36; Found: C, 35.93; H, 1.65; N, 19.38%. IR spectrum (KBr disc, cm^{-1}): ν(CN), 2205vs; ν(C=C) of mnt^{2-}, 1475s.

*[N-NH_2Ql][Ni(mnt)$_2$] (**2**).* This complex (312 mg) was obtained in terms of the procedure above-described for **1**, but [N-NH_2Py]$_2$[Ni(mnt)$_2$] replaced with [N-NH_2Ql]$_2$[Ni(mnt)$_2$] as the starting material. Yield: 64.4%. Anal. Calcd for $C_{17}H_9N_6NiS_4$: C, 42.16; H,

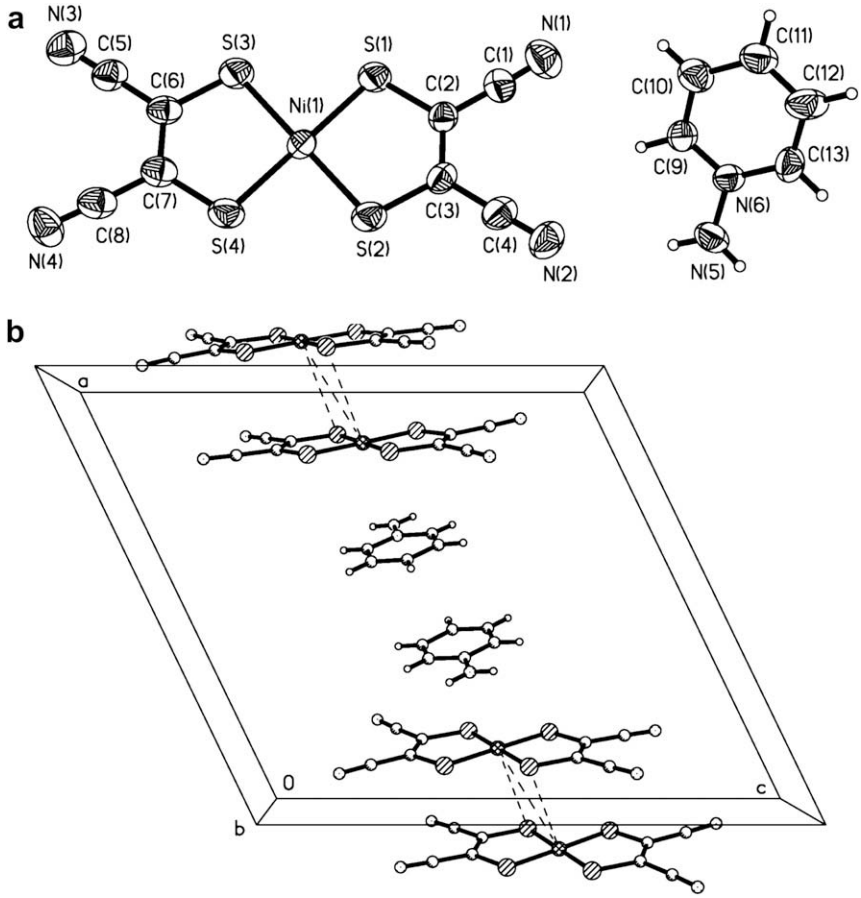


Fig. 1. (a) Molecular structure of **1** with non-hydrogen atoms labeling and (b) anionic and cationic dimers alternate to form a columnar arrangement along *a*-axis for **1**.