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Novel molecular staircases constructing from H-bonding interactions based on the building blocks of $[Ni(mnt)2]^-$ ions: syntheses, crystal structures, EPR spectra and magnetic properties

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Abstract

Two new ion-pair compounds, consisting of 1-(4′-R-phenacyl)pyridinium derivatives and bis(maleonitriledithiolato)nickelate, have been synthesized and characterized structurally (R = NMe_2 (**1**) and H (**2**)). In crystal **1**, H-bonding interactions connecting the cations and anions lead a molecular staircase to form. The adjacent paramagnetic anions are effectively separated by nonmagnetic cations, and the magnetic behavior of **1** is nearly an isolated spin-system, which is supported by the results both EPR (which possesses the very narrow half-width at half-height of ~18 Gs) and temperature dependence of magnetic susceptibility. While the cations and anions arrange alternately layered structure in crystal **2**. In an anionic layer, the neighboring dimers form an anionic chain via peripheral S···S stacking interactions. The magnetic feature of **2** denotes the presence of antiferromagnetic interactions between the nearest-neighboring spins, but deviates from any dimer or alternating chain magnetic model.

Keywords: Bis(maleonitriledithiolato)nickelate compound; Crystal structure; H-Bonding interaction; EPR spectra; Magnetic property

1. Introduction

Considerable interest has been focused on $[M(mnt)_2]^-$ compounds (M = Ni, Pd or Pt; mnt^{2-} = maleonitriledithiolate) due to their unusual properties in magnetism and conductivity [1–5].

We have been paying attention to the study on quasi-one-dimensional spin system of molecules, because such a system displays a wide range of ground states [for example, Peierls- and spin-Peierls transition, charge density wave (CDW), spin density wave (SDW) and charge ordering and so on due to the inherent instability of one-dimensional electron gas] [2]. The flat-shaped anions, $[M(mnt)_2]^-$ (M = Ni, Pd or Pt), possess $S = 1/2$ spin and are favorable to form face-to-face stack via the intermolecular M···M, M···S and S···S interactions, moreover the stacking pattern of $[M(mnt)_2]^-$ anions depends intensely on the geometric feature of the countercation, accordingly, it is possible to control the arrangement of $[M(mnt)_2]^-$ anions through modifying the countercation geometric nature. More recently, the benzylpyridinium derivatives ($[RBzPy]^+$) were employed as the countercation of $[M(mnt)_2]^-$ anion (M = Ni, Pd or Pt), and a series of ion-pair compounds, which possess the separated columnar stacks of cations and anions and the quasi-one-dimensional magnetic nature, were prepared and characterized structurally in our Lab [6,7]. Some of which exhibit a spin-Peierls-like transition [7]. It appears that the nature of the substituting groups in the benzylpyridinium derivative affect quite on the stacking pattern of $[M(mnt)_2]^-$ and magnetic property of the ion-pair compound. To gain more insight understanding into the magnetostructural relationship in these series of compounds, it is necessary to design and prepare the new cation that possesses a different molecular geometry. Herein we presented two new compounds, [1-(4′-R-phenacyl)pyridinium]$[Ni(mnt)_2]$ (R = NMe_2 or H), which syntheses, crystal structures, EPR spectra and magnetic susceptibilities are described.

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Table 1
Crystal and structural refinement data of **1** and **2**

	1	2
Chemical formula	$C_{23}H_{17}N_6OS_4Ni$	$C_{21}H_{12}N_5OS_4Ni$
Formula weight	580.38	537.31
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Space group	$P-1$	$P2(1)/n$
a (Å)	8.5068(14)	16.481(4)
b (Å)	10.7633(18)	7.809(2)
c (Å)	15.433(3)	17.951(5)
α (°)	74.912(3)	90
β (°)	81.513(3)	101.930(4)
γ (°)	70.118(3)	90
V (Å^3), Z	1280.3(4)/2	2260.4(10)/4
Density (calc)/g/cm^3	1.505	1.579
Abs coeff. (mm^{-1})	1.113	1.252
F(000)	594	1092
θ Range for data collection	2.07–25.00	1.88–25.00
Index ranges	$-10\leq h\leq 9$ $-12\leq k\leq 12$ $-18\leq l\leq 12$	$-19\leq h\leq 14$ $-9\leq k\leq 7$ $-21\leq l\leq 20$
Reflns collected	6428	10670
Independent reflns	4427 ($R_{int}=0.0537$)	3971 ($R_{int}=0.0750$)
Refinement method on F^2	Full-matrix least-squares	
Data/restraints/params	4427/0/316	3971/0/289
Goodness-of-fit on F^2	0.928	0.792
Final R indices [$I>2\sigma(I)$]	$R_1=0.0531$, $wR_2=0.1104$	$R_1=0.0389$, $wR_2=0.1065$
R indices (all data)	$R_1=0.0908$, $wR_2=0.1235$	$R_1=0.0463$, $wR_2=0.1127$
Residual (eÅ^{-3})	0.448 and -0.277	0.389 and -0.319

$R_1=\Sigma(||F_0|-|F_c||)/|F_0|$, $wR_2=\Sigma w(|F_0|^2-|F_c|^2)^2/\Sigma w(|F_0|^2)^2]^{1/2}$.

2. Experiment

1-(4′-R-Phenacyl)pyridinium bromide (abbreviated as [RPhacPy]Br), disodium maleonitriledithiolate (abbreviated as Na_2mnt) were prepared according to the published procedures [8]. [RPhacPy][Ni(mnt)$_2$] (R = NMe_2 (1) and H (2)) were synthesized using a similar procedure described in the literature [6]. Anal. Calcd for $C_{23}H_{17}N_6OS_4Ni$ (1): C, 47.6; N, 14.5; H, 2.95%. Found: C, 47.7; N, 14.3; H, 2.97%. IR (KBr disc): 2212.0 (s), 2225.3(sh) cm^{-1} for $\nu_{C\equiv N}$ and 1452.1(m) cm^{-1} for $\nu_{C=C}$ of mnt^{2-}. Calcd for $C_{21}H_{12}N_5OS_4Ni$ (2): C, 46.9; N, 13.0; H, 2.25%. Found: C, 46.8; N, 12.6; H, 2.30%. IR (KBr disc): 2208.1(s) cm^{-1} for $\nu_{C\equiv N}$ and 1450.2(m) cm^{-1} for $\nu_{C=C}$ of mnt^{2-}.

All single crystals suitable for X-ray analysis were obtained by dispersing Et_2O into MeCN solution of the corresponding [RPhacPy][Ni(mnt)$_2$] for 1 week.

2.1. X-ray crystallography

The diffraction data for **1** and **2** were collected at 293 K with graphite-monochromated Mo K$_\alpha$ ($\lambda=0.71073$ Å) on a CCD area detector (Bruker-SMART). Structures were solved by direct method and refined by the full-matrix least-squares procedure on F^2 using SHELXL-97 program [9]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced at calculated positions. The crystallographic details about data collection and structure refinement are summarized in Table 1.

2.2. EPR spectra and magnetic susceptibility measurements

X-band EPR spectra were recorded on a Bruker EMX spectrometer near 9 GHz on polycrystalline samples at 293 K. Temperature dependent magnetic susceptibilities on polycrystalline samples of **1** and **2** were measured between 2 and 300 K using a Quantum Design MPMS XL superconducting quantum interference device (SQUID) magnetometer.

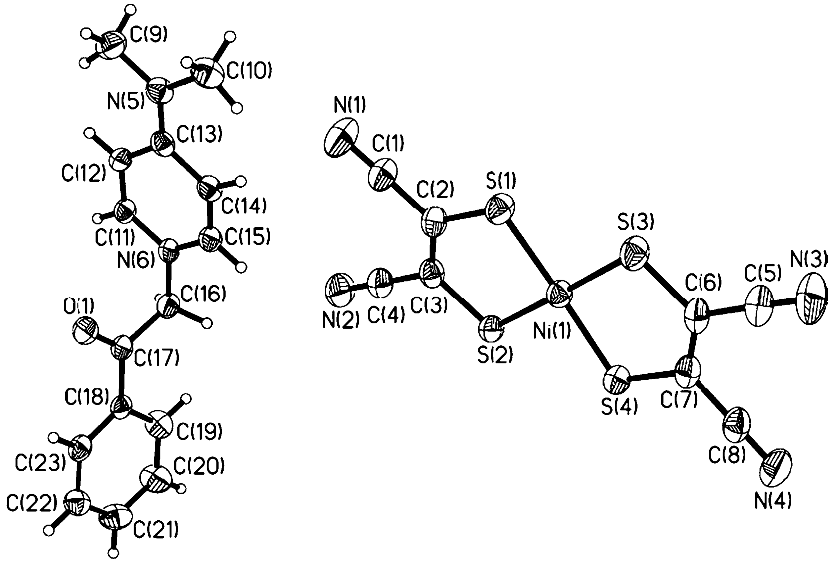

Fig. 1. ORTEP view of **1** with non-hydrogen atomic labeling at 30% probability thermal ellipsoids.