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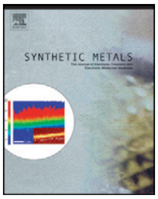

Syntheses, crystal structures, and magnetic properties of four new molecular solids based on $Ni(mnt)_2^-$ monoanion (mnt^{2-} = maleonitriledithiolate)

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ABSTRACT

Four new molecular solids, [1-(2′-F-4′-R-benzyl)pyridinium][bis(maleonitrile dithiolato)nickel] (abbreviated as $[RFBzPy][Ni(mnt)_2]$, R = F (**1**), Cl (**2**), I (**3**), H (**4**)), have been prepared and characterized. The Ni(III) ions in **1**–**3** form a 1D zig-zag chain within a $Ni(mnt)_2^-$ column. The chain is uniform in **2** and **3**, while it is alternating in **1**. The cations and $Ni(mnt)_2$ ions of **4** stack in complicated way in which the stacking of Ni(III) ions shows an ACA-type repeat unit. Magnetic susceptibility measurements in the temperature range 1.8–300 K show that **1** and **4** are diamagnetic, whereas **2** and **3** exhibit ferromagnetic coupling behavior. The $\chi_M T$ of **2** and **3** can be well reproduced by the Baker equation for a 1D $S = 1/2$ magnetic chain with $g = 2.01$, $J = 17.8\ cm^{-1}$ for **2**, and $g = 2.04$, $J = 41.1\ cm^{-1}$ for **3**.

1. Introduction

The investigation of molecular solids based on transition metal complexes of bis-dithiolenes has become a fascinating subject in the field of molecular-based materials [1]. Considerable efforts have been directed towards preparation and characterization of new transition metal bis-dithiolene complexes that can display superconductivity, electrical conductivity, strong near-infrared absorptions, optical properties, and interesting magnetic properties [2,3]. The $[M(mnt)_2]^-$ (mnt^{2-} = maleonitriledithiolate, M = Ni, Pd or Pt ion) complexes are very useful building blocks for magnets [4,5]; in particular, the discovery in 1996 of the ferromagnetic complex containing $Ni(mnt)_2^-$ ion, $NH_4 \cdot Ni(mnt)_2 \cdot H_2O$ [6], strongly stimulated renewed interest in $Ni(mnt)_2$-based molecular solids. One of the interesting works in our laboratory is to develop a new class of ion-pair complexes $[RbzPy]^+[M(mnt)_2]^-$ ($[RbzPy]^+$ = benzylpyridinium derivative, M = Ni, Pd, Pt ion) in which the $Ni(mnt)_2^-$ anions and $[RbzPy]^+$ cations stack into well-segregated columns, and exhibit versatile magnetic properties such as ferromagnetic ordering at low temperature, magnetic transition from ferromagnetic coupling to diamagnetism, metamagnetism, spin–gap transitions and spin-Peierls-like transitions [7–9]. In our continuing work with molecular solids based on $[M(mnt)_2]^-$ anion, we sought to further find some multifunctional organic cations to control the stacking pattern of $[M(mnt)_2]^-$ anions with a view to obtaining ideal molecular magnets. Herein, we succeeded in synthesizing four novel molecular solids, $[FFBzPy][Ni(mnt)_2]$ (**1**), $[ClFBzPy][Ni(mnt)_2]$ (**2**), $[IFBzPy][Ni(mnt)_2]$ (**3**), and $[HFBzPy][Ni(mnt)_2]$ (**4**). Their crystal structures and magnetic properties have been systemically investigated. It is interesting that **2** and **3** show ferromagnetic coupling behavior. To the best of our knowledge, the uniform chain exhibiting ferromagnetic coupling behavior is very rare for molecular solids containing $Ni(mnt)_2^-$ monoanion [4b,6,8c].

2. Experimental

2.1. Materials and methods

All chemicals purchased were of reagent grade and used without further purification. The starting materials, disodium maleonitriledithiolate (Na_2mnt) and 1-(2′-F-4′-R-benzyl)pyridinium bromide ([RFBzPy]Br) (R = F, Cl, I or H) were synthesized following the literature procedures [10]. A similar method for preparing $[BrFBzPy]_2[Ni(mnt)_2]$ was utilized to prepare $[RFBzPy]_2[Ni(mnt)_2]$ [8c]. Elemental analyses were run on a Model 240 PerkinElmer C H N instrument. IR spectra were recorded on an IF66V FT-IR (400–4000 cm^{-1} region) spectrophotometer in KBr pellets. Magnetic susceptibility data on crushed polycrystalline samples of **1**–**4**

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Table 1
Crystallographic data for **1**–**4**

	1	**2**	**3**	**4**
CCDC number	298945	298944	298948	298946
Empirical formula	$C_{20}H_{10}F_2N_5NiS_4$	$C_{20}H_{10}ClFN_5NiS_4$	$C_{20}H_{10}IFN_5NiS_4$	$C_{20}H_{11}FN_5NiS_4$
Formula weight	545.28	561.73	653.18	527.29
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P*-1	*P*2$_1$/*c*	*P*2$_1$/*c*	*P*-1
a (Å)	7.1996(17)	12.048(2)	11.896(3)	13.239(3)
b (Å)	10.377(3)	26.228(5)	26.548(6)	14.765(3)
c (Å)	14.470(4)	7.4277(13)	7.610(2)	17.864(4)
α (°)	105.685(4)	90	90	106.140(10)
β (°)	95.606(4)	101.664(4)	101.660	99.750(10)
γ (°)	96.105(5)	90	90	92.360(10)
V (Å^{-3})	1096.7(5)	2298.6(7)	2353.6(10)	3291.5(13)
Z	2	4	4	6
$\rho_{Calcd.}$ (g cm^{-3})	1.651	1.623	1.843	1.596
Absorption coeff. (mm^{-1})	1.301	1.351	2.518	1.291
θ range (°)	2.1–25.0	1.9–25.0	2.3–26.0	2.0–25.0
F(0 0 0)	550	1,132	1,276	1,602
Reflections collected	5485	11,379	12,387	16,399
Unique reflections	3784	4030	4,597	11,360
R_{int}	0.024	0.036	0.031	0.021
Goodness-of-fit on F^2	1.051	1.057	1.095	0.956
R indexes [$I > 2\sigma(I)$][a]	$R_1 = 0.0537$	$R_1 = 0.0504$	$R_1 = 0.0548$	$R_1 = 0.0573$
	$wR_2 = 0.1212$	$wR_2 = 0.0996$	$wR_2 = 0.1431$	$wR_2 = 0.1216$
R (all data)[a]	$R_1 = 0.0756$	$R_1 = 0.0727$	$R_1 = 0.0677$	$R_1 = 0.0872$
	$wR_2 = 0.1285$	$wR_2 = 0.1061$	$wR_2 = 0.1486$	$wR_2 = 0.1306$

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

were collected over the temperature range of 1.8–300 K using a SQUID MPMS-XL magnetometer.

2.2. Synthesis

2.2.1. Synthesis of [FFBzPy][Ni(mnt)$_2$] (**1**)

[FFBzPy]$_2$[Ni(mnt)$_2$] (752 mg, 1.0 mmol) was dissolved in 30 cm^3 MeCN, then a MeCN solution (10 cm^3) of I_2 (150 mg, 0.59 mmol) was slowly added, the mixture was stirred for 1 h, and then 100 mL CH_3OH was added. After the mixture was allowed to stand overnight, 462 mg dark microcrystals produced were filtered off, washed with CH_3OH and Et_2O and dried in a vacuum. Yield: ~85%. Anal. Calc. for $C_{20}H_{10}F_2N_5NiS_4$: C, 44.05; H, 1.85; N, 12.84. Found: C, 44.13; H, 1.89; N, 13.03%. IR spectrum (cm^{-1}): ν(CN), 2202 s; ν(C=C) of mnt^{2-}, 1487 s.

2.2.2. Syntheses of [ClFBzPy][Ni(mnt)$_2$] (**2**), [IFBzPy][Ni(mnt)$_2$] (**3**) and [HFBzPy][Ni(mnt)$_2$] (**4**)

The procedures for preparing **2**, **3** and **4** are similar to that for **1**. Yield of **2**: ~87%. Anal. Calc. for $C_{20}H_{10}ClFN_5NiS_4$: C, 44.05; H,

Table 2
Bond distances (Å), bond angles (°), intermolecular contacts (Å) and dihedral angles (°) for **1**–**4**

	1	**2**	**3**	**4**
Bond distances (Å)				
Ni(1)–S(1)	2.1365(15)	2.1440(12)	2.1336(16)	2.1413(13)
Ni(1)–S(2)	2.1470(15)	2.1267(12)	2.1400(16)	2.1384(14)
Ni(1)–S(3)	2.1566(15)	2.1254(12)	2.1544(16)	2.1372(14)
Ni(1)–S(4)	2.1411(15)	2.1511(12)	2.1380(160	2.1438(14)
Ni(2)–S(5)				2.1455(14)
Ni(2)–S(6)				2.1433(14)
Ni(2)–S(7)				2.1352(14)
Ni(2)–S(8)				2.1377(14)
Bond angles (°)				
S(1)–Ni(1)–S(2)	92.75(5)	92.32(4)	92.25(6)	92.38(5)
S(2)–Ni(1)–S(3)	88.76(5)	85.49(4)	89.90(6)	87.62(5)
S(1)–Ni(1)–S(4)	86.06(5)	89.70(4)	85.35(6)	87.70(5)
S(3)–Ni(1)–S(4)	92.53(5)	92.46(4)	92.51(6)	92.31(5)
S(5)–Ni(2)–S(6)				92.77(5)
S(5)–Ni(2)–S(8)				87.56(5)
S(6)–Ni(2)–S(7)				87.39(5)
S(7)–Ni(2)–S(8)				92.28(5)
Intrachain distances (Å)				
Ni···Ni	3.674, 4.212	3.940	3.998	3.539, 4.420, 4.228, 3.539
Ni···S	3.659, 3.655	3.645	3.650	3.870, 3.673, 3.665, 3.705
S···S	3.764, 3.715	3.719	3.757	3.591, 3.784, 4.197, 3.617
Dihedral angles (°)				
C_{Ar}–CH_2–N_{Py} and Φ_{Ar}	60.5	105.5	101.1	98.3, 93.5, 82.6
C_{Ar}–CH_2–N_{Py} and Φ_{Py}	78.8	97.1	96.0	82.6, 85.0, 99.2
Φ_{Ar} and Φ_{Py}	112.0	112.9	113.2	67.6, 69.5, 70.4