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Syntheses, crystal structures, and magnetic properties of Ni(mnt)₂-based molecular solids containing substituted isoquinolinium

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Abstract

Two novel ion-pair complexes, $[RBzIQl]^+[Ni(mnt)_2]^ (mnt^{2-} = maleonitriledithiolate, <math>[RBzIQl]^+ = 4$ -R-benzylisoquinolinium; R = H(1), Cl (2)) have been characterized structurally and magnetically. The Ni(mnt)₂⁻ anions and $[BzIQl]^+$ cations of 1 form 1D column of alternating between cations and anions via $\pi \cdots \pi$ stacking interaction between Ni(mnt)₂ plane and isoquinoline ring, and the Ni(mnt)₂ anions between adjacent columns exist C···N, C···N, and N···N interaction. The anions and cations of 2 stack into well-segregated columns in the solid state; and the Ni(III) ions form a 1D zigzag chain in a Ni(mnt)₂ column through intermolecular Ni···S, S···S, Ni···Ni or $\pi \cdots \pi$ interactions. The chain is uniform in 2 with the Ni···Ni distances of 3.784 Å. Magnetic susceptibility measurements for these complexes in the temperature range 1.8–300 K show that 1 exhibits antiferromagnetic coupling behavior, and 2 exhibits unusual magnetic phase transitions around 45 K. The overall magnetic behavior for 2 indicates the presence of antiferromagnetic interaction in the high-temperature phase (HT) and spin gap in the low-temperature phase (LT). © 2006 Elsevier B.V. All rights reserved.

Keywords: Maleonitriledithiolate; Isoquinolinium; Nickel(III) complex; Crystal structure; Antiferromagnetic coupling; Spin gap

1. Introduction

In the past few years, a considerable number of molecular solids based on $M(dithiolene)_2$ as building blocks have been investigated due to their novel properties such as magnetism, conducting, and non-linear optics [1–10]. Especially, the discovery of the first $Ni(mnt)_2$ complex with ferromagnetic ordering, $NH_4 \cdot Ni(mnt)_2 \cdot H_2O$ [11], has led to new development of $Ni(mnt)_2$ chemistry, and prompted us to investigate the magnetic interaction in simple ionic complexes composed of $Ni(mnt)_2$ anions.

Recently, we have developed a surprising new class of ion-pair complexes $[RbzPy][Ni(mnt)_2]$ $(RbzPy^+ = ben$ zylpyridinium derivative) [12-19] and found that the significant structural feature of these ion-pair complexes is that the Ni(mnt)_2 ions and $[RbzPy]^+$ cations stack into well-segregated columns in the solid state, and Ni(mnt)_2 ions form ideal 1D magnetic chains of S = 1/2 through intermolecular Ni \cdots S, S \cdots S, Ni \cdots Ni or $\pi \cdots \pi$ interactions. These ionpair complexes exhibit versatile magnetic properties such as ferromagnetic ordering, magnetic transition from ferromagnetic to diamagnetic coupling, meta-magnetism, and spin-Peierls-like transitions. One of the advantages of using substituted benzylpyridinium as countercation is that the topology and size of the countercation in Ni(mnt)_2 complex may play an important role in controlling the stacking

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pattern of anions and cations, which further influence the magnetic properties of these complexes. Our continuing research with $[Ni(mnt)_2]^-$ complexes is to find more suitable multifunctional organic cations to tune the crystal stacking structure of the [Ni(mnt)₂] anion, and establish a relationship between the magnetic interactions and the stacking pattern of anions or cations. The structure of isoquinoline is similar to pyridine, but its electronic conjugating system is larger than that of the latter. We have introduced substituted benzylisoquinolinium into the Ni(mnt)₂ system and obtained two newly prepared Ni(mnt)₂-based molecular solids: [BzIQl][Ni(mnt)₂] (1) and $[ClBzIQl][Ni(mnt)_2] \cdot 0.75MeCN \cdot 0.5 H_2O$ (2). Although these molecular solids show antiferromagnetic coupling behavior, 2 exhibit unusual spin-gap around 60 K. To the best of our knowledge, a spin gap system the $Ni(mnt)_2$ complex is very rare.

2. Experimental

Benzyl bromide, 4-chlorobenzyl bromide, and isoquinoline were purchased from Aldrich and were used without further purification. 1-Benzylisoquinolinium bromide ([BzIQl]Br) and 1-(4'-chlorobenzyl)isoquinolinium bromide ([ClBzIQl]Br) were prepared by the literature methods [20]. Disodium maleonitriledithiolate (Na₂mnt) was synthesized by a published procedure [21].

2.1. Synthesis of [BzIQl]₂[Ni(mnt)₂] and [ClBzIQl]₂[Ni(mnt)₂]

These two compounds were prepared by the direct combination of NiCl₂ · 6H₂O, Na₂mnt and [BzIQl]Br or [ClBzIQl]Br in H₂O in 1:2:2 molar ratio. The brown precipitate that formed was filtered off, washed with water and dried under vacuum. Yield: 85%. *Anal.* Calc. for [BzIQl]₂-[Ni(mnt)₂] (C₄₀H₂₈N₆NiS₄): C, 61.62; H, 3.62; N, 10.78. Found: C, 61.51; H, 3.74; N, 10.69%. IR spectrum (cm⁻¹): v(CN), 2202.6 s; v(C=C) of mnt^{2–}, 1450.3 s. Yield: 91% *Anal.* Calc. for [ClBzIQl]₂[Ni(mnt)₂] (C₄₀H₂₆N₆-NiCl₂S₄): C, 56.62; H, 3.09; N, 9.90. Found: C, 56.57; H, 3.13; N, 9.86%. IR spectrum (cm⁻¹): v(CN), 2196.0 s; v(C=C) of mnt^{2–}, 1444.7 s.

2.2. Synthesis of $[BzIQl][Ni(mnt)_2]$ (1)

A MeCN solution (20 cm³) of I₂ (160 mg, 0.62 mmol) was slowly added to a MeCN solution (50 cm³) of [BzIQl]₂[Ni(mnt)₂] (780 mg, 1 mmol) and the mixture was stirred for 1 h. MeOH (90 cm³) was then added, and the mixture allowed to stand overnight, 466 mg of black micro-crystals formed were filtered off, washed with MeOH and dried in vacuum.Yield: 83%. *Anal.* Calc. for C₂₄H₁₄N₅NiS₄: C, 51.53; H, 2.52; N, 12.52. Found: C, 51.50; H, 2.61; N, 12.46%. IR spectrum (cm⁻¹): v(CN), 2208.5 s; v(C=C) of mnt²⁻, 1451.3 s.

2.3. Synthesis of $[ClBzIQl][Ni(mnt)_2]$ (2)

The procedure for preparing **2** is similar to that for **1**. Yield: 87%. *Anal.* Calc. for $C_{24}H_{13}N_5NiClS_4 \cdot 0.75CH_3C-N \cdot 0.5H_2O$ (**2**): C, 48.34; H, 2.58; N, 12.71. Found: C, 48.50; H, 2.73; N, 12.54%. IR (KBr, cm⁻¹): IR spectrum (cm⁻¹): v(CN), 2207.5 s; v(C=C) of mnt²⁻, 1445.3 s. Yield: 85%.

The black single crystals suitable for the X-ray structure analysis were obtained by evaporating the MeCN and *i*-PrOH (v/v = 1:1) mixed solution of **1** and **2** about two weeks at room temperature.

2.4. Instrumental procedures

Elemental analyses of C, H, and N were run on a Model 240 Perkin–Elmer C H N instrument. IR spectra were recorded on an IF66V FT-IR spectrophotometer in $4000-400 \text{ cm}^{-1}$ region as KBr pellets. Magnetic susceptibility data on polycrystals sample was collected over the temperature range of 1.8–300 K using a Quantum Design MPMS-5S super-conducting quantum interference device (SQUID) magnetometer, and diamagnetic corrections were made using Pascal's constants.

Table 1 Crystal data and structure refinement for **1** and **2**

Empirical formula $C_{24}H_{14}N_5NiS_4$ $C_{24}H_{13}N_5NiClS_4 \cdot 0.75$ $CH_3CN \cdot 0.5H_2O$ Formula weight 559.35 633.59 T (K) 293(2) 293(2) Wavelength (Å) 0.71073 0.71073 Crystal system triclinic monoclinic Space group $P\bar{1}$ $P2_1/c$ a (Å) 7.216(1) 18.669(4) b (Å) 11.042(2) 23.580(5) c (Å) 15.840(1) 7.234(2) a (°) 93.34(3) 90 B (°) 98.10(3) 99.89(1) ϕ (°) 105.80(3) 90 Volume (ų) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m³) No 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) R 1.011 1.065 parameters Goodness	Compounds	1	2
CH3CN $\cdot 0.5H_2O$ Formula weight559.35633.59 T (K)293(2)293(2)Wavelength (Å)0.710730.71073Crystal systemtriclinicmonoclinicSpace group $P\bar{1}$ $P2_1/c$ a (Å)7.216(1)18.669(4) b (Å)11.042(2)23.580(5) c (Å)15.840(1)7.234(2) a (°)93.34(3)90 B (°)98.10(3)99.89(1) v (°)105.80(3)90 V olume (Å3)1196.1(4)3137.2(13) Z 24Density (calculated)1.5531.342(Mg/m3)0.60 × 0.50 × 0.300.40 × 0.35 × 0.20Reflections collected11 47116748(Independent reflections4197 (0.021)6131 (0.034)(R_{int})full-matrixfull-matrixRefinement methodfull-matrixfull-matrix $parameters$ Goodness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$,Final R indices $[I > 2\sigma(I)]$ $wR_2 = 0.0626$ $wR_2 = 0.1120$ $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data)	Empirical formula	$C_{24}H_{14}N_5NiS_4\\$	$C_{24}H_{13}N_5NiClS_4\cdot 0.75$
Formula weight 559.35 633.59 T (K) 293(2) 293(2) Wavelength (Å) 0.71073 0.71073 Crystal system triclinic monoclinic Space group $P\bar{1}$ $P2_1/c$ a (Å) 7.216(1) 18.669(4) b (Å) 11.042(2) 23.580(5) c (Å) 15.840(1) 7.234(2) a (Å) 93.34(3) 90 β (°) 98.10(3) 99.89(1) p (°) 105.80(3) 90 Volume (ų) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m³) 1.184 0.996 Crystal size (mm³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) Refinement method full-matrix full-matrix Refinement method full-matrix full-matrix parameters Goodness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0$			$CH_3CN \cdot 0.5H_2O$
T (K) 293(2) 293(2) Wavelength (Å) 0.71073 0.71073 Crystal system triclinic monoclinic Space group $P\bar{1}$ $P2_1/c$ a (Å) 7.216(1) 18.669(4) b (Å) 11.042(2) 23.580(5) c (Å) 15.840(1) 7.234(2) a (°) 93.34(3) 90 g (°) 98.10(3) 99.89(1) v (°) 105.80(3) 90 Volume (Å ³) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections coefficient 1.184 0.996 (mm ⁻¹) 70 70 1290 Crystal size (mm ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) Reflections collected 1.011 1.065 parameters Goodness-of-fit on F^2 $R_1 = 0.0308$, <td>Formula weight</td> <td>559.35</td> <td>633.59</td>	Formula weight	559.35	633.59
Wavelength (Å) 0.71073 0.71073 Crystal system triclinic monoclinic Space group $P\bar{1}$ $P2_1/c$ a (Å) 7.216(1) 18.669(4) b (Å) 11.042(2) 23.580(5) c (Å) 15.840(1) 7.234(2) a (°) 93.34(3) 90 g (°) 98.10(3) 99.89(1) g (°) 98.10(3) 99.89(1) g (°) 98.10(3) 90 Volume (Å ³) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 /0/361 Data/restraints/ 1.011 1.065 parameters Goodness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, Final R indices (all data) $wR_2 = 0.0626$	T (K)	293(2)	293(2)
Crystal system triclinic monoclinic Space group $P\bar{1}$ $P2_1/c$ a (Å) 7.216(1) 18.669(4) b (Å) 11.042(2) 23.580(5) c (Å) 15.840(1) 7.234(2) a (°) 93.34(3) 90 b (°) 98.10(3) 99.89(1) p (°) 105.80(3) 90 Volume (Å ³) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m ³) Absorption coefficient 1.184 0.996 (rmm ⁻¹) $F(000)$ 570 1290 Crystal size (mm ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) Reflections collected 11471 16748 Independent method full-matrix least-squares on F^2 4197/0/307 Quarterstraints/ 1.011 1.065 <	Wavelength (Å)	0.71073	0.71073
Space group $P\bar{1}$ $P2_1/c$ $a(\bar{A})$ 7.216(1) 18.669(4) $b(\bar{A})$ 11.042(2) 23.580(5) $c(\bar{A})$ 15.840(1) 7.234(2) $a(\bar{C})$ 93.34(3) 90 $b(\bar{C})$ 98.10(3) 99.89(1) $a(\bar{C})$ 98.10(3) 99.89(1) $p(\bar{C})$ 105.80(3) 90 Volume (Å^3) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 /0/361 Data/restraints/ 1.011 1.065 parameters Goodness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, Final R indices $[I > 2\sigma(I)]$ $wR_2 = 0.0626$ $wR_2 = 0.1120$ $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data)	Crystal system	triclinic	monoclinic
a (Å) 7.216(1) 18.669(4) b (Å) 11.042(2) 23.580(5) c (Å) 15.840(1) 7.234(2) a (°) 93.34(3) 90 B (°) 98.10(3) 99.89(1) p (°) 105.80(3) 90 Volume (Å ³) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m ³) 1 16.1(4) 0.996 (mm ⁻¹) 660 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11.471 16.748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) Reflections collected 11.471 16.748 Independent reflections 4197 (0.021) 6131 (0.034) R^2 (R_{int}) Reflections collected 11.011 1.065 1.011 1.065 parameters Goodness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) $wR_2 = 0.0626$ $wR_2 = 0.1120$ $R_1 = 0.0992$	Space group	$P\overline{1}$	$P2_1/c$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	a(A)	7.216(1)	18.669(4)
$(2, \dot{A})$ 15.840(1) 7.234(2) $(2, \dot{C})$ 93.34(3) 90 $(3, \dot{C})$ 98.10(3) 99.89(1) $(3, \dot{C})$ 98.10(3) 90 $(3, \dot{C})$ 98.10(3) 90 $(2, \dot{C})$ 105.80(3) 90 Volume (\dot{A}^3) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m^3) 1.184 0.996 (mm^{-1}) 570 1290 Crystal size (mm ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) Refinement method full-matrix Refinement method full-matrix full-matrix least-squares on F^2 least-squares on F^2 4197/0/307 Data/restraints/ 1.011 1.065 parameters Goodness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, Final R indices (all data) $wR_2 = 0.0626$ $wR_2 = 0.1120$	b (Å)	11.042(2)	23.580(5)
(\circ) 93.34(3) 90 β (°) 98.10(3) 99.89(1) β (°) 105.80(3) 90 Volume (Å ³) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m ³) Absorption coefficient 1.184 0.996 (mm ⁻¹) F(000) 570 1290 Crystal size (mm ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) Refinement method full-matrix full-matrix (R_{int}) Reflections of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, parameters Goodness-of-fit on F^2 $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) $wR_2 = 0.0638$ $wR_2 = 0.1196$	c (Å)	15.840(1)	7.234(2)
$g(^{\circ})$ 98.10(3) 99.89(1) $y(^{\circ})$ 105.80(3) 90 Volume (Å ³) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m ³) 1 1.184 0.996 (mm ⁻¹) 570 1290 Crystal size (mm ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) rule 1.011 1.065 parameters 1.011 1.065 1.011 Data/restraints/ 1.011 1.065 1.011 parameters Goodness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, Final R indices $[I > 2\sigma(I)]$ $wR_2 = 0.0626$ $wR_2 = 0.1120$ $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) $wR_2 = 0.0638$ $wR_2 = 0.1196$	χ (°)	93.34(3)	90
$(^{\circ})$ 105.80(3) 90 Volume (Å ³) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m ³) 1 1.184 0.996 (mm ⁻¹) 570 1290 Crystal size (mm ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) rulematrix full-matrix Refinement method full-matrix full-matrix parameters 63000 6131/0/361 Data/restraints/ 1.011 1.065 parameters 650000 $R_1 = 0.0308$, $R_1 = 0.0576$, Final R indices [$I > 2\sigma(I)$] $wR_2 = 0.0626$ $wR_2 = 0.1120$ $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) $wR_2 = 0.0638$ $wR_2 = 0.1196$	β (°)	98.10(3)	99.89(1)
Volume (Å ³) 1196.1(4) 3137.2(13) Z 2 4 Density (calculated) 1.553 1.342 (Mg/m ³) 1.184 0.996 (mm ⁻¹) 570 1290 Crystal size (mm ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R _{int}) rulematrix full-matrix Refinement method full-matrix full-matrix parameters 6131/0/361 Data/restraints/ 1.011 1.065 parameters Goodness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, Final R indices $[I > 2\sigma(I)]$ wR ₂ = 0.0626 wR ₂ = 0.1120 $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) wR ₂ = 0.0638 wR ₂ = 0.1196	y (°)	105.80(3)	90
Z 2 4 Density (calculated) 1.553 1.342 (Mg/m ³) 1.184 0.996 (mm ⁻¹) 570 1290 Crystal size (mm ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R _{int}) rulematrix full-matrix Refinement method full-matrix full-matrix parameters 6131/0/361 Data/restraints/ 1.011 1.065 parameters 6000ness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, Final R indices $[I > 2\sigma(I)]$ wR ₂ = 0.0626 wR ₂ = 0.1120 $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) wR ₂ = 0.0638 wR ₂ = 0.1196	Volume ($Å^3$)	1196.1(4)	3137.2(13)
Density (calculated) 1.553 1.342 (Mg/m^3) 1.184 0.996 (mm^{-1}) 70 1290 $F(000)$ 570 1290 Crystal size (mm ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) rest-squares on F^2 least-squares on F^2 Refinement method full-matrix full-matrix parameters 1.011 1.065 Goodness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, Final R indices $[I > 2\sigma(I)]$ w $R_2 = 0.0626$ w $R_2 = 0.1120$ $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) w $R_2 = 0.0638$ w $R_2 = 0.1196$	Z	2	4
Absorption coefficient (mm ⁻¹) 1.184 0.996 (mm^{-1}) 570 1290 Crystal size (mm ³) 0.60 × 0.50 × 0.30 0.40 × 0.35 × 0.20 Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) rest-squares on F^2 least-squares on F^2 Refinement method full-matrix least-squares on F^2 $A197/0/307$ 6131/0/361 0.405 Data/restraints/ 1.011 1.065 parameters Goodness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, Final R indices $[I > 2\sigma(I)]$ wR2 = 0.0626 wR2 = 0.1120 $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) wR2 = 0.0638 wR2 = 0.1196	Density (calculated) (Mg/m ³)	1.553	1.342
$F(000)$ 570 1290 Crystal size (mm ³) $0.60 \times 0.50 \times 0.30$ $0.40 \times 0.35 \times 0.20$ Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) full-matrix full-matrix Refinement method full-matrix least-squares on F^2 $4197/0/307$ $6131/0/361$ Data/restraints/ 1.011 1.065 parameters $Goodness-of-fit$ on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, Final R indices $[I > 2\sigma(I)]$ $wR_2 = 0.0626$ $wR_2 = 0.1120$ $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) $wR_2 = 0.0638$ $wR_2 = 0.1196$	Absorption coefficient (mm ⁻¹)	1.184	0.996
Crystal size (mm ³) $0.60 \times 0.50 \times 0.30$ $0.40 \times 0.35 \times 0.20$ Reflections collected 11471 16748 Independent reflections $4197 (0.021)$ $6131 (0.034)$ (R_{int}) K K Refinement method full-matrix full-matrix least-squares on F^2 least-squares on F^2 $4197/0/307$ $6131/0/361$ Data/restraints/ 1.011 1.065 parameters $K_1 = 0.0308$, $R_1 = 0.0576$, Final R indices $[I > 2\sigma(I)]$ $wR_2 = 0.0626$ $wR_2 = 0.1120$ $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) $wR_2 = 0.0638$ $wR_2 = 0.1196$	F(000)	570	1290
Reflections collected 11471 16748 Independent reflections 4197 (0.021) 6131 (0.034) (R_{int}) full-matrix full-matrix Refinement method full-matrix least-squares on F^2 $4197/0/307$ 6131/0/361 Data/restraints/ 1.011 1.065 parameters Goodness-of-fit on F^2 $R_1 = 0.0308$, $R_1 = 0.0576$, Final R indices $[I > 2\sigma(I)]$ $wR_2 = 0.0626$ $wR_2 = 0.1120$ $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) $wR_2 = 0.0638$ $wR_2 = 0.1196$	Crystal size (mm ³)	$0.60 \times 0.50 \times 0.30$	$0.40 \times 0.35 \times 0.20$
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least-squares on F^2 least-squares on F^2 4197/0/3076131/0/361Data/restraints/1.0111.065parameters $R_1 = 0.0308$, $R_1 = 0.0576$,Final R indices $[I > 2\sigma(I)]$ $wR_2 = 0.0626$ $wR_2 = 0.1120$ $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) $wR_2 = 0.0638$ $wR_2 = 0.1196$	Refinement method	full-matrix	full-matrix
$\begin{array}{cccc} & 4197/0/307 & 6131/0/361 \\ \mbox{Data/restraints/} & 1.011 & 1.065 \\ \mbox{parameters} & & & & \\ \mbox{Goodness-of-fit on } F^2 & R_1 = 0.0308, & R_1 = 0.0576, \\ \mbox{Final } R \mbox{ indices } [I > 2\sigma(I)] & wR_2 = 0.0626 & wR_2 = 0.1120 \\ & R_1 = 0.0334 & R_1 = 0.0992 \\ \mbox{Final } R \mbox{ indices (all data)} & wR_2 = 0.0638 & wR_2 = 0.1196 \\ \end{array}$		least-squares on F^2	least-squares on F^2
Data/restraints/ 1.011 1.065 parameters		4197/0/307	6131/0/361
Goodness-of-fit on F^2 $R_1 = 0.0308$, $wR_2 = 0.0626$ $R_1 = 0.0576$, $wR_2 = 0.1120$ Final R indices $[I > 2\sigma(I)]$ $wR_2 = 0.0626$ $R_1 = 0.0334$ $wR_2 = 0.1120$ $R_1 = 0.0992$ Final R indices (all data) $wR_2 = 0.0638$ $wR_2 = 0.1196$	Data/restraints/ parameters	1.011	1.065
Final R indices $[I > 2\sigma(I)]$ $wR_2 = 0.0626$ $wR_2 = 0.1120$ $R_1 = 0.0334$ $R_1 = 0.0992$ Final R indices (all data) $wR_2 = 0.0638$ $wR_2 = 0.1196$	Goodness-of-fit on F^2	$R_1 = 0.0308$,	$R_1 = 0.0576$,
Final <i>R</i> indices (all data) $R_1 = 0.0334$ $R_1 = 0.0992$ $wR_2 = 0.0638$ $wR_2 = 0.1196$	Final R indices $[I > 2\sigma(I)]$	$wR_2 = 0.0626$	$wR_2 = 0.1120$
Final <i>R</i> indices (all data) $wR_2 = 0.0638$ $wR_2 = 0.1196$		$R_1 = 0.0334$	$R_1 = 0.0992$
	Final R indices (all data)	$wR_2 = 0.0638$	$wR_2 = 0.1196$

Table 2 Selected bond lengths, bond angles and dihedral angles for **1** and **2**

Compounds	1	2	
Bond length (Å)			
Ni(1)–S(1)	2.152(1)	2.144(1)	
Ni(1)–S(2)	2.152(1)	2.141(1)	
Ni(1)–S(3)	2.150(1)	2.141(1)	
Ni(1)–S(4)	2.152(1)	2.139(1)	
S(1)-C(2)	1.723(3)	1.744(3)	
S(2)-C(3)	1.722(2)	1.701(3)	
S(3)-C(6)	1.723(3)	1.699(4)	
S(4)-C(7)	1.723(2)	1.699(4)	
Bond angles (°)			
S(1)-Ni(1)-S(2)	92.63(4)	92.84(4)	
S(1)-Ni(1)-S(4)	87.11(4)	87.10(4)	
S(2)-Ni(1)-S(3)	87.57(4)	87.78(4)	
S(3)-Ni(1)-S(4)	92.69(5)	92.26(4)	
Dihedral angles (°)			
C_{Ar} -CH ₂ -N _{Py} and Φ_{Ar}	91.7	66.1	
C_{Ar} -CH ₂ -N _{Py} and Φ_{IQI}	96.3	65.3	
$\Phi_{\rm Ar}$ and $\Phi_{\rm IQI}$	75.7	97.6	

2.5. Crystal structure determination

Crystals with dimensions $0.2 \times 0.3 \times 0.4$ mm for 1 and $0.30 \times 0.35 \times 0.4$ mm for 2 were selected for indexing and intensity data collections at 293(2) K on a Bruker Smart APEX CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) by ω scan mode within the angular range $1.8 \le \theta \le 26.0$ for **1** and $1.7 \le \theta \le 26.0$ for 2, respectively. Space group, lattice parameters, and other relevant information are listed in Table 1, and selected bond lengths, bond angles, and dihedral angles for 1 and 2 are listed in Table 2. The structures were solved by direct methods and refined on F^2 by full-matrix leastsquares, employing Bruker's SHELXTL [22]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were placed in calculated positions, assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic U value of the attached atom, and allowed to ride on their respective parent atoms.

3. Results and discussion

3.1. Crystal structures

Crystallographic data for 1 and 2 are listed in Table 1. An ORTEP view of 1 with non-hydrogen atomic labeling is shown in Fig. 1. An asymmetric unit of 1 includes one $Ni(mnt)_2^-$ anion and one $[BzIQ1]^+$ cation, The Ni(1) of the $Ni(mnt)_2^-$ anion exhibits the square-planar coordination geometry. The Ni–S bond distances and the S–Ni–S bond angles (Table 2) within the five-membered rings agree well with those found in Ni(mnt)₂⁻ complexes comprised of benzylpyridinium derivatives [18]. The $[BzIQ1]^+$ cation adopts a conformation where both the phenyl and isoquinoline rings are twisted to the C(14)–C(15)–N(5) reference plane. The dihedral angles that the isoquinoline ring and



Fig. 1. ORTEP plot (30% probability ellipsoids) showing the molecule structure of 1.

phenyl ring make with the reference plane are 96.3° and 91.7° (Table 2), respectively. The $Ni(mnt)_2^{-}$ anions and [BzIQl]⁺ cations are alternately stacked as revealed by the projection along the crystallographic a-axis (Fig. 2) and form a column through $\pi \cdots \pi$ interactions between the isoquinoline rings and the planes of $Ni(mnt)_2^-$ ions (Fig. 3a). The nearest distance between isoquinoline rings and the Ni(III) of the planes of Ni(mnt)₂⁻ ions is 3.632 Å, and the isoquinoline rings are not completely parallel with the plane of $Ni(mnt)_2^-$ anion (the dihedral angle of 2.0°). As shown in Fig. 2, there are two significant interactions between adjacent columns. One is $\pi \cdots \pi$ interactions of benzene rings of cations between column A and column A' (Fig. 3a), and the contact distances of C(9), C(10) and C(11) atoms to the centre of neighboring benzene ring are 3.824, 3.582 and 3.750 Å, respectively. The other is $C \cdots N$, $C \cdots C$, and $N \cdots N$ interactions of $Ni(mnt)_2^-$ anions between column A and column B and two overlap modes

Fig. 2. The packing diagram of a unit cell for 1 as viewed along *a*-axis.



Fig. 3. (a) The $\pi \cdot \cdot \pi$ interactions between the isoquinoline rings and the planes of Ni(mnt)₂⁻ ions in column A and the $\pi \cdot \cdot \cdot \pi$ interactions of cations between column \tilde{A} and column A' for 1. (b) Modes of overlapping of $[Ni(mnt)_2]^-$ anions between column A and column B for 1.

of adjacent anions are expected (Fig. 3b). For mode M, the contacts of $C(1) \cdots C(1A)$, $C(1) \cdots N(1A)$, $N(1) \cdots C(2A)$, and N(1)···C(3A) are 3.813, 3.737, 3.737, and 3.594 Å, respectively; and the nearest contact for mode N is 3.454 Å. The weak magnetic interactions between Ni(III) ions through $C \cdots N$, $C \cdots C$, $N \cdots N$ exchange pathways are expected from the structural point.

An asymmetric unit of **2** contains one $Ni(mnt)_2^-$ anion and one $[ClBzIQl]^+$ cation, half and quarter of acetonitrile molecule, and half of water molecule. The water molecule is disordered, and the occupancies of both O(1) and O(2)are 25%. The coordination geometry of anion and the conformation of cation in 2 are essentially identical to those described above for 1 (the Ni-S band distances and the S-Ni-S bond angle and the dihedral angles that the isoquinoline ring and phenyl ring make with the reference plane C(14)-C(15)-N(5) are listed in Table 2), while the stacking pattern of anions and cations for 2 (Fig. 4) are significantly different from those of 1. The Ni(III) ions form a 1D zigzag chain within a $Ni(mnt)_2^-$ column through intermolecular Ni \cdots S, S \cdots S, Ni \cdots Ni or $\pi \cdots \pi$ interactions (Fig. 5a), and the overlap mode of adjacent anions is shown in Fig. 6. Within a $Ni(mnt)_2^-$ anions stacking column, the nearest Ni \cdots S and S \cdots S distances are 3.585 and 3.788 Å, respectively; the Ni ··· Ni distance is 3.785 Å, while the closest Ni...Ni separation between anion columns is 14.392 Å, which is significantly longer than the distance of Ni...Ni separation within a column. Therefore,



Fig. 4. The packing diagram of a unit cell for 2 as viewed along *a*-axis.



Fig. 5. (a) Side view of the anions stack of 2 showing the alternating space linear-chain of [Ni(mnt)_2]⁻. (b) Boat-type conformation of the cations in 2.



Fig. 6. Mode of overlapping of $[Ni(mnt)_2]^-$ anions for 2.

the Ni(mnt)₂⁻ anion chain can be considered as a 1D uniform magnetic one. In a [ClBzIQl]⁺cation column, the adjacent cations stack into a boat-type conformation through $\pi \cdots \pi$ interactions between isoquinoline rings (Fig. 5b), which is significantly different form that of the [RBzPy]⁺ system [23]. The isoquinoline rings are nearly parallel with respect to each other, and the contact distance C(18), C(19), and C(20) atoms to centre of the neighboring isoquinoline rings are 3.862, 3.482, and 3.692 Å.

By comparing the structures of 1 and 2, we conclude that the stacking and overlapping modes are different when we have changed the *p*-substituted group in the benzene, and the Cl group favors separated columnar molecular stacking. In addition, some intermolecular contacts of hydrogen bonds were found between the adjacent cationic and anionic columns (Table 3), which play important roles in the molecular stacking and stabilizing.

3.2. Magnetic properties of 1 and 2

The temperature dependence of the magnetic susceptibilities for 1 and 2 were measured under an applied field of 2000 Oe in the temperature range 1.8–300 K. The plots of χ_m versus T for 1 and 2 are shown in Fig. 7 with χ_m being the magnetic susceptibility per nickel atom corrected by the diamagnetic contribution. For the complexes 1 and 2, the overall magnetic behaviors correspond to a paramagnetic system with an antiferromagnetic coupling interaction. At 300 K, the $\chi_m T$ values of 1 and 2 are 0.347,

Table 3					
Hydrogen	bonds	for	1	and	2

D–H···A	$d(\mathbf{D}\cdot\cdot\cdot\mathbf{H})$	$d(H \cdots A)$	$d(\mathbf{D}\cdots\mathbf{A})$	∠(DHA)
Complex 1				
$C(16) - H(16) \cdots N(4) \# 1$	0.93	2.43	3.349(4)	168.0
$C(23)-H(23)\cdots N(1)#2$	0.93	2.57	3.340(4)	141.0
Complex 2				
$C(9) - H(9) \cdots N(1) #3$	0.93	2.53	3.449(5)	169.0
$C(15)-H(15B)\cdots N(6)#4$	0.97	2.60	3.424(7)	143.0
$C(17)-H(17A)\cdots N(4)\#5$	0.93	2.59	3.447(5)	152.0

Symmetry transformations used to generate equivalent atoms: #1: x, y - 1, z; #2: x, y, z + 1; #3: x, -y + 1/2, z + 1/2; #4: -x + 1, y - 1/2, -z + 3/2; #5: x + 1, -y + 1/2, z + 1/2.



Fig. 7. (a) Plots of χ_m vs. *T* for **1** (inset: plots of $\chi_m T$ vs. *T*) (b) Plots of χ_m vs. *T* for **2** (inset: plots of $d\chi_m T$ vs. dT). The solid line is reproduced from the theoretical calculations and detailed fitting procedure described in the text.

 $0.362 \text{ emu K mol}^{-1}$, the values are slightly lower than the expected for magnetically isolated Ni(III) ions. As the temperature is lowered, the χ_m value of 2 varies in a complex way (Fig. 7b): it increases slightly from $0.00120 \text{ emu mol}^{-1}$ at 300 K to 0.00336 emu mol⁻¹ at 60 K, then decreases abruptly to a minimum $(0.00287 \text{ emu mol}^{-1} \text{ at } 30 \text{ K})$ and finally increases to $0.0314 \text{ emu mol}^{-1}$ again upon further cooling to 1.8 K. It is worthy to note that the χ_m values decrease exponentially at 60 K for 2, indicating that 2 exhibits the characteristics of a spin gap system [24]. On increase of temperature back to the original temperature, the same $\chi_m - T$ curves are obtained without hysteresis effect being detected. These findings indicate that 2 undergoes a reversible phase transition and the phase transition temperature (\sim 45 K) is evaluated as the temperature at the maximum of the $d(\chi_m T)/dT$ derivative (inset of Fig. 7b).

The magnetic susceptibility data of **1** were quantitatively analysed by the Curie–Weiss law with a Curie constant of 0.42 emu K mol⁻¹ and a negative Weiss constant $\theta =$ -4.2 K, indicating an overall antiferromagnetic interaction between Ni(III) ions (Fig. 7a). The theoretical calculations [25–27] and experimental determination [28] had shown that about 0.15 of the unpaired electron resides on ligand C and N atoms of Ni(mnt)₂⁻ anion, while the rest resides in the NiS₄ core, so this weak magnetic interactions between Ni(III) ions of **1** through C···N, C···C, N···N exchange pathways are expected.

The magnetic susceptibilities of 2 may be estimated by the formula $\chi_{\rm m} = [\alpha \exp(-\Delta/k_{\rm B}T)]/T + C/T + \chi_0$, where α is a constant value corresponding to the dispersion of excitation energy, Δ is the magnitude of the spin gap, γ_0 contributes from the core diamagnetism and the possible Van Vleck paramagnetism, and the other symbols have their usual meanings [29], The best fit curve is shown in Fig. 7b, and the corresponding parameters are given as follows: $\alpha = 0.54$, $\Delta/k_b = 72.4$ K, $\chi_0 = 4.2 \times 10^{-4}$ emu mol⁻¹, $C = 5.6 \times 10^{-2}$ emu K mol⁻¹, and $R = 2.3 \times 10^{-4}$ (*R* is defined as $\sum (\chi_m^{calc} - \chi_m^{obsd})^2 / (\chi_m^{obsd})^2$). The origins of the phase transition for 2 is attributed to cooperative interactions of Ni···S bonding, interplane repulsion of the $[Ni(mnt)_2]^-$ anions [30], $\pi \cdot \cdot \pi$ stacking interactions between adjacent cations, spin-lattice interactions [31], and spin-spin coupled interaction between nearest-neighbor anions [32]. In recent years, the spin-gapped system has attracted extensive interest [33-36], but it is very rare for Ni(III) complexes[16,19].

4. Conclusions

In this paper, two novel ion-pair complexes containing the Ni(mnt)₂⁻ anion have been structurally characterized and their magnetic behaviors investigated. 1 forms 1D alternating column of cations and anions via $\pi \cdot \cdot \pi$ stacking interactions between the Ni(mnt)₂ plane and isoquinoline ring, and the Ni(mnt)₂ anions between adjacent columns exhibit $C \cdots N$, $C \cdots N$, and $N \cdots N$ interaction. The anions and cations of 2 stack into well-separated uniform columns in the solid state, and the Ni(III) ions form a 1D zigzag chain within a Ni(mnt)₂-column through intermolecular Ni \cdots S, S \cdots S, Ni \cdots Ni or $\pi \cdots \pi$ interactions. Magnetic susceptibility measurements show that 1 exhibits antiferromagnetic coupling behavior, and 2 exhibits unusual magnetic phase transitions around 45 K. The overall magnetic behavior for 2 indicates the presence of antiferromagnetic interaction in the high-temperature phase (HT) and spin gap in the low-temperature phase (LT).

5. Supplementary materials

The detailed crystallographic data for 1 and 2 have been deposited at the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 260424 and No. CCDC 260425. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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