



Three ion–pair complexes containing bis(maleonitriledithiolate) copper(II) anion and substituted 2-aminopyridinium cations: Syntheses, crystal structures, and magnetic properties

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ABSTRACT

Three new ion–pair complexes, $[2\text{-ClBz-2'-NH}_2\text{Py}]_2[\text{Cu}(\text{mnt})_2]$ (**1**), $[2\text{-Cl-4-ClBz-2'-NH}_2\text{Py}]_2[\text{Cu}(\text{mnt})_2]$ (**2**) and $[2\text{-Cl-4-BrBz-2'-NH}_2\text{Py}]_2[\text{Cu}(\text{mnt})_2] \cdot \text{C}_2\text{H}_5\text{OH}$ (**3**) ($[2\text{-Cl-4-RBz-2'-NH}_2\text{Py}]^+ = 1\text{-(2'-chloro-4'-Rbenzyl)-2-aminopyridinium}$, R = H, Cl, Br; $\text{mnt}^{2-} = \text{maleonitriledithiolate}$), were synthesized and characterized by elemental analyses, IR, UV–visible, single crystal X-ray diffraction and magnetic measurements. Both **1** and **2** crystallize in the monoclinic space group $P2(1)/c$, and the $[\text{Cu}(\text{mnt})_2]^{2-}$ anions and the cations form a 1D network structure through the N–H...N hydrogen bonds. While the anions in **3** form a ladder-like chain through the C–H...N interactions between the $[\text{Cu}(\text{mnt})_2]^{2-}$ anions and $\text{CH}_3\text{CH}_2\text{OH}$ molecules. Some weak interactions such as $\pi \cdots \pi$, $\text{Cu} \cdots \text{N}$, $\text{Cl} \cdots \text{C}$, and C–H...Cl, O–H...Cl, C–H...S, N–H...O, N–H...N and C–H...N hydrogen bonds in three molecular solids generate further a 3D network structure. The magnetic measurement reveals that **1** shows a very weak ferromagnetic interaction, and **2** exhibits a transition from ferromagnetic to antiferromagnetic coupling about 15 K, while **3** shows an antiferromagnetic coupling feature with $\theta = -12.51$ K when the temperature is lowered.

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1. Introduction

In recent decades, much attention has been focused on organic–inorganic hybrid materials based on bis(dithiolene) transition metal complex anions and organic cations, and those materials are frequently characterized by their various physical and chemical properties that could lead to potential applications in the areas of electro-conductive, ferroelectric, magnetic and nonlinear optical materials [1–6]. Inorganic complex anions $[\text{M}(\text{mnt})_2]^{n-}$ (M = Ni, Pd, Pt, Cu, Fe; $\text{mnt}^{2-} = \text{maleonitriledithiolate}$, $n = 1$ or 2) are especially interesting because they have been proved to be very useful and potential building block over the past few years and the overlapping of the neighboring anions are influenced by the size and configuration of the organic counter-cation as well as some non-covalent interactions such as weak $\text{p} \cdots \pi$ or $\pi \cdots \pi$ stacking interactions and H-bonding interactions [7–13]. In this area, one important branch is the design and synthesis of molecular solids

containing the $[\text{Ni}(\text{mnt})_2]^-$ anion and some organic cations due to their versatile magnetic properties such as ferromagnetism, magnetic transition from ferromagnetic to diamagnetic coupling, spin-Peierls-like transitions, and meta-magnetism [14–19]. To tune the overlapping mode of the $[\text{Ni}(\text{mnt})_2]^-$ anions, many attempts have been focused on finding appropriate organic cations, and the derivatives of substituted benzylpyridinium (abbreviated as $[\text{RBzPy}]^+$) have been confirmed to be flexible and multifunctional cations containing two aromatic rings in which the molecular configuration was determined by the dihedral angles between these rings. The change of the magnitude and configuration of the counteraction results in the change of the overlapping mode of the neighboring $[\text{Ni}(\text{mnt})_2]^-$ anions and the magnetic coupling of these molecular solids [7,8,15–20]. Recently, we have been interested in the incorporation of substituted 2-aminopyridinium cations into the $[\text{Ni}(\text{mnt})_2]^-$ anion system to obtain some new organic–inorganic hybrid solids, such as $[\text{BzPyNH}_2][\text{Ni}(\text{mnt})_2]$, $[2\text{-NpCH}_2\text{PyNH}_2][\text{Ni}(\text{mnt})_2]$ [21], $[2\text{-FBzPy-2'-NH}_2][\text{Ni}(\text{mnt})_2]$ and $[4\text{-FBzPy-2'-NH}_2][\text{Ni}(\text{mnt})_2]$ (**2**) [22], in which the Ni(III) ions form a 1D magnetic chain within a $[\text{Ni}(\text{mnt})_2]^-$ column through $\text{Ni} \cdots \text{N}$, $\text{Ni} \cdots \text{Ni}$, $\text{Ni} \cdots \text{S}$,

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Table 1
Crystal data and structure refinement for **1**, **2** and **3**.

Compound	1	2	3
Empirical formula	C ₃₂ H ₂₄ CuN ₈ S ₄ Cl ₂	C ₃₂ H ₂₂ CuN ₈ S ₄ Cl ₄	C ₃₄ H ₂₈ CuN ₈ S ₄ Cl ₂ Br ₂ O
Formula weight	783.27	852.16	987.14
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2 ₁ /c	P2 ₁ /c	P-1
Unit cell dimensions			
<i>a</i> (Å)	10.423(1)	10.804(6)	7.869(2)
<i>b</i> (Å)	11.141(1)	11.191(7)	11.678(3)
<i>c</i> (Å)	15.602(2)	16.386(10)	11.847(3)
α (°)	90	90	89.57(1)
β (°)	98.45 (1)	109.05(1)	81.08(1)
γ (°)	90	90	80.22(1)
<i>V</i> /Å ³	1792.1(4)	1872.7(19)	1059.7(5)
<i>Z</i>	2	2	1
<i>D_c</i> /Mg m ⁻³	1.452	1.511	1.547
Absorption coefficient/mm ⁻¹	1.027	1.128	2.761
<i>F</i> (000)	795	862	493
Reflection collected	12722	12051	7672
Independent reflections(<i>R</i> _{int})	3160 (0.043)	3446(0.040)	3703(0.043)
Data/restraints/parameters	3160/0/214	3446/0/223	3703/0/246
Goodness-of-fit on <i>F</i> ²	1.012	1.009	1.007
<i>R</i> ₁	0.0306, 0.0383	0.0314, 0.0429	0.0796, 0.1032
<i>wR</i> ₂	0.0785, 0.0820	0.0845, 0.0902	0.2108, 0.2287
Largest diff. peak and hole/Å ⁻³	0.22 and -0.41	0.28 and -0.25	0.25 and -1.42

Table 2
Selected bond parameters for **1**, **2** and **3**.

Compound	1	2	3
Bond lengths (Å)			
Cu(1)–S(1)	2.284(1)	2.286(2)	2.280(2)
Cu(1)–S(2)	2.262(1)	2.266(2)	2.273(2)
S(1)–C(2)	1.729(2)	1.737(3)	1.713(7)
S(2)–C(3)	1.729(2)	1.736(3)	1.714(8)
N(1)–C(1)	1.144(3)	1.144(3)	1.168(12)
N(2)–C(4)	1.142(3)	1.151(3)	1.148(13)
N(3)–C(11)	1.473(3)	1.480(3)	1.489(11)
N(4)–C(12)	1.321(3)	1.331(3)	1.300(14)
Cl(1)–C(5)	1.738(3)	1.741(3)	1.765(9)
Bond angles (°)			
S(1)–Cu(1)–S(2)	91.34(2)	91.18(3)	90.76(8)
Cu(1)–S(1)–C(2)	100.8(1)	101.0(1)	101.6(3)
Cu(1)–S(2)–C(3)	101.2(1)	101.6(1)	101.5(3)
Cl(1)–C(5)–C(6)	119.1(2)	118.7(1)	113.2(7)
N(3)–C(11)–C(10)	113.9(1)	114.7(2)	112.6(7)
N(4)–C(12)–C(13)	121.6(2)	121.4(2)	123.8(10)
S(1)–C(2)–C(1)	117.3(1)	117.7(2)	118.3(6)
S(2)–C(3)–C(3)	123.0(2)	123.0(2)	122.3(6)

Ni...C, S...C, N...C or $\pi \cdots \pi$ interactions, and the amino group in the pyridine ring may result in the forming of the intermolecular hydrogen bonds which result in the stacking and stabilizing of the molecular solids. It is interesting that the latter three solids display a novel spin-gap transition upon the temperature is lowered. This work is a part of our project dealing with the synthesis, crystal structure, and magnetic properties of new molecular solids based on substituted benzyl 2-aminopyridinium cations. In this paper, the synthesis, characterization, molecular structures and magnetic properties of three new ion–pair complexes, [2-ClBz-2'-NH₂Py]₂[Cu(mnt)](**1**), [2-Cl-4-ClBz-2'-NH₂Py]₂[Cu(mnt)](**2**) and [2-Cl-4-BrBz-2'-NH₂Py]₂[Cu(mnt)](**3**) ([2-Cl-4-RBz-2'-NH₂Py]⁺ = 2-chloro-4Rbenzyl)-2-aminopyridinium, R = H, Cl, Br) are reported. It has been observed that when the atom in 2-position is Cl atom, and the 4-substituted group in the benzyl ring is changed from H to Cl and Br atom, the difference in the crystal structure, weak interaction and the neighboring Cu...Cu contact results in the change in magnetic properties of **1**, **2** and **3** when the

temperature is lowered.

2. Experimental

2.1. General materials and physical measurements

2-Chlorobenzyl bromide, 2, 4-dichlorobenzyl bromide, 2-chloro-4-bromobenzyl bromide, 2-aminopyridine and CuCl₂·2H₂O were purchased from Aldrich and were used without further purification. 1-(2'-Chlorobenzyl)-2-aminopyridinium bromide ([2-ClBz-2'-NH₂Py]Br), 1-(2',4'-dichlorobenzyl)-2-aminopyridinium bromide ([2-Cl-4-ClBz-2'-NH₂Py]Br) and 1-(2'-chloro-4'-bromobenzyl)-2-aminopyridinium bromide ([2-Cl-4-BrBz-2'-NH₂Py]Br) were prepared by literature methods [23]. Disodium maleonitriledithiolate (Na₂mnt) was synthesized by a published procedure [24].

The elemental analyses (C, H, N) were carried out using a Perkin–Elmer 240C elemental analyzer. The IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer between 400 and 4000 cm⁻¹, using KBr pellet method. The UV–Vis absorption spectra of the three samples in MeCN in the region of 250–700 nm are obtained by Shimadzu UV-2500 spectrophotometer.

2.2. Syntheses

A similar method for preparing [BzDMP]₂[Cu(mnt)]₂ was utilized to prepare [2-Cl-4-RBz-2'-NH₂Py]₂[Cu(mnt)]₂ (R = H, Cl, Br) [25]. Slow evaporating a solution of them in a mixture of MeCN/EtOH (v/v = 2:1) at room temperature gave the brownish black crystals suitable for X-ray single crystal structure analyses.

[2-ClBz-2'-NH₂Py]₂[Cu(mnt)]₂(**1**), Yield: 78.5%. *Anal.* Calc. For C₃₂H₂₄Cl₂CuN₈S₄: C, 49.07; H, 3.09; N, 14.31%. Found: C, 49.18; H, 3.21; N, 13.45%.

[2-Cl-4-ClBz-2'-NH₂Py]₂[Cu(mnt)]₂(**2**), Yield: 82.1%. *Anal.* Calc. For C₃₂H₂₂Cl₄CuN₈S₄: C, 45.10; H, 2.60; N, 13.15%. Found: C, 45.19; H, 2.73; N, 13.04%.

[2-Cl-4-BrBz-2'-NH₂Py]₂[Cu(mnt)]₂·C₂H₅OH(**3**)Yield: 87.4%. *Anal.* Calc. For C₃₄H₂₈Cl₂Br₂CuN₈S₄O: C, 41.37; H, 2.86; N, 11.35%. Found: C, 41.52; H, 3.07; N, 11.24%.

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