



Syntheses, crystal structures and magnetic properties of three new molecular metals based on bis(maleonitriledithiolate)copper(II) anion and substituted benzyl isoquinolinium cations



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ABSTRACT

Syntheses, crystal structures and magnetic properties of three novel molecular metals, $[4RBzIQ]_2[Cu(mnt)_2]$ (mnt^{2-} = maleonitriledithiolate; $[4RBzIQ]^+$ = 1-(4'-R-benzyl)isoquinolinium, R = H(**1**), Cl(**2**) and NO_2 (**3**)) are systemically investigated. The crystal structural analysis reveals that three molecular metals crystallize in the triclinic space group $P-1$, and the $[4RBzIQ]^+$ cations stack into a one-dimensional column through C–H... π and π ... π interactions. The anions (A) and cations (C) are arranged alternatively into a column in the sequence of ...A-CC-A-CC... for **1** and ...AA-CC-AA-CC... for **2** and **3** though Cu...N, C...N, C...O, C–H... π or/and π ... π interactions. The magnetic susceptibilities measured in the temperature range 2.0–300 K reveals that these molecular show a change of magnetic exchange from weak ferromagnetic to antiferromagnetic around 20 K, 19 K and 47.6 K for **1**, **2** and **3**.

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1. Introduction

The possible mechanisms for magnetic exchange have been a major area of study for decades and numerous empirical and theoretical descriptions have been presented [1–3]. The magnetic properties of molecular solids containing π -planar metal complex $[M(mnt)_2]^{n-}$ (M = Ni, Pd, Pt, Cu; mnt = maleonitriledithiolate, $n = 1$ or 2) anions with inorganic or organic cations have been studied for a long time owing to their application as potentially building blocks in molecular-based materials [4–8]. The successful demonstrations of the usefulness of organic counter cation was discovery of a class of molecular solids, $[RBzPy][Ni(mnt)_2]$ ($RBzPy^+$ = benzylpyridinium derivative) whose significant structural feature is that the $[Ni(mnt)_2]^-$ anions and $[RBzPy]^+$ cations stack into well-segregated columns and $[Ni(mnt)_2]^-$ anions form ideal one-dimensional $s = 1/2$ magnetic chain in which the magnetic exchange could propagate through the non-covalent interactions through intermolecular Ni...S, S...S, Ni...Ni or π ... π interactions, and the small change of the topology and size of the $[RBzPy]^+$ counter cation of these solids lead to the significant difference in their stacking pattern of anions, weak interactions

and magnetic properties. Especially, these molecular solid have shown versatile magnetic properties such as ferromagnetic ordering at low temperature [9,10], magnetic transitions from ferromagnetic coupling to diamagnetism [11], meta-magnetism [12], spin-gap and spin-Peierls-like transitions [13–15]. The structure of isoquinoline is similar to pyridine, but as compared to benzylpyridinium derivative, its electronic conjugating system is larger than that of the latter. So, we have used substituted benzylisoquinolinium ($[RBzIQ]^+$) as the counter ion of $[Ni(mnt)_2]^-$ anion and obtained several molecular solids with usual magnetic properties, $[BzIQ][Ni(mnt)_2]$ and $[4ClBzIQ][Ni(mnt)_2]$ [16], $[2FBzIQ][Ni(mnt)_2]$ [17], $[4NO_2BzIQ][Ni(mnt)_2]$ [18], $[IFBzIQ][Ni(mnt)_2]$ and $[IClBzIQ]_2[Ni(mnt)_2]_2 \cdot MeCN$ [19]. With a view to extending our study in this field, the $[4RBzIQ]^+$ (R = H, Cl and NO_2) cations have employed into the system containing the $[Cu(mnt)_2]^{2-}$ anion, and have synthesized three molecular metals, $[BzIQ]_2[Cu(mnt)_2]$ (**1**), $[4ClBzIQ]_2[Cu(mnt)_2]$ (**2**) and $[4NO_2BzIQ]_2[Cu(mnt)_2]$ (**3**). There are few examples covering the system containing the $[Cu(mnt)_2]^{2-}$ anion and substituted pyridinium cation, $[4,4'-H_2bpy][Cu(mnt)_2]$ [20], $[BrBzPy]_2[Cu(mnt)_2]$ [21], $[NO_2BzPy]_2[Cu(mnt)_2]$ [21], $[BzDMAP]_2[Cu(mnt)_2]$ and $[NO_2BzDMAP]_2[Cu(mnt)_2]$ [22], but the literature are scarce. In this paper, the syntheses, structural characterization, magnetic behaviors and theoretical analysis of three molecular solids based on $[Cu(mnt)_2]^{2-}$ anion, and the influence of the substituted groups

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on the crystal stacking structures and magnetic properties of the solids is investigated when the *p*-substituted group in the benzyl ring has changed from H or Cl and NO₂ atom.

2. Experimental

2.1. Materials and physical measurements

Benzyl bromide, 4-chlorobenzyl bromide, 4-nitrobenzyl bromide, CuCl₂·2H₂O and isoquinoline were of analytical grade and used without further purification. Disodium maleonitriledithiolate (Na₂mnt) and 1-(4'-R-benzyl)isoquinolinium bromide ([4RBz-IQ]Br, R=H, Cl, NO₂) were synthesized following the literature procedures [23,24]. Elemental analyses for C, H and N were determined using a Perkin-Elmer 240 analyzer. Infrared spectra were obtained in the 400–4000 cm⁻¹ region by a Nicolet Avatar 360 FT-IR spectrophotometer with KBr pellets. Electronic spectra were recorded on a SHIMADZU UV-4000 spectrophotometer. Variable-temperature magnetic data of crushed polycrystalline samples for **1**, **2** and **3** were obtained over the temperature range of 2–300 K using a Quantum Design MPMS-XL super-conducting quantum interference device (SQUID) magnetometer, and the experimental data were corrected for diamagnetism of the constituent atoms estimated from Pascal's constants.

2.2. Syntheses

[BzIQ]₂[Cu(mnt)₂] (**1**) was prepared according to a similar method described in literature [22]. A solution of CuCl₂·2H₂O (0.17 g, 1.0 mmol) in methanol (10 ml) was added dropwise to a solution of Na₂mnt (0.37 g, 2.0 mmol) in methanol (20 ml) with vigorous stirring at room temperature. A brown precipitate formed immediately after adding a methanol (20 ml) solution containing [BzIQ]Br (0.60 g, 2.0 mmol) into the above mixture, which was filtered off another 2 h later, washed with cool methanol and ether, dried in vacuum. Yield: 600 mg (76.5%). *Anal.* Calc. for C₄₀H₂₈CuN₆S₄: C, 61.24; H, 3.60; N, 10.71%. Found: C, 61.18; H, 3.75; N, 10.65%. IR (KBr, cm⁻¹): 3071(m), 3043(m), 2995(w), 2873(m), 2192(vs), 1641(m), 1461(vs), 1395(s), 753(s), 721(m). UV–vis (nm, lg ε): 263(4.73), 323(4.51), 475(3.65).

The procedure for preparing [4ClBzIQ]₂[Cu(mnt)₂] (**2**) is analogous to that for **1**. Yield: 667 mg (78.2%). *Anal.* Calc. for C₄₀H₂₆CuCl₂N₆S₄: C, 56.29; H, 3.07; N, 9.85%. Found: C, 56.35; H, 3.17; N, 9.77%. IR (KBr, cm⁻¹): 3089(w), 3041(w), 2994(w), 2881(m), 2194(vs), 1641(m), 1459(vs), 1392(s), 819(s), 743(s). UV–vis (nm, lg ε): 262(4.63), 326(4.36), 476(3.59).

The procedure for preparing [4NO₂BzIQ]₂[Cu(mnt)₂] (**3**) is similar to that for **1**. Yield: 713 mg (81.6%). *Anal.* for C₄₀H₂₆CuN₈O₄S₄: C, 54.94; H, 3.00; N, 12.81%. Found: C, 55.01; H, 3.07; N, 12.69%. IR (KBr, cm⁻¹): 3062(m), 3002(m), 2950(w), 2852(w), 2195(vs), 1639(m), 1525(s), 1466(s), 1395(s), 1347(s), 854(s), 804(s). UV–vis (nm, lg ε): 262(5.23), 321(4.93), 475(4.04).

2.3. Crystal structure determination

Brownish black crystals suitable for the X-ray structure analysis were grown by evaporating solution of **1**, **2** and **3** in mixtures of MeCN/*i*-PrOH (1:2, v/v) at room temperature, and data were collected at room temperature using a Bruker SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å). Cell parameters were retrieved using SMART software [25] and refined using SAINTPlus [26] on all observed reflections. Data reduction was performed using the SAINTPlus software. The structure was solved by direct method and refined by least-squares methods on F² using the SHELXTL program package [27]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in the Fourier map and their

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

Compound	1	2	3
Empirical formula	C ₄₀ H ₂₈ CuN ₆ S ₄	C ₄₀ H ₂₆ CuN ₆ S ₄ Cl ₂	C ₄₀ H ₂₆ CuN ₈ S ₄ O ₄
Formula weight	784.46	853.35	874.47
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions			
<i>a</i> /Å	8.515(2)	11.458(1)	11.141(1)
<i>b</i> /Å	8.941(2)	13.437(1)	13.584(2)
<i>c</i> /Å	13.271(3)	14.459(1)	14.611(2)
<i>α</i> /°	70.41(1)	110.60(1)	110.41(1)
<i>β</i> /°	74.56(1)	101.87(1)	99.63(1)
<i>γ</i> /°	78.56(1)	98.63(1)	98.26(1)
<i>V</i> /Å ³	910.9(4)	1978.3(4)	1993.8(4)
<i>Z</i>	1	2	2
<i>D_c</i> /Mg m ⁻³	1.430	1.433	1.457
Absorption coefficient/mm ⁻¹	0.868	0.936	0.810
<i>F</i> (000)	403	870	894
Reflection collected	6331	6939	14,661
Independent reflections (<i>R</i> _{int})	3164 (0.022)	5408(0.043)	6967 (0.034)
Data/restraints/parameters	3164/12/232	6939/0/478	6967/0/515
Goodness-of-fit on <i>F</i> ²	1.028	1.016	1.004
<i>R</i> ₁	0.0762, 0.1044	0.0442, 0.0578	0.0398, 0.0678
<i>wR</i> ₂	0.1534, 0.1762	0.1083, 0.1156	0.0868, 0.0983
Largest diff. peak and hole/Å ⁻³	1.44 and -1.24	0.47 and -0.41	0.35 and -0.31

positions refined with fixed isotropic thermal parameters. Details of the data collection, refinement and crystallographic data are summarized in Table 1. Further details are provided in the Supporting Information. Selected bond lengths and angles are listed in Tables 2 and 3.

3. Results and discussion

3.1. IR and UV–vis spectra

The ν(C–H) bands of aromatic rings and the methylene are at 3071, 3043, 2995, 2873 cm⁻¹ for **1**, 3089, 3041, 2994, 2881 cm⁻¹ for **2** and 3062, 3002, 2950, 2852 cm⁻¹ for **3**. The strong bands at 2192 cm⁻¹ for **1**, 2194 cm⁻¹ for **2**, and 2195 cm⁻¹ for **3** are assigned to the CN stretching bands [28]. The bands at 1641 and 1461 cm⁻¹ for **1**, 1641 and 1459 cm⁻¹ for **2**, 1639 and 1466 cm⁻¹ for **3** can be assigned to the ν(C=C) stretching bands for the aromatic rings and mnt²⁻, respectively. The C–Cl stretching band of **2** is seen at 647 cm⁻¹, and the stretching bands of NO₂ group for **3** are found at 1525 and 1347 cm⁻¹. The UV–vis absorption spectra of **1**, **2** and **3** in MeCN in the region of 200–800 nm are attributed to the anionic portions of these solids. The characteristic bands at 263, 323, 475 nm for **1**, 262, 326, 476 nm for **2**, and 262, 321, 475 nm for **3** are assigned

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

Bond lengths (Å)	Bond angles (°)		
Cu(1)–S(1)	2.262(2)	S(1)–Cu(1)–S(2)	90.74(7)
Cu(1)–S(2)	2.279(2)	S(1)–Cu(1)–S(2)#1	89.26(7)
S(1)–C(2)	1.719(8)	Cu(1)–S(1)–C(2)	101.9(3)
S(2)–C(3)	1.731(7)	Cu(1)–S(2)–C(3)	101.6(2)
N(1)–C(1)	1.132(13)	N(1)–C(1)–C(2)	176.9(9)
N(2)–C(4)	1.141(10)	S(1)–C(2)–C(1)	116.6(6)
N(3)–C(11)	1.473(9)	S(1)–C(2)–C(3)	123.4(6)
N(3)–C(12)	1.385(13)	S(2)–C(3)–C(2)	122.2(5)
N(3)–C(20)	1.373(9)	S(2)–C(3)–C(4)	117.4(5)

Symmetry transformations used to generate equivalent atoms: #1 = -*x*+1, -*y*, -*z*+1.

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