



## Syntheses, crystal structures, weak interactions and magnetic properties of two salts with tetrachlorocuprate(II) and substituted benzylpyridinium

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### ABSTRACT

Two tetrachlorocuprate(II) salts,  $[4\text{-RBzPy}]_2[\text{CuCl}_4]$  ( $[4\text{-RBzPy}]^+ = 4\text{-R-benzylpyridinium}$ ,  $\text{R} = \text{Cl}(\mathbf{1})$ ,  $\text{NO}_2(\mathbf{2})$ ), have been prepared and characterized by elemental analysis, IR, MS, single-crystal X-ray diffraction and magnetic susceptibility. Compound **1** crystallizes in the orthorhombic system with space group  $Pca2_1$ , while **2** in the monoclinic  $P2_1/c$ . Two salts comprise a tetrahedral  $[\text{CuCl}_4]^{2-}$  anion and two flexuous  $[4\text{-RBzPy}]^+$  cations. The cations both **1** and **2** form a column through  $\text{p}\cdots\pi$  and  $\pi\cdots\pi$  interactions, while the  $[\text{CuCl}_4]^{2-}$  anions only in **2** form a dimer through  $\text{Cl}\cdots\text{Cl}$  interaction. The  $\text{C-H}\cdots\text{Cl}$  and  $\text{C-H}\cdots\text{Cu}$  weak hydrogen bonds between the anions and the cations give further rise to a 3D network structure. Magnetic susceptibility measurements in the temperature range 2–300 K show that **1** exhibits a ferromagnetic coupling behavior with  $\theta = 3.57$  K, while **2** shows an antiferromagnetism with  $J = -11.09$   $\text{cm}^{-1}$ .

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## 1. Introduction

The coordination compounds of metal halides have been interesting for their rich photo-luminescent and magnetic properties [1–8]. Salts of the type  $\text{A}_2\text{MX}_4$  ( $\text{A} = \text{cation}$ ,  $\text{M} = \text{metal ion}$ ,  $\text{X} = \text{halide}$ ) have played an important role in the development in low-dimensional magnetism duo to their two-dimensional layer perovskite structure [9,10]. The magnetic properties of this family are related to the interionic distances between the  $[\text{MX}_4]^{2-}$  anions and the properties of the cations [9–11]. Therefore, to find more suitable and multifunctional organic cations to link the metal ions through hydrogen bonding has proven to be one of the most powerful methods to obtain novel hybrid organic–inorganic materials. Our own interests have in particular focused on the design and synthesis of some organic cations that adjust the stacking mode of some anions such as  $[\text{M}(\text{mnt})_2]^{x-}$  ( $\text{M} = \text{Cu(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Ni(III)}$ ,  $\text{mnt} = \text{maleonitriledithiolate}$ ,  $x = 1$  or  $2$ ),  $[\text{Ni}(\text{i-mnt})_2]^{2-}$  ( $\text{i-mnt} = \text{iso-maleonitriledithiolate}$ ),  $[\text{Ni}(\text{tdas})_2]^{2-}$  ( $\text{tdas} = 1,2,5\text{-thiadiazole-3,4-dithiolate}$ ), and  $[\text{Co}(\text{NCS})_4]^{2-}$ , and some materials with special physical properties have been obtained [12–18]. Substituted benzylpyridinium (abbreviated as  $[\text{RBzPy}]^+$ ) has been confirmed to be a series of fine and flexible organic cations containing two aromatic rings [19–22]. Very recently, we have introduced  $[\text{RBzPy}]^+$  into the system containing  $[\text{CuBr}_4]^{2-}$  anion and obtained two new salts,  $[\text{BzPy}]_2[\text{CuBr}_4]$  and  $[4\text{NO}_2\text{BzPy}]_2[\text{CuBr}_4]$ , in which some weak interactions such as

$\text{p}\cdots\pi$ ,  $\pi\cdots\pi$ ,  $\text{C-H}\cdots\pi$ ,  $\text{C-H}\cdots\text{Br}$  or  $\text{C-H}\cdots\text{O}$  are found, and the two salts show good antibacterial activities for *colibacillus* and *aurococcus* [23]. As part of our continuing studies, we have introduced  $[\text{RBzPy}]^+$  into the system containing  $[\text{CuCl}_4]^{2-}$  anion and obtained two new salts,  $[4\text{-ClBzPy}]_2[\text{CuCl}_4](\mathbf{1})$  and  $[4\text{-NO}_2\text{BzPy}]_2[\text{CuCl}_4](\mathbf{2})$ , and their components, structures and properties have been characterized by elemental analyses, IR, MS spectra, single crystal X-ray diffraction and magnetic susceptibility.

## 2. Experimental

### 2.1. General materials and techniques

4-Chlorobenzyl chloride, 4-nitrobenzyl chloride,  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ , pyridine and all solvents were obtained from commercial sources and used as received. 1-(4-Chlorobenzyl)pyridinium chloride ( $[4\text{-ClBzPy}]\text{Cl}$ ) and 1-(4-nitrobenzyl)pyridinium chloride ( $[4\text{-NO}_2\text{BzPy}]\text{Cl}$ ) were prepared by the literature method [24]. The chemical compositions for C, N and H were analyzed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra were collected on a Nicolet Acvatar 360 FT-IR (400–4000  $\text{cm}^{-1}$  region) spectrophotometer using KBr pellets of the samples. The electro spray mass spectra [ESI-MS] were determined from  $1.0 \times 10^{-5}$   $\text{mol L}^{-1}$  with a Finnigan LCQ mass spectrometer. Magnetic susceptibility data of **1** and **2** were collected over the temperature range of 2–300 K using a Quantum Design MPMS super-conducting quantum interference device (SQUID) magnetometer.

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## 2.2. Syntheses of **1** and **2**

### 2.2.1. [4-ClBzPy]<sub>2</sub>[CuCl<sub>4</sub>](**1**)

[4-ClBzPy]Cl (0.48 g, 2 mmol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (0.17 g, 1 mmol) were dissolved in 20 mL of methanol acidified with 3 mL of concentrated hydrochloric acid. The green solution was heated and stirred under reflux for 2 h. The dark orange crystals were developed by evaporation of the solution at room temperature. Yield: 78%. *Anal.* Calc. for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>CuCl<sub>6</sub>: C, 46.90; H, 3.61; N, 4.56; Found: C, 46.79; H, 3.75; N, 4.47%.

[4-NO<sub>2</sub>BzPy]<sub>2</sub>[CuCl<sub>4</sub>](**2**) was prepared by a method analogous to that of **1**. Yield: 81%. *Anal.* Calc. for C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>CuCl<sub>4</sub>: C, 45.34; H, 3.49; N, 8.81; Found: C, 45.26; H, 3.62; N, 8.67%.

### 2.3. Crystal structure determination

The crystals of two salts were simply prepared from HCl acidic methanol media. The X-ray single-crystal data of **1** and **2** were collected using a Bruker SMART CCD area detector (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) at 291 K. Their structures were solved by direct method using SHELXS 97 and refined on  $F^2$  by full-matrix least-squares methods (SHELXL 97) [25]. All the non-hydrogen atoms were easily found from Fourier map and refined anisotropically. Hydrogen atoms were constrained to ride on the respective carbon atoms with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of their parent atom. The details of data collection, refinement and crystallographic data of **1** and **2** are summarized in Table 1. Selected bond lengths and bond angles for **1** and **2** are listed in Tables 2 and 3, respectively.

## 3. Results and discussion

### 3.1. Synthesis, IR spectra and ESI-MS

The crystals of two salts were simply prepared from HCl acidic methanol media containing CuCl<sub>2</sub> and [4-RBzPy]Cl (R = Cl, NO<sub>2</sub>).

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

Compounds	<b>1</b>	<b>2</b>
Empirical formula	C <sub>24</sub> H <sub>22</sub> N <sub>2</sub> CuCl <sub>6</sub>	C <sub>24</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> CuCl <sub>4</sub>
Formula weight	614.68	635.80
T (K)	291(2)	291(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	<i>Pca</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	29.792(3)	7.336(2)
<i>b</i> (Å)	7.206(1)	29.567(8)
<i>c</i> (Å)	12.637(1)	12.851(4)
$\alpha$ (°)	90	90
$\beta$ (°)	90	96.46(1)
$\gamma$ (°)	90	90
Volume (Å <sup>3</sup> )	2712.8(4)	2769.7(14)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.505	1.525
Absorption coefficient (mm <sup>-1</sup> )	1.412	1.212
<i>F</i> (000)	1244	1292
Crystal size (mm <sup>3</sup> )	0.11 × 0.15 × 0.21	0.12 × 0.17 × 0.21
Reflections collected	18541	19682
Independent reflections ( <i>R</i> <sub>int</sub> )	4719 (0.041)	4880 (0.047)
Data/restraints/parameters	4719/1/298	4880/204/334
Goodness of fit (GOF) on $F^2$	1.040	1.070
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	<i>R</i> <sub>1</sub> = 0.0279, <i>wR</i> <sub>2</sub> = 0.0700	<i>R</i> <sub>1</sub> = 0.0480, <i>wR</i> <sub>2</sub> = 0.1330
Final <i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0316, <i>wR</i> <sub>2</sub> = 0.0729	<i>R</i> <sub>1</sub> = 0.0543, <i>wR</i> <sub>2</sub> = 0.1370

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

Bond length (Å)			
Cu(1)–Cl(1)	2.256(1)	N(1)–C(7)	1.500(4)
Cu(1)–Cl(2)	2.257(1)	N(1)–C(8)	1.343(4)
Cu(1)–Cl(3)	2.256(1)	N(1)–C(12)	1.340(4)
Cu(1)–Cl(4)	2.247(1)	N(2)–C(19)	1.501(4)
Cl(5)–C(3)	1.740(3)	N(2)–C(20)	1.336(4)
Cl(6)–C(15)	1.740(4)	N(2)–C(24)	1.347(4)
Bond angles (°)			
Cl(1)–Cu(1)–Cl(2)	124.75(4)	C(20)–N(2)–C(24)	122.2(3)
Cl(1)–Cu(1)–Cl(3)	100.43(3)	Cl(5)–C(3)–C(2)	119.5(3)
Cl(1)–Cu(1)–Cl(4)	99.82(4)	Cl(5)–C(3)–C(4)	118.8(2)
Cl(2)–Cu(1)–Cl(3)	100.16(3)	Cl(6)–C(15)–C(14)	120.1(3)
Cl(2)–Cu(1)–Cl(4)	100.86(3)	Cl(6)–C(15)–C(16)	118.4(3)
Cl(3)–Cu(1)–Cl(4)	134.56(3)	N(1)–C(7)–C(6)	110.5(2)
C(7)–N(1)–C(8)	120.1(2)	N(1)–C(8)–C(9)	119.9(3)
C(7)–N(1)–C(12)	119.2(2)	N(1)–C(12)–C(11)	120.5(3)
C(8)–N(1)–C(12)	120.7(2)	N(2)–C(19)–C(18)	110.9(2)
C(19)–N(2)–C(20)	119.9(3)	N(2)–C(20)–C(21)	119.9(3)
C(19)–N(2)–C(24)	117.8(3)	N(2)–C(24)–C(23)	119.9(3)

**Table 3**  
Selected bond lengths and bond angles for **2**.

Bond length (Å)			
Cu(1)–Cl(1)	2.272(1)	N(1)–C(7)	1.486(7)
Cu(1)–Cl(2)	2.233(2)	N(1)–C(8)	1.325(7)
Cu(1)–Cl(3)	2.240(2)	N(1)–C(12)	1.339(7)
Cu(1)–Cl(4)	2.256(2)	N(2)–C(3)	1.459(7)
O(1)–N(2)	1.208(7)	N(3)–C(19)	1.497(6)
O(2)–N(2)	1.215(7)	N(3)–C(20)	1.334(6)
O(3)–N(4)	1.232(7)	N(3)–C(24)	1.347(6)
O(4)–N(4)	1.213(7)	N(4)–C(15)	1.459(8)
Bond angles (°)			
Cl(1)–Cu(1)–Cl(2)	132.59(5)	C(20)–N(3)–C(24)	121.1(4)
Cl(1)–Cu(1)–Cl(3)	98.92(5)	O(3)–N(4)–C(15)	118.7(5)
Cl(1)–Cu(1)–Cl(4)	99.89(4)	O(3)–N(4)–O(4)	123.2(5)
Cl(2)–Cu(1)–Cl(3)	98.99(5)	O(4)–N(4)–C(15)	118.1(5)
Cl(2)–Cu(1)–Cl(4)	101.42(5)	N(2)–C(3)–C(2)	118.4(4)
Cl(3)–Cu(1)–Cl(4)	129.84(5)	N(2)–C(3)–C(4)	119.4(5)
C(7)–N(1)–C(8)	116.3(4)	N(4)–C(15)–C(14)	118.1(5)
C(7)–N(1)–C(12)	121.9(5)	N(4)–C(15)–C(16)	119.6(5)
C(8)–N(1)–C(12)	121.8(5)	N(1)–C(7)–C(6)	112.4(4)
O(1)–N(2)–C(3)	119.1(5)	N(1)–C(8)–C(9)	119.8(5)
O(1)–N(2)–O(2)	122.9(5)	N(1)–C(12)–C(11)	120.3(5)
O(2)–N(2)–C(3)	118.0(5)	N(3)–C(19)–C(18)	111.3(4)
C(19)–N(3)–C(20)	119.5(4)	N(3)–C(20)–C(21)	119.8(5)
C(19)–N(3)–C(24)	119.4(4)	N(3)–C(24)–C(23)	120.5(5)

Elementary analyses indicated the observed values are in agreement with actual values. In the IR spectra of **1** and **2**, bands at 3051 and 2993 cm<sup>-1</sup> and 3056 and 2965 cm<sup>-1</sup> in the IR spectra of **1** and **2** are assigned to the  $\nu$ (C–H) bands of the aromatic ring and methylene, respectively. Bands at 1631 and 1596 cm<sup>-1</sup> for **1** and 1632 and 1578 cm<sup>-1</sup> for **2** can be assigned to  $\nu$ (C=N) and  $\nu$ (C=C) of the pyridine and phenyl rings. The bands at 1526 and 1347 cm<sup>-1</sup> are the  $\nu$ (N–O) bands for **2**. The positive-ion ESI-MS spectra of **1** and **2** in MeOH solution show that the mass spectra is dominated by 204.3 and 215.1 peaks, which are assigned to [4-ClBzPy]<sup>+</sup> and [4-NO<sub>2</sub>BzPy]<sup>+</sup>, respectively.

### 3.2. Crystal structures

The molecular structure of **1**, which crystallizes in orthorhombic system with space group *Pca*2<sub>1</sub>, is shown in Fig. 1. The asymmetric unit within the unit cell is comprised of one tetrahedral [CuCl<sub>4</sub>]<sup>2-</sup> anion and two flexuous [4-ClBzPy]<sup>+</sup> cations. For the [CuCl<sub>4</sub>]<sup>2-</sup> anion, the average bond length of Cu–Cl was 2.254 Å, and the average angle of Cl–Cu–Cl was 110.10°, these values are in agreement with those of the [CuCl<sub>4</sub>]<sup>2-</sup> salts previously reported

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