

## 烟酰胺合铜固体化合物中的分子间氢键

陈彩虹 蔡继文\* 冯小龙 陈小明

(中山大学化学化工学院、测试中心, 广州 510275)

合成了三个烟酰胺配位的铜(II)化合物  $[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4]$  (bpds) **1**,  $[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4] (2, 6\text{-nds}) \cdot 2\text{H}_2\text{O}$  **2** 和  $[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4][\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_2(1, 5\text{-nds})_2] \cdot 4\text{H}_2\text{O}$  **3** (nia = 烟酰胺, bpds = 4, 4'-联苯二磺酸, nds = 萘二磺酸), 并通过 X-射线单晶衍射确定了其晶体结构。化合物 **1**~**3** 中的配合阳离子都是四个水和两个烟酰胺配位的铜(II)离子, 八面体  $\text{CuO}_4\text{N}_2$  具有不同程度的畸变。在化合物 **3** 中, 阴离子是由 Cu(II)与两个水、两个烟酰胺和两个磺酸形成的配离子。在 **1** 和 **2** 中, 配合阳离子间由酰胺以头对头的氢键模式相互连成一维带状结构, 再分别通过吡啶环上的 C-H 与酰胺 N 或配位水所形成的氢键扩展成二维结构。在 **3** 中, 配合阳离子间通过配位水和烟酰胺间的氢键连成一维锯齿状结构。这三个化合物的配合阳离子构成相同, 不同的阴离子导致了阳离子间不同模式氢键的形成。

关键词: 铜(II) 烟酰胺 磺酸 氢键  
分类号: O614.121

## Variation of Intermolecular Hydrogen Bonding Modes in Nicotinamide-Coordinated Copper (II) Complex Cations

CHEN Cai-Hong CAI Ji-Wen\* FENG Xiao-Long CHEN Xiao-Ming

(School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275)

Three nicotinamide-coordinated copper (II) complexes have been synthesized and structurally characterized by X-ray single crystal diffraction.  $[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4]$  (bpds) **1** and  $[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4] (2, 6\text{-nds}) \cdot 2\text{H}_2\text{O}$  **2** (nia = nicotinamide, bpds = 4, 4'-biphenyldisulfoante, nds = naphthalenedisulfonate) have the same complex structures of four water molecules and two nicotinamides coordinated to a copper (II) ion. The complex cations are connected to each other through complementary amide-amide hydrogen bonds in a head-to-head fashion, creating one-dimensional cationic ribbons. In  $[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4][\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_2(1, 5\text{-nds})_2] \cdot 4\text{H}_2\text{O}$  **3**, the complex anion is formed by two water molecules, two nicotinamides and two 1, 5-nds anions coordinated to Cu (II). While the complex cation has the same component as that in **1** and **2**, the inter-cationic hydrogen bonding interactions are different. The cations are linked by hydrogen bonds between coordinated water molecules and amide carbonyl oxygens into 1-dimensional zigzag chain.

Keywords: copper (II) nicotinamide sulfoacid hydrogen bond

## 0 Introduction

Covalent bonds have been extensively exploited to

create coordination polymers, as indicated by numerous compounds constructed with spacer ligands such as 4,

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\* 通讯联系人。E-mail: puscjw@zsu.edu.cn

第一作者: 陈彩虹, 女, 28 岁, 博士研究生; 研究方向: 功能配合物和配位化学。

4'-bipyridine<sup>[1]</sup> and dicarboxylates<sup>[2]</sup>. Meanwhile, the ability to design and control the assembly of coordination networks through both coordination and H-bonding interactions has been of great interest in recent years<sup>[3]</sup>. As an extension of our previous effects of constructing extended 1-dimensional structure of silver (I) complexes using nicotinamide as both ligand and functional group for hydrogen bonds<sup>[4]</sup>, a series of copper (II) analogues were prepared and characterized, namely  $[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4]$  (bpds) **1**,  $[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4](2, 6\text{-nds}) \cdot 2\text{H}_2\text{O}$  **2** and  $[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4][\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_2(1, 5\text{-nds})_2] \cdot 4\text{H}_2\text{O}$  **3**. All cations in these complexes are propagated by inter-cationic hydrogen bonds into 1-dimensional structures.

## 1 Experimental

### 1.1 Materials and Methods

All materials were commercially available and used as received. Elemental analyses were carried out with an elemental Vario EL elemental analyzer. FTIR spectra were obtained on a Bruker EQUINOX 55 FTIR spectrometer with KBr pellet.

### 1.2 Syntheses and Characterization

$[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4]$  (bpds) **1**. Nicotinamide (0.13 g, 1mmol) was added with constant stirring to an aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.12g, 0.5 mmol). The solution was then treated with disodium 4, 4'-biphenyldisulfonate (0.18g, 0.5mmol). Azure plate-like crystals of **1** were collected after 3 days (80% yield based on Cu). Required for  $\text{C}_{24}\text{H}_{28}\text{O}_{12}\text{N}_4\text{S}_2\text{Cu}$ : C, 41.65; H, 4.08; N, 8.09; Found: C, 41.69; H, 4.15; N, 8.45. IR data ( $\text{cm}^{-1}$ , KBr): 3416s, 3325s, 3270, 3215s, 3193s, 3061m, 1662s, 1623s, 1579m, 1482w, 1443w, 1392s, 1196s, 1130s, 1038s, 997s, 822m, 726s, 694m, 619s.

Compounds **2** and **3** were prepared using the same procedure as that of **1**.

$[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4](2, 6\text{-nds}) \cdot 2\text{H}_2\text{O}$  **2**. (85% yield based on Cu). Required for  $\text{C}_{24}\text{H}_{32}\text{O}_{14}\text{N}_4\text{S}_2\text{Cu}$ : C, 37.63; H, 4.31; N, 7.98; Found: C, 37.66; H, 4.26; N, 7.87. IR data ( $\text{cm}^{-1}$ , KBr): 3414s, 3325s, 3270s, 3216s, 3188s, 1663s, 1622s, 1601s,

1574m, 1479w, 1443m, 1406m, 1234s, 1183s, 1141m, 1090s, 1035s, 891m, 780m, 692m, 665s, 625s.

$[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4][\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_2(1, 5\text{-nds})_2] \cdot 4\text{H}_2\text{O}$  **3**. (80% yield based on Cu). Required for  $\text{C}_{44}\text{H}_{58}\text{O}_{30}\text{N}_8\text{S}_4\text{Cu}_2$ : C, 36.85; H, 4.08; N, 7.81; Found: C, 37.26; H, 4.43; N, 7.54. IR data ( $\text{cm}^{-1}$ , KBr): 3577s, 3417s, 3325s, 3270s, 3216s, 1663s, 1624s, 1579m, 1500w, 1444w, 1407m, 1205s, 1161s, 1045s, 941w, 826w, 789m, 693m, 616s.

## 2 Crystallography Studies

Experimental details of the X-ray analyses are provided in Table 1. All diffraction data were collected on a Bruker Smart 1000 CCD diffractometer with graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. Absorption corrections were applied by SADABS<sup>[5]</sup>. Space groups of these compounds were determined from systematic absences and further justified by the results of refinement. In all cases, the structures were solved by direct methods and refined using full-matrix least-squares/difference Fourier techniques using SHELXTL<sup>[6, 7]</sup>. All non-hydrogen atoms were refined with anisotropic displacement parameters. After that, all hydrogen atoms of the ligands were placed at idealized positions and refined as riding atoms with the relative isotropic parameters of the heavy atoms to which they are attached. Hydrogen atoms of some water molecules were located from the difference Fourier map at the finale state of refinement and refined as fixed atoms. Selected hydrogen bonds for compounds **1** ~ **3** were provided in Table 2.

## 3 Results and Discussion

The IR spectra show the N-H stretching vibrations of amide groups at  $3200 \sim 3580 \text{ cm}^{-1}$  for all of these compounds. And all compounds have absorptions at  $3000\text{-}3200$ , corresponding to the presence of water molecules. The well-resolved frequencies of aromatic rings spans over the region of  $1240 \sim 1670\text{cm}^{-1}$  and  $600 \sim 930\text{cm}^{-1}$ . Bands characteristic of the fundamental and split  $\nu_3$  S-O stretching modes are observed

Table 1 Crystal Data and Structure Refinement for compounds 1 ~ 3

compound	1	2	3
formula	C <sub>12</sub> H <sub>14</sub> Cu <sub>0.50</sub> N <sub>2</sub> O <sub>6</sub> S	C <sub>22</sub> H <sub>30</sub> CuN <sub>4</sub> O <sub>14</sub> S <sub>2</sub>	C <sub>44</sub> H <sub>52</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>30</sub> S <sub>4</sub>
formula weight	346.08	702.16	1428.26
crystal class	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
$a/\text{\AA}$	7.0932(12)	6.2193(9)	46.797(7)
$b/\text{\AA}$	7.1459(12)	8.6526(12)	7.5832(11)
$c/\text{\AA}$	14.029(2)	13.8641(18)	16.233(2)
$\alpha/^\circ$	96.827(3)	95.601(2)	90
$\beta/^\circ$	90.587(3)	97.922(2)	95.915(3)
$\gamma/^\circ$	96.074(3)	99.057(2)	90
$V/\text{\AA}^3$	701.9(2)	724.29(17)	5730.1(14)
Z	2	1	4
density (calc.)/(g·cm <sup>-3</sup> )	1.638	1.610	1.656
absorption coefficient/mm <sup>-1</sup>	0.998	0.973	0.988
$F(000)$	357	363	2936
$\theta$ range for data collection/ $^\circ$	4.07 ~ 29.98	3.98 ~ 30.04	4.08 ~ 30.02
reflections collected/unique	5424/3845	5258/4008	19989/8276
observed reflections ( $I > 2\sigma(I)$ )	3009	3194	5607
transmission factors	0.8103 ~ 0.9425	0.8000 ~ 0.9350	0.7492 ~ 0.9163
data/restraints/parameters	3845/0/200	4008/0/202	8276/0/407
goodness of fit	1.230	1.011	1.044
$R(F)$ ; $R_w(F)$ ( $I > 2\sigma(I)$ )	0.0441; 0.1445	0.0399; 0.1063	0.0511; 0.1453

in the range of 1000 ~ 1240cm<sup>-1</sup>[8].

[Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](bpd)s **1**: The compound comprises discrete [Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> cations and bpd<sup>2-</sup> anions. Both the complex cation and bpd<sup>2-</sup> anion are located on inversion centers. Structure of [Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> is shown in Fig. 1(a). The Cu(II) center is six-coordinated with four water molecules and two nicotinamide nitrogen atoms in trans fashion. The CuN<sub>2</sub>O<sub>4</sub> chromophores are elongated to different extents along the axial positions, which are occupied by water molecules. The distances between Cu(II) and water molecules are Cu(1)-O(1W) = 1.988(2) Å and Cu(1)-O(2W) = 2.428(3) Å. The distances between Cu(II) and pyridine nitrogen atom are Cu-N = 2.023(2) Å, which is shorter than that in [Cu<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(nia)<sub>2</sub>]<sup>[9]</sup>, slightly longer than that in [Cu(nia)<sub>2</sub>F<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>[10]</sup>. The amide moieties arrange trans with respect to each other. The complex cations are linked by four complementary N-H...O hydrogen bonds between amide moieties on neighboring complexes, generating infinite one-dimensional ribbons. Adjacent ribbons are connected by C-H...N hydrogen bonds (C...N = 3.321 Å, ∠C-H...N = 132.7°) formed between meta C-H

and amide nitrogen atom, leading to extended two-dimensional cationic sheets as illustrated in Fig. 1(b). The bpd<sup>2-</sup> anions are sandwiched between the cationic layers, anchored by hydrogen bonds between the sulfonate oxygen atoms and water/amide hydrogen atoms, resulting in three-dimensional structures as depicted in Fig. 1(c).

[Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](2,6-nds)·2H<sub>2</sub>O **2**: Both the complex cation and 2,6-nds anion are located on inversion centers. Cu(II) has a similar coordination environment as that observed in **1**, with Cu-O<sub>w</sub> = 2.0118(14) Å and 2.3908(15) Å, respectively, while the Cu-N bond distance is 2.0034(16) Å. The amide moieties align in trans with respect to each other, and the cations are propagated into infinite one-dimensional ribbons through amide-amide hydrogen bonds in a 'head-to-head' R<sub>2</sub><sup>2</sup>(8) mode. Neighboring ribbons are linked via C-H...O hydrogen bonds (C...O = 3.372 Å, ∠C-H...O = 152.9°) between ortho C-H and coordinated water molecules, leading to two-dimensional cationic sheets, as illustrated in Fig. 2(a). These cationic sheets interact with anions through extensive hydrogen bonds, resulting in three-dimensional

Table 2 Selected Hydrogen Bond Interactions(Å, °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
<b>[Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](bpd<sub>s</sub>) (1)</b>				
O(1W) - H(1WA)···O(1)	0.86	1.88	2.722(3)	166.2
O(1W) - H(1WB)···O(3) <sup>i</sup>	0.78	1.89	2.672(3)	171.1
O(2W) - H(2WA)···O(2) <sup>ii</sup>	0.86	2.05	2.868(3)	158.3
O(2W) - H(2WB)···O(1) <sup>iii</sup>	0.88	2.26	3.045(4)	149.5
N(2) - H(2A)···O(4) <sup>iv</sup>	0.86	2.17	3.011(3)	167.2
N(2) - H(2B)···O(2) <sup>v</sup>	0.86	2.17	3.018(4)	170.2
<b>[Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](2,6-nds) · 2H<sub>2</sub>O (2)</b>				
O(1W) - H(1WA)···O(3) <sup>vi</sup>	0.83	1.98	2.788(2)	162.9
O(1W) - H(1WB)···O(2) <sup>vii</sup>	0.83	2.08	2.900(2)	168.0
O(2W) - H(2WA)···O(1) <sup>viii</sup>	0.87	1.89	2.761(2)	174.0
O(2W) - H(2WB)···O(3W)	0.89	1.79	2.656(2)	166.1
O(3W) - H(3WA)···O(3) <sup>ix</sup>	0.85	2.03	2.862(3)	165.6
O(3W) - H(3WB)···O(2) <sup>x</sup>	0.92	2.02	2.934(3)	175.4
N(2) - H(2A)···O(4) <sup>xi</sup>	0.86	2.07	2.917(2)	166.7
N(2) - H(2B)···O(2) <sup>xii</sup>	0.86	2.14	2.987(3)	167.6
<b>[Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] · [Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(1,5-nds)<sub>2</sub>] · 4H<sub>2</sub>O (3)</b>				
O(1W) - H(1WA)···O(2)	0.88	1.89	2.759(3)	168.4
O(1W) - H(1WB)···O(2) <sup>xiii</sup>	0.86	2.07	2.873(3)	155.9
O(2W) - H(2WA)···O(4) <sup>xiv</sup>	0.91	2.17	2.973(4)	146.5
O(2W) - H(2WA)···O(4W) <sup>xv</sup>	0.91	2.46	3.019(8)	120.1
O(2W) - H(2WB)···O(5) <sup>xvi</sup>	0.93	2.02	2.944(4)	173.4
O(5W) - H(5WA)···O(3) <sup>xvii</sup>	0.88	2.00	2.767(3)	144.7
O(5W) - H(5WA)···O(3) <sup>xviii</sup>	0.88	2.43	2.986(3)	121.8
O(5W) - H(5WB)···O(1W) <sup>xix</sup>	0.92	1.86	2.779(3)	176.4
O(6W) - H(6WA)···O(5) <sup>xx</sup>	0.82	1.95	2.769(3)	173.0
O(6W) - H(6WB)···O(8) <sup>xxi</sup>	0.82	2.07	2.837(5)	155.9
N(2) - H(2B)···O(2W)	0.86	2.02	2.870(3)	172.4
N(2) - H(2C)···O(1W) <sup>xxii</sup>	0.86	2.30	3.154(3)	169.7
N(4) - H(4B)···O(4) <sup>xxiii</sup>	0.86	2.13	2.977(4)	168.2
N(4) - H(4C)···O(3W) <sup>xxiv</sup>	0.86	2.13	2.961(6)	161.4

Symmetry codes for 1: i:  $-x+2, -y+2, -z+2$ ; ii:  $-x+1, -y+2, -z+2$ ; iii:  $x-1, y, z$ ; vi:  $-x+1, -y, -z+1$ ;  $x, y-1, z$ .

Symmetry codes for 2: i:  $-x, -y+2, -z+1$ ; ii:  $-x, -y+1, -z+1$ ; iii:  $x, y-1, z+1$ ; iv:  $x, y, z+1$ ;  $v: -x+1, -y+2, -z+1$ ; vi:  $-x-1, -y+1, -z+1$ .

Symmetry codes for 3: i:  $-x+1/2, -y+3/2, -z+1$ ; ii:  $-x, y, -z+1/2$ ; iii:  $-x+1/2, y-1/2, -z+1/2$ ;  $iv: x, -y+1, z+1/2$ ;  $v: -x+1/2, -y+1/2, -z+1$ ; vi:  $x, y+1, z$ ;  $vii: -x+1/2, y+1/2, -z+1/2$ ;  $viii: x, -y+2, z+1/2$ ;  $ix: x-1/2, -y+3/2, z-1/2$ .

structures, as shown in Fig. 2(b).

[Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>][Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(1,5-nds)<sub>2</sub>] · 4H<sub>2</sub>O **3** is composed of discrete [Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> cation, [Cu(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(1,5-nds)<sub>2</sub>]<sup>2-</sup> anion and water molecules. The complex anion is formed by Cu(II) coordinated by two 1,5-nds anions (Cu-O = 2.3859(18) Å), two nicotinamide nitrogens (Cu-N = 2.003(2) Å) and two water molecules (Cu-O<sub>w</sub> = 1.998(2) Å), all in trans fashion, as indicated in Fig. 3(b). The distance between Cu and coordinated

sulfonate oxygen is shorter than those we reported previously<sup>[10]</sup>. The anions are linked into one-dimensional chain through hydrogen bonds formed between coordinated sulfonate groups and water molecules.

The cation in **3** has the same coordination environment as that in **1** and **2**. However, the coordination geometry can be described as regular octahedral, with Cu(II) ion coordinated to four water molecules and two pyridine nitrogen atoms in similar distances, Cu(2)-O(6w) = 2.126(2) Å, Cu(2)-O(7w) = 2.095(5) Å and

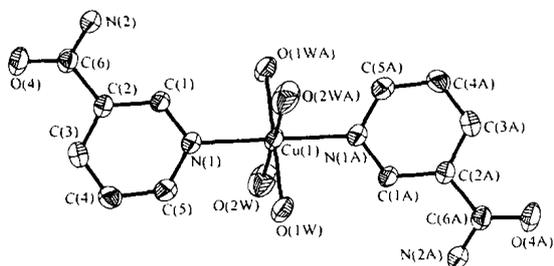


Fig. 1 (a) Cationic complex in **1**, with 30% probability displacement ellipsoids

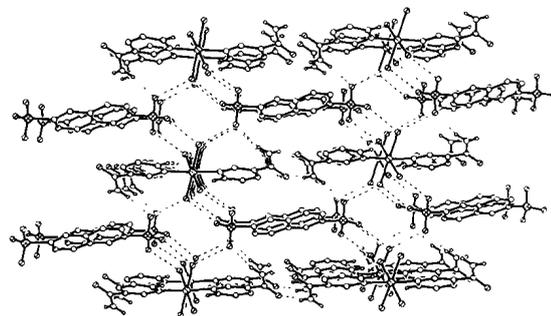


Fig. 2 (b) 3-D network constructed by alternating cationic sheets and anions in **2**

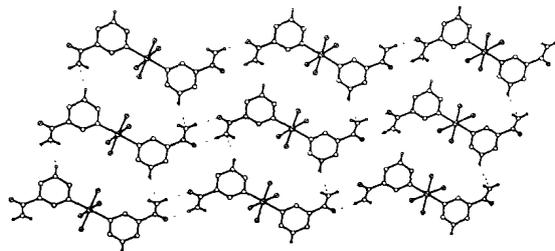


Fig. 1 (b) 2-D cationic sheet constructed by hydrogen bonds in **1**

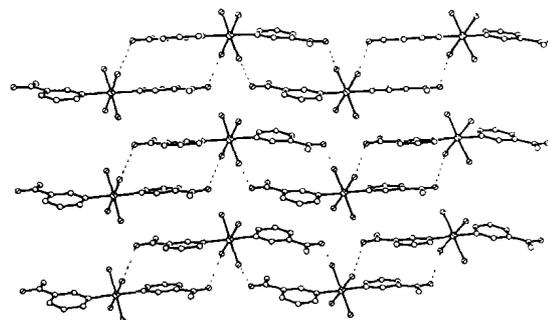


Fig. 3 (a) 1-D chains formed by the complex cations in **3**

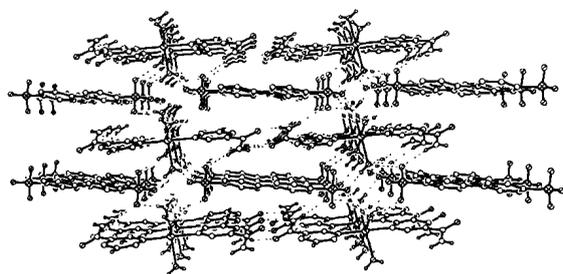


Fig. 1 (c) 3-D network constructed by alternating cationic sheets and anions in **1**

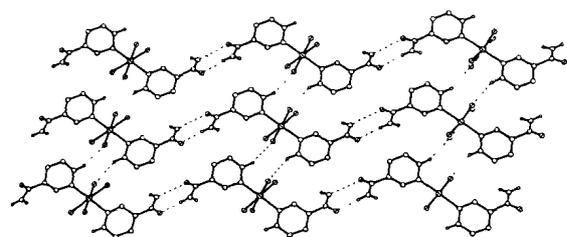


Fig. 2 (a) 2-D cationic sheet constructed by hydrogen bonds in **2**

$\text{Cu}(2)-\text{N} = 2.044(3) \text{ \AA}$ . Interestingly, unlike in **1** and **2** in which the cations are located on inversion centers, in **3**, the cation is located on a 2-fold axis. Therefore, the cation in **3** is not centro-symmetric. The two pyridine rings are not co-planar to each other. They form a dihedral angle of  $15.4^\circ$ . Furthermore, the amide group is almost co-planar with the pyridine ring, as indicated

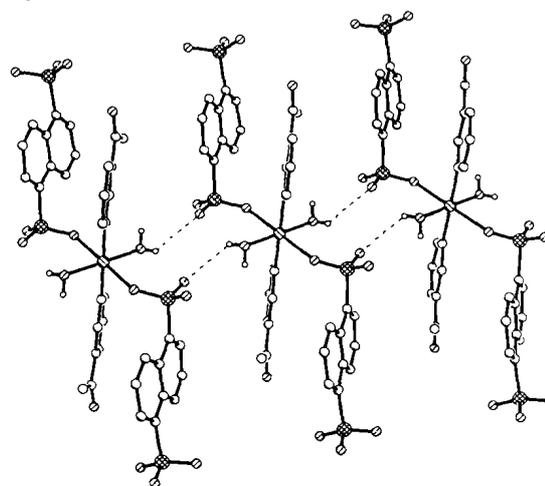


Fig. 3 (b) 1-D chain formed by the complex anions in **3**

by the torsion angle of  $\text{C}(17)-\text{C}(18)-\text{C}(22)-\text{O}(10)$   $178.9^\circ$ . In the case of **1** and **2**, the corresponding torsion angles are  $155.1$  and  $-144.7^\circ$  respectively.

The hydrogen bonding mode in **3** is also very different from that in **1** and **2**. In **3**, each cation interact with two other adjacent cations *via*  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds formed between coordinated water molecules and amide carbonyl oxygens, creating infinite one-dimensional zigzag chains, as shown in Fig. 3(a). Complex

cations and anions interact through extensive hydrogen bonds formed between sulfonate oxygens, water molecules and amide groups, as illustrated in Fig. 3(c).

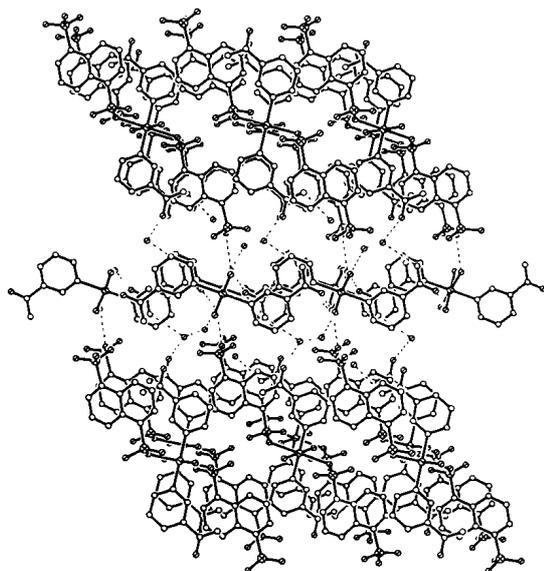


Fig. 3 (c) Packing diagram of 3

In summary, complex cations in **1**~**3** have the same component described as  $[\text{Cu}(\text{nia})_2(\text{H}_2\text{O})_4]^{2+}$ . However, they demonstrate variant inter-molecular hydrogen bonding behaviors which are tuned by the nature of counter anions.

#### 4 Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 176799 ~ 176801 for compounds **1**~**3**, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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