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Dinuclear copper(II) complexes with different bridging connectors

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Abstract

One novel triply-bridged dicopper(II) complex formulated as $[Cu_2(dpa)_2(\mu-Cl)(\mu-OH)(\mu-HCOO)] \cdot (ClO_4)$ **1** and two terephthalate anions bridged 2,2'-bipyridine (2,2'-bpy) dicopper(II) complexes with formulae of $[Cu_2(2,2'-bpy)_4(\mu-terephthalate)] \cdot (NO_3)_2$ **2** and $[Cu_2(2,2'-bpy)_4(\mu-terephthalate)] \cdot (terephthalate)$ **3**, respectively, have been synthesized and characterized by infrared and electrospray mass spectra as well as X-ray single-crystal determination. In addition, thermal properties of all compounds have been studied.

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1. Introduction

Over the past two decades the use of transition metal centers and coordination chemistry for directing the high-yielding formation of complexes has generated one of the most widely used strategies for organizing molecular building blocks into supramolecular arrays. More and more supramolecular coordination complexes with a wide range of sizes and shapes have been prepared by this directionalbonding approach due to their interesting topologic structures and possible functions. The assembly of well-designed ligands with metal ions possessing certain coordination geometry has led to the generation of diversiform 1D, 2D and 3D networks via

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coordination bonding as well as weak surpramolecular interactions [1–8]. Among these ligands, rigid bifunctional linear ligands and tri-functional tripodal ligands such as two or three pyridine-based bridging ligands have been actively utilized as construction units to obtain lots of supramolecular arrays with certain metal ion connectors [9–12]. In addition, transition metals with specific coordination geometries have also been employed for the rational design and construction of highly ordered structures. Furthermore, the weak forces such as hydrogen bonding, van der Walls forces, $\pi - \pi$ interactions, and dipole– dipole interactions are very common in constructing these supramolecular systems.

In our recent study, we have designed and prepared a few of bi-terminal tetradentate ligands containing 2,2'-dipyridylamine (dpa) units, attempting to obtain supramolecular compounds or ordered coordination

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polymers via self-assembly with transition metal ions. It is known to us now that when N,N'-bis(2,2'dipyridyl)isophthaloylamide is used to react with copper(II) ions, a copper(II) complex formulated as $[Cu(dpa)_2] \cdot (ClO_4)_2$ could be found as the major product, which suggests that the amide C-N bonds of the ligand which are longer than the normal value have been broken [13]. But what will happen when N,N'-bis(2,2'-dipyridyl)trimesoylamide is assembled with copper(II) ions. Once again, instead of an expected supramolecular framework, a dinuclear copper(II) complex with free dpa molecules which come from the amide C-N bonds decomposition of the N.N'-bis(2,2'-dipyridyl)trimesoylamide has proved to be yielded. In this paper, we report the syntheses and the crystal structures of three dinuclear copper(II) complexes by assembling Cu^{II} ions with bior multi-dentate ligands containing N- or O-donors, namely, one novel triply-bridged complex formulated as $[Cu_2(dpa)_2(\mu-Cl)(\mu-OH)(\mu-HCOO)] \cdot (ClO_4)$ 1, and two terephthalate anions bridged 2,2'-bipyridine (2,2'bpy) dicopper(II) complexes with the formulae of $[Cu_2(2,2'-bpy)_4(\mu-terephthalate)] \cdot (NO_3)_2$ 2 and $[Cu_2(2,2'-bpy)_4(\mu-terephthalate)] \cdot (terephthalate) 3,$ respectively.

2. Experimental section

2.1. Materials and measurements

2,2'-Bipyridine, terephthalic acid, trimesoyl chloride and 2,2'-dipyridylamine were purchased as commercial chemicals from Aldrich. All other solvents and reagents were of analytical grade and used without further purification. $[Cu(2,2'-bpy)](NO_3)_2 \cdot 3H_2O$ was prepared by a literature method [14].

Analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 1400C analyzer. Infrared spectra (4000–400 cm⁻¹) were recorded with a Nicolet FT-IR 170X spectrophotometer on KBr disks. Electrospray (ES) ionization mass spectra were recorded on a Finnigan MAT SSQ 710 mass spectrometer in a scan range of 100–1200 amu. TGA-DTA data were recorded by a CA Instrument DTA-TGA 2960 type simultaneous analyzer in nitrogen atmosphere. *Caution*: Although no problem was encountered in all our experiments, transition metal perchlorates are potentially explosive and should be handled in small quantities.

2.2. Synthesis of complex 1

The syntheses of the ligand and its Cu^{II} complex **1** are shown in scheme 1. Trimesoyl chloride (1.03 g, 4 mmol) and 2,2'-dipyridylamine (2.00 g, 12 mmol) were dissolved in 80 cm³ dry DMF and stirred at 70 °C for one day, and the same amount of water was added, then the solution was condensed to nearly dry under reduced pressure. The residue was washed by 40 cm³ hot acetonitrile, and then the colorless crystals came into being when the filtrate was cooled in an ice bath. Finally the precipitate was collected and dried in a vacuum to obtain *N*,*N*'-bis(2,2'-dipyridyl)trimesoy-lamide. Anal Calc for C₃₉H₂₇N₉O₃·H₂O C: 68.11; H: 4.25; N: 18.33. Found: C: 68.32; H: 4.34; N: 18.61. FT-IR: ν [cm⁻¹]: 3353, 1666, 1602, 1560, 1506, 1482, 1453, 1248, 843 and 777.

The resulting colorless crystals obtained above (0.67 g, 1 mmol) and CuCl₂·2H₂O (0.17 g, 1 mmol) were dissolved in CH₃CN-C₂H₅OH (40 cm³), and the mixture was refluxed for 1 h, then an ethanol solution (10 cm^3) of sodium perchlorate (0.12 g)1 mmol) was added dropwise. A deep green precipitate formed immediately, which was filtered off, washed with a small amount of ethanol, and dried in a vacuum. The single crystal sample suitable for X-ray diffraction measurements was grown from the mixed solution of CH₃CN/DMF (1:1) by slow evaporation at room temperature. Anal. Calc for the green crystals C₂₁H₂₀Cl₂N₆O₇Cu₂ (1): C, 37.85; H, 3.02; N, 12.61. Found: C, 37.62; H, 3.21; N, 12.89. FT-IR data for the green crystals: ν [cm⁻¹]: 3296, 3207, 3141, 1634, 1585, 1525, 1477, 1432, 1383, 1230, 1157, 1118, 1083, 776 and 625. Es-ms: m/z 297 (100%), $[Cu(dpa)(\mu-HCOO)(H_2O)]^+$.

2.3. Synthesis of complex 2

An aqueous solution of NaOH (0.08 g, 2 mmol) and terephthalate acid (0.17 g, 1 mmol) was added to the solution of $[Cu(2'2-bpy)](NO_3)_2\cdot 3H_2O$ (0.40 g, 1 mmol) in 20 cm³ ethanol (scheme 2). The liquid immediately became dark blue, and the mixture was



Scheme 1. Synthesis of the ligand and its $\mbox{Cu}^{\mbox{II}}$ complex 1.



Scheme 2. The synthetic routes for copper(II) complexes 2 and 3.

refluxed for 2 h, blue micro-crystals precipitated, which were filtered out and dried in a vacuum. Single crystals suitable for X-ray crystallography were grown from the aqueous solution of **2**. Anal Calc for C₄₈H₄₀N₁₀O₁₂Cu₂ C: 53.58; H: 3.75; N: 13.02. Found: C: 53.42; H: 3.98; N: 13.29. FT-IR: ν [cm⁻¹]: 1688, 1616, 1604, 1593 and 1397. Es-ms: *m*/*z* 190 (100%), [Cu(2'2-bpy)₂]²⁺/2.

2.4. Synthesis of complex 3

Complex **3** was prepared in the same way as **2** except that the molar ratio of sodium terephthalate salt to $[Cu(2'2-bpy)](NO_3)_2 \cdot 3H_2O$ was 2:1, namely, NaOH (0.16 g, 4 mmol) and terephthalate acid (0.34 g, 2 mmol) dissolved in 40 cm³ water were added to the solution of $[Cu(2'2-bpy)](NO_3)_2 \cdot 3H_2O$ (0.40 g, 1 mmol) in 20 cm³ ethanol. Anal Calc for C₅₆H₆₈N₈O₂₂Cu₂ C: 50.49; H: 5.14; N: 8.41. Found: C: 50.22; H: 5.08; N: 8.59. FT-IR: ν [cm⁻¹]: 1688, 1614, 1604, 1592 1400. Es-ms: *m*/*z* 190 (100%), [Cu(2'2-bpy)_2]²⁺/2. Green single crystals of **2** and **3** suitable for X-ray determination were developed from their DMF (**2**) and water (**3**) solutions, respectively, which were slowly evaporated at room temperature.

2.5. Crystal structure determination

As crystals of 1, 2 and 3 are unstable in the absence of their mother liquors, these single crystal samples were glue-covered for measurements. Reflection data for 1, 2 and 3 crystals were measured on a Bruker SMART 1 K CCD diffractometer at 293(2) K using mono-chromated Μο Κα graphite radiation $(\lambda = 0.71073 \text{ Å})$ at a detector distance of 4 cm and swing angle of -35° . The collected data were reduced by using the program SAINT [15] and empirical absorption correction was done by using the SADABS [16] program. Both structures were solved by direct methods and refined by least squares method on F_{obs}^2 by using the SHELXTL-PC [17] software package, with 3142 of 8728 (1), 3947 of 4722 (2) and 5508 of 8216 (3) $[I > 2\sigma(I)]$ unique absorption corrected reflections, respectively. All non-H atoms were anisotropically refined; other hydrogen atoms were geometrically fixed and allowed to ride on the attached atoms. The summary of the crystal data, experimental details and refinement results for 1, 2

and **3** is listed in Table 1, selected bond distances and bond angles are given in Table 2. Further details are provided in supporting information.

3. Results and discussion

3.1. Synthesis and spectral characterization

In the process of preparing N,N'-bis(2,2'-dipyridyl)trimesoylamide ligand, the results of the microanalytical and the IR spectral data (a sharp C=O stretching vibration band assigned to the amide group at 1666 cm⁻¹ and the signals corresponding to the dpa units and the benzene group) suggest that the expected ligand has been yielded. But the elemental analyses of complex **1** show that it is not an expected product. The IR spectral data indicate that dpa molecules still exist but the sharp C=O stretching vibration band has disappeared compared with those of the ligand. In addition, complex **1** is characterized by perchlorate absorptions at 1118, 1083 and 625 cm⁻¹.

As mentioned above, when Cu(ClO₄)₂·6H₂O was reacted directly with such a kind of ligands, only $[Cu(dpa)_2] \cdot (ClO_4)_2$ could be obtained because of the cleavage of imide C-N bond, but at this time CuCl₂·2H₂O was used for comparison. As the X-ray crystal structural study shown, the imide C-N bonds of the ligand are broken and a triply-bridged dinuclear copper(II) perchlorate complex with three kinds of different bidentate bridging ligands (a chloride anion, a hydroxy anion and a formate anion) $[Cu_2(dpa)_2(\mu Cl)(\mu-OH)(\mu-HCOO)] \cdot (ClO_4)$ 1 has been yielded. It is believed that chloride and perchlorate anions are derived from the addition of CuCl₂·2H₂O and NaClO₄, respectively, and the hydroxy anions may arise from the ionization of water molecules in solution. Up till now, we could not specify certainly where formate anions come from, but there have been many reports in literature about metal-catalyzed (Cu, Zn, Co, Fe, Ru, et al.) hydrogenation of carbon dioxide to formic acids [18-21]. It is assumed that formate anions in 1 could be resulted from the catalytic reduction of copper(II) ions to carbon dioxide in atmosphere absorbed by mother liquor during the formation of single crystals. The IR frequencies of the antisymmetric and symmetric O-C-O stretching modes of the coordinated formate ion

| Table 1 | | | | | | | |
|-----------------------|--------------|------|-----|----|---|-----|---|
| Crystal and structure | refinemental | data | for | 1, | 2 | and | 3 |

| Compound | 1 | 2 | 3 |
|---|--|--------------------------------|--|
| Empirical formula | C ₂₁ H ₂₂ 'Cl ₂ Cu ₂ N ₆ O ₈ | $C_{48}H_{40}Cu_2N_{10}O_{12}$ | C ₅₆ H ₆₈ Cu ₂ N ₈ O ₂₂ |
| Formula weight | 684.43 | 1075.98 | 1332.26 |
| Crystal size (mm) | $0.46 \times 0.36 \times 0.22$ | $0.65 \times 0.60 \times 0.40$ | $0.20 \times 0.20 \times 0.30$ |
| Crystal system | Orthorhombic | Triclinic | Triclinic |
| Space group | Cmc21 | P-1 | <i>P</i> -1 |
| a, Å | 16.8109(3) | 9.578(3) | 10.432(2) |
| b, Å | 7.78600(10) | 10.819(5) | 11.767(2) |
| <i>c</i> , Å | 19.31540(10) | 12.030(6) | 14.278(2) |
| α , deg | 90 | 77.33(4) | 92.160(10) |
| β , deg | 90 | 68.46(3) | 106.300(10) |
| γ, deg | 90 | 89.98(3) | 106.960(10) |
| V,Å ³ | 2528.19(6) | 1126.9(9) | 1595.4(5) |
| $Z, D_{calcd}, (Mg/m^3)$ | 4, 1.798 | 1, 1.586 | 1, 1.387 |
| F(000) | 1384 | 552 | 694 |
| μ , $M \text{ mm}^{-1}$ | 1.954 | 1.023 | 0.747 |
| Temperature (K) | 293(2) | 293(2) | 293(2) |
| h_{\min}/h_{\max} | - 22/13 | - 1/11 | - 10/12 |
| k_{\min}/k_{\max} | - 10/10 | - 12/12 | - 13/13 |
| l_{\min}/l_{\max} | - 25/24 | - 13/14 | - 16/12 |
| Refl. collected/unique | 8728/3142 | 4722/3947 | 8216/5508 |
| Parameters | 191 | 331 | 397 |
| Max./min. transmissions | 0.6731/0.4668 | 0.6728/0.5193 | 0.861/0.836 |
| Final <i>R</i> indices $[I > 2\sigma(I)]$ | R1 = 0.0405, wR2 = 0.1016 | R1 = 0.0747, wR2 = 0.1834 | R1 = 0.0521, wR2 = 0.1476 |
| R indices (all data) | R1 = 0.0435, wR2 = 0.1030 | R1 = 0.1112, wR2 = 0.2087 | R1 = 0.0573, wR2 = 0.1508 |
| Goodness-of-fit on F^2 | 1.020 | 1.047 | 1.080 |
| Max./min., $\Delta \rho$ (e Å ⁻³) | 0.550/ - 0.583 | 0.852/ - 1.399 | 0.703 / - 0.457 |

in 1 are assigned at ν_a (CO₂) = 1585 cm⁻¹ and ν_s (CO₂) = 1383 cm⁻¹, respectively. The separation between them (Δ) is 202 cm⁻¹. Deacon and Phillips [22] have reported that for bidentate carboxylates the value is similar to, or less than, that found in the free formate, taken as those for the sodium (Δ = 241 cm⁻¹) [23] or potassium (Δ = 233 cm⁻¹) [24] salts. Furthermore, a vibration of δ (OCO) mode at 776 cm⁻¹ has also been observed. Thus it is suggested that what is observed experimentally for complex 1 in this case has proved the existence of bidentate formate bridging groups.

 $[Cu(2,2'-bpy)](NO_3)_2\cdot 3H_2O$ is often used to generate coordinating polymers and supramolecular compounds [25-27], in which two coordinating sites of its copper(II) ions have been preoccupied by 2,2'-bpy which serves as a shape-defining unit [28]. In our experiments, equal or double molar ratios of sodium terephthalate to $[Cu(2,2'-bpy)](NO_3)_2\cdot 3H_2O$ are performed to yield dissimilar infinite supramolecular arrays. The outcome of microanalytical and IR

spectral data of **2** and **3** reveals different products, but their ES-MS spectral results are analogous, so it is necessary for us to determine their crystal structures to specify how they are arranged. Contrary to our expectation, the X-ray diffraction structures of **2** and **3** are only five-coordinated dinuclear copper(II) complexes in which two 2,2'-bpy molecules are bonded to each metal atom.

3.2. *Crystal structure of* [*Cu*₂(*dpa*)₂(μ-*Cl*)(μ-*OH*) (μ-*HCOO*)]·(*ClO*₄) **1**

An X-ray crystal structural study indicated that compound **1** consists of discrete dimeric copper(II) cations countered by a hydroxy anion, a chloride anion, a formate anion and an independent perchlorate anion (Fig. 1). The coordination environment around each Cu(II) atom is five-coordinated distorted pyrimidal. A dpa molecule occupies two coordinating positions of each copper atom and three different ligands, i.e. a chloride anion, a hydroxy anion and

| 1 | | 2 | | 3 | |
|-----------------------|------------|-------------------------|------------|---------------|------------|
| Cu(1)-O(2) | 1.913(2) | Cu(1)-N(1) | 1.993(5) | Cu(1)–O(1) | 1.980(2) |
| Cu(1)-N(2) | 1.972(3) | Cu(1)-O(1) | 1.995(4) | Cu(1) - N(4) | 1.993(2) |
| Cu(1)-N(1) | 2.024(3) | Cu(1)–N(3) | 2.007(5) | Cu(1) - N(1) | 2.017(2) |
| Cu(1)–O(1) | 2.160(2) | Cu(1) - N(2) | 2.010(5) | Cu(1) - N(3) | 2.036(2) |
| Cu(1)-Cl(1) | 2.4788(11) | Cu(1)-N(4) | 2.198(5) | Cu(1) - N(2) | 2.199(2) |
| O(1)-C(11) | 1.256(3) | O(1)-C(21) | 1.256(8) | C(4)-O(2) | 1.263(3) |
| | | O(2)-C(21) | 1.230(8) | C(4) - O(1) | 1.271(4) |
| | | $C(22) - C(24)^{a}$ | 1.383(9) | C(28)-O(3) | 1.253(5) |
| | | | | C(28)-O(4) | 1.254(5) |
| O(2)-Cu(1)-N(2) | 173.32(12) | N(1)-Cu(1)-O(1) | 91.9(2) | O(1)-Cu(1)-N4 | 91.59(9) |
| O(2)-Cu(1)-N(1) | 94.40(12) | N(1)-Cu(1)-N(3) | 174.9(2) | O(1)-Cu(1)-N1 | 88.59(9) |
| N(2)-Cu(1)-N(1) | 91.81(11) | O(1)-Cu(1)-N(3) | 92.0(2) | N(4)-Cu(1)-N1 | 177.16(9) |
| O(2)-Cu(1)-O(1) | 87.73(11) | N(1)-Cu(1)-N(2) | 80.8(2) | O(1)-Cu(1)-N3 | 158.88(10) |
| N(2)-Cu(1)-O(1) | 86.19(10) | O(1) - Cu(1) - N(2) | 164.49(19) | N(4)-Cu(1)-N3 | 80.78(10) |
| N(1)-Cu(1)-O(1) | 133.82(11) | N(3)-Cu(1)-N(2) | 94.6(2) | N(1)-Cu(1)-N3 | 98.09(10) |
| O(2)-Cu(1)-Cl(1) | 82.75(9) | N(1)-Cu(1)-N(4) | 104.8(2) | O(1)-Cu(1)-N2 | 103.32(9) |
| N(2)-Cu(1)-Cl(1) | 96.46(9) | O(1) - Cu(1) - N(4) | 95.08(19) | N(4)-Cu(1)-N2 | 104.28(10) |
| N(1)-Cu(1)-Cl(1) | 118.34(9) | N(3)-Cu(1)-N(4) | 78.1(2) | N(1)-Cu(1)-N2 | 78.42(10) |
| O(1) - Cu(1) - Cl(1) | 107.71(8) | N(2)-Cu(1)-N(4) | 100.0(2) | N(3)-Cu(1)-N2 | 97.66(10) |
| C(11)-O(1)-Cu(1) | 126.9(2) | O(2)-C(21)-O(1) | 125.3(6) | O(2)-C(4)-O1 | 123.6(3) |
| Cu(1)-Cl(1)-Cu(1A) | 75.33(4) | $C(23)-C(22)-C(24)^{a}$ | 118.9(6) | O(3)-C(28)-O4 | 123.9(3) |
| O(1)-C(11)-O(1A) | 126.5(4) | | | | |
| Cu(1) - O(2) - Cu(1A) | 104.72(17) | | | | |

Table 2 Selected bond lengths (Å) and angles(°) for complexes $1,\,2$ and 3

^a -x, -y, -z+1.



Fig. 1. A perspective view of the molecular structure of the complex cation (1) with the atom-numbering scheme, hydrogen atoms and perchlorate anions are omitted for clarity.

a formate anion, all serve as bidentate ligands linking two copper(II) ions. Two nitrogen atoms of dpa molecules, a chlorine atom and an oxygen atom of hydroxy group offer the base plane, and the apical position was placed by one oxygen atom of the formate anion. The related bonds are Cu(1)-O(1)2.160(2) Å, Cu(1)-O(2) 1.913(2) Å, Cu(1)-N(1) 2.024(3) Å, Cu(1)-N(2) 1.972(3) Å, Cu(1)-Cl(1)2.4788(11) Å and O(1)-C(11) 1.256(3) Å. The two copper atoms are separated only by 3.0291(6) Å with a Cu(1)-O(2)-Cu(1A) bridge angle of $104.72(17)^{\circ}$ and Cu(1)-Cl(1)-Cu(1A) angle of 75.33(4)°. The related angle of bridged formate anions are C(11)-O(1)-Cu(1) 126.9(2)° and O(1)-C(11)-O(1A)126.5(4)°. Two pyridine rings of each dpa molecule are nearly at the same plane, and the dihedral angle of them is 6.9° .

Hathaway has pointed out that triply-bridged dimeric complexes are unusual in copper(II) chemistry [29], up till now there are several triply-bridged copper(II) dimers reported. An early case is a $Cs_3[Cu_2Cl_2(H_2O)_2]$ compound where three chloride anions act as bridging connectors linking two copper(II) ions with a Cu···Cu separation of 3.45 Å [30]. Recent examples are a $[Cu_2(dpa)_2(\mu-OH)_2(\mu-O$ H₂O)]Cl₂·2H₂O complex containing two hydroxy anions and one water molecule bridging two copper(II) ions which are separated by 2.799(1) Å [31], and a [Cu₂(dpa)₂(µ-OMe)₂(µ-Cl)]Cl·MeOH complex synthesized in anhydrous condition in which two OMe⁻ and one Cl⁻ anions serve as bridging ligands with a $Cu \cdots Cu$ distance of 2.792(2) Å [32]. But dimeric copper(II) complex triply-bridged by three different bridging ligands in our case is unique.

In the crystal packing of molecule 1 exists N- $H \cdots O$ type H-bonding interactions between two oxygen atoms of each formate anion and two N-H units in dpa molecules of neighboring bimetallic units (2.8582 Å, 142.47°) (Table 3). There are also O- $H \cdots O$ typed H-bonds between one oxygen atom of perchlorate anion and the hydroxy group with the length of 2.9280 Å and in an angle of 103.76°. Furthermore, weak C-H···O kind hydrogen bonding interactions have been observed between the hydroxy anion and α -positioned hydrogen of pyridine rings, such C-H···O H-bonds are 2.9109 Å, 118.80°. In addition, pyridine rings of complex 1 are all packed in a parallel fashion via $\pi - \pi$ interactions. The distance

| Table 3 | | | | |
|-----------------------|-------|----------|-----------|---------|
| Table3 Hydrogen bonds | (Å, ' |) in com | plexes 1, | 2 and 3 |

| D–H···A | D–H | H–A | D· · ·A | ∠DHA |
|---|--------|--------|----------|--------|
| 1 | | | | |
| $O(2)-H(2A)\cdots O(4)^a$ | 0.9300 | 2.5640 | 2.9280 | 103.76 |
| $N(3)-H(3A)\cdots O(1)^{b}$ | 0.8600 | 2.1278 | 2.8582 | 142.47 |
| $C(1)-H(1A)\cdots O(2)^{c}$ | 0.9300 | 2.3455 | 2.9109 | 118.80 |
| 2 | | | | |
| $O(1W) - H(1A) \cdot \cdot \cdot O(2)^e$ | 0.7581 | 2.2743 | 2.9081 | 141.82 |
| $C(1)-H(1A)\cdots O(1)$ | 0.9300 | 2.4898 | 3.0107 | 115.59 |
| $C(7)-H(7A)\cdots O(2)^d$ | 0.9300 | 2.3885 | 3.1186 | 135.27 |
| $C(10)-H(10A)\cdots N(3)$ | 0.9301 | 2.6259 | 3.1379 | 115.29 |
| $C(12)-H(12A)\cdots O(3)^{e}$ | 0.9300 | 2.5409 | 3.3973 | 153.27 |
| $C(17)-H(17A)\cdots O(1A)^{f}$ | 0.9301 | 2.3957 | 3.3156 | 170.02 |
| 3 | | | | |
| $C(5)-H(5)\cdots O(2)$ | 0.9304 | 2.5815 | 3.178(4) | 122.36 |
| $C(6)-H(6)\cdots O(12)^g$ | 0.9297 | 2.5410 | 3.365(5) | 147.85 |
| $C(15)-H(15)\cdots O(14)^h$ | 0.9306 | 2.5134 | 3.379(6) | 154.75 |
| $C(21)-H(21)\cdots O(2)^i$ | 0.9298 | 2.4078 | 3.324(3) | 168.26 |
| $C(23) - H(23) \cdots O(13)$ | 0.9295 | 2.4860 | 3.362(6) | 157.12 |
| $C(24)-H(24)\cdots O(1)$ | 0.9309 | 2.5218 | 2.997(4) | 111.95 |
| ^a $1/2 - x$, $1/2 - y$, $-1/2$ | z + z | | | |

- ^b 1/2 x, -1/2 + y, z.
- ^c 1/2 + x, 1/2 y, -1/2 + z.

e -x, 1 - y, 1 - z.

^d 1 - x, 1 - y, 1 - z.

^f x, -1 + y, 1 + z.

g = -1 + x, y, z.^h 1 - x, 1 - y, 1 - z.

x, -1 + y, z.

between adjacent pyridine rings is ca. 3.58 Å. Under the assistance of these above-mentioned weak interactions, a two-dimensional network has been formed (Fig. 3).

3.3. Crystal structures of $[Cu_2(2,2'-bpy)_4(\mu$ terephthalate)]·(NO₃)₂ **2** and $[Cu_2(2,2'-bpy)_4(\mu$ terephthalate)]·(terephthalate) 3

The structure of 2 is made up of dinuclear cations with two copper(II) centers bridged by terephthalic dianions, coordinated in a monodentate fashion to Cu(1) and Cu(1A), through the oxygen atoms of their carboxylic groups, two NO₃⁻ anions and two water molecules (Fig. 2).

The geometry of each copper(II) ion may be described as a trigonal bipyramid with N(2), O(1) and N(4) in the basal plane and N(1) and N(3) in axial positions. The Cu ion deviates only by 0.0196 Å from the basal plane, and the trigonal axis does not show too much deviation from linearity, N(1)-Cu(1)-N(3)



Fig. 2. Molecular structure of the complex cation (2) with the atom-numbering scheme, hydrogen atoms are omitted for clarity.

being 174.9°. However, the angles in the basal plane depart significantly from the theoretical 120° value, with values of 100, 164.5, and 95.1°.

The Cu–Cu distance inside the same dinuclear unit is 11.027 Å. The shortest Cu–Cu distance, equal to 6.883 Å, involves metal ions belonging to two different dinuclear units, as shown in Fig. 2. Both pyridine planes in one 2,2'-bpy molecule, staggered with a dihedral angle of 11.7° and paralleled with their counterparts which linked another copper(II) ion, are nearly perpendicular to the adjacent 2,2'-bpy (the dihedral angle is 103.2°). The bond lengths of C(21A)–O(1A) and C(21A)–O(2A) are 1.256(8) Å and 1.230(8) Å, respectively. The Cu–N distances vary from 1.994–2.198 Å.

It is worthwhile to point out, as listed in Table 2, the existence of a hydrogen bond between the oxygen atom O(3) of the carboxylic group and the carbon atom C(12) of the 2,2'-bpy. The distance between C(12)-O(3) is 3.3973 Å and C(12)-H···O(3) angle is 153.27°. A 1D chain comes into being under the assistance of these above-mentioned hydrogen-bonding interactions (Fig. 4). Moreover, the $\pi-\pi$ interactions between two adjacent 2,2'-bpy belonging to two different units are also observed. The centroidcentriod distance of two different 2,2'-bpy is ca 3.6 Å.

In complex 3, the coordination environments of the metal atoms are similar to those of in 2, where



Fig. 3. View of the 2D network depicting the connection via hydrogen bonds and $\pi - \pi$ interactions along *c*-axis in 1.



Fig. 4. View of the 2D network depicting the connection via hydrogen bonds and $\pi - \pi$ interactions along *c*-axis in 2.

the geometry of a copper(II) ion is also trigonal bipyramid and the angles of O(1)-Cu(1)-N(4), O(1)-Cu(1)-N(2), N(4)-Cu(1)-N(2), O(1)-Cu(1)-N(1), N(4)-Cu(1)-N(1), O(1)-Cu(1)-N(3), N(4)-Cu(1)-N(3), N(1)-Cu(1)-N(3), N(1)-Cu(1)-N(2), N(3)-Cu(1)-N(2) are 91.59(9), 103.32(9), 104.28(10), 88.59(9), 177.16(9), 158.88(10), 80.78(10), 98.09(10), 78.42(10) and 97.66(10), respectively. It is interesting to note that only one simple terephthalic divalent anion and seven water molecules were found in a unit cell, and NO_3^- that is present in 2 was absent. In the crystal packing of 3, a 1D chain structure comes into being (Fig. 5) under the assistance of hydrogen bonds between the oxygen atoms O(1) and O(2) of the carboxylic group and the carbon atoms C(24) and C(5)of the 2,2'-bpy, respectively. The H-bond lengths and relative angles are C(24)-O(1) 2.997(4) Å and C(24)- $H(24) \cdots O(1)$ 111.95°, C(5) - O(2) 3.178(4) Å and $C(5)-H(5)\cdots O(2)$ 122.36°, respectively.

That μ -terephthalato acting as a bi(monodentate) bridging ligand has been reported by Ma and his

co-workers [33], in which only the IR spectra of $[(VO)_2(TPHA)(H_2O)_2(bpy)_2](Ac)_2$, $[(VO)_2(-TPHA)(H_2O)_2(Me_2bpy)_2](Ac)_2$ and $[(VO)_2(TPHA)(H_2O)_2(bpu)_2](Ac)_2$. (0.5H₂O were recorded. However, it is regretted that crystal structures of three abovementioned complexes were not given, so the detailed structural comparison could not be carried out here.

3.4. Thermal analyses

TGA-DTA analysis on **1** denotes that the compound is stable in a large range of 293-568 K, then a quick weight loss (68.73%) in a range of 569-596 K indicating the decomposition of the compound. The thermal analyses of **2** show that it loses coordinating terephthalate molecules in the range of 398-428 K (15.94% weight loss) and chelating 2'2-bpy units from 517 to 579 K (59.96% weight loss), respectively. Compared with **2**, the thermal property of **3** observed is similar, namely, the sample can keep unchangeable in the range of 298-368 K, then it loses coordinating



Fig. 5. View of the 2D network depicting the connection via hydrogen bonds along *b*-axis in 3.

terephthalate molecules from 369 to 453 K with a loss of weight 30.65% and 2'2-bpy units from 503 to 564 K with a loss of weight 57.62%), respectively.

4. Supplementary material

Crystallographic data have been deposited to the Cambridge Crystallographic Data center (CCDC) (12 Union Road, Cambridge, CB2 1EZ, UK) and are available on request quoting the deposition number 195306 (1), 195307 (2) and 195308 (3).

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