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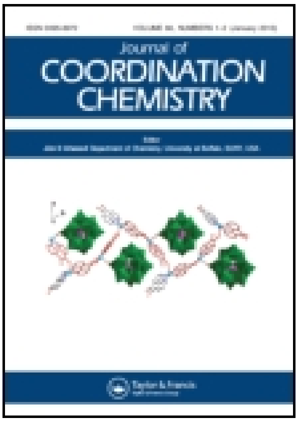

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Three copper(II) complexes of 4-formylbenzoate obtained from degradation of the Schiff base

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A 1-D copper(II) coordination polymer and two mononuclear copper(II) complexes of 4-formylbenzoate, $[Cu(L)_2(H_2O)_2]_n$ (**1**), $[Cu(L)_2$(D,L-cam)] (**2**), and $[Cu(L)(bpy)_2]\cdot(ClO_4)(H_2O)$ (**3**) (HL = 4-formylbenzoic acid, D,L-cam = D,L-camphoric diamine, bpy = 2,2′-bipyridine), have been obtained from cleavage of C=N double bonds of a bis-Schiff-base compound. 4-Formylbenzoate exhibits bidentate chelating and bidentate μ_2-bridging modes by terminal carboxylic and aldehydic groups in 1-D coordination polymer **1**. In contrast, it shows bidentate chelating in **2** and monodentate and bidentate bonding in **3** by its terminal carboxylic group where the aldehydic group does not coordinate. Offset π–π stacking interactions and two types of 8-membered hydrogen-bonding rings are found between neighboring molecules of the copper(II) complexes.

Keywords: Copper(II) complexes; 4-Formylbenzoate; Coordination polymers; Supramolecular interactions

1. Introduction

Coordination polymers with transition-metal ions have intriguing structures and potential applications in molecular recognition, nonlinear optics, porous materials, microelectronics, catalysis, liquid crystals, etc. [1–4]. Schiff bases have been widely used to react with transition-metal ions to obtain such coordination polymers for applications in the biological activities, magnetic, optical, and catalytic properties [5–12]. However, C=N double bond cleavage of Schiff-base units in these complexes often takes place during metal-ion complexation mainly because of reversible formation and decomposition of Schiff-base units, size-matching effect of the ligands, and the configuration and stereochemical restriction of the metal [13–16]. In some cases, degradation products of Schiff-base complexes are important for understanding

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mechanisms for related reactions [17]. Degradation products themselves are interesting candidates for studies of coordination and supramolecular chemistry [18–21].

In our previous work, scission of C=N double bonds in [3 + 3] macrocyclic Schiff bases has been found in reaction with several transition-metal ions, resulting in [2 + 2], [2 + 1], and [1 + 2] types of ring-degradation complexes [22–24]. In this article, we report the syntheses and structures of three copper(II) complexes, **1**–**3**, from degradation of a Schiff-base ligand condensed from 4-formylbenzoic acid and D,L-camphoric diamine; 4-formylbenzoate exhibits different coordination modes by its terminal carboxylic and aldehydic groups.

2. Experimental

2.1. *Materials and measurements*

All reagents were of analytical grade from commercial sources and used without purification. Elemental analyses were measured with a Perkin-Elmer 1400°C analyzer. Infrared spectra (IR, 4000–400 cm^{-1}) were collected on a Nicolet FT-IR 170X spectrophotometer at 25°C using KBr plates. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan MAT SSQ 710 mass spectrometer in a scan range 100–1200 amu. Ultraviolet-Visible (UV-Vis) spectra were recorded on a Shimadzu UV-3100 double-beam spectrophotometer using a Pyrex cell with a path length of 10 mm at room temperature. $[Cu^{II}(bpy)_2(ClO_4)](ClO_4) \cdot 2H_2O$ and D,L-camphoric diamine were synthesized by literature methods [25, 26].

2.2. *Preparation of $[Cu(L)_2(H_2O)_2]_n$ (1)*

A mixture of $Cu(OAc)_2 \cdot H_2O$ (0.099 g, 0.5 mmol), sodium hydroxide (0.040 g, 1.0 mmol), and 4-formylbenzoic acid (HL, 0.150 g, 1.0 mmol) was dissolved in ethanol (30 cm^3) and refluxed for 1 h. The solution was allowed to evaporate slowly in air, and dark blue crystals of **1** (0.118 g, 60% yield) suitable for X-ray diffraction determination were collected after 5 days. Elemental Anal. Calcd for $C_{16}H_{14}CuO_8$ (%): C 48.31; H 3.55. Found (%): C 48.04; H 3.86. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3448(m), 1689(s), 1594(vs), 1555(vs), 1428(s), 1399(s), 1206(m), 871(m), 766(m). ESI-MS in methanol: m/z $[Cu(L)_2(OH)]^+$ 378, $[Cu(L)_2(H_2O)(OH)]^+$ 396. UV-Vis in CH_3OH: $\lambda_{max} = 231$ nm.

2.3. *Preparation of $[Cu(L)_2(D,L\text{-}cam)]$ (2)*

A mixture of $Cu(OAc)_2 \cdot H_2O$ (0.099 g, 0.5 mmol), D,L-camphoric diamine (0.071 g, 0.5 mmol), sodium hydroxide (0.040 g, 1.0 mmol), and 4-formylbenzoic acid (HL, 0.150 g, 1.0 mmol) was dissolved in ethanol (30 cm^3) and refluxed for 2 h. The solution was allowed to evaporate slowly in air, and blue crystals of **2** (0.150 g, 60% yield) suitable for X-ray diffraction determination were collected after 1 week. Elemental Anal. Calcd for $C_{24}H_{28}CuN_2O_6$ (%): C 57.19; H 5.60; N 5.56. Found (%): C 58.08; H 5.92; N 5.20. Main FT-IR absorptions (KBr, cm^{-1}): 3425(m), 2971(m), 1688(s), 1601(s), 1559(m), 1388(vs), 1206(m), 817(m). ESI-MS in methanol: *m/z* [Cu(L)$_2$(D,L-cam)(C$_2$H$_5$OH)]$^{2+}$/2, 275.17. UV-Vis in CH$_3$OH: $\lambda_{max} = 251$ nm.

2.4. *Preparation of [Cu(L)(bpy)$_2$] · (ClO$_4$)(H$_2$O) (3)*

A solution of [Cu^{II}(bpy)$_2$(ClO$_4$)](ClO$_4$) · 2H$_2$O (0.122 g, 0.2 mmol) in acetonitrile (10 cm^3) was added to a mixture of sodium hydroxide (0.008 g, 0.2 mmol) and 4-formylbenzoic acid (0.030 g, 0.2 mmol) in 10 cm^3 ethanol. The resulting mixture was stirred and refluxed for 2 h, then cooled to room temperature. The blue solution was allowed to evaporate slowly in air, and blue crystals of **3** (0.090 g, 70% yield) suitable for X-ray diffraction determination were collected after 1 week. Elemental Anal. Calcd for $C_{28}H_{23}ClCuN_4O_8$ (%): C 52.34; H 3.61; N 8.72. Found (%): C 51.06; H 3.14; N 9.25. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3070(m), 2953(w), 1719(s), 1688(s), 1447(s), 1089(vs), 770(s), 623(s). UV-Vis in CH$_3$OH: $\lambda_{max} = 203$, 243, 297 nm. ESI-MS in methanol (*m/z*): 278 ([Cu(bpy)$_2$(L)(CH$_3$OH)]$^{2+}$/2), 331 ([Cu(bpy)$_2$(L)(CH$_3$OH)$_2$]$^{2+}$/2), 471 ([Cu(bpy)$_2$(L)$_2$(CH$_3$CN)$_2$(CH$_3$OH)]$^{2+}$/2).

2.5. *Crystal structural determination and refinement*

Single-crystal samples of **1**–**3** were measured on a Bruker SMART 1K CCD area detector at 291(2) K using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The collected data were reduced with SAINT and empirical absorption correction was done with SADABS [27]. The structures were solved by direct methods where all non-H atoms were anisotropically refined and all hydrogen atoms were inserted in calculated positions. One oxygen atom of one ClO_4^- in **3** is refined disordered with different site occupancy factors of 0.53(2) : 0.47(2). In the case of **2**, several "simu" and "dfix" instructions, which give rise to 26 restraints, are used to restrain the *U*eq(max)/*U*eq(min) of some carbon atoms in one 4-formylbenzoate molecule (C1 to C8) and camphoric diamine ligand (C17 to C24). Furthermore, ADDSYM was used to try to solve the structure by using the *C*2/*c* space group for **2**, but the result is obviously unreasonable in the case of five-membered camphoric carbon ring. The summary of the crystal data, experimental details, and refinement results for **1**–**3** is listed in table 1. Selected bond distances and angles are given in table SI1, while O–H · · · O and C–H · · · O hydrogen-bonding interactions in **1**–**3** are listed in table SI2.

3. Results and discussion

3.1. *Synthesis and spectral characterizations*

As illustrated in scheme 1, three copper(II) complexes **1**–**3** arise from degradation of a Schiff-base ligand condensed between 4-formylbenzoic acid and D,L-camphoric diamine instead of the expected Schiff-base copper(II) complexes. Control experiments have been carried out by using the corresponding starting materials directly to check and compare the characterizations of products, and the results clearly show the formation of **1**–**3** in high yields. ESI-MS analyses for copper(II) complexes **1**–**3**

Table 1. Crystal and structural refinement data for **1**–**3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{16}H_{14}CuO_8$	$C_{24}H_{28}CuN_2O_6$	$C_{28}H_{23}ClCuN_4O_8$
Formula weight	397.82	504.03	642.50
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	Cc	$P1$
Unit cell dimensions (Å, °)			
a	7.548(5)	23.112(17)	15.295(3)
b	19.166(13)	9.920(8)	15.487(2)
c	11.698(7)	10.819(8)	15.489(3)
α	90	90	99.741(4)
β	99.283(8)	107.335(9)	112.643(4)
γ	90	90	115.530(3)
Volume (Å^3), Z	1670.1(19), 4	2368(3), 4	2797.2(10), 4
Calculated density (g cm^{-3})	1.582	1.414	1.526
Absorption coefficient (Mo-Kα, mm^{-1})	1.349	0.964	0.934
$F(000)$	812	1052	1316
Reflections collected	8223	5620	13,983
Independent reflection	2915	2882	9670
Observed reflections [$I > 2\sigma(I)$]	1157	1384	5392
Parameters	227	299	767
R_1 [$I > 2\sigma(I)$]	0.0718	0.0715	0.0715
wR_2 (all data)	0.1733	0.1933	0.1625
Goodness of fit (S)	0.88	0.88	0.96
Largest difference peak and hole (e Å^{-3})	1.15 and −0.64	0.54 and −0.58	0.63 and −0.32

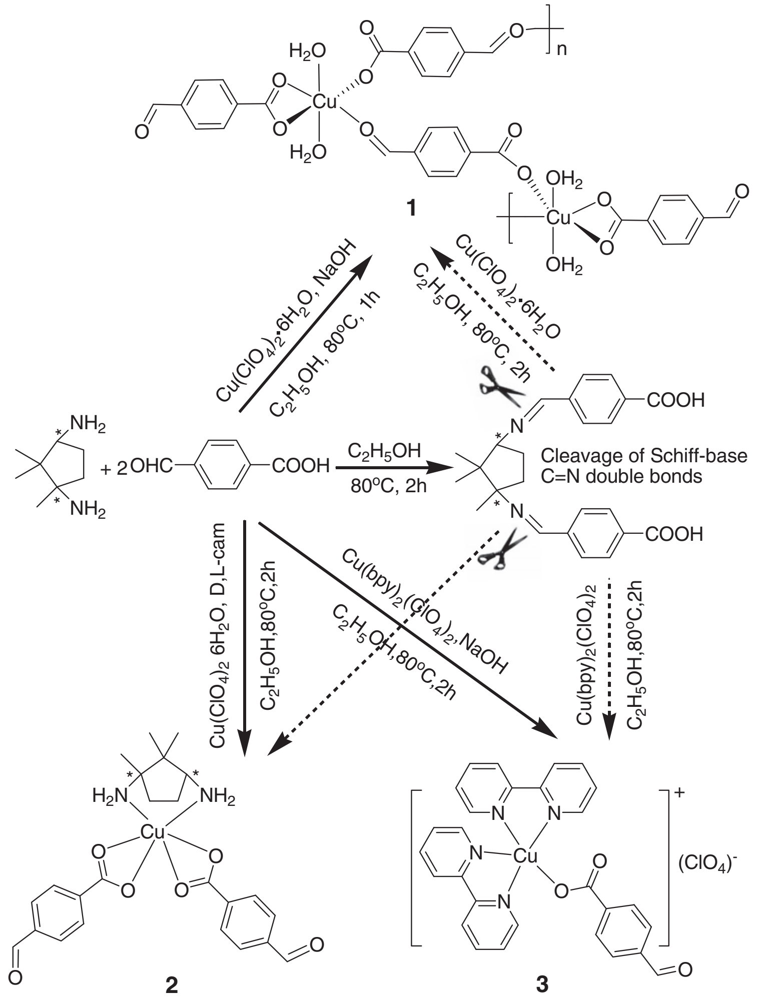
$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

demonstrate the existence of molecular ion peaks. FT-IR spectra reveal the presence of carboxylic and aldehydic groups of 4-formylbenzoate and the absence of typical absorptions of Schiff-base C=N units around 1640 cm^{-1}.

3.2. *Structural elucidation of [Cu(L)$_2$(H$_2$O)$_2$]$_n$ (1)*

Figure 1 shows the molecular structure of **1** with anisotropic displacement ellipsoids and atom-numbering scheme. It crystallizes in the monoclinic $P2_1/c$ space group (table 1) and the coordination geometry around the Cu^{II} center can be described as a six-coordinate severely distorted and Jahn–Teller elongated octahedron. Two carboxylic oxygen atoms (O1 and O4) from two 4-formylbenzoate anions and two oxygen atoms (O7 and O8) from two water molecules constitute the equatorial plane with Cu–O bond lengths ranging from 1.965(6) to 2.012(6) Å (table SI1). The two apical positions are occupied by one carboxylic oxygen (O2) from one 4-formylbenzoate and one aldehydic oxygen (O6^a, x, $1/2-y, -1/2+z$) of a third 4-formylbenzoate, having longer Cu–O bond lengths of 2.639(7) and 2.723(7) Å.

The two 4-formylbenzoates in the crystallographically independent unit adopt different coordination modes and the dihedral angle between two phenyl rings is 19.1°. One is bidentate chelating, while the other is bidentate μ_2-bridging by terminal carboxylic and aldehydic groups linking adjacent Cu^{II} centers into an infinite 1-D chain coordination polymer (figure 2a). In addition, offset interchain π–π stacking interactions are found between neighboring phenyl rings of 4-formylbenzoate with



Scheme 1. Schematic illustration for preparation of **1**–**3**. * denotes Chiral atoms.

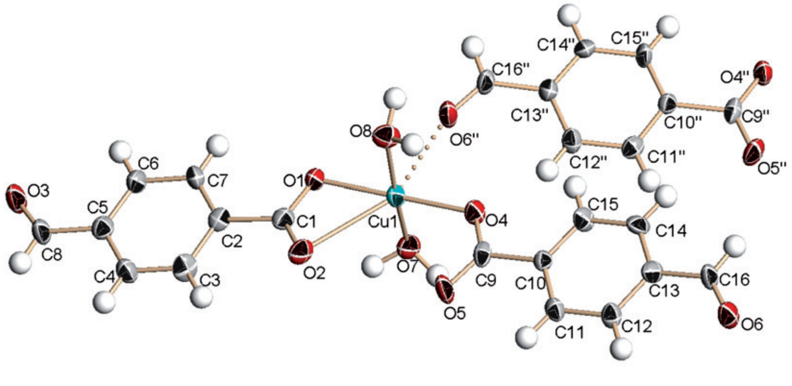


Figure 1. ORTEP drawing (30% probability level) of **1** with the atom-numbering scheme.

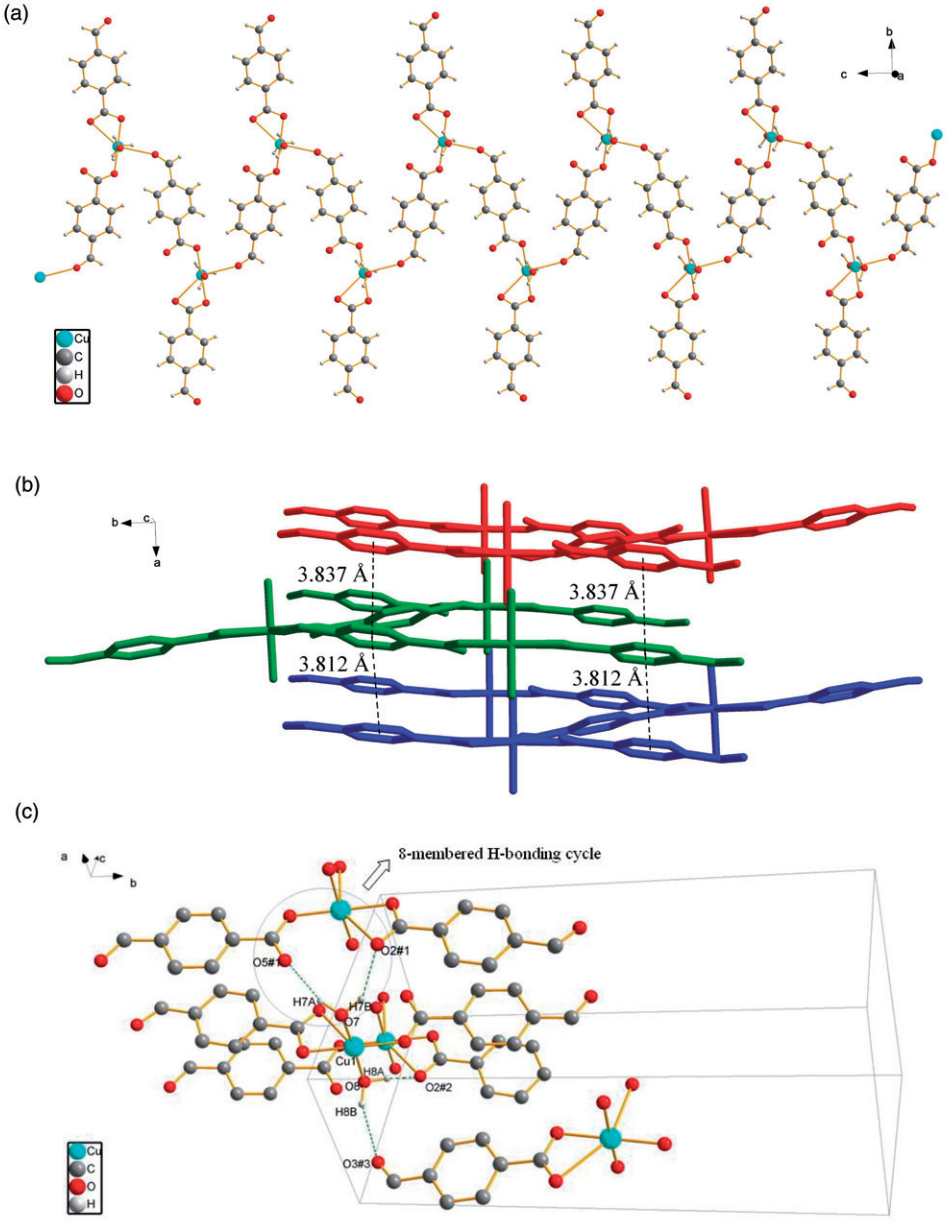


Figure 2. View of the 1-D coordination polymer (a), π–π stacking (b), and hydrogen-bonding interactions with the unit cell (c) in **1**. Symmetry codes: #1: $2 - x, -y, 1 - z$; #2: $1 - x, -y, 1 - z$; #3: $1 - x, 1/2 + y, 1/2 - z$.

centroid–centroid separations of 3.812 Å and 3.837 Å, respectively, as shown in figure 2(b). Furthermore, eight-membered $CuCO_4H_2$ hydrogen-bonding rings are observed (table SI2) extending the 1-D chain into a 3-D supramolecular network (figure 2c).

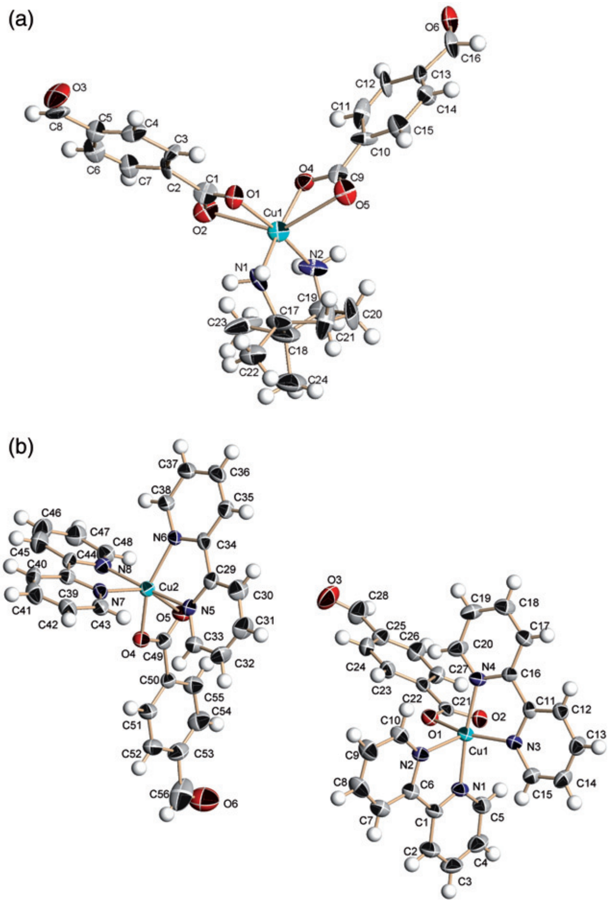


Figure 3. ORTEP drawings (30% probability level) of **2** (a) and **3** (b) with the atom-numbering scheme. Perchlorate anions and water molecules in **3** are omitted for clarity.

3.3. *Structural elucidation of [Cu(L)$_2$(D,L-cam)] (2) and [Cu(L)(bpy)$_2$]·(ClO$_4$)(H$_2$O) (3)*

The molecular structures of **2** and **3** with atom-numbering scheme are shown in figure 3(a) and (b), respectively. Complex **2** crystallizes in the monoclinic *Cc* space group and the coordination geometry around Cu$^{\text{II}}$ is a six-coordinate distorted octahedron where two nitrogen atoms from the camphoric diamine and two oxygen atoms from the terminal carboxylic groups of 4-formylbenzoate occupy equatorial sites, while the other two oxygen atoms occupy axial sites. Different from **1**, both carboxylic groups of 4-formylbenzoate are bidentate chelating and their aldehydic groups do not coordinate.

There are equal amounts of D-(+)- and L-(−)-camphoric diamine ligands in the crystal packing of **2** because a racemic ligand is used. Typical π–π stacking interactions are found between adjacent phenyl rings with centroid–centroid separation of 3.812 Å (figure 4) forming an infinite 1-D chain. Moreover, continuous eight-membered

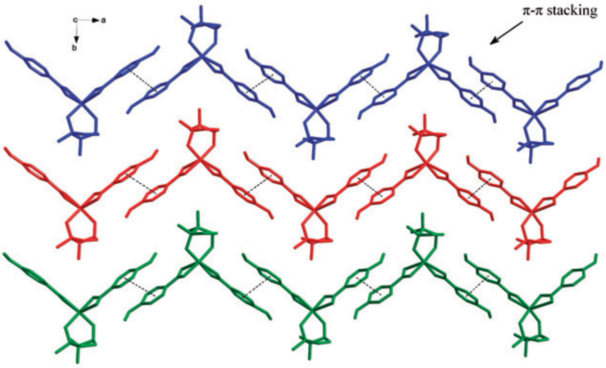


Figure 4. Perspective view along the *c*-axis of π–π stacking in **2**.

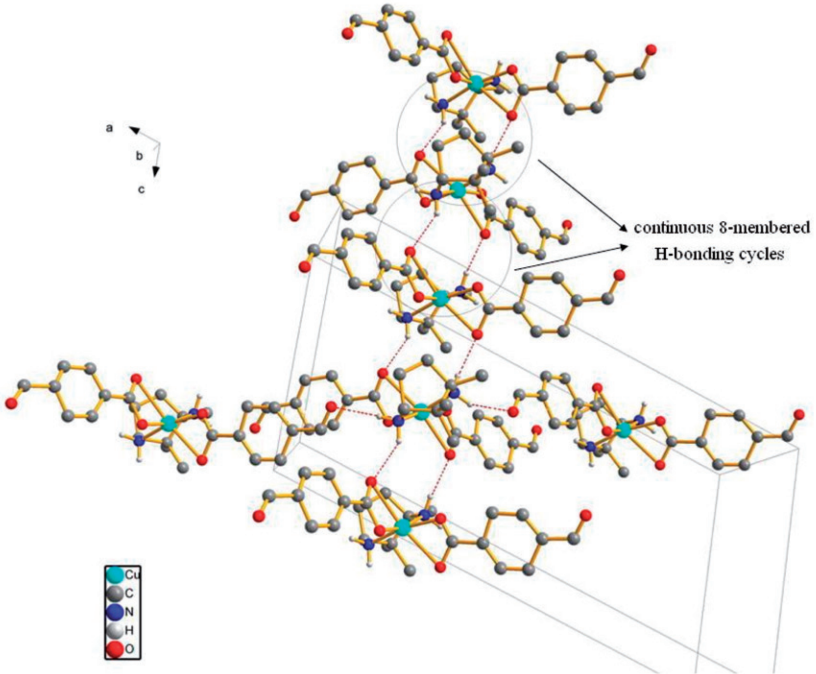


Figure 5. Perspective view of the hydrogen-bonding interactions in **2**.

$Cu_2O_2N_2H_2$ hydrogen-bonding rings are observed extending the above-mentioned 1-D chain into a 3-D supramolecular network (figure 5).

In contrast, **3** crystallizes in the triclinic $P1$ space group and there are two crystallographically independent mononuclear Cu^{II} units in the asymmetric unit. The coordination geometries around the two Cu^{II} centers are different: a five-coordinate distorted pyramid for Cu1 and a six-coordinate distorted octahedron for Cu2. Both Cu^{II} centers coordinate with two bpy molecules and one 4-formylbenzoate. However, the terminal carboxylic group of L is monodentate for Cu1 but bidentate for Cu2. Like in **2**, the aldehydic group of L in **3** does not coordinate.

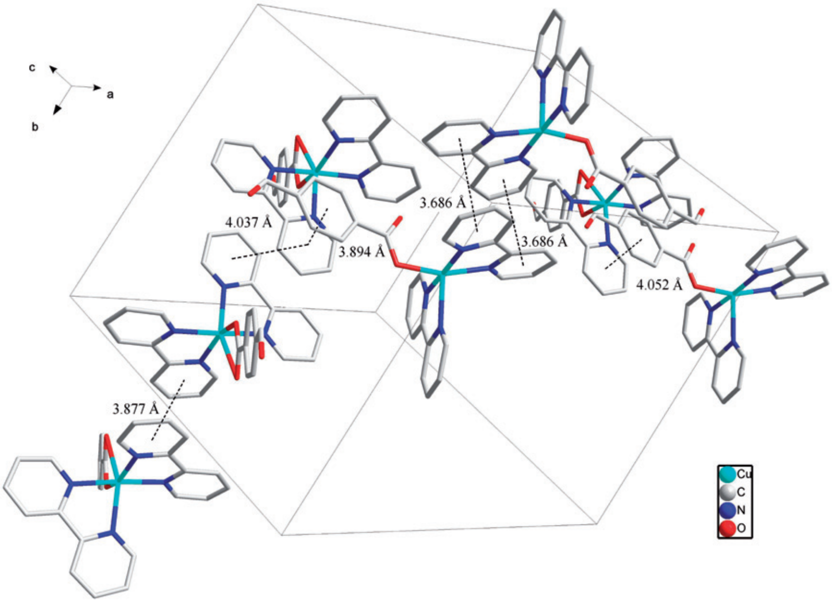


Figure 6. View of the π–π stacking interactions in the crystal structure of **3**.

Offset π–π stacking interactions are observed between adjacent aromatic rings in the crystal packing of **3** (figure 6). Various intermolecular weak C–H···O type of hydrogen-bonding interactions can be found to link contiguous molecules into a 3-D supramolecular network.

4. Conclusion

Three copper(II) complexes of 4-formylbenzoate, obtained from cleavage of C=N double bonds of a bis-Schiff-base compound condensed between 4-formylbenzoic acid and D,L-camphoric diamine, have been structurally and spectrally characterized. 4-Formylbenzoate exhibits bidentate chelating and bidentate μ_2-bridging modes in 1-D coordination polymer **1**, but bidentate chelating in **2**, and monodentate and bidentate in **3** by its terminal carboxylate with the aldehydic group not coordinated. Offset π–π stacking and hydrogen-bonding interactions including two types of eight-membered H-bonding rings are found between neighboring molecules of these copper(II) complexes.

Supplementary material

CCDC reference numbers 775274, 775275, and 709270 contain the supplementary crystallographic data for **1**–**3**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic

Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk

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