Solvent-controlled formation of monomeric and dimeric species containing Cu(II) acetate and 4-phenylpyridine

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ABSTRACT:

Three copper(II) acetate complexes with 4-phenylpyridine (4-Phpy), namely [Cu(MeCO2)2(4-Phpy)2(H2O)2] (1), [Cu(MeCO2)2(4-Phpy)2(H2O)1.5] (2) and [Cu(MeCO2)2(4-Phpy)]2 (3), were synthesized and characterized by analytical and spectroscopic methods. Experimental conditions as solvent or temperature determine the species obtained. Crystal and molecular structure of 2 was determined by Xray diffraction. Compound 2 presents a singular structure, containing two crystallographic independent mononuclear units [Cu(MeCO2)2(4-Phpy)2(H2O)2] (2A) and [Cu(MeCO2)2(4-Phpy)2(H2O)] (2B) in its unit cell and each of these forms an independent 1-D chain through H-bonding.

1. INTRODUCTION

The formation of secondary building units (SBUs) with interesting supramolecular features in a controlled fashion, such as 1D chains, 2D sheets or 3D porous frameworks is a current milestone in inorganic chemistry [1–3]. In this topic, the combination of metal centers with carboxylates and pyridines has attracted attention due the fact that pyridines provide structural rigidity and could force the direction of the hydrogen bond propagation [4]. Cu(II) is a typical choice for metal center due its variety of coordination modes and molecular topologies. An important family of Cu (II) based SBUs are dimeric paddle-wheel like complexes [5,6]. Interestingly, when paddle-wheel like dimers crystallize, usually mononuclear species with octahedral, square pyramidal or square planar geometries are also formed. This dimer-monomer equilibrium in Cu(II) carboxylate derivatives with pyridines or other auxiliary ligands has been known since decades and thoroughly studied [7–10]. Despite their efforts, most studies do not provide a clear explanation of the mechanism that governs the formation of either the dimeric or the monomeric compound. Furthermore, reports in the literature where the monomeric and dimeric structures for the same choice ligands are isolated and characterized are scarce [11–13]. Recently in our group, we have assayed the reaction between M (MeCO2)2⨂ H2O (M = Cu(II), Zn(II) or Cd(II); MeCO2 = acetate), 1,3- benzodioxole-5-carboxylic acid (HPip) and different bulky pyridine derivatives. Thus, dimeric and monomeric compounds were obtained [14–16]. Specifically, we have assayed the reaction of Cu(MeCO2)2⨂ H2O, with HPip and 3-phenylpyrydine (3-Phpy) or 4-benzylpyrydine (4-Bzpy), obtaining paddle-wheel dimers and mononuclear compounds in the same reaction. However using 4-phenylpyrydine (4-Phpy) only a dimeric compound [Cu(m-Pip) (Pip)(4-Phpy)]2 is obtained [16].

As a continuation of these works, in this paper we study the reaction between [Cu(MeCO2)2(H2O)]2 and 4-Phpy, a system that yields two new monomeric hydrated complexes besides the known paddle-wheel dimeric compound [17]. All reactions were assayed at room temperature, and the obtaining of one or another compound depends on the solvent employed in the preparations. All compounds were fully characterized and the X-ray crystal structure of 2 is presented.

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2. RESULTS AND DISCUSSION

2.1. Synthesis and general characterization

The reaction between Cu(MeCO2)2· H2O and 4-Phpy in a methanol: water (MeOH:H2O, 1:1) mixture as solvent at room temperature, using 1:1 Cu:4-Phpy molar ratio, yielded compound [Cu (MeCO2)2(4-Phpy)2(H2O)2] (1). However, the same reaction assayed in an ethanol:water (EtOH:H2O, 1:1) mixture as solvent results in the formation of compound [Cu(MeCO2)2(4-Phpy)2(H2- O)1.5] (2). The same reactions in absence of H2O, using EtOH or MeOH as solvent, result in the formation of paddle-wheel dimer [Cu(MeCO2)2(4-Phpy)]2 (3). Compound 2 can also be obtained via recrystallization of 3 in MeOH:H2O (1:1) mixture (Scheme 1). Therefore, the formation of a monomeric, 1 and 2, or a dimeric, 3, compound is controlled by the presence of a sizeable quantity H2O in the reaction media (50%). Our results agree with the fact that the role of water as one of the key factors governing the formation of either monomeric or dimeric compounds has been already identified in the literature [7–11,13,18]. Furthermore, the use of different alcohols as co-solvents also results in the isolation of two differentiate compounds, 1 in MeOH and 2 in EtOH.

Dimer 3 has already been described in the literature [17] but herein we report a different synthetic procedure. In the reported procedure, the dimer was obtained working in a 1:1 metal to 4- Phpy ratio, using a MeCN:MeOH:H2O mixture (1:1:1, MeCN = acetonitrile) as solvent and heating at 60 ꟷ C for 15 min. Despite the presence of H2O as co-solvent in the reported synthesis, the dimeric compound (3) is obtained. This fact is probably due the heating at 60 ꟷ C, as it will be demonstrated later in this work. The elemental analyses of 1–3 are consistent with the proposed formulas. Phase purity of 1–3 was confirmed via Powder X-ray diffraction (PXRD) (Figs. S1–S3). ATR-FTIR spectrum of 1 and 2 show significant shifts in the m(C@O) and m(CAO) stretching with respect to the spectra of [Cu(MeCO2)2(H2O)]2 (Figs. S4–S5), hence confirming the different coordination mode of the Cu(II) to the carboxylate groups of MeCO2 ligands. However, for compound 3 no significant variations could be found in m(C@O) and m(CAO) stretching (Fig. S6). For 1–3, the presence of m(C@C)ar and m(C@N)ar bands confirm the coordination of 4-Phpy. Additionally, the coordination mode of the carboxylate groups can be inferred from the difference between the asymmetric and symmetric vibrations of the COOꟷ groups (D = mCOOasym–mCOOsym) [19]. The values of D = 215 cmꟷ 1 for 1 and D = 213 cmꟷ 1 for 2 show a monodentate mode whereas for compound 3 D = 189 cmꟷ 1 shows bidentate bridging mode [19]. For compound 2, the value (D) is coherent with its elucidated X-ray crystal structure.

As described in Section 4.5, heating blue monomeric compounds 1 or 2 at 50 ꟷ C during 32 h resulted in the formation of the green dimer 3. This conversion processes were confirmed via PXRD (Fig. 1). This monomeric to dimeric conversion has also been reported previously in the literature [7–10,13]. It is also noteworthy that this transformation also happens at room temperature when monomeric species are treated with EtOH.

111 2.2. Crystal and extended structure of complex 2

112 Suitable crystals for X-ray diffraction where obtained via recrystallization of compound 3 in an

113 EtOH:H2O mixture in a 1:1 proportion. The X-ray crystallographic analyses reveal that the crystal

114 structure of compound 2 contains two crystallographic independent monomers [Cu(MeCO2)2(4-

115 Phpy)2(H2O)2] (2A) and [Cu (MeCO2)2(4-Phpy)2(H2O)] (2B) in its unit cell (Fig. 2). In each

116 monomer, the copper cation is linked to two monodentate MeCO2 and two 4-Phpy ligands. The main

117 difference between the two monomers is due the number of coordinated H2O molecules that in turn

118 depends on the different conformations assumed by the acetate anions. Monomer 2A presents an

119 asymmetric unit consisting of a Cu(II) atom in a special position (inversion center), one monodentate

120 MeCO2 anion, one 4-Phpy, and one H2O molecule. Each of the independent Cu(II) center is six-

121 coordinated, having a distorted octahedral geometry. Monomer 2B, on the other hand, contains only one

122 H2O molecule, resulting in a slightly distorted square pyramidal geometry (s = 0.093) [20]. In the

123 asymmetric unit the Cu1B atom is located on a twofold axis passing through Cu1B–O3B.

124 Therefore, the difference between the numbers of H2O determines the coordination geometry of each

125 metal center. Selected distances and angles are provided on Table 1. For 2A, the basal plane is formed

126 by trans-coordinated 4-Phpy (Cu1A–N1A 2.028 (3) Å) and trans-coordinated monodentate MeCO2

127 (Cu1A–O1A 1.984(2) Å). The apical positions are occupied by two weakly bonding oxygen atoms from

128 H2O molecules (Cu1A–O3A 2.381(3) Å). This longer distance respect to the basal plane can be

129 attributed to Jahn–Teller effect. The other O2A atom of the acetate lies at a large distance (Cu1A

130 O2A 3.300 Å) and is therefore, uncoordinated. Bond angles are in the range 85.24(11) –94.76(11) .

131 For 2B, 4-Phpy and acetate ligands form the basal plane (Cu1B–N1B 2.023(3) Å and Cu1A–O1A

132 1.951(2) Å) and a H2O ligand is in the apical position (Cu1B–O3B 2.222(4) Å). Once again, the

133 uncoordinated O2B atom of the acetate ligand lies at a long distance (Cu1B   O2B 3.126 Å). Short

134 bond angles are in the range of 88.18(8) –94.16(9) and long ones in the range of 170.77(18) –

135 176.36(16) . All these distances and angles are in good agreement with related acetate-pyridine

136 compounds [21–28].

137 The presence of two crystallographic monomeric subunits generates an intriguing supramolecular

138 structure, in which the coordinated H2O molecules play a key role. Each subunit interacts exclusively

139 with its symmetry related subunits to generate 1D supramolecular chains, and each include only 2A

140 subunits or 2B subunits (Fig. 3, up). Those chains grow in a parallel fashion in the b direction and are

141 stacked alternatively in the a direction, forming a layered structure. Cu   Cu distance between units

142 in the same chain is 5.867 Å for both Cu1A   Cu1A and Cu1B   Cu1B. Interlayer Cu1A

143 Cu1B distance is 8.361 Å. A similar supramolecular structure is seen in the closely related compounds

144 {[Cu(2,4-bipy)2(MeCO2)2(H2O)2] [Cu(2,4-bipy)2(MeCO2)2(H2O)]} (2,4-bipy = 2,40-bipyridine)

145 [27] and {[Cu(stpy)2(MeCO2)2(H2O)2] [Cu(stpy)2(MeCO2)2(H2O)]} (stpy = trans-4-styrylpyridine)

146 [28]. These two compounds also contain two crystallographic independent monomeric subunits, one

147 having an octahedral geometry and the other having a square pyramidal one, which form independent

148 1D chain containing only either octahedral or square pyramidal subunits. Furthermore, intrachain and

149 interlayer Cu⋯Cu distances show similar values for the three compounds. Interestingly, for these

150 two combinations of acetate and pyridine derivative ligands no dimeric structures have been found in the

151 literature.

152 The study of each individual chain reveals that their H-bridging interactions are different. Each

153 monomer 2A has a symmetric quadruple H-bond, involving O1A from the acetate ligand (which is the

154 coordinating oxygen) and H3OB from the H_2O molecule (O3A–H3OB 0.832 Å, O1A⋯O3A–

155 H3OB 2.849 Å, O1A⋯H3OB– O3A 2.050 Å, O1A⋯H3OB-O3A 160.92°). Each Monomer

156 2B forms an asymmetric double bond, involving O2B from the acetate ligand (note that this is the non-

157 coordinating oxygen) and H3OC from the H_2O molecule (O3B-H3OC 0.830 Å, O2B⋯O3C–

158 H3OC 2.719 Å, O2B⋯H3OC–O3B 1.903 Å, O2B⋯H3OC–O3B 167.13°) (Fig. 3, down).

159

3. CONCLUSIONS

Direct reaction of Cu(II) acetate with 4-phenylpyridine (4-Phpy) at room temperature and alcohol (EtOH or MeOH) and H_2O as solvent, allowed the preparation of monomeric and dimeric compounds. The formation of the monomeric or dimeric compounds depends on the solvent. When this solvent is alcohol (EtOH or MeOH), the formation of the paddle-wheel compound (3) is observed, however, when the solvent is an alcohol:H_2O (1:1) mixture, the monomeric compounds (1, 2) are obtained. The formation of compounds 1 and 2 depends on the alcohol used, MeOH and EtOH, respectively, as confirmed via PXRD. The three compounds have been fully characterized, and for the compound 2 the crystal and molecular structure was determined by X-ray diffraction. The crystal structure reveals the presence of two independent monomers (2A, 2B). Monomers 2A and 2B differ in the number of H_2O molecules coordinated to the metal, two in the former, and one in the second. In the crystal packing of this compound, the coordinated H_2O molecules play a key role generating two different 1D chains.

174 **4. EXPERIMENTAL**

175

176 4.1. General details

177 Copper(II) acetate monohydrate (Cu(MeCO2)2· H2O), 4-phenylpyridine (4-Phpy) reagents, methanol

178 (MeOH) and ethanol (EtOH) were purchased from Sigma–Aldrich and used without further purification.

179 All the reactions and manipulations were carried out in air. Elemental analysis (C, H, N) were carried

180 out by the staff of Chemical Analysis Service of the Universitat Autònoma de Barcelona on a Thermo

181 Scientific Flash 2000 CHNS analyses. IR spectra were recorded on a Tensor 27 (Bruker) spectrometer,

182 equipped with and attenuated total reflectance (ATR) accessory model MKII Golden Gate with diamond

183 window in the range 4000–600 cm⁻1. PXRD patterns were measured with Siemens D5000 apparatus

184 using the Cu Ka radiation of 0.15418 nm. Patterns were recorded from 2h = 5 –50 , with a step scan

185 of 0.02 counting for 1 s. at each step.

186

187 4.2. Synthesis of [Cu(MeCO2)2(4-Phpy)2(H2O)2] (MeCO2 = acetate, 4-Phpy = 4-phenylpyridine) (1)

188 To a solution containing 4-phenylpyridine (155 mg, 1.00 mmol) in MeOH (20 mL), a green solution of

189 Cu(MeCO2)2· H2O (198 mg, 0.99 mmol) in H2O (20 mL) was added. The resulting light blue solution

190 was left to evaporate at room temperature. When the solution volume was reduced to 20 mL, a blue

191 crystalline solid appeared; it was filtered, washed with MeOH:H2O (10 mL) and dried in the air.

192 1. Yield: 0.316 g (60.45%) (respect to Cu(MeCO2)2· H2O). Elemental Analyses: Calc. for

193 C26H28N2O6Cu (528.06): C 59.14; H 5.34; N 5.31. Found C 59.08; H 5.23; N 5.12%. ATR-FTIR

194 (wavenumber, cm⁻1): 3336(br) [m(O–H), (H2O)], 1654(m), 1612(s) [mas(COO)], 1562(s) 1484(m),

195 1397(s), 1332(s) [ms(COO)], 1332(m), 1231(w), 1162(w), 1073(w), 1044(w), 1016(m) [m(CO)],

196 931(w), 833(m), 764(m), 727(w), 688(m), 666(m), 623(w).

197

198 4.3. Synthesis of [Cu(MeCO2)2(4-Phpy)2(H2O)1.5] (MeCO2 = acetate, 4-Phpy = 4-phenylpyridine)

199 (2)

200 To a solution containing 4-phenylpyridine (155 mg, 1.00 mmol) in EtOH (20 mL), a green solution of

201 Cu(MeCO2)2· H2O (198 mg, 0.99 mmol) in H2O (20 mL) was added. The resulting light blue solution

202 was left to evaporate at room temperature. When the solution volume was reduced to 20 mL, a blue

203 crystalline solid appeared; it was filtered, washed with EtOH:H2O (10 mL) and dried in the air. Suitable

204 crystals of 2 for X-ray diffraction (XRD) single crystal elucidation were obtained via recrystallization of

205 3 in an EtOH:H2O mixture.

206 2. Yield: 0.365 g (71.03%). Elemental Analyses: Calc. for C52H54-N4O11Cu2 (1038.07): C, 60.16; H,

207 5.24; N, 5.40. Found C 60.24; H 5.07; N 5.33%. ATR-FTIR (wavenumber, cm⁻1): 3358(br) [m(OH),

208 (H2O)], 1591 [mas(COO)], 1567(s), 1483(m), 1393(s) [ms(COO)], 1378(m), 1332(w), 1221(w),

209 1072(w), 1038(w), 1016(m) [m(CO)], 928(w), 832(m), 762(m), 729(w), 690(m), 665(m), 618(w).

210

4.4. Synthesis of [Cu(MeCO2)2(4-Phpy)]2 (MeCO2 = acetate, 4-Phpy = 4-phenylpyridine) (3)

To a solution containing 4-phenylpyridine (157 mg, 1.01 mmol) in EtOH (20 mL), a green solution of Cu(MeCO2)2꞉ H2O (200 mg, 1.00 mmol) in EtOH (20 mL) was added. The resulting green solution was allowed to evaporate at room temperature. When the solution volume was reduced to 20 mL, a green crystalline solid appeared; it was filtered, washed with EtOH (5 mL) and dried in the air.

3. Yield: 0.313 g (92.93%) (respect to Cu(MeCO2)2꞉ H2O). Elemental Analyses: Calc. for C30H30N2O8Cu2 (673.64): C 53.49; H 4.49; N 4.16. Found C 53.28; H 4.37; N 4.09%. ATR-FTIR (wavenumber, cm꞉ 1): 1606(s) [mas(COO)], 1547(w), 1488(m), 1417(s) [ms(COO)], 1344(m), 1225 (w) 1073(w), 1048(w), 1026(w), 1012(m) [m(CO)], 923(w), 837(m), 759(m), 730(w), 692(m), 679(m), 619(w).

The same reaction has been assayed in MeOH resulting in the formation of the same compound with similar yields.

4.5. Monomer–Dimer conversion

1 to 3: After heating a (107 mg, 0.20 mmols) of 1 for 32 h at 50 ꞉ C, the blue solid turned green. Yield: 0.049 g (71.7%).

2 to 3: Heating compound 2 (65 mg, 0.063 mmols) for 32 h. at 50 ꞉ C resulted in the formation of 3 in a quantitative yield.

These conversion processes were confirmed via PXRD. These two transformations imply both dehydration and sublimation of half of the coordinated 4-Phpy. In a separate experiment, we confirmed that a sample of pure 4-Phpy in the same conditions sublimates completely.

4.6. X-ray crystal structure of 2

The X-ray intensity data for the crystallographic analysis were measured on a D8 Venture system equipped with a multilayer mono-chromate and a Mo microfocus (k = 0.71073 Å) at 100 K. For the compound [Cu(MeCO2)2(4-Phpy)2(H2O)2] [Cu(MeCO2)2(4- Phpy)2(H2O)] (2) a blue prism-like specimen was used. The frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6580 and 0.7454.

The structure was solved using the Bruker SHELXTL Software, package and refined using SHELX [29]. The final cell constants and volume, are based upon the refinement of the XYZ-centroids of reflections above 20 r(I). Crystal data and relevant details of structure refinement are reported in Table 2. Complete information about the crystal structure and molecular geometry is available in CIF format as Supporting Information. Molecular graphics were generated Mercury 3.6 software [30,31]. Color codes for all molecular graphics: orange (Cu), blue (N), red (O), gray (C), White (H).

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300

301   **Legends to figures**

302

303   **Figure. 1** PXRD patterns of 1 (top), 2 (middle) and 3 (bottom).

304

305   **Figure. 2** Monomers 2A and 2B, and their corresponding numbering scheme for relevant atoms.

306   Hydrogens are omitted for the sake of clarity.

307

308   **Figure. 3** View of the stacking of Monomers 2A and 2B along the a axis (up). Detailed view of the H-

309   bonding interactions in the individual chains (down).
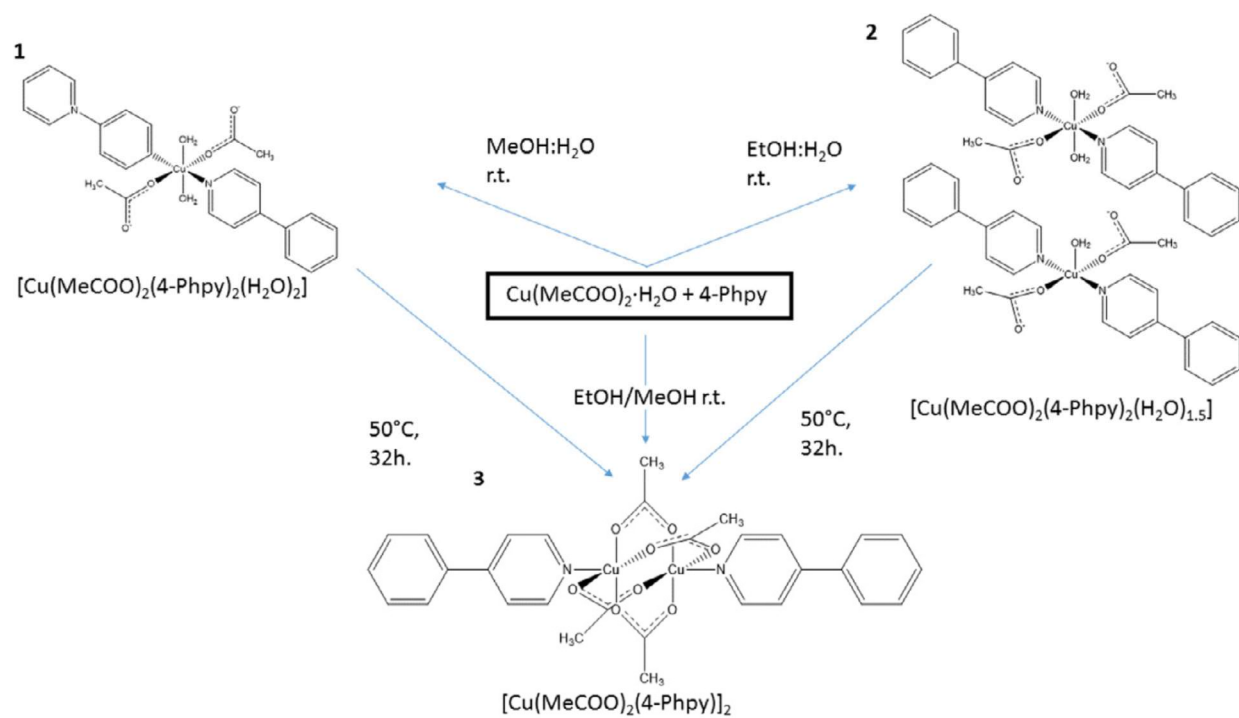
310

311

SCHEME 1
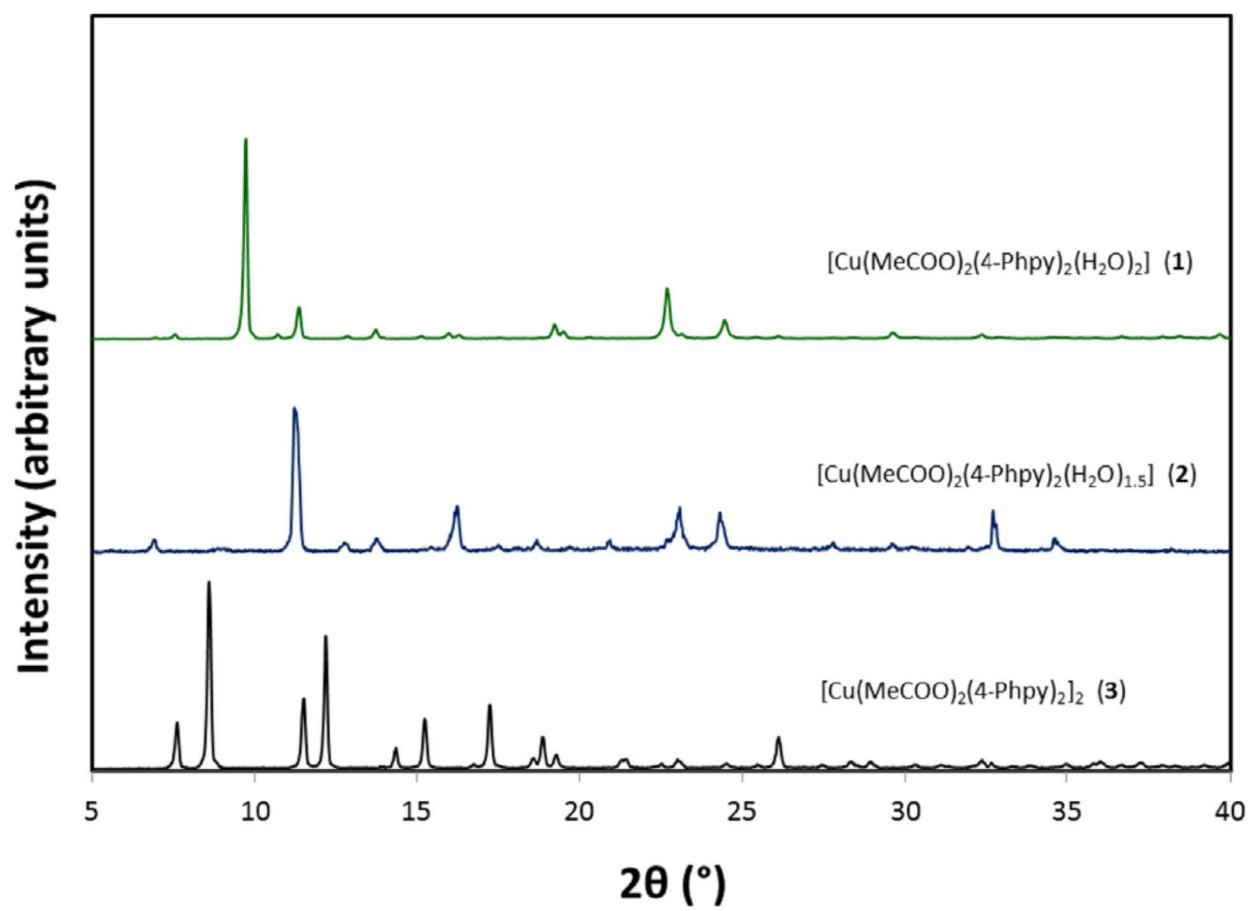
1

[Cu(MeCOO)$_2$(4-Phpy)$_2$(H$_2$O)$_2$]

2

[Cu(MeCOO)$_2$(4-Phpy)$_2$(H$_2$O)$_{1.5}$]

Cu(MeCOO)$_2$·H$_2$O + 4-Phpy

MeOH:H$_2$O
r.t.

EtOH:H$_2$O
r.t.

EtOH/MeOH r.t.

50°C,
32h.

50°C,
32h.

3

[Cu(MeCOO)$_2$(4-Phpy)]$_2$

FIGURE 1

[Cu(MeCOO)$_2$(4-Phpy)$_2$(H$_2$O)$_2$] (**1**)

[Cu(MeCOO)$_2$(4-Phpy)$_2$(H$_2$O)$_{1.5}$] (**2**)

[Cu(MeCOO)$_2$(4-Phpy)$_2$]$_2$ (**3**)

Intensity (arbitrary units)

2θ (°)

322
323   **FIGURE 2**
324
325
326
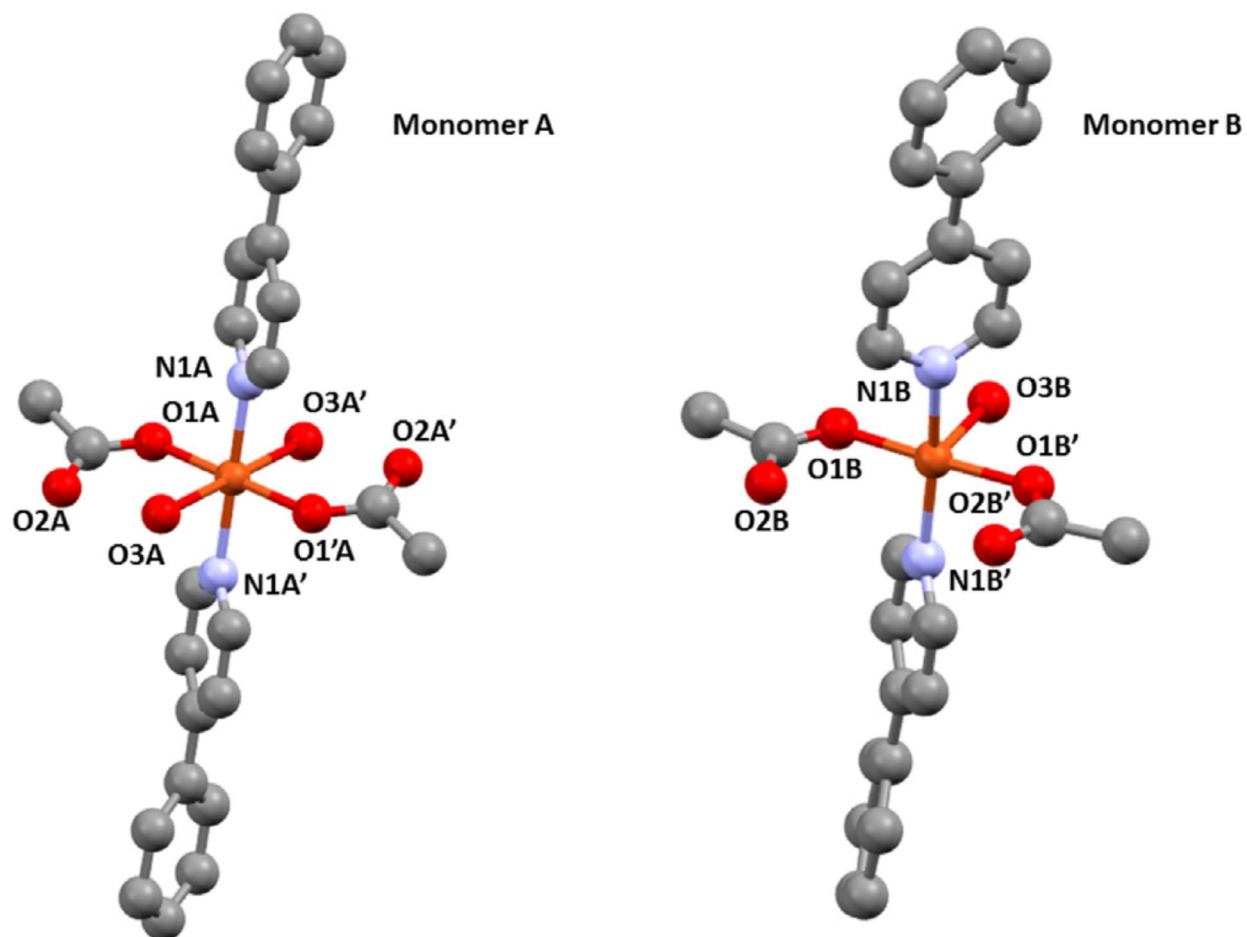

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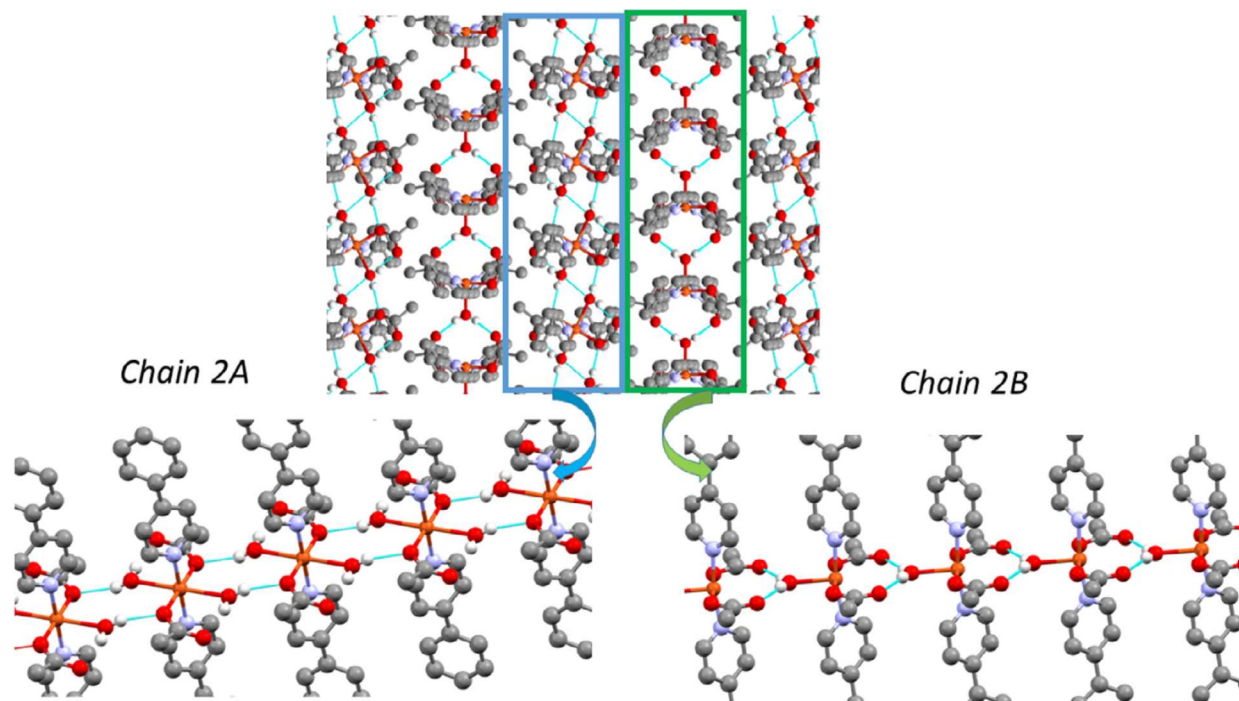
FIGURE 3

Chain 2A

Chain 2B

334

335

336 **Table 1** Selected bond lengths (Å) and bond angles (⬚) values for (2A) and (2B). The estimated
337 standard deviations (e.s.d.s.) are shown in parentheses.

338

Molecule A			
Bond lengths (Å)			
Cu(1A)–O(1A)	1.984(2)	Cu(1A)–O(3A)	2.381(3)
Cu(1)–N(1A)	2.028(3)		
Bond angles (°)			
O(1A)–Cu(1A)–O(1A)#1	180.0	N(1A)–Cu(1)–O(3A)#1	85.24(11)
O(1A)–Cu(1A)–N(1A)#1	88.11(11)	O(1A)–Cu(1A)–O(3A)	86.80(10)
O(1A)–Cu(1A)–N(1A)	91.89(11)	N(1A)–Cu(1A)–O(3A)	94.76(11)
N(1A)#1–Cu(1A)–N(1A)	180.0	O(3A)#1–Cu(1A)–O(3A)	180.0
O(1A)–Cu(1A)–O(3A)#1	93.20(10)		
Molecule B			
Bond lengths (Å)			
Cu(1B)–O(1B)	1.951(2)	Cu(1B)–O(3B)	2.222(4)
Cu(1B)–N(1B)	2.023(3)		
Bond angles (°)			
O(1B)–Cu(1B)–O(1B)#2	176.36(16)	N(1B)#2–Cu(1B)–N(1B)	170.77(18)
O(1B)–Cu(1B)–N(1B)#2	89.34(11)	O(1B)–Cu(1B)–O(3B)	88.18(8)
O(1B)–Cu(1B)–N(1B)	90.95(11)	N(1B)–Cu(1B)–O(3B)	94.61(9)
#1 = –x + 1, –y, –z + 1; #2 = –x + 1, y, –z + 1/2			

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343 **Table 2** Crystallographic data for [Cu(MeCO2)2(4-Phpy)2(H2O)2] [Cu(MeCO2)2(4-Phpy)2(H2O)] (2).

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Formula	$C_{52}H_{54}N_4O_{11}Cu_2$
Formula weight	1038.07
T (K)	100(2)
λ (Å)	0.71073
System, space group	monoclinic, $C2/c$
a (Å)	25.181(2)
b (Å)	5.8668(5)
c (Å)	30.879(3)
α (°)	90
β (°)	94.496(4)
γ (°)	90
U (Å^3)/Z	4547.7(7)/4
D_{calc} (g cm^{-3})/μ (mm^{-1})	1.516/1.005
$F(000)$	2160
Crystal size (mm^3)	0.279x0.075x0.063
hkl ranges	$-31 \leq h \leq 31$,
	$-7 \leq k \leq 7$,
	$-38 \leq l \leq 38$
2θ range (°)	2.173–26.440
Reflections collected/unique/[R_{int}]	38487/4682 [R_{int} = 0.0570]
Completeness to θ (%)	99.9
Absorption correction	semi-empirical
Maximum and minimum trans.	0.7454 and 0.6580
Data/restrains/parameters	4682/4/325
Goodness-of-fit (GOF) on F^2	1.279
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0542$, $wR_2 = 0.1200$
R indices (all data)	$R_1 = 0.0605$, $wR_2 = 0.1223$
Extinction coefficient	n/a
Largest difference peak and hole (e Å^{-3})	+0.709, −1.441

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