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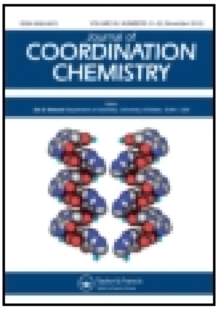

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Three trinuclear copper(II) complexes bridged by μ $_3$- with different coordination modes

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Three trinuclear copper(II) complexes bridged by μ_3-CO_3^{2-} with different coordination modes

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Three trinuclear copper(II) complexes bearing the same μ_3-CO_3^{2-} bridge and triangular geometry, $\{[Cu_3(bpy)_6(CO_3)](ClO_4)_4(CH_3OH)(H_2O)_2\}$ (**1**), $\{[Cu_3(bpy)_6(CO_3)](ClO_4)_4(C_2H_5OH)_4(H_2O)_2\}$ (**2**), and $\{[Cu_3(bpy)_6(CO_3)](PF_6)_4(H_2O)_2\}$ (**3**) (bpy = 2,2′-bipyridine), have been synthesized and structurally characterized. The common $[Cu_3(bpy)_6(CO_3)]^{4+}$ cationic unit is found in **1**–**3** but distinguishable coordination is observed for the central CO_3^{2-} bridge, namely μ_3-η^2, η^2, η^2 in **1**, μ_3-η^1, η^1, η^1 in **2**, and μ_3-η^1, η^1, η^2 in **3**. Five-coordinate trigonal bipyramidal and square pyramidal as well as six-coordinate octahedral structures for the copper(II) centers in **1**–**3** are observed. The presence of different counterions and solvent is responsible for the variations of coordination spheres of copper(II) and crystal packing modes in **1**–**3**.

Keywords: Copper(II) complexes; Trinuclear complexes; μ_3-$CO_3{}^{2-}$ Bridge; Coordination fashions

1. Introduction

Polynuclear copper(II) complexes connected by a variety of bridging ligands and anions have been investigated because of their supramolecular structures, optoelectronic, and magnetic properties [1–4]. Most commonly used bridging anions are OH^-, X^-, $C_2O_4^{2-}$, NO_3^- etc., however, CO_3^{2-} has been seldom employed in polynuclear copper(II) complexes although three oxygen atoms are in the anion. Due to versatile coordination of carbonate, dimers, trimers, and tetramers, as well as 1-D, 2-D, and 3-D complexes, have been reported [5–21].

Carbonate-bridged copper(II) complexes are formed from *in situ* fixation of atmospheric CO_2 in many cases [22–25]. Fixation of greenhouse atmospheric CO_2 is of special interest for coordination and environmental chemistry [26–30]. In our previous work, C–C bond cleavage of acetonitrile has been catalyzed by some copper(II) complexes with bpy, such as $[Cu(bpy)_2(ClO_4)](ClO_4) \cdot 2H_2O$ [31]. In addition

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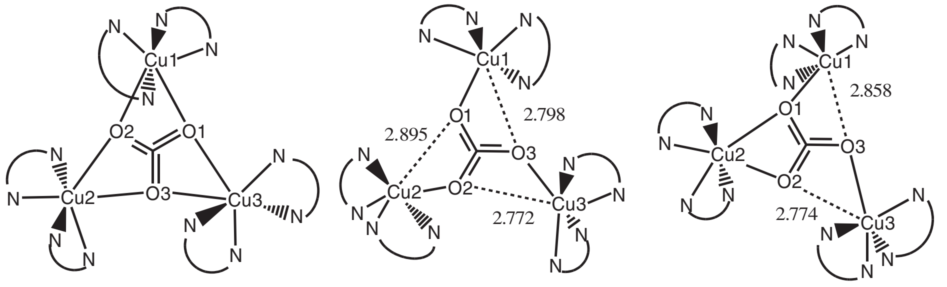


μ_3-η^2,η^2,η^2 in **1** μ_3-η^1,η^1,η^1 in **2** μ_3-η^1,η^1,η^2 in **3**

Scheme 1. Different coordination modes of the trinulear $[Cu_3(bpy)_6(CO_3)]^{4+}$ cationic units in **1–3**. The dotted lines (Å) show the uncoordinated Cu–O distances (>2.525(6) Å).

to formation of mono-, di-, tri-, and tetranuclear cyano-bridged mixed-valent copper complexes, some unexpected carbonate-bridged trinuclear copper(II) by-products were isolated and structurally characterized, obtained from fixation of atmospheric CO_2. In this article, we report three trinuclear copper(II) complexes bearing μ_3-CO_3^{2-} bridge andtriangular geometry, $\{[Cu_3(bpy)_6(CO_3)](ClO_4)_4(CH_3OH)(H_2O)_2\}$ (**1**), $\{[Cu_3(bpy)_6(CO_3)](ClO_4)_4(C_2H_5OH)_4(H_2O)_2\}$ (**2**), and $\{[Cu_3(bpy)_6(CO_3)](PF_6)_4(H_2O)_2\}$ (**3**). The common $[Cu_3(bpy)_6(CO_3)]^{4+}$ cation exhibits distinguishable coordination for the central CO_3^{2-} bridge, namely μ_3-η^2, η^2, η^2 in **1**, μ_3-η^1, η^1, η^1 in **2**, and μ_3-η^1, η^1, η^2 in **3** (scheme 1).

2. Experimental

2.1. *Materials and measurements*

All reagents were of analytical grade from commercial sources and used without purification. $[Cu^{II}(bpy)_2(ClO_4)](ClO_4) \cdot 2H_2O$ and $[Cu^{II}(bpy)_2(ONO_2)](NO_3) \cdot H_2O$ were prepared by a literature method [32]. Infrared (IR) spectra (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 from 100 to 1200 amu. Ultraviolet-Visible (UV-Vis) spectra were recorded on a Shimadzu UV-3100 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm at room temperature.

Caution! Although no problem was encountered in our experiments, transition metal perchlorates are potentially explosive and should be handled in small quantities.

2.2. *Preparation of* $\{[Cu_3(bpy)_6(CO_3)](ClO_4)_4(CH_3OH)(H_2O)_2\}$ *(1) and* $\{[Cu_3(bpy)_6(CO_3)](ClO_4)_4(C_2H_5OH)_4(H_2O)_2\}$ *(2)*

A solution of $[Cu^{II}(bpy)_2(ClO_4)](ClO_4) \cdot 2H_2O$ (0.2444 g, 0.4 mmol) in CH_3CN (15 cm^3) was added to a solution of benzaldehyde in CH_3OH (20 cm^3, 0.04 mmol cm^{-3}). The mixture was refluxed for 50 h and allowed to evaporate slowly at room temperature in air. Blue crystals of $[Cu^{II}(bpy)_2(ClO_4)](ClO_4) \cdot 2H_2O$ and $[Cu^{II}(bpy)_3](ClO_4)_2$ as well as a few dark blue crystals of **1** (~20% yield) suitable for X-ray diffraction determination were collected after two weeks. Main FT-IR absorptions, (KBr pellets): $v = 3434$(b, m), 3064(w), 1604(m), 1472(w), 1444(s), 1380(s), 1084(vs), 840(m), 780(s), 623(m). Anal. Calcd for $[C_{62}H_{56}Cl_4Cu_3N_{12}O_{22}]$ (%): C, 45.03; H, 3.41; N, 10.16. Found (%): C, 44.79; H, 3.60; N, 10.37. UV-Vis (CH_3OH): $\lambda_{max} = 212$, 240, and 298 nm. ESI-MS (*m*/*z*): 188 ($[Cu(bpy)_2]^{2+}/2$), 250 ($[Cu_2(bpy)_2(CO_3)]^{2+}/2$), and 266 ($[Cu(bpy)_3]^{2+}/2$).

If the solvent was replaced by C_2H_5OH, the reaction gave $[Cu^{II}(bpy)_2(ClO_4)](ClO_4) \cdot 2H_2O$ and $[Cu^{II}(bpy)_3](ClO_4)_2$ as well as a few dark blue crystals of **2** (~10% yield). The single crystal of **2** suitable for X-ray diffraction determination is obtained by slow evaporation at room temperature in air for two weeks. Main FT-IR absorptions, (KBr pellets): $v = 3440$(b, m), 3054(w), 1607(m), 1477(w), 1440(s), 1382(s), 1089(vs), 840(m), 776(s), 623(m). Anal. Calcd for $[C_{62}H_{56}Cl_4Cu_3N_{12}O_{22}]$ (%): C, 45.89; H, 4.24; N, 9.31. Found (%): C, 45.61; H, 4.52; N, 9.55. UV-Vis (CH_3OH): $\lambda_{max} = 209$, 241, and 297 nm. ESI-MS (*m*/*z*): 188 ($[Cu(bpy)_2]^{2+}/2$), 250 ($[Cu_2(bpy)_2(CO_3)]^{2+}/2$), and 266 ($[Cu(bpy)_3]^{2+}/2$).

2.3. *Preparation of* $\{[Cu_3(bpy)_6(CO_3)](PF_6)_4(H_2O)_2\}$ *(3)*

A solution of $[Cu^{II}(bpy)_2(ONO_2)](NO_3) \cdot H_2O$ (0.2072 g, 0.4 mmol) in CH_3CN (15 cm^3) and KPF_6 (0.3680 g, 2.0 mmol) in H_2O (5 cm^3) was added to a solution of benzaldehyde in C_2H_5OH (20 cm^3, 0.04 mmol cm^{-3}). The mixture was refluxed for 50 h and the solution was allowed to evaporate slowly at room temperature in air. Blue crystals of $[Cu^{II}(bpy)_3](PF_6)_2$ and $[Cu^{II}(bpy)_2(ONO_2)](PF_6)$ as well as a few green crystals of **3** (~10% yield) suitable for X-ray diffraction were collected after two weeks. Main FT-IR absorptions, (KBr pellets): $v = 3421$(b, m), 3089(w), 1603(m), 1475(w), 1446(s), 1384(s), 1294(m), 1163(m), 1032(m), 845(vs), 771(s), 661(w), 557(s). Anal. Calcd for $[C_{62}H_{56}Cl_4Cu_3N_{12}O_{22}]$ (%): C, 41.03; H, 2.82; N, 9.41. Found (%): C, 41.38; H, 3.09; N, 9.61. UV-Vis (CH_3OH): $\lambda_{max} = 211$, 238, and 298 nm. ESI-MS (*m*/*z*): 188 ($[Cu(bpy)_2]^{2+}/2$), 250 ($[Cu_2(bpy)_2(CO_3)]^{2+}/2$), and 266 ($[Cu(bpy)_3]^{2+}/2$).

2.4. *Crystal structural determination and refinement*

Single crystals of **1**–**3** were covered in glue and mounted on glass fibers and used for data collection. Crystallographic data of **1**–**3** were collected at 291(2) K on a Bruker SMART 1 K CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences using XPREP. Absorption corrections were performed to all data and the structures were solved by direct methods and refined by full-matrix least-squares on F^2_{obs} by using the SHELXTL-PC software package [33]. All non-H atoms were anisotropically refined and all hydrogen atoms were inserted in calculated positions, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent. The common cationic structure of ($[Cu_3(bpy)_6(CO_3)]^{4+}$) in **1**–**3** can be easily solved, but the severely disordered anions and solvent molecules are very difficult to be fully located because of the low-quality diffraction data, even though many attempts were carried out. The summary of the crystal data, experimental details, and refinement results for **1**–**3** is listed in table 1.

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

Compound	**1**	**2**	**3**
Formula	$C_{62}H_{54}Cl_4Cu_3N_{12}O_{21}$	$C_{69}H_{74}Cl_4Cu_3N_{12}O_{24}$	$C_{122}H_{98}Cu_6F_{48}N_{24}O_7P_8$
Formula weight	1635.59	1787.82	3553.30
Temperature (K)	291(2)	291(2)	291(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	13.681(4)	14.1453(14)	12.971(6)
b	13.703(4)	14.2593(14)	14.032(6)
c	21.633(6)	24.200(2)	22.124(10)
α	84.952(4)	97.299(2)	91.137(7)
β	74.183(4)	98.635(2)	105.751(6)
γ	62.631(4)	118.438(1)	115.124(7)
Volume (Å^3), Z	3461.9(17), 2	4131.4(7), 2	3466(3), 1
Calculated density (g cm^{-3})	1.586	1.452	1.702
Absorption coefficient (mm^{-1})	1.153	0.973	1.125
F(000)	1686	1838	1780
Crystal size (mm^3)	0.10 × 0.10 × 0.12	0.10 × 0.10 × 0.12	0.10 × 0.12 × 0.14
h, k, l limiting indices	$-8 \le h \le 16$; $-15 \le k \le 16$; $-25 \le l \le 25$	$-16 \le h \le 16$; $-16 \le k \le 16$; $-23 \le l \le 28$	$-15 \le h \le 14$; $-16 \le k \le 14$; $-26 \le l \le 26$
Reflections collected	17,031	20,778	17,633
Independent reflection	11,893	14,290	12,038
Reflections [$I > 2\sigma(I)$]	4670	4162	3082
Parameters	904	943	973
Goodness-of-fit on F^2	1.040	0.996	0.679
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0921$, $wR_2 = 0.2179$	$R_1 = 0.0988$, $wR_2 = 0.2586$	$R_1 = 0.0634$, $wR_2 = 0.1017$
R indices (all data)	$R_1 = 0.1962$, $wR_2 = 0.2504$	$R_1 = 0.2375$, $wR_2 = 0.2877$	$R_1 = 0.2217$, $wR_2 = 0.1317$
Max./min. $\Delta\rho$ (e Å^{-3})	1.468 and −1.128	1.105 and −0.583	0.682 and −0.522

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

Selected bond distances and angles related to copper are given in table 2, while weak C–H···O hydrogen bonds in **1**–**3** are listed in table 3.

3. Results and discussion

3.1. *Synthesis and spectral characterization*

We previously employed $[Cu^{II}(bpy)_2]^{2+}$ with different anions to catalyze C–C bond cleavage of acetonitrile in the presence of reductants such as aryl aldehydes. To better understand these reactions, we have carried out many control experiments. Although no CN^- containing products have been obtained under some reactions by using excess reductants, mononuclear $[Cu^{II}(bpy)_2]^{2+}$ and $[Cu^{II}(bpy)_3]^{2+}$ based complexes with different counterions proved to be the main products. Among them, several unexpected μ_3-CO_3^{2-}-bridged Cu^{II} complexes **1**–**3** are obtained where the carbonate may come from atmospheric CO_2 when the solutions are exposed to air in the process of growing single crystals.

Table 2. Selected bond lengths (Å) and angles (°) for **1–3**.

1			
Cu1–O1	2.395(7)	Cu3–O1	2.403(7)
Cu1–O2	2.467(7)	Cu3–O3	2.368(6)
Cu1–N1	2.047(8)	Cu3–N9	2.048(8)
Cu1–N2	1.962(8)	Cu3–N10	1.964(8)
Cu1–N3	2.102(9)	Cu3–N11	1.963(7)
Cu1–N4	1.951(7)	Cu3–N12	2.105(7)
Cu2–O2	2.551(7)	O1–C61	1.241(11)
Cu2–O3	2.279(6)	O2–C61	1.178(11)
Cu2–N5	1.985(8)	O3–C61	1.195(12)
Cu2–N6	2.060(7)		
Cu2–N7	1.978(8)		
Cu2–N8	2.116(11)		
O1–Cu1–O2	52.0(2)	O3–Cu2–N8	82.3(3)
O1–Cu1–N1	159.7(3)	N5–Cu2–N6	80.4(3)
O1–Cu1–N2	96.2(4)	N5–Cu2–N7	173.6(4)
O1–Cu1–N3	89.9(4)	N5–Cu2–N8	106.2(4)
O1–Cu1–N4	83.9(3)	N6–Cu2–N7	94.8(3)
O2–Cu1–N1	108.0(3)	N6–Cu2–N8	103.1(3)
O2–Cu1–N2	89.5(3)	N7–Cu2–N8	79.0(4)
O2–Cu1–N3	141.7(3)	O1–Cu3–O3	50.4(2)
O2–Cu1–N4	91.3(3)	O1–Cu3–N9	166.8(3)
N1–Cu1–N2	79.1(4)	O1–Cu3–N10	97.4(3)
N1–Cu1–N3	110.3(3)	O1–Cu3–N11	85.2(3)
N1–Cu1–N4	101.2(3)	O1–Cu3–N12	85.3(3)
N2–Cu1–N3	99.5(4)	O3–Cu3–N9	116.4(3)
N2–Cu1–N4	179.0(4)	O3–Cu3–N10	89.9(3)
N3–Cu1–N4	79.5(3)	O3–Cu3–N11	92.0(3)
O2–Cu2–O3	50.9(2)	O3–Cu3–N12	135.6(3)
O2–Cu2–N5	88.3(3)	N9–Cu3–N10	80.6(3)
O2–Cu2–N6	124.2(3)	N9–Cu3–N11	97.4(3)
O2–Cu2–N7	90.9(3)	N9–Cu3–N12	107.9(3)
O2–Cu2–N8	132.4(3)	N10–Cu3–N11	177.4(3)
O3–Cu2–N5	94.9(3)	N10–Cu3–N12	100.2(3)
O3–Cu2–N6	173.7(4)	N11–Cu3–N12	79.5(3)
O3–Cu2–N7	89.5(3)		
2			
Cu1–O1	1.998(8)	Cu3–O3	2.021(7)
Cu1–N1	2.033(10)	Cu3–N9	1.948(10)
Cu1–N2	1.981(10)	Cu3–N10	2.126(10)
Cu1–N3	2.178(9)	Cu3–N11	1.977(11)
Cu1–N4	2.015(10)	Cu3–N12	2.092(11)
Cu2–O2	1.948(8)	O1–C61	1.282(12)
Cu2–N5	1.969(9)	O2–C61	1.289(14)
Cu2–N6	2.049(10)	O3–C61	1.276(13)
Cu2–N7	2.166(10)		
Cu2–N8	2.024(9)		
O1–Cu1–N1	157.6(3)	N5–Cu2–N7	100.5(4)
O1–Cu1–N2	92.2(4)	N5–Cu2–N8	176.5(4)
O1–Cu1–N3	102.2(3)	N6–Cu2–N7	98.2(4)
O1–Cu1–N4	89.9(3)	N6–Cu2–N8	97.4(4)
N1–Cu1–N2	81.0(5)	N7–Cu2–N8	78.5(4)
N1–Cu1–N3	100.1(3)	O3–Cu3–N9	94.0(4)
N1–Cu1–N4	95.8(4)	O3–Cu3–N10	131.8(4)
N2–Cu1–N3	104.7(4)	O3–Cu3–N11	93.2(4)
N2–Cu1–N4	176.0(4)	O3–Cu3–N12	124.2(4)
N3–Cu1–N4	78.1(4)	N9–Cu3–N10	79.7(4)
O2–Cu2–N5	94.8(4)	N9–Cu3–N11	172.6(4)

(*continued*)

Table 2. Continued.

O2–Cu2–N6	163.5(4)	N9–Cu3–N12	97.5(5)
O2–Cu2–N7	98.0(3)	N10–Cu3–N11	94.5(4)
O2–Cu2–N8	88.6(3)	N10–Cu3–N12	104.0(4)
N5–Cu2–N6	79.4(5)	N11–Cu3–N12	79.5(5)
3			
Cu1–O1	2.043(6)	Cu3–O3	2.059(7)
Cu1–N1	2.020(7)	Cu3–N9	2.012(6)
Cu1–N2	1.994(6)	Cu3–N10	2.119(8)
Cu1–N3	2.153(8)	Cu3–N11	1.996(6)
Cu1–N4	2.024(7)	Cu3–N12	2.039(7)
Cu2–O1	2.525(6)	O1–C61	1.215(10)
Cu2–O2	2.102(6)	O2–C61	1.263(11)
Cu2–N5	1.996(6)	O3–C61	1.298(12)
Cu2–N6	2.106(7)		
Cu2–N7	2.048(7)		
Cu2–N8	1.999(6)		
O1–Cu1–N1	163.8(3)	O2–Cu2–N8	94.8(3)
O1–Cu1–N2	94.2(3)	N5–Cu2–N6	78.3(3)
O1–Cu1–N3	89.1(2)	N5–Cu2–N7	93.9(3)
O1–Cu1–N4	91.0(3)	N5–Cu2–N8	172.9(3)
N1–Cu1–N2	80.5(3)	N6–Cu2–N7	93.1(3)
N1–Cu1–N3	107.0(3)	N6–Cu2–N8	100.5(3)
N1–Cu1–N4	93.2(3)	N7–Cu2–N8	79.2(3)
N2–Cu1–N3	106.3(4)	O3–Cu3–N9	91.9(3)
N2–Cu1–N4	172.9(3)	O3–Cu3–N10	97.5(3)
N3–Cu1–N4	78.6(4)	O3–Cu3–N11	93.2(3)
O1–Cu2–O2	54.5(2)	O3–Cu3–N12	152.8(3)
O1–Cu2–N5	96.0(2)	N9–Cu3–N10	79.1(3)
O1–Cu2–N6	161.5(2)	N9–Cu3–N11	174.4(3)
O1–Cu2–N7	104.8(2)	N9–Cu3–N12	95.5(3)
O1–Cu2–N8	87.3(2)	N10–Cu3–N11	98.0(3)
O2–Cu2–N5	92.2(3)	N10–Cu3–N12	109.6(3)
O2–Cu2–N6	107.8(3)	N11–Cu3–N12	80.9(3)
O2–Cu2–N7	159.0(3)		

In their infrared spectra, frequencies of the antisymmetric and symmetric stretches of carbonate in **1**–**3** are $\nu_a = 1472$, 1477, and 1475 cm^{-1} and 1444, 1440, and 1446 cm^{-1}, respectively. The strong bands at 1084, 1089, and 845 cm^{-1} in **1**–**3** are the typical absorptions of ClO_4^- and PF_6^- counterions.

3.2. *Structural elucidation of trinuclear copper(II) complexes 1–3*

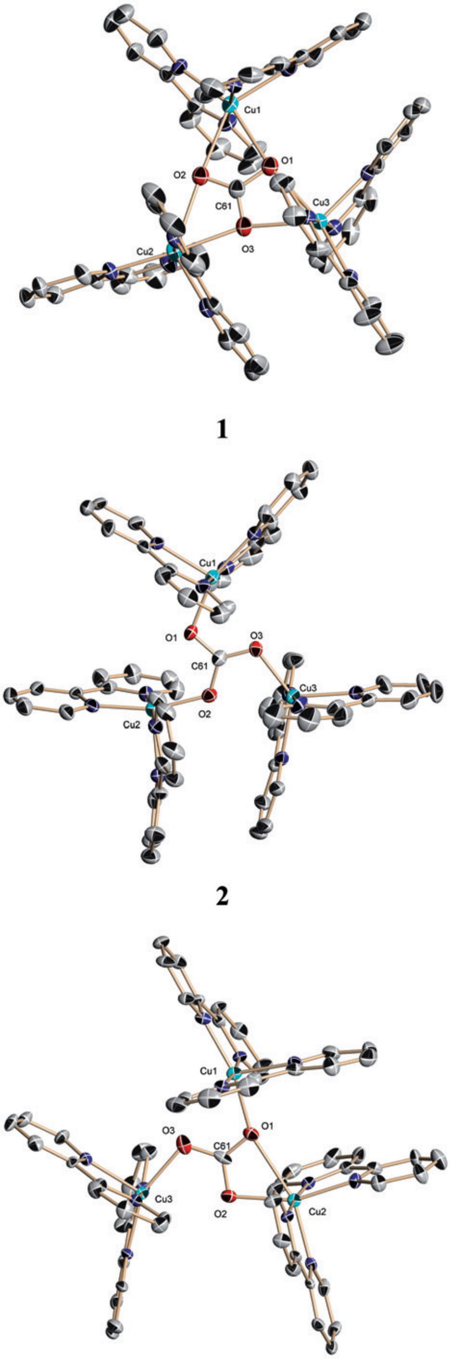
The cationic structures of the trinuclear copper(II) complexes with the anisotropic displacement ellipsoids and atom-numbering scheme are shown in figure 1. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with one $[Cu_3(bpy)_6(CO_3)]^{4+}$, four perchlorates, one free methanol, and two half crystalline water molecules in the asymmetric unit. The coordination sphere of each copper(II) is a severely distorted octahedron with four nitrogen atoms from two bpy and two oxygen atoms from carbonate. The Cu–N bond lengths of 1.951(7)–2.116(11) Å are shorter than the Cu–O bond lengths of 2.279(6)–2.551(7) Å, where Jahn–Teller effects have not been observed. The carbonate is μ_3-CO_3^{2-} linking three adjacent copper(II) centers and forming trinuclear copper(II) complexes. The central μ_3-CO_3^{2-} bridge adopts a μ_3-η^2, η^2, η^2 coordination mode in **1**.

Table 3. Intermolecular hydrogen-bonding interactions (Å, °) in **1–3**.

D–H···A	D–H	H–A	D···A	∠DHA	Symmetry transformations
1					
C11–H11···O19	0.93	2.53	3.31(2)	141.0	$x, -1+y, z$
C13–H13···O10	0.93	2.44	3.24(2)	139.0	$x, -1+y, z$
C14–H14···O6	0.93	2.48	3.24(2)	139.0	$1-x, 1\text{-}y, 1-z$
C19–H19···O11	0.93	2.54	3.23(2)	131.0	$-1+x, y, z$
C22–H22···O13	0.93	2.55	3.28(2)	135.0	$-x, 1-y, 1-z$
C27–H27···O19	0.93	2.39	3.26(2)	156.0	$1-x, 1-y, -z$
C28–H28···O2	0.93	2.52	3.31(2)	139.0	$1-x, -y, -z$
C34–H34···O7	0.93	2.49	3.30(2)	146.0	$x, -1+y, z$
C37–H37···O4	0.93	2.45	3.35(2)	158.0	$x, -1+y, z$
C54–H54···O11	0.93	2.59	3.37(2)	141.0	$-1+x, y, z$
2					
C2–H2···O18	0.93	2.40	3.08(3)	130.0	$-1+x, y, z$
C3–H3···O11	0.93	2.52	3.13(3)	123.0	$-1+x, y, z$
C11–H11···O10	0.93	2.38	3.11(3)	135.0	$-x, 1-y, -z$
C24–H24···O11	0.93	2.56	3.36(2)	145.0	$x, 1+y, z$
C32–H32···O12	0.93	2.50	3.26(3)	139.0	$x, 1+y, z$
C49–H49···O5	0.93	2.52	3.38(3)	154.0	$1-x, 2-y, 1-z$
3					
C1–H1···F15	0.93	2.55	3.22(2)	130.0	$1-x, 1-y, -z$
C4–H4···F23	0.93	2.39	3.23(2)	150.0	$1-x, 1-y, -z$
C14–H14···F24	0.93	2.41	3.21(2)	145.0	$1-x, 2-y, -z$
C17–H17···F21	0.93	2.49	3.36(2)	156.0	$1-x, 2-y, -z$
C22–H22···F16	0.93	2.46	3.23(2)	131.0	$x, 1+y, z$
C30–H30···F11	0.93	2.46	3.31(2)	151.0	$2-x, 1-y, 1-z$
C33–H33···F13	0.93	2.54	3.27(2)	135.0	$1+x, 1+y, z$
C34–H34···F7	0.93	2.45	3.29(2)	152.0	$1+x, 1+y, z$
C37–H37···F7	0.93	2.48	3.25(2)	141.0	$1+x, 1+y, z$
C48–H48···F20	0.93	2.51	3.30(2)	143.0	$-x, 1-y, -z$
C59–H59···F10	0.93	2.50	3.26(2)	139.0	$1-x, 1-y, 1-z$

Complex **2** crystallizes in the triclinic space group $P\bar{1}$ where one $[Cu_3(bpy)_6(CO_3)]^{4+}$, four perchlorates, one crystalline water molecule, and four free ethanols are found in the asymmetric unit. In comparison with **1**, coordination between copper(II) centers and carbonate are different in addition to differences in solvent. The coordination spheres of copper(II) centers are distorted five-coordinate square pyramids for Cu1 and Cu2 and trigonal bipyramid for Cu3 ($\tau = 0.307$ for Cu1, 0.217 for Cu2, and 0.680 for Cu3), respectively [34]. Each copper(II) is coordinated with four nitrogen atoms from two bpy and one oxygen atom from carbonate The central μ_3-CO_3^{2-} bridge is μ_3-η^1, η^1, η^1 and the Cu–O bond lengths (1.948(8)–2.021(7) Å) are comparable to Cu–N bond lengths (1.948(10)–2.126(10) Å).

Complex **3** also crystallizes in the triclinic space group $P\bar{1}$, consisting of one $[Cu_3(bpy)_6(CO_3)]^{4+}$, four hexafluorophosphorates, and half a crystalline water molecule in the asymmetric unit. The coordination of copper(II) is distorted square pyramids for Cu1 and Cu3 ($\tau = 0.152$ for Cu1 and 0.360 for Cu3) and distorted octahedron for Cu2. Coordination of Cu1 and Cu3 is quite similar to those in **2** with the Cu–O and Cu–N bond lengths of 2.043(6)–2.525(6) Å and 1.994(6)–2.153(8) Å, respectively. However, two bonds are formed between Cu2 and carbonate with lengths of 2.102(6) and 2.525(6) Å, exhibiting a μ_3-η^1, η^1, η^2 coordination.



1

2

3

Figure 1. ORTEP plots of the cations of **1**–**3**. Thermal ellipsoids are drawn at 20% probability (hydrogen atoms and solvent molecules are omitted for clarity).

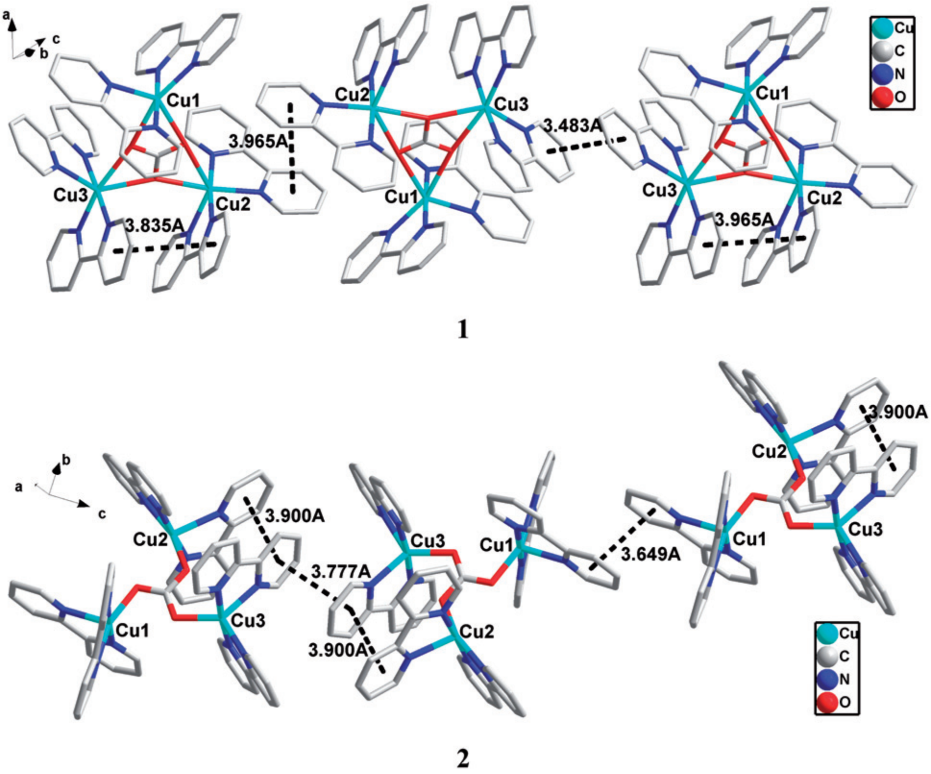


Figure 2. Intermolecular and intramolecular π–π stacking interactions in **1** and **2**.

In the crystal packing of **1**, intramolecular and intermolecular π–π stacking interactions are found between neighboring pyridine rings of bpy with centroid–centroid separations of 3.835, 3.965, and 3.483 Å, forming a 1-D supramolecular chain [35], as shown in figure 2(a). Similar π–π stacking interactions and 1-D supramolecular chains are also observed in **2**. The centroid–centroid separations are 3.900, 3.777, and 3.649 Å, respectively, as can be seen in figure 2(b). No π–π stacking interactions can be found in **3**. However, weak intermolecular C–H···O hydrogen-bonding interactions are abundant in **1**–**3**, as listed in table 3, due to the presence of large numbers of counterions and crystalline solvent. The presence of different counterions and solvent molecules in **1**–**3** is responsible for the variations of coordination, coordination spheres of copper(II), and crystal packing.

4. Conclusion

Three triangular trinuclear copper(II) complexes bridged by carbonate have been synthesized and structurally characterized. Carbonate anions originate from atmospheric CO_2 when the solutions are exposed to air for a long time. The common $[Cu_3(bpy)_6(CO_3)]^{4+}$ unit in **1**–**3** shows distinguishable coordination fashions, i.e., μ_3-η^2,

η^2, η^2 in **1**, μ_3-η^1, η^1, η^1 in **2**, and μ_3-η^1, η^1, η^2 in **3**. The copper(II) centers are five-coordinate trigonal bipyramidal and square pyramidal as well as six-coordinate octahedral. Similar 1-D supramolecular chains are formed in **1** and **2** with the help of intramolecular and intermolecular π–π stacking interactions. Various weak hydrogen-bonding interactions are observed in all three complexes.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC 878456∼878 458 for trinuclear copper(II) complexes **1**–**3** (The Director, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: request@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Copies of this information are available free of charge on request quoting the deposition CCDC number.

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