Polyhedron 29 (2010) 434–440

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Copper(II) α-hydroxycarboxylate complexes of bis(2-pyridylcarbonyl)amine ligand: From mononuclear complex to one-dimensional coordination polymer

Partha Halder [a], Ennio Zangrando [b], Tapan Kanti Paine [a,*]

[a] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, 2A & 2B Raja S.C. Mullick Road, Jadavpur, Kolkata 700032, India*
[b] *Dipartimento di Scienze Chimiche, University of Trieste, Via Licio Giorgieri 1, 34127 Trieste, Italy*

ARTICLE INFO

Article history:
Available online 7 August 2009

Keywords:
Copper
Hydroxy acids
Hydrogen bonds
Coordination polymer
Solid-state structure

ABSTRACT

The coordination geometry and supramolecular structures of three copper(II) complexes of two α-hydroxycarboxylates and one α-methoxycarboxylate with nitrogen donor co-ligands are discussed. The complexes have been characterized by elemental analysis, ESI-MS, IR and electronic spectroscopy, thermogravimetric analysis and magnetic measurements. The X-ray structure analysis of all the complexes, namely [(BPCA)Cu^{II}(MA)] (**1**), [(BPCA)Cu^{II}(MPA)(H$_2$O)] (**2**) and [(BPCA)Cu^{II}(BA)]$_n$ (**3**), where BPCA = bis(2-pyridylcarbonyl)amidate, MA = racemic mandelate, MPA = racemic α-methoxy phenylacetate and BA = benzilate anion, shows the copper(II) ion in a distorted square-pyramidal geometry. In **1** the mandelate anion is coordinated to the copper(II) center in a bidentate fashion while in **2** the α-methoxycarboxylate is monodentate. In both cases a one-dimensional supramolecular array is formed through hydrogen bonds: the mononuclear units are directly connected in **1** by the MA hydroxyl group, whereas in **2** is the coordinated water that operates as H donor towards the MPA carboxylate group and the BPCA carbonyl oxygens of nearby complexes. In **3** the benzilate anion, acting as bridging ligand between copper ions, gives rise to a one-dimensional coordination polymer. In the latter, intra- and inter-chain π···π stacking interactions between pyridines and one phenyl ring of benzilate anions are observed in the packing.

1. Introduction

Coordination compounds of appropriate metal–ligand combination are used as molecular building blocks for self-organized structures with diverse topologies and potential application [1–8]. Beside covalent linkages between the building blocks, non-covalent intermolecular interactions, like H-bonds, π···π, and C–H···π, direct the formation of self-assembled structures of variable dimensions [9–13]. The coordination chemistry of metal complexes containing α-hydroxy acids has been extensively studied over the last years for their unusual structural features as well as various physical and chemical properties [14–31]. These carboxylate species reveal various coordination modes (i.e., denticity) since they can behave as monodentate or bidentate chelating (through the carboxylate group or *via* one oxygen of the carboxylate and the α-OH group). In addition, different coordination patterns were reported in the same compound, as well as bridging behavior between two metal ions as observed for simple carboxylate ligands. The coordination mode eventually adopted by the α-hydroxy anions may depend on the metal ion and co-ligands used in complex synthesis and, to a certain extent, also on the ratio of the reactants. Moreover, the α-hydroxy acids or their monoanionic forms can act as source of H-bonds and are suitable for π···π stacking and/or C–H···π interactions with aromatic nitrogen donor ligands. It is also possible to fine tune such non-covalent interaction by suitable functionalization on α-hydroxy acids.

In spite of a large number of copper(II) α-hydroxycarboxylates reported in literature [17–22,24–29,31–33], study on the effect of ligand functionality in directing the self-assembled product is rare [20,31]. We decided to investigate copper(II) complexes of α-hydroxy acids and α-methoxy carboxylic acid with bis(2-pyridylcarbonyl)amidate (BPCA) as nitrogen donor coligand (Chart 1). We report herein the complexes [(BPCA)Cu^{II}(MA)] (**1**), [(BPCA)-Cu^{II}(MPA)(H$_2$O)] (**2**), and [(BPCA)Cu^{II}(BA)]$_n$ (**3**) [MA = racemic mandelate, MPA = racemic α-methoxy phenylacetate and BA = benzilate anion], comparing the effect of carboxylic acids on their solid state structure. It is expected that the tridentate bis(2-pyridylcarbonyl)amidate ligand and packing requirements may induce the hydroxy carboxylate to adopt different coordination modes in the copper(II) complexes. Moreover, the benzilate with two phenyl rings at α-carbon would engender more steric crowding, affecting its binding mode beside the possibility to form extra π···π interaction in comparison to mandelate. The effect of ligand

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* Corresponding author. Tel.: +91 33 2473 4971; fax: +91 33 2473 2805.
E-mail address: ictkp@iacs.res.in (T.K. Paine).

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doi:10.1016/j.poly.2009.06.087

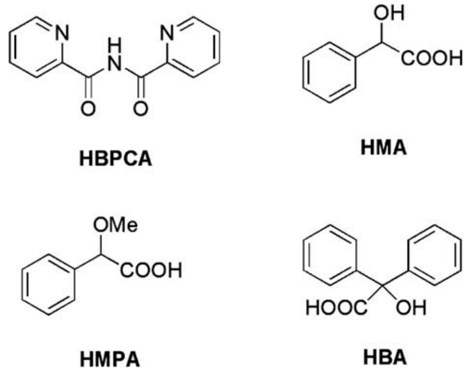


Chart 1.

functionality, coordination geometry of metal complex and other non-covalent interactions in stabilizing such self-assembled structures is described.

2. Experimental

2.1. Chemicals

The chemicals were purchased from commercial sources and used as received. The solvents were distilled and dried before use. Although no problems were encountered during the synthesis of complexes, perchlorate salts are potentially explosive and should be handled with care. The ligand HBPCA was synthesised according to a literature procedure [34].

2.2. Syntheses

2.2.1. Complex [(BPCA)Cu^{II}(MA)] (**1**)

To a methanolic solution (20 mL) of HBPCA ligand (0.227 g, 1 mmol) was added $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1 mmol). To the resulting solution was added a methanolic solution (3 mL) of mandelic acid (1 mmol) and triethylamine (1 mmol). The solution turned immediately to blue and was stirred further for 3 h to yield a pale blue solid. The solid was isolated by filtration and air-dried. The filtrate was kept at room temperature for a week to isolate blue single crystals suitable for X-ray crystallography. Yield: 0.26 g (59%). *Anal.* Calc. for $C_{20}H_{15}CuN_3O_5$: C, 54.48; H, 3.43; N, 9.53. Found: C, 54.5; H, 3.3; N, 9.7%. IR (KBr, cm^{-1}): 3423 (br), 3101–3032 (br), 1705 (s), 1599 (s), 1355–1342 (s), 1093, 1043, 766, 704. ESI-MS (positive ion mode, water–methanol): $m/z = 751.02$ (20%, $[(BPCA)_2Cu_2(MA)+Na]^+$), 479.01 (25%, $[(BPCA)Cu(MA)+K]^+$), 463.04 (100%, $[(BPCA)Cu(MA)+Na]^+$), 289.00 (70%, $[BPCA)Cu]^+$). UV–Vis in DMF (λ, nm; ε, $M^{-1}\ cm^{-1}$): 629 (100), 429 (sh), 342 (sh), 309 (sh), 285 (11 300), 274 (13 400).

2.2.2. Complex [(BPCA)Cu^{II}(MPA)(H_2O)] (**2**)·0.5 MeOH·0.5 H_2O

The complex was synthesised according to the procedure described for complex **1** except for α-methoxy phenylacetic acid was used instead of mandelic acid. The solution was kept at room temperature for slow evaporation of solvent for 5 days to isolate dark blue needles. Yield: 0.35 g (70%). *Anal.* Calc. for $C_{21.5}H_{22}CuN_3O_7$: C, 51.86; H, 4.45; N, 8.44. Found: C, 51.9; H, 4.4; N, 8.7%. IR (KBr, cm^{-1}): 3448 (br), 2931, 1713 (s), 1635 (s), 1599 (s), 1363(s), 1097, 1029, 761, 704. ESI-MS (positive ion mode, water–methanol): $m/z = 931.51$ (50%, $[(BPCA)_2Cu_2(MPA)_2+Na]^+$), 743.43 (25%, $[(BPCA)_2Cu_2(MPA)]^+$), 477.28 (100%, $[(BPCA)Cu(MPA)+Na]^+$), 312.14 (70%, $[BPCA)Cu+Na]^+$), 289.05 (50%, $[BPCA)Cu]^+$). UV–Vis in MeOH (λ, nm; ε, $M^{-1}\ cm^{-1}$): 632 (115), 303 (sh), 274 (15 600).

2.2.3. Complex $[(BPCA)Cu^{II}(BA)]_n$ (**3**)

The complex was synthesised according to the procedure described for complex **1** except for benzilic acid was used instead of mandelic acid. Yield: 0.34 g (66%). *Anal.* Calc. for $C_{26}H_{19}CuN_3O_5$: C, 60.40; H, 3.70; N 8.13. Found: C, 59.8; H, 3.5; N, 8.2%. IR (KBr, cm^{-1}): 3502–3406 (br), 3063 (br), 1713 (s), 1625, 1600 (s), 1382–1359 (s), 1300, 766, 704. ESI-MS (positive ion mode, water–methanol): $m/z = 1057.19$ (25%, $[(BPCA)_2Cu_2(BA)_2+Na]^+$), 805.18 (75%, $[(BPCA)_2Cu_2(BA)]^+$), 555.12 (10%, $[(BPCA)Cu(BA)+K]^+$), 539.15 (100%, $[(BPCA)Cu(BA)+Na]^+$), 289.04 (50%, $[BPCA)Cu]^+$). UV–Vis in DMF (λ, nm; ε, $M^{-1}\ cm^{-1}$): 634 (100), 429 (sh), 342 (sh), 308 (sh), 285 (11 350), 274 (13 400).

2.3. Physical methods

Fourier transform infrared spectroscopy on KBr pellets was performed on a Shimadzu FT-IR 8400S instrument. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN series. Solution electronic spectra were measured on an Agilent 8453 diode array spectrophotometer. Electro-spray mass spectra were recorded with a Waters QTOF Micro YA263. Room temperature magnetic data were collected on a Gouy balance (Sherwood Scientific, Cambridge, UK). Diamagnetic contributions were estimated for each compound by using Pascal's constants. TGA measurements were carried out on a TA instruments SDT Q 600 thermal analyzer with the heating rate of 10 °C/min from room temperature to 800 °C under nitrogen atmosphere.

2.3.1. X-ray crystallographic data collection and refinement of the structures

Crystallographic data for the complexes are summarized in Table 1. Diffraction data for **1** were collected at RT on a Nonius DIP-1030H system (Mo Kα radiation, $\lambda = 0.71073$ Å). Intensities data collections for **2** and **3** were performed on a Bruker Smart APEX II (Mo Kα radiation, $\lambda = 0.71073$ Å) at 150 K. Cell refinement, indexing and scaling of the data sets were carried out using Denzo and Scalepack packages [35], and the APEX2 v2.1-0 software [36]. The structure was solved by direct methods and subsequent Fourier

Table 1
Crystallographic data for complexes **1**–**3**.

	1	**2**·0.5MeOH·0.5H_2O	**3**
Empirical formula	$C_{20}H_{15}CuN_3O_5$	$C_{21.50}H_{22}CuN_3O_7$	$C_{26}H_{19}CuN_3O_5$
Formula weight	440.89	495.95	516.98
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a (Å)	5.515(3)	10.0649(4)	8.8400(11)
b (Å)	9.402(3)	15.4982(6)	12.7073(17)
c (Å)	18.333(4)	14.6418(5)	19.617(3)
α (°)	90.49(3)		
β (°)	98.47(3)	108.692(1)	100.998(4)
γ (°)	108.21(3)		
V (Å^3)	891.6(6)	2163.48(14)	2163.2(5)
Z	2	4	4
D_{calc} (Mg/m^3)	1.642	1.529	1.587
μ (Mo Kα) (mm^{-1})	1.265	1.059	1.056
F(0 0 0)	450	1028	1060
θ Range data collection (°)	1.12–26.37	1.97–24.06	1.92–27.60
Reflections collected	10 742	18 765	22 238
Reflections unique	3184	3420	4917
R_{int}	0.0378	0.0525	0.0810
Data [$I > 2\sigma(I)$]	1952	2752	3794
Parameters	265	298	317
Goodness-of-fit (GOF) on F^2	0.846	1.048	1.031
R_1 [$I > 2\sigma(I)$]	0.0387	0.0371	0.0488
wR_2	0.0781	0.0877	0.1204
Residuals (e Å^{-3})	0.202, −0.248	0.724, −0.327	1.240, −0.838

analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections [37]. H atoms bonded to carbon (and to hydroxyl group in **3**) were included at calculated positions, those of the hydroxyl group in **1** and of the aquo ligand in **2** were located from electron density map and refined. In the ΔF map of **2** an area of disordered solvent was interpreted as occupied by a molecule of MeOH and of water, both at half occupancy (H atoms not assigned). All the calculations were performed using the WinGX System, Ver 1.70.01 [38].

3. Results and discussion

3.1. Syntheses and characterization

The complexes **1**–**3** were synthesised by reacting HBPCA ligand with copper(II) perchlorate and appropriate acids in methanol in the presence of one equivalent of triethylamine (Scheme 1).

The IR spectra of copper(II) complexes exhibit bands at around 1600 cm^{-1}, and in the range of 1330–1380 cm^{-1}, attributable to $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$, respectively. Complexes **1** and **3** show sharp bands in the 3050–3470 cm^{-1} due to OH stretching of α-hydroxy acid anion and for complex **1** weak broad band is observed around 2600 cm^{-1}, due to hydrogen bonded OH stretching frequency. In addition, sharp bands are observed at 1705 cm^{-1} for **1** and at 1712 cm^{-1} for **2** and **3** corresponding to $\nu(C{=}O)$ vibrations of BPCA ligand [39]. ESI-MS in positive ion mode (in water–methanol) shows peaks at m/z = 479.01 (25%), 463.04 (100%), and 289.00 (70%) for **1** with isotope distribution patterns calculated for $[(BPCA)Cu(MA)+K]^+$, $[(BPCA)Cu(MA)+Na]^+$, and $[(BPCA)Cu]^+$, respectively. Apart from this, a peak observed at m/z = 751.03 (20%) can be assigned to $[(BPCA)_2Cu_2(MA\text{-}H)+Na]^+$. Similar mass spectral pattern (in methanol) is observed for complex **2** which shows peaks in the ESI-MS at m/z = 931.51 (50%), 743.43 (25%), 477.28 (100%), 312.14 (70%) and 289.05 (50%) with isotope distribution patterns calculated for $[(BPCA)_2Cu_2(MPA)_2+Na]^+$, $[(BPCA)_2Cu_2(MPA)]^+$, $[(BPCA)Cu(MPA)+Na]^+$, $[BPCA)Cu+Na]^+$ and $[BPCA)Cu]^+$, respectively. The presence of higher molecular weight mass peaks suggests that in solution the mononuclear copper(II) units of complexes **1** and **2** are arranged in polymeric fashion through some intermolecular interactions. The ESI-MS of **3** shows peaks at m/z = 1057.19 (25%), 843.13 (10%), 827.16 (60%), 805.18 (75%), 555.12 (10%), 539.15 (100%) and 289.04 (50%) with expected isotope distribution patterns calculated for $[\{(BPCA)Cu(BA)\}_2+Na]^+$, $[(BPCA)_2Cu_2(BA\text{-}H)+K]^+$, $[(BPCA)_2Cu_2(BA\text{-}H)+Na]^+$, $[(BPCA)_2Cu_2(BA)]^+$, $[(BPCA)Cu(BA)+K]^+$, $[(BPCA)Cu(BA)+Na]^+$ and $[(BPCA)Cu]^+$, respectively. This indicates the polymeric nature of complex **3**. The complexes show effective magnetic moments between 1.79 and 1.84 BM (per copper) at room temperature, as expected for Cu(II) ion in d^9 electronic configuration. The thermogravimetric behavior of **1** and **3** is very similar. Decomposition of the hydroxy carboxylate ligands begins at about 200 °C and continues up to 300 °C. A further weight loss takes place in the range 300–390 °C and then very slowly up to 800 °C, which corresponds to the decomposition of the tridentate BPCA ligand. Complex **2** contains lattice solvent that is lost at 140 °C, while the loss of a coordinated water molecule is observed at 220 °C. The α-methoxy phenylacetate ligand (MPA) decomposes at ca. 310 °C and then BPCA ligand decomposes slowly up to 800 °C.

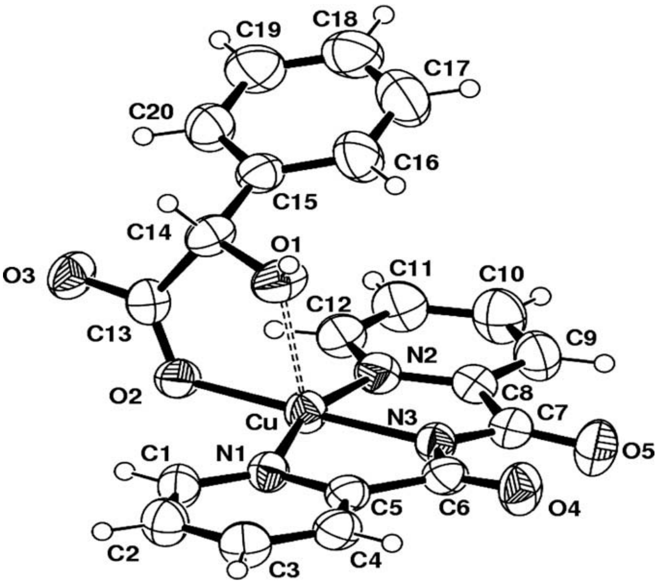


Fig. 1. Molecular structure of $[(BPCA)Cu^{II}(MA)]$ (**1**).

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

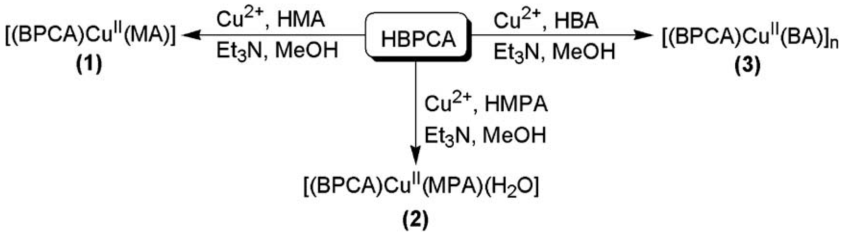
	1	2	3[a]
Cu–N(1)	1.999(3)	2.014(3)	1.983(2)
Cu–N(2)	2.005(3)	2.009(3)	1.979(2)
Cu–N(3)	1.931(3)	1.933(3)	1.935(2)
Cu–O(1)	2.297(3)	2.255(2)	2.482(2)
Cu–O(2)	1.945(2)	1.947(2)	1.959(2)
N(1)–Cu–N(2)	163.32(11)	163.45(10)	164.09(10)
N(1)–Cu–N(3)	82.64(11)	81.73(10)	82.18(10)
N(1)–Cu–O(1)	91.20(11)	90.13(10)	91.23(8)
N(1)–Cu–O(2)	100.05(10)	97.19(10)	96.43(9)
N(2)–Cu–N(3)	82.04(12)	81.75(10)	82.41(10)
N(2)–Cu–O(1)	98.94(11)	93.88(10)	92.73(8)
N(2)–Cu–O(2)	95.26(11)	98.72(10)	99.40(9)
N(3)–Cu–O(1)	104.31(10)	100.70(10)	118.80(9)
N(3)–Cu–O(2)	177.30(10)	167.42(10)	160.08(9)
O(2)–Cu–O(1)	76.01(9)	91.82(9)	81.04(7)
C(13)–O(2)–Cu	121.4(2)	114.3(2)	112.79(18)

[a] In **3** O(1) represents the symmetry related hydroxyl oxygen at $-x+1$, $y-1/2$, $-z+1/2$ (see Fig. 5).

3.2. X-ray structures

3.2.1. Crystal structure of $[(BPCA)Cu^{II}(MA)]$(**1**)

The X-ray structural determination of **1** reveals that the copper(II) center is surrounded by the chelating MA anion and



Scheme 1. Syntheses of complexes **1**–**3**.

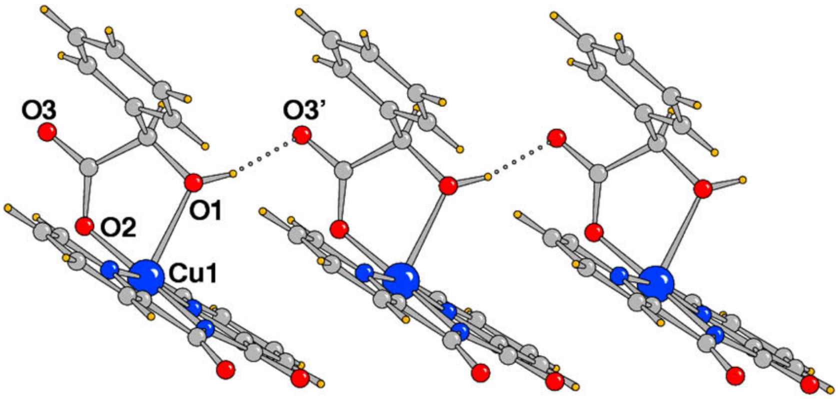


Fig. 2. Crystal packing of **1** shows linear one-dimensional polymer along axis *a* formed by H-bonds (O3′ at 1 + *x*, *y*, *z*).

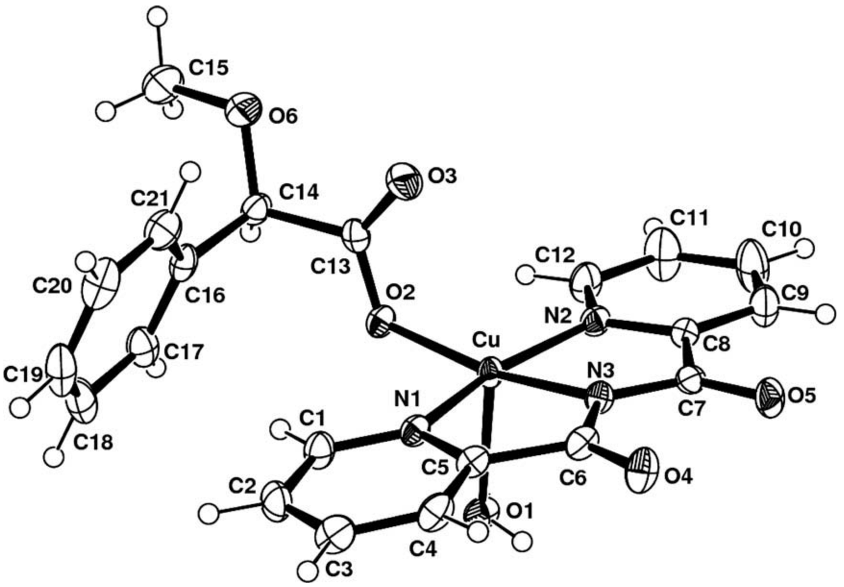


Fig. 3. ORTEP drawing of the molecular structure of [(BPCA)Cu^{II}(MPA)(H$_2$O)] (**2**).

the tridentate BPCA ligand in a distorted square-pyramidal coordination geometry (τ = 0.233) [40], indicating that the amide nitrogen undergoes deprotonation upon complexation (Fig. 1). The imido and two pyridyl nitrogen donors from BPCA ligand and the carboxylate oxygen atom O2 from MA form the basal plane whereas the hydroxyl oxygen atom (O1) is located at the apical position of the distorted square pyramid. Among the Cu–N bond distances, that involving the amide nitrogen (Cu–N(3) = 1.931(3) Å) is slightly shorter in comparison with the Cu–N(py) distances of 1.999(3) and 2.005(3) Å (Table 2). The basal Cu–O bond length is 1.945(2) Å, while the apical hydroxyl oxygen donor is located, as expected, at considerably longer distance 2.297(3) Å, forming an O(2)–Cu–O(1) angle of 76.01(9)°.

The Cu–N and Cu–O bond length values are in agreement with those found in other BPCA-containing copper(II) complexes [39,41] and among these it is of interest the close comparable values found in the complex containing an oxalate anion double bridging two Cu(BPCA) entities [42].

The atoms in BPCA are practically coplanar and the dihedral angle between the pyridine planes is 4.8(2)°. The phenyl ring is oriented to form an angle of 21.51° with the pyridine N(2). These aromatic rings with a distance of 4.193 Å between their centroids may be indicative of a weak intra-molecular $\pi \cdots \pi$ stacking interaction at least in the solid state. The mononuclear units are connected through hydrogen bonds involving the MA hydroxyl group with the carboxylate oxygen of another symmetry related unit to form a one-dimensional polymer developing along axis *a*, as shown in Fig. 2 (O(1)$\cdots$O(3) distance = 2.630(4) Å, the collinear metal ions being separated by 5.515(3) Å). The crystal packing shows also non-conventional C–H$\cdots$O hydrogen bond interactions (C$\cdots$O distance of ca. 3.2 Å) occurring between BPCA carbonyl oxygens O4 and O5 and pyridyl H atoms of an adjacent array. Since the chain construction is merely due to crystallographic translation, each array contains mandelate anions of same chirality.

Table 3
H-bond parameters for complexes **1**–**3**.

D - H	A	Symmetry	D - H/Å	H. . .A/Å	D. . .A/Å	D - H. . .A/Å
Complex ***1***						
O1–H	O(3)	1 + x, y, z	0.92(4)	1.74(4)	2.630(4)	163(3)
Complex ***2***						
O1–Ha	O(2)	−x, −y, 1−z	0.83(3)	2.03(4)	2.834(4)	163(3)
O1–Hb	O(4)	1−x, −y, 1−z	0.82(3)	2.18(4)	2.910(3)	148(4)
O1–Hb	O(5)	1−x, −y, 1−z	0.82(3)	2.37(3)	2.994(3)	133(4)
Complex ***3***						
O1–H	O(3)		0.84	2.07	2.587(3)	120

3.2.2. Crystal structure of $[(BPCA)Cu^{II}(MPA)(H_2O)]$(**2**)

A perspective view of complex **2**, reported in Fig. 3, indicates the methoxy carboxylate monocoordinated to copper(II) ion. The square-pyramidal coordination geometry ($\tau = 0.066$) [40], beside the BPCA nitrogen donors, is completed by an aquo ligand at the apical position. The trend of Cu–N and Cu–O coordination bond distances is very similar to that found in **1** with a slight shortening of the apical Cu–OH_2 bond (2.255(2) Å). The C13–O2–Cu angle is 114.3(2)° (Table 2). The complex geometry is similar to the formato $[(BPCA)Cu^{II}(formato)(H_2O)]$ [39] and to two acetato $[(BPCA)Cu^{II}(acetato)(H_2O)]$ derivatives [43,44], where the Cu–OH_2 bond was found slightly elongated (ca. 2.33 Å).

The conformation adopted by the methoxy carboxylate allows the formation of infinite one-dimensional hydrogen bonded chains where metal ions are separated by 5.51 and 6.65 Å. The aquo ligand O1 plays a crucial role in connecting the complex units by means of H-bonds: on one side it links a coordinated carboxylate oxygen O2′ (O···O distance = 2.834(4) Å) and in the opposite direction, the carbonyl BPCA oxygens of another complex through a bifurcate interaction (O···O = 2.910(3), 2.994(3) Å) (Table 3). The complex units (Fig. 4) are related by centers of symmetry so that pairs of H-bond interactions are operative along the chain. Finally a methanol molecule at half occupancy is H-bond appended to the uncoordinated carboxylate oxygen (O3···O7 = 2.616(8) Å). In the same area it is also present a water molecule (occupancy = 0.5, O3···Ow = 2.938(9) Å, see Section 2). By means of H-bonds these solvent molecules (at half occupancy) eventually lead to a two-dimensional sheet arrangement of the complexes, but the disorder observed does not allow to detailing this feature further.

3.2.3. Crystal structure of $[(BPCA)Cu^{II}(BA)]_n$ (**3**)

Complex **3** exhibits a five-coordinate distorted square-pyramidal coordination geometry ($\tau = 0.067$) [40] at copper(II) defined by the BPCA imido and pyridyl nitrogen donors and by two oxygen atoms coming from two different BA ligands (Fig. 5). The coordination structural features of BPCA are comparable to those observed in complexes **1** and **2**, with the Cu–N(amide) bond distance (1.935(2) Å) slightly shorter with respect to the Cu–N(py) ones of 1.983(2) and 1.979(2) Å (Table 2). The dihedral angle between the pyridine mean planes is 7.42(5)°. Here the benzilate acts as

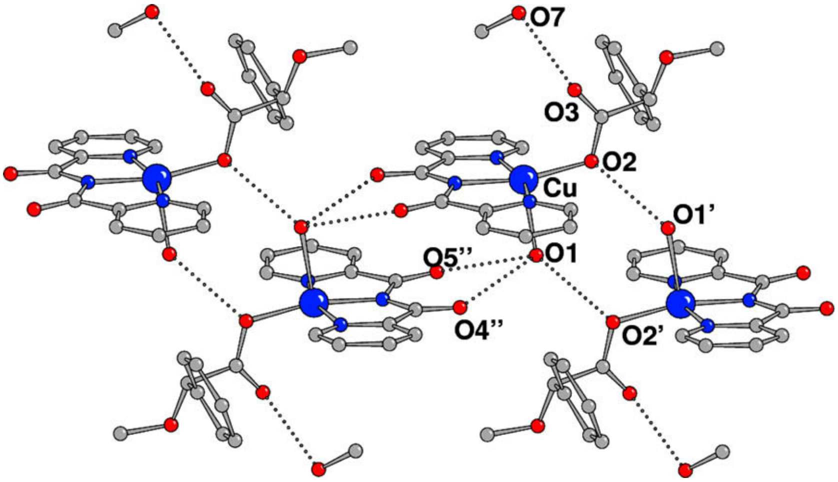


Fig. 4. Crystal packing of **2** showing one-dimensional polymer running parallel to axis *a* formed by H-bonds (Symmetry codes: (‘) at $-x$, $-y$, $1-z$, (“) at $1-x$, $-y$, $1-z$; O7 is a disordered methanol oxygen).

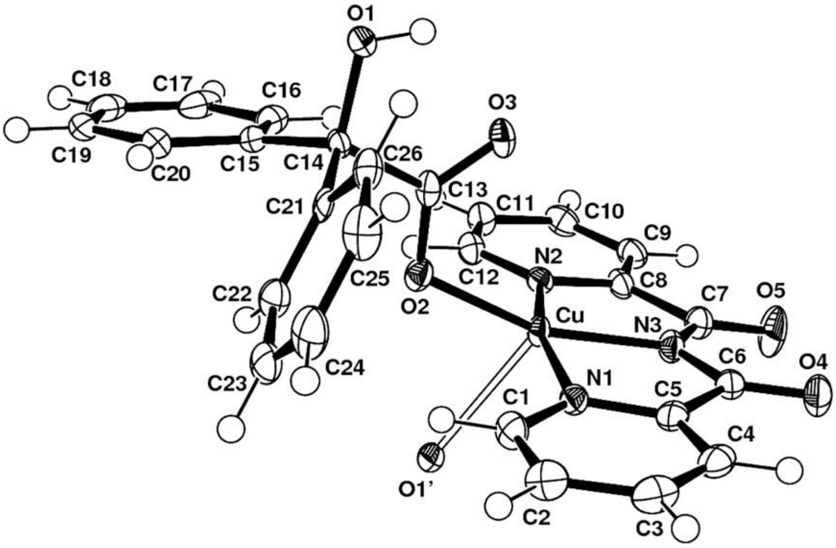


Fig. 5. ORTEP drawing of the monomeric unit forming the coordination polymer in **3** (O1′ at $-x+1$, $y-1/2$, $-z+1/2$).

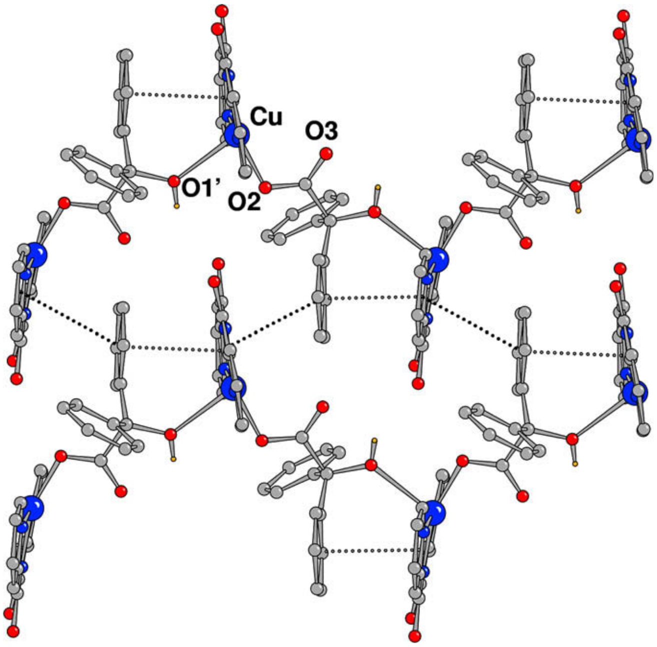


Fig. 6. Crystal packing of **3** viewed approx. down [1 0 1] direction with indication of the intra- and inter-chain π–π stacking interactions. The one-dimensional coordination polymers run parallel to axis *b*.

bridging ligand between two metal centers through a carboxylate oxygen (Cu–O(2) 1.959(2) Å) and the hydroxyl oxygen O1 that completes the square-pyramidal coordination sphere of the metal (Cu–O(1′) 2.482(2) Å). The hydroxyl group, which behaves as efficient group to stabilize the supramolecular structure in **1**, is positioned at a distance of 2.587(3) Å from oxygen O3 with the O1–H···O3 angle of 120° (Fig. 5).

Thus in the present case the behavior of BA is responsible for the formation of a one-dimensional zigzag coordination polymer, running along axis *b* (Fig. 6). The metal ions are spaced by 7.546 Å and the intermetallic angle is 114.71°. As a matter of fact the rather long Cu–O(1′) distance (2.482(2) Å), as observed in a coordination polymeric complex $[Cu(BA)_2(1,10\text{-phen})]_n$ [32], is such to allow the formation of intra- and inter-chain face-to-face π···π stacking interactions (Fig. 6), between the BPCA pyridine N1 and a BA phenyl ring (centroid-to-centroid distances of 3.556(2), 3.600(2) Å, dihedral angles between the ring planes of 5.19 and 8.86°, respectively), that contribute in stabilizing the coordination polymer.

4. Conclusions

We have isolated and structurally characterized three copper(II) complexes supported by a tridentate nitrogen donor ligand and α-hydroxy- or α-methoxy carboxylate anions. The anionic ligands manifest different denticity towards the metal ions resulting in different supramolecular structures. The crystal packing of mandelate and α-methoxy phenylacetate complexes evidences one-dimensional polymeric chains formed through H-bonds, but the presence of an aquo ligand in the latter complex leads to chain of different topology. On the other hand benzilate anions bridge copper(II) ions obtaining coordination chain stabilized by aromatic/heteroaromatic π···π interactions.

Supplementary data

CCDC 724059, 724060, and 724061 contains the supplementary crystallographic data for this paper. 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.

Acknowledgments

We are grateful to the Department of Science and Technology (DST), Government of India (Project: SR/S1/IC-10/2006) and PRIN 2007HMTJWP_002 (Rome) for the financial support. Crystal structure determination was performed at the DST-funded National Single Crystal Diffractometer Facility at the Department of Inorganic Chemistry, IACS. P.H. acknowledges Council of Scientific and Industrial Research (CSIR), India for a fellowship.

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