

Chiral and achiral 1D copper(II) coordination polymers based on glycolato and chelating aromatic diamine ligands

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Rosa Carballo^{*a}, Alfonso Castiñeiras^b, Berta Covelo^a, Ana B. Lago^{‡*a}, Ezequiel M. Vázquez-López^a, Olaya Gómez-Paz^a, Susana Balboa^b and Inmaculada Prieto^c

Achiral glycolic acid and chelating aromatic diamine ligands were employed at room temperature to prepare five 1D copper(II) coordination polymers which were structurally characterized. The polymers $\infty^1\{\text{Cu}(\text{HG})(\text{dipyam})\}(\text{HG})$ (**1**) (dipyam = 2,2'-dipyridylamine) and $\infty^1\{\text{Cu}(\text{HG})(\text{ClO}_4)(\text{NN})\}$ (NN = 2,2'-bipyridine (**2**), NN = 1,10-phenanthroline (**3**)) adopt homochiral helical structures in the crystal state and undergo spontaneous chiral resolution in the solid state. On the other hand, the polymers containing bideprotonated glycolato ligand G, $\infty^1\{\text{Cu}(\text{G})(\text{dipyam})\} \cdot \text{H}_2\text{O}$ (**1a**), obtained from a solution of **1** in MeOH/PrOH and $\infty^1\{\text{Cu}_2(\mu\text{-G})(\text{ClO}_4)(\text{H}_2\text{O})(\text{dipyam})_2\}(\text{ClO}_4)(\text{H}_2\text{O})_2$ (**4b**) are achiral. Crystals of **4b** have been obtained together with crystals of the molecular complex $[\text{Cu}(\text{HG})(\text{H}_2\text{O})(\text{dipyam})](\text{ClO}_4)$ (**4a**). Analysis by Hirshfeld surface generation and two-dimensional fingerprinting was carried out to study the nature of the interactions and their contributions towards the crystal packing.

Introduction

In recent years there has been intense research on the synthesis and characterization of coordination polymers of transition metals and this has led to significant advances in their theoretical description and the search for potential applications [1]. A commonly used strategy to obtain coordination polymers is the selection of ligands that can divergently coordinate metal ions and, if the ligand provides potential intermolecular interaction sites, the dimensionality of the coordination polymer can be increased by supramolecular interactions. In this sense, the possibilities of α -hydroxycarboxylato anions as bridging ligands [2] have been explored. Several papers have been published on the formation of 2D and 3D coordination polymers that contain as the only ligand a bridging α -hydroxycarboxylato anion: $\infty^2\{\text{Cu}(\text{HG})_2\}$ [**3a**], $\infty^3\{\text{Pb}(\text{HG})_2\}$ [**3b**], $\infty^2\{\text{Ag}_2(\text{HG})_2\} \cdot 1/2\text{H}_2\text{O}$ [**3c**],

$\infty^2\{\text{Co}(\text{HG})_2\}$ [**3d**] and $\infty^2\{\text{Zn}(\text{HL})_2\}$ [**3e**], where HG = glycolato and HL = lactate, which are the smallest α -hydroxycarboxylato anions. A number of interesting mixed ligand complexes containing bridging glycolato or lactate have also been reported: the chiral 2D coordination polymer (S-(–)-lactate)(isonicotinato)zinc(II) [4] and the cyclic tetranuclear complexes $[\text{Cu}_4(\text{HG})_4(\text{NN})_4](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$; NN = 2,2'-bipy; phen [5,6]. In this respect, previous work by our group on copper(II) complexes that contain both glycolato and chelating N,N-diamine ligands allowed the preparation and characterization of several types of compounds and these are summarized in Table 1. Discrete mononuclear [7,8] and dinuclear [9] compounds were isolated as well as a 1D polymeric compound containing glycolato and oxalato mixed ligands [9]. These previous and diverse results in the investigation of the copper(II)/glycolato/chelating aromatic N,N-diamine system show the great versatility of the small anion glycolato to generate discrete or polymeric metal complexes. This fact stimulated our interest in the exploration of new reactions to yield novel compounds. We report here the synthesis and structural characterization of five new 1D coordination polymers: $\infty^1\{\text{Cu}(\text{HG})(\text{dipyam})\}(\text{HG})$ (**1**), $\infty^1\{\text{Cu}(\text{G})(\text{dipyam})\} \cdot \text{H}_2\text{O}$ (**1a**), (dipyam = 2,2'-dipyridylamine); $\infty^1\{\text{Cu}(\text{HG})(\text{ClO}_4)(\text{NN})\}$ (NN = 2,2'-bipyridine (**2**), NN = 1,10-phenanthroline (**3**)) and $\infty^1\{\text{Cu}_2(\mu\text{-G})(\text{ClO}_4)(\text{H}_2\text{O})(\text{dipyam})_2\}(\text{ClO}_4)(\text{H}_2\text{O})_2$ (**4b**) which has been obtained together with the molecular compound $[\text{Cu}(\text{HG})(\text{H}_2\text{O})(\text{dipyam})](\text{ClO}_4)$ (**4a**). The most striking feature of complexes **1**, **2** and **3** is that each single crystal is spontaneously resolved as chiral in the solid state and this

^a Departamento de Química Inorgánica, Instituto de Investigación Sanitaria Galicia Sur (IISGS)- Universidade de Vigo, 36310 Vigo, Galicia, Spain.

e-mail: rcrial@uvigo.es A. B. Lago, e-mail: ablago@uvigo.es

^b Departamento de Química Inorgánica, Facultade de Farmacia, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Galicia, Spain.

^c Departamento de Química Física, Facultade de Química, Universidade de Vigo, 36310 Vigo, Galicia, Spain.

[†] CCDC 1824713–1824718. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ce00279g

[‡] Current address: Laboratorio de Rayos X y Materiales Moleculares,

Departamento de Física Fundamental, Facultad de Ciencias Universidad de La Laguna. Avda. Astrofísico Francisco Sánchez s/n. 38204 La Laguna, Tenerife, Spain

leads to the formation of three chiral coordination polymers generated from achiral ligands without any chiral auxiliary. It should be noted that the construction of chiral crystals from achiral components is difficult because molecules intrinsically assemble to cancel out their polarity and asymmetric properties. In the literature there are some examples of the formation of chiral 1D coordination polymers from achiral components [11] but this phenomenon remains unusual in coordination chemistry.

Table 1. Known complexes in the copper(II)/glycolato/aromatic N,N-diamine system^a

Compound/ [Reference]/Synthesis	Glycolato coordination mode/metal environment	Species/ space group
$[Cu(HG)(NN)(NO_3)]_4$ [5,6] $Cu(NO_3)_2 \cdot H_2G/NN/NaHCO_3$ 1:1:1:1; RT; $H_2O/MeOH$ or EtOH	Chelate bridging HG^- SPY-5	Tetramer $P-42_1c$ $I4_1/a$
$[Cu(HG)(phen)_2]HG \cdot H_2G \cdot CH_3CN$ [7] $CuCO_3 \cdot Cu(OH)_2 \cdot H_2G/phen$ 1:4.5:2.2; 75 °C; EtOH/ CH_3CN	Monodentate HG^- , counterion HG^- , solvate H_2G SPY-5	Monomer $P2_1/c$
$[Cu(HG)_2(bipy)]$ [8] $CuCO_3 \cdot Cu(OH)_2 \cdot H_2G/bipy$ 1:4.5:2.2; reflux; EtOH/ CH_3CN - H_2O	Chelating HG^- OC-6	Monomer $P\bar{1}$
$\{[Cu(G)_{1-x}(ox)_x(bipy)] \cdot 2.5H_2O\}$ $x =$ 0.56 or 0.71; ox = oxalate [8] $CuCO_3 \cdot Cu(OH)_2 \cdot H_2G/bipy$ 1:1:1 and 1.1:2.3:4.5; reflux; H_2O	Chelate bridging G^{2-} SPY-5	1D polymer $P\bar{1}$
$[CuG(bipy)]_2 \cdot nH_2O$ [9] $CuCO_3 \cdot Cu(OH)_2 \cdot H_2G/bipy$ 1:2:2; reflux; EtOH	Chelate bridging G^{2-} SPY-5	Dimer $P\bar{1}$; $C2/c$
$[Cu(HG)_2(phen)]$ [10] $CuAc_2 \cdot H_2G/phen$ 1:2:1; RT; $H_2O/MeOH$	Chelating HG^- OC-6	Monomer $C2/c$

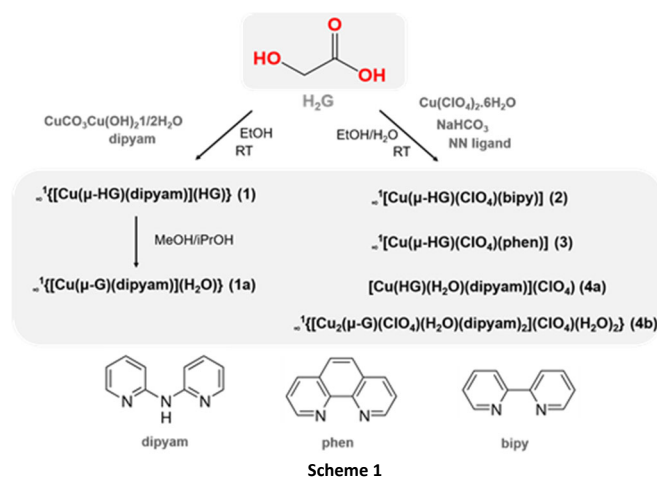
^aNN = phen, bipy (bipy = 2,2'-bipyridine, phen = 1,10-phenanthroline); SPY-5 : square pyramid; OC-6: octahedron. [12]

Results and discussion

The previously isolated monomeric, dimeric, tetrameric and polymeric complexes (Table 1) based on the Cu(II)/glycolato/chelating aromatic diamines show that slight variations in the reaction conditions have a significant effect on the resulting solid state structure since the glycolate anion can adopt different coordination modes such as monodentate HG^- , O,O' -chelating HG^- and O,O' -chelate bridging HG^- or G^{2-} . In view of these previous results we investigated new reactions at room temperature in EtOH (Scheme 1).

The reaction between $CuCO_3 \cdot Cu(OH)_2 \cdot 1/2H_2O$ and glycolic acid (H_2G) in the presence of 2,2'-dipyridylamine (dipyam) resulted in the formation of a green powdery solid of formula $\{[Cu(\mu-HG)(dipyam)](HG)\}_n$ (**1**). When a small amount of **1** was dissolved in MeOH/iPrOH (1:1), green crystals of **1** and blue crystals of $\{[Cu(G)(dipyam)] \cdot H_2O\}$ **1a** were deposited upon slow evaporation of the solvent. Consequently, compound **1a** is formed from compound **1** after several days in solution. The formation of **1a** from **1** involves

two main changes: (i) the deprotonation of the hydroxyl group of the coordinated glycolato ligand and (ii) in the outer coordination sphere the replacement of glycolato by a water molecule. Since this transformation takes place in solution and stops when the crystals are taken out of the solution, the mechanism is very probably a solvent-assisted one. Compounds of general formula $[Cu(ClO_4)(HG)(NN)]$ (NN = bipy (**2**), NN = phen (**3**)) were obtained as blue powders and single crystals from the reaction of glycolic acid (H_2G), $NaHCO_3$, $Cu(ClO_4)_2$ and 2,2'-bipyridine or phenanthroline. Nevertheless, the same reaction with 2,2'-dipyridylamine give rise to the diprotonated glycolato (G^{2-}) ligand in the polymeric complex **4b** mixed with the HG^- form in the molecular complex **4a**. Moreover, when the same mixture of reagents was irradiated in a microwave oven the resulting crystals after evaporation at room temperature correspond to **4a** and to blue-violet crystals of $[Cu(dipyam)_2](ClO_4)_2$ [12a]. It is interesting to note that the diprotonated G^{2-} ligand is only present in the complexes with 2,2'-dipyridylamine and only these compounds incorporate water molecules in the second coordination sphere (**1a** and **4b**) or also as ligand (**4b**). All of the isolated copper complexes are air stable.



The IR spectra of all complexes contain bands in the 3200–3500 cm^{-1} region corresponding to the OH stretching vibration of the HG^- ligand in **1–3** and **4a**, crystallization water in **1a** and the NH stretching vibration in **1**, **1a** and **4a**. The precise identification of the carboxylate bands is complicated by the presence in the same region of the spectrum of bands due to the aromatic amine ligands but the bands close to 1600 cm^{-1} can be attributed to $\nu_{asym}(OCO)$ and those around 1400 cm^{-1} to $\nu_{sym}(OCO)$. The difference between the asymmetric and symmetric stretching vibrations is in the range 147–163 cm^{-1} and this suggests bidentate bridging behavior of the carboxylate groups [13]. The IR spectra of complexes **2** and **3** contain bands that are characteristic of monodentate perchlorate groups [14]. The electronic spectra of complexes **1–3** obtained by diffuse reflectance show a broad band, centered in the range 14000–15000 cm^{-1} , that can be attributed to d-d transitions [15].

The room temperature magnetic moments of 1.80 B.M. for **1** and 1.82 B.M. for **1a** fall in the range expected for essentially magnetically diluted d^9 species but the values of 1.59 B.M. (**2**) and

1.52 B.M. (**3**) are lower than the spin only value (1.73 B.M.), thus suggesting the possibility of antiferromagnetic coupling between metal centers.

The EPR spectrum of **1** displays a rhombic pattern ($g_1 = 2.20$, $g_2 = 2.08$, $g_3 = 2.03$) and this is consistent with the trigonal-bipyramidal stereochemistry [15] confirmed by the X-ray data. However, closer examination of the g values suggests a roughly axial situation where g_1 can be assimilated with $g_{||}$, while g_2 and g_3 , which are close one to another, would be related to the equatorial plane. The X-band EPR spectra at room temperature for crystalline samples of compounds **2** and **3** are typical of axial symmetry with $g_{||} = 2.23$ and $g_{\perp} = 2.06$. These axial spectra, with $g_{||} > g_{\perp}$, indicate that the unpaired electron occupies a $d_{x^2-y^2}$ orbital and this suggests an elongated octahedral environment around Cu(II) [15], which is in good agreement with the X-ray data presented below. According to the criterion of Kivelson and Neiman [16], M–L bonds in compounds with $g_{||} \leq 2.3$ indicate a covalent character, so in these complexes a covalent character can be suggested for the metal–ligand bond.

Reaction of $\text{Cu}(\text{ClO}_4)_2$ with 2,2'-dipyridylamine under different synthetic conditions give rise to mixed phase products that make spectroscopic or magnetic studies of pure phases difficult to perform. Nevertheless, **4a** that is the majority compound in all the synthetic procedures, could be separated by hand to perform IR studies.

Crystal structures

Selected interatomic distances and angles are listed in Table 2 and the main hydrogen bonds are provided in Table 3.

The X-ray crystal structure analysis of compounds **2** and **3** revealed that they are isomorphous with very similar cell parameters. Complexes **1** and **2–3** crystallized in the monoclinic $P2_1$ and orthorhombic $P2_12_12_1$ chiral space groups, respectively. The analysis unambiguously established their absolute stereochemistry by refinement of the corresponding Flack parameters (Table 5) [17], which indicate the enantiomeric purity of the single crystals. Nevertheless the polymers **1a** and **4b** crystallized in the orthorhombic $Pbca$ and monoclinic $P2_1/c$ non chiral space groups, respectively.

The copper(II) compounds **1**, **1a**, **2**, **3** and **4b** are 1D coordination polymers constructed from similar achiral building units, but in the crystals of **1**, **2** and **3** a spontaneous chiral resolution occurs and this phenomenon has only rarely been observed for coordination polymers [18]. **4a** is the only molecular compound obtained in this work.

The 1D coordination polymers consist of cationic units $[\text{Cu}(\text{HG})(\text{dipyam})]^+$ in **1** and $[\text{Cu}_2(\text{G})(\text{ClO}_4)(\text{dipyam})_2(\text{H}_2\text{O})]^+$ in **4b**, neutral units $[\text{Cu}(\text{G})(\text{dipyam})]$ in **1a** and neutral $[\text{Cu}(\text{HG})(\text{ClO}_4)(\text{NN})]$ in **2** and **3**. The mononuclear **4a** contains the cationic units $[\text{Cu}(\text{HG})(\text{H}_2\text{O})(\text{dipyam})]^+$.

In **1** and **1a** (Figures 1 and 2), each copper atom is bound to the bidentate 2,2'-dipyridylamine and one glycolato anionic ligand through the hydroxyl function (O13), which is deprotonated in **1a**, and two oxygen atoms of two carboxylate groups; one of these, O12, arises from the glycolato ligand of a neighboring Cu atom. As such, the glycolato ligand behaves as a bidentate chelating bridge through the carboxylate in a *syn,anti* fashion. In complex **1** the glycolato ligand (HG^-) acts as a monoanion and in **1a** (G^{2-}) it is a dianion. In the two complexes the pentacoordinated metal ions have different coordination geometries and these were evaluated using the Addison parameter τ [19]: 0.67 for **1** and 0.06 for **1a**. Compound **1** has a 3+2 coordination with a geometry close to trigonal bipyramidal, with axial Cu–O11 and Cu–N2 distances (1.953(2) and 1.964(2) Å) that are shorter than the equatorial ones (ranging between 2.017–2.133 Å). In **1a** the resulting coordination polyhedron is a square pyramid in which the apical position is occupied by the carboxyl O12 atom with a Cu–O12 distance of 2.417(2) Å. The stereochemical descriptor [priority order 1, O11; 2, O12; 3, O13; 4, N1, N2] [20] for compound **1** is BPTY-5-14-C and for **1a** is SPY-5-24 (the centrosymmetric nature of the crystal mean that both configurations C/A are present).

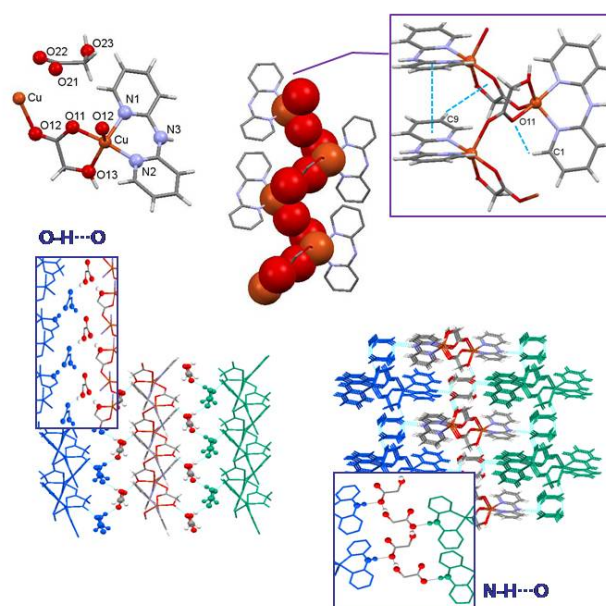


Figure 1. Compound **1** (BPTY-5-14-C), views of the coordination environment around Cu(II), the 1D helix and the supramolecular association of the helices.

In the isomorphous compounds **2** and **3** (compound **3** is shown in Figure 3) the copper atoms are hexacoordinated by an N,N-chelating aromatic diamine (2,2'-bipyridine or 1,10-phenanthroline), one bidentate chelating monoanionic glycolato ligand HG^- acting as a bridge through the carboxylate group in a *syn,anti* fashion as in compounds **1** and **1a**, and one oxygen atom of a perchlorate anion. In both cases the coordination geometry corresponds to an elongated octahedron due to the Jahn–Teller effect. This elongation involves the axial Cu– $\text{O}_{\text{hydroxyl}}$ and Cu– $\text{O}_{\text{perchlorate}}$ bonds with distances in the range 2.445(2)–2.479(6) Å and average equatorial distances of 1.987 Å in **2** and 1.993 Å in **3**.

The stereochemical descriptors [20] are OC-6-45-C for **2** and OC-6-45-A for **3** (priority order 1, O21; 2, O11; 3, O12; 4, O13; 5, N11, N13). The coordination polyhedra of **2** and **3** are further stabilized by means of anion- π interactions (in Figure 3 for compound **3**) involving one oxygen atom of a coordinated perchlorate anion and the metal chelate ring with the N,N-diamine ligand. The O-centroid distances are 3.3388 Å (**2**) and 3.2600 Å (**3**) and the Cl–O–centroid angles are 96° (**2**) and 95° (**3**). These values are similar to those observed in other systems with perchlorate-aromatic plane interactions [21]. This kind of π interaction is not usually described and provides evidence of the metalloaromaticity or aromatic character of the corresponding metal chelate ring.

In **4b** (Figure 4) there are two coordinatively different copper metal centers linked by one dianionic (G^{2-}) glycolato which acts as tridentate chelating bridge ligand through the carboxylate in a *syn,anti* fashion and the deprotonated hydroxyl group. In this way, Cu2 is chelated by the G^{2-} ligand and the deprotonated hydroxyl group (O13) additionally coordinates Cu1, which is also coordinated by the carboxylate oxygen not involved in chelation (O12). Each copper atom is also bounded to one bidentate 2,2'-dipyridylamine ligand and one oxygen atom belonging to one water molecule in Cu1 and one perchlorate anion in Cu2.

Table 2. Selected bond lengths (Å) and bond angles (°).

Compound	1	1a (i = x+1/2, y, -z+1/2)	2	3	4a	4b (i = 1 - x+1, y-1/2, -z+3/2)
Cu–O11	1.953(2)	1.964(2)	1.979(2)	1.985(4)	1.9484(10)	1.940(2)
Cu–O12/O12'	2.133(2)	2.417(2)	1.989(2)	1.978(4)		1.981(2)
Cu1–O13	2.017(2)	1.9058(19)	2.445(2)	2.450(5)	2.0843(10)	1.951(2)
Cu2–O13						1.936(2)
Cu–N1/N11	2.020(2)	1.985(2)	2.007(3)	2.022(5)	1.9898(12)	Cu2–N1/N2 1.986(3) / 1.971(2)
Cu–N2/N12	1.964(2)	1.992(2)	1.973(2)	1.988(5)	1.9621(12)	Cu1–N4/N5 2.006(3) / 1.987(3)
Cu–O21 Cu2–O1A Cu1–O1W			2.464(3)	2.479(6)	2.1456(12)	2.525(3) 2.213(2)
O11–Cu–N2/N12	172.31(10)	172.05(9)	176.06(10)	176.3(2)	173.03(5)	93.4(1) / 171.6(1)
O11–Cu–O13	80.51(10)	85.47(8)	74.54(8)	74.39(17)	81.75(4)	83.66(9)
N2/N12–Cu–O13	91.81(10)	91.61(8)	103.91(8)	106.16(17)	94.19(5)	89.07(9) / 166.42(9)
N4/N5–Cu1–O13	93.69(10)	91.16(8)	94.43(9)	93.4(2)	93.49(5)	
O11–Cu–N1/N11	93.69(10)	91.16(8)	94.43(9)	93.4(2)	93.49(5)	
N2/N12–Cu–N1/N11			81.90(10)	83.0(2)	93.27(5)	88.0(1) / 92.1(1)
N4–Cu1–N5	91.40(10)	90.27(9)				
N1–Cu2–N2						
O13–Cu–N1/N11	131.13(12)	168.51(9)	89.88(8)	90.04(17)	139.30(5)	162.7(1) / 93.0(1)
O13–Cu2–N1/N2						
O11–Cu–O12/O12'	91.14(10)	88.14(8)	91.34(9)	91.75(19)		
N2/N12–Cu–O12/O12'	93.93(10)	99.35(8)	92.38(9)	91.8(2)		159.6(1) / 87.8(1)
N4/N5–Cu1–O12						
O13–Cu–O12/O12'	131.09(11)	91.76(8)	93.77(8)	95.42(17)		90.31(9)
N1/N11–Cu–O12/O12'	97.25(9)	99.12(8)	173.82(9)	173.36(19)		
N2/N12–Cu–O21			94.71(10)	91.8(2)		97.9(1) / 84.6(1)
O1A–Cu2–N1/N2						
O11–Cu–O21			86.55(8)	87.1(2)		88.39(9)
O1A–Cu2–O11						
O12–Cu–O21			90.38(9)	92.6(2)		
N1/N11–Cu–O21			87.79(10)	83.5(2)		

	160.71(8)	160.04(17)	99.02(9)
O13–Cu–O21			
O1A–Cu2–O13			
O1W–Cu1–O13		90.80(5)	99.45(9)
O1W–Cu1–N4/N5		129.13(5) / 90.21(5)	93.2(1) / 94.0(1)
O1W–Cu1–N1/N2			
O1W–Cu1–O12		84.22(4)	106.96(9)
O1W–Cu1–O11			
τ	0.67	0.06	0.56
			0.11 (Cu1) / 0.15 (Cu2)

Table 3. Main hydrogen bonds (Å) and angles (°).

D–H...A	D–H	H...A	D...A	D–H...A
Compound 1				
Intrachain				
C1–H1...O11	0.93	2.51	2.978(4)	111.4
Interchain				
O23–H23...O21 ⁱⁱⁱ	0.82	1.93	2.746(3)	171.7
O13–H13...O22 ⁱ	0.837(18)	1.73(2)	2.536(3)	162(3)
N3–H3B...O21 ^{iv}	0.842(16)	1.943(17)	2.783(3)	176(3)
C7–H7...O21 ^{iv}	0.93	2.59	3.309(4)	134.7
C12–H12A...O23 ⁱ	0.97	2.46	3.219(4)	134.8
i = -x+2, y-1/2, -z+1; iii = -x+1, y+1/2, -z; iv = x, y, z+1				
Compound 1a				
Intrachain				
C1–H1...O11	0.93	2.44	2.877(4)	108.4
C10–H10...O13	0.93	2.46	2.890(4)	108.1
Interchain				
O1W–H1B...O13 ⁱⁱⁱ	0.77(4)	1.88(4)	2.647(3)	174(4)
O1W–H1A...O12 ⁱ	0.76(4)	2.07(4)	2.815(3)	171(4)
N3–H3B...O1W ^{iv}	0.77(4)	2.00(3)	2.763(3)	172(3)
C3–H3...O12 ^v	0.93	2.52	3.413(4)	160.9
i = x+1/2, y, -z+1/2; iii = x+1, y, z; iv = x-1/2, -y+1/2, -z+1, v = -x, y+1/2, -z+1/2				
Compound 2				
Intrachain				
O13–H13A...O11 ⁱ	0.78	2.00	2.700(3)	149.0
C19–H19...O22 ⁱⁱ	0.94	2.47	3.348(4)	155.9
C20–H20...O12	0.91	2.42	2.985(4)	119.8
C11–H11...O11	0.91	2.62	3.127(4)	116.2
Interchain				
C14–H14...O24 ⁱⁱⁱ	0.91	2.65	3.406(5)	140.4
C17–H17...O23 ^{iv}	0.93	2.60	3.091(4)	113
i = x-1/2, -y+1/2, ii = -1+x, y, z -z, iii = -x+3/2, -y, z+1/2, iv = 1/2-x, -y, 1/2+z				
Compound 3				
Intrachain				
O13–H13A...O11 ⁱ	0.82	1.96	2.710(7)	152.3
C2–H2B...O21 ⁱ	0.97	2.54	3.308(9)	136.5
C20–H20...O12 ⁱ	0.93	2.53	3.030(6)	114
C20–H20...O21 ⁱⁱ	0.93	2.64	3.332(10)	131.3
Interchain				
C15–H15...O22 ⁱⁱⁱ	1.08	2.37	3.256(8)	138
C18–H18...O23 ^{iv}	1.03	2.43	3.031(6)	132
i = x+1/2, -y+1/2, -z, ii = x+1, y, z, iii = 1/2-x, 1-y, 1/2+z, iv = 3/2-x, 1-y, 1/2+z				
Compound 4a				
O1w–H1wA...O4 ⁱ	0.79(3)	2.02(2)	2.7993(17)	169(3)
O1w–H1wB...O1	0.76(2)	2.02(2)	2.7670(17)	170(2)
N3–H3...O12 ⁱⁱ	0.79(2)	2.06(2)	2.8412(17)	171.3(19)
O13–H13...O12 ⁱⁱⁱ	0.84(2)	1.76(3)	2.5971(15)	173(2)
i = -x, 1-y, 1-z; ii = 1/2+x, 1/2-y, 1/2+z; iii = 1/2-x, -1/2+y, 1/2-z				
Compound 4b				
Intrachain				
O1w–H1wA...O4 ⁱ	0.83(3)	1.98(3)	2.809(4)	175(4)
C101–H101...O11	0.95	2.26	2.860(4)	120
C110–H110...O13	0.95	2.48	2.914(4)	108
Interchain				
O1w–H1wB...O8 ⁱⁱ	0.84(4)	2.11(4)	2.935(3)	167(4)
N3–H3...O6	0.84(3)	2.12(3)	2.905(4)	156(3)
O2w–H2wA...O3w	0.86(4)	2.03(4)	2.713(4)	136(4)
O2w–H2wB...O2A ⁱⁱⁱ	0.84(3)	2.15(3)	2.910(4)	151(4)
O3w–H3wA...O2w ^{iv}	0.87(5)	1.99(5)	2.831(4)	162(5)
O3w–H3wB...O5	0.88(4)	1.98(4)	2.851(4)	177(6)
N6–H6...O2w	0.85(3)	2.06(4)	2.901(4)	168(4)
i = 1-x, 1/2+y, 3/2-z; ii = x, 1/2-y, 1/2+z; iii = -1+x, y, z; iv = -x, -y, 1-z				

Both pentacoordinated metal centers are in square pyramidal coordination polyhedron (Addison parameter τ [19] 0.11 for Cu1 and 0.15 for Cu2) with the apical position occupied by the O1w

atom from the water molecule or by the O1A atom from the perchlorate anion with Cu–O distances of 2.213(2) Å and 2.525(3) Å, respectively. The stereochemical descriptor [20] for both metal centers is SPY-5-34A (Cu1, priority order 1, O12; 2, O13; 3, O1w; 4, N4, N5; Cu2, priority order 1, O11; 2, O13; 3, O1A; 4, N1, N2) showing that each chain is chiral but the presence of chains of opposite chirality produces an achiral crystal.

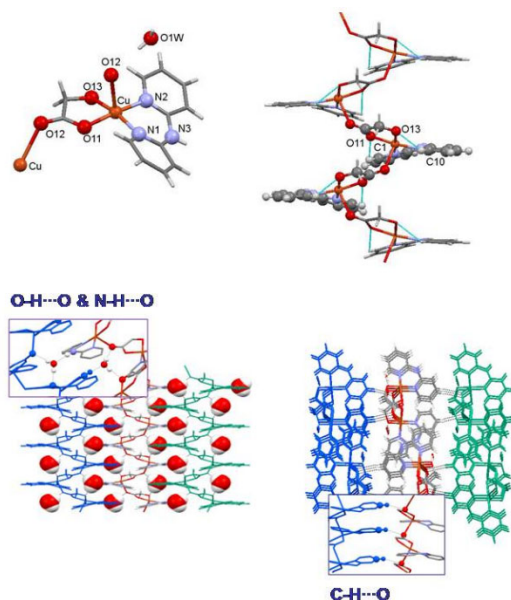


Figure 2. Compound **1a** (SPY-5-24), views of the coordination environment around Cu(II), the 1D chain and the supramolecular association.

The cationic unit in the molecular compound **4a** (Figure 5) presents structural similarities with the cationic unit observed in the polymer **1**. As in compound **1**, **4a** shows a coordination geometry close to trigonal bipyramidal (Addison parameter τ [19]: 0.56), with axial Cu–O11 and Cu–N2 bonds. As in **1**, the stereochemical descriptor [20] for **4a** is BPTY-5-14. The coordination polyhedron of **4a** is stabilized by a H(H₂O)- π interaction (Figure 5) involving the coordinated water molecule and the metal glycolato chelate ring. The H-centroid distance is 2.67 Å and the O–H–centroid angle is 78°. Again, this kind of π interaction is not usually described in a coordination compound and provides evidence of the metalloaromaticity of the corresponding metal chelate ring.

In polymeric complexes **1**, **1a**, **2** and **4b**, the Cu–O_{carboxy} distances in the chelate ring are shorter than the Cu–O_{carboxy} distances in the bridge and this is more asymmetric in compound **1a**, which contains G²⁻, with a particularly long Cu–O_{carboxy} distance (2.417(2) Å) in the bridge. However, in compound **3** the two Cu–O_{carboxy} distances are very similar, with the distance involved in the bridging role being slightly shorter (Table 2). Due to its bridging character, the carboxylate groups of the glycolato ligands have a delocalized π system rather than a formal double bond (C–O distances between 1.239(4) Å and 1.270(3) Å). In **1**, the carboxylate group of the ionic glycolato, with C–O distances of 1.258(4) and 1.248(3) Å, also has a delocalized π system due to its involvement in strong hydrogen bonds (Table 3). The distances between the copper atoms bridged by the carboxylate groups are around 5.20 Å in **1**, **2**, **3** and **4b** but in **1a** this distance is slightly longer (5.5891(8) Å). In **4b**, the distance between copper atoms bridged by the deprotonated hydroxyl group is around 3.508 Å.

Table 4. Crystal data and structure refinement

Compound	1	1a	2	3	4a	4b
Empirical formula	C ₁₂ H ₁₅ N ₃ O ₆ Cu	C ₁₂ H ₁₃ N ₃ O ₄ Cu	C ₁₂ H ₁₁ N ₂ O ₇ CuCl	C ₁₄ H ₁₁ N ₂ O ₇ CuCl	C ₁₂ H ₁₄ N ₃ O ₈ CuCl	C ₂₂ H ₂₆ N ₆ O ₁₄ Cu ₂ Cl ₂
Formula weight	360.81	326.79	394.22	418.24	427.25	796.47
Temperature (K)	293	293	293	293	100	100
Wavelength (Å)	0.71073	0.71073	0.71073	1.54184	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	P2 ₁	Pbca	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /n	P2 ₁ /c
Unit cell dimensionsa (Å)	10.3927(17)	7.0214(12)	6.5406(13)	6.4852(2)	10.2071(6)	13.1280(9)
b (Å)	7.2489(12)	18.010(3)	14.063(3)	14.3549(4)	9.4026(5)	8.7729(6)
c (Å)	11.1460(18)	19.735(3)	15.063(3)	15.7193(11)	16.5141(9)	25.0767(16)
β (°)	116.460(2)				91.226(2)	90.356(2)
V (Å ³)	751.7(2)	2495.7(7)	1385.5(5)	1463.38(12)	1584.55(15)	2888.0(3)
Z	2	8	4	4	4	4
D _{calc} (g cm ⁻³)	1.700	1.740	1.890	1.898	1.791	1.832
μ (mm ⁻¹)	1.491	1.768	1.810	4.223	1.596	1.739
F(000)	394	1336	796	844	868	1616
Crystal size	0.34x0.15x0.10	0.45x0.35x0.30	0.53x0.15x0.12	0.64x0.24x0.16	0.23x0.22x0.12	0.26x0.02x0.02
Max/min transmission	0.765/0.861	0.481-0.588	0.729/0.805	0.341/0.509	0.7457/0.6069	0.7454/0.6662
Reflections collected	4856	13769	15747	3279	23261	36559
Independent reflections	2700	2967	2837	2908	3966	5908
reflections	(R _{int} = 0.0236)	(R _{int} = 0.0402)	(R _{int} = 0.0594)	(R _{int} = 0.0538)	(R _{int} = 0.0262)	(R _{int} = 0.0633)
Goodness-of-fit on F ²	0.996	1.157	1.088	1.129	1.075	1.038
Final R indices [I > 2 σ (I)]	R1 = 0.0286 wR2 = 0.0606	R1 = 0.0445 wR2 = 0.0892	R1 = 0.0215 wR2 = 0.0542	R1 = 0.0532 wR2 = 0.1470	R1 = 0.0236 wR2 = 0.0600	R1 = 0.0379 wR2 = 0.0757
R indices (all data)	R1 = 0.0339 wR2 = 0.0622	R1 = 0.0605 wR2 = 0.0943	R1 = 0.0242 wR2 = 0.0556	R1 = 0.0556 wR2 = 0.1492	R1 = 0.0272 wR2 = 0.0616	R1 = 0.0581 wR2 = 0.0819
Flack parameter	0.003(12)		-0.001(15)	0.04(5)		
CCDC numbers						

The cationic chains of **1** and **4b** and the homochiral neutral chains of **2** and **3** run along the *b* and *a* axes, respectively, and the achiral chain of **1a** runs along the *a* axis. The pitch of the chains in **1a**, **2** and **3** corresponds to the length of *a* in the unit cell and in **1** it corresponds to the length of *b*. The achiral chain of **1a** results in alternating $\Delta\Lambda\Lambda\dots$ configurations at the metal centers. The direction of the rotation in **3** is a left-handed screw (*M*-sense) involving $\Lambda\Lambda\Lambda\dots$ configurations at the metal centers. In **1** and **2**, right-(*P*)-handed helices associated with $\Delta\Delta\Delta\dots$ configurations at the Cu atoms were structurally identified. In compound **1**, the uncoordinated glycolato anion forms a hydrogen bonded ($\text{OH}\cdots\text{O}_{\text{carboxylate}}$, Figure 1, Table 3) *P*-handed helix that runs parallel to the cationic helix.

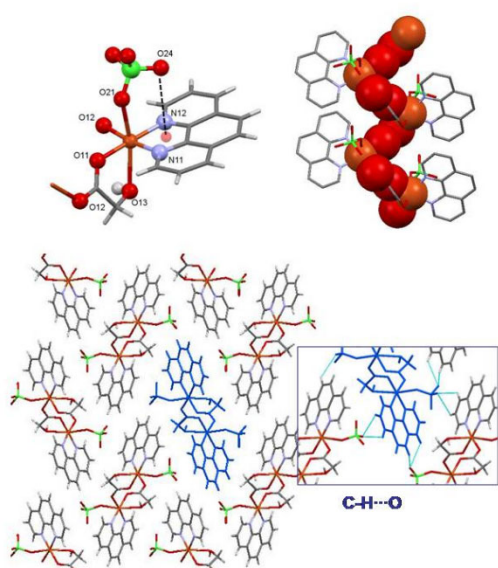


Figure 3. Compound **3** (OC-6-45-A), views of the coordination environment around Cu(II), the 1D helical chain and the supramolecular association.

The chains of compounds **1** and **1a** are stabilized by a similar intrachain C–H \cdots O hydrogen bond involving the dipyam hydrogen atom *ortho* to nitrogen, H1, and the coordinated carboxylate oxygen O11 (Table 3), with a shorter C \cdots O distance in compound **1a**, which also has another C–H \cdots O hydrogen bond involving the other dipyam hydrogen atom *ortho* to nitrogen, H10, and as acceptor the oxygen of the hydroxyl group of glycolato. In addition, the chain in compound **1** is stabilized by weak π – π interactions between the aromatic rings of the dipyam ligands, with centroid-centroid distances of 3.782 Å (**1**), and by intrachain C–H \cdots π (Cu/glycolato chelate ring) interactions with an H \cdots ring centroid distance of 3.119 Å (Figure 1). According to DFT calculations [22], this interaction may be considered as structural evidence for the metalloaromaticity of the Cu/glycolato chelate ring.

Several kinds of intrachain interactions are involved in the stabilization of the chiral chains of compounds **2** and **3**. The strongest interaction, with a donor-acceptor distance close to 2.700

Å, is the hydrogen bond between the hydroxyl (O13) of the glycolato ligand and the coordinated carboxylate oxygen (O11) of an adjacent unit. This $\text{O}_{\text{hydroxyl}}\text{--H}\cdots\text{O}_{\text{carboxylate}}$ interaction is usually found in α -hydroxycarboxylato metal complexes and it is responsible for the supramolecular assembly of monomeric and 1D polymeric units. A second type of interaction is based on $\text{C}_{\text{NN}}\text{--H}\cdots\text{O}$ hydrogen bonds (Table 3) in which the acceptor is a perchlorate oxygen or the uncoordinated carboxylate oxygen, with $\text{C--O}_{\text{perchlorate}}$ distances around 3.3 Å and $\text{C--O}_{\text{carboxylate}}$ distances close to 3.0 Å. As in the chain of compound **1**, the chains of **2** and **3** have weak π – π interactions between the aromatic rings of the diamine ligands, with centroid-centroid distances 3.6902 and 3.791 Å, which are slightly shorter than that found in **1**.

The chains in **4b** are connected to give a 3D supramolecular architecture through hydrogen bonds involving water molecules and perchlorate anion in the second coordination sphere. The two crystallographically independent free water molecules and their equivalents are associated by $\text{Ow}\cdots\text{Ow}$ hydrogen bonds forming a discrete 4-membered ring (R4) which is hydrogen bonded with the uncoordinated perchlorate anion. The $\text{O}\cdots\text{O}$ distances in this associations are in the range 2.713–2.851 Å (Table 3). This motif acts as a glue between the chains by means of $\text{N--H}\cdots\text{O}$ hydrogen bonds between the –NH group of dipyam ligands as donors and oxygen atoms of water and perchlorate motif as acceptors (Figure 4). As a result, this water-perchlorate motif is responsible for the 3D supramolecular arrangement of the structure in **4b**.

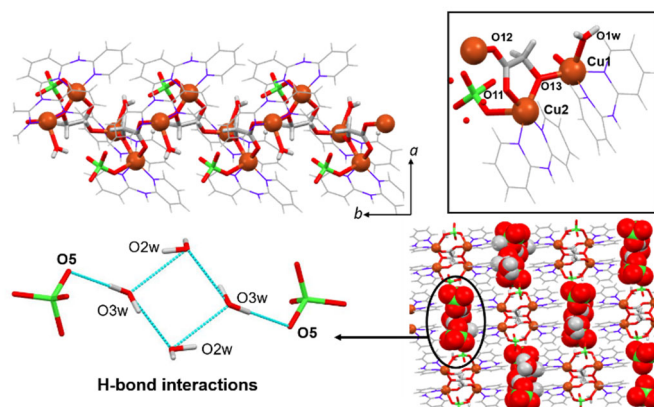


Figure 4. Top: Compound **4b**, view of the coordination environment around Cu(II) and coordination mode of glycolato anion. Down: water and perchlorate hydrogen bonds motif and final 3D supramolecular organization

The crystal packing in **1** and the consequent transfer of chirality from the 1D chiral chain to the crystal is due to several $\text{O--H}\cdots\text{O}$, $\text{N--H}\cdots\text{O}$ and $\text{C--H}\cdots\text{O}$ hydrogen bonds (Figure 1, Table 3) in which the O acceptor atom belongs to the free glycolato anion. The strongest of these hydrogen bonding interactions corresponds to $\text{O13--H13}\cdots\text{O22}$ (2.536(3) Å), which connects the 1D coordination polymer and the supramolecular chain of free glycolato anions. The packing in the achiral **1a** results from the contribution of several $\text{O--H}\cdots\text{O}$, $\text{N--H}\cdots\text{O}$ and $\text{C--H}\cdots\text{O}$ hydrogen bonds (Figure 2, Table 3) in such a way that the crystallization water molecule acts as hydrogen bond acceptor and donor (Figure 2). The $\text{D}\cdots\text{A}$ distances are

between 2.647 and 2.815 Å and the D–H...A angles between 171 and 174°, with the chains assembled into layers that are connected through a weak C–H...O bond into a 3D arrangement. In both compounds, the –NH group of the 2,2'-dipyridylamine (dipyam) ligand plays an active role in the supramolecular assembly of the chains through a hydrogen bonding interaction with the free glycolate anion in **1** and with the crystallization water in **1a**.

The chiral chains of compounds **2** and **3** are packed into chiral crystals by means of C–H...O hydrogen bonds (Figure 3, Table 3) in which the acceptors are perchlorate oxygen atoms.

The monomers in **4a** are connected to give a 3D supramolecular architecture through hydrogen bonds involving coordinated water molecule and perchlorate anion and the –NH group of dipyam ligand that establish interactions with the O12 oxygen atom of the glycolate anion.

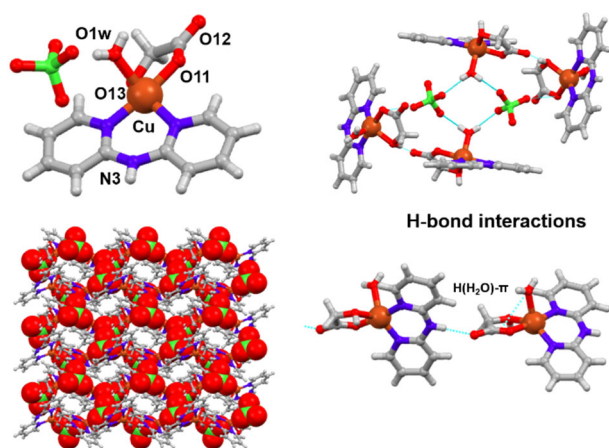


Figure 5. Compound **4a**, view of the monomer and the coordination environment around Cu(II). Main hydrogen bonds interactions and the final 3D supramolecular organization

Hirshfeld surface study

Hirshfeld surface studies are used to gain a fuller appreciation of the importance of the interactions at the surface of the crystal structures. The decomposition of contributions from different interaction types, which overlap in the full fingerprint, proves helpful to highlight graphically the regions of the surface that are involved in a specific type of intermolecular contact.

This study provides us with six different molecular environments and the resulting histogram is provided in Figure 6. Despite the different crystal packing arrangements, in general hydrogen bonding O...H contacts stand out from the other interactions (Figure 6). In this sense, the Hirshfeld analysis revealed that around 51% of the total surface area can be identified with H...O contacts in **2**, **4a** and **4b** (46% in **3**) and this value decreases by almost half in **1** and **1a**. Although the percentage of interactions is lower in **1** and

1a, the role of these interactions had a greater influence on the final supramolecular arrangements.

Fingerprint plots for the two isomorphous structures show that the contacts in **2** and **3** are strikingly similar. An analogous behavior is observed for **4b**. A pair of sharp and symmetric crossed spikes representing C–O contacts associated with C–H...O hydrogen bonds is observed in **2** and **3**, whereas another less sharp spike is attributed to H–O contacts. The C...O interactions represent around 10% of the interactions in these structures but are almost negligible in the other structures, thus emphasizing the observed differences between the intermolecular interaction patterns. The fingerprint plot for **4b** is similar to those for **2** and **3**, but the amount of H-bonds interactions are considerable higher than the C...O contacts. Moreover, these C...O interactions were shorter in **2** and **3** whereas the H...O contacts are shorter in **1** and **1a**.

The unsaturated coordination environment of the copper metal centers give rises to weak Cu...O interactions in structures **1**, **1a** and **4b**. These contacts are stronger in **1** and **1a** than in **4b** and are not present in the other saturated structures (**2**, **3** and **4a**). Finally, other interactions such as C...C and N...H contacts with lower percentage values also contribute to the crystal stability of the structures. The relative areas associated with C...C contacts (often referred to as π ... π contacts) represented around 5% of the surface in all the structures.

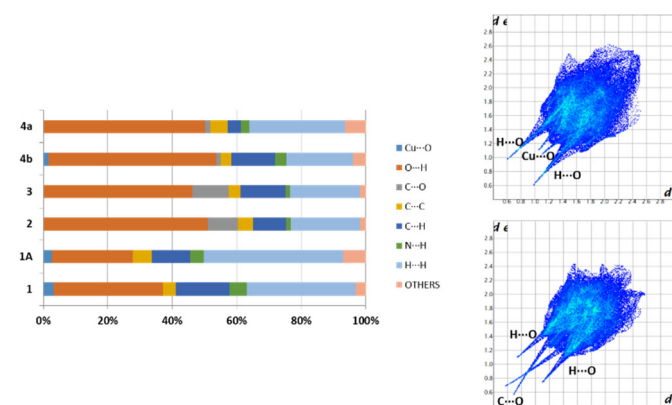


Figure 6. (Left) Relative contributions to the Hirshfeld surface area for the close contacts in the different crystal structures. (Right) Fingerprint plots for **1** (top) and **3** (bottom) with the sharpest spike contacts labeled.

Conclusions

The reactions carried out at room temperature in EtOH with copper(II)/glycolic acid/chelating aromatic diamine allowed the isolation of five crystalline 1D coordination polymers formed due to the bridging role of the glycolato(–1) ligand and a mononuclear cationic copper(II) compound. These results complement those described previously and show that slight changes in the synthetic and crystallization conditions lead to the stabilization of different compounds in the solid state. Three of the 1D coordination polymers (**1**, **2** and **3**) described here are examples of chiral compounds obtained from simple and inexpensive achiral components that form homochiral chains organized in space in a

homochiral way due to interchain hydrogen bonds. The intrachain anion- π interaction in **2** and **3** and the π - π and C-H \cdots π interactions in **1** provide structural evidence of the copier(II) chelate rings metalloaromaticity which is also observed in the molecular compound **4a**. The achiral compounds (**1a** and **4b**) contain the bridging bideprotonated glycolato(-2) ligand which is only formed when 2,2'-dipyridylamine is used.

Conflicts of interest

There are no conflicts to declare

Experimental

Materials and physical measurements

All reagents were commercially available and were used as received. Elemental analyses (C, H, N) were performed on a Carlo Erba 1108 microanalyser. The FT-IR spectra were obtained on a Bruker IFS66v spectrophotometer. A Shimadzu UV-3101PC spectrophotometer was used to obtain electronic spectra in the region 1000–300 nm. Magnetic susceptibility measurements were made at room temperature using a Johnson Matthey magnetic susceptibility balance. Solid state EPR measurements were carried out on a Bruker ER200D system at X-band frequencies.

Synthesis of complexes

Preparation of $\infty^1\{[\text{Cu}(\text{HG})(\text{dipyam})](\text{HG})\}$ (**1**) and $\infty^1\{[\text{Cu}(\text{G})(\text{dipyam})]\cdot\text{H}_2\text{O}\}$ (**1a**)

To a suspension of $\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2\cdot 1/2\text{H}_2\text{O}$ (1 mmol) in 10 mL of EtOH were slowly added a solution of glycolic acid (H_2G) (4 mmol) in 10 mL of EtOH followed by a solution of 2,2'-dipyridylamine (dipyam) (2 mmol) in 10 mL of EtOH. The resulting green solution was stirred for 2 d at room temperature. The green solid **1** was filtered off and dried over CaCl_2 .

Data for **1**. Yield: 60%. Anal. Calc. for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_6\text{Cu}$ (360.81): C, 43.3; H, 3.8; N, 10.9. Found: C, 42.9; H, 3.4; N, 10.5%. IR (KBr), ν (cm^{-1}): 3326m, $\nu(\text{OH})+\nu(\text{NH})$; 1663s, 1625s, 1538m, $\nu(\text{CC})+\nu(\text{CN})$; 1589s, $\nu_{\text{asym}}(\text{OCO})$; 1426s, $\nu_{\text{sym}}(\text{OCO})$; 1017m, $\nu(\text{C}-\text{OH})$. μ (293 K): 1.80 B.M. UV-Vis (diffuse reflectance, cm^{-1}): 14750. EPR (300 K): $g_1 = 2.20$, $g_2 = 2.08$, $g_3 = 2.03$.

A small portion of **1** was dissolved in MeOH/iPrOH 1:1 and, after slow evaporation at room temperature of the resulting solution, green crystals of **1** and a few blue crystals of $\infty^1\{[\text{Cu}(\text{G})(\text{dipyam})]\cdot\text{H}_2\text{O}\}$ (**1a**) were obtained.

Data for **1a**. IR (KBr), ν (cm^{-1}): 3402m, $\nu(\text{OH})+\nu(\text{NH})$; 1669sh, 1584m, 1536m, $\nu(\text{CC})+\nu(\text{CN})$; 1598s, $\nu_{\text{asym}}(\text{OCO})$; 1445s, $\nu_{\text{sym}}(\text{OCO})$; 1019w, $\nu(\text{C}-\text{OH})$. μ (293 K): 1.82 B.M.

Preparation of $\infty^1\{\text{Cu}(\mu\text{-HG})(\text{ClO}_4)(\text{bipy})\}$ (**2**) and $\infty^1\{\text{Cu}(\mu\text{-HG})(\text{ClO}_4)(\text{phen})\}$ (**3**).

A solution of glycolic acid (H_2G) (1 mmol) and NaHCO_3 (1 mmol) in 10 mL of H_2O was added to a previously obtained solution of $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (1 mmol) in 10 mL of EtOH and a NN ligand (2,2'-bipyridine for **2**, 1,10-phenanthroline for **3**) (1 mmol) in 10 mL of EtOH. The mixture was stirred for 2 d at room temperature. The blue crystalline solids of **2** and **3** were

filtered off and dried over CaCl_2 and the slow concentration of the filtrates at room temperature afforded blue crystals of **2** and **3**.

Data for **2**: Yield: 83%. Anal. Calc. for $\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_7\text{ClCu}$ (394.23): C, 36.6; H, 2.8; N, 7.1. Found: C, 36.8; H, 2.8; N, 7.2%. IR (KBr), ν (cm^{-1}): 3423m, 3262m, $\nu(\text{OH})$; 1607s, $\nu(\text{CC})$; 1560m, $\nu_{\text{asym}}(\text{OCO})$; 1445m, $\nu(\text{CC})+\nu(\text{CN})$; 1413m, $\nu_{\text{sym}}(\text{OCO})$; 1135s, 1120s, 1092s, 928w, $\nu(\text{ClO}_4)$. μ (293 K): 1.59 B.M. UV-Vis (diffuse reflectance, cm^{-1}): 14880. EPR (300 K): $g_{\parallel} = 2.23$, $g_{\perp} = 2.06$.

Data for **3**: Yield: 89%. Anal. Calc. for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_7\text{ClCu}$ (418.25): C, 40.2; H, 2.6; N, 6.7. Found: C, 39.9; H, 2.6; N, 6.3%. IR (KBr), ν (cm^{-1}): 3429m, 3261m, $\nu(\text{OH})$; 1597s, $\nu(\text{CC})$; 1555m, $\nu_{\text{asym}}(\text{OCO})$; 1518m, 1429m, $\nu(\text{CC})+\nu(\text{CN})$; 1408m, $\nu_{\text{sym}}(\text{OCO})$; 1147s, 1120s, 1078s, 929w, $\nu(\text{ClO}_4)$. μ (293 K): 1.52 B.M. UV-Vis (diffuse reflectance, cm^{-1}): 14685. EPR (300 K): $g_{\parallel} = 2.23$, $g_{\perp} = 2.06$.

Preparation of $[\text{Cu}(\text{HG})(\text{H}_2\text{O})(\text{dipyam})]\text{ClO}_4$ (**4a**) and $\infty^1\{[\text{Cu}_2(\mu\text{-G})(\text{ClO}_4)(\text{H}_2\text{O})(\text{dipyam})_2]\text{ClO}_4\cdot 2\text{H}_2\text{O}\}$ (**4b**)

A solution of glycolic acid (H_2G) (1 mmol) and NaHCO_3 (1 mmol) in 10 mL of H_2O was added to a solution of $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (1 mmol) in 10 mL of EtOH and 2,2'-dipyridylamine (1 mmol) in 10 mL of EtOH. The mixture was stirred for 2 d at room temperature. The slow evaporation at room temperature of the blue resulting solution afforded a mixture of green crystals **4a** and a few blue crystals of **4b**.

When the same mixture of reagents was irradiated for 10 min in a microwave oven, a similar blue solution is obtained. After slow evaporation at room temperature, green crystals of **4a** and blue-violet crystals of $[\text{Cu}(\text{dipyam})_2](\text{ClO}_4)_2$ [**12a**] were obtained.

Data for **4a**: Yield: 33%. Anal. Calc. for $\text{C}_{12}\text{H}_{14}\text{N}_3\text{O}_8\text{ClCu}$ (427.25): C, 33.80; H, 3.31; N, 9.86. Found: C, 33.63; H, 3.49; N, 9.86%. IR (KBr), ν (cm^{-1}): 3400m,b $\nu(\text{OH})+\nu(\text{NH})$; 1575m, $\nu_{\text{asym}}(\text{OCO})$; 1532m, 1419m, $\nu(\text{CC})+\nu(\text{CN})$; 1482s, $\nu_{\text{sym}}(\text{OCO})$; 1164s, 1057s, 621s, $\nu(\text{ClO}_4)$. μ (293 K): 1.69 B.M. UV-Vis (diffuse reflectance, cm^{-1}): 14600.

X-ray diffraction analyses

A summary of the key crystallographic information is given in Table 4. Crystallographic data were collected on a Bruker SMART 1000 CCD diffractometer for **1**, **1a** and **2**, on an Enraf Nonius CAD4 diffractometer for **3** and Bruker D8 Venture diffractometer for **4a** and **4b**. Data reduction and cell refinements were performed using the SAINT program [23]. Scaling and empirical absorption corrections were carried out using the SADABS program [24] in all cases except for **3**, which corrected by semi-empirical method (ψ -scans) [25]. The structures were solved by direct methods using the program SHELXS-97 [26]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the program SHELXL-97 [27]. Hydrogen atoms were generally inserted at calculated positions and constrained with isotropic thermal parameters, except those of the -NH group of dipyam, the hydroxyl group and water molecule, which were generally located using a Fourier

difference map and refined isotropically. Drawings were produced with MERCURY [28].

Hirshfeld surface study

Hirshfeld surfaces and their associated two-dimensional fingerprint plots [28-31] were drawn by using CrystalExplorer3.0 software [32]. The d_{norm} (normalized contact distance) surface and the breakdown of two-dimensional fingerprint plots were used to analyze intermolecular interactions in the different crystal lattices. The sizes and shapes of the fingerprint illustrate the significant differences between the intermolecular interaction patterns.

Acknowledgements

Financial support from ERDF (EU), MEC (Spain) and the Xunta de Galicia (Spain) (research projects CTQ2015-71211-REDT, CTQ2015-7091-R and ED431D 2017/01) are gratefully acknowledged.

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