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Copper(II) assembling with bis(2-pyridylcarbonyl)amidate and N,N'-2,2-phenylenebis(oxamate)†

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We herein present the synthesis and X-ray structures of five copper(1) complexes of formulae [Cu(bpca)-(CF₃SO₃)(H₂O)]·H₂O (1), [Cu(bpca)(Phpr)(H₂O)]·3/2H₂O (2), {[Cu(bpca)]₂[Cu(opba)(H₂O)]}·H₂O (3), {[Cu- $(bpca)]_{2}(H_{2}opba)]_{2}(H_{2}opba)]_{2}(H_{2}opba)]_{2}(5)$, where bpca = bis(2-pyridylcarbonyl)amidate, Phpr = 3-phenylpropionate, $CF_3SO_3^-$ = triflate (anion of the trifluoromethanesulphonic acid), H_4 opba = N,N'-1,2-phenylenebis(oxamic acid), and EtH₃opba = monoethyl ester derivative of the H₄opba. 1 and 2 are mononuclear copper(\mathbf{u}) complexes where the copper atom is five-coordinate in distorted square pyramidal surroundings with a tridentate bpca and a water molecule (1)/carboxylate oxygen (2) building the basal plane and a triflate oxygen (1)/water molecule (2) filling the apical position. 3 is a neutral tricopper(1) complex where the $[Cu(opba)(H_2O)]^{2-}$ unit acts as a bis-bidentate ligand toward two peripheral [Cu-(bpca)]⁺ fragments. The three crystallographically independent copper(1) ions in 3 are five-coordinate with two nitrogen and two oxygen atoms (inner copper atom)/three bpca-nitrogen and an oxamate oxygen (outer copper atom) building the basal plane plus a water molecule (inner copper)/an oxamate oxygen (outer copper) in the apical position (inner copper atom) of somewhat distorted square pyramidal surroundings. **4** is a centrosymmetric tetracopper($_{\parallel}$) compound where four [Cu(bpca)]⁺ fragments are assembled by two H_2 opba²⁻ groups adopting an unusual bidentate/bis-monodentate bridging mode. The two crystallographically independent copper(11) ions in 4 are also five-coordinate having the three bpca-nitrogens in basal positions, the other two sites of the distorted square pyramid being filled by two oxygens of either a bidentate oxamate (at one copper centre) or two bis-monodentate oxamates (at the other copper atom). 5 is a zigzag chain of $[Cu(bpca)(H_2O)]^+$ units which are connected through the EtH₂opba⁻ ligand adopting a bidentate/monodentate bridging mode across the monodeprotonated oxamate group. Each copper(\mathfrak{n}) ion in 5 is six-coordinate in an elongated octahedral CuN₃O₃ chromophore. The magnetic properties of 3-5 were investigated in the temperature range 1.9-300 K. 3 exhibits an intermediate intramolecular antiferromagnetic interaction [J = -65.8(2) cm⁻¹ with the Hamiltonian $H = -J(S_{Cu_1} \cdot S_{Cu_2} + S_{Cu_2} \cdot S_{Cu_3})]$ which leads to a low-lying spin doublet at low temperatures. A weak antiferromagnetic coupling between the inner copper(1) ions occurs in 4 [J = -2.36(2) cm⁻¹, $H = -J S_1 S_2$)] and a very small intrachain antiferromagnetic interaction is observed in 5 [J = -0.17(1) cm⁻¹ with $H = -J\sum_{i} S_{i}S_{i+1}$]. These values are analyzed by means of simple orbital symmetry considerations and compared with those previously reported for parent systems.

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Introduction

Substituted s-triazines such as tris(2-pyridyl)-1,3,5-triazine (tpyt) and tris(2-pyrimidyl)-1,3,5-triazine (tpymt) undergo copper(II)-assisted hydrolysis under mild conditions yielding the [bis(2-pyridylcarbonyl)amido]copper(II) ($[Cu(bpca)]^+$) and 2-pyridylformamide fragments in the case of tpyt and [bis(2-pyrimidulcarbonyl)amido]copper(II) ($[Cu(bpcam)]^+$) and 2-pyrimidylformamide when using tpymt (see Scheme 1).¹ Interestingly, these fragments could be characterized by single crystal X-ray diffraction occurring as ligands in the same copper(II) complex or apart from each other in two different $copper(\pi)$ species, the composition of the products being monitored by modifying the starting triazine : Cu(II) molar ratio.²

According to kinetic and thermodynamic data,^{3,4} this hydrolytic reaction could take place through a nucleophilic attack at the triazine ring by the OH⁻ or H₂O and geometrical constraints have been pointed out to be highly significant on the basis of the structural data obtained for the mononuclear species [Cu(bpcam)(H₂O)₃]NO₃·2H₂O and [Cu(bpca)(H₂O)₂]-NO₃·2H₂O.^{1b,2b} Although first-row transition metal ions other than Cu(II) have been unable to cause this hydrolytic reaction, the heavier Rh(III)/Rh(II) ions have been demonstrated to be able to hydrolyze tpyt affording the same fragments.⁵ In this latter case, the authors suggest that an electron-withdrawing effect of the metal ion, rather than the angular strain, would be responsible for the metal-promoted hydrolysis of the tpyt. Theoretical molecular orbital calculations of M(tpyt) [M = Ru(II), Cu(II) and Rh(III) support that the main hydrolytic effect is the electron-withdrawing effect of the metal ions.⁶

The stability of the $[Cu(bpca)(H_2O)_2]^+$ and [Cu(bpcam)- $(H_2O)_3$ ⁺ species in solution together with the easy replacement

 $[Cu(bpca)]^+$ (X = C-H) 2-pyridylformamide (X = C-H) 2-pyrimidylformamide (X = N) $\left[Cu(bpcam)\right]^+ (X = N)$

Scheme 1

Cu⁺²/ H₂O

NH₂

of the coordinated water molecules by better donor atoms have made possible their use as Lewis bases against potential mono- or polyatomic bridges (organic linkers) and preformed complexes acting as donors in order to prepare homo-7-9 and heteropolymetallic compounds.^{10,11} The isolation of the Hbpca monoprotic acid¹² conducted for the preparation of mononuclear compounds such as $[M(bpca)_x]^{(m-x)+}$ (M = 3d metal ion).12-15 Their use as ligands has afforded heterodinuclear complexes,16 homo- and heterotrinuclear compounds,^{12a,14b,17,18} chains^{15,17b,19,20} as well as honeycomb lavered materials^{17b,21} whose magnetic properties have been investigated, some of them being examples of single molecule magnets (SMMs)^{16,18} and single chain magnets (SCMs).¹⁹

Having in mind the good coordinating properties of the oxamato-containing complexes and the remarkable ability of the oxamato to mediate strong magnetic interactions,²² we explored the possibility of preparing polynuclear [Cu(bpca)]⁺/ oxamate polynuclear compounds by using preformed oxamatecontaining complexes as ligands towards the [Cu(bpca)]⁺ unit. Our first results through this approach are presented herein and they concern the synthesis and X-ray structures of the compounds [Cu(bpca)(CF₃SO₃)(H₂O)]·H₂O (1), [Cu(bpca)(Phpr)- (H_2O)]·3/2H₂O (2), {[Cu(bpca)]₂[Cu(opba)(H₂O)]]·H₂O (3), {[Cu- $(bpca)]_2(H_2opba)]_2 \cdot 6H_2O$ (4) and $[Cu(bpca)(EtH_2opba)]_n$ (5) [Phpr = 3-phenylpropionate, H_4 opba = N, N'-1,2-phenylenebis-(oxamic acid) and EtH₃opba = monoethyl ester derivative of the H₄opba molecule] together with the variable-temperature magnetic study of 3-5.

Experimental

Materials

tpyt (X = C-H)

tpymt (X = N)

 NH_4^+

Tpyt, copper(II) triflate and 3-phenylpropionic acid were purchased from commercial sources and they were used without further purification. (Bu₄N)₂[Cu(opba)], Me₄N[Mn- $(opba)(H_2O)_2$ and the Et_2H_2opba proligand $[Bu_4N^+ = tetra$ *n*-butylammonium, Me_4N^+ = tetramethylammonium and $Et_2H_2opba = diethyl ester derivative of H_4opba]$ were prepared according to procedures reported elsewhere.²³⁻²⁵ Elemental analyses (C, H, N) were performed with a Perkin Elmer 2400 analyzer and the copper contents were determined by means of a Hitachi-Z8200 spectrophotometer.

Preparation of the complexes

 $[Cu(bpca)(CF_3SO_3)(H_2O)]$ ·H₂O (1). The addition of solid tpyt (0.156 g, 0.49 mmol) to a warm (50 °C) aqueous solution (30 cm^3) of copper(II) triflate (0.534 g, 1.48 mmol) led to a blue solution that was heated at 70 °C for half an hour under continuous stirring. The resulting dark blue solution was filtered and allowed to evaporate in a hood at room temperature. X-ray quality crystals of 1 as deep blue squares were obtained after a few days. They were collected on a filter paper, washed with a small amount of cold water (10 °C) and dried in the open air. Yield is ca. 70%. The 3:1 Cu(II): tpyt molar ratio used in the synthesis of 1 avoids the formation of the heteroleptic $[Cu(bpca)(NC_5H_4CONH_2)]CF_3SO_3 \text{ complex which is the only product when a 1:1 Cu(II): tpyt molar ratio is used.^{2b} Anal. Calcd for C₁₃H₁₂CuF₃N₃O₇S (1): C, 32.89; H, 2.53; N, 8.85; Cu, 13.38. Found: C, 32.65; H, 2.48; N, 8.67; Cu, 13.28%.$

[Cu(bpca)(Phpr)(H₂O)]-3/2H₂O (2). Solid sodium hydroxide was added to an aqueous solution (20 cm³) of 3-phenylpropionic acid (0.042 g, 0.28 mmol) under continuous stirring until pH *ca.* 9.0. This solution was poured into another aqueous solution (10 cm³) of 1 (0.133 g, 0.28 mmol) with stirring and gentle warming (60 °C) for half an hour. Slow evaporation of the resulting solution under ambient conditions afforded deep blue hexagons of 2 which were suitable for X-ray diffraction. They were collected on a filter paper, washed with a small amount of cold water (10 °C) and dried in the open air. Yield is *ca.* 50%. Calcd for C₂₁H₂₂CuF₃N₃O_{6.5} (2): C, 52.14; H, 4.55; N, 8.68; Cu, 13.13. Found: C, 52.03; H, 4.41; N, 8.53; Cu, 13.05%.

{[Cu(bpca)]₂[Cu(opba)(H₂O)]}·H₂O (3). Compound 3 was obtained as a blue polycrystalline powder in a practically quantitative yield by mixing concentrated aqueous solutions of 1 (0.095 g, 0.20 mmol) and (Bu₄N)₂[Cu(opba)] (0.080 g, 0.10 mmol). Blue needles of 3 suitable for X-ray diffraction were grown by slow diffusion in an H-shaped tube (h = 10 cm; w = 4 cm; d = 1 cm) of aqueous solutions of the complex 1 at one arm and the (Bu₄N)₂[Cu(opba)] species at the other one. The crystals were collected, washed with a small amount of cold water (10 °C) and air dried. Calcd for C₃₄H₂₄Cu₃N₈O₁₂ (3): C, 44.05; H, 2.59; N, 12.08; Cu, 20.56. Found: C, 43.95; H, 2.48; N, 11.96; Cu, 20.44%.

 $\{ [Cu(bpca)]_2(H_2opba) \}_2 \cdot 6H_2O$ (4). An aqueous solution (85 cm³) of 1 (0.095 g, 0.20 mmol) was poured into an aqueous solution (12 cm³) of Me₄N[Mn(opba)(H₂O)₂] (0.124 g, 0.27 mmol) under continuous stirring. The resulting blue solution was allowed to evaporate at 20 °C. X-ray quality crystals of 4 as blue needles were grown after 20 days. Yield is ca. 11%. This compound was obtained in a practically quantitative yield by reacting H_2 opba²⁻ (generated *in situ*) and **1** in water: solid hydroxide (0.040 g, 1.0 mmol) dissolved in a minimum amount of water was added to a suspension of Et₂H₂opba (0.154 g, 0.5 mmol) in 10 cm³ of a 9:1 water-ethanol (v/v) mixture; the mixture was stirred at 60 °C for 5 min. Then, a warm aqueous solution (20 cm^3) of 1 (0.474 g, 1.0 mmol) was added under continuous stirring. Compound 4 separates as a blue polycrystalline solid on standing. Calcd for C₆₈H₅₆Cu₄N₁₆O₂₆ (4): C, 46.22; H, 3.17; N, 12.68; Cu, 14.39. Found: C, 46.01; H, 3.09; N, 12.39; Cu, 14.10%.

 $[Cu(bpca)(EtH_2opba)]_n$ (5). An aqueous solution (50 cm³) of 1 (0.266 g, 0.56 mmol) was added dropwise to an acetone solution (10 cm³) of Et₂H₂opba (0.088 g, 0.56 mmol) and the resulting blue solution (pH *ca.* 3.7) was filtered and allowed to evaporate under ambient conditions. Plate-like blue plates of 5 were grown after seven days. They were collected by filtration, washed with a small amount of cold water (10 °C) and air dried. Yield is *ca.* 34%. Calcd for C₂₄H₁₉CuN₅O₈ (5): C, 50.68; H, 3.34; N, 12.31; Cu, 11.17. Found: C, 50.45; H, 3.25; N, 12.23; Cu, 11.02%.

Physical techniques

Infrared spectra were recorded with Bruker IF S55 (1 and 2) and Perkin-Elmer FTIR (3–5) spectrometers as KBr pellets in the 4000–400 cm⁻¹ region. The magnetic susceptibility measurements were carried out on polycrystalline samples of 3–5 in the temperature range 1.9–295 K with a Quantum Design SQUID susceptometer and using applied magnetic fields of 0.1 T ($T \ge 100$ K) and 0.025 T (T < 100 K). The complex (NH₄)₂Mn(SO₄)₂·6H₂O was used as a susceptibility standard. Diamagnetic corrections of the constituent atoms were calculated from Pascal's constants²⁶ and found to be -372×10^{-6} (3), -627×10^{-6} (4) and -337×10^{-6} cm³ mol⁻¹ (5) per three (3), four (4) and one (5) mole of copper(π) ions. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism of [60×10^{-6} cm³ mol⁻¹ per Cu(π)] and the magnetization of the sample holder.

Crystallography

X-ray data for 1 and 2 were collected on an Agilent Supernova X-ray source at 293(2) K with mirror monochromated Cu radiation ($\lambda = 1.5418$ Å) whereas those for 3–5 were performed using an Oxford-Diffraction GEMINI diffractometer by using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293 (3), 260 (4) and 120 K (5). Accurate cell dimensions and orientation matrices were determined by least-squares refinement of the reflections obtained by $\theta - \chi$ scans for 1–5. The data for 1-5 were indexed and scaled with the CrysalisPro program.²⁷ Analytical absorption corrections of the diffracted intensities based on a multifaceted crystal model using CrysalisPro²⁷ were applied in 1–5. The indexes of the data collection were $-12 \le h \le 18, -9 \le k \le 9, -15 \le l \le 17$ (1), $-33 \le h \le 34$, $-12 \le k \le 12, -24 \le l \le 19$ (2), $-14 \le h \le 14, -16 \le k \le 16$, $-17 \le l \le 17$ (3), $-12 \le h \le 12$, $-14 \le k \le 14$, $-22 \le l \le 22$ (4) and $-17 \le h \le 16$, $-12 \le k \le 12$, $-24 \le l \le 24$ (5). Of the 3296 (1), 4151 (2), 6982 (3), 7869 (4) and 5254 (5) measured independent reflections in the θ range 3.99–71.83° (1), 4.32–73.50° (2), 3.0-26.4 (3), 2.7-27.5° (4) and 3.1-27.5° (5), 2873 (1), 3955 (2), 5451 (3), 6221 (4) and 4722 (5) were considered as observed $[I \ge 2\sigma(I)]$. The crystal structure of **1** was solved by using the SIR92 software,²⁸ while those of 2-5 were solved by direct methods using the SHELX-97 package.²⁹ The structures of 1-5 were refined by a full-matrix least-squares technique on F^2 using the SHELX-97 programs²⁹ included in the WINGX software package.³⁰ All non-hydrogen atoms in 1-5 were refined anisotropically. The crystallization water molecule O(3W) in 2 is in a special position and the free water molecule O(12W) in 3 was found to be disordered in two positions and partial occupancy factors of 0.5 [O(2W1)] and 0.5 [O(2W2)] were assigned. The hydrogen atoms of the organic ligands in 1-5 were placed in calculated positions and refined with a riding model. However, those of the coordinated (1-5) and free (1 and 2) water molecules were located from Fourier differences although their hydrogen isotropic displacement has been constrained to their respective oxygen atom. The final geometrical calculations were carried out with PARST,³¹

whereas the graphical manipulations were performed with the DIAMOND³² and ORTEP³³ programs. The crystal data and structure refinements of 1-5 are listed in Table 1. Selected bond lengths and angles and hydrogen bonds are given in Tables 2 (1), 3 (2), 4 (3) 5 (4) and 6 (5).

Results and discussion

Synthesis and IR characterization

The copper(II)-promoted hydrolysis of tpyt in aqueous solution affords the [Cu(bpca)]⁺ fragment (see Scheme 1) which is isolated as the mononuclear compounds 1 and 2 where the positive charge has been neutralized by the trifluoromethanesulphonate (1) and 3-phenylpropionate (2). The strong peak at 1717 (1) and 1708 cm^{-1} (2) in the infrared spectra of these complexes, which corresponds to an imide group, is diagnostic of the presence of the bpca ligand in them.^{1,2,34} Another common feature in the i.r. spectra of 1 and 2 is the occurrence of a strong and broad absorption in the high-frequency region [continuous absorption in the range 3600-3250 cm⁻¹ with maxima centered at *ca.* 3435 (1) and 3450 cm^{-1} (2)] which is indicative of the presence of hydrogen bonded coordinated/ free water molecules.^{35,36} Evidence for unidentate sulphonate coordination of the triflate group ($C_{3\nu}$ symmetry) in **1** is provided by the set of peaks due to this anion:37-39 two SO3 stretching modes at 1282s and 1254s cm⁻¹ [$\nu_4(E)$], an SO₃ deformation mode at 520m cm⁻¹ $[\nu_5(E)]$ plus three absorptions at 1032s $[\nu_1(A_1)]$, 800w $[\nu_2(A_1)]$ and 650s cm⁻¹ $[\nu_3(A_1)]$ to be compared with the set of peaks for the ionic CF₃SO₃⁻ as the Na⁺ salt [stretching vibrations of the SO₃ at 1280 and 1240 cm^{-1} and the CF₃ stretching modes at 1175 and 1035 cm⁻¹].⁴⁰ As far as the 3-phenylpropionate group in 2 is

The use of the $[Cu(opba)]^{2-}$ unit as a ligand towards the $[Cu(bpca)]^+$ in aqueous solution yields compound 3 as a polycrystalline blue solid. Single crystals of this complex were grown by slow diffusion in an H-shape tube. The broad absorption centered at *ca.* 3400 cm⁻¹ [ν (OH)] and the strong peak at 1717 cm⁻¹ [ν (CO)_{imide}] in the i.r. spectrum of 3 are due to the presence of water molecules and the [Cu(bpca)]⁺ fragment, respectively. Interestingly, the pattern of peaks in the 1700–1600 cm⁻¹ region from the i.r. spectrum of the mononuclear (Bu₄N)₂[Cu(opba)] complex [1676sh, 1648s and 1614s cm^{-1} is simplified to only one strong peak at 1619 cm^{-1} with a shoulder at 1600 cm⁻¹ in the i.r. spectrum of 3. These features are consistent with the different coordination mode of the carbonyl groups of the opba ligand in 3 (bridging bisbidentate) versus that in the mononuclear complex (bidentate).

The reaction of stoichiometric amounts of 1 and Me₄N[Mn- $(opba)(H_2O)_2$ in aqueous solution afforded a small amount of single crystals of 4 where four [Cu(bpca)]⁺ fragments are assembled through two H₂opba²⁻ ligands. The partial decomposition of the $[Mn(opba)(H_2O)_2]^+$ species in aqueous solution (after the mixture of the starting chemicals in the preparation of 4, the pH of the resulting solution was 5.6) accounts for the formation of single crystals of 4 in a low yield. Anyway, this compound was obtained as a blue polycrystalline solid in a good yield by the reaction of stoichiometric amounts of 1 and H₂opba²⁻ (generated in situ) in a water-ethanol mixture. The i.r. spectrum of 4 exhibits a strong and broad

Fable 1 Summary of the crystal data and refinement details for 1–5					
Compound	1	2	3	4	5
Formula	C13H12CuF3N3O7S	C21H22CuN3O6.5	C34H24Cu3N8O12	C68H56Cu4N16O26	C24H19N5O8
Fw	474.86	483.95	927.23	1767.49	568.98
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	C2/c	$P(\bar{1})$	$P(\bar{1})$	$P2_1/c$
a/Å	14.6006(3)	28.5694(7)	11.6502(3)	9.4297(4)	13.2927(3)
b/Å	8.0694(2)	10.23660(10)	13.4289(4)	11.2189(9)	9.66889(15)
c/Å	14.7344(3)	20.1856(5)	13.6461(5)	17.0787(13)	18.7558(4)
$\alpha/^{\circ}$	90.0	90.0	61.971(3)	75.037(7)	90.0
β/°	98.067(2)	134.242(4)	65.206(3)	80.294(5)	107.619(2)
γ/°	90.0	90.0	80.022(3)	89.324(5)	90.00
$V/Å^3$	1718.80(7)	4229.2(3)	1710.05(11)	1719.6(2)	2297.52(8)
Ζ	4	8	2	1	4
λ/Å	1.54184	1.54184	0.71073	0.71073	0.71073
$\rho/\mathrm{g~cm}^{-3}$	1.835	1.867	1.797	1.707	1.645
T/K	293(2)	293(2)	293(2)	260(1)	120(1)
$u(Mo-K\alpha)/cm^{-1}$	3.667	1.867	19.1	13.2	10.1
No. parameters	253	288	544	531	350
Goodness-of-fit on F^2	1.033	1.044	1.06	1.02	1.04
$R^a, WR^b \left[I > 2\sigma(I) \right]$	0.037, 0.100	0.036, 0.099	0.027, 0.075	0.039, 0.084	0.027, 0.068
R^a w R^b (all data)	0.042, 0.106	0.037, 0.101	0.037, 0.077	0.057, 0.091	0.031, 0.071
Largest diffraction peak and hole/e A^{-3}	0.27, -0.43	0.38, -0.46	0.78, -0.47	0.63, -0.47	0.43, -0.42

 ${}^{a}R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b}WR = \left[\sum (|F_{o}|^{2} - |F_{c}|^{2})^{2} / \sum |F_{o}|^{2}\right]^{1/2}.$

Table 2 Selected bond distances (Å) and angles (°) for 1^a

Copper(II) environment				
Cu(1)-N(1)	2.002(3)	Cu(1)-O(1W)	1.971(2)	
Cu(1) - N(2)	1.931(2)	Cu(1) - O(3)	2.297(2)	
Cu(1) - N(3)	2.001(2)			
N(1) - Cu(1) - N(2)	82.32(9)	N(2)-Cu(1)-O(1W)	172.14(8)	
N(1) - Cu(1) - N(3)	163.33(8)	N(2) - Cu(1) - O(3)	102.08(8)	
N(1)-Cu(1)-O(1W)	95.50(8)	N(3) - Cu(1) - O(1W)	99.01(8)	
N(1) - Cu(1) - O(3)	99.37(8)	N(3) - Cu(1) - O(1W)	99.01(8)	
N(2) - Cu(1) - N(3)	82.20(8)	O(1W) - Cu(1) - O(3)	85.71(8)	
Bpca ligand				
N(2)-C(6)	1.359(3)	N(2)-C(7)	1.370(3)	
C(6) - O(1)	1.219(3)	C(7) - O(2)	1.214(3)	
C(5) - C(6)	1.508(4)	C(7) - C(8)	1.500(3)	
C(4) - C(5)	1.374(4)	C(8) - C(9)	1.373(4)	
C(3) - C(4)	1.382(5)	C(9) - C(10)	1.385(4)	
C(2) - C(3)	1.373(5)	C(10) - C(11)	1.366(5)	
C(1) - C(2)	1.383(4)	C(11) - C(12)	1.384(4)	
C(1) - N(1)	1.324(4)	C(12) - N(3)	1.334(3)	
N(1) - C(5)	1.352(3)	N(3) - C(8)	1.352(3)	
N(2) - C(6) - O(1)	128.9(3)	N(2) - C(7) - O(2)	128.3(2)	
N(2) - C(6) - C(5)	111.1(2)	N(2) - C(7) - C(8)	111.09(19)	
O(1) - C(6) - C(5)	120.0(2)	O(2) - C(7) - C(8)	120.6(2)	
C(6) - C(5) - C(4)	122.3(2)	C(7) - C(8) - C(9)	121.8(2)	
C(6) - C(5) - N(1)	115.8(2)	C(7) - C(8) - N(3)	115.9(2)	
C(4) - C(5) - N(1)	121.8(3)	C(9) - C(8) - N(3)	122.3(2)	
C(5) - N(1) - Cu(1)	112.66(17)	C(8) - N(3) - Cu(1)	112.97(15)	
C(5)-N(1)-C(1)	119.2(2)	C(8) - N(3) - C(12)	118.7(2)	
C(1) - N(1) - Cu(1)	128.02(18)	C(12) - N(3) - Cu(1)	128.09(17)	
N(1) - C(1) - C(2)	121.7(3)	N(3) - C(12) - C(11)	121.6(3)	
C(1) - C(2) - C(3)	119.4(3)	C(12) - C(11) - C(10)	119.6(3)	
C(2) - C(3) - C(4)	118.9(3)	C(11) - C(10) - C(9)	119.3(3)	
C(3) - C(4) - C(5)	118.9(3)	C(10) - C(9) - C(8)	118.5(3)	
Cu(1) - N(2) - C(6)	117.60(17)	Cu(1) - N(2) - C(7)	117.49(16)	
C(6) - N(2) - C(7)	124.9(2)			
Hydrogen bonds ^{b,c}				
D-H···A	D–H (Å)	H····A (Å)	D…A (Å)	D-H…A (°)
$O(1W)-H(1WA)\cdots O(2Wa_1)$	0.87(2)	2.00(2)	2.777(3)	149.50(13)
O(1W)-H(1WB)O(2W)	0.87(2)	1.84(2)	2.696(3)	170.90(14)
$O(2W) - H(2WB) \cdots O(2b_1)$	0.88(2)	2.13(2)	2.761(3)	127.80(14)
$O(2W) - H(2WB) \cdots O(1b_1)$	0.90(2)	2.00(2)	2.815(3)	149.6(2)
		~ /		. /

^{*a*} Estimated standard deviations in the last significant digits are given in parentheses. ^{*b*} D and A stand for donor and acceptor, respectively. ^{*c*} Symmetry code: $(a_1) = -x + 3/2$, y - 1/2, -z + 1/2; $(b_1) = x - 1/2$, -y + 1/2, z - 1/2.

absorption in the range $3600-3100 \text{ cm}^{-1}$ due to the OH stretching of the water molecules that masks the observation of the expected N–H amide of the H₂opba^{2–} ligand around 3200 cm^{-1} . As for the preceding compounds, the peak at 1711s,sh supports the presence of the [Cu(bpca)]⁺ fragment in 4. Finally, four medium intensity peaks at 1690, 1660, 1640 and 1608 cm⁻¹ are tentatively attributed to amide and carboxylate stretching vibration of the H₂opba^{2–} group.

The partial hydrolysis of the Et₂H₂opba proligand (the pH of the initial mixture of **1** and Et₂H₂opba is *ca.* 3.8) which is assisted by the subsequent coordination of its resulting mono-hydrogenoxamate arm to the $[Cu(bpca)]^+$ unit would account for the formation of **5**. The i.r. spectra of **5** also exhibit the strong absorption at 1710 cm⁻¹ characteristic of the ν (CO)_{imide} vibration from the bpca ligand. The presence of a medium intensity peak at 3164 cm⁻¹ [ν (N–H)_{amide}] together with the set of peaks at 1738m, 1665m, 1643s and 1615m cm⁻¹ [ν (COO)_{ester} and ν (CO)_{amide}] supports the occurrence in **5** of the monoethyl ester derivative EtH₂opba⁻. All these spectroscopic features for **1–5** were confirmed by their X-ray structures (see below).

Description of the structures

 $[Cu(bpca)(CF_3SO_3)(H_2O)] \cdot H_2O$ (1). The structure of 1 consists of neutral [Cu(bpca)(H₂O)(CF₃SO₃)] mononuclear units and crystallization water molecules (Fig. 1) which are interlinked by hydrogen bonds involving all the water molecules and the carbonyl-oxygens (see the end of Table 2) and π - π type interactions between the pyridyl rings of the bpca ligands. These weak intermolecular interactions lead to a supramolecular two-dimensional structure growing in the diagonal of the ac plane (Fig. 2). Additional weak π - π type stacking interactions between pyridyl rings of pairs of bpca ligands [N(1)C(1)- $C(2)C(3)C(4)C(5)/N(3c_1)C(8c_1)C(9c_1)C(10c_1)C(11c_1)C(12c_1)$ with a centroid–centroid distance of 3.769(2) Å; symmetry operation: $(c_1) = -x + 2, -y, -z + 1$ contribute to the stabilization of the resulting supramolecular layered structure. The shorter intermolecular copper-copper separation in 1 is 4.6006(4) $[Cu(1)\cdots Cu(1c_1)].$

Each copper(n) ion in **1** is five-coordinate in a somewhat distorted square pyramidal CuN₃O₂ environment, the value of

Paper

Copper(II) environment				
Cu(1)-N(1)	2.012(2)	Cu(1)–O(3)	1.9365(13)	
Cu(1)-N(2)	1.9391(13)	Cu(1)-O(1W)	2.365(2)	
Cu(1)-N(3)	2.007(2)	Cu(1)-O(4)	2.852(2)	
N(1)-Cu(1)-N(2)	81.64(6)	N(2)-Cu(1)-O(3)	175.22(6)	
N(1)-Cu(1)-N(3)	163.10(6)	N(2)-Cu(1)-O(1W)	90.88(6)	
N(1)-Cu(1)-O(3)	97.05(6)	N(3)-Cu(1)-O(3)	99.44(7)	
N(1)-Cu(1)-O(1W)	90.60(6)	N(3)-Cu(1)-O(1W)	92.01(6)	
N(2) - Cu(1) - N(3)	81.63(6)	O(3) - Cu(1) - O(1W)	93.73(6)	
Bpca ligand				
N(2) - C(6)	1.360(2)	N(2)-C(7)	1.360(2)	
C(6) - O(1)	1.215(2)	C(7) - O(2)	1.215(2)	
C(5) - C(6)	1.511(2)	C(7)-C(8)	1.508(2)	
C(4) - C(5)	1.375(3)	C(8) - C(9)	1.370(3)	
C(3) - C(4)	1.389(3)	C(9) - C(10)	1.384(3)	
C(2) = C(3)	1 368(3)	C(10) = C(11)	1 376(3)	
C(1) - C(2)	1 378(3)	C(11) - C(12)	1.370(3)	
C(1) - N(1)	1.370(3)	C(12) - N(3)	1 338(2)	
N(1) - C(5)	1 339(2)	N(3) - C(8)	1.330(2)	
N(1) = O(3) N(2) = O(6) = O(1)	1.339(2)	N(3) = C(3) N(2) = C(7) = O(2)	1.344(2) 100 12(17)	
N(2) - C(6) - C(1) N(2) - C(6) - C(5)	128.01(10) 111.00(14)	N(2) - C(7) - C(2) N(2) - C(7) - C(9)	120.13(17) 111.07(14)	
O(1) C(6) C(5)	120.29(16)	O(2) = O(7) = O(8)	111.07(14) 120.90(16)	
C(f) = C(f) = C(f)	120.38(10)	C(2) = C(1) = C(0)	120.80(10)	
C(6) - C(5) - C(4)	121.74(17)	C(7) - C(8) - C(9)	122.00(16)	
C(6) = C(5) = N(1)	115.84(15)	C(7) = C(8) = N(3)	115.62(15)	
C(4) - C(5) - N(1)	122.41(17)	C(9) - C(8) - N(3)	122.38(17)	
C(5) - N(1) - Cu(1)	113.37(11)	C(8) - N(3) - Cu(1)	113.53(12)	
C(5) - N(1) - C(1)	118.6/(16)	C(8) - N(3) - C(12)	118.21(16)	
C(1) - N(1) - Cu(1)	127.80(13)	C(12)-N(3)-Cu(1)	128.15(13)	
N(1)-C(1)-C(2)	122.07(19)	N(3)-C(12)-C(11)	122.59(19)	
C(1)-C(2)-C(3)	119.13(19)	C(12)-C(11)-C(10)	118.93(19)	
C(2)-C(3)-C(4)	119.27(19)	C(11)-C(10)-C(9)	119.0(2)	
C(3)-C(4)-C(5)	118.42(19)	C(10)-C(9)-C(8)	118.86(19)	
Cu(1)-N(2)-C(6)	117.79(11)	Cu(1)-N(2)-C(7)	117.92(11)	
C(6)-N(2)-C(7)	124.12(14)			
Hydrogen bonds ^{<i>b</i>,<i>c</i>}				
D-H···A	D–H (Å)	$H \cdots A(A)$	D…A (Å)	$D-H\cdots A(^{\circ})$
$O(1W)-H(1WB)\cdots O(1a_2)$	0.87(2)	2.55(3)	2.872(4)	102.71(14)
$O(1W)-H(1WB)\cdots O(2Wb_2)$	0.87(2)	2.40(2)	2.873(2)	114.00(13)
$O(2W)-H(2WA)\cdots O(4)$	0.89(2)	1.94(2)	2.808(2)	164.80(15)
$O(2W)-H(2WB)\cdots O(2c_2)$	0.87(3)	2.39(2)	3.065(3)	134.56(13)
$O(3W) - H(3WA) \cdots O(3d_2)$	0.89(2)	2.09(2)	2.885(2)	149.35(4)

^{*a*} Estimated standard deviations in the last significant digits are given in parentheses. ^{*b*} D and A stand for donor and acceptor, respectively. ^{*c*} Symmetry code: $(a_2) = -x, -y, -z + 2; (b_2) = x - 1/2, -y + 1/2, z - 1/2; (c_2) = -x + 1/2, y + 1/2, -z + 5/2; (d_2) = -x, y, -z + 3/2.$

the trigonality parameter τ being 0.2 ($\tau = 0$ and 1 for square pyramidal and trigonal bipyramidal surroundings, respectively).43 The basal positions are occupied by the three bpcanitrogen atoms and a water molecule whereas the apical site is filled by a sulphonate-oxygen atom from the triflate group. The Cu-N bond distances [1.931(2)-2.002(3) Å] are close to those reported for previous structural reports concerning [bis(2-arylcarbonyl)amido]copper(II) complexes^{1,2,7b-d,8-11,15} and the remaining basal Cu– O_w bond length [1.971(2) Å] is shorter than the apical Cu–O_{triflate} interaction [2.297(2) Å]. The copper(π) ion is shifted by 0.0114(3) Å from the mean basal plane towards the apical site. The reduced bite of the two fused fivemembered chelate rings subtended at the $copper(\pi)$ ion by the tridentate bpca ligand accounts for significant departure of the values of the angles N(1)-Cu(1)-N(2) [82.32(9)°] and N(2)-Cu(1)-N(3) [82.20(8)°] from the ideal value of 90°.

The two pyridylcarbonyl halves of the bpca ligand form a dihedral angle of $3.38(6)^\circ$, a value which is in the range of those reported for other [bis(2-arylcarbonyl)amido]copper(π)

complexes $(1.5-8.6^{\circ})$.^{1,2,7b-d,8-11,15} The bonding parameters of the CF₃SO₃⁻ ligand are similar to those found in other complexes and it adopts a staggered-ethane conformation about the S–C bond and the O–S–O angles are greater than the C–S–O ones. The S(1)–O(3) bond length [1.440(2) Å] is somewhat longer than those involving the terminally bound oxygen atoms [mean value 1.429(2) Å] because of the monodentate coordination through O(3) to the copper(π) ion.

 $[Cu(bpca)(Phpr)(H_2O)]\cdot 3/2H_2O$ (2). The structure of 2 is made up of discrete neutral $[Cu(bpca)(Phpr)(H_2O)]$ units and water of crystallization (Fig. 3) which are interlinked by van der Waals forces and hydrogen bonds (see the end of Table 3) leading to a supramolecular three-dimensional network (Fig. 4).

Each copper(II) ion in 2 exhibits a somewhat distorted square pyramidal CuN₃O₂ chromophore ($\tau = 0.20$) comprising a tridentate bpca ligand [values of the Cu–N bond lengths in the range 1.9391(13)–2.012(2) Å], a carboxylate-oxygen atom [Cu(1)–O(3) = 1.9365 Å] forming the equatorial plane and a

Copper(II) environments				
Cu(1)-N(1)	1.9956(19)	Cu(2)–O(6)	1.9766(14)	
Cu(1)-N(2)	1.9163(17)	Cu(2)-O(1W)	2.425(2)	
Cu(1)-N(3)	2.0111(19)	Cu(3) - N(6)	2.0129(17)	
Cu(1) - O(4)	1.9683(14)	Cu(3) - N(7)	1.9293(17)	
Cu(1) - O(3)	2.3277(15)	Cu(3) - N(8)	1.9894(17)	
Cu(2) - N(4)	1.9221(16)	Cu(3) - O(7)	1.9553(14)	
Cu(2) - N(5)	1.9177(16)	Cu(3) - O(8)	2.3201(14)	
Cu(2) - O(5)	1.9846(15)			
N(1)-Cu(1)-N(2)	82.54(8)	N(5)-Cu(2)-O(5)	165.65(7)	
N(1)-Cu(1)-N(3)	162.39(7)	N(5)-Cu(2)-O(1W)	96.35(7)	
N(1)-Cu(1)-O(3)	94.19(7)	O(5) - Cu(2) - O(6)	107.77(6)	
N(1)-Cu(1)-O(4)	99.71(7)	O(5)-Cu(2)-O(1W)	91.41(7)	
N(2)-Cu(1)-N(3)	82.40(8)	O(6) - Cu(2) - O(1W)	90.07(7)	
N(2)-Cu(1)-O(3)	108.52(7)	N(6)-Cu(3)-N(7)	81.99(8)	
N(2)-Cu(1)-O(4)	172.86(7)	N(6) - Cu(3) - N(8)	163 48(7)	
N(3)-Cu(1)-O(3)	99.21(6)	N(6) - Cu(3) - O(7)	96 16(7)	
N(3)-Cu(1)-O(4)	94 21(7)	N(6) - Cu(3) - O(8)	92 47(6)	
O(3)-Cu(1)-O(4)	78 17(5)	N(7) - Cu(3) - N(8)	82 51(8)	
N(4) - Cu(2) - N(5)	82 99(7)	N(7) - Cu(3) - O(7)	173 86(7)	
N(4) - Cu(2) - O(5)	83 76(6)	N(7) = Cu(3) = O(8)	106.89(6)	
N(4) - Cu(2) - O(6)	164 46(7)	N(2) - Cu(3) - O(7)	100.09(0)	
N(4) - Cu(2) - O(0) N(4) - Cu(2) - O(1W)	104.40(7) 100.24(7)	N(8) - Cu(3) - O(7) N(8) - Cu(3) - O(8)	98.00(7)	
N(4) - Cu(2) - O(W)	100.24(7)	O(7) Cu(2) O(8)	79.00(x)	
N(3)-Cu(2)-O(0)	84.34(0)	O(7) - Ou(3) - O(8)	78.99(X)	
C(12) $O(2)$	1 240(2)	C(17) $C(19)$	1 202(2)	
C(13) - O(3) C(12) - O(5)	1.240(2) 1.266(2)	C(17) = C(10)	1.362(3) 1.291(2)	
C(13) = O(3) C(12) = C(14)	1.200(3)	C(10) - C(19)	1.301(3)	
C(13) - C(14)	1.352(5)	V(5) - C(20)	1.390(3)	
C(14) - O(4)	1.200(2)	N(5) = C(20)	1.397(3)	
C(14) - N(4)	1.293(2)	C(21) = N(5)	1.315(2)	
N(4) = C(15)	1.408(3)	C(21) - O(8)	1.244(2)	
C(15) - C(16)	1.381(3)	C(21) - C(22)	1.556(3)	
C(15) - C(20)	1.41/(3)	C(22) = O(6)	1.253(2)	
C(16) - C(17)	1.337(2)	C(22) = O(7)	1.255(2)	
C(13)-O(3)-Cu(1)	106.8/(13)	C(17)-C(18)-C(19)	120.4(2)	
C(14) - O(4) - Cu(1)	116.28(13)	C(18)-C(19)-C(20)	119.94(19)	
O(3)-C(13)-O(5)	125.98(19)	C(19)-C(20)-N(5)	126.96(18)	
O(3)-C(13)-C(14)	116.92(18)	C(19)-C(20)-C(15)	119.10(19)	
O(5)-C(13)-C(14)	117.09(18)	N(5)-C(20)-C(15)	113.92(17)	
C(13)-O(5)-Cu(2)	111.39(13)	C(20)-N(5)-Cu(2)	114.99(12)	
C(13)-C(14)-O(4)	118.79(17)	C(20)-N(5)-C(21)	129.61(17)	
C(13)-C(14)-N(4)	111.74(17)	C(21)-N(5)-Cu(2)	115.37(13)	
O(4)-C(14)-N(4)	129.45(19)	N(5)-C(21)-O(8)	131.20(19)	
C(14)-N(4)-Cu(2)	115.51(14)	N(5)-C(21)-C(22)	109.69(17)	
C(14)-N(4)-C(15)	129.84(17)	O(8)-C(21)-C(22)	119.12(17)	
C(15)-N(4)-Cu(2)	114.64(13)	C(21)-O(8)-Cu(3)	104.19(12)	
N(4)-C(15)-C(16)	126.25(18)	C(21)-C(22)-O(6)	119.23(18)	
N(4)-C(15)-C(20)	113.45(17)	C(21)-C(22)-O(7)	117.17(17)	
C(16)-C(15)-C(20)	120.27(18)	O(6)-C(22)-O(7)	123.60(18)	
C(15)-C(16)-C(17)	119.44(19)	C(22)-O(6)-Cu(2)	110.31(13)	
C(16)-C(17)-C(18)	120.8(2)	C(22)-O(7)-Cu(3)	116.11(12)	
Hydrogen bonds ^{b,c}		-		
D-H···A	D-Н (Å)	H…A (Å)	D…A (Å)	D-H…A
$O(2W2)-H(222)\cdots O(5a_3)$	0.89(2)	2.06(4)	2.885(6)	154(7)
$O(2W2) - H(221) \cdots O(9b_3)$	0.91(2)	2.12(6)	2.773(6)	128(6)
$O(1W) - H(1W1) - O(3a_3)$	0.891(10)	2.071(12)	2.945(2)	167(3)
O(1W) - H(2W1) - O(2W2)	0.891(10)	2.02(2)	2.867(19)	159(3)
		• •		

^{*a*} Estimated standard deviations in the last significant digits are given in parentheses. ^{*b*} D and A stand for donor and acceptor, respectively. ^{*c*} Symmetry code: $(a_3) = -x + 2, -y + 1, -z; (b_3) = -x + 2, -y, -z + 1.$

water molecule [Cu(1)–O(1W) = 2.365(2) Å] in the apical position. In fact, although the copper(II) ion in 2 can be considered as basically five-coordinate, the O(4) carboxylate-oxygen atom is occupying a sixth coordinating position at a distance of 2.852(2) Å. As in 1, some of the angles subtended at the ligating atoms are far from the ideal 90 and 180° [81.64(6), 81.63(6) and 163.10(6)° for N(1)–Cu(1)–N(2), N(2)–

Cu(1)–N(3) and N(1)–Cu(1)–N(3), respectively]. The rigidity of the tridentate bpca ligand is at the origin of these deviations. The copper atom is displaced by 0.0071(3) Å from the mean basal plane toward O(1W).

No unusual bonds lengths and angles are observed in the bpca ligand and the dihedral angle between its two pyridylcarbonyl halves is $6.63(8)^{\circ}$. The C(14)C(13)(O3)O(4) set of

(°)

Copper(II) environments				
Cu(1) - N(1)	1.994(2)	Cu(2)-N(6)	1.990(2)	
Cu(1) - N(2)	1.9053(19)	Cu(2) - N(7)	1.9253(18)	
Cu(1) - N(3)	1.996(2)	Cu(2) - N(8)	2.007(2)	
Cu(1) - O(3)	1.9271(16)	Cu(2) - O(7)	1.9300(16)	
$Cu(1) - O(3a_4)$	2.6692(19)	Cu(2) - O(8)	2.2386(17)	
N(1) - Cu(1) - N(2)	82.66(8)	N(6)-Cu(2)-N(7)	82.26(8)	
N(1)-Cu(1)-N(3)	164.61(8)	N(6) - Cu(2) - N(8)	160.99(8)	
N(1)-Cu(1)-O(3)	97.06(8)	N(6) - Cu(2) - O(7)	97.07(8)	
$N(1)-Cu(1)-O(3a_4)$	93.60(7)	N(6)-Cu(2)-O(8)	95.79(7)	
N(2)-Cu(1)-N(3)	82.58(8)	N(7)-Cu(2)-N(8)	82.01(8)	
N(2)-Cu(1)-O(3)	176.44(9)	N(7)-Cu(2)-O(7)	177.46(8)	
$N(2)-Cu(1)-O(3a_4)$	99.28(8)	N(7)-Cu(2)-O(8)	102.41(7)	
N(3)-Cu(1)-O(3)	97.95(8)	N(8)-Cu(2)-O(7)	98.17(8)	
$N(3)-Cu(1)-O(3a_4)$	93.05(7)	N(8)-Cu(2)-O(8)	97.96(7)	
$O(3)-Cu(1)-O(3a_4)$	77.19(7)	O(7)-Cu(2)-O(8)	80.09(6)	
Hydrogen bonds ^{b,c}	_		_	
D-H···A	D–H (Å)	H…A (Å)	D…A (Å)	$D-H\cdots A(^{\circ})$
$N(5)-H(5)\cdots O(9b_4)$	0.86	2.29	3.026(3)	144.3
$N(5)-H(5)-O(10b_4)$	0.86	2.26	2.877(3)	128.6
$N(4)-H(4)\cdots O(9b_4)$	0.86	2.15	2.990(3)	164.6
$O(1W)-H(11A)-O(4c_4)$	0.856(18)	2.80(4)	2.890(4)	87(3)
$O(2W)-H(12A)\cdots O(2d_4)$	0.850(18)	2.03(2)	2.858(3)	165(3)
O(2W)-H(12B)-O(1)	0.850(18)	2.17(3)	2.875(3)	141(3)
$O(3W)-H(13B)-O(6e_4)$	0.819(13)	2.376(19)	3.046(4)	140(3)
$O(3W)-H(13A)-O(4b_4)$	0.815(13)	2.419(18)	3.045(4)	134(2)
$O(3W)-H(13B)-O(7e_4)$	0.819(13)	2.47(2)	3.162(3)	143(3)
<i>a</i>		<i>h</i> _		

^{*a*} Estimated standard deviations in the last significant digits are given in parentheses. ^{*b*} D and A stand for donor and acceptor, respectively. ^{*c*} Symmetry code: $(b_4) = 1 + x, +y, +z; (c_4) = 1 - x, 1 - y, 1 - z; (d_4) = 2 - x, 1 - y, 1 - z; (e_4) = 1 - x, -y, 2 - z; (e_4) = 1 - x, -y, 2 - z;$

atoms from the Phpr ligand are planar and the different C-O values [1.284(2) and 1.220(2) Å for C(13)-O(3) and C(13)-O(4), respectively] are consistent with its equatorial and pseudoaxial coordination through O(3) and O(4) atoms, respectively. A supramolecular one-dimensional arrangement of the mononuclear copper(II) units involving the coordinated water molecule O(1W), the crystallization water molecule O(2W) and the carboxylate-oxygen O(4) $[O(1W)\cdots O(2Wb_2) = 2.873(2)$ Å and $O(2W)\cdots O(4) = 2.808(2)$ Å] is observed in the crystal packing of 2 (see Fig. 4a). These chains are interlinked through an additional hydrogen bond between the coordinated water molecule [O(1W)] and the bpca carbonyl-oxygen O(1) [O(1W)... $O(1a_2) = 2.872(4)$ Å] affording layered motifs, which are in turn connected through another hydrogen bond between the free water molecule O(3W) and the carboxylate-oxygen $O(3d_2)$ $[O(3W)\cdots O(3d_2) = 2.885(2) \text{ Å}]$ to afford a supramolecular threedimensional structure (see Fig. 4b). Finally, weak π - π type interactions between the phenyl ring of the Phpr ligand and the pyridyl-bpca rings [values of the angle between the normal to the phenyl-Phpr and centroid pyridyl-bpca rings of 21.82(6) and 18.35(6)° and centroid-centroid distances of 3.9401(3) and 3.7825(3) Å] contribute to the stabilization of the supramolecular arrangement of 2.

The shorter intermolecular copper-copper separation in 2 is $6.6474(6) \text{ Å} [Cu(1) \cdots Cu(1d_2)].$

{[Cu(bpca)]₂[Cu(opba)(H₂O)]]·H₂O (3). The structure of 3 consists of the neutral tricopper(π) unit of formula {[Cu-(bpca)]₂[Cu(opba)(H₂O)]} and a crystallization water molecule [O(2W)] (Fig. 5), the inner [Cu(opba)(H₂O)]²⁻ unit from each

trinuclear entity acting as a bis-bidentate ligand towards two peripheral $[Cu(bpca)]^+$ fragments. Centrosymmetric bis-trinuclear motifs result by hydrogen bonds involving the coordinated water molecule [O(1W)] and one oxamate-oxygen $[O(3a_3)]$, the disordered water molecule O(2W) contributing also to the stabilization of this supramolecular assembling by additional hydrogen bonds (see Fig. 6 and the end of Table 4).

The central copper(π) ion [Cu(2)] in 3 is five-coordinate in distorted square pyramidal surroundings with $\tau = 0.02$. Two deprotonated amidate-nitrogens and two carboxylate-oxygen atoms from the opba ligand build the basal plane and a water molecule [O(1W)] fills the apical position. The average Cu(2)-N and Cu(2)-O bond lengths in the basal plane [1.919(2) and 1.981(2) Å, respectively] agree with those previously reported for the [Cu(opba)]^{2–} unit in other structurally characterized tricopper(II) compounds where this entity adopts the bis-chelating coordination mode,44 the shorter value for the coppernitrogen interaction being due to the stronger basicity of the amidate-nitrogen compared to that of the carboxylateoxygen.⁴⁵ Cu(2) is shifted by 0.1385(9) Å from the mean basal plane towards O(1W). The geometrical constraints caused by the occurrence of the three fused five-membered chelate rings subtended by the opba ligand at the Cu(2) account for the severe distortion of the ideal basal square at the copper environment: an opening of the less constrained O(5)-Cu(2)-O(6) angle $[107.77(6)^{\circ}]$ whereas the bite angles at the 5-5-5 fused chelate rings are smaller than 90° [82.99(7), 83.76(6) and 84.34(6)° for N(4)-Cu(2)-N(5), N(4)-Cu(2)-O(5) and N(4)-Cu(2)–O(6), respectively].

Table 6 Selected bond distances (Å) and angles (°) for **5**^{*a,b*}

Copper environment Cu(1)-N(3) Cu(1)-N(4) Cu(1)-N(5) N(3)-Cu(1)-N(4) N(3)-Cu(1)-N(5) N(3)-Cu(1)-O(5) N(3)-Cu(1)-O(4) $N(3)-Cu(1)-O(6a_5)$ N(4)-Cu(1)-N(5) N(4)-Cu(1)-O(5)	$\begin{array}{c} 1.9937(13) \\ 1.9438(13) \\ 1.9987(13) \\ 87.71(5) \\ 162.71(5) \\ 96.82(5) \\ 90.41(5) \\ 86.29(5) \\ 82.61(5) \\ 174.13(5) \end{array}$	$\begin{array}{c} Cu(1)-O(5)\\ Cu(1)-(O4)\\ Cu(1)-O(6a_5)\\ N(4)-Cu(1)-O(6a_5)\\ N(5)-Cu(1)-O(5)\\ N(5)-Cu(1)-O(4)\\ N(5)-Cu(1)-O(4a_5)\\ O(5)-Cu(1)-O(4)\\ O(5)-Cu(1)-O(6a_5)\\ O(4)-Cu(1)-O(6a_5)\\ \end{array}$	$\begin{array}{c} 1.9583(11)\\ 2.4649(11)\\ 2.4255(11)\\ 95.28(5)\\ 98.71(5)\\ 100.79\\ 86.02(5)\\ 75.46(4)\\ 90.52(4)\\ 165.13(4) \end{array}$	
N(4)-Cu(1)-O(4) EtH ₂ opba ⁻ ligand C(23)-C(24) C(22)-O(2)	98.69(5) 1.448(3) 1.470(2)	C(6)-C(7)	1.384(2)	
C(23)-O(2) C(1)-O(2) C(1)-O(1) C(1)-C(2)	1.470(2) 1.322(2) 1.198(2) 1.544(2)	C(7)-C(8) C(8)-C(9) C(9)-C(10) C(10)-N(2)	1.380(2) 1.387(2) 1.388(2) 1.4302(19)	
C(2)-O(3) C(2)-N(1) C(5)-N(1)	1.215(2) 1.349(2) 1.418(2)	N(2)-C(4) C(4)-O(4) C(3)-C/4)	1.3375(19) 1.2351(18) 1.556(2)	
C(5)-C(10) C(5)-C(6) C(3)-O(5)-Cu(1)	1.402(2) 1.397(2) 122.52(9)	C(3)-O(5) C(3)-O(6) C(6)-C(7)-C(8)	1.2720(18) 1.2275(18) 120.38(15)	
$C(3)-O(6)-Cu(1b_5)$ $O(5)-C(3)-O(6)$ $O(5)-C(3)-C(4)$ $O(5)-C(3)-C(4)$	128.35(10) 127.27(14) 115.19(13)	C(7)-C(8)-C(9) C(8)-C(9)-C(10) C(10)-C(5)-N(1) C(2)-N(1)	$119.51(16) \\120.80(15) \\119.64(14) \\121.04(14) \\121.$	
O(b)-C(3)-C(4) C(3)-C(4)-O(4) C(3)-C(4)-N(2) O(a)-C(4)-N(2)	$ \begin{array}{c} 117.53(13) \\ 120.78(13) \\ 113.68(12) \\ 125.52(14) \end{array} $	C(6)-C(5)-N(1) C(5)-N(1)-C(2) N(1)-C(2)-O(3) N(1)-C(2)-C(1)	$121.34(14) \\125.27(14) \\127.18(16) \\111.23(14)$	
$\begin{array}{c} C(4) - N(2) \\ C(4) - N(2) - C(10) \\ N(2) - C(10) - C(5) \\ N(2) - C(10) - C(9) \end{array}$	$123.32(14) \\126.96(13) \\123.78(14) \\116.39(13)$	$\begin{array}{c} N(1) - C(2) - C(1) \\ O(3) - C(2) - C(1) \\ C(2) - C(1) - O(2) \\ C(2) - C(1) - O(1) \end{array}$	111.23(14) $121.56(15)$ $110.00(14)$ $123.71(15)$	
C(9) - C(10) - C(5) C(10) - C(5) - C(6) C(5) - C(6) - C(7)	119.78(14) 118.97(15) 120.54(15)	$\begin{array}{c} O(1) - O(2) \\ C(1) - O(2) - C(23) \\ O(2) - C(23) - C(24) \end{array}$	$126.29(16) \\116.01(14) \\106.38(15)$	
Hydrogen bonds ^c D-H···A N(1)-H(1)···O(1) N(1)-H(1)···O(4)	D–H (Å) 0.887(10) 0.887(10)	H…A (Å) 2.32(3) 2.014(19)	D…A (Å) 2.7114(19) 2.7704(17)	D-H···A (°) 107(2) 142(3)
$N(2)-H(2)-O(8a_5)$	0.891(10)	2.012(17)	2.8149(17)	149(3)

^{*a*} Estimated standard deviations in the last significant digits are given in parentheses. ^{*b*} D and A stand for donor and acceptor, respectively. ^{*c*} Symmetry code: $(a_5) = x, y + 1, z$.

The terminal copper(π) ions [Cu(1) and Cu(3)] are also fivecoordinate in distorted square pyramidal surroundings with $\tau = 0.17$ [Cu(1) and Cu(3)]. The basal positions at each peripheral copper(II) ion are occupied by the three bpca-nitrogen atoms [N(1), N(2) and N(3) at Cu(1) and N(6), N(7) and N(8) at Cu(3)] and one outer carboxylate-oxygen [O(7) at Cu(3)] and an oxamate-oxygen [O(4) at Cu(1) from the [Cu(2)(opba)] fragment whereas the apical position is filled by the remaining oxamate- [O(8) at Cu(3)] and carboxylate-oxygen [O(3) at Cu(1)] atoms of such a fragment. The supramolecular bis-trinuclear assembling through the O(1W)...O(3a₃) and its symmetryrelated pair (see Fig. 6) is most likely responsible for the axial coordination of O(3) towards Cu(1) versus the equatorial one of O(7) towards Cu(3). The pattern of the Cu–N_{bpca} bond lengths [the Cu-N_{imido} bond being shorter than the two Cu-N_{pyridyl} ones] is as observed in 1 and 2. Cu(1) and Cu(3) are shifted by 0.1419(0) and 0.1068(8) Å respectively, from the mean basal plane towards the apical position.

The central $[Cu(2)(opba)]^{2-}$ moiety is quite flat indicating a π -conjugating system extended to the CuN₂O₂ chromophore. Within a trinuclear unit the dihedral angles between the central Cu(2) and the terminal Cu(1) and Cu(3) basal planes are 83.98(6) and 78.24(5)°, respectively. The values of the intra-molecular copper-copper separation are 5.3492(4) [Cu(1)- \cdots Cu(2)] and 5.2507(4) Å [Cu(2) \cdots Cu(3)], whereas that of the shortest intermolecular metal-metal distance is 5.3936(5) Å [Cu(3) \cdots Cu(3c₃); symmetry code: (c₃) = -x + 3, -y, -z + 1].

 $\{[Cu(bpca)]_2(H_2opba)\}_2 \cdot 6H_2O$ (4). The crystal structure of 4 consists of centrosymmetric, neutral $\{[Cu(bpca)]_2(H_2opba)\}_2$ tetrameric units and crystallization water molecules (Fig. 7). Within each tetracopper(II) unit, the dideprotonated H_2opba^{2-} entity acts as a bridging ligand adopting simultaneously bidentate [through the oxamate O(7) and O(8) oxygen atoms towards Cu(2)] and bis-monodentate [through the carboxylate-oxamate O(3) towards Cu(1) and Cu(1a₄)] coordination modes, whereas the bpca exhibits the usual tridentate coordination at

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Fig. 1 ORTEP view of complex 1 with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.



Fig. 2 (a) View of fragments of the supramolecular chain growing in the [101] direction. (b) View of the supramolecular two-dimensional structure of **1** extending in the (101) plane. The hydrogen bonds are drawn as dashed lines.

each copper(II) ion. An extensive network of hydrogen bonds involving all the water molecules and the two N–H amide groups as donors and the carbonyl-oxygens from the bpca ligands plus three of the four carboxylate-oxygen atoms from the two oxamate groups as acceptors lead to a supramolecular two-dimensional structure (see the end of Table 5 and Fig. 8). π – π type interactions between the planes defined by N (6)C(27)C(26)C(25)C(24)C(13) and N(3c_3)C(8c_3)C(9c_3)C-(10c_3)C-(11c_3)C(12c_3) also occur [symmetry operation: (c_3) = 1 + x, +y, +z]. The distance of each aromatic ring centroid is 3.6181(4) Å. The least-square planes defined by aromatic rings are 6.6(2)° from each other showing the formation of π ··· π interaction.



Fig. 3 ORTEP view of complex 2 with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.



Fig. 4 (a) Details of the hydrogen bonding pattern in **2** leading to a supramolecular three-dimensional arrangement. (b) A view of the packing in **2** down the crystallographic *b* axis. The hydrogen bonds are drawn as dashed lines.

Two crystallographically independent copper(II) ions [Cu(1) and Cu(2)] occur in 4. They are both five-coordinate in distorted square pyramidal CuN₃O₂ surroundings with values of the trigonality parameter of 0.20 [Cu(1)] and 0.27 [Cu(2)]. The bpca-nitrogen atoms [N(1), N(2) and N(3) at Cu(1) and N(6), N(7) and N(8) at Cu(2)] and the carboxylate(oxamate)-oxygens from an opba^{2–} ligand [O(3) at Cu(1) and O(7) at Cu(2)] build the basal plane whereas the apical position is occupied by



Fig. 5 ORTEP view of complex 3 with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.



Fig. 6 View of the supramolecular bis-trinuclear assembling in **3**. The hydrogen bonds are represented as dashed lines and the hydrogen atoms are omitted for clarity.

either one carbonyl-oxygen from this bis-oxamate ligand [O(8) at Cu(2)] or a carboxylate(oxamate)-oxygen atom from a symmetry-related opba²⁻ ligand [O(3a₄) at Cu(1)]. The Cu-N_{bpca} bond lengths vary in the ranges 1.9053(19)–1.9996(2) and 1.9253(18)–2.007(2) Å around Cu(1) and Cu(2) respectively, values which agree with those observed in 1–3. The values of the basal copper to carboxylate(oxamate) bond distance in 4 [1.9271(16) and 1.9300(16) Å] are very close to the equatorial copper to carboxylate(3-phenylpropionate) in 2 [Cu(1)–O(3) = 1.9365(13) Å]. Whereas Cu(1) lies in the basal plane defined by the N(1)N(2)N(3)O(3) set of atoms, Cu(2) is shifted by 0.1106 Å from its mean basal plane towards the apical O(8) atom.

The phenyl ring of the H₂opba²⁻ ligand and one of its two oxamate arms [O(3)C(13)O(4)C(14)N(4)O(5)] are quasi-planar and their mean planes form a dihedral angle of 17.0(1)°. However, the other oxamate fragment [N(5)C(21)O(8)C(22)O(6)-O(7)] exhibits a significant twisting, the value of the dihedral angle between the planes of the carboxylate and amide groups being 71.06(8)°. This structural flexibility of the H₂opba²⁻



Fig. 7 (a) ORTEP view of the crystallographically independent unit of **4** with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level and the hydrogen atoms are omitted for clarity. (b) Perspective view of the tetranuclear motif of **4**.



Fig. 8 View of the assembling of the tetranuclear units of **4** along two different directions. The hydrogen bonds are drawn as dashed lines and the hydrogen atoms are omitted for clarity.

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Fig. 9 (a) ORTEP view of the crystallographically independent unit of **5** with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. (b) View of a fragment of the neutral chain of **5** running parallel to the crystallographic *b* axis (hydrogen bonds are drawn as dashed lines and the hydrogen atoms are omitted for clarity).

ligand in 4 compared to the planarity of its fully deprotonated opba^{4–} form in 3 is due to the different coordination modes that they exhibit which are related to their different protonation degrees. The low basicity of the amide-nitrogen atoms of the H₂opba^{2–} ligand accounts for the coordination to the $[Cu(bpca)]^+$ fragments through its carboxylate-oxygen atoms. The two crystallographically independent bpca ligands are practically planar [max. deviation from the mean plane being 0.1207(27) Å at the C(32) atom]. The intramolecular copper-copper distances amount to 3.6220(7) Å [Cu(1)…Cu(1a₄)] and 10.2014(9) Å [Cu(1)…Cu(2)] whereas the shortest intermolecular metal-metal separation is 4.8312(7) Å [Cu(2)…Cu(2f4); symmetry code: (f₄) = -x - 1, -y, -z + 2].

 $[Cu(bpca)(EtH_2opba)]_n$ (5). The crystal structure of 5 is made up of neutral zigzag chains of copper(II) ions where the [Cu(bpca)] units are connected through the EtH_2opba^- ligand which adopts a bidentate/outer monodentate bridging mode (Fig. 9). Intra- and interchain hydrogen bonds involving N–H and opba/bpca carbonyl-oxygens are observed (see the end of Table 6 and Fig. 9b). There are two types of $\pi \cdots \pi$ interactions that contribute to stabilize the structure of 5 leading to a supramolecular two-dimensional structure. One of them is between phenyl rings of $EtH_2opba [C(5)C(6)C(7)C(8)C(9)C(10)]/$



Fig. 10 View of the packing in **5** showing interchain π - π type interactions.

 $[C(5d_5)C(6d_5)C(7d_5)C(8d_5)C(9d_5)C(10d_5)]$ with a centroidcentroid distance of 3.8730 Å [symmetry code: $(d_5) = 1 - x$, 2 - y, 1 - z] (see Fig. 10). An additional π - π stacking interaction arises from pyridyl rings of pairs of bpca ligand [N(5)C(18)-C(19)C(20)C(21)C(22)/N(5e_5)C(18e_5)C(19e_5)C(20e_5)C(21e_5)C(22e_5)] with a centroid-centroid distance of 3.8225 Å [symmetry code: $(e_5) = 2 - x$, 1 - y, 1 - z].

The crystallographically independent copper(II) ion is sixcoordinate in a somewhat distorted elongated octahedral CuN₃O₃ environment. Three equatorial positions at each copper(II) ion are occupied by the N(3), N(4) and N(5) nitrogen atoms from the tridentate bpca ligand whereas the remaining equatorial site and one of the axial positions are filled by the O(5) carboxylate- and the O(4) carbonyl-oxygen atoms respectively, from the monodeprotonated oxamate group of the EtH₂opba⁻ monoester derivative. The other axial position is occupied by the O(6a₅) carboxylate-oxygen from a symmetryrelated EtH₂opba⁻ ligand. The copper atom is shifted by only 0.0220(6) Å from the mean equatorial plane towards the axial O(4) atom. The Cu–N_{bpca} [values in the range [1.9438(13)– 1.9987(13) Å] and Cu–O_{eq} [Cu(1)–O(5) = 1.9583(11) Å] bond lengths agree with those reported for the above structures.

The monodeprotonated oxamate group in 5 exhibits a bidentate/outer monodentate bridging mode, the N(2) amidenitrogen being not involved in the coordination given its low basicity. This non-coordination of the amide nitrogen is also observed in the two monoprotonated oxamate groups in the structure of compound 4, the difference being that these act as bidentate (one of them) and bridging bis-monodentate (the other one) in 4. The bpca ligand and the bridging monoprotonated oxamate group are practically planar [max. deviation from the mean planes being 0.2963(16) Å at the C(13) atom and -0.1452(10) Å at the O(5) atom, respectively]. The values of the dihedral angle between the bridging monoprotonated oxamate [O(5)O(4)O(6)C(4)C(3)N(2)] and the mean equatorial planes of two adjacent copper(II) ions [O(5)N(5)N(4)N(3)] within each chain are 86.28(3) and 89.99(3)°. The intrachain



Fig. 11 $\chi_M T$ versus T plot for compound **3**: (O) experimental; (–) best-fit curve through eqn. (2) (see text).

copper-copper separation is 5.5356(2) Å [Cu(1)-Cu(1b₅); symmetry code: (b₅) = 2 - x, -0.5 + y, 1.5 - z], a value which is smaller than the shortest interchain metal-metal separation [7.9459(4) Å for Cu(1)···Cu(1c₅); symmetry code: (c₅) = 2 - x, 1 - y, 1 - z].

Magnetic properties of 3-5

The magnetic properties of 3 in the form of the $\chi_M T$ versus T plot [χ_M is the magnetic susceptibility per three copper(II) ions] are shown in Fig. 11. At room temperature, $\chi_M T$ is equal to 1.03 cm³ mol⁻¹ K, a value which is smaller than that expected for three magnetically isolated copper(II) ions ($\chi_M T = 1.20$ cm³ mol⁻¹ K with $g_{Cu} = 2.09$). Upon cooling, $\chi_M T$ continuously decreases to reach a plateau in the temperature range 20–6.0 K with $\chi_M T = 0.406$ cm³ mol⁻¹ K, a value which is as expected for a spin doublet state with g = 2.08. Finally, $\chi_M T$ exhibits a very small decrease in the very low temperature range attaining a value of 0.395 cm³ mol⁻¹ K at 1.9 K. These features are indicative of a relatively strong intramolecular antiferromagnetic interaction leading to a low lying spin doublet, the incipient decrease of $\chi_M T$ at very low temperatures being due to an extremely weak intermolecular magnetic interaction.

The spin Hamiltonian appropriate to describe the magnetic properties of the tricopper(π) unit of 1 is given by eqn (1)

$$\boldsymbol{H} = -J_{12} \boldsymbol{S}_{\mathrm{Cu}_1} \cdot \boldsymbol{S}_{\mathrm{Cu}_2} - J_{23} \boldsymbol{S}_{\mathrm{Cu}_2} \cdot \boldsymbol{S}_{\mathrm{Cu}_3}$$
(1)

where J_{12} and J_{23} denote the exchange coupling parameters between the central and peripheral copper(II) ions. The expression for the magnetic susceptibility deduced from this Hamiltonian is given by eqn (2)

$$\chi_{\rm M} = (Ng^2\beta^2/4kT) \ [A/B] \tag{2}$$



Scheme 2 Relative orientations of magnetic orbitals for the oxamato bridges.

with

and

$$A = \{1 + \exp[-J/kT] + 10 \, \exp[J/2kT]\}$$

$$B = \{1 + \exp[-J/kT] + 2 \exp[J/2kT]\}$$

where *g* is the average Landé factor for the three copper(II) ions and it has been assumed that $J_{12} = J_{23} = J$. The quasi negligible deviation of the Curie law behaviour for a spin doublet in the very low temperature range, which can be seen in Fig. 11, accounts for the lack of magnetic coupling between peripheral copper(II) ions in **3**. Excellent agreement between calculated and experimental magnetic data has been obtained with the parameters $J = -65.8(2) \text{ cm}^{-1}$, $g = 2.08(1) \text{ cm}^{-1}$ and R = 2.1×10^{-5} (*R* is the agreement factor defined as $\sum_i [(\chi_M T)_{obs}(i) - (\chi_M T)_{calcd}(i)]^2 / \sum_i [(\chi_M T)_{obs}(i)]^2$).

Two families of oxamato-bridged trinuclear copper(II) complexes have been magneto-structurally characterized: one with bidentate diamines as capping ligands and the other one with tridentate triamines as blocking ligands. Both families exhibit intramolecular antiferromagnetic couplings, but they are much larger in the former one [-J] values in the ranges 330-380 cm⁻¹ (diamines) and 84-196 cm⁻¹ (triamines)].^{44,46-48} The type of interacting magnetic orbitals [that is the molecular orbital which describes the unpaired electron on each copper(II) ion] and their relative orientation account for these two extreme situations. In the case where a bidentate diamine acts as the terminal ligand, the peripheral copper(II) ions exhibit a square pyramidal surrounding. The involved magnetic orbitals are of the $d_{x^2-y^2}$ type and they are localized in the basal plane (see Scheme 2a). The good σ in-plane overlap between the peripheral magnetic orbitals and the central one through the OCN and OCO arms of the two oxamato bridges is responsible for the strong antiferromagnetic coupling observed (-J values



Fig. 12 $\chi_M T$ versus T plot for compound **4**: (O) experimental; (–) best-fit curve through eqn. (3) (see text).

of *ca.* 330–380 cm⁻¹). Subtle structural factors such as the deviation of the coplanarity of the three basal planes or the shift of the copper(II) ion from the basal plane are at the origin of small changes of the value of the antiferromagnetic coupling in this family. Concerning the second family, the magnetic orbital at each peripheral copper(π) ion can be described by d_{22} (Scheme 2b) or $d_{x^2-y^2}$ (Scheme 2c) type magnetic orbitals or by an intermediate situation. In the two cases, the overlap is reduced (σ pathway through the OCN arm of each oxamato bridge) and then, the antiferromagnetic coupling is decreased, the weakening of the magnetic coupling being greater for the case of Scheme 2c, as discussed in a previous contribution.^{46c,49} The situation in 3 corresponds to Scheme 2c and the value of the observed magnetic coupling $(J = -65.8 \text{ cm}^{-1})$ is close to the lowest value previously reported for this family $[J = -84 \text{ cm}^{-1} \text{ for the compound } \{[Cu(terpy)]_2Cu(pba)\}(ClO_4)_2$ with terpy = 2,2':6',2''-terpyridine and H₄pba = N,N'-1,3-propylenebis(oxamic acid)].46c

The magnetic properties of 4 in the form of the $\chi_{\rm M}T$ versus *T* plot [$\chi_{\rm M}$ is the magnetic susceptibility per four copper(II) ions] are shown in Fig. 12. At room temperature, $\chi_{\rm M}T$ is 1.63 cm⁻¹ mol⁻¹ K, a value which is as expected for four magnetically isolated spin doublets ($\chi_{\rm M}T = 1.65$ cm³ mol⁻¹ K with $g_{\rm Cu} = 2.1$). Upon cooling, this value remains constant until *ca*. 60 K and then, it decreases smoothly to 1.22 cm³ mol⁻¹ K at 1.9 K. This behaviour agrees with an overall weak antiferromagnetic interaction.

Following the tetranuclear structure of **4**, its magnetic data were treated through eqn (3)

$$\chi_{\rm M} = (2N\beta^2 g^2/kT)[3 + \exp(-J/kT)]^{-1} + N\beta^2 g^2/2kT \qquad (3)$$

where the first term is the Bleaney-Bowers expression for a coupled binuclear copper(π) species and the second term is





Scheme 3 Equatorial–axial pathway through the parallel $d_{x^2-y^2}$ magnetic orbitals.

the Curie law for two magnetically non-interacting spin doublets. *N*, β , *g* and *k* have their usual meaning and *J* is the magnetic coupling between the inner copper(II) ions [Cu(1) and Cu(1a₄)]. A common *g* factor has been assumed for the two crystallographically independent Cu(1) and Cu(2) centers. Best-fit parameters are: $J = -2.36(2) \text{ cm}^{-1}$, g = 2.08(1) and $R = 1.7 \times 10^{-6}$ (*R* is the agreement factor defined as $\sum_i [(\chi_M T)_{obs}(i) - (\chi_M T)_{calcd}(i)]^2 / \sum_i [(\chi_M T)_{obs}(i)]^2$).

The weak intramolecular antiferromagnetic coupling between the symmetry-related Cu(1) and $Cu(1a_4)$ centers in 4 can be understood by simple orbital symmetry considerations. The unpaired electron on each copper(II) ion is of the $d_{x^2-y^2}$ type with the x and y axes being roughly defined by the short equatorial bonds [mainly located on the N(1)N(2)N(3)O(3) (at Cu(1)) and $N(1a_4)N(2a_4)N(3a_4)O(3a_4)$ (at $Cu(1a_4)$) basal planes]. These magnetic orbitals are parallel to each other and they are connected in an equatorial-axial pathway by a double oxocarboxylate bridge (see Scheme 3), the poor overlap between them allows the prediction of a weak antiferromagnetic interaction which could be ferromagnetic in the case of accidental orthogonality. Well known magneto-structural examples of this out-of-plane exchange pathway have been observed in other di-µ-chloro,⁵⁰ di-µ-oximato,⁵¹ di-µ-1,1-azido/cyanato⁵² and di-µ-oxo-carboxylato bridged dicopper(II) units (see Table 7), the sign and magnitude of the magnetic coupling depending mainly on the value of the bond angle at the bridgehead atom (θ) and the basal to apical Cu-X bond length (R_{ax}) . The values of these parameters for 4 [102.81(7)° and 2.6692(19) Å, respectively] are at the origin of the weak antiferromagnetic coupling $(J = -2.36(2) \text{ cm}^{-1})$ observed in this compound.

The magnetic properties of compound 5 in the form of the $\chi_{\rm M}T$ versus T plot [$\chi_{\rm M}$ is the magnetic susceptibility per copper(n) ion] are shown in Fig. 13. $\chi_{\rm M}T$ at room temperature is equal to 0.405 cm³ mol⁻¹ K, a value which is as expected for a magnetically isolated spin doublet. Upon cooling, this value remains constant until *ca*. 40 K and then decreases smoothly to 0.377 cm³ mol⁻¹ K at 1.9 K. The occurrence of a weak intrachain antiferromagnetic interaction accounts for this slight decrease of the $\chi_{\rm M}T$ product at low temperature.

Bearing in mind that the structure of 5 is made up of a zigzag chain of copper(II) ions bridged by a monodeprotonated oxamate group exhibiting the bidentate/outer monodentate coordination mode, its magnetic data were analyzed through

Table 7 Selected magneto-structural data for double µ-oxo carboxylate-bridged copper(1) complexes

Compound ^a	$R_{\mathrm{ax}}/\mathrm{\AA}$	$ heta/\circ$	J/cm ⁻¹	Ref.
$\{ [CuL^1(MeCO_2)]_2 \}$	2.665(4)	96.3(5)	-1.84	53
$\left[CuL^2 (MeCO_2) \right]_2$	2.577(2)	96.1(1)	-1.51	53
$\left[CuL^{3} (MeCO_{2}) \right]_{2}$	2.512(5)	96.9(2)	-1.33	54, 55
$\left[CuL^4 (MeCO_2) \right]_2 \cdot 2H_2O_n$	2.498(8)	98.1(3)	$-1.54(-2.26)^{b}$	55
$\left[CuL^{5}(MeCO_{2}) \right]_{2} \cdot 2MeOH \right]_{n}$	2.495(6)	98.3(5)	$-1.50(-7.88)^{b}$	56
$\left[CuL^{6}(MeCO_{2}) \right]_{2} \cdot H_{2}O \cdot 2EtOH$	2.446(2)	95.7(1)	+0.63 ^c	57
	2.651(1)	102.6(1)		
$\{ [Cu(PhCONHCH_2CO_2)(H_2O)_2]_2 \} \cdot 2H_2O \}$	2.37(1)	107.0(59	-2.15	58, 59
$[CuL7(MeCO2)]_2$	2.490(1)	95.34(5)	-0.25	60
$\left[Cu(tzq)_2(HCO_2) \right]_2(\mu - HCO_2)_2 \cdot 4H_2O$	2.331(4)	102.2(2)	-0.52	61
$[Cu(H_2O)_3][Cu(Phmal)_2]]_n$	2.443(2)	97.38(7)	$+1.95^{d}$	62
${[Cu(bpca)]_2(H_2opba)}_2 \cdot 6H_2O$	2.669(2)	102.81(7)	-2.36(2)	This work

^{*a*} HL¹ = *N*-(5-Bromosalicylidene)-*N*-methylpropane-1,3-diamine, HL² = *N*-methyl-*N*'-(5-nitrosalicylidene)propane-1,3-diamine, HL³ = *N*-methyl-*N*'-salicylidenepropane-1,3-diamine, HL⁴ = *N*-(5-methoxysalicylidene)-*N*'-methylpropane-1,3-diamine, HL⁵ = *N*,*N*'-[bis(2-*o*-hydroxybenzylideneamino)-ethyl]ethane-1,2-diamine, HL⁶ = *N*-(2-hydroxy-1,1-dimethylethyl)-salicyleneamine, HL⁷ = 7-amino-4-methyl-5-azahept-3-en-2-onate and H₂Phmal = phenylmalonic acid. ^{*b*} Magnetic analysis through an alternating chain model. ^{*c*} This is the only compound whose Cu₂O₂ core is non-centrosymmetric. ^{*d*} This value is *zj* and it has derived from a molecular mean field term.



Fig. 13 $\chi_M T$ versus T plot for compound **5**: (O) experimental; (–) best-fit curve through eqn. (4) (see text).

the theoretical expression proposed by Hall^{63*a*} for a uniform chain of local spins S = 1/2 [eqn. (4)]

with

$$A = 0.25 \pm 0.14995x \pm 0.30094x^2$$

 $\chi_{\rm M} = (N\beta^2 g^2/kT)[A/B]$

and

$$B = 1 + 1.9862x + 0.68854x^2 + 6.0626x^2$$

the Hamiltonian being $H = -J\sum_i S_i \cdot S_{i+1}$ and x = |J|/kT. This expression was derived from the numerical results from Bonner and Fisher^{63b} and it has been widely used for the treatment of the magnetic data of uniform copper(π) chains. Best-

fit parameters through eqn. (4) are: $J = -0.17(1) \text{ cm}^{-1}$, g = 2.08 and $R = 3.2 \times 10^{-5}$ (*R* is the agreement factor defined as $\sum_i [(\chi_M T)_{obs}(i) - (\chi_M T)_{calcd}(i)]^2 / \sum_i [(\chi_M T)_{obs}(i)]^2$).

The intrachain magnetic coupling in 5 is very weak. This can be understood having in mind the equatorial-axial exchange pathway involved through the monodeprotonated oxamate ligand that adopts the bidentate/outer monodentate coordination mode. Just focusing on the Cu(1)–O(5)–C(3)–O(6)–Cu(1a₅) skeleton, one can see that the carboxylate bridge exhibits the *anti–syn* conformation (equatorial–axial), a pathway which is well known to mediate very weak ferro- or antiferromagnetic interactions.⁶⁴ Anyway, we would like to outline that to our mind, 5 is the first structurally characterized example where the monodeprotonated oxamate group acts as a bridge.

Conclusions

(4)

In this work we report on the synthesis and structural characterization of five copper(II) complexes on the basis of rational design and serendipity: two mononuclear (1 and 2) bpca-based compounds, a trinuclear (3) containing two building blocks $[Cu(bpca)]^+$ and $[Cu(opba)]^{2-}$, a tetranuclear (4) with H₂opba²⁻ bridging [Cu(bpca)]⁺ units, and an unusual zigzag chain (5). The magnetic studies of the polynuclear compounds (3-5) show antiferromagnetic couplings dependent on the opba bridging mode. For 3, that presents the $[Cu(opba)(H_2O)]^{2-}$ unit acting as a bis-bidentate ligand toward two peripheral [Cu(bpca)]⁺ fragments, relatively strong intramolecular antiferromagnetic interaction leads to a low lying spin doublet, although the J value found $[J = -65.8(2) \text{ cm}^{-1}]$ is an intermediate in relation to the family of compounds with diamines as terminal ligands (-I values in the ranges 330–380 cm⁻¹). The weak intramolecular antiferromagnetic coupling [I = -2.36(2)] cm^{-1} in 4 can be understood by simple orbital symmetry

considerations. The magnetic $d_{x^2-y^2}$ orbitals on each copper(II) are parallel and present poor overlap between them due to the equatorial-axial connection through the double oxo-carboxylate bridge promoted by the H_2 opba²⁻ ligand. It is worthy of note that besides this bis-monodentate coordination mode, H_2 opba²⁻ acts simultaneously as a bidentate ligand in 4. The present work has also demonstrated that the opba ligand can still provide us with more bridging modes in spite of the numerous compounds described in the literature with these building blocks and derivatives. In fact, within the 5 zigzag chain the monodeprotonated EtH₂opba⁻ oxamato group acts as a bidentate/monodentate bridge connecting unconventional six-coordinate copper(II) of $[Cu(bpca)(H_2O)]^+$ units. The magnetic properties for 5 reveal an isolated spin doublet behaviour [the $\chi_{\rm M}T$ value almost constant at 0.405 cm³ mol⁻¹ K] with weak intrachain antiferromagnetic interaction $\chi_{M}T$ decreases smoothly below 40 K; $J = -0.17(1) \text{ cm}^{-1}$ as a consequence of the equatorial-axial [anti-syn conformation] exchange pathway involved through the monodeprotonated oxamate ligand. Finally, for all the complexes herein described, theoretically a further application as building blocks is possible since they present free coordination sites (principally the carbonyloxygens of bpca or opba ligands), even when considering the inherent difficulty of the solubility decrease with increasing nuclearity.

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