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# Copper(II)-phenylmalonate complexes with the bifunctional ligands nicotinamide and isonicotinamide

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# ABSTRACT

The use as coligands of the nicotinamide (nia) and isonicotinamide (inia) molecules in the complex formation between copper(II) and phenylmalonate [Phmal = dianion of phenylmalonic acid] yielded the compounds of formula [Cu(inia)(Phmal)(H<sub>2</sub>O)] (1) and [Cu(inia)(Phmal)(H<sub>2</sub>O)]<sub>n</sub> (2). Although single crystals of 1 of appropriate size were grown, their unresolved twinning and space group ambiguity prevented a satisfactory X-ray structure determination. The crystal structure 2 consists of corrugated layers of copper(II) ions with intralayer carboxylate-phenylmalonate bridges in the anti-syn (equatorial-apical) coordination mode. A water molecule and the isonicotinamide group are coordinated to the copper atom in trans position being located above and below each layer. The Phmal ligand adopts the bidentate/monodentate coordination mode with the bidentate coordination involving one equatorial and one apical bonds, a feature which is unprecedented for the copper(II) complexes with alkyl(aryl)substituted-malonate derivatives. Intra- and interlayer H-bonds together with intralayer  $\pi - \pi$  type interactions between the phenyl and inia aromatic groups contribute to the stabilization of the three-dimensional supramolecular structure. Magnetic susceptibility measurements of complexes 1 and 2 in the temperature range 1.9–300 K are quasi identical and they correspond to a very weak ferromagnetic interaction between the copper(II) ions  $[J = +0.091(2) \text{ cm}^{-1}(1) \text{ and } +0.097(2) \text{ cm}^{-1}(2)$  through the spin Hamiltonian for an isotropic square grid of interacting spin doublets which is defined as  $H = -J\sum_i S_i \cdot S_{i+1}$ ]. The strong similarity in the magnetic properties of 1 and 2 allow us to conclude that although they are not isostructural species, their structures have to be very close.

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### 1. Introduction

The design of coordination polymers lies at the interface of coordination and supramolecular chemistry, and it is a part of crystal engineering, whose ultimate goal is to obtain solids with technologically useful functionalities (molecular magnetic materials, conducting solids, zeolite-like materials, catalysts, luminescent materials, etc.) [1]. The metal ions plays both *structural* (directing and sustaining the solid-state architecture) and *functional* roles (spin carrier, optical or redox properties, etc.). An important point concerning the general architecture of crystals containing coordination polymers is their packing which is the result of the hierarchic organization determined by the primary (metal-ligand bonds which generate the coordination polymer) and the secondary structures (a concert of electrostatic and non-covalent forces such as hydrogen bonds and  $\pi$ - $\pi$  type interactions). Their subtle interplay makes difficult the prediction of the final structure.

Among the metal ions used to build molecule-based magnetic materials, copper(II) has played a prominent role both from experimental and theoretical points of view [2]. However, looking at the structural aspects, the plasticity of the coordination sphere of the copper(II) ion, which accounts for the richness and variety of its coordination chemistry, is at the origin of the diversity of the topologies and connectivities occurring in the extended assemblies containing this metal ion.

In contrast with the rigidity of the aromatic dicarboxylate spacers, the aliphatic dicarboxylate ligands exhibit a greater conformational freedom and then, a greater coordination versatility being considered as highly flexible connectors. Under mild conditions, the self-assembly of metal ions with  $\alpha, \omega$ -dicarboxylate ligands, such as the malonate (dianion of propanedioic acid, H<sub>2</sub>mal) [3], afforded a variety of supramolecular motifs where the discrete metal–oxygen polyhedra could be interconnected by organic linkers into polymeric chains, layers and 3D frameworks. Focusing on the malonate-bridged copper(II) complexes, it has been shown that



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the carboxylate–malonate bridge is able to mediate significant ferromagnetic interactions between the copper(II) ions [3k,3o]. More recently, we have started a systematic study on the copper(II) complexation by substituted malonate ligands such as phenylmalonate (dianion of phenylmalonic acid, H<sub>2</sub>Phmal) [4] and methylmalonate (dianion of methylmalonic acid, H<sub>2</sub>Memal) [5]. One of the aims of this study is to analyze the influence that factors such as the steric hindrance, the rigidity and the possibility of specific attractive interactions between phenyl rings can exert on the structure and magnetic coupling of copper(II) complexes with aryl(alkyl)-substituted malonate derivatives.

In the present work, we have explored the magneto-structural effects caused by the presence of the bifunctional ligands nicotinamide (nia) and isonicotinamide (inia) in the copper(II)-phenylmalonate system. Two compounds of formula [Cu(inia)(Phmal)(H<sub>2</sub>O)] (1) and  $[Cu(inia)(Phmal)(H_2O)]_n$  (2) were prepared, the crystal of **2** determined and the variable-temperature magnetic properties of 1 and 2 investigated. Our aim in this work has been to combine the well established molecular inorganic chemistry with well established aspects of supramolecular organic chemistry. Hydrogen bonds combine the most favorable aspects of directionality and strength among intermolecular interactions and in spite of being weaker than the metal-ligand covalent bonds, they offer a greater flexibility and there are well developed principles for fostering mutual recognition by functional groups through hydrogen bonding [6]. The choice of the nia and inia as coligands was made for two reasons: (i) firstly, the higher affinity of the copper(II) ion for the nitrogen-donors, which ensures its coordination to the nia and inia pyridyl-nitrogen atom, the amide fragment remaining uncoordinated; (ii) and secondly, amide moieties have a well established propensity to be engaged in complementary hydrogen bonds resulting either in ribbons (through head-to-head interactions), or in chains via equivalent N-H···O type contacts [amide-amide interactions in organic molecular solids typically involve "headto-head"  $R_2^2(8)$  or catemer  $C_1^1(4)$  hydrogen bonds] [7]. In the case of 2, the latter motif is observed and its structure contains quasi linear N-H···O hydrogen bonds that connect neighboring amide moieties.

# 2. Experimental

# 2.1. Materials and methods

Reagents and solvents used in all the syntheses were purchased from commercial sources and used without further purification.  $\{[Cu(H_2O)_3][Cu(Phmal)]\}_n$  was prepared as previously reported [4a]. Elemental analyses (C, H, N) were performed on an EA 1108 CHNS-O microanalytical analyzer.

#### 2.2. Preparation of the complexes

### 2.2.1. Synthesis of $[Cu(inia)(Phmal)(H_2O)](1)$

An aqueous solution  $(3 \text{ cm}^3)$  of  $\{[Cu(H_2O)_3][Cu(Phmal)]\}_n$ (0.125 mmol, 134 mg) was introduced into one arm of an H-shape tube while a 50:50 (v/v) water/methanol solution  $(1 \text{ cm}^3)$  of nicotinamide (0.5 mmol, 61 mg) was added in the other arm. Water was added dropwise to fill the H-tube and the tubes were covered with parafilm. Pale blue single crystals of **1** as extremely thin plates were grown in the H-shaped tube on standing after one month at room temperature. Although single crystals of **1** of adequate size were synthesized in several attempts, they always exhibit twin growth. The thinnest plates of **1** exhibit the characteristic differentiation in color areas when they are looked through polarized light (Fig. S1). Unfortunately, to date all data sets exhibit unresolved twinning and have space group ambiguity preventing satisfactory refinement. Nevertheless, this is an important observation as it is indicative of the difficulty in predicting the overall structural arrangement. Yield *ca.* 80%. *Anal.* Calc. for  $C_{15}H_{14}O_6N_2Cu$  (1): C, 47.18; H, 3.70; N, 7.34. Found: C, 47.12; H, 3.57; N, 7.27%. Main IR peaks (values in cm<sup>-1</sup>/KBr pellets): 1696s, 1668s, 1640s, 1605vs, 1420m, 1384s, 1298m, 1284m; 726m, 700m.

# 2.2.2. Synthesis of $[Cu(inia)(Phmal)(H_2O)]_n$ (2)

Complex **2** was synthesized following the same procedure than that described for **1**, but using isonicotinamide (0.5 mmol, 61 mg) instead of nicotinamide. X-ray quality crystals of **2** as thin blue plates appeared in the H-shaped tube on standing at room temperature after three weeks. Yield *ca.* 82%. *Anal.* Calc. for  $C_{15}H_{14}O_6N_2Cu$  (**2**): C, 47.18; H, 3.70; N, 7.34. Found: C, 47.15; H, 3.59; N, 7.27%. Main IR peaks (values in cm<sup>-1</sup>/KBr pellets): 1674s, 1616s, 1595vs; 1550s, 1449m, 1398s, 1380s, 1284m, 1220m, 845m, 818m, 722m.

#### 2.3. Physical techniques

The IR spectra (450–4000 cm<sup>-1</sup>) of **1** and **2** were recorded on a Bruker IF S55 spectrophotometer with samples prepared as KBr pellets. Magnetic susceptibility measurements on polycrystalline samples of **1** and **2** were performed with a Quantum Design SQUID magnetometer in the temperature range 1.9–300 K operating at 1 *T* ( $T \ge 50$  K) and 1000 G (T > 50 K). Diamagnetic corrections for the constituent atoms were estimated from Pascal's constants as  $155.8 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup> per mol of copper(II) for **1** and **2** [8]. Experimental magnetic susceptibilities were also corrected for the temperature independent paramagnetism ( $60 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup> per copper(II) ion) and the magnetization of the sample holder.

#### 2.4. X-ray crystallography

A single crystal of 2 was mounted on a Bruker-Nonius KappaCCD diffractometer and the diffraction data were collected at 293(2) K using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The data collection was carried out with  $\varphi$ - $\omega$  scans in the 6.43-30.0°  $\theta$  range. Data were collected with the COLLECT [9] program and indexed, integrated and scaled with EVALCCD [10]. SADABS absorption correction was applied to these data [11]. The crystal structure of 2 was solved by direct methods and refined with the full-matrix least-squares technique on F<sup>2</sup> using the SHELXS-97 and SHEXL-97 programs [12] included in the WINGX software package [13]. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms of **2** were located from Fourier differences and refined isotropically. The absolute configuration of the chiral crystal could be reliably solved with a Flack parameter of 0.018(11). Measurements on different crystals yielded a racemic mixture of the two enantiomeric forms. The final geometrical calculations and the graphical manipulations were carried out with PARST95 [14] and DIAMOND [15] programs. A summary of the crystallographic data and structure refinement for 2 is given in Table 1 while main bond lengths and angles and hydrogen bonds are listed in Tables 2 and 3.

#### 3. Results and discussion

#### 3.1. Description of the crystal structure of 2

The structure of **2** consists of a quasi square grid of *trans*-aqua(isonicotinamide)copper(II) units linked through phenylmalonate-carboxylate bridges running parallel to the *ab* plane (Figs. 1 and 2), similar to that of the compound of formula [Cu (pym)(Phmal)]<sub>n</sub> (pym = pyrimidine) [4d]. The corrugated layers are stacked along the crystallographic *c* axis being linked through hydrogen bonds involving the amide group of the isonicotinamide

**Table 1**Crystallographic data for complex 2.

	2
Formula	C15H14O6N2Cu
Formula weight	381.82
Crystal system	monoclinic
Space group	P2 <sub>1</sub>
a (Å)	7.3012(10)
b (Å)	7.2406(12)
<i>c</i> (Å)	14.852(4)
β (°)	104.020(11)
V (Å <sup>3</sup> )	761.8(3)
Ζ	2
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	14.69
T (K)	293(2)
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.665
λ (Å)	0.71073
Index ranges	$-10\leqslant h\leqslant$ 3,
	$-10 \leqslant k \leqslant 7$ ,
	$-16 \leqslant l \leqslant 20$
Independent reflections $(R_{int})$	3445 (0.0182)
Obs. reflections $[I > 2\sigma(I)]$	3039
Parameters	273
Flack parameter	0.018(11)
Goodness-of-fit	0.899
$R \left[ I > 2\sigma(I) \right]$	0.0260
$R_w \left[ I > 2\sigma(I) \right]$	0.0523
R (all data)	0.0337
R. (all data)	0.0543

Table 2
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Selected bond lengths (Å) and bond angles (°) for compound  $\mathbf{2}^{a,b}$ 

2 (1) 2(2)			1 = 0 0 0 (0)
Cu(1) - O(2)	2.2154(17)	O(4) - Cu(1) - O(1a)	173.38(8)
Cu(1)-O(4)	1.9729(16)	O(4)-Cu(1)-O(3b)	93.65(7)
Cu(1)-O(1a)	1.9740(16)	O(4)-Cu(1)-N(1)	90.43(8)
Cu(1)-O(3b)	2.3651(18)	O(4)-Cu(1)-O(1w)	89.22(7)
Cu(1)-N(1)	2.0360(19)	O(1a)-Cu(1)-O(3b)	92.13(7)
Cu(1)-O(1w)	2.0235(17)	O(1a)-Cu(1)-N(1)	86.87(7)
O(2)-Cu(1)-O(4)	85.92(7)	O(1a)-Cu(1)-O(1w)	94.28(7)
O(2)-Cu(1)-O(1a)	88.27(7)	O(3b)-Cu(1)-N(1)	84.94(7)
O(2)-Cu(1)-O(3b)	179.23(7)	O(3b)-Cu(1)-O(1w)	87.16(7)
O(2)-Cu(1)-N(1)	94.42(8)	N(1)-Cu(1)-O(1w)	172.05(8)
O(2)-Cu(1)-O(1w)	93.47(8)		

<sup>a</sup> Estimated standard deviations in the last significant digits are given in parentheses.

<sup>b</sup> Symmetry code: (a) -x, y + 1/2, -z + 1; (b) -x - 1, y + 1/2, -z + 1.

**Table 3** Hydrogen bonds in **2**.

D–H…A <sup>a</sup>	D–H (Å)	H· · ·A (Å)	D–H···A (°)	$D \cdots A$ (Å)
Interlayer N(2)−H· · · O(5)	0.67(2)	2.28(2)	172.4(8)	2.946(4)
Intralayer $O(1w)-H\cdots O(2)$ $O(1w)-H\cdots O(4)$	0.79(3) 0.82(3)	1.84(2) 1.88(2)	164.7(9) 178.1(9)	2.616(3) 2.703(3)

<sup>a</sup> D and A stand for donor and acceptor, respectively.

ligand (see Table 3 and Fig. 2) affording a supramolecular threedimensional network. The inia and Phmal ligands located in *trans*-position respect to the copper atom and inversely located respect to the adjacent [Cu(inia)(Phmal)(H<sub>2</sub>O)] units, these bulky groups being located in an hydrophobic area which separates the layers as occur in the previously reported [Cu(pym)(Phmal)]<sub>n</sub> complex (the shortest interlayer copper–copper separation being 13.390(3) Å (see Fig. 2)). Intralayer hydrogen bonds between the water molecule O(1w) and the coordinated phenylmalonate-oxygens O(2) and O(4) occur (see Table 3). Weak intralayer  $\pi$ -type interactions between the phenyl (Phmal) and pyridyl (inia) rings contribute to the stabilization of the three-dimensional supramolecular structure. The shortest centroid–centroid separation and off-set angle are 4.773(2) Å and 29.9(3)° respectively, values which are somewhat longer than those previously reported for this type of interactions [16].

Each copper atom exhibits a distorted octahedral environment with the parameters s/h and  $\phi$  being 1.32° and 56.5°, respectively (values to be compared with those for an ideal octahedron: s/h = 1.22 and  $\phi = 60°$ ) [17]. Two oxygen atoms from two different phenylmalonate ligands [O(4) and O(1a); (a) = -x, y + 1/2, -z + 1], a isonicotinamide nitrogen atom [N(1)] and a water molecule [O(1w)] build the basal plane (mean value of the equatorial bond lengths being 2.0016(19) Å; see Table 2), while two phenylmalonate oxygen atoms [O(2) and O(3b)] occupy the axial positions



Fig. 1. A view of the asymmetric unit of 2 along with the numbering scheme.



**Fig. 2.** A perspective view of the crystal packing of **2** along the *a* axis (left). Views of the square grid of carboxylate-bridged copper(II) ions (top, right) and the hydrogen bonding scheme involving the isonicotinamide ligands of adjacent layers (bottom, right).

(average Cu–O(ax) bond distance being 2.2902(18) Å; (*b*) = -x - 1, y + 1/2, -z + 1).

The phenylmalonate ligand adopts simultaneously the bidentate (through O(2) and O(4) toward Cu(1), the angle subtended at the copper atom being  $85.92(7)^\circ$ ) and bis-monodentate (across O(1)) and O(3) toward Cu(1c) and Cu(1d), respectively; (c) = -x, y = 1/2, -z + 1; (*d*) = -x - 1, y - 1/2, -z + 1) coordination modes. The bidentate coordination of the Phmal ligand involves one equatorial [O(4)] and one axial [O(2)] bonds (see Scheme 1). This structural feature which has been scarcely observed in copper(II) complexes with alkyl(aryl)-substituted malonate ligands [3h,4c,18], although it is not uncommon for copper(II)-oxalate complexes [19]. Two different anti-syn carboxylate bridges are present in the structure of 2 (namely O(1)-C(1)-O(2) and O(3)-C(3)-O(4)) with values for the copper-copper separation of 5.3362(6) and 5.3856(6) Å, respectively. Both carboxylate bridges connect an equatorial [O(1)] and O(4) with one axial position [O(2) and O(3)] at the copper environments. The shortest interlayer copper-copper separation is 13.390(3) Å.

The inia ligand acts as a monodentate ligand [through N(1)], the amide group participating in interlayer hydrogen bonds (Table 3). The dihedral angle between the plane of the amide group and



Scheme 1. Coordination mode of the Phmal ligand in 2.

the pyridyl ring is 27.9(2)°. This unprecedented behavior of the inia molecule illustrates the potential of combining coordination chemistry and hydrogen bonding aiming at designing and controlling new crystalline materials. Coordination chemistry is able to provide a good prediction of the coordinating behavior of a given ligand which can be used to direct its ability in hydrogen bonding *through* suitable substituents. Nowadays, hydrogen bonding arrangements exhibit a high degree of predictability, but their inherent weakness leaves open different structural possibilities with similar energy values [20].

A survey on the Cambridge Structural Database [21] was carried out in order to compare the functionality of the inia ligand in **2** with other related systems. A total of twenty-two inia-containing copper(II) complexes has been found [22]. Although the inia ligand establishes intermolecular hydrogen bonds with neighboring units in most of them, compound **2** is revealed as the first example where the inia group is used with the final purpose of act as a pillar for a two-dimensional coordination polymer. The amide groups recognize each other forming interlayer hydrogen bonds. The same structural survey performed for the case of the nia ligand reveals that this pillar functionality was neither reported.

#### 3.2. Structural remarks

The copper atom in **2** exhibits an octahedral environment with the inia and water ligands occupying equatorial positions. This feature makes the phenylmalonate ligand to chelate the copper atom through one equatorial and one axial positions, the remaining coordination sites being filled by oxygen atoms from adjacent Phmal ligands (Fig. 3). Considering an ideal octahedral metal environment, such a situation is achiral. However, due to the Jahn–Teller effect, the ideal O<sub>h</sub> symmetry is lowered and the resulting environment becomes chiral. The  $\Lambda$  and  $\Delta$  conformations are shown in Fig. 3. An identical situation was found in the complex  $[Cu(2,4'-bpy)(Phmal)(H_2O)]_n$  [4c] (2,4'-bpy = 2,4'-bipyridine) but



**Fig. 3.** Views of the  $\Delta$  (left) and  $\Lambda$  (right) conformations of the copper(II) environment in **2**. The arrows indicate the direction of the pseudo-Jahn–Teller elongation. The aromatic rings of the Phmal and inia ligands are omitted for clarity.

exhibiting a static Jahn–Teller disorder within the crystal. The 2,4'bpy and water ligands which occupy the equatorial positions are unaffected by the *J*–*T* disorder.

Also looking in the previously reported copper(II) complex  $[Cu(4,4'-bpy)(Phmal)]_n \cdot 2nH_2O$  [4c] (4,4'-bpy = 4,4'-bipyridine), the square pyramidal environment at the copper atom is built by two 4,4'-bpy nitrogen atoms occupying equatorial positions, two oxygen atoms from a bidentate Phmal ligand in one equatorial and apical positions and another oxygen atom from an adjacent Phmal group in the remaining equatorial position. The equatorial-apical bidentate coordination and the fact that the Phmal ligand has two different substituents (a phenyl ring and a hydrogen atom) in the central carbon atom of the malonate skeleton account for the chirality of the copper environment. The superposition of the metal environment with its inversion related one shows that the unique difference is the relative situation of the substituents of the methylene carbon atom of the malonate ligand.

Let us finish with an important point: the structure of **2** shows that all complexes exhibiting the equatorial-axial bidentate coordination of the phenylmalonate ligand will lead to chiral environments, a situation which was not observed in the related copper(II)-malonate complexes.

#### 3.3. Magnetic properties of 1 and 2

The magnetic properties of **1** and **2** under the form of a  $\chi_M T$  versus *T* plot ( $\chi_M$  is the magnetic susceptibility per copper(II) ion) are shown in Fig. 4 (top (**1**) and middle (**2**)]. At room temperature,  $\chi_M T$  is equal to 0.44 cm<sup>3</sup> mol<sup>-1</sup> K for **1** and **2**, a value which is as expected for a magnetically isolated spin doublet. Upon cooling,  $\chi_M T$  remains almost constant down to 50 K, and further increases to reach values of 0.50 (**1**) and 0.51 cm<sup>3</sup> mol<sup>-1</sup> K for (**2**) at 2.0 K. This behavior is indicative of the existence of a very weak ferromagnetic interaction between the copper(II) ions. The magnetization (*M*) versus *H* plot for **1** and **2** at 2.0 K (Fig. 4, bottom) confirms this behavior: the magnetization data for both compounds are slightly above the Brillouin curve (dashed line) for a magnetically isolated spin doublet.

Although **1** and **2** are not isostructural species, the similarity of their magnetic properties strongly supports a close structure for them. Having in mind this similarity from a magnetic point of view and the fact that the structure of **2** consists of a quasi square grid of copper(II) ions linked by *anti-syn* carboxylate bridges, the magnetic data of **1** and **2** have been analyzed by means of the derived high-



**Fig. 4.**  $\chi_M T$  vs. *T* plots for **1** (top) and **2** (middle): ( $\bigcirc$ ) experimental data; (-) best-fit curve through Eq. (1) (see text). The inset shows a detail of the low temperature region. *M* vs. *H* plot (bottom) for **1** (triangles) and **2** (circles) together with the Brillouin function for a magnetically isolated spin doublet with *g* = 2.0 (dashed line).

temperature expansion series for the isotropic ferromagnetic quadratic lattice with local spin doublets (Eq. (1)) [23].

$$\chi_{M} = \left(\frac{N\beta^{2}g^{2}}{3kT}S(S+1)\right) \left[1 + \sum_{n=1}^{10} a_{n}\frac{x^{n}}{2^{n}}\right]$$
(1)

In this expression, N, g,  $\beta$  and  $k_B$  have their usual meanings, x = J/kT, J is the intralayer magnetic coupling,  $a_n$  are coefficients which run up to n = 10 with the spin Hamiltonian being defined as

#### Table 4

Selected magneto-structural data for some equatorial-apical carboxylate-bridged malonato- and phenylmalonato-containing copper(II) complexes.

Compound <sup>a</sup>	Cu∙ · ·Cu (Å)	Cu···O(ap) (Å)	$Cu \cdots O(eq) (Å)$	$\tau$ Cu1/Cu2 <sup>b</sup>	$J^{c}(cm^{-1})$	Ref.
$[Cu(H_2O)_4][Cu(mal)_2(H_2O)_2]$	5.781(1)	2.393(4)	1.948(3)	O <sub>h</sub> /0.05	+1.8	[3a]
$\{[Cu(H_2O)_4]_2[Cu(mal)_2(H_2O)]\}$	5.857(2)	2.381(3)	1.941(2)	O <sub>h</sub> /0.12	+1.2	[3a]
$\{[Cu(H_2O)_3][Cu(mal)_2(H_2O)]\}_n$	4.640(1)	2.185(2)	1.930(2)	0.24/0.28	+1.9	[3a]
$[Cu(Im)_2(mal)]_n$	6.036(2)	2.394(2)	1.962(2)	0.016	+1.6(1)	[3g]
$[Cu(2-MeIm)_2(mal)]_n$	6.099(2)	2.270(4)	1.961(3)	0.18	+0.4(1)	[3g]
$\{(H_2 bpe)[Cu(mal)_2]\}_n \cdot 4nH_2O$	4.8831(10)	2.6107(14)	1.9314(11)	O <sub>h</sub>	+0.049(1)	[3h]
$[{Cu(2,2'-bpym)(Phmal)}]_n$	4.6853(7)	2.262(3)	1.900(3)	0.08	+0.10(1)	[4b]
$[{Cu(phen)(Phmal)}]_n \cdot 3nH_2O$	5.014(3)	2.314(2)	1.934(2)	0.10	+0.31(1)	[4b]
$\{(H_2ade)_2[Cu(\mu-mal)_2]\cdot 2H_2O\}_n$	5.081	2.705(2)	1.928(2)	O <sub>h</sub>	+0.6	[26]
$\{[Cu(mal)_2](Hpic)_2 \cdot 2H_2O\}_n$	6.0910(2)	2.6143(10)	1.9458(9)	O <sub>h</sub>	+0.3(2)	[27]
1	_	-	_	-	+0.091(2)	_
2	5.3362(6) 5.3856(6)	2.2154(17) 2.3651(18)	1.9740(16) 1.9729(16)	O <sub>h</sub>	+0.097(2)	-

<sup>a</sup> Abbreviations used:  $H_2$ mal = malonic acid, Im = imidazole, 2-MeIm = 2-methylimidazole, bpe = 1,2-bis(4-pyridyl)ethylene,  $H_2$ Phmal = phenylmalonic acid, 2,2'-bpym = 2,2'-bipyrimidine, phen = 1,10-phenanthroline, ade = adenine, pic = 2-amino-4-picoline.

<sup>b</sup> Distortion of the five-coordinated copper environment ( $\tau$  = 1 for trigonal bipyramidal and 0 for square pyramidal); O<sub>n</sub> stands for octahedral.

<sup>c</sup> Values of the magnetic coupling.



Scheme 2. Magnetic coupling between the copper(II) ions through the carboxylate bridge in the anti-syn conformation.

 $H = -J\Sigma_i S_i \cdot S_{i+1}$ . Least-squares best-fit parameters in the temperature range 1.9–300 K are  $J = +0.092(2) \text{ cm}^{-1}$ , g = 2.10(2) and  $R = 1.1 \times 10^{-4}$  for **1** and  $J = +0.099(2) \text{ cm}^{-1}$ ; g = 2.10(2) and  $R = 1.3 \times 10^{-4}$  for **2** (*R* is the agreement factor defined as  $\sum_i [(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2 / \sum_i [(\chi_M T)_{calc}(i)]^2$ ). The calculated curves (solid lines in Fig. 4 (top and middle) match very well the experimental data in the whole temperature range.

The weak magnetic interactions in **1** and **2** are as expected for anti-syn carboxylate-bridges which connect equatorial with apical positions of adjacent copper(II) ions. The magnetic orbital (that is the unpaired electron) of the copper(II) ion with elongated octahedral surrounding is of the  $d_{x^2-y^2}$  character (the *x* and *y* axes being roughly defined by the equatorial bonds) with some admixture of the  $d_{z^2}$  (the *z* axis corresponding to the axial bonds). According to the Kahn's model [24], the magnetic orbital  $d_{x^2-y^2}$  interacts with the  $d_{r^2}$  across the equatorial-axial exchange pathway provided by the carboxylate bridge. The weak spin density, which is predicted for the axial position together with the poor overlap (S) between these two magnetic orbitals [25], would lead to a very weak magnetic interaction. As the antiferromagnetic contribution in a dicopper(II) unit is proportional to the square of the overlap integral  $(S^2)$ between the magnetic orbitals and given that it is minimized in the case of **1** and **2**, the resulting magnetic coupling is certainly weak

but most likely ferromagnetic. The computed magnetic interactions in **1** and **2** are within the range observed for this kind of bridge in other related copper(II)-malonate complexes as shown in Table 4.

The magnitude of the ferromagnetic behavior observed in **1** and **2** is significantly weaker than that observed for copper(II) complex of formula  $[Cu(pym)(Phmal)]_n$  [ $J = +5.6(1) \text{ cm}^{-1}$ ] [4d], the three compounds exhibiting the same carboxylate-bridged (*anti-syn* conformation) square-grid of copper(II) ions. The fact that the nicotinamide (**1**) and the isonicotinamide (**2**) ligands occupy equatorial positions at the metal environment causes one of the oxygen atoms from the phenylmalonate ligand to fill an apical position, and then the carboxylate-bridge becomes of the equatorial-apical type. This situation alters completely the magnetic behavior since this kind of carboxylate-bridge is much less efficient than the equatorial-equatorial exchange pathway which occurs in  $[Cu(pym)(Phmal)]_n$  (see Scheme 2).

## 4. Conclusions

The structure of the complexes **1** and **2** consists of carboxylatebridged copper(II) layers which are linked through hydrogen bonds involving the amide groups of the nia (1) or inia (2) ligands. This situation is as expected for their use as coligands, analogously to the case of the complex  $[Cu(pym)(Phmal)]_n$ . However, the weakness of the intralayer ferromagnetic coupling between the copper(II) ions across the carboxylate bridge in 1 and 2 when compared to that in  $[Cu(pym)(Phmal)]_n$  is due to the occurrence of equatorial-axial (former compounds) versus equatorial-equatorial (latter compound) exchange pathways involved. The equatorial-axial connection through the carboxylate-bridge in 1 and 2 appears as a consequence of the equatorial coordination at the copper atom of the nia and inia ligands. Moreover, a water molecule is also present in the coordination sphere of the copper(II) ion in **1** and **2** while this is not the case for the pym-containing copper(II) compound. Summarizing, the present work shows that the subtle but predictable structural changes which are associated to the introduction of the amide group of the coligand in the Phmal-containing copper(II) system are relevant for a magnetic point of view and consequently. the investigation about how different magnetic properties could arise from similar structures remains an open subject.

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### Appendix A. Supplementary data

A figure of a single crystal of **1** is supplied as complementary information (Fig. S1). CCDC 765760 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly. 2011.06.006.

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