Phenylmalonate-Containing Copper(II) Complexes: Synthesis, Crystal Structure and Magnetic Properties

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Three new copper(II) complexes of formula $[Cu(2,2'\text{-bpy})(Phmal)(H_2O)]\cdot 2H_2O$ (**1**), $[\{Cu(2,2'\text{-bpym})(Phmal)\}]_n$ (**2**) and $[\{Cu(phen)(Phmal)\}]_n\cdot 3nH_2O$ (**3**) (Phmal = phenylmalonate; 2,2′-bpy = 2,2′-bipyridine; 2,2′-bpym = 2,2′-bipyrimidine; phen = 1,10-phenanthroline) have been prepared and their structures determined by X-ray diffraction techniques. Complex **1** is mononuclear whereas **2** and **3** are uniform chain compounds. The copper atoms in **1**–**3** are distorted square-pyramidal: two nitrogen atoms from the bidentate nitrogen heterocycle and two carboxylate oxygen atoms from the phenylmalonate ligand build the equatorial plane; the axial position is filled either by a water molecule (**1**) or a carboxylate oxygen atom from another phenylmalonate group (**2** and **3**). The values of the intrachain copper–copper separation through the phenylmalonate-carboxylate bridge in the *anti-syn* conformation are 4.6853(7) (**2**) and 5.014(3) Å (**3**). The phenyl ring of the Phmal ligand in **1** produces an unusual intramolecular π–π stacking interaction with the Cu^{II}–(aromatic 2,2′-bpy) chelate ring. Intrachain edge-to-face phenyl–pyridyl and offset phen–phen-type interactions occur in **2** and **3**, respectively. Magnetic susceptibility measurements of **2** and **3** in the temperature range 1.9–290 K show the occurrence of weak intrachain ferromagnetic interactions between the copper(II) ions through the phenylmalonate-carboxylate bridge [$J = +0.10(1)$ (**2**) and $+0.31(1)\ cm^{-1}$ (**3**)]. These values are compared with those reported for malonate-containing copper(II) complexes with the same exchange pathway through the *anti-syn* carboxylate bridge.

Introduction

The design of synthetic pathways to obtain systems with desired properties continues to be a challenge for inorganic chemists. In this context, a great interest has been devoted to the development of rational synthetic routes to novel polynuclear compounds of tuneable dimensionality which may have applications as molecule-based magnetic materials.[1–3] Many recent reports have focused on the synthesis and magneto-structural characterization of polymeric transition metal compounds using malonate (dianion of propanedioic acid, H_2mal) as both blocking and bridging ligand.[4–10] In the framework of our research with malonate-containing metal complexes[8–13] we have been able to prepare a large number of compounds with different structures and properties whose dimensionality goes from zero in the mononuclear species [Cu(mal)(2,2′-bpym)][14] (2,2′-bpym = 2,2′-bipyrimidine) to three in the compound $[Cu(mal)(pyz)]_n$ (pyz = pyrazine).[15] The variety of the coordination modes of the malonate ligand in these compounds has been reviewed very recently.[9] From a magnetic point of view, the parameters governing the nature and magnitude of the magnetic interactions between copper(II) ions are the conformation of the bridge (*anti-anti*, *anti-syn*, *syn-syn*), the environment of the metal atom,[16,17] and the relative orientation of the malonate-carboxylate bridge with respect to the metal environment (equatorial-equatorial, equatorial-apical and apical-apical with relatively strong, weak and negligible interactions, respectively), in addition to the Cu−O(carboxylate) distances.[10]

More recently, we have started a systematic study on copper(II) complexation by substituted malonate ligands such as phenylmalonate (dianion of phenylmalonic acid, H_2Phmal). One of the aims of this study is to analyze the influence that factors such as the withdrawing effect, the rigidity and the possibility of specific attractive interactions between phenyl rings can exert on the structure and magnetic coupling of phenylmalonate-containing copper(II) complexes.[17] In a previous work, we have observed that

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the complex $[\{Cu(H_2O)_3\}\{Cu(Phmal)_2\}]_n$ has a layered structure induced by the phenyl groups and intralayer ferromagnetic couplings through phenylmalonate-carboxylate and -oxo bridges. Here we show how the structure and magnetic properties of this layered system are modified by the presence of coligands such as 2,2′-bipyridine (2,2′-bpy), 2,2′-bipyrimidine (2,2′-bpym) and 1,10-phenanthroline (phen). These are all aromatic nitrogen heterocycles that, in addition to their good coordinating ability (metal−ligand bonds), can interact with the phenyl ring of the Phmal group (supramolecular interactions), making this system very appropriate to illustrate the effects of both types of interactions.

We report herein the synthesis, crystallographic analysis and magnetic study of the copper(II) complexes of formula $[Cu(2,2'\text{-bpy})(Phmal)(H_2O)]\cdot 2H_2O$ (**1**), $[\{Cu(2,2'\text{-bpym})(Phmal)\}]_n$ (**2**) and $[\{Cu(phen)(Phmal)\}]_n\cdot 3nH_2O$ (**3**). Complex **1** is a magnetically isolated mononuclear species whereas **2** and **3** are uniform chains with intrachain ferromagnetic interactions.

Results and Discussion

Synthesis of the Complexes

Complexes **1**−**3** were prepared by reaction of stoichiometric amounts copper(II) phenylmalonate with the appropriate heterocyclic N-donor in a methanol water mixture. X-ray quality crystals of the mononuclear complex **1** and the chain compounds **2** and **3** were grown from concentrated solutions by slow solvent evaporation.

Description of the Crystal Structures

[Cu(2,2′-bpy)(Phmal)(H₂O)]·2H₂O (1)

The structure of **1** consists of neutral $[Cu(Phmal)(2,2'\text{-bpy})(H_2O)]$ mononuclear entities (Figure 1a) and crystallization water molecules. The molecular units are linked by hydrogen bonding involving the uncoordinated phenylmalonate oxygen atoms and the crystallization water molecules, with O···O distances ranging from 2.667(3) to 2.972(4) Å (see Table 1). A surprising two-dimensional (6,3) net results (Figure 2) which contributes to the stabilization of the whole structure. Adjacent layers are linked by weak offset π−π-stacking interactions between pyridyl rings. The shortest offset angle between pyridyl rings is 28.5° while the shortest centroid−centroid contact is 3.966(4) Å, values which are slightly larger than the average values in π−π interactions with pyridine-like groups previously reported.[18]

The molecular structure of **1** is remarkably similar to that of the recently reported[19,20] complexes $[Cu(Bzmal)(phen)(H_2O)]\cdot 3H_2O$ and $[Cu(Bzmal)(2,2'\text{-bpy})(H_2O)]\cdot 2H_2O$ (Bzmal = 2-benzylmalonate) compounds. The phenyl rings of Bzmal and Phmal are located over the N−C−C−N−Cu chelate ring in the three complexes and metalloaromaticity was pointed out to be the factor responsible for this structural feature.[19] A search in the Cambridge Structural Database has shown the existence of several compounds which present the same conformation (listed in Table 2). The value of the dihedral angle between the mean planes in complex **1** is larger (25.5°) than in the other compounds (1.2−14.5°) due to geometrical constraints that preclude the parallel arrangement of the phenyl group above the chelate ring. All the structures found in the search contain a ligand with the nitrogen atoms inside the aromatic rings (i.e. always 2,2′-bpy or phen but never *N,N′*-ethylenediamine). According to Janiak,[18] phenyl rings do not like to stack above each other but to adopt an offset (parallel displaced) arrangement, thus leading to C−H···π-type interactions. Therefore, we suggest that this is responsible for the situation of the phenyl group above the chelate ring (i.e. displaced from the stacked position over the pyridyl groups). We can compare this structure with that of the reported mononuclear complex $[Cu(2,2'\text{-bpy})(mal)(H_2O)]\cdot H_2O$,[30] where the monomeric units are distributed in bilayers in the *bc* plane through hydrogen bonds involving the malonate-carboxylate groups and the coordinated and uncoordinated water molecules. The hydrophobic interactions in **1** form layers of different hydrophilic character with the aromatic rings in one and the phenylmalonate oxygen atoms and water molecules in the other one. A remarkable difference between both compounds is the position of the methylene group: it is directed toward the coordinated water molecule in the malonate compound whereas the metalloaromaticity in the case of **1** causes the methylene C−H bond to point towards the opposite side of the coordinated water molecule.

Each copper atom in **1** exhibits a somewhat distorted square-pyramidal environment, with a τ value[31] of 0.14. The copper atom is bound to two 2,2′-bpy nitrogen atoms [2.001(2) and 1.998(2) Å for Cu(1)−N(1) and Cu(1)−N(2), respectively] and to two carboxylate oxygen atoms from the Phmal ligand [1.954(2) and 1.933(2) Å for Cu(1)−O(2) and Cu(1)−O(4)] in the basal plane, and to a water molecule in the apical position [2.143(2) Å for Cu(1)−O(1w)]. The 2,2′-bpy and Phmal groups in **1** adopt a bidentate coordination mode, the values of the angles subtended at the copper atom by them being 80.53(8)° and 90.09(7)°, respectively. The 2,2′-bpy ligand is practically planar [the value of the dihedral angle between the mean pyridyl planes is 1.1(1)°] and its bond lengths and angles are in agreement with those reported for free 2,2′-bpy.[32] The Phmal group exhibits the boat conformation as in $[\{Cu(H_2O)_3\}\{Cu(Phmal)_2\}]_n$.[17] However, the Phmal group in this last compound simultaneously exhibits bidentate (through two oxygen atoms of the two carboxylate groups) and bis(monodentate) (through two *trans* carboxylate oxygen atoms from two Phmal ligands) coordination modes, leading to a layered structure. The $[Cu(Phmal)_2]^{2-}$ units in this compound tend also to align their aromatic rings in the same direction, preventing the occupation of one of the axial positions of the copper(II) coordination sphere, while the other apical site is filled by another $[Cu(Phmal)_2]^{2-}$ unit. This also occurs in **1** where the aromatic ring practically fills one of the axial

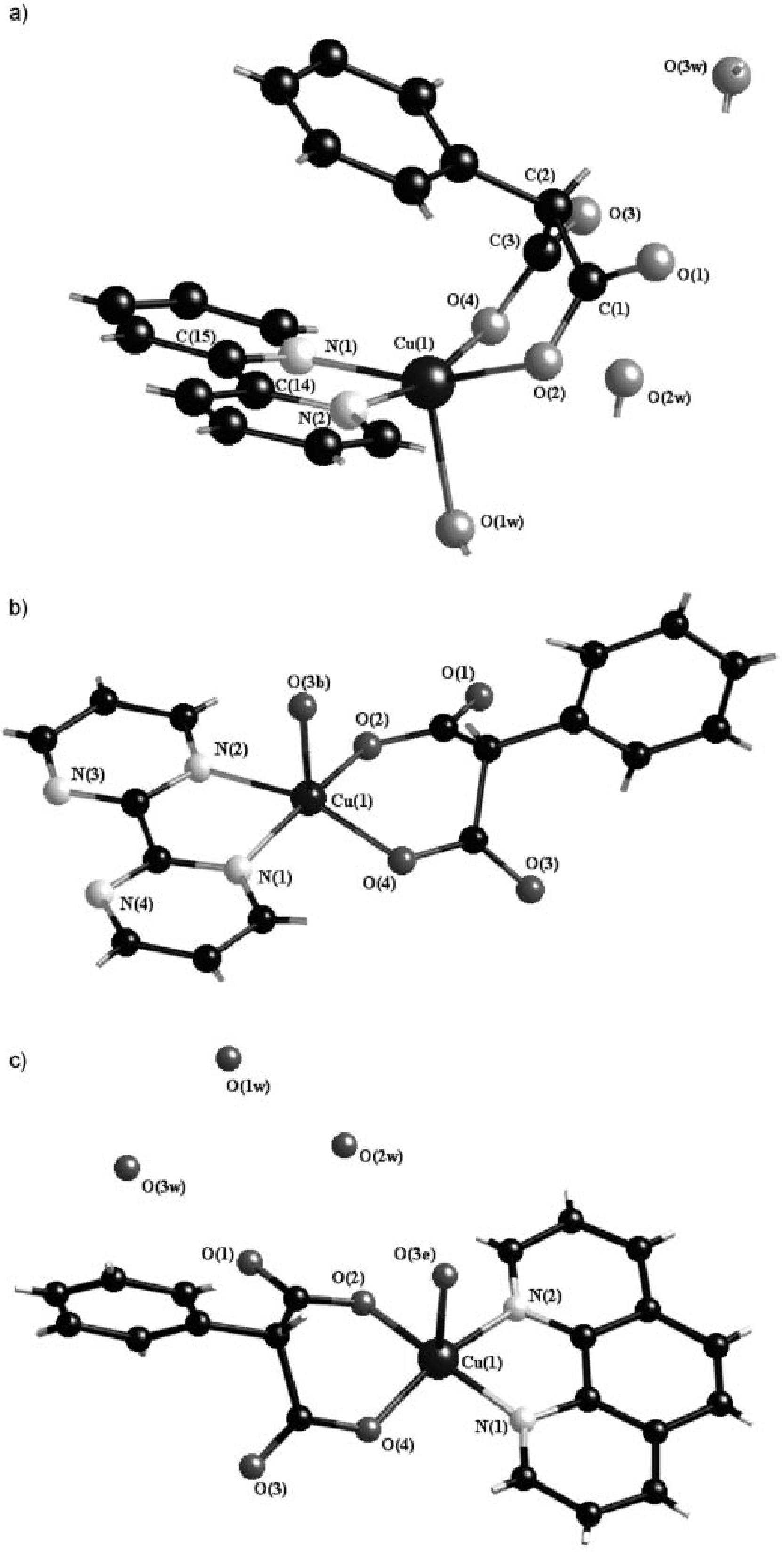


Figure 1. Asymmetric unit of $[Cu(2,2'\text{-bpy})(Phmal)(H_2O)]\cdot 2H_2O$ (**1**) (a) and molecular fragments of $[\{Cu(2,2'\text{-bpym})(Phmal)\}]_n$ (**2**) (b) and $[\{Cu(phen)(Phmal)\}]_n\cdot 3nH_2O$ (**3**) (c) with the numbering scheme

Table 1. Hydrogen bonds in complex **1**

D−H···A[a]	D···A	∠D−H···A[b]	Symmetry operator[c]
O(1w)−H(1wa)···O(2w)	2.667(3)	170(4)	$x, y - 1, z + 1$
O(1w)−H(1wb)···O(3)	2.735(3)	172(4)	$x + 1/2, -y, -z + 5/2$
O(2w)−H(2wa)···O(1)	2.881(4)	172(6)	$x, y + 1/2, -z + 3/2$
O(2w)−H(2wb)···O(3w)	2.763(4)	171(4)	$x + 1, y, z$
O(3w)−H(3wa)···O(3)	2.972(4)	167(5)	$x - 1/2, -y + 1/2, z - 1$
O(3w)−H(3wb)···O(1)	2.815(3)	158(5)	$x - 1/2, -y + 1, -z + 3/2$

[a] Values of the distances and angles in Å and °, respectively. [b] D = donor and A = acceptor. [c] Symmetry operation concerning the acceptor atom.

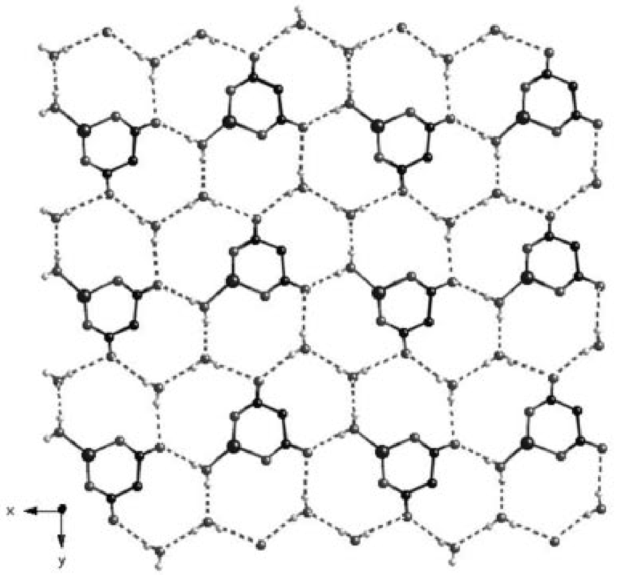


Figure 2. (6,3) pattern formed by hydrogen bonding involving the coordinated and crystallization water molecules and the malonate oxygen atoms; such a regular net contributes to the stabilization of the structure; the 2,2′-bpy ligands have been omitted for clarity

positions of the copper coordination sphere and the other one is occupied by a water molecule. The shortest intermolecular copper−copper separation in **1** is 7.6494(5) Å [Cu(1)−Cu(1a); (a) = $-x + 2, -y, -z + 2$].

[{Cu(2,2′-bpym)(Phmal)}]$_n$ (2)

The structure of **2** consists of chains of [Cu(2,2′-bpym)(Phmal)] units that are linked through one phenylmalonate-carboxylate group in an *anti-syn* conformation (Figure 1b). These chains run parallel to the *a* axis and interact between themselves by means of π−π- and C−H···π-type interactions (Figure 3). There are two hydrophobic cavities where 2,2′-bpym molecules and the phenyl rings from the Phmal groups are constrained. The 2,2′-bpym groups are involved in π−π interactions, with the shortest centroid−centroid contact being 3.798(6) Å and the shortest parallel displacement angle between pyrimidyl rings being 25.7°, values which are similar to the average ones observed in π−π interactions with pyridine-like groups.[18] Weak C−H···π interactions are also present between the phenyl rings and 2,2′-bpym groups inside the chains and between phenyl groups of different chains, with the shortest H···centroid distance being 2.86(4) Å, and C−H···centroid

Table 2. Stacking parameters of some compounds found in the Cambridge Structural Database with the same conformation as complex **1**

Compound	Stacking parameters[a]			Ref.
	$d(c_1-c_2)$ [Å]/α [°]	$d[\perp c_1-P(2)]$ [Å]/β [°]	$d[\perp c_2-P(1)]$ [Å]/γ [°]	
$[Cu(L1)(L2)]SbF_6 \cdot CH_2Cl_2$ [b]	3.58/1.2	3.49/13.1	3.49/13.2	[21]
$[Cu(L3)(L4)(L5)]$	3.49/7.2	3.45/14.3	3.38/8.2	[22]
$[Cu(L3)(L4)](NO_3)_2 \cdot 3H_2O$	3.50/10.2	3.43/18.5	3.32/11.4	
catena-$[Cu(L4)(L6)]ClO_4 \cdot H_2O$	3.44/6.46	3.37/8.0	3.41/12.1	[23]
$[Cu(L7)(L8)H_2O]BF_4 \cdot 3H_2O$	3.39/10.1	3.38/14.2	3.29/4.3	[24]
$[Cu(L9)(L8)H_2O]Cl \cdot H_2O$	3.53/14.5	3.32/15.8	3.39/19.7	[25]
$[Cu(L10)(L4)H_2O] \cdot 3H_2O$	3.49/2.1	3.39/15.5	3.36 /13.9	[19]
$[Cu(L10)(L8)H_2O] \cdot 2H_2O$	3.51/8.2	3.37/10.7	3.45/16.4	[20]
$[Cu(L11)(L8)H_2O]NO_3 \cdot MeOH \cdot H_2O$	3.48/5.2	3.41/15.7	3.35/11.3	[26]
$[Cu(L9)(L4)H_2O]ClO_4 \cdot 1.5H_2O$	3.38/8.8, 3.38/5.4	3.31/16.6, 3.32/12.0	3.24/11.8, 3.30/10.3	[27]
$[Cu(L12)(L4)Cl] \cdot 3H_2O$	3.45/6.7	3.41/5.6	3.44/9.2	[27]
$[Cu(L12)(L8)H_2O]ClO_4$	3.37/7.4	3.35/13.2	3.28/5.8	[28]
$[Cu(L9)(L13)H_2O]ClO_4 \cdot H_2O$	3.42/3.7	3.29/17.1	3.27/16.1	[29]
1	3.683/25.5	3.152/31.5	3.562/14.7	this work

[a] P(1) = plane 1; P(2) = plane 2; c_1 = centroid of P(1); c_2 = centroid of P(2); α = angle between mean planes; β = angle between the normal of P(1) and P(2); γ = angle between the normal of P(2) and P(1). [b] L1 = (*S,S*)-2,6-bis(4-phenyl-2-oxazolin-2-yl)pyridine; L2 = benzyloxyacetaldehyde; L3 = L-4,5-dihydroxyphenylalanine; L4 = 1,10-phenanthroline; L5 = *n*-propanol; L6 = L-tryptophanate; L7 = D,L-2,5-dihydroxytyrosine; L8 = 2,2′-bipyridine; L9 = L-tyrosinate; L10 = 2-benzylmalonate; L11 = L-3-iodotyrosinate; L12 = L-phenylalanine; L13 = 1,4,8,9-tetraazatriphenylene.

groups being almost collinear. The building units of the chain are rotated 90° through the normal axis of the planar 2,2′-bpym group in a twist fashion (i.e. odd units in the same position and even units rotated by 90°; Figure 3).

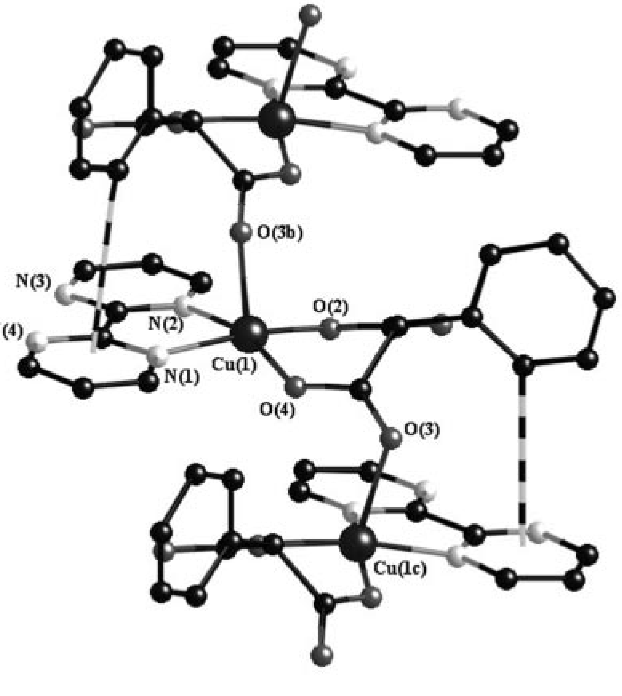


Figure 3. Fragment of the uniform chain of compound **2** showing the rotation of the units by 90° and the intrachain C−H···π interaction (dashed line)

Each copper(II) atom has a slightly distorted square-pyramidal surrounding, the τ value[31] being 0.08. Two nitrogen atoms of the 2,2′-bpym ligand [N(1) and N(2)] and two carboxylate oxygen atoms from the Phmal ligand [O(2) and O(4)] build the basal plane, whereas the symmetry-related carboxylate oxygen atom [O(3b); (b) = $-1/2 + x$, $1/2 - y$, z] occupies the apical position. The equatorial bond lengths vary in the range 1.900(3)−2.003(3) Å and the apical bond length is 2.262(3) Å. The 2,2′-bpym ligand is quasi planar [the dihedral angle between the pyrimidyl rings being 3.5(1)°] and it acts as a bidentate ligand through two [N(1) and N(2)] of its four nitrogen atoms. This coordination mode has previously been observed in several mono- and polynuclear 2,2′-bpym-containing copper(II) complexes.[14,33,34] The outer N(3) and N(4) 2,2′-bpym nitrogen atoms remain free, the N(3)···N(4) bite distance being somewhat longer [2.811(6) Å] than the N(1)···N(2) one [2.584(5) Å] due to the bidentate coordination of the 2,2′-bpym to the copper atom through N(1) and N(2). The inter-ring carbon−carbon bond length of 2,2′-bpym in **2** [1.480(6) Å for C(13)−C(14)] is close to that found in the free ligand in the solid state [1.497(1) and 1.502(4) Å].[35] As in **1**, the Phmal ligand adopts a boat conformation; the phenyl ring in **2** is placed perpendicular to the boat skeleton of the malonate in order to establish the weak intrachain C−H(phenyl)···π (pyrimidyl) interactions mentioned above. Finally, a comparison between the structure of **2** and that of the related mononuclear complex [Cu(2,2′-bpym)(mal)(H_2O)]·6H_2O[14] shows once more the structural influence of the hydrophobic phenyl ring of the Phmal ligand. The complexation reaction between the preformed [Cu(2,2′-bpym)]$^{2+}$ species and the dicarboxylate mal and Phmal ligands affords neutral hydrated mononuclear (mal) and anhydrous chain (Phmal, **2**) compounds. The structure of the former exhibits extensive hydrogen bonds involving coordinated and uncoordinated water molecules, whereas carboxylate-bridging and supramolecular C−H···π-type interactions counterbalance the lack of hydrogen bonds in the latter.

The shortest intrachain copper−copper separation in **2** is 4.6853(7) Å [Cu(1)···Cu(1c); (c) = $1/2 + x$, $1/2 - y$, z], a value which is much shorter than the shortest interchain metal−metal distance [7.3634(8) Å for Cu(1)···Cu(1d); (d) = $-x$, $1 - y$, $1 - z$].

[{Cu(phen)(Phmal)}]$_n$·3nH$_2$O (3)

The structure of complex **3** consists of chains of [Cu(phen)(Phmal)] units linked through *anti-syn* carboxylate bridges and crystallization water molecules (Figure 1c). The chains run parallel to the *a* axis and they are linked by pairs along the [011] direction through hydrogen bonds involving the water molecules and noncoordinated carboxylate oxygen atoms [the values of the O···O distance range from 2.338(13) to 3.084(5) Å; Figure 4]. Intrachain offset π−π interactions between phen ligands occur, the shortest centroid−centroid distance being 3.907(4) Å and parallel displacement angle being 28.6°, in agreement with previously reported values.[18]

Each copper(II) atom presents a slightly distorted square-pyramidal environment, with a τ value[31] of 0.10. Two carboxylate oxygen atoms from the Phmal ligand [O(2) and O(4)] and the two nitrogen atoms of phen [N(1) and N(2)] form the equatorial plane, whereas a symmetry-related carboxylate oxygen atom [O(3e); (e) = $x + 1$, y, z] occupies the apical position. The equatorial bond lengths vary in the range 1.913(2)−2.026(3) Å and the apical bond amounts to 2.314(3) Å. The angle subtended by the planar bidentate phen ligand at the copper atom is 81.86(11)°. The bond lengths and angles of the phen ligand in **3** agree well with those reported for the free molecule.[36] The conformation and coordination mode of the Phmal ligand in **3** are identical to those in **2**. However, π−π stacking between phen ligands occurs in **3** instead of the C−H(phenyl)···π(N-heterocycle)-type interaction which occurs in **2**. Moreover, the [Cu(phen)(Phmal)] chain units in **3** are not rotated by 90°, in contrast to what it is observed in **2**; this modification of the crystal packing in **3** is due most likely to the crystallization water molecules which are present in the structure of the latter compound. A comparison between the structure of **3** and that of the mononuclear complex [Cu(phen)(mal)(H_2O)]·1.5H_2O[37] reveals that weak π−π stacking interactions between phen ligands are present in both compounds. However, the mononuclear units are grouped by pairs in the malonato-containing complex, whereas a uniform chain is formed in **3**.

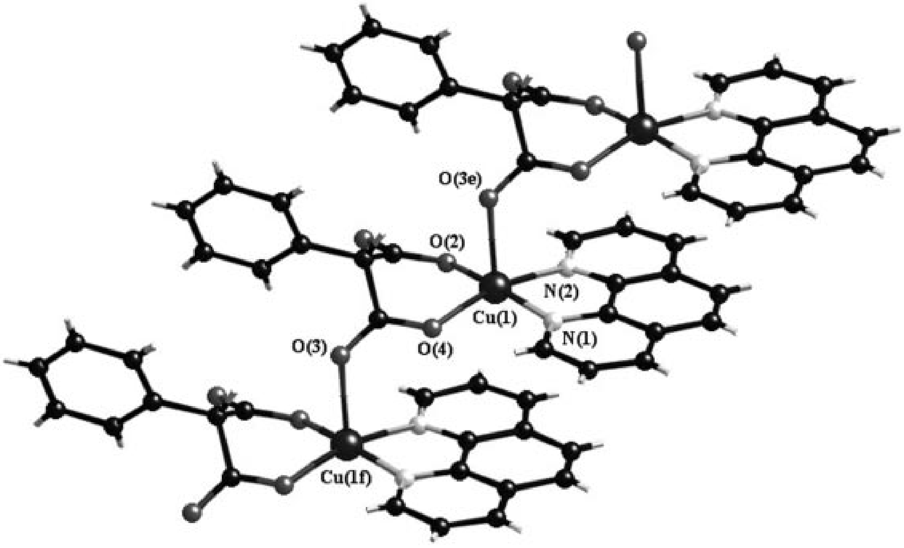


Figure 4. View of the uniform chain of compound **3** showing the phenylmalonate-carboxylate bridge in axial-equatorial *anti-syn* conformation

The shortest intrachain copper−copper separation is 5.014(3) Å [Cu(1)−Cu(1f); (f) = $-1 + x, y, z$], a value which is much shorter than the shortest interchain metal−metal distance [7.5872(16) Å for Cu(1)−Cu(1g); (g) = $-1/2 + x, 1/2 - y, -1/2 + z$].

Magnetic Properties

The $\chi_M T$ product of compound **1** obeys the Curie law in the 5−300 K temperature range. Its value is 0.365 cm^{3}mol^{-1}K, as expected for a magnetically isolated spin doublet of a copper(II) ion. This is in agreement with its mononuclear nature.

The magnetic properties of compounds **2** and **3** in the form of $\chi_M T$ vs. T plots [χ_M being the molar susceptibility per copper(II) ion] are shown in Figure 5; $\chi_M T$ at room temperature is 0.41 cm^{3}mol^{-1}K for both compounds, a value which is as expected for a magnetically isolated spin doublet. Upon cooling, $\chi_M T$ remains almost constant for compound **2** down to 10 K and then smoothly increases at lower temperatures to reach a value of 0.44 cm^{3}mol^{-1}K at 1.9 K; $\chi_M T$ remains constant upon cooling down to 25 K for compound **3** and then it increases at lower temperatures reaching a value of 0.50 cm^{3}mol^{-1}K at 2.0 K. These features are indicative of an overall weak ferromagnetic coupling between the copper(II) ions in both compounds. Given that the structures of **2** and **3** consist of uniform chains, where the copper(II) ions are bridged by the phenylmalonate-carboxylate group, we analyzed their magnetic properties through the numerical expression proposed by Baker and Rushbrooke[38] for a ferromagnetic uniform copper(II) chain [Equation (1)]:

$$\chi_M = (N\beta^2 g^2/4kT)(A/B)^{2/3} \quad (1)$$

where

$$A = 1.0 + 5.7979916y + 16.902653y^2 + 29.376885y^3 + 29.832959y^4 + 14.036918y^5 \quad (2)$$

$$B = 1.0 + 2.7979916y + 7.0086780y^2 + 8.6538644y^3 + 4.5743114y^4 \quad (3)$$

and $y = J/2kT$, the spin Hamiltonian, H, being defined as $\Sigma_i -J\, S_i\, S_{i+1}$; J is the intrachain magnetic-coupling parameter and N, g, and β have their usual meanings.

The best fit obtained using a nonlinear regression analysis leads to $J = +0.10(1)$ cm^{-1}, $g = 2.091(1)$ and $R = 2.6 \times 10^{-5}$ for compound **2** and $J = +0.31(1)$ cm^{-1}, $g = 2.092(1)$ and $R = 2.1 \times 10^{-6}$ for compound **3** (R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obsd.}(i) - (\chi_M T)_{calcd.}(i)]^2/\Sigma[(\chi_M T)_{obsd.}(i)]^2$. The calculated curves match very well the experimental data in the whole temperature range, as seen in Figure 5. The fact that the magnetization data of **3** at 2.0 K (see inset of Figure 5) are clearly above the Brillouin function for a magnetically isolated spin doublet (this is also observed for the corresponding plot in **2**) confirms the ferromagnetic nature of the intrachain magnetic coupling.

The weak ferromagnetic interactions in **2** and **3** can be understood in a simple manner by analysing the exchange pathway which is involved and the relative arrangement of the magnetic orbitals. The unpaired electron of the copper(II) ion in **2** and **3** (square-pyramidal environment) lies in the equatorial plane [N(1)N(2)O(2)O(4)] and it is defined by a $d_{x^2-y^2}$-type magnetic orbital [the x and y axes corre-

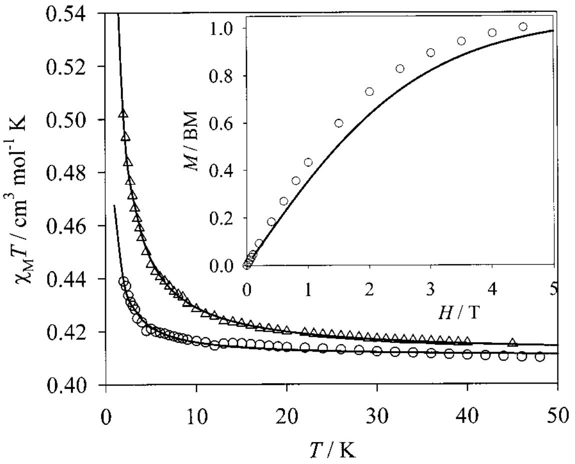
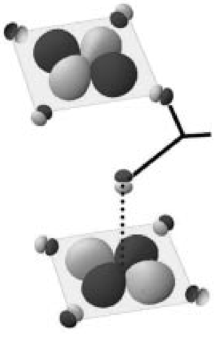


Figure 5. Experimental temperature dependence of the $\chi_M T$ product of **2** (circles) and **3** (triangles) at $T < 50$ K; (—) curves calculated from Equation (1); the inset shows the magnetization versus H plot for **3** at 2.0 K, experimental data (circles), (—) Brillouin function for a magnetically isolated spin doublet with $g = 2.09$

sponding roughly to the equatorial bonds to the copper atom]. The O(4)C(3)O(3) carboxylate bridge provides the intrachain exchange pathway in **2** and **3**: it links one equatorial position from Cu(1) [O(4)] with the axial one [O(3)] at Cu(1c) (**2**) and Cu(1f) (**3**) (see Scheme 1) adopting the *anti-syn* bridging mode. This exchange pathway produces a very poor overlap between the magnetic orbitals due to the weak spin density in the apical site.[39] Thus, the antiferromagnetic contribution, which is proportional to the square of the overlap between the magnetic orbitals, is minimized and the resulting magnetic coupling is most likely ferromagnetic, as observed.[40]



Scheme 1

Previous examples of carboxylate-(*anti-syn*-)bridged copper(II) complexes with an axial-equatorial exchange pathway exhibit ferromagnetic couplings with values of J ranging from +0.05 to +1.9 cm^{-1} (see Table 3).[8,10,16,41–43] The intensity of the magnetic coupling is affected by the Cu–O(axial) distance and the distortion of the metal environment — the longer the distance and the greater the distortion, the weaker the coupling is. The values of J for **2** and **3** fall in this range, but they are smaller than those with similar structural parameters [distortion and Cu–O(axial) distance]. The low value observed for the coupling constant for **2** [$J = +0.10(1)$ cm^{-1}] could be due to the greater value of the angle between the apical-oxygen-to-copper vector and the normal to the equatorial mean plane of the copper atom (7° in **2** and only 3.6° in **3**). In general, this shift influences the effectiveness of the bridge in the transmission of the magnetic coupling because it modifies the overlap between the magnetic orbitals.

Another interesting point looking at the results listed in Table 3 concerns compounds **3** and [{Cu(mal)(Im)}]$_n$. Although the structural parameters of **3** are similar to those of [{Cu(mal)(Im)}]$_n$, the value of the ferromagnetic coupling for **3** is somewhat smaller. Most likely, the carboxylate group of the phenylmalonate is less effective in the transmission of the magnetic coupling than the carboxylate group of the malonate ligand. The magnetic coupling is essentially an electronic effect and the phenylene ring of the phenylmalonate exerts an electron-withdrawing effect that delocalizes some electron density of the copper(II) towards the aromatic ring, decreasing the electronic delocalization towards the carboxylate bridge. The decrease of the electron delocalization towards the bridge would decrease the size of the magnetic coupling. This could be one of the factors to account for the weaker magnetic interaction between the copper(II) ions in **3** (and also in **2**) through the phenylmalonate-carboxylate bridge with respect to the malonate-carboxylate one.

Conclusions

Three new compounds have been prepared in which the phenylmalonate ligand acts either as blocking (**1**) or as bridging ligand (**2** and **3**). Weak interactions (hydrogen bonding and π–π stacking) govern the structure of the compounds leading to molecular (**1**) and one-dimensional (**2** and **3**) structures. A comparison with the related malonato-containing complexes reveals that the influence of the phenyl group in the Phmal compounds is decisive: [Cu(2,2′-bpy)(mal)(H_2O)]·H_2O presents different conformation and crystal packing of the mononuclear units from those in compound **1**; compounds **2** and **3** are uniform chains whereas the malonato-containing copper(II) complexes of 2,2′-bpym and phen are mononuclear compounds. The nature of the magnetic coupling between copper(II) ions through the phenylmalonate-carboxylate bridge (ferromagnetic) is the same as that through the malonate-carboxylate, but its magnitude is somewhat smaller, probably due to the electron-withdrawing effect which is exerted by the phenyl ring. In the near future, magneto-structural studies on phenylmalonate-containing copper(II) complexes will be pursued to check this observation and to gain further insights into the structural possibilities they provide.

Experimental Section

General: Phenylmalonic acid (H_2Phmal), copper(II) acetate hydrate ([Cu($CH_3COO)_2$·H_2O]), 2,2′-bipyridine (2,2′-bpy), 2,2′-bipyrim-

Table 3. Selected magneto-structural data for some (malonate-/phenylmalonate-)carboxylate-bridged copper(II) complexes

Compound[a]	Carboxylate pathway	Cu−(O)ap	τ[31] Cu1/Cu2	J [cm^{-1}][b]	Ref.
$[Cu(H_2O)_4][Cu(mal)_2(H_2O)_2]$	equatorial-apical	2.383	oct[c]/0.05	+1.8	[8]
$[Cu(H_2O)_4]_2[Cu(mal)_2(H_2O)]^{2+}$	equatorial-apical	2.381	oct[c]/0.12	+1.2	[8]
$[\{Cu(H_2O)_3\}\{Cu(mal)_2(H_2O)\}]_n$	equatorial-apical	2.185	0.24/0.28	+1.9	[8]
$[Cu(Im)_2(mal)]_n$	equatorial-apical	2.394	0.02/0.02	+1.6	[16]
$[Cu(2\text{-}MeIm)_2(mal)]_n$	equatorial-apical	2.270	0.18/0.18	+0.4	[16]
$\{(H_2bpe)[Cu(mal)_2\}]_n{\cdot}4nH_2O$	equatorial-apical	2.611	oct[c]/oct[c]	+0.049	[41]
2	equatorial-apical	2.262	0.08/0.08	+0.10	this work
3	equatorial-apical	2.314	0.10/0.10	+0.31	this work

[a] Abbreviations: Im = imidazole; 2-MeIm = 2-methylimidazole; bpe = 1,2-bis(4-pyridyl)ethylene. [b] Values of the coupling constant (J). [c] Octahedral.

idine (2,2′-bpym), 1,10-phenanthroline (phen) and methanol were purchased from Aldrich and used as received. Elemental analyses (C, H and N) were performed with an EA 1108 CHNS-O microanalytical analyzer. IR spectra (450−4000 cm^{-1}) were recorded with a Bruker IF S55 spectrophotometer with the sample prepared as KBr pellets. Magnetic susceptibility measurements on polycrystalline samples of compounds **1**−**3** were carried out in the temperature range 1.9−290 K with a Quantum Design SQUID magnetometer. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants[44] as -228×10^{-6}, -189×10^{-6} and -251×10^{-6} cm^3·mol^{-1} for compounds **1**, **2** and **3**, respectively. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism (60×10^{-6} cm^3·mol^{-1} per Cu^{II}) and the magnetization of the sample holder.

Synthesis: The general procedure to prepare compounds **1**−**3** starts with the preparation of an aqueous solution (15 mL) of copper(II) phenylmalonate (1 mmol) which was prepared by adding phenylmalonic acid (0.180 g, 1 mmol) to a warm methanolic solution (20 mL) of copper(II) acetate (1 mmol, 0.200 g) under continuous stirring. The resulting pale-blue solution was concentrated to dryness in a rotary evaporator. The green solid obtained was washed thoroughly with acetone to remove the acetic acid and then the green product was dissolved in water (15 mL).

$[Cu(2,2'\text{-}bpy)(Phmal)(H_2O)]{\cdot}2H_2O$ (1): 2,2′-Bipyridine (0.156 g, 1 mmol) was dissolved in methanol/water (50:50, 10 mL) and then an aqueous solution (15 mL) of copper(II) phenylmalonate was added whilst stirring. The solution was allowed to concentrate in a fumehood at room temperature. Prismatic blue single crystals of **1** had grown after a few days. Yield: 0.34 g (75% based on copper). $C_{19}H_{20}CuN_2O_7$ (451.55): calcd. C 50.49, H 4.43, N 6.20; found C 50.41, H 4.40, N 6.05. IR (KBr): ν(C−H, =C−H): 3090, 3062, 2950, 2923; ν(C=C, COO): 1637, 1605, 1590, 1577, 1445, 1409 cm^{-1}.

$[\{Cu(2,2'\text{-}bpym)(Phmal)\}]_n$ (2): Compound **2** was prepared similarly to **1** but using a solution of 2,2′-bpyrimidine (0.158 g, 1 mmol) instead of 2,2′-bipyridine. Prismatic greenish-blue single crystals of **2** were grown after a few days. Yield: 0.24 g (60% based on copper).

Table 4. Crystallographic data for complexes **1**−**3**

	1	**2**	**3**
Empirical formula	$C_{19}H_{20}CuN_2O_7$	$C_{17}H_{12}CuN_4O_4$	$C_{21}H_{20}CuN_2O_7$
Formula mass	451.91	399.85	475.88
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$Pcab$	$Pcab$	$P2_1/n$
a [Å]	14.6113(5)	8.9331(3)	5.014(3)
b [Å])	16.1928(4)	11.7577(3)	26.403(3)
c [Å]	16.5067(5)	29.8171(4)	14.685(3)
β [°]	90	90	94.75
V [Å^3]	3905.5(2)	3131.77(14)	1937.3(12)
Z	8	8	4
μ(Mo-K_α) [cm^{-1}]	11.63	14.28	11.76
T [K]	293(2)	293(2)	293(2)
$\rho_{calcd.}$ [gcm^{-3}]	1.537	1.696	1.611
λ [Å]	0.71073	0.71073	0.71073
Index ranges	$-18 \le h \le 20$	$-12 \le h \le 9$	$-7 \le h \le 5$
	$-22 \le k \le 22$	$-16 \le k \le 16$	$-32 \le k \le 37$
	$-23 \le l \le 13$	$-41 \le l \le 41$	$-13 \le l \le 20$
Independent reflections (R_{int})	5537 (0.060)	4545 (0.132)	5284 (0.051)
Observed reflections [$I > 2\sigma(I)$]	3552	2985	2872
Parameters	343	283	336
Goodness-of-fit	1.043	1.138	1.012
R [$I > 2\sigma(I)$]	0.0429	0.0742	0.0591
R_w [$I > 2\sigma(I)$]	0.0837	0.1462	0.1098
R (all data)	0.0866	0.1217	0.1376
R_w (all data)	0.1004	0.1615	0.1302

$C_{17}H_{12}CuN_4O_4$ (399.55): calcd. C 51.05, H 3.00, N 14.02; found C 51.20, H 3.14, N 14.10. IR (KBr): ν(C−H, =C−H): 3057, 3027, 2925; ν(C=C, COO): 1646, 1606, 1578, 1557, 1420, 1403 cm^{-1}.

[{Cu(phen)(Phmal)}]$_n$·3nH$_2$O (3): Compound **3** was prepared similarly to **1** but using a solution of 1,10-phenanthroline (0.180 g, 1 mmol) instead of 2,2′-bipyridine. Prismatic blue single crystals of **3** separated from the mother liquor on standing at room temperature after a week. Yield: 0.38 g (80% based on copper). $C_{21}H_{20}CuN_2O_7$ (475.55): calcd. C 52.99, H 4.21, N 5.89; found C 52.79, H 4.32, N 5.80. IR (KBr): ν(C−H, =C−H): 3060, 3030, 2923, 2850; ν(C=C, COO): 1628, 1615, 1595, 1576, 1425, 1405 cm^{-1}.

X-ray Crystallographic Study: Single crystals of **1**−**3** were used for data collection with a Nonius KappaCCD diffractometer. The data collection was carried out at 293 K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). A summary of the crystallographic data and structure refinement is given in Table 4 and selected interatomic distances and angles are listed in Table 5. The structures were solved by direct methods and refined with a full-matrix least-squares technique on F^2 using the SHELXL-97[45] program included in the WINGX[46] software package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms of structures **1**−**3** were located from difference maps and refined with isotropic temperature factors, except those of the water molecules of complex **3**. The final geometrical calculations and graphical manipulations were carried out with PARST97[47] and CRYSTALMAKER[48] programs. CCDC-235074 (**1**), -235075 (**2**) and -235076 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 5. Selected bond lengths [Å] and bond angles [°] for compounds **1**−**3**[a]

1			
Cu(1)−O(2)	1.954(2)	Cu(1)−N(2)	1.998(2)
Cu(1)−O(4)	1.933(2)	Cu(1)−O(1w)	2.143(2)
Cu(1)−N(1)	2.001(2)		
O(2)−Cu(1)−O(4)	90.09(7)	O(4)−Cu(1)−N(2)	166.47(8)
O(2)−Cu(1)−N(1)	158.23(8)	O(4)−Cu(1)−O(1w)	97.46(9)
O(2)−Cu(1)−N(2)	92.89(8)	N(1)−Cu(1)−N(2)	80.53(8)
O(2)−Cu(1)−O(1w)	96.85(9)	N(1)−Cu(1)−O(1w)	104.38(9)
O(4)−Cu(1)−N(1)	91.89(8)	N(2)−Cu(1)−O(1w)	95.29(9)
2			
Cu(1)−O(2)	1.922(3)	Cu(1)−N(2)	1.996(3)
Cu(1)−O(4)	1.900(3)	Cu(1)−O(3b)	2.262(3)
Cu(1)−N(1)	2.003(3)		
O(2)−Cu(1)−O(4)	92.93(11)	O(4)−Cu(1)−N(2)	162.02(14)
O(2)−Cu(1)−N(1)	166.90(14)	O(4)−Cu(1)−O(3b)	100.05(12)
O(2)−Cu(1)−N(2)	93.31(13)	N(1)−Cu(1)−N(2)	80.53(13)
O(2)−Cu(1)−O(3b)	106.32(12)	N(1)−Cu(1)−O(3b)	85.78(12)
O(4)−Cu(1)−N(1)	89.79(12)	N(2)−Cu(1)−O(3b)	94.33(12)
3			
Cu(1)−O(2)	1.913(2)	Cu(1)−N(2)	2.026(3)
Cu(1)−O(4)	1.934(2)	Cu(1)−O(3e)	2.314(2)
Cu(1)−N(1)	1.992(3)		
O(2)−Cu(1)−O(4)	92.80(9)	O(4)−Cu(1)−N(2)	162.66(10)
O(2)−Cu(1)−N(1)	168.52(11)	O(4)−Cu(1)−O(3e)	101.46(9)
O(2)−Cu(1)−N(2)	90.63(10)	N(1)−Cu(1)−N(2)	81.86(11)
O(2)−Cu(1)−O(3e)	92.74(10)	N(1)−Cu(1)−O(3e)	96.59(10)
O(4)−Cu(1)−N(1)	91.90(10)	N(2)−Cu(1)−O(3e)	95.35(10)

[a] Estimated standard deviations in the last significant digits are given in parentheses. Symmetry codes: (b) −1/2 + x, 1/2 − y, z; (e) x + 1, y, z.

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