$\{[Cu(H_2O)_3][Cu(phmal)_2]\}_n$: a new two-dimensional copper(II) complex with intralayer ferromagnetic interactions (phmal = phenylmalonate dianion)

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The novel sheet-like copper(II) compound of formula $\{[Cu(H_2O)_3][Cu(Phmal)_2]\}_n$ (**1**) (Phmal = dianion of phenylmalonic acid) has been synthesized and its crystal structure determined by X-ray diffraction. The structure of **1** consists of 2_1 chains of carboxylate(phenylmalonate)-bridged copper(II) ions which are linked through double μ-oxo(carboxylate) units to afford a two-dimensional network. The interlayer space is filled by the phenyl rings of the phenylmalonate ligands that exhibit offset face-to-face interactions. Variable-temperature magnetic measurements of **1** show the occurrence of significant intralayer ferromagnetic interactions between the copper(II) ions through *anti–syn* carboxylate- and double μ-oxo-bridges which are analyzed and discussed in the light of the values found in related magneto-structurally characterized systems.

Introduction

There has been considerable interest in inorganic–organic hybrid materials with variable dimensionality and different coordination frameworks.[1] The studies on these inorganic–organic hybrid pillared structures focus on aspects concerning materials science and structural chemistry because of their potential applications in catalysis,[2] sorption processes,[3] photochemistry[4] and magnetism.[5] A reasonable synthetic approach to build three-dimensional structures in crystal engineering consists of connecting layers of transition-metal ions through bridging ligands.[6] The choice of parameters such as bridging ability of the spacer and its length and topology is very important in determining the resulting architecture of the three-dimensional network and the transmission of electronic effects between the metal centres. In this respect, the use of bifunctional groups such as diphosphonate, carboxyphosphonate and dicarboxylate ligands has afforded a large variety of crystal structures depending on the synthetic conditions, the nature of the metal ions, and the characteristics and flexibility of the co-ligands which are present.[7]

The structure and physical properties of polynuclear coordination compounds with different carboxylate-type ligands such as α,ω-dicarboxylate,[8] phthalate,[9] and biphenyldicarboxylate (bpdc)[10] have been the subject of recent reports. In this respect, in the framework of our current research work with malonate-bridged copper(II) complexes, we have observed that the carboxylate–malonate bridge through both the *anti–syn* and *anti–anti* coordination is able to mediate significant ferromagnetic interactions between the copper(II) ions it links.[11,12] From a magnetic point of view, we have found that the parameters governing the magnetic interaction between metal centres are the relative position of the carboxylato bridge of the malonate respect to the copper(II) ions: equatorial–equatorial (relatively strong interaction), equatorial–apical (weak interaction) and apical–apical (negligible interaction). Inside this division, two additional structural parameters become important: the value of the dihedral angle β between the mean basal planes of the interacting copper(II) ions in the equatorial–equatorial exchange pathway and the distortion τ[$\tau = 0$ and 1 for square pyramidal and trigonal bipyramidal copper(II) environments, respectively][13] in the equatorial–apical one.[14]

In the light of these results, the question of whether other conformations of malonate–copper(II) complexes are possible remains open. Keeping this in mind, we have started a systematic study with substituted malonate ligands such as the phenylmalonate dianion (hereafter noted Phmal). The presence of a phenyl ring on the methylene carbon group could induce different conformations of the malonate bridging modes due to geometrical constraints and would make possible specific attractive interactions between phenyl rings which would contribute to the overall stability of the resulting compound. Their role in molecular recognition, and more generally in supramolecular chemistry, has now been widely examined.[15–21]

In this paper, we report the synthesis, crystallographic analysis and magnetic properties of the first phenylmalonate-containing copper(II) complex of formula $\{[Cu(H_2O)_3][Cu(Phmal)_2]\}_n$ (**1**). This compound has a two-dimensional structure with single carboxylate- and double oxo-malonate bridges which mediate ferromagnetic interactions between the copper(II) ions.

Results and discussion

Description of the structure of 1

The crystal structure of **1** consists of a two-dimensional arrangement of copper(II) ions which is made up of 2_1 chains with regular alternation of bis(phenylmalonato)cuprate(II) anions and triaquacopper(II) cations that are linked through a double μ-oxo bridge (Fig. 1). These 2_1 chains run parallel to the *b* axis (Fig. 2) and the resulting layers are stacked parallel to the [101] direction. These layers are well separated from each other, the interlayer distance being 8.187(2) Å. The interlayer space is filled by the malonate-phenyl rings that create hydrophobic layers (Fig. 3). where offset face-to-face π–π stacking between the phenyl rings occurs, the shortest distance between the mean planes of adjacent phenyl rings being 3.495(3) Å. The centre to centre distance between adjacent phenyl rings is 3.954(5) Å, a value which is a bit longer than the average distances in π–π interactions with pyridine-like groups previously reported.[22] Intralayer hydrogen bonds involving water molecules and phenylmalonate oxygen atoms, [O(w)···O distances ranging from 2.672(4) Å to 2.830(3) Å] contribute to stabilize the structure. Selected bonds lengths and angles are listed in Table 1.

The two crystallographically independent copper(II) ions [Cu(1) and Cu(2)] have slightly distorted square pyramidal surroundings. Four coplanar carboxylate oxygen atoms [O(2), O(4), O(5), and O(8)], define the basal plane at Cu(1) [copper to oxygen bond lengths varying in the range 1.915(2)–1.945(2) Å], whereas the apical position is occupied by the symmetry related carboxylate oxygen atom O(8a) [2.433(2) Å for Cu(1)–O(8a) (a) = $-x+1, -y+1, -z+2$]. Cu(1) is shifted by 0.0282(4) Å from the mean basal plane towards O(8a). The difference between the length of the axial and equatorial bonds (0.503 Å) is in agreement with the R_L–R_S value (0.51 Å) reported by Hathaway.[23] The angles subtended at Cu(1) by the chelating phenylmalonate groups are 93.20(8) and 91.39(8)°. Two water molecules, [O(2w) and O(3w)], and two carboxylate-oxygen atoms [O(1) and O(6b) (b) = $-x+3/2, y+1/2, -z+5/2$], build the basal plane at Cu(2), whereas the apical position is filled by another water molecule [O(1w)]. The equatorial copper to oxygen bond distances [1.952(2) to 1.980(2) Å] are shorter than the apical one [2.120(2) Å]. Cu(2) is shifted by 0.2130(3) Å from the mean basal plane towards O(1w). The calculated values of the τ factor[13] are 0.02, and 0.06 for Cu(1) and Cu(2), respectively; indicating a quasi perfect square pyramidal environment in both copper(II) ions.

The two phenylmalonate ligands simultaneously adopts bidentate [through O(2) and O(4) and O(5) and O(8)] and monodentate [through O(1) and O(6)] coordination modes at Cu(1) and Cu(2), respectively, affording the 2_1 chain with regular alternating Cu(1) and Cu(2). In addition, one of two phenylmalonate ligands [O(5)/O(8)] acts as a monodentate [through O(8) atom] towards a symmetry-related copper atom [Cu(1a)] from an adjacent chain (Fig. 1), the 2_1 chains being thus linked by double μ-oxo bridges. The bridging network Cu_2O_2 is strictly planar owing to the inversion centre, with a Cu(1)···Cu(1a) separation of 3.3042(5) Å. The value of the angle at the oxo bridge Cu–O–Cu is 97.38(7)°, whereas the

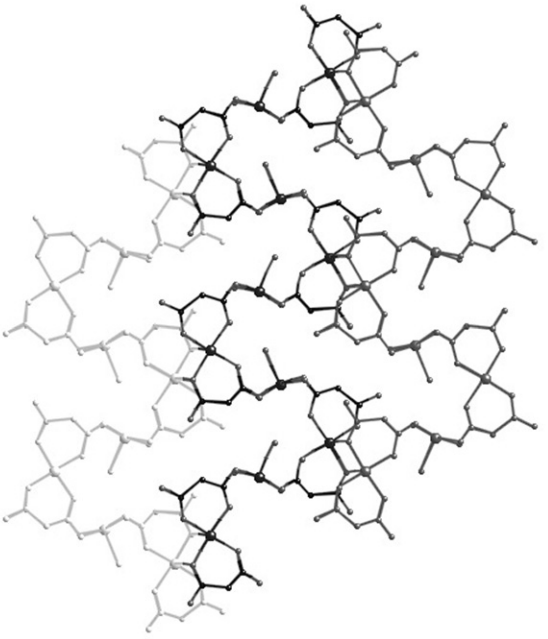


Fig. 2 Sheet-like arrangement of the three 2_1 chains running parallel to the *b* axis. The phenyl groups of the Phmal ligand are omitted for clarity.

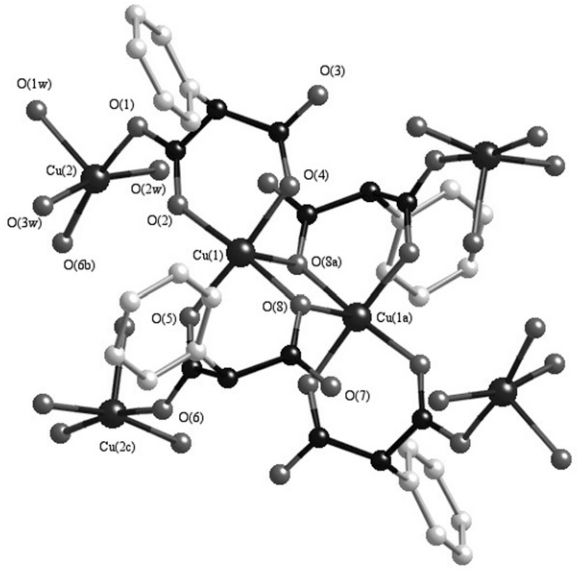


Fig. 1 A view of a fragment of the carboxylato-bridged copper(II) chains linked by the double μ-oxo bridge. The numbering of the carbon atoms is omitted for clarity.

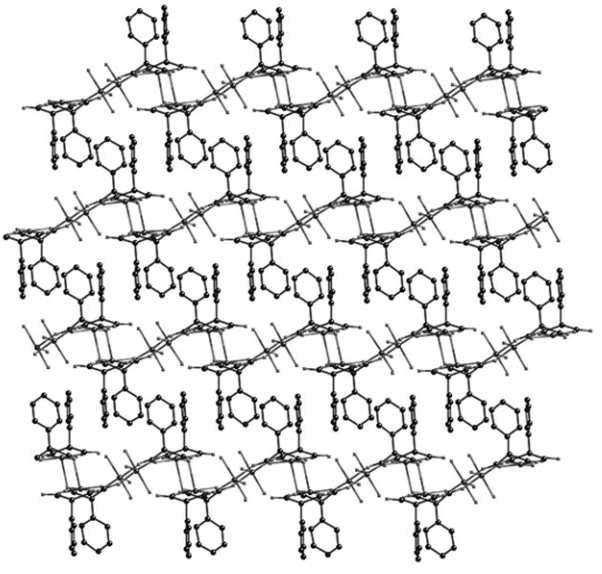


Fig. 3 A view of the structure of complex **1** along the *b* axis showing the interlayer π–π interactions.

Table 1 Selected bond lengths (Å) and bond angles (°) for compound **1**[a,b]

Bond lengths			
Cu(1)–O(2)	1.926(2)	Cu(2)–O(1)	1.952(2)
Cu(1)–O(4)	1.915(2)	Cu(2)–O(1w)	2.120(2)
Cu(1)–O(5)	1.919(2)	Cu(2)–O(2w)	1.978(2)
Cu(1)–O(8)	1.945(2)	Cu(2)–O(3w)	1.961(3)
Cu(1)–O(8a)	2.433(2)	Cu(2)–O(6b)	1.980(2)
Bond angles			
Cu(1)–O(8)–Cu(1a)	97.38(7)	O(1)–Cu(2)–O(1w)	92.99(10)
O(2)–Cu(1)–O(4)	93.20(8)	O(1)–Cu(2)–O(2w)	89.40(9)
O(2)–Cu(1)–O(5)	84.48(8)	O(1)–Cu(2)–O(3w)	92.65(12)
O(2)–Cu(1)–O(8a)	99.13(8)	O(1)–Cu(2)–O(6b)	168.59(8)
O(2)–Cu(1)–O(8)	175.64(8)	O(1w)–Cu(2)–O(2w)	101.90(12)
O(4)–Cu(1)–O(5)	177.04(9)	O(1w)–Cu(2)–O(3w)	93.12(13)
O(4)–Cu(1)–O(8)	90.87(8)	O(1w)–Cu(2)–O(6b)	98.41(10)
O(4)–Cu(1)–O(8a)	87.13(8)	O(2w)–Cu(2)–O(3w)	164.72(12)
O(5)–Cu(1)–O(8)	91.39(8)	O(2w)–Cu(2)–O(6b)	88.53(9)
O(5)–Cu(1)–O(8a)	95.05(8)	O(3w)–Cu(2)–O(6b)	86.49(12)
O(8)–Cu(1)–O(8a)	82.62(7)	Cu(2)–O(1)–C(1)	116.7(2)
Cu(1)–O(8)–C(12)	126.2(2)	Cu(2c)–O(6)–C(10)	129.1(2)
Cu(1a)–O(8)–C(12)	110.4(2)}		

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] Symmetry code: (a) $-x+1$, $-y+1$, $-z+2$; (b) $-x+3/2$, $y+1/2$, $-z+5/2$; (c) $-x+3/2$, $y-1/2$, $-z+5/2$.

out-of-plane distance is 2.433(2) Å. The phenyl groups point always to the stacking direction of the layers [10–1]. The average C–O bond distances and O–C–O bond angles are 1.251(3) Å and 122.2(3)°, respectively. Two slightly different carboxylate bridges [O(1)C(1)O(2) and O(6)C(10)O(5)] that exhibit the *anti–syn* conformation and link equatorial positions of the two copper atoms involved, alternate regularly within each chain. The values of the intrachain copper–copper separation through these carboxylate bridges are 4.6511(5) [Cu(1)···Cu(2)] and 5.0736(7) Å [Cu(1)···Cu(2c) (c) = $-x+3/2$, $y-1/2$, $z+5/2$]. The bond angles at the bridging O(1) and O(6) atoms are 116.7(2)° and 129.1(2)°, respectively. The values of the dihedral angle between the equatorial plane at Cu(1) and those of the O(1)C(1)O(2) and O(6)C(10)O(5) bridging carboxylates are 15.0(2) and 28.6(2)°, respectively. These values are far from the corresponding values between the equatorial plane at Cu(2) and the O(1)C(1)O(2) and O(6b)C(10b)O(5b) carboxylate planes, which are 82.67(12) and 89.9(2)°, respectively. The value of the angle between the two mean basal planes of the two crystallographically independent copper(II) ions is 87.62(7)°, indicating a quasi orthogonality between them. Curiously, the two Phmal ligands have different conformation: that containing O(2)/O(3) has the boat conformation whereas O(5)/O(8) exhibits the envelope one.

Let us finish this part with a comparison of the structure of **1** with that of the chain compound $\{[Cu(H_2O)_3][Cu(mal)_2(H_2O)]\}_n$ (**2**) (mal = dianion of malonic acid).[11] The structure of **2** is made up of neutral uniform chains of copper(II) ions where the $[Cu(mal)_2(H_2O)]^{2-}$ unit acts as a bis-monodentate ligand through malonate-oxygen atoms in *trans* positions of the two malonate ligands towards $[Cu(H_2O)_3]^{2+}$ entities. Both copper atoms have square pyramidal surroundings and the two carboxylate-malonate bridges exhibit the *anti–syn* conformation but one of them connects two equatorial copper sites and the other one links an equatorial with one axial site. In the case of compound **1**, one can observe an alternating arrangement of bis(phenylmalonato)cuprate(II) and triaquacopper(II) units, the former being linked to the latter as bis-monodentate ligands through two *cis*-malonato oxygen atoms. The carboxylato-bridge in the resulting chain of **1** has also the *anti–syn* conformation but connects equatorial positions of adjacent copper atoms. The presence of the phenyl ring introduces an apolar part and it exerts thus a strong influence on the resulting structure. In addition to the differences in the chelating/monodentate coordination mode of mal and Phmal within the copper(II) chain, the phenylmalonate in **1** is involved in π–π interactions between the phenyl rings to build a hydrophobic intralayer space which accounts for the *cis* arrangement of the phenyl groups in each $[Cu(Phmal)_2]^{2-}$ unit. At a molecular scale, the phenylmalonate ligands of the $[Cu(Phmal)_2]^{2-}$ units tend to align their aromatic rings in the same direction, preventing the occupation of one of the axial positions of the copper(II) coordination sphere. As the other axial position is readily available, the lack of steric effects allows bulky groups to be introduced leading to the formation of the $[Cu_2(Phmal)_4]^{4-}$ dinuclear species through double μ-oxo(carboxylate) bridge. This dimerization has neither been observed in **2** nor in other malonate-bridged complexes. The chains are interconnected through these units leading to a 2D system. The intrachain magnetic interaction in **1** is ferromagnetic as in **2**, but in addition, these chains are also ferromagnetically coupled through the double μ-oxo bridges in **1** (see below), the phenylmalonate allowing to increase the structural and magnetic dimensionality with respect to parent malonate-bridged copper(II) complexes.

Magnetic properties of 1

The magnetic properties of compound **1** under the form of $\chi_M T$ *vs.* T plot (χ_M being the molar susceptibility per copper(II) ion) are shown in Fig. 4. $\chi_M T$ at room temperature is 0.42 cm^3 mol^{-1} K, a value which is as expected for a magnetically isolated spin doublet. Upon cooling, $\chi_M T$ increases smoothly until 50 K and sharply at lower temperatures reaching a value of 1.77 cm^3 mol^{-1} K at 2 K. This behaviour is indicative of an overall ferromagnetic coupling between the copper(II) ions.

Two exchange pathways are operative in the structure of **1**: the carboxylate bridge in the *anti–syn* conformation within the copper(II) 2_1 chain and the double μ-oxo(carboxylate) bridge between the chains. Because of the occurrence of the same conformation in both carboxylate bridges and the similarity between the angles in the bridging skeleton, the carboxylate-bridged copper(II) chain may be considered as a regular chain (see Scheme 1). Neglecting the interchain interactions in a first approximation, we analyzed the magnetic data of **1** through the Baker and Rushbrooke numerical expression for a ferromagnetically coupled uniform copper(II) chain[24]

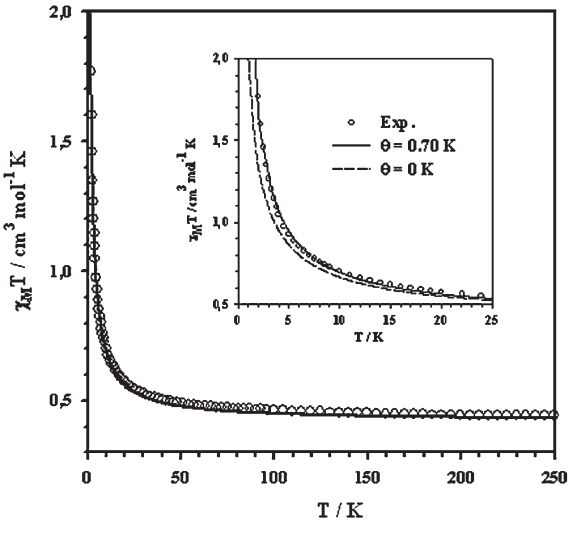
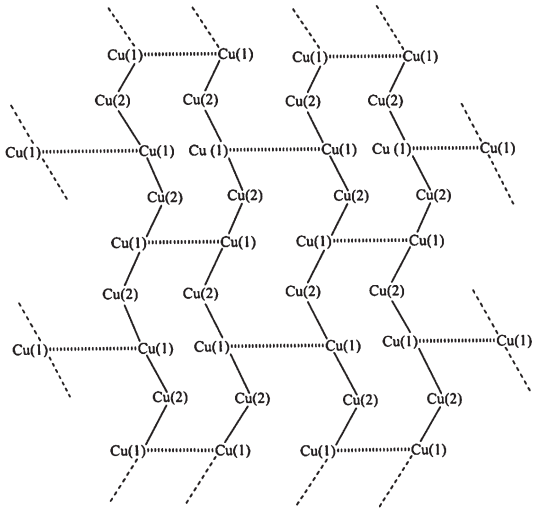


Fig. 4 Thermal dependence of the $\chi_M T$ product for complex **1**:(○) experimental data and (—) best fit curve. The inset shows the fits with θ = 0 (---) and 0.70 K (—) in the low temperature range (see text).



Scheme 1

[(eqns. (1)–(4)]

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

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

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

$$\hat{H} = -J\Sigma_i \hat{S}_i \cdot \hat{S}_{i+1} \quad (4)$$

with $y = J/2kT$. J is the intrachain magnetic coupling parameter, and the other symbols have their usual meanings. Best least-squares fit parameters are $J = +6.2(1)$ cm^{-1}, $g = 2.086(9)$ and $R = 5.4 \times 10^{-3}$. R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2/\Sigma\,[(\chi_M T)_{obs}(i)]^2$. The calculated curve matches the experimental data well in the high temperature range (above 30 K), but it lies below them in the lower temperature range. This suggests that an additional ferromagnetic interchain interaction is involved and most likely the interaction linking through the double μ-oxo bridge has to be the responsible form. Consequently, a molecular mean field term (θ) is introduced to evaluate it. Under this approach, best-fit parameters are $J = +4.44(5)$ cm^{-1}, $g = 2.131(3)$, $\theta = 0.70(2)$ K and $R = 1.1 \times 10^{-4}$. A value of the interchain coupling (zj) of *ca.* $+1.95$ cm^{-1} is derived from the relation $\theta = \frac{zjS(S+1)}{3k}$. The magnitude of this value must be taken with caution because of the inclusion in this parameter of the possible interactions through the weak π–π stacking. In any case, it is clear that the two magnetic interactions (J and zj) are ferromagnetic. The calculated curve with this last set of best-fit parameters reproduces very well the experimental data in the whole temperature range.

Let us analyse and discuss the nature and values of the two magnetic couplings observed in **1**. The ferromagnetic coupling between Cu(1) and Cu(2) through the *anti–syn* carboxylate-malonate bridge in **1** is in agreement with the data reported in the literature for copper(II) complexes with this type of bridge, as shown in Table 2.[11,12,14] Simple magnetic orbital considerations allow us to understand the ferromagnetic interaction through this type of bridge. The unpaired electron of Cu(1) [the same applies for Cu(2)] is of the $d_{x^2-y^2}$, the x and y axes being roughly defined by the Cu(1)–O(2) and Cu(1)–O(4) bonds [Cu(2)–O(1) and Cu(2)–O(6b) at Cu(2)], and it is mainly located in the equatorial plane. As the mean basal planes of the adjacent Cu(1) and Cu(2) atoms make a dihedral angle very close to 90° [87.7(1)°], their magnetic orbitals are orthogonal and the magnetic coupling is ferromagnetic.[14,25–28] As far as the weak ferromagnetic coupling observed through the double μ-oxo bridge is concerned, the comparison with previously magneto-structural results which are listed in Table 3 provides a less clear picture. As one can see in this table, the magnetic coupling through this type of bridge in most of the reported examples is weak and antiferromagnetic.[29–33] This family has in common the parallel arrangement of the $d_{x^2-y^2}$ type magnetic orbitals of the two

Table 2 Selected magneto-structural data for some carboxylate-(malonate)-bridged copper(II) complexes

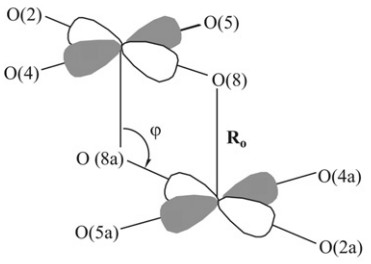
Compound[a]	Carboxylate pathway[b]	J[c] /cm^{-1}	Ref
$[Cu(H_2O)_4][Cu(mal)_2(H_2O)_2]$	Eq–Ap	+1.8	11
$\{[Cu(H_2O)_4]_2[Cu(mal)_2(H_2O)]\}$	Eq–Ap	+1.2	11
$\{[Cu(H_2O)_3][Cu(mal)_2(H_2O)]\}_n$	Eq–Ap	+1.9	11
$[Cu(Im)_2(mal)]_n$	Eq–Ap	+1.6	12b
$[Cu(2\text{-}MeIm)_2(mal)]_n$	Eq–Ap	+0.4	12b
$\{(H_2bpe)[Cu(mal)_2]\}_n \cdot 4nH_2O$	Eq–Ap	+0.049	12g
$[Cu_4(mal)_4(bpe)_3]_n \cdot 6nH_2O$	Eq–Ap	+6.5	12g
$\{[Cu(H_2O)_3][Cu(mal)_2(H_2O)]\}_n$	Eq–Eq	+3.0	11
$\{[Cu(bpy)(H_2O)][Cu(bpy)(mal)(H_2O)]\}$ $n \cdot 2n(ClO_4)$	Eq–Eq	+4.6	12a
$[Cu_4(mal)_4(2,4'\text{-}bpy)_4(H_2O)_4] \cdot 8H_2O$	Eq–Eq	+12.3	12f
$[Cu_2(mal)_2(H_2O)_2(4,4'\text{-}bpy)_n]$	Eq–Eq	+12.4	12c
$\{Cu_3(mal)_2(bpa)_3(H_2O)_2\} n \cdot 2n(NO_3)$	Eq–Eq	+22	42
$[Cu_4(mal)_4(bpe)_3]_n \cdot 6nH_2O$	Eq–Eq	+23	12g
Compound **1**	Eq–Eq	+4.44	

[a] Abbreviations used: Im = imidazole, 2-MeIm = 2-methylimidazole, bpy = 2,2′-bipyridine, 2,4′-bpy = 2,4′-bipyridine, 4,4′-bpy = 4,4′-bipyridine, bpe = 1,2-bis(4-pyridyl)ethylene and bpa = 1,2-bis(4-pyridyl)ethane. [b] Eq and Ap stand for equatorial and apical, respectively. [c] Values of the magnetic coupling.

Table 3 Relevant data for the magneto-structurally characterized double μ-oxo carboxylate-bridged copper(II) systems

Compound[a]	R_o/Å	ϕ/°	J/cm^{-1}	Ref
$\{[CuL^1(MeCO_2)]_2\}$	2.665(4)	96.3(5)	−1.84	34[a]
$\{[CuL^2(MeCO_2)]_2\}$	2.577(2)	96.1(1)	−1.51	34[a]
$\{[CuL^3(MeCO_2)]_2\}$	2.512(5)	96.9(2)	−1.33	29,34[b]
$\{[CuL^4(MeCO_2)]_2 \cdot 2H_2O\}_n$	2.498(8)	98.1(3)	−1.54 (−2.26)[b]	34[b]
$\{[CuL_5(MeCO_2)]_n\} \cdot 2n$MeOH	2.495(6)	98.3(5)	−1.50 (−7.88)[b]	34[c]
$\{[CuL^6(MeCO_2)]_2\} \cdot H_2O \cdot$EtOH	2.446(2) 2.651(1)	95.7(1) 102.6(1)	+0.63[c]	36
$\{[Cu(PhCONHCH_2CO_2)(H_2O)]_2\} \cdot 2H_2O$	2.37(1)	101.0(5)	−2.15	30,31
$\{[CuL^7(MeCO_2)]_2\}$	2.490(1)	95.34(5)	−0.25	32
$\{[Cu(tzq)_2(HCO_2)]_2(\mu\text{-}HCO_2)_2\} \cdot 4H_2O$	2.331(4)	102.2(2)	−0.52	33
Compound **1**	2.433(2)	97.38(7)	+1.95[d]	

[a] HL^1 = *N*-(5-Bromosalicylidene)-*N*-methylpropane-1,3-diamine, HL^2 = *N*-methyl-*N*′-(5-nitrosalicylidene)propane-1,3-diamine, HL^3 = *N*-methyl-*N*′-salicylidenepropane-1,3-diamine, HL^4 = *N*-(5-methoxysalicylidene)-*N*-methylpropane-1,3-diamine, HL^5 = *N*,*N*′-[bis(2-*o*-hydroxybenzylideneamino)ethyl]ethane-1,2-diamine, HL^6 = *N*-(2-hydroxy-1,1-dimethylethyl)-salicyleneamine, HL^7 = 7-amino-4-methyl-5-azahept-3-en-2-onate. [b] Magnetic analysis through an alternating chain model. [c] This is the only compound whose Cu_2O_2 system is non-centrosymmetric. [d] This value is zj (see text).



Scheme 2

copper(II) ions involved, each oxo atom occupying simultaneously an equatorial position at one copper atom and the axial one at the other copper atom (see Scheme 2).

The poor overlap between the two magnetic orbitals through the out-of-plane exchange pathway allows prediction of a weak antiferromagnetic interaction which can be ferromagnetic in the case of accidental orthogonality, the value of the angle at the oxo bridge and the basal to apical Cu–O bond length being the most important structural parameters in determining the sign and magnitude of the magnetic coupling.[33,34] The trigonal distortion of the copper environment seems to be another relevant parameter as already noted in the di-μ-chloro-bridged copper(II) complexes (out-of-plane exchange pathway).[35] In this respect, the compounds exhibiting antiferromagnetic coupling in Table 3 have important trigonal distortions that mix the d_{z^2} orbital in the magnetic orbital of the Cu(II) ions, whereas the only case exhibiting ferromagnetic coupling has a very little trigonal distortion of the Cu(II) environment (τ being 0.09 and 0.06).[36] It seems that the very small trigonal distortion of the square pyramid of Cu(1) in **1** ($\tau = 0.02$) minimizes the overlap between their magnetic orbitals through the double μ-oxo bridge leading the ferromagnetic term to become dominant. Additional ferromagnetically coupled examples with this type of bridge are needed in order to establish a clear magneto-structural correlation.

Conclusions

The two main conclusions of the present work are: (i) the carboxylate–Phmal bridge is able to transmit ferromagnetic interactions between copper(II) ions through the *anti–syn* conformation as the malonate, (ii) the inclusion of the phenyl ring in the malonate skeleton makes possible supramolecular interactions (offset π–π stacking) and allows the increase of the structural [π–π stacking of the layers of copper(II) ions] and magnetic dimensionalities [intra- and interchain magnetic interactions between copper(II) ions through the Phmal ligand]. Finally, the phenyl substituent induces subtle changes in the coordinating behaviour of the phenylmalonate ligand such as the bridging mode through double μ-oxo(carboxylate) which is unprecedented in the coordination chemistry of the related malonate ligand.

Experimental

Materials

H_2Phmal and $Cu(CH_3COO)_2{\cdot}H_2O$ were purchased from commercial sources and used as received. Elemental analyses (C, H) were performed on an EA 1108 CHNS-O microanalytical analyzer.

Synthesis of $\{[Cu(H_2O)_3][Cu(Phmal)_2]\}_n$ (1). Copper(II) acetate (1 mmol, 200 mg) was dissolved in warm methanol (20 cm^3) under stirring. Phenylmalonic acid (1 mmol, 180 mg) was added and the resulting clear blue solution was evaporated to dryness in a rotatory evaporator. The green solid obtained was thoroughly washed with acetone to remove the acetic acid. Next, it was dissolved in water (25 cm^3) and the solution was allowed to evaporate at room temperature. Prismatic blue single crystals of **1** were grown after a few days. Yield *ca.* 65%. Anal. calc. for $C_{18}H_{18}O_{11}Cu_2$ (1): C, 40.23; H, 3.38. Found: C, 40.18; H, 3.39%. IR (KBr, cm^{-1}): 1669s, 1570vs; 1449m, 1380s, 1284m; 811m, 722m.

Physical techniques

IR spectrum (450–4000 cm^{-1}) was recorded on a Bruker IF S55 spectrophotometer with the sample prepared as a KBr pellet. Magnetic susceptibility measurements on a polycrystalline sample of **1** was carried out in the temperature range 1.9–290 K with a Quantum Design SQUID magnetometer operating at 100 ($T < 50$ K) and 1000 G ($T > 50$ K). Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants[37] as -215×10^{-6}. 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.

Crystallographic data collection and structure determination

A crystal of dimensions $0.23 \times 0.17 \times 0.17$ mm was used for data collection on a Nonius KappaCCD diffractometer. Indexing and unit cell refinement were based on all observed reflections of 8 frames collected at 293 K with the φ–χ scan technique, exposure time of 15 s per frame and sample to detector distance of 35 mm. The data collection was carried out at 293 K with an exposure time of 30 s per frame, a distance of 35 mm and using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A summary of the crystallographic data and structure refinement is given in Table 4. The index ranges of data collection were $-17 \le h \le 17$, $-14 \le k \le 12$ and $-11 \le l \le 21$. Of the 5292 measured independent reflections in the θ range 6.40–30.00°, 3823 have $I > 2\sigma(I)$. All the measured independent reflections were used in the analysis.

The structure of **1** was solved by direct methods and refined with full-matrix least-squares technique on F^2 using SHELXL-97[38] program included in the WINGX[39] package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Full-matrix least-squares refinement was performed minimizing the function $w(|F_o|^2 - |F_c|^2)$ with $w = 1/[\sigma^2(F_o)^2 + (mP)^2 + nP]$ and $P = (F_o^2 + 2F_c^2)/3$ with

Table 4 Crystallographic data for compound **1**

Formula	$C_{18}H_{18}O_{11}Cu_2$
FW	537.4
Crystal system	Monoclinic
Space group	$P\,2_1/n$
a/Å	12.1329 (9)
b/Å	10.4929 (9)
c/Å	15.2841 (17)
β/deg	98.315 (8)
V/Å^3	1925.4 (3)
Z	4
μ(Mo Kα)/cm^{-1}	22.72
T/K	293 (2)
ρ_{calc}/g cm^{-3}	1.854
λ/Å	0.71073
Indep. reflect. (R_{int})	5292 (0.0424)
Obs. reflect. [$I > 2\sigma(I)$]	3823
Parameters	352
R^a	0.0414
$R_w{}^b$	0.0831

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma_w(|F_o|^2 - |F_c|^2)^2/\Sigma_w|F_o|^2]^{1/2}$.

$m = 0.0389$ and $n = 1.3648$. The values of the discrepancy indices R and R_w for all data were 0.0732 and 0.0932 respectively [those listed in Table 4 correspond to the data with $I > 2\sigma(I)$]. The final Fourier-difference map showed maximum and minimum height peaks of 0.604 and -0.466 e Å^{-3}. The value of the number of reflections/number of parameters ratio is 15.0, and the value of the goodness-of-fit is 1.003. The final geometrical calculations and graphical manipulations were carried out with PARST97[40] and CRYSTALMAKER[41] programs.

CCDC reference number 214031(**1**). See http://www.rsc.org/suppdata/nj/b3/b304471h/ for crystallographic data in CIF or other electronic format.

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