

Polymeric Networks of Copper(II) Phenylmalonate with Heteroaromatic N-donor Ligands: Synthesis, Crystal Structure, and Magnetic Properties

Jorge Pasán,[†] Joaquín Sanchiz,[‡] Catalina Ruiz-Pérez,^{*†} Francesc Lloret,[§] and Miguel Julve[§]

Laboratorio de Rayos X y Materiales Moleculares, Departamento de Física Fundamental II, Universidad de La Laguna, Av. Astrofísico Francisco Sánchez s/n, 38206 La Laguna (Tenerife), Spain, Laboratorio de Rayos X y Materiales Moleculares, Departamento de Química Inorgánica, Universidad de La Laguna, Av. Astrofísico Francisco Sánchez s/n, 38204 La Laguna (Tenerife), Spain, and Departament de Química Inorgànica/ Instituto de Ciencia Molecular, Facultat de Química, Universitat de València, Av. Dr. Moliner 50, 46100 Burjassot (València), Spain

Received March 17, 2005

Two new phenylmalonate-bridged copper(II) complexes with the formulas $[\text{Cu}(4,4'\text{-bpy})(\text{Phmal})]_n \cdot 2n\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(2,4'\text{-bpy})(\text{Phmal})(\text{H}_2\text{O})]_n$ (**2**) (Phmal = phenylmalonate dianion, 4,4'-bpy = 4,4'-bipyridine, 2,4'-bpy = 2,4'-bipyridine) have been synthesized and characterized by X-ray diffraction. Complex **1** crystallizes in monoclinic space group $P2_1$, $Z = 4$, with unit cell parameters of $a = 9.0837(6)$ Å, $b = 9.3514(4)$ Å, $c = 11.0831(8)$ Å, and $\beta = 107.807(6)^\circ$, whereas complex **2** crystallizes in orthorhombic space group $C2cb$, $Z = 8$, with unit cell parameters of $a = 10.1579(7)$ Å, $b = 10.3640(8)$ Å, and $c = 33.313(4)$ Å. The structures of **1** and **2** consist of layers of copper(II) ions with bridging bis-monodentate phenylmalonate (**1** and **2**) and 4,4'-bpy (**1**) ligands and terminal monodentate 2,4'-bpy (**2**) groups. Each layer in **1** contains rectangles with dimensions of 11.08×4.99 Å², the edges being defined by the Phmal and 4,4'-bpy ligands. The intralayer copper–copper separations in **1** through the anti–syn equatorial–apical carboxylate-bridge and the 4,4'-bpy molecule are 4.9922(4) and 11.083(1) Å, respectively. The anti–syn equatorial–equatorial carboxylate bridge links the copper(II) atoms in complex **2** within each layer with a mean copper–copper separation of 5.3709(8) Å. The presence of 2,4'-bpy as a terminal ligand accounts for the large interlayer separation of 15.22 Å. The copper(II) environment presents a static pseudo-Jahn–Teller disorder which has been studied by EPR and low-temperature X-ray diffraction. Magnetic susceptibility measurements of both compounds in the temperature range 2–290 K show the occurrence of weak antiferromagnetic [$J = -0.59(1)$ cm⁻¹ (**1**)] and ferromagnetic [$J = +0.77(1)$ cm⁻¹ (**2**)] interactions between the copper(II) ions. The conformation of the phenylmalonate–carboxylate bridge and other structural factors, such as the planarity of the exchange pathway in **1**, account for the different nature of the magnetic interaction.

Introduction

The investigation of properties, such as porosity, guest inclusion, chirality, and magnetism, and their cooperative effects in self-assembled multifunctional molecular materials are of current interest. The design and exploration of new synthetic routes to obtain this type of metal–organic coordination network are topics of the recent research of inorganic chemists.^{1–5} In the context of molecular magnetism, the study of the magnetostructural correlations aimed

at understanding the structural and chemical factors that govern the exchange coupling between paramagnetic centers through multiatom bridges are of continuing interest.^{3,6–8}

* To whom correspondence should be addressed. E-mail: caruiz@ull.es.
[†] Departamento de Física Fundamental II, Universidad de La Laguna.
[‡] Departamento de Química Inorgánica, Universidad de La Laguna.
[§] Departament de Química Inorgànica/Instituto de Ciencia Molecular, Universitat de València.

- (1) Picketing, M.; Decurtins, S. *Crystal Design: Structure and Function*; Desiraju, G. R., Ed.; Wiley: Chichester, U.K., 2003.
- (2) (a) Janiak, C. *Dalton Trans.* **2003**, 2781. (b) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (c) Zaworotko, M. J. *Chem. Commun.* **2001**, 1.
- (3) *Molecular Magnetism: From Molecular Assemblies to the Devices*; Coronado, E., Delhaès, P., Gatteschi, D., Miller, J. S. Eds.; NATO ASI Series E321; Kluwer: Dordrecht, The Netherlands, 1996.
- (4) *Magnetism: A Supramolecular Function*; Kahn, O., Ed.; NATO ASI Series C484; Kluwer: Dordrecht, The Netherlands, 1996.
- (5) *Supramolecular Engineering of Synthetic Metallic Materials*; Veciana, J., Rovira, C., Amabilino, D. B., Eds.; NATO ASI Series C518; Kluwer: Dordrecht, The Netherlands, 1999.

A reasonable synthetic approach to build three-dimensional structures in crystal engineering consists of connecting layers of transition metal ions through bridging ligands.^{1,2} The dimensionality of the structure can be controlled by a careful selection of the metal coordination structure and the organic spacer. Recent reports have focused on the malonate ligand (anion of the malonic acid, hereafter noted mal) as a flexible and fruitful tool for the design of magnetic systems with different dimensionalities when an appropriate coligand is used.^{9–11} The introduction of substituents on the methylene group of the malonate ligand could induce different conformations because of geometrical constraints, and it would make possible specific interactions between substituents, which would contribute to the overall stability of the resulting compound. In the first steps of these investigations, we have focused on the phenylmalonate dianion (Phmal), and recent reports were devoted to its complexation of copper(II).¹²

The dimensionality of the structures of the copper(II)–phenylmalonate coordination complexes can be modified with the presence of adequate ligands such as 4,4′-bipyridine (4,4′-bpy) and 2,4′-bipyridine (2,4′-bpy). The efficiency of these ligands stems from their rigidity, which allows for some degree of control to be exerted upon the steric constraints of the assembly process. The use of these ligands has yielded a great variety of coordination polymers, some of them featuring unprecedented physical phenomena (porosity, catalysis, gas and small molecule sorption, magnetism, etc). The current state of the knowledge in this topical area is described in several recent reviews.^{2,13}

In previous reports, these ligands were incorporated into copper(II)–malonate complexes producing, for instance, the isolated tetranuclear unit $[\text{Cu}_4(\text{mal})_4(2,4′\text{-bpy})_4(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$ and the two-dimensional compound $[\text{Cu}_4(\text{mal})_4(4,4′\text{-bpy})_2(\text{H}_2\text{O})_4]_n$.¹⁴ In addition to the stacking interactions between the pyridyl groups that stabilize the structure in both malonate compounds, π – π interactions between the pyridyl and phenyl rings are expected in the Phmal–copper(II) complexes.

We report herein the synthesis, crystallographic study, and magnetic properties of two new phenylmalonate–copper(II) complexes with the formulas $[\text{Cu}(4,4′\text{-bpy})(\text{Phmal})]_n \cdot 2n\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(2,4′\text{-bpy})(\text{Phmal})(\text{H}_2\text{O})]_n$ (**2**). Complexes

1 and **2** are two-dimensional compounds that are structurally very different because of the terminal and bridging coordination modes of the 2,4′-bpy and 4,4′-bpy ligands, respectively. Intralayer antiferromagnetic and ferromagnetic interactions are observed in **1** and **2**, respectively.

Experimental Section

Materials. Phenylmalonic acid (H_2Phmal), copper(II) acetate hydrate $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2.5\text{H}_2\text{O}]$, 4,4′-bipyridine (4,4′-bpy), 2,4′-bipyridine (2,4′-bpy), and methanol (MeOH) were purchased from Aldrich and used as received. Elemental analyses (C, H, N) were performed on an EA 1108 CHNS-O microanalytical analyzer.

Synthesis of $[\text{Cu}(4,4′\text{-bpy})(\text{Phmal})]_n \cdot 2n\text{H}_2\text{O}$ (1**).** An aqueous solution of copper(II) phenylmalonate (120 mg, 0.5 mmol), prepared as previously described,¹² was placed into one arm of an H-shaped tube, and a 50/50 MeOH/water solution of the 4,4′-bpy (78 mg, 0.5 mmol) was put into the other arm. A 50/50 MeOH/water solution was added dropwise to fill the H-shaped tube. Rectangular blue single crystals of **1** appeared within a week by slow diffusion at room temperature and were used for all measurements. Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_6\text{Cu}$ (**1**): C, 52.59; H, 4.15; N, 6.46. Found: C, 52.30; H, 4.25; N, 6.38. IR (KBr, cm^{-1}): ν 1614 vs, 1580 vs, 1494 m, 1430 s, 790 m.

Synthesis of $[\text{Cu}(2,4′\text{-bpy})(\text{Phmal})(\text{H}_2\text{O})]_n$ (2**).** Compound **2** was obtained by following a similar procedure to that of **1**, but 2,4′-bpy was used instead of 4,4′-bpy. Single crystals of **2** as blue rods appeared within a week by slow diffusion at room temperature and were used for all measurements. Anal. Calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_5\text{Cu}$ (**2**): C, 54.87; H, 3.69; N, 6.74. Found: C, 54.58; H, 3.76; N, 6.72. IR (KBr, cm^{-1}): ν 1614 vs, 1593 vs, 1452 m, 1410 vs, 788 s.

Physical Techniques. IR spectra (450–4000 cm^{-1}) of **1** and **2** were recorded on a Bruker IF S55 spectrophotometer with samples prepared as KBr pellets. EPR spectra on a polycrystalline sample of **2** were carried out on a Bruker EleXsys E580 EPR spectrometer operating at Q-band (34 GHz) frequency. Magnetic susceptibility measurements on polycrystalline samples of **1** and **2** were performed in the temperature range of 1.9–290 K with a Quantum Design SQUID magnetometer. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants¹⁵ to be -238×10^{-6} and $-225 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for **1** and **2**, respectively. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism [$60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ per Cu(II) ion] and the magnetization of the sample holder.

- (6) *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer: Dordrecht, The Netherlands, 1991.
- (7) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.
- (8) (a) Olivier Kahn Special Issue. *Polyhedron* **2001**, *20* (11–14). (b) Proceedings of the 8th International Conference on Molecule-Based Magnets. *Polyhedron* **2003**, *22* (14–17).
- (9) Rodríguez-Martín, Y.; Hernández-Molina, M.; Delgado, F. S.; Pasán, J.; Ruiz-Pérez, C.; Sanchiz, J.; Lloret, F.; Julve, M. *CrystEngComm* **2002**, *4*, 522.
- (10) Ruiz-Pérez, C.; Rodríguez-Martín, Y.; Hernández-Molina, M.; Delgado, F. S.; Pasán, J.; Sanchiz, J.; Lloret, F.; Julve, M. *Polyhedron* **2003**, *22*, 2111.
- (11) Pasán, J.; Delgado, F. S.; Rodríguez-Martín, Y.; Hernández-Molina, M.; Ruiz-Pérez, C.; Sanchiz, J.; Lloret, F.; Julve, M. *Polyhedron* **2003**, *22*, 2143.
- (12) (a) Pasán, J.; Sanchiz, J.; Ruiz-Pérez, C.; Lloret, F.; Julve, M. *New J. Chem.* **2003**, *27*, 1557. (b) Pasán, J.; Sanchiz, J.; Ruiz-Pérez, C.; Lloret, F.; Julve, M. *Eur. J. Inorg. Chem.* **2004**, 4081.
- (13) (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1461. (b) Batten, S. R. *CrystEngComm*, **2001**, *3*, 67. (c) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276.

- (14) For malonate containing Cu(II) complexes, see: (a) Chattopadhyay, D.; Chattopadhyay, S. K.; Lowe, P. R.; Schwalbe, C. H.; Mazumder, S. K.; Rana, A.; Ghosh, S. *J. Chem. Soc., Dalton Trans.* **1993**, 913. (b) Gil de Muro, I.; Mautner, F. A.; Insausti, M.; Lezama, L.; Arriortua, M. I.; Rojo, T. *Inorg. Chem.* **1998**, *37*, 3243. (c) Ruiz-Pérez, C.; Sanchiz, J.; Hernández-Molina, M.; Lloret, F.; Julve, M. *Inorg. Chim. Acta* **2000**, *298*, 245. (d) Ruiz-Pérez, C.; Sanchiz, J.; Hernández-Molina, M.; Lloret, F.; Julve, M. *Inorg. Chem.* **2000**, *39*, 1363. (e) Ruiz-Pérez, C.; Hernández-Molina, M.; Lorenzo-Luis, P.; Lloret, F.; Cano, J.; Julve, M. *Inorg. Chem.* **2000**, *39*, 3845. (f) Ruiz-Pérez, C.; Sanchiz, J.; Hernández-Molina, M.; Lloret, F.; Julve, M. *Inorg. Chim. Acta* **2000**, *298*, 245. (g) Rodríguez-Martín, Y.; Sanchiz, J.; Ruiz-Pérez, C.; Lloret, F.; Julve, M. *Inorg. Chim. Acta* **2001**, *326*, 20. (h) Rodríguez-Martín, Y.; Ruiz-Pérez, C.; Sanchiz, J.; Lloret, F.; Julve, M. *Inorg. Chim. Acta* **2001**, *318*, 159. (i) Sanchiz, J.; Rodríguez-Martín, Y.; Ruiz-Pérez, C.; Mederos, A.; Lloret, F.; Julve, M. *New J. Chem.* **2002**, *26*, 1624. (j) Rodríguez-Martín, Y.; Hernández-Molina, M.; Delgado, F. S.; Pasán, J.; Ruiz-Pérez, C.; Sanchiz, J.; Lloret, F.; Julve, M. *CrystEngComm* **2002**, *4*, 440. (k) Sain, S.; Maji, T. K.; Mostafa, G.; Lu, T. H.; Chanduri, N. R. *New J. Chem.* **2003**, *27*, 185.
- (15) Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: London, 1968.

Table 1. Crystallographic Data for Complexes **1** and **2**

	1	2	2
formula	C ₁₉ H ₁₈ O ₆ N ₂ Cu	C ₁₉ H ₁₃ O ₅ N ₂ Cu	C ₁₉ H ₁₃ O ₅ N ₂ Cu
fw	433.86	412.88	412.88
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	<i>P</i> 2 ₁	<i>C</i> 2 <i>cb</i>	<i>C</i> 2 <i>cb</i>
<i>a</i> (Å)	9.0837(6)	10.1579(7)	10.2178(4)
<i>b</i> (Å)	9.3514(4)	10.3640(8)	10.2909(5)
<i>c</i> (Å)	11.0831(8)	33.313(4)	32.825(2)
β (deg)	107.807(6)	—	—
<i>V</i> (Å ³)	896.35(10)	3507.1(6)	3451.6(3)
<i>Z</i>	4	8	8
μ (Mo K α) (cm ⁻¹)	12.59	12.84	13.01
<i>T</i> (K)	293(2)	293(2)	100(2)
ρ_{calc} (g cm ⁻³)	1.593	1.642	1.612
λ (Å)	0.71073	0.71073	0.71073
index ranges	-12 ≤ <i>h</i> ≤ 12 -13 ≤ <i>k</i> ≤ 12 -15 ≤ <i>l</i> ≤ 13	-14 ≤ <i>h</i> ≤ 13 -14 ≤ <i>k</i> ≤ 13 -46 ≤ <i>l</i> ≤ 43	-14 ≤ <i>h</i> ≤ 12 -14 ≤ <i>k</i> ≤ 11 -46 ≤ <i>l</i> ≤ 36
independent reflns (<i>R</i> _{int})	4940 (0.050)	4904 (0.085)	4571 (0.079)
observed reflns [<i>I</i> > 2 σ (<i>I</i>)]	4242	4224	4247
parameters	254	263	263
GOF	1.025	1.038	1.132
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0394	0.0485	0.0678
<i>R</i> _w [<i>I</i> > 2 σ (<i>I</i>)]	0.0858	0.1228	0.1807
<i>R</i> (all data)	0.0525	0.0577	0.0754
<i>R</i> _w (all data)	0.0907	0.1282	0.1905

Crystallographic Data Collection and Structural Determination. Single crystals of **1** and **2** were used for data collection with a Nonius Kappa CCD diffractometer. The data collection was carried out using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K, and it was also done at 100 K for compound **2**. A summary of the crystallographic data and structure refinement is given in Table 1. The structures were solved by direct methods and refined with a full-matrix least-squares technique on *F*² using the SHELXL-97¹⁶ program included in the WINGX¹⁷ software package. All non-hydrogen atoms were refined anisotropically. The C(13) and C(14) carbon atoms from the 2,4'-bpy ligand in **2** were delocalized between two positions with the *sof* parameter being 0.48 and 0.52. The hydrogen atoms in both structures were set in calculated positions and isotropically refined as riding atoms. The final geometrical calculations and graphical manipulations were carried out with the PARST97¹⁸ and CRYSTALMAKER¹⁹ programs.

Description of the Structures

[Cu(4,4'-bpy)(Phmal)]_{*n*}·2*n*H₂O (**1**). The structure of complex **1** consists of chains of carboxylate(phenylmalonate)-bridged copper(II) ions which are linked through bis-monodentate 4,4'-bpy ligands to produce a sheetlike polymer growing in the *bc* plane (Figures 1a and 2a). Rectangles with dimensions of 11.08 × 4.99 Å² are repeated within each layer, the longer edge corresponding to the 4,4'-bpy ligand (*c* axis), whereas the shorter side is defined by the phenylmalonate-carboxylate group (*b* axis). The separation between adjacent layers is 8.64 Å. The layers are not stacked parallel along the *a* axis but form an angle of 17.807(6)° with the normal plane vector. They are staggered in the ABCABCABC trend and the nearest neighbors are shifted by *c*/3 from each other. Adjacent layers are linked through

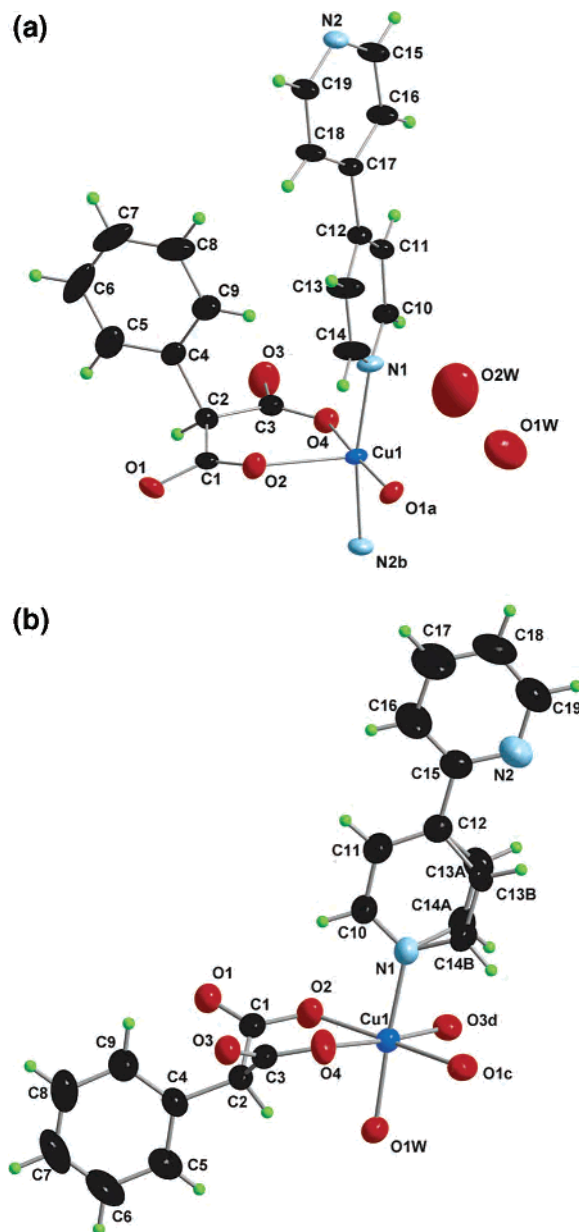


Figure 1. View of a fragment of the structures of (a) **1** and (b) **2** with the numbering scheme.

hydrogen bonds involving two carboxylate oxygens [O(1) and O(3)] and the crystallization water molecules (Figure 3); the values of the O...O distances range from 2.839(5) to 3.085(6) Å. It should be noted that the crystallization water molecules are placed between the layers close to the carboxylate groups because of the hydrogen bonds they form. Thus, the water molecules avoid the rectangular cavities because of their hydrophobic character. The π - π interactions play an important role in the packing of this structure as observed in previous reports concerning Phmal-containing copper(II) complexes.¹² Several intra- and interlayer C-H... π contacts can be identified,²⁰ the shortest centroid...centroid distance being 4.8781(4) Å, a value which is close to the molecular dynamics calculation for benzene²¹ (optimum distance of 4.99 Å between two ring centers in the T-shaped orientation). The values of the dihedral angle between the aromatic rings range from 52.2° to 89.31°.

(16) Sheldrick, G. M. *SHELXL-97* and *SHELXS-97*; Universität Göttingen: Göttingen, Germany, 1998.

(17) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(18) Nardelli, M. *PARST95*, *J. Appl. Crystallogr.* **1995**, *28*, 659.

(19) *CrystalMaker*, version 4.2.1; CrystalMaker Software: Bicester, U.K.

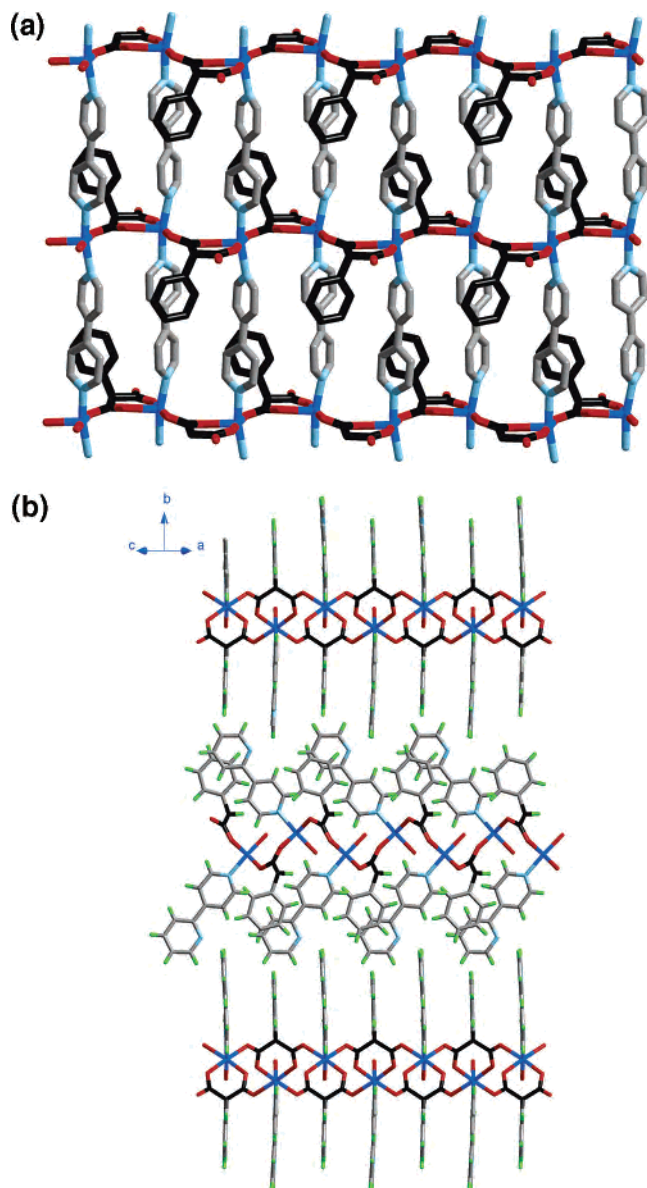


Figure 2. (a) View through the [100] direction of a fragment of complex **1**. The 4,4'-bpy ligand connects chains of phenylmalonate-bridged copper(II) ions. Hydrogen atoms are omitted for clarity. (b) Crystal packing of complex **2** with the corrugated layers viewed through the [101] direction.

Each copper atom exhibits a somewhat distorted square pyramidal environment, the geometric τ value being 0.13 ($\tau = 0$ for square pyramidal and $\tau = 1$ for trigonal bipyramidal).²² Two nitrogen atoms from the 4,4'-bpy molecule [N(1) and N(2a); (a) $x, y, z + 1$] and two carboxylate-oxygen atoms from the Phmal ligand [O(4) and O(1b); (b) $-x, y - 1/2, -z$] build the basal plane, whereas another carboxylate-oxygen atom [O(2)] occupies the apical position (selected interatomic distances and angles are listed in Table 2). The

(20) For examples of C–H $\cdots\pi$ interactions, see: (a) Janiak, C.; Temizdemir, S.; Dechert, S.; Deck, W.; Girgsdies, F.; Heinze, J.; Kolm, M. J.; Scharmann, T. G.; Zipfel, O. M. *Eur. J. Inorg. Chem.* **2000**, 1229. (b) McNelis, B. J.; Nathan, L. C.; Clark, C. J. *J. Chem. Soc., Dalton Trans.* **1999**, 1831. (c) Biradha, K.; Seward, C.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 492.

(21) Cox, E. G.; Cruickshank, D. W.; Smith, J. A. S. *Proc. R. Soc. London, Ser. A* **1958**, *247*, 1

(22) Addison, A. W.; Rao, T. N. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

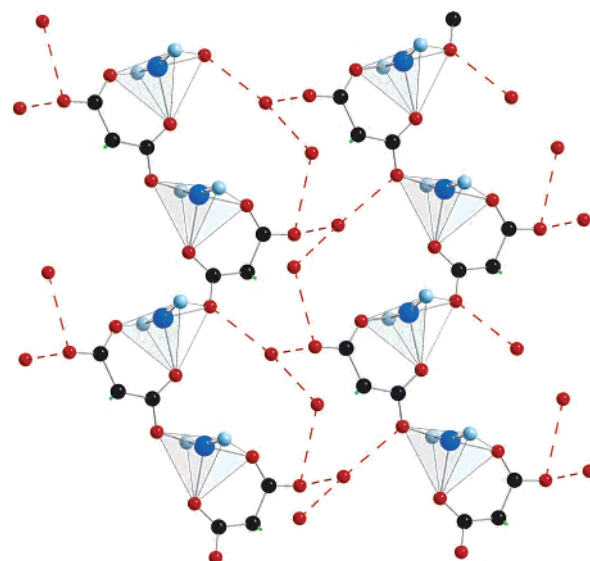


Figure 3. Supramolecular layers of phenylmalonate-copper(II) chains bridged through hydrogen bonds with the crystallization water molecules. Phenyl rings of Phmal, carbon atoms of 4,4'-bpy, and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds **1** and **2**^{a,b}

1			
Cu(1)–O(1a)	1.952(2)	Cu(1)–N(1)	2.041(2)
Cu(1)–O(2)	2.185(2)	Cu(1)–N(2b)	2.0220(19)
Cu(1)–O(4)	1.928(2)		
O(4)–Cu(1)–O(1a)	176.69(9)	N(2b)–Cu(1)–N(1)	168.70(12)
O(4)–Cu(1)–N(2b)	90.60(9)	O(4)–Cu(1)–O(2)	89.40(8)
O(1a)–Cu(1)–N(2b)	88.94(9)	O(1a)–Cu(1)–O(2)	93.90(8)
O(4)–Cu(1)–N(1)	89.26(9)	N(2b)–Cu(1)–O(2)	94.72(11)
O(1a)–Cu(1)–N(1)	90.55(9)	N(1)–Cu(1)–O(2)	95.29(9)
2			
Cu(1)–O(2)	2.128(3)	Cu(1)–O(3d)	2.110(3)
Cu(1)–O(4)	2.076(3)	Cu(1)–N(1)	2.026(3)
Cu(1)–O(1c)	2.208(3)	Cu(1)–O(1w)	2.004(2)
O(1w)–Cu(1)–N(1)	176.32(11)	O(4)–Cu(1)–O(2)	84.79(14)
O(1w)–Cu(1)–O(4)	90.71(12)	O(3d)–Cu(1)–O(2)	90.18(13)
N(1)–Cu(1)–O(4)	90.73(12)	O(1w)–Cu(1)–O(1c)	89.50(10)
O(1w)–Cu(1)–O(3d)	91.68(11)	N(1)–Cu(1)–O(1c)	87.13(11)
N(1)–Cu(1)–O(3d)	87.19(11)	O(4)–Cu(1)–O(1c)	89.41(13)
O(4)–Cu(1)–O(3)	174.49(13)	O(3d)–Cu(1)–O(1c)	95.57(12)
O(1w)–Cu(1)–O(2)	91.59(11)	O(2)–Cu(1)–O(1c)	174.12(14)
N(1)–Cu(1)–O(2)	91.91(12)		

^a Estimated standard deviations in the last significant digits are given in parentheses. ^b Symmetry code is as follows: (a) $-x, y - 1/2, -z$; (b) $x, y, z + 1$; (c) $x, y + 1/2, -z + 1/2$; and (d) $x + 1/2, y, -z + 1/2$.

equatorial bond lengths vary in the range of 1.928(2)–2.041(2) Å, and the apical bond distance is 2.185(2) Å. The copper atom is shifted by 0.0989(3) Å from the mean basal plane toward the apical position. The copper–copper separation through the phenylmalonate–carboxylate bridge is 4.9922(4) Å, a value which is much shorter than the metal–metal separation through the 4,4'-bpy ligand [11.083(1) Å].

The phenylmalonate ligand simultaneously adopts monodentate [through O(1) to Cu(1e); (e) $-x, y + 1/2, -z$] and bidentate [through O(2) and O(4) to Cu(1)] coordination modes. The bidentate coordination of the Phmal ligand involves one equatorial O(4) bond and one apical O(2) bond, a feature which is unprecedented for Phmal- or malonate-containing copper(II) complexes,^{12,14} although it is not

uncommon for copper(II)–oxalate complexes.^{23,24} The preference of the copper(II) ion for the nitrogen donor atoms versus the oxygen ones and the fact that the two 4,4'-bpy nitrogen atoms in **1** occupy trans positions in the coordination sphere of the copper atom account for this singularity. The value of the angle subtended at the copper atom by the bidentate Phmal ligand is 89.40(8)°. The pyridyl rings of the 4,4'-bpy molecule are planar, but the ligand as a whole is far from being planar [the dihedral angle between the two pyridyl rings is 19.99(10)°]. As far as we know, there are two recently reported compounds whose structures are very similar to that of **1**: [Cu₃(μ-ox)₃(μ-4,4'-bpy)(4,4'-bpy)₂]_n²⁴ and {[Cu(Hsal)₂(4,4'-bpy)]·H₂O·H₂sal}_n²⁵ (ox = oxalate dianion and H₂sal = salicylic acid). In light of these structures (see Supporting Information), it is clear that the rectangular moiety observed in **1** is not unique, but layered motifs are ensured by the reaction of copper(II) with the appropriate bridging ligand and 4,4'-bpy.

We would like to finish the present structural description with a comparison of the structure of **1** with that of the previously reported malonato copper(II) complex [Cu₄(mal)₄(H₂O)₄(4,4'-bpy)₂]_n^{14h} (H₂mal = malonic acid). This structure consists of layers of tetranuclear entities of carboxylate–malonato-bridged copper(II) ions linked by 4,4'-bpy ligands. The tetranuclear units are small squares with the copper(II) ions at the corners and the bridging-malonato ligand defining the edges. These units are linked by the 4,4'-bpy groups to form large squares of 15.784(1) × 15.784(1) Å². Although the dimensionality of this structure as a whole is identical to that of **1**, the presence of the phenyl ring in **1** provides additional interactions (C–H⋯π- and π–π-type interactions, steric effects, etc.) which account for the new coordination mode of the Phmal ligand and the hydrophobic character in the structure.

[Cu(2,4'-bpy)(Phmal)(H₂O)]_n (**2**). The structure **2** consists of a sheetlike arrangement of *trans*-aqua(2,4'-bipyridine)-copper(II) units bridged by phenylmalonate ligands running parallel to the *ac* plane (see Figures 1b and 2b). A corrugated square grid of copper atoms results (Figure 4) where the 2,4'-bpy terminal ligands are alternatively located above and below each layer and, at the same time, inversely to the position of the phenyl group of the Phmal ligand. These sheets are stacked parallel along the *b* axis but rotated 90° through this axis in a twisted fashion (i.e., odd units in the same position and even units rotated by 90°) exhibiting the ABABAB sequence. Intralayer hydrogen bonds involving the coordinated water molecule [O(1w)] and oxygen atoms from the carboxylate–phenylmalonate groups [2.615(4) and

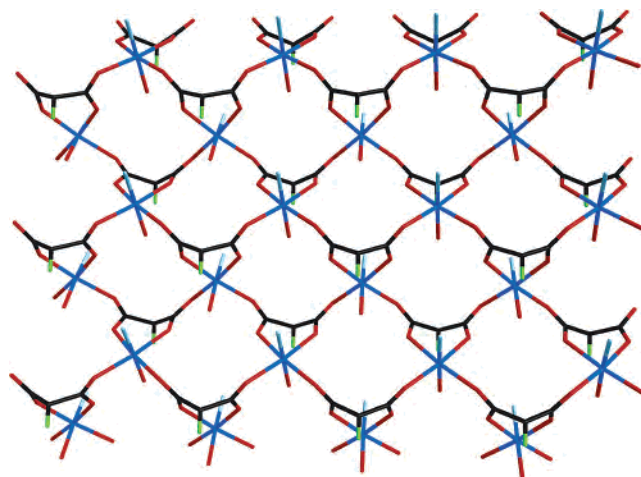


Figure 4. View of the corrugated layer of the phenylmalonate-bridged copper(II) atoms of complex **2** forming a square grid. The phenyl (Phmal) pyridyl (2,4'-bpy) rings are omitted for the sake of clarity.

Table 3. Bond Distances at Cu(1) and Calculated ΔMSDA Values for Compound **2** at Different Temperatures^a

bond	<i>T</i> = 293 K		<i>T</i> = 100 K	
	<i>d</i> (Å)	ΔMSDA (×10 ⁻⁴ Å ²)	<i>d</i> (Å)	ΔMSDA (×10 ⁻⁴ Å ²)
Cu(1)–O(2)	2.128(3)	269	2.111(5)	355
Cu(1)–O(4)	2.076(3)	255	2.087(5)	301
Cu(1)–O(1c)	2.208(3)	293	2.187(5)	247
Cu(1)–O(3d)	2.110(3)	315	2.156(5)	201
Cu(1)–O(1w)	2.004(2)	59	1.992(3)	29
Cu(1)–N(1)	2.026(3)	64	2.014(4)	36

^a Symmetry code is as follows: (c) *x*, *y* + 1/2, *-z* + 1/2 and (d) *x* – 1/2, *y*, *-z* + 1/2.

2.633(4) Å for O(1w)⋯O(2c) and O(1w)⋯O(4f), respectively; (c) *x*, *y* + 1/2, *-z* + 1/2; (f) *x* – 1/2, *y*, *-z* + 1/2] contribute to stabilize the structure. Weak π-type interactions occur between the phenyl rings and the 2,4'-bpy groups, the shortest centroid⋯centroid distance being 4.154(6) Å and the shortest off-set angle being 29.6°, values which are somewhat larger than the average ones observed in π–π interactions with pyridyl-like groups.²⁶

Each copper atom exhibits a six-coordinated environment defined by four carboxylate–phenylmalonate oxygen atoms, one 2,4'-bpy-nitrogen atom, and a water molecule. The CuNO₅ chromophore could be described as an unusual compressed tetragonal octahedron with two short distances [2.004(2) and 2.026(3) Å for Cu(1)–O(1w) and Cu(1)–N(1), respectively] and four long ones [values ranging from 2.076(3) to 2.208(3) Å] (see Table 2). A low-temperature crystallographic study has been carried out to give a clear-cut answer to this compression. In light of Table 3, one can see that the bond distances and angles at 293 and 100 K do not vary significantly, and hence, the presence of a static pseudo-Jahn–Teller disorder could be suspected.^{27–30} The

- (23) (a) Oshio, H.; Nagashima, U. *Inorg. Chem.* **1992**, *31*, 3295. (b) Castillo, O.; Luque, A.; Lloret, F.; Román, P. *Inorg. Chim. Acta* **2001**, *324*, 141. (c) Luo, J.; Hong, M.; Liang, Y.; Cao, R. *Acta Crystallogr., Sect. E*, **2001**, *57*, m361. (d) Cavalca, L.; Villa, A. C.; Manfredotti, A. G.; Tomlinson, A. A. G. *J. Chem. Soc., Dalton Trans.* **1972**, 391. (e) Castillo, O.; Luque, A.; Julve, M.; Lloret, F.; Román, P. *Inorg. Chim. Acta*, **2001**, *315*, 9. (f) Castillo, O.; Luque, A.; Román, P.; Lloret, F.; Julve, M. *Inorg. Chem.* **2001**, *40*, 5526. (g) Suárez-Varela, J.; Domínguez-Vera, J. M.; Colacio, E.; Ávila-Rosón, J. C.; Hidalgo, M. A.; Martín-Ramos, D. *J. Chem. Soc., Dalton Trans.* **1995**, 2143. (24) Castillo, O.; Alonso, J.; García-Couceiro, U.; Luque, A.; Román, P. *Inorg. Chem. Commun.* **2003**, *6*, 803. (25) Zhu, L.-G.; Kitagawa, S. *Inorg. Chem. Commun.* **2003**, *6*, 1051.

- (26) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885. (27) Hathaway, B. J. *Struct. Bonding*, **1984**, *57*, 55. (28) Falvello, L. R. *J. Chem. Soc., Dalton Trans.* **1997**, 4463. (29) Halcrow, M. A. *Dalton Trans.* **2003**, 4375. (30) Solanki, N. K.; Leech, M. A.; McInnes, E. J. L.; Mabbs, F. E.; Howard, J. A. K.; Kilner, C. A.; Rawson, J. M.; Halcrow, M. A. *J. Chem. Soc., Dalton Trans.* **2002**, 1295.

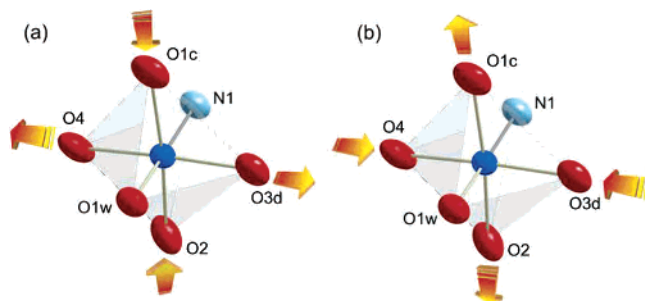


Figure 5. Two different copper(II) environments [(a) and (b)] which occur in complex **2** because a static pseudo-Jahn–Teller disorder. Arrows indicate the atoms that fill equatorial (compressed) or apical (elongated) positions at the metal environment.

vibrational amplitudes of the ligand donor atoms along the metal–ligand bonds represented by the quantity $\langle d^2 \rangle$ or equivalently $\Delta\text{MSDA}^{27-30}$ are also listed in Table 3. These values correspond to the difference in the mean-square displacements parameters (MSDAs) of a given donor atom and the Cu atom along their common vector (eqs 1 and 2).

$$\text{MSDA} = \frac{\sum_{i=1}^3 \sum_{j=1}^3 U_{ij} n_i n_j}{|n|^2} \quad (1)$$

$$\langle d \rangle^2 = \Delta\text{MSDA} = \text{MSDA}(\text{donor}) - \text{MSDA}(\text{Cu}) \quad (2)$$

where U_{ij} is an element of the 3×3 matrix of thermal parameters and n_i and n_j are elements of the vector describing the bond. Values of ΔMSDA are typically found in the range of $(10-100) \times 10^{-4} \text{ \AA}^2$.²⁸ The values of the ΔMSDA for O(1w) and N(1) are within this range but the four carboxylate oxygen atoms present ΔMSDA s in the range of $(255-315) \times 10^{-4} \text{ \AA}^2$. This disparity from the “static” values can be attributed to the presence of a static pseudo-Jahn–Teller disorder of two of the three axes of the octahedral copper environment. The shorter bond distances correspond with the Cu(1)–O(1w) and Cu(1)–N(1) bonds indicating that these two atoms belong to the basal plane of Cu(1). The O(2), O(4), O(1c), and O(3d) [(d) $x + 1/2, y, -z + 1/2$] are statically disordered in pairs between the equatorial and axial positions [two different environments are found within the crystal, one with O(1w), N(1), O(2), and O(1c) in equatorial positions and O(4) and O(3d) in axial positions; the other with O(1w), N(1), O(4), and O(3d) in equatorial positions and O(2) and O(1c) in axial positions] (Figure 5). The analysis of the EPR spectrum at room temperature (see Supporting Information) reveals three different effective g values ($g_1 = 2.27, g_2 = 2.20, g_3 = 2.15$) indicating a rhombic environment of the copper(II) ion or, according to our approximation, the averaged values of a static pseudo-Jahn–Teller disorder in the crystal as they appear in the X-ray crystal structure. EPR spectra at low temperatures do not change significantly from the rhombic distortion; the slight variations in the g values are most likely associated with the spin coupling.

The phenylmalonate ligand acts simultaneously as a bidentate ligand [through O(2) and O(4) to Cu(1)] and as a

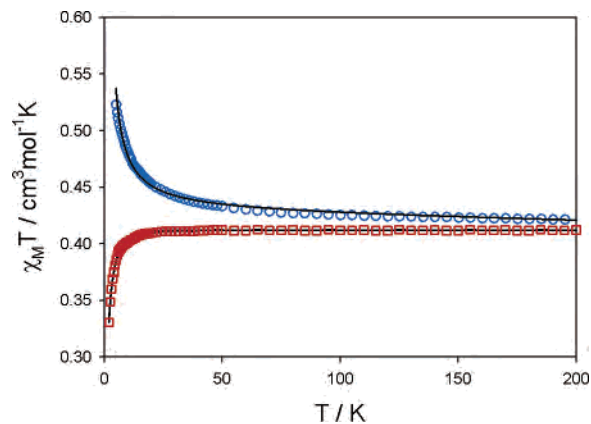


Figure 6. Thermal dependence of the $\chi_M T$ product for complexes **1** and **2** (**1**, red squares; **2**, blue circles). The solid line represents the best fit through eqs 3 and 4 for complexes **1** and **2**, respectively.

bis-monodentate ligand [through O(1) and O(3) to Cu(1) g) and Cu(1d), respectively; (g) $x, y - 1/2, -z + 1/2$]. The 2,4'-bpy ligand is quasi-planar [the dihedral angle between pyridyl rings is 4°]. The pyridyl ring formed by the N(1)–C(10)–C(11)–C(12)–C(13)–C(14) set of atoms is slightly distorted, and two crystallographic positions are found for the C(13) and C(14) atoms [0.977(16) and 1.012(15) Å for C(13A)–C(13B) and C(14A)–C(14B), respectively]. These two positions are also found in the low-temperature X-ray study of a different crystal; hence, a static disorder within the crystal could be the responsible for this feature. The copper–copper separations through the two crystallographically independent anti-syn carboxylate bridges are 5.3217(9) and 5.4202(6) Å, values which are much shorter than the interlayer Cu \cdots Cu distance [15.221(2) Å].

The comparison of the structure of **2** with that of the previously reported³¹ malonato–manganese(II) complex of formula $[\text{Mn}(\text{mal})(\text{H}_2\text{O})(2,4'\text{-bpy})]_n$ reveals that both are very similar, fact that cannot be extended to the compound $[\text{Cu}_4(\text{mal})_4(2,4'\text{-bpy})_4(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$.^{14j} Therefore, from a structural point of view and in the presence of the 2,4'-bpy ligand, the copper(II) ion acts as the manganese(II) cation when the malonate is substituted by the phenylmalonate ligand.

Magnetic Properties

The magnetic properties of compounds **1** and **2** under the form of the $\chi_M T$ vs T plot [χ_M is the molar susceptibility per copper(II) ion] are shown in Figure 6. The values of $\chi_M T$ at room temperature are 0.41 and 0.42 $\text{cm}^3 \text{mol}^{-1} \text{K}$ for **1** and **2**, respectively. These values are as expected for magnetically isolated spin doublets. The $\chi_M T$ values remains almost constant down to 10 K for compound **1** and then smoothly decreases to 0.34 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 2.0 K indicating that there is a very weak antiferromagnetic coupling between the copper(II) ions. For compound **2**, $\chi_M T$ remains almost constant until 30 K and then it increases to reach a value of 0.53 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 2.0 K, a feature which is indicative of an overall ferromagnetic coupling in **2**.

(31) Rodríguez-Martín, Y.; Hernández-Molina, M.; Sanchiz, J.; Ruiz-Pérez, C.; Lloret, F.; Julve, M. *Dalton Trans.* **2003**, 2359.

Two different magnetic exchange pathways between copper atoms are present in **1**: the 4,4'-bpy bridging ligand and the carboxylate bridge in the anti-syn conformation linking one apical position with an equatorial position at the copper(II) atoms. Since the distance between the copper(II) ions through the 4,4'-bpy bridge is 11.083(1) Å and the values of $-J$, from previous reports^{14d,32} on 4,4'-bpy-bridged copper dimers, vary in the range of 0.05–0.1 cm⁻¹, the magnetic coupling has to be very small compared with that of the anti-syn carboxylate bridge. Therefore, from a magnetic point of view, compound **1** can be seen as uniform chains of antiferromagnetically coupled copper(II) ions, and the magnetic data can be analyzed by means of the following numerical expression:³³

$$\chi_M = \frac{Ng^2\beta^2}{kT} \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \quad (3)$$

where $x = |J|/kT$, the Hamiltonian is defined as $\sum_i JS_i \cdot S_{i+1}$, J is the magnetic coupling constant, and N , g , β , and k have their usual meaning. Best-fit parameters using a nonlinear regression analysis are as follows: $J = -0.59(1)$ cm⁻¹, $g = 2.21(2)$, and $R = 5.2 \times 10^{-5}$ (R is the agreement factor defined as $\sum_i [(\chi_M T)_{\text{obs}}(i) - (\chi_M T)_{\text{calc}}(i)]^2 / \sum_i [(\chi_M T)_{\text{obs}}(i)]^2$). The calculated curve matches well the experimental data in the whole temperature range (Figure 6).

According to the square lattice layer defined by the copper(II) ions of compound **2** (Figure 4), its magnetic data were analyzed by the high-temperature series expansion derived from the two-dimensional Heisenberg model for a $S = 1/2$ ferromagnetic square lattice³⁴

$$\chi = [Ng^2\beta^2/(3kT)]S(S+1)(1 + \sum_{n=1}^{10} a_n K^n) \quad (4)$$

with $K = J/kT$. The coefficients for the square lattice are represented by a_n , and J is the intralayer magnetic coupling between the local spins of the nearest-neighbors with the Hamiltonian of eq 4 defined as

$$H = -\sum_i JS_i \cdot S_{i+1} \quad (5)$$

Best-fit parameters using a nonlinear regression analysis are as follows: $J = 0.77(1)$ cm⁻¹, $g = 2.22(1)$, and $R = 1.2 \times 10^{-5}$ (R is the agreement factor defined as $\sum_i [(\chi_M T)_{\text{obs}}(i) - (\chi_M T)_{\text{calc}}(i)]^2 / \sum_i [(\chi_M T)_{\text{obs}}(i)]^2$). The calculated curve matches well the experimental data in the temperature range explored (Figure 6). The calculated value of g is in agreement with that obtained from the EPR spectra.

The analysis of the magnetic data shows that compounds **1** and **2** exhibit weak antiferromagnetic (**1**) and ferromagnetic

(**2**) interactions. Let us try to analyze, first, the magnitude and, second, the nature of the magnetic interaction. The carboxylate group can adopt three different bis-monodentate bridging modes: syn-syn, anti-anti, and anti-syn. From moderate to strong antiferromagnetic coupling is observed for the first two modes, whereas weak either ferromagnetic or antiferromagnetic interactions occur in the third.³⁵ This ability of the carboxylate group has been substantiated by DFT-type calculations.³⁶ As the copper(II) ions in compounds **1** and **2** are bridged by carboxylate groups in the anti-syn conformation, the weak values of the magnetic coupling observed are as expected.

In addition to the conformation of the bridge, the relative orientation of the magnetic orbitals centered on the metal ions in both compounds is very unfavorable for a strong magnetic coupling. In the case of compound **1**, the carboxylate bridge links an equatorial position of one copper(II) ion with an axial position of the adjacent copper(II) ion. The magnetic orbital for copper(II) ions in a square pyramidal surrounding is of the $d_{x^2-y^2}$ -type; the x and y axes are roughly defined by the equatorial bonds. Some admixture of the d_z^2 orbital is present as a result of trigonal distortion. The magnetic coupling is very weak because it is the result of the interaction of a $d_{x^2-y^2}$ -type orbital with a d_z^2 -type orbital, the latter having a very small spin density. In the case of compound **2**, the environment of the copper(II) ion is distorted octahedral and the magnetic orbital also has $d_{x^2-y^2}$ character. Each copper(II) ion is connected to four other copper(II) ions through anti-syn carboxylate bridges to give a quadratic layer. The magnetic coupling in this compound is also very weak because the equatorial plane of the copper environment (Scheme 1) is quasi-perpendicular to the plane of the bridging carboxylate (the exchange pathway) and only two of the four exchange pathways have important spin density (half of the exchange pathways are inactive). This situation is very unfavorable for a large magnetic interaction and leads to a very weak coupling constant.

We will now try to explain the different nature of the magnetic coupling for compounds with apparently similar chemical and structural features. The exchange constant can be expressed as the sum of two contributions, one ferromagnetic (small and positive) and another antiferromagnetic (negative and proportional to the square of the overlap between the orbitals on the bridge with those of the metal ions bearing the unpaired electrons), in such a way that the lower the overlap is, the smaller the antiferromagnetic contribution [$J = J_F + J_{AF}$].³⁷ In the case of compound **1**, the copper(II) ions and carboxylate groups lie in a plane with an out-of-plane maximum deviation of 0.321(2) Å for O(2). This situation enhances the overlap between the interacting magnetic orbitals of the metal ions and those of the atoms of the bridge and makes the antiferromagnetic term dominant. On the other hand, the copper(II) ions in compound **2** lie in

(32) (a) Haddad, M. S.; Hendrickson, D. N.; Cannady, J. P.; Drago, R. S.; Bieksza, D. S. *J. Am. Chem. Soc.* **1979**, *101*, 898. (b) Julve, M.; Verdager, M.; Faus, J.; Tinti, F.; Moratal, J.; Monge, A.; Gutiérrez-Puebla, E. *Inorg. Chem.* **1987**, *26*, 3520.

(33) Estes, W. E.; Gavel, D. P.; Hatfield, W. E.; Hodgson, D. *Inorg. Chem.* **1978**, *17*, 1415.

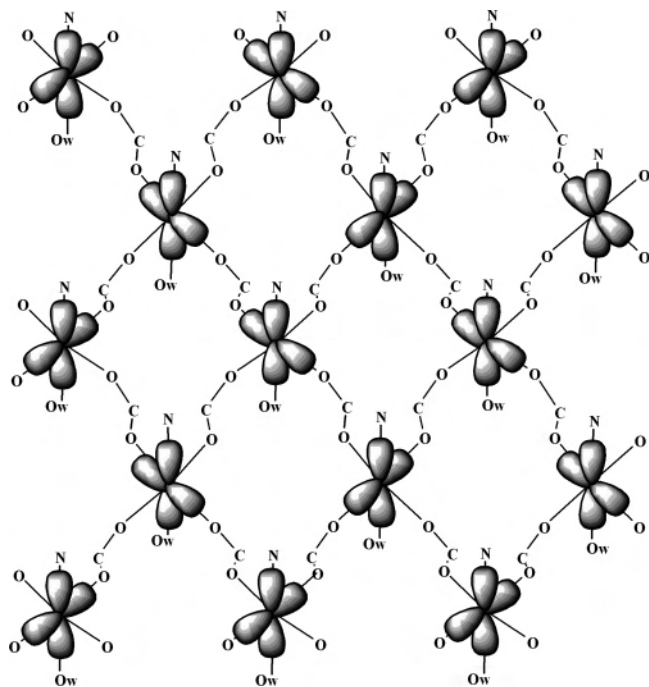
(34) Navarro, R. *Application of High- and Low-Temperature Series Expansions to Two-Dimensional Magnetic Systems*; de Jongh, L. J.; Ed., Kluwer: Dordrecht, The Netherlands, **1990**.

(35) Pasán, J.; Delgado, F. S.; Rodríguez-Martín, Y.; Hernández-Molina, M.; Ruiz-Pérez, C.; Sanchiz, J.; Lloret, F.; Julve, M. *Polyhedron*, **2003**, *22*, 2143.

(36) Rodríguez-Fortea, A.; Alemany, P.; Álvarez, S.; Ruiz, E. *Chem.—Eur. J.* **2001**, *7*, 627.

(37) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

Scheme 1



a corrugated layer that makes the magnetic orbitals of the metal ions form an angle of $87.8(4)^\circ$ in the bridge (Figure 4). This situation leads to a very poor overlap making the antiferromagnetic contribution very small and causing the ferromagnetic contribution to be dominant.

Conclusions

The compounds $[\text{Cu}(4,4'\text{-bpy})(\text{Phmal})]_n \cdot 2n\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(2,4'\text{-bpy})(\text{Phmal})(\text{H}_2\text{O})]_n$ (**2**) were prepared, and their structures and magnetic properties were investigated. Although both compounds are sheetlike polymers, their structures are very different. There are two bridging ligands in **1** (Phmal and 4,4'-bpy), and only one in **2** (Phmal). Addition-

ally, the layers in **1** are almost planar, whereas they are corrugated in **2** with angles of 87.8° . The structures of **1** and **2** are also very different from those of the malonate copper(II) derivatives $[\text{Cu}(\text{mal})(\text{H}_2\text{O})(4,4'\text{-bpy})_{0.5}]$ and $[\text{Cu}(\text{mal})(\text{H}_2\text{O})(2,4'\text{-bpy})]$, demonstrating that the phenyl ring of the phenylmalonate exerts important structural effects. Nevertheless the structure of **2** is similar to that of $[\text{Mn}(2,4'\text{-bpy})(\text{mal})(\text{H}_2\text{O})]$.³¹

Under a magnetic point of view, both compounds display very weak interactions mainly caused by the anti-syn conformation of the carboxylate bridge. However, compound **2** exhibits a ferromagnetic coupling between the copper(II) ions, but magnetic ordering down to 2.0 K is not achieved because of the weak magnetic interaction. It seems interesting to determine if other potentially bridging ligands such as pyrazine or pyrimidine lead to similar structures in which the magnetic coupling could be stronger. The work of our group will be oriented in that direction trying to increase the intralayer magnetic coupling and paying attention to the effect of introducing smaller ligands that may lead to a shorter interlayer separation.

Acknowledgment. We thank the Ministerio Español de Ciencia y Tecnología (Projects CTQ2004-03633 and BQU2001-3794), the Consejería de Educación, Cultura y Deportes of Gobierno Autónomo de Canarias (Project PI2002/175), and the Ministerio Español de Educación y Ciencia (Project MAT2004-03112) for financial support. J.P. also thanks the Ministerio Español de Educación y Ciencia for a predoctoral fellowship (Ref. AP2001-3322).

Supporting Information Available: Crystallographic data in CIF format for **1** (CCDC 266328) and **2** (CCDC 266329) and the Q-band EPR spectra of complex **2** at different temperatures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0503986