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Magnetic Coupling through the Carbon Skeleton of Malonate in Two Polymorphs of $\{[Cu(bpy)(H_2O)][Cu(bpy)(mal)(H_2O)]\}(ClO_4)_2$ (H_2mal = Malonic Acid; bpy = 2,2′-Bipyridine)

**Catalina Ruiz-Pérez,*[1a] María Hernández-Molina,[1a] Pablo Lorenzo-Luis,[1b]
Francesc Lloret,*[1c] Juan Cano,[1c] and Miguel Julve[1c]**

Departamento de Física Fundamental II, Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez s/n, 38204 La Laguna, Tenerife, Spain, Departamento de Química Inorgánica, Universidad de la Laguna, 38204 La Laguna, Tenerife, Spain, and Departament de Química Inorgànica, Facultat de Química, Universitat de València, Dr. Moliner 50, 46100 Bujassot, València, Spain

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Two polymorphic malonato-bridged copper(II) complexes of formula $\{[Cu(bpy)(H_2O)][Cu(bpy)(mal)(H_2O)]\}(ClO_4)_2$ (**1** and **2**) (bpy = 2,2′-bipyridine and mal = malonate dianion) have been prepared and their structures solved by X-ray diffraction methods. Compound **1** crystallizes in the monoclinic space group $P2_1/a$, with $a = 23.743(3)$ Å, $b = 9.7522(5)$ Å, $c = 27.731(2)$ Å, $\beta = 114.580(10)°$, and $Z = 4$. Compound **2** crystallizes in the orthorhombic space group *Pbcn*, with $a = 23.700(5)$ Å, $b = 25.162(5)$ Å, $c = 9.693(5)$ Å, and $Z = 4$. The structures of **1** and **2** are made up of uncoordinated perchlorate anions and malonate-bridged zigzag copper(II) chains grouped in an isosceles triangle running parallel to the *b* (**1**) and *c* (**2**) axes. These chains are built by a $[Cu(bpy)(mal)(H_2O)]$ unit acting as bis-monodentate ligand toward two $[Cu(bpy)(H_2O)]$ adjacent units through its OCCCO skeleton in an *anti*−*anti* conformation, whereas the OCO carboxylate bridges exhibit the *anti*−*syn* conformation. Compounds **1** and **2** contain four crystallographically independent copper(II) atoms, but the environment of all of them is distorted square pyramidal: the axial position is occupied by a water molecule, whereas the equatorial plane is formed by a chelating bpy and either a bidentate malonate or two carboxylate oxygens from two malonate groups. The equatorial Cu−O(mal) (1.911(4)−1.978(4) (**1**) and 1.897(5)−1.991(4) Å (**2**)) and Cu−N(bpy) (1.983(4)−2.008(5) (**1**) and 1.971(6)−2.007(6) Å (**2**)) bonds are somewhat shorter than the axial Cu−O(w) one (2.257(5)−2.524(5) (**1**) and 2.236(5)−2.505(6) Å (**2**)). The angles subtended at the copper atom by the chelating bpy vary in the ranges 80.9(2)−81.8(2)° (**1**) and 80.4(2)−82.1(2)° (**2**), values which are somewhat smaller than those of the chelating malonate (80.4(2)−82.1(2)° (**1**) and 93.0(2)−93.6(2)° (**2**)). The intrachain copper−copper separations through the OCCCO fragment are 8.227(1) (**1**) and 8.206(2) Å (**2**), whereas those through the OCO bridging unit are 4.579(1)−5.043(1) (**1**) and 4.572(2)−5.040(2) Å (**2**). The magnetic behavior of **1** and **2** in the temperature range 2.0−290 K is very close, and it corresponds to an overall ferromagnetic coupling, the $\chi_M T$ versus T curve exhibiting a maximum at 18 K. The analysis of the magnetic data through a numerical expression derived for the real topology of **1** and **2**, that is, chains of isosceles triangles with two intrachain exchange pathways J_1 (exchange coupling through the OCO carboxylate) and J_2 (exchange coupling through the OCCCO malonate), indicates the occurrence of ferro- ($J_1 = +4.6$ cm^{-1}) and antiferromagnetic couplings ($J_2 = -4.2$ cm^{-1}). The magnetic coupling through these exchange pathways is further analyzed and substantiated by density functional theory calculations on a malonate-bridged trinuclear copper(II) model system.

Introduction

During the past 2 decades, one-dimensional magnetic systems have been thoroughly investigated, mainly because they are suitable examples for developing theoretical models aimed at understanding the exchange interaction in extended lattices.[2−6] Among the great variety of homometallic one-dimensional magnetic complexes which have been characterized, one of the more interesting is that where regular alternating ferro- and antiferromagnetic interactions occurs.[7−14] This is a rare situation

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(1) (a) Departamento de Física Fundamental II, Universidad de La Laguna. (b) Departamento de Química Inorgánica, Universidad de La Laguna. (c) Departament de Química Inorgànica, Universitat de València.

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because the difficulty of designing a ferromagnetically coupled unit which could act as complex ligand toward the same metal ion yielding a chain with regular alternating bridges and sign of magnetic interactions. The regular alternating of bis(chelating) 2,2′-bipyrimidine (bpm, the antiferromagnetic coupler) and di-μ-hydroxo groups (the ferromagnetic coupler) in copper(II) chains provided examples of these materials.[11] The same type of ligand but with different bridging modes can be used in designing these systems as demonstrated by the azide group in the family of formula $[M(2,2'\text{-bpy})(N_3)_2]$ (M = Mn(II), Fe(II), Co(II), and Ni(II); 2,2′-bpy = 2,2′-bipyridine).[12,14] The complex magnetic behavior of the type of chains has motivated the development of new models in order to account for it.[12b,15,16]

Research works using malonate (dianion of the propanedioic acid, hereafter noted mal) as bridging ligand in copper(II) complexes have shown the versatility of this ligand.[17−20] The structural complexity in its metal complexes is associated with the simultaneous adoption of chelating bidentate and different carboxylato-bridging coordination modes. The use of $[Cu(mal)_2]^{2-}$ as a complex ligand allowed the preparation of dimers,[17] trimers,[20] and one-[19] and two-dimensional[18] complexes whose structure and magnetic properties were subject of recent investigation. In the course of our current research work concerning the building block strategy to design polynuclear complexes,[21] we have obtained two new malonato-bridged copper(II) chains of formula $\{[Cu(bpy)(H_2O)][Cu(bpy)(mal)(H_2O)]\}(ClO_4)_2$ (**1** and **2**), where the copper atoms define isosceles triangles sharing two vertices. Remarkably, alternating significant ferro- (through the OCO bridge) and antiferromagnetic (through the OCCCO skeleton) occur in them. Their preparation, structural and magnetic characterization, and density functional theory (DFT) calculations are presented in this work.

Experimental Section

Materials. Malonic acid, diethylmalonate, copper(II) perchlorate hexahydrate, and 2,2′-bipyridine were purchased from commercial sources and used as received. Elemental analyses (C, H, N) were performed on a EA 1108 CHNS−O microanalytical analyzer.

Synthesis of the Complexes $\{[Cu(bpy)(H_2O)]$ $[Cu(bpy)(mal)(H_2O)]\}(ClO_4)_2$. Compound 1. Aqueous solutions of malonic acid (5 mmol, 20 mL) and copper(II) perchlorate (10 mmol, 30 mL) were mixed under continuous stirring. An ethanolic solution of 2,2′-bipyridine (10 mmol, 25 mL) was added dropwise to the aqueous one, and the resulting solution was left undisturbed. Polyhedral sky blue crystals of **1** which were suitable for X-ray diffraction were obtained by slow evaporation at room temperature. They were filtered off, washed with a small amount of cold water, and dried on filter paper. Anal. Calcd for $C_{23}H_{22}O_{14}Cu_2N_4Cl_2$ (**1**): C, 35.56; H, 2.83; N, 7.21. Found: C, 35.43; H, 2.74; N, 7.17.

Compound 2. This compound was prepared by following a procedure analogous to that of **1** but replacing malonic acid by diethylmalonate. A typical synthesis is as follows: diethylmalonate (5 mmol) was added to a warm aqueous solution of copper(II) perchlorate (10 mmol, 30 mL) under continuous stirring. The resulting clear blue solution was allowed to cool at room temperature, and then 2,2′-bipyridine (10 mmol) dissolved in 50 mL of a water/ethanol (3:1) mixture was added under stirring. Polyhedral sky blue crystals of **2** were grown by slow evaporation at room temperature. They were filtered off, washed with a small amount of cold water, and dried on filter paper. Anal. Calcd for $C_{23}H_{22}O_{14}Cu_2N_4Cl_2$ (**2**): C, 35.53; H, 2.83; N, 7.21. Found: C, 35.34; H, 2.92; N, 7.35.

Physical Measurements. Magnetic susceptibilty measurements on polycrystalline samples of **1** and **2** were carried out in the temperature range 1.9−300 K with a Quantum Design SQUID magnetometer operating at 100 G ($T \leq 50$ K) and 1000 G ($T > 50$ K). Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants[22] as -267×10^{-6} cm^3 mol^{-1} (**1** and **2**). Experimental susceptibilities were also corrected for the temperature-independent paramagnetism (60×10^{-6} cm^3 mol^{-1}/Cu(II)) and the magnetization of the sample holder.

Computational Methodology. The computational strategy used in this work has been fully described elsewhere,[23] and it is briefly outlined here. Density functional theory[24] is used to evaluate the coupling constants in **1**. The model system we have used to carry out the calculations is the trinuclear copper(II) compound shown in Chart 3 (see below), where the bond lengths and angles are those of the real molecule. The copper surrounding is kept square planar, and ammonia molecules are used as terminal ligands for simplicity. Three separate calculations were done, one for the quadruplet and the other two for the broken-symmetry doublet states. The hybrid B3LYP method[25] has been used in the calculations as implemented in Gaussian-94,[26] mixing the exact Hartree−Fock exchange with the Becke's expression for the exchange[27] and using the Lee−Yang−Parr correlation functional.[28] Basis sets of triple-ζ[29] (copper atoms) and of double-ζ quality[30] (atoms other than copper) were used in all calculations.

The exchange coupling constants for the trinuclear copper(II) model compound were evaluated through eqs 1 and 2, where E_Q, E_{D1}, and E_{D2} correspond to the energies of the quadruplet (↑↑↑) and doublet (D1, ↑↓↑; D2, ↑↑↓) states, respectively.[31] Positive and negative values for the

$$E_Q - E_{D1} = -3J_1/2 \tag{1}$$

$$E_{D2} - E_{D1} = -J_1 + J_2 \tag{2}$$

coupling constant J_i indicate ferro- and antiferromagnetic interactions, respectively. The presence of low-energy doublet states close to the D1 and D2 doublets makes difficult the evaluation of their energies within a single-determinant method. To solve this problem, Noodleman

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Table 1. Crystallographic Data for $\{[Cu(bpy)(H_2O)][Cu(bpy)(mal)(H_2O)]\}(ClO_4)_2$ (**1** and **2**)

	1	**2**
formula	$C_{23}H_{22}O_{14}N_4Cl_2Cu_2$	$C_{23}H_{22}O_{14}N_4Cl_2Cu_2$
fw	776.1	776.1
space group	$P2_1/a$	Pbcn
a, Å	23.743(3)	23.700(5)
b, Å	9.7522(5)	25.162(5)
c, Å	27.731(2)	9.693(5)
β, deg	114.580(10)	90.0
V, Å^3	5839.1(9)	5780(3)
Z	4	4
T, K	293(2)	293(2)
ρ_{calcd}, g cm^{-3}	1.757	1.798
λ, Å	1.541 79	1.541 79
μ(Cu Kα), cm^{-1}	41.71	42.15
R^a	0.0597	0.0453
$R_w{}^b$	0.1591	0.1264

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

et al.[32−35] proposed a broken-symmetry approach. Although the broken-symmetry wave function is not a pure spin state, we have used its energy as an approximation to that of the doublet state, as suggested by different authors.[36,37] It deserves to be noted that although the broken-symmetry wave function is not able to provide correct values for the spin densities, it allows correct predictions of total density and energy for the ground state. Recently, we have shown that this methodology is able to reproduce theoretically the experimental data.[23,37−39]

Crystallographic Data Collection and Structure Determination. Crystals of dimensions 0.45 × 0.30 × 0.24 and 0.45 × 0.60 × 0.27 mm for **1** and **2**, respectively, were used for data collection on a Siemens AED four circle diffractometer. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data of 15 reflections in the range $6 < \theta < 18°$.[40,41] Data were collected at 293(2) K using graphite-monochromatized Cu Kα radiation (λ = 1.541 79 Å) and the ω-scan technique. A summary of the crystallographic data and structure refinement is given in Table 1. Examination of two standard reflections monitored every 2 h showed no sign of crystal deterioration. The index ranges of data collection were $0 \leq h \leq 25$, $0 \leq k \leq 11$, $-30 \leq l \leq 29$ for **1** and $0 \leq h \leq 28$, $-30 \leq k \leq 30$, $0 \leq l \leq 11$ for **2**. Of the 9148 (**1**) and 8971 (**2**) measured independent reflections in the θ range 3.51−65.05° (**1**) and 3.51−70.02° (**2**), 7287 (**1**) and 7364 (**2**) have $I \geq 2\sigma(I)$. All the measured independent refletions were used in the analysis. Intensity data were corrected for Lorentz−polarization and absorption.[42] The maximum and minimum transmission factors were 0.923 and 0.564 for **1** and 0.978 and 0.496 for **2**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**[a,b]

Cu(1)−N(11)	1.987(5)	Cu(3)−N(31)	1.997(5)
Cu(1)−N(12)	2.008(5)	Cu(3)−N(32)	1.998(6)
Cu(1)−O(1)	1.968(3)	Cu(3)−O(5)	1.978(4)
Cu(1)−O(4a)	1.974(4)	Cu(3)−O(8b)	1.963(4)
Cu(1)−O(1w)	2.257(5)	Cu(3)−O(3w)	2.260(5)
Cu(2)−N(21)	1.987(6)	Cu(4)−N(41)	1.983(4)
Cu(2)−N(22)	1.984(5)	Cu(4)−N(42)	1.987(6)
Cu(2)−O(2)	1.912(5)	Cu(4)−O(6)	1.919(5)
Cu(2)−O(3)	1.914(4)	Cu(4)−O(7)	1.911(4)
Cu(2)−O(2w)	2.524(5)	Cu(4)−O(4w)	2.497(5)
N(11)−Cu(1)−N(12)	81.1(2)	N(31)−Cu(3)−N(32)	80.9(2)
N(11)−Cu(1)−O(1)	95.2(2)	N(31)−Cu(3)−O(5)	157.0(2)
N(11)−Cu(1)−O(4a)	158.6(2)	N(31)−Cu(3)−O(8b)	95.0(2)
N(11)−Cu(1)−O(1w)	98.0(2)	N(31)−Cu(3)−O(3w)	99.0(2)
N(12)−Cu(1)−O(1)	175.4(2)	N(32)−Cu(3)−O(5)	89.2(2)
N(12)−Cu(1)−O(4a)	89.3(2)	N(32)−Cu(3)−O(8b)	175.1(2)
N(12)−Cu(1)−O(1w)	92.4(2)	N(32)−Cu(3)−O(3w)	93.3(2)
O(1)−Cu(1)−O(4a)	93.3(2)	O(5)−Cu(3)−O(8b)	93.6(2)
O(1)−Cu(1)−O(1w)	90.8(2)	O(5)−Cu(3)−O(3w)	102.3(2)
O(4a)−Cu(1)−O(1w)	101.5(2)	O(8b)−Cu(3)−O(3w)	90.1(2)
N(21)−Cu(2)−N(22)	81.2(2)	N(41)−Cu(4)−N(42)	81.8(2)
N(21)−Cu(2)−O(2)	172.6(2)	N(41)−Cu(4)−O(6)	92.4(2)
N(21)−Cu(2)−O(3)	93.3(2)	N(41)−Cu(4)−O(7)	174.5(2)
N(21)−Cu(2)−O(2w)	92.2(2)	N(41)−Cu(4)−O(4w)	94.9(2)
N(22)−Cu(2)−O(2)	92.6(2)	N(42)−Cu(4)−O(6)	168.3(2)
N(22)−Cu(2)−O(3)	169.4(2)	N(42)−Cu(4)−O(7)	92.7(2)
N(22)−Cu(2)−O(2w)	95.0(2)	N(42)−Cu(4)−O(4w)	97.3(2)
O(2)−Cu(2)−O(3)	93.4(2)	O(6)−Cu(4)−O(7)	93.0(2)
O(2)−Cu(2)−O(2w)	84.4(2)	O(6)−Cu(4)−O(4w)	93.3(2)
O(3)−Cu(2)−O(2w)	94.3(2)	O(7)−Cu(4)−O(4w)	85.7(2)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] Symmetry code: (a) $^3/_2 - x$, $y - {}^1/_2$, $2 - z$.; (b) $^1/_2 - x$, $^1/_2 + y$, $1 - z$.

The structures of **1** and **2** were solved by direct methods followed by successive Fourier synthesis through SIR97.[43] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques on F^2 by using the SHELXL97[44] computational program. The hydrogen atoms of the malonate ligand were either found (**1**) or set in calculated positions (**2**) and isotropically refined as riding atoms. The remaing hydrogen atoms were neither found nor calculated. Full-matrix least-squares refinement was performed by minimizing the function $\sum w(|F_o|^2 - |F_c|^2)$ with $w = 1/[\sigma^2(F_o)^2 + mP^2 + nP]$ and $P = (F_o{}^2 + 2F_c{}^2)/3$ with $m = 0.064$ (**1**) and 0.0669 (**2**) and $n = 4.4143$ (**1**) and 14.6387 (**2**). The values of the discrepancy indices R (R_w) for all data were 0.075 (0.211) for **1** and 0.069 (0.215) for **2**, whereas those listed in Table 1 correspond to the data with $I \geq 2\sigma(I)$. The final Fourier difference map showed maximum and minimum height peaks of 1.07 and −0.83 e Å^{-3} for **1** and 0.61 and −0.53 e Å^{-3} for **2**. The largest and mean Δ/σ are 0.21 and 0.01 (**1**) and 0.01 and 0.001 (**2**). The values of the number of reflections/number of variable parameters are 17.5 (**1**) and 20.5 (**2**), and those of the goodness-of-fit are 1.08 (**1**) and 1.09 (**2**). Analytical expressions of neutral scattering factors were used, and anomalous dispersion corrections were incorporated.[45] The final geometrical calculations and the graphical manipulations were carried out with PARST95[46] and PLATON[47] programs, respectively. Selected interatomic bond distances and angles for **1** and **2** are listed in Tables 2 and 3, respectively.

Results and Discussion

Description of the Structures. Compound 1. The structure of **1** consists of two cationic zigzag chains of copper(II) ions, Cu(1) and Cu(2) (Figure 1a) and Cu(3) and Cu(4) (Figure 1b), which exhibit a regular alternating of aqua(2,2′-bipyridyl)-

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **2**[a,b]

Cu(1)−N(11)	1.991(6)	Cu(3)−N(31)	2.007(6)
Cu(1)−N(12)	1.983(6)	Cu(3)−N(32)	1.993(6)
Cu(1)−O(1)	1.961(4)	Cu(3)−O(3)	1.963(4)
Cu(1)−O(8c)	1.991(4)	Cu(3)−O(6)	1.963(4)
Cu(1)−O(1w)	2.238(5)	Cu(3)−O(3w)	2.236(5)
Cu(2)−N(21)	1.978(6)	Cu(4)−N(41)	1.982(6)
Cu(2)−N(22)	1.971(6)	Cu(4)−N(42)	1.986(5)
Cu(2)−O(2)	1.902(5)	Cu(4)−O(5)	1.907(5)
Cu(2)−O(4)	1.925(5)	Cu(4)−O(7)	1.897(5)
Cu(2)−O(2w)	2.498(6)	Cu(4)−O(4w)	2.505(6)
N(11)−Cu(1)−N(12)	80.9(2)	N(31)−Cu(3)−N(32)	80.4(2)
N(11)−Cu(1)−O(1)	94.8(2)	N(31)−Cu(3)−O(4)	89.0(2)
N(11)−Cu(1)−O(8c)	157.7(2)	N(31)−Cu(3)−O(5)	175.5(2)
N(11)−Cu(1)−O(1w)	99.1(2)	N(31)−Cu(3)−O(3w)	91.7(2)
N(12)−Cu(1)−O(1)	174.8(2)	N(32)−Cu(3)−O(4)	158.3(2)
N(12)−Cu(1)−O(8c)	89.8(2)	N(32)−Cu(3)−O(5)	96.2(2)
N(12)−Cu(1)−O(1w)	94.0(2)	N(32)−Cu(3)−O(3w)	97.1(2)
O(1)−Cu(1)−O(8c)	93.2(2)	O(4)−Cu(3)−O(5)	93.3(2)
O(1)−Cu(1)−O(1w)	89.5(2)	O(4)−Cu(3)−O(3w)	102.1(2)
O(8c)−Cu(1)−O(1w)	101.8(2)	O(5)−Cu(3)−O(3w)	91.7(2)
N(21)−Cu(2)−N(22)	82.1(2)	N(41)−Cu(4)−N(42)	81.1(2)
N(21)−Cu(2)−O(2)	174.0(2)	N(41)−Cu(4)−O(6)	93.3(2)
N(21)−Cu(2)−O(3)	92.5(2)	N(41)−Cu(4)−O(7)	173.4(2)
N(21)−Cu(2)−O(2w)	92.6(2)	N(41)−Cu(4)−O(4w)	93.8(2)
N(22)−Cu(2)−O(2)	92.5(2)	N(42)−Cu(4)−O(6)	168.8(2)
N(22)−Cu(2)−O(3)	169.6(2)	N(42)−Cu(4)−O(7)	92.8(2)
N(22)−Cu(2)−O(2w)	95.5(2)	N(42)−Cu(4)−O(4w)	96.2(2)
O(2)−Cu(2)−O(3)	93.2(2)	O(6)−Cu(4)−O(7)	93.1(2)
O(2)−Cu(2)−O(2w)	85.3(2)	O(6)−Cu(4)−O(4w)	93.8(2)
O(3)−Cu(2)−O(2w)	93.7(2)	O(7)−Cu(4)−O(4w)	84.4(2)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] Symmetry code: (c) *x*, *y*, *z*. − 1.

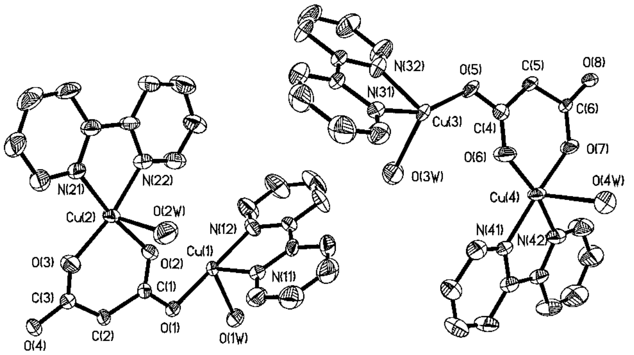

Figure 1. Perspective view of the asymmetric units of **1** (fragments of the chains containing Cu(1) and Cu(2) (a, left) and for Cu(3) and Cu(4) (b, right)) along with the atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

(malonato)copper(II) (Cu(2) and Cu(4)) and aqua(2,2′-bipyridyl)copper(II) (Cu(1) and Cu(3)) units, the former being linked to the latter as a bis-monodentate ligand through two carboxylate−malonate oxygen atoms in a *cis* arrangement. The charges are counterbalanced by uncoordinated perchlorate anions. The chains run parallel to the *b* axis (Figure 2), and they are interconnected through hydrogen bonds involving the coordinated water molecules and three of the four perchlorate oxygen atoms [the O(water)···O(perchlorate) distances are 2.916(7) (O(1w)···O(3D)), 2.806(9) (O(3w)···O(1A)), 2.804(10) (O(4w)···O(3Dd)), and 2.787(8) Å (O(3w)···O(3B)); (d) = −*x* + 1, −*y*, −*z* + 1] (Figure 3). Additional intrachain C−H(bpy)···O(perchlorate) and C−H···O(malonate) interactions contribute to the stabilization of the crystal structure.

The four crystallographic independent copper(II) ions [Cu(1), Cu(2), Cu(3), and Cu(4)] exhibit a distorted CuN$_2$O$_3$ square-pyramidal surrounding. The basal sites of the Cu(1) and Cu(3) atoms are occupied by the N-bpy atoms and two carboxylate oxygen atoms from two diferent malonate ligands, the mean value of the former bonds being somewhat longer (1.997(5) Å for Cu−N) than the latter ones (1.970(4) Å for Cu−O]. The apical position of these copper atoms is occupied by a relatively strongly coordinated water molecule [2.257(5) and 2.260(5) Å for Cu(1)−O(1w) and Cu(3)−O(3w) bonds, respectively], and they are shifted by 0.1966(8) (Cu(1)) and 0.2167(8) Å (Cu(3)) from the mean basal plane toward the O(1w) and O(3w) water molecules. Two bpy nitrogen atoms and two carboxylate oxygens from bidentate 2,2′-bipyridyl and malonate ligands build the equatorial plane around the Cu(2) and Cu(4) atoms. The bpy nitrogen to Cu(2) and Cu(4) bond distances are nearly identical, and they are somewhat longer [mean value Cu−N 1.985(5) Å] than those of the malonate oxygen to copper [mean value Cu−O 1.914(4) Å]. The apical position of both copper atoms is occupied by a weakly coordinated water molecule [2.524(5) and 2.497(5) Å for Cu(2)−O(2w) and Cu(4)−O(4w)]. Cu(2) and Cu(4) are shifted by 0.0524(12) and 0.0593(12) Å from the mean basal plane toward O(2w) and O(4w), respectively. These structural data are in agreement with that of the monomeric copper(II) complex [Cu(bpy)(mal)(H$_2$O)]·H$_2$O[48] which exhibits the same chromophore. The difference between the mean values of the axial and equatorial bonds around Cu(2) and Cu(4) atoms (0.596 Å) is in agreement with the $R_L - R_S$ value (0.51 Å) reported by Hathaway,[49] R_L and R_S representing the lengths of the axial and equatorial oxygen to copper bonds, respectively.

Each malonate group adopts simultaneously bidentate (at Cu(2) and Cu(4)) and bis-monodentate (at Cu(1) and Cu(3)) coordination modes, and it exhibits an envelop conformation in which only the methylene group is significantly shifted from the chelate ring plane. The angles subtended at Cu(2) and Cu(4) by the chelating malonato groups are 93.4(2) and 93.0(2)°. The average C−O bond distances and O−C−O bond angles are 1.256(7) Å and 122.1(6)°. Two slightly different carboxylate

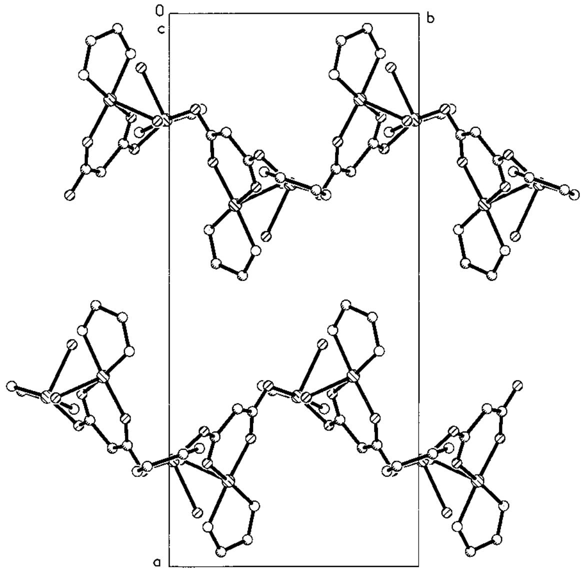

Figure 2. Projection of the cell of **1** down the *c* axis showing the parallel arrangement of the A (Cu(1) and Cu(2)) and B (Cu(3) and Cu(4)) chains. Hydrogen atoms and the perchlorate anions have been omitted for clarity.

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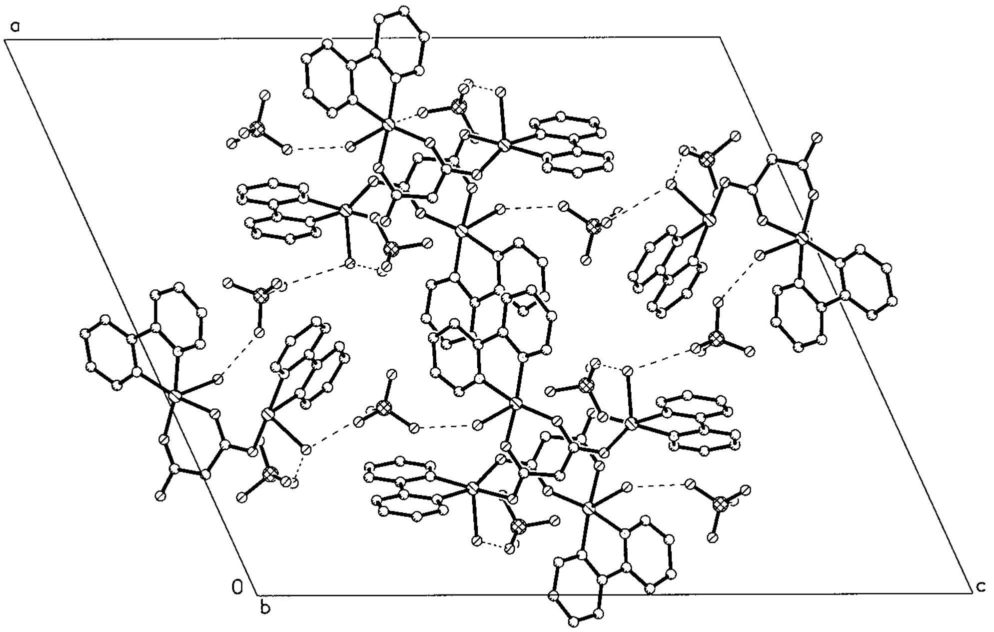


Figure 3. Projection of the contents of the cell down the *b* axis illustrating the hydrogen bonding interactions (broken lines).

bridges, O(1)C(1)O(2) and O(3)C(3)O(4) (chain with Cu(1) and Cu(2)) and O(5)C(4)O(6) and O(7)C(6)O(8) (chain with Cu(3) and Cu(4)) exhibiting the *anti*−*syn* conformation alternate regularly within each copper(II) chain. The bond angles at the bridging O(1) and O(4) atoms are 112.4(3) and 128.1(3)° and at the O(5) and O(8) 127.7(3) and 112.5(3)°, respectively. The values of the dihedral angle between the equatorial plane at Cu(2) and that of the O(1)C(1)O(2) and O(3)C(3)O(4) bridging carboxylates are 13.3(2) and 16.4(2)°, and those between the equatorial plane at Cu(4) and that of the O(5)C(4)O(6) and O(7)C(6)O(8) bridging carboxylates are 17.9(2) and 13.5(2)°.

The bpy molecules are nearly planar [largest deviation of atoms from the mean planes is 0.017(6) Å], the dihedral angle between the mean planes of the two pyridyl rings being 3.7(2)° (mean value). The intraring C−N [mean value 1.340(4) Å] and C−C [mean value 1.389(11) Å] bond distances are as expected. The angles subtended by the bidentate bpy ligand at the copper atoms in **1** vary in the range 80.9(2)−81.8(2)°.

The intrachain copper−copper separations through carboxylato are 4.5953(13) [Cu(1)···Cu(2)], 5.0368(12) [Cu(1)···Cu(2a)], 5.0434(14) [Cu(3)···Cu(4)], and 4.5768(11) Å [Cu(3)···Cu(4b)], values which are much shorter than those through malonato [8.2270(12) and 8.2264(13) Å for Cu(1)···Cu(1c) and Cu(3)···Cu(3e) with (c) = $^3/_2 - x$, $^1/_2 + y$, $2 - z$ and (e) = $^1/_2 - x$, $y - {}^1/_2$, $1 - z$]. The shortest interchain copper−copper separation is 8.367(2) Å.

Compound 2. The structure of **2** consists of uncoordinated perchlorate anions and cationic copper(II) chains containing four crystallographically independent copper atoms (Figure 4) with a regular alternation of aqua(2,2′-bipyridyl)(malonato)copper(II) (Cu(2) and Cu(4)) and aqua(2,2′-bipyridyl)copper(II) (Cu(1) and Cu(3)) units. This situation resembles that found in **1**, the main differences being the presence in **2** of only one type of chain and the fact that the chains in the present compound run papalell to the *c* axis (Figure 5) (*b* axis in **1**). As in the preceding structure, an extensive network of hydrogen bonds involving the coordinated water molecules and three of the four perchlorate anions contribute to the stabilization of the lattice (Figure 6) [2.787(10), 2.810(8), 2.833(10), 2.894(9), 2.809(9), and 2.833(10) Å for O(1w)···O(4A), O(1w)···O(1Dh), O(2w)···O(1Cf), O(3w)···O(2Cg), O(3w)···O(4Bi), and O(4w)···O(4Dj), respectively; symmetry codes: (h) = $-x + 1$, $y + {}^1/_2$, $-z + 1$; (f) = x, $y - 1$, z; (g) = $-x + 1$, $y - {}^1/_2$, $-z + 1$; (i) = $x - {}^1/_2$, y, $-z + 1$; (j) = $x - {}^1/_2$, y, $-z + 2$].

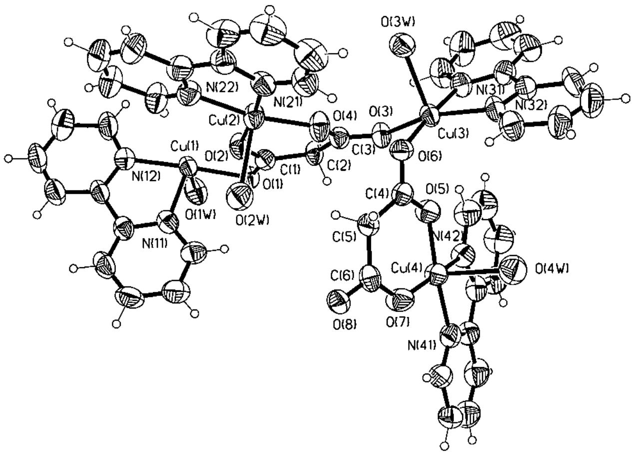


Figure 4. Perspective view of the asymmetric unit of **2** along with the atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

The four crystallographically independent copper atoms exhibit a distorted CuN_2O_3 square-pyramidal surrounding. The basal sites for the aqua(bpy)copper(II) units [Cu(1) and Cu(3)] are occupied by the bpy nitrogen atoms and two carboxylate oxygen atoms from two diferent malonate ligands [mean values Cu−N and Cu−O are 1.993(6) and 1.969(4) Å, respectively], whereas the apical position is occupied by strongly coordinated water molecule [2.238(5) Å for Cu(1)−O(1w) and 2.236(5) Å Cu(3)−O(3w)]. Cu(1) and Cu(3) are shifted by 0.2136(10) and 0.1973(10) Å from their mean basal plane toward O(1w) and O(3w), respectively. These structural features are very close to those observed in the related units in **1**. Concerning the aqua(2,2′-bpy)(mal)copper(II) units [Cu(2) and Cu(4)], two bpy nitrogen atoms and two carboxylate oxygens from bidentate bpy and malonato build the equatorial plane. The pattern of the Cu−N and Cu−O bond distances is as observed in **2** [the average Cu−N and Cu−O bonds being 1.978(6) and 1.907(5)

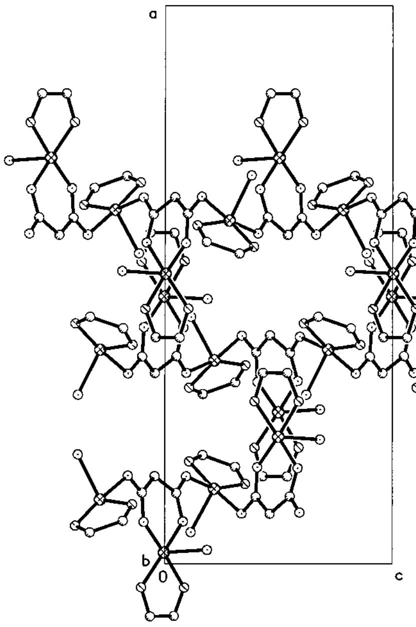


Figure 5. Projection of the cell of **2** down the *b* axis showing the parallel arrangement of the chains. Hydrogen atoms and the perchlorate anions have been omitted for clarity.

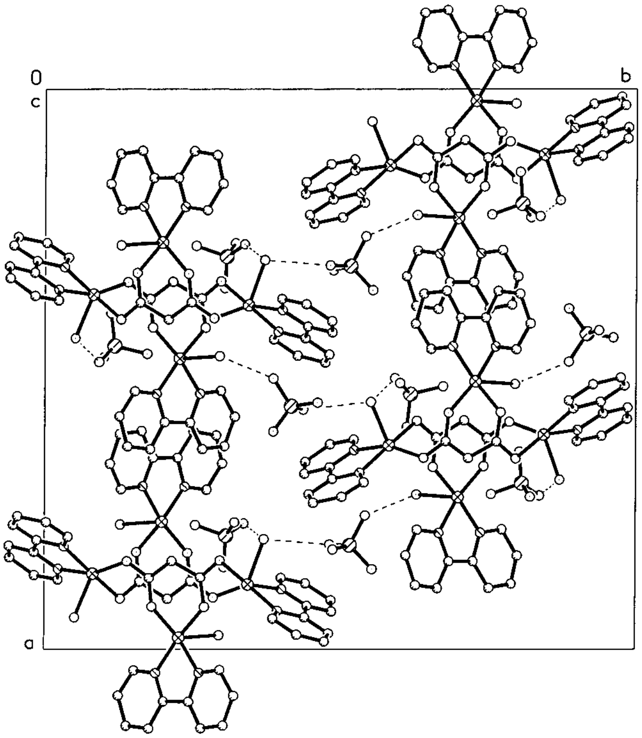


Figure 6. Projection of the contents of the cell down the *c* axis illustrating the hydrogen bonding pattern (broken lines).

Å]. The apical position is occupied by a weakly coordinated water molecule [2.498(6) and 2.505(6) Å for Cu(2)−O(2w) and Cu(4)−O(4w), respectively]. Cu(2) and Cu(4) are somewhat shifted from the mean basal plane toward O(2w) (0.0524(12) Å) and O(4w) (0.0593(12) Å). The angles subtended at Cu(2) and Cu(4) by the chelating malonato groups are 93.2(2) and 93.1(2)°, and those subtended by bpy at Cu(1) and Cu(3) are 80.9(2) and 80.4(2)°.

As in **1**, each malonate group adopts simultaneously bidentate (at Cu(2) and Cu(4)) and monodentate (at Cu(1) and Cu(3)) coordination modes and exhibits an envelop conformation in which only the methylene group is significantly shifted from the chelate ring plane. The average C−O bond distances and O−C−O bond angles are 1.256(7) Å and 122.1(6)°. Two slightly different carboxylate bridges (O(1)C(1)O(2) and O(3)C(3)O(4) (involving Cu(2)) and O(5)C(4)O(6) and O(7)C(6)O(8) (involving Cu(4)) which exhibit the anti−syn conformation alternate regularly within each copper(II) chain. The bond angles at the bridging O(1) and O(4) atoms are 112.4(3) and 128.1(3)°, whereas those at the O(5) and O(8) atoms are 127.7(3) and 112.5(3)°. The values of the dihedral angle between the equatorial plane at Cu(2) [Cu(4)] and those of the O(1)C(1)O(2) [O(5)C(4)O(6)] and O(3)C(3)O(4) [O(7)-C(6)O(8)] bridging carboxylates are 13.3(2) [13.5(2)] and 16.4(2) [18.7(2)]°.

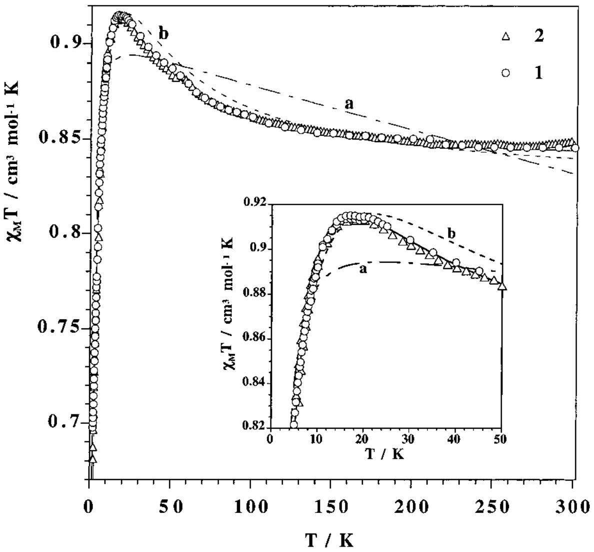


Figure 7. Thermal dependence of the $\chi_M T$ product for complexes **1** and **2**: (○, △) experimental data; (−•−), (•••) and (−) best-fits through eq 3, Baker's et al. expression, and eq 4, respectively (see text). The inset shows the quality of the different fits in the lower temperature region.

The bpy molecules are nearly planar [the largest deviation of atoms from the mean planes is 0.026(9) Å]. The mean planes of the two pyridine rings are inclined at 3.7(2)° (mean value) with respect to one other.

The intrachain copper−copper separations through the carboxylate bridge are 4.584(2) [Cu(1)•••Cu(2)], 5.040(2) [Cu(2)•••Cu(3)], 4.572(2) [Cu(3)•••Cu(4)], and 5.006(2) Å [Cu(1)•••Cu(4c)], whereas those through malonato are 8.198(2) [Cu(1)•••Cu(3)] and 8.206(2) [Cu(1)•••Cu(3c)]. The shortest interchain copper−copper separation is 8.476(2) Å.

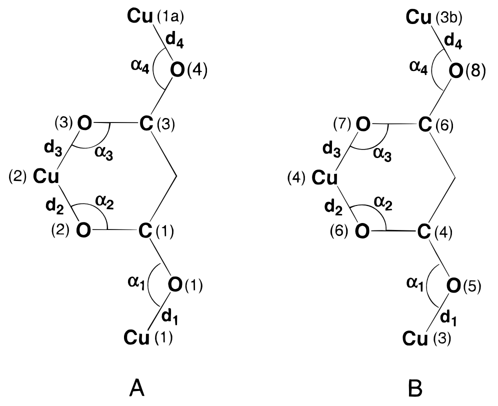
Magnetic Properties of 1 and 2. The temperature dependence of $\chi_M T$ (χ_M being the magnetic susceptibility per two copper(II) ions) for complexes **1** and **2** is shown in Figure 7. As one can see, the corresponding curve for **2** is practically identical to that of complex **1**, both magnetic curves matching well each other. This surprising fact can be easily understood through a detailed comparison between **1** and **2**, but we will come back to this point after the analysis and discussion of their magnetic behavior. $\chi_M T$ at 290 K is 0.86 cm^3 mol^{-1} K for both complexes, a value which is as expected for two magnetically isolated spin doublets. $\chi_M T$ gradually increases when cooling; it attains a maximum value of 0.96 cm^3 mol^{-1} K at 18 K and further decreases sharply to reach 0.68 cm^3 mol^{-1} K at 1.9 K. The shape of these curves is characteristic of the occurrence of weak ferro- and antiferromagnetic interactions in the high- and low-temperature ranges, respectively. As indicated in the

Table 4. Selected Bond Lengths (d_i) and Angles (α_i) for the Malonatocopper(II) Fragment in Compounds **1**[a] and **2**[b]

complex	d_1/Å	d_2/Å	d_3/Å	d_4/Å	α_1/deg	α_2/deg	α_3/deg	α_4/deg
1 (A)	1.968(3)	1.912(5)	1.914(4)	1.974(4)	112.4(3)	128.8(4)	128.5(4)	128.1(3)
1 (B)	1.978(4)	1.919(5)	1.911(4)	1.963(4)	112.4(3)	129.1(4)	128.4(4)	127.7(3)
2	1.977(4)	1.916(5)	1.899(5)	1.962(4)	112.7(4)	128.3(4)	129.2(4)	128.2(4)

[a] A and B refer to the copper(II) chains of **1** containing Cu(1) and Cu(2) (A) and Cu(3) and Cu(4) (B). [b] Average values concerning the four crystallographically independent copper atoms of compound **2**.

Chart 1



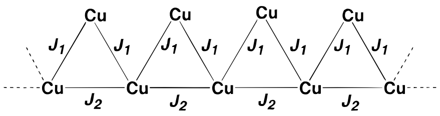
structural description, these compounds are made up of carboxylato-bridged copper(II) chains where the carboxylate adopts the *anti*−*syn* conformation. Previous magnetostructural studies have shown that the magnetic coupling between copper(II) ions through this type of bridged is always weak and usually ferromagnetic.[20,50−54] Although two crystallographically independent copper(II) chains occur in **1**, the small structural differences between them (see Chart 1A,B and Table 4) allow us to predict a practically identical magnetic behavior. In the case of **2**, only one copper(II) chain occurs, and it is so close to the two copper(II) chains occurring in **1** (seeTable 4) that a practically identical magnetic behavior for **1** and **2** could be expected, as observed.

Keeping in mind these considerations and given that the magnetic curves reveal the occurrence of ferro- and antiferromagnetic interactions, we have assumed in a first approach that their magnetic properties could be modelized by a chain of local spin doublets with regular alternating ferro- and antiferromagnetic interactions through the two carboxylate bridges (one carboxylato with α_1 ca. 112° and the other one with α_4 ca. 128°). The analysis of the magnetic data by means of the numerical expression derived through the appropriate Hamiltonian (eq 3)[15]

$$\hat{H} = -\sum_{i=1}^{n-1}[(J_1\hat{S}_{2i}\cdot\hat{S}_{2i+1} + J_2\hat{S}_{2i}\cdot\hat{S}_{2i-1}] \qquad (3)$$

led to the following set of least-squares fit parameters: $J_1 = 1.81$ cm^{-1}, $J_2 = -1.79$ cm^{-1}, and $g = 2.19$. The calculated curve (that noted a in Figure 7) with them is far from matching the magnetic data in the whole temperature range. However, the results of this fit point out that the interaction through the two carboxylate groups has to be of the same sign (that is ferromagnetic) and magnitude given the similarity between the structural parameters of the two carboxylate bridges. In a second approach, we assumed that the magnetic behavior would correspond to a regular ferromagnetically coupled copper(II) chain with interchain antiferromagnetic interactions. The latter ones would account for the decrease of $\chi_M T$ in the lower temperature region. The fit of the magnetic data through the expression of Baker et al.[55] and based on the Padé approximants led to the following best fit parameters: $J = 12.9$ cm^{-1}, $\theta = -12.7$ K, and $g = 2.10$. θ was introduced to account for the interchain interactions via a mean-field approximation.[56] The calculated curve with this set of parameters (curve noted b in Figure 7) hardly reproduces the magnetic data of both compounds, but this fit is much better than the previous one. Of course, the computed values of J and θ are too large. This is clear that a value of −13 K for θ is unreasonable because of the large interchain copper−copper separation (ca. 8.4 Å). Anyway, the important point of this fit is that two exchange interactions of opposite sign but close in magnitude have to be involved. This led us to the third approach where the possibility of two intrachain exchange interactions are considered: one through the carboxylato in the *anti*−*syn* conformation (the ferromagnetic one, J_1) and another through the malonato skeleton in the *anti*−*anti* conformation (the antiferromagnetic one, J_2), as sketched in Chart 2.

Chart 2



According to this scheme of exchange interactions, we are faced with a copper(II) chain made up of isosceles triangles sharing the two vertices of their base (real topology of **1** and **2**). The appropriate Hamiltonian for treating this chain is given by eq 4. As far as we know, there is no analytical expression to

$$\hat{H} = -[J_1\sum_{i=1}^{n}\hat{S}_{2i}\cdot\hat{S}_{2i-1} + J_1\sum_{i=1}^{n}\hat{S}_{2i}\cdot\hat{S}_{2i+1} + J_2\sum_{i=1}^{n}\hat{S}_{2i-1}\cdot\hat{S}_{2i+1}] \quad (4)$$

describe the magnetic behavior of such a copper(II) chain. This is why we have used a general numerical procedure based on closed spin chains of increasing length similarly to that previously done to modelize the alternating chains with alternating ferro- and antiferromagnetic interactions.[15] In our case, we have investigated rings of N local spin doublets up to $N = 14$. Given that the curves of $N = 12$ and $N = 14$ match each other,

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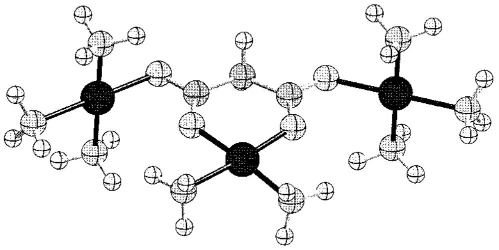
Chart 3



we have used the numerical expression concerning the case with $N = 14$ to treat the magnetic data of both compounds. The best fit parameters are $J_1 = +4.6(1)$ cm^{-1}, $J_2 = -4.2(1)$ cm^{-1}, and $g = 2.11(1)$. Within the experimental errors, the same values are obtained for **1** and **2**. The calculated curve (solid line in Figure 7) matches very well the magnetic data in the whole temperature range.

To check the validity of these parameters and that of the approximations we have made, we carried out DFT calculations on the trinuclear model system in Chart 3 (see computational paragraph for more details). The calculated values of J_1 and J_2 are $+2.24$ and -1.78 cm^{-1}, respectively. This calculation shows that the magnetic interaction through *anti*−*syn* carboxylato is ferromagnetic and that through malonato in the *anti*−*anti* conformation is antiferromagnetic in agreement with the values obtained through the previous fit. Although the absolute value of the magnetic couplings obtained through this *ab initio* calculation is somewhat smaller, the agreement in sign strongly supports the validity of our approach.

To conclude, the main aspects of the present work are the following: (i) first, **1** and **2** are examples of a new topology of copper(II) chains which illustrate the use of the [Cu(bpy)(mal)]-(H_2O)] mononuclear unit as a complex ligand; (ii) second, the fact is that polymorphism (compounds **1** and **2**) in coordination chemistry is associated in the present case to the nature of the starting products (malonate versus diethylmalonate); (iii) and third, the ability of the malonate ligand to mediate simultaneously weak but significant ferro- (through the carboxylato bridge in *anti*−*syn* conformation) and antiferromagnetic (through the OCCCO skeleton in *anti*−*anti* conformation) interactions has been evidenced for the first time and substantiated by theoretical calculations.

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Supporting Information Available: X-ray crystallographic files for complexes **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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