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Article

$[Cu_3(Hmesox)_3]^{3-}$: a Precursor for the Rational Design of Chiral Molecule-Based Magnets (H_4mesox = 2-dihydroxymalonic acid)

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Two new compounds $K_3[Cu_3(Hmesox)_3(H_2O)]\cdot 4H_2O$ (**1**) and $\{(PPh_4)_2[CoCu_3(Hmesox)_3Cl]\}$ (**2**) [H_4mesox = mesoxalic acid (2-dihydroxymalonic acid) and PPh_4^+ = tetraphenylphosphonium cation] have been prepared and magneto-structurally characterized. Compound **1** contains the $[Cu_3(Hmesox)_3]^{3-}$ entity which can be considered as a new precursor for molecular magnetism. In **1** the triangular arrangement of three copper(II) ions bridged by alkoxo groups are further connected to a symmetry-related tricopper(II) unit through a double oxo(carboxylate) bridge. The resulting hexacopper(II) entities are joined further through *anti-syn* carboxylate groups into an anionic three-dimensional network of formula $[Cu_3(Hmesox)_3(H_2O)]_n^{3n-}$ whose charge is neutralized by univalent potassium cations. The strong decrease of the $\chi_M T$ product [per three copper(II) ions] in the high temperature range with the occurrence of a plateau for a spin doublet at $T < 65$ K is as expected for the coexistence of two antiferromagnetic interactions within the quasi isosceles tricopper(II) core of **1** [$J = -194(1)$ cm^{-1} and $j = -3(4)$ cm^{-1}, the Hamiltonian being defined as $\hat{H} = -J(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_2\cdot\hat{S}_3) - j(\hat{S}_1\cdot\hat{S}_2)$]. Compound **2** exhibits a chiral three-dimensional structure which is made up of an anionic $[Co^{II}Cu^{II}_3(\mu_3\text{-}Cl)(Hmesox)_3]_n^{2n-}$ framework with a (10,3)-a topology whose cavities are filled by PPh_4^+ cations. The $[Cu^{II}_3(\mu_3\text{-}Cl)(Hmesox)_3]^{3-}$ tricopper(II) unit in **2** acts as a tris-bidentate ligand through the Hmesox groups toward three cobalt(II) ions, these latter ones being tris-chelated. Alternating current (ac) and direct current (dc) magnetic susceptibility measurements of **2** show a ferrimagnetic behavior with a magnetic ordering at $T_c = 18.5$ K and a coercive field $H_c = 5000$ G. As shown by the magneto-structural study of **2**, the use as a ligand of **1** versus metal ions other than cobalt(II) or preformed complexes whose coordination sphere is partially blocked represents a new and rational preparative route toward multifunctional heterometallic compounds.

Introduction

The area of molecular magnetism is expanding because of the fascinating new physics displayed by both molecular species (single molecule magnets, frustrated systems, high-spin molecules) and extended networks (single chain magnets, molecule-based magnets with high critical temperatures, etc.).[1−5] Regarding the applicability of these materials, strong magnetic interactions are required to shift the blocking temperature toward the high temperature domain. At the

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preparative level and envisaging a rational synthetic approach to these materials, the possibilities that the chemist has on his hands concern the control of the nature of the ground state and the size of the molecule as well as its topology and order of magnitude of the magnetic anisotropy.[6] The synthesis of high-spin molecules has been considered as one possible route to the preparation of molecule-based magnets.[7] In this respect, a general and rational synthetic method which consists of using a stable paramagnetic complex as a ligand (the precursor) toward metal ions whose coordination sphere is partially blocked has been highly rewarding. The precursor can be obtained as separated compounds or generated *in situ* in an initial step of the global reaction. Selected examples which illustrate the richness and possibilities of this complex as ligand strategy are the oxalato-,[8] cyano-,[1a,4h,8e,9] and oxamato-containing metal complexes.[10] However, the most widely used precursors

are mononuclear complexes having at least one potentially bridging ligand in their coordination sphere. To improve the efficiency of the precursors and open new routes of rational design of nuclearity tailored magnetic complexes, higher nuclearity precursors are currently investigated.[10a,b,11]

Focusing on trinuclear array of copper(II) ions, they may be essential functional units in a number of multicopper blue oxidases,[12] such as laccase and ascorbate oxidases, which catalyze the four-electron reduction of dioxygen to water with concomitant one-electron oxidation of a variety of substrates, such as ascorbate and polyphenols, and aromatic polyamines.[13] It is of importance to synthesize low molecular weight trinuclear copper(II) complexes having a triangular arrangement of metal atoms and to study the conditions leading these compounds to mimic the behavior of natural products. Trinuclear triangular and chains of trinuclear copper(II) complexes, with[14,15] or without[16] a $Cu^{II}_3(\mu_3$-OH), core have been reported. In addition to that, there is an increasing interest in cyclic trinuclear metal complexes because they can be geometrically frustrated systems which offer the opportunity to test magnetic exchange models (spin frustration, spin delocalization, or antisymmetric exchange).[17-19]

Two triangular tricopper(II) motifs with α-hydroxycarboxylate [tartronate and malate (anions of the triprotic 2-hydroxymalonic and 2-hydroxybutanedioic acids, respectively; see Scheme 1)] as bridging ligands have been reported.[17,20]

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Scheme 1. Molecular Structure of Tartronic (H$_3$tar), Mesoxalic (H$_4$mesox), and Malic H$_3$malc) Acids[a]

tartronic acid

mesoxalic acid
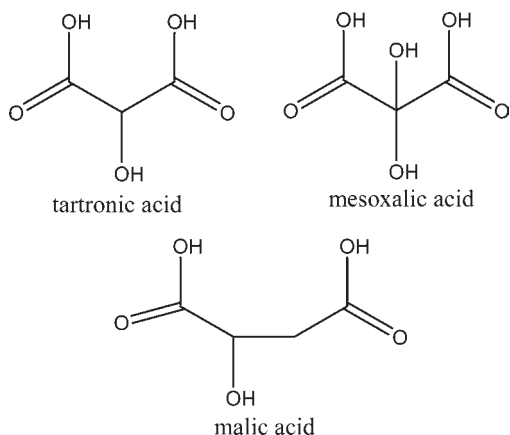
malic acid

[a] The two carboxylic and one of the hydroxo groups of the mesoxalic acid are deprotonated upon its coordination to the copper(II) (**1**) and cobalt(II) ions (**2**).

In particular, the three copper(II) ions from the [Cu$_3$(tar)$_3$]$^{3-}$ species are bridged by the μ-alkoxo groups and leave a void position in which another paramagnetic metallic ion can be inserted yielding *anti-anti* carboxylate bridges, both types of bridges being well-known mediators of magnetic coupling (Scheme 2).

To rationalize these preliminary findings, and in the light of our previous results with malonate and substituted malonate ligands,[21,22] we present herein the first results of an ongoing research project dealing with the study of the reactivity of copper(II) with α-hydroxycarboxylates as magnetic precursors. One could expect that a tartronate derivative such as the mesoxalate [deprotonated form of 2-dihydroxymalonic acid (H$_4$mesox); Scheme 1] would yield analogous tricopper(II) species with a similar structure. With this idea we have prepared the compound K$_3$[Cu$_3$(Hmesox)$_3$(H$_2$O)]·4H$_2$O (**1**) and we have tested the behavior of the [Cu$_3$(Hmesox)$_3$]$^{3-}$ species as a ligand toward first-row transition metal ions. Our results show that the paramagnetic [Cu$_3$(Hmesox)$_3$]$^{3-}$ trinuclear core from **1** seems to be a very suitable complex to act as a ligand toward paramagnetic centers, as illustrated by the crystal structure of the compound {(Ph$_4$P)$_2$[CoCu$_3$(Hmesox)$_3$Cl]} (**2**) which is indeed a chiral, three-dimensional molecule-based magnet. The preparation, crystal structure determination, and magnetic study of both

Scheme 2. Bridging Pattern within the Core of the Copper(II)-Tartronate Complexes

μ-alkoxo
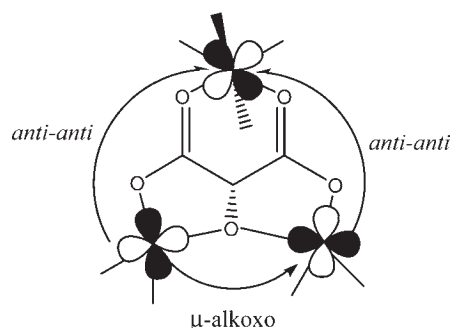
compounds are the subject of the present work, representing a new strategy toward the rational design of extended magnetic systems.

Experimental Section

Synthesis Procedure. Copper(II) acetate hydrate, basic copper(II) carbonate CuCO$_3$·Cu(OH)$_2$, cobalt(II) acetate tetrahydrate, mesoxalic acid, potassium hydrogencarbonate, tetraphenylphosphonium chloride, ethanol and diethylether were purchased from commercial sources and used as received. Elemental analyses (C, H) were performed on an EA 1108 CHNS-O microanalytical analyzer.

K$_3$[Cu$_3$(Hmesox)$_3$(H$_2$O)]·4H$_2$O (1). Mesoxalic acid (136 mg, 1 mmol) was added to a solution of copper(II) acetate (200 mg, 1 mmol) in water (8 cm^3) at 30 °C, under continuous stirring. Potassium hydrogencarbonate KHCO$_3$ (190 mg, 1.9 mmol) dissolved in water (10 cm^3) was added to afford a deep blue solution which was filtered and allowed to evaporate at room temperature. X-ray quality blue prisms of **1** separated from the mother liquor within a week. Yield 146 mg, 55%. Found: C, 13.60; H, 1.65%. Calc. for C$_9$H$_{13}$O$_{23}$K$_3$Cu$_3$ (**1**): C, 13.55; H, 1.63. IR peaks (KBr disk/cm^{-1}): the most important absorptions are those of the O−H stretching of the water molecules associated by hydrogen bonds (3409s,br) and the carboxylate ν_{as} (1622s,m/br) and the ν_s (1350 m) stretchings; other relevant peaks occur at are 1444 m, 1404 m, 1165 m, 1087 m, 867 m, 819 m, 701 m, 641 m and 475 m.

{(Ph$_4$P)$_2$[CoCu$_3$(Hmesox)$_3$Cl]} (2). Solid basic copper(II) carbonate (110 mg, 0.5 mmol) was added in small fractions to an aqueous solution (2 cm^3) of mesoxalic acid (136 mg, 1 mmol), allowing the CO$_2$ to evolve after the addition of each fraction. The reaction was performed at 40−50 °C in a hot plate during 10 min. When the reaction was finished the solution was filtered and diluted to 12 cm^3 by the addition of distilled water. At this point the trinuclear precursor is already formed. Cobalt(II) acetate (82 mg, 0.33 mmol) and Ph$_4$PCl (250 mg, 0.66 mmol) were added to the resulting pale blue solution under stirring. The mother liquor was allowed to evaporate on standing at room temperature. Chunky blue crystals of **2** suitable for X-ray diffraction were separated from this solution after several days. They were filtered, washed with a small amount of ethanol and diethylether, and dried under vacuum. Yield 148 mg, 32%. The yield of the reaction can be improved by increasing the evaporation time, but co-precipitation of by-side products occurred. Found: C, 49.94; H, 3.08%. Calc. for C$_{57}$H$_{43}$ClCoCu$_3$K$_3$O$_{18}$P$_2$ (**2**): C, 50.21; H, 3.15. IR peaks (KBr disk/cm^{-1}): the most intense bands are those of the tetraphenylphosphonium cation (ca. 1609, 1586, 1481, 1437, 11081, 990, 723, 690 and 528) and the carboxylate ν_{as} (1650−1550 s,br) and ν_s (1390s) stretchings.

Physical Techniques. IR spectra (400−4000 cm^{-1}) were recorded on a Bruker IF S55 spectrophotometer with the samples prepared as a KBr pellets. Magnetic susceptibility measurements

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Table 1. Crystal Data and Experimental Details for Complexes **1** and **2**

	1	**2**
formula	$C_9H_{13}O_{23}K_3Cu_3$	$C_{57}H_{43}ClCoCu_3O_{18}P_2$
M	797.03	1362.85
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a, Å	7.8804(10)	17.709(6)
b, Å	24.870(4)	17.992(12)
c, Å	10.8961(5)	18.445(11)
β, deg	94.315(7)	
V, Å³	2129.4(4)	5877(6)
Z	4	4
index ranges	$-10 \leq h \leq 5$	$-16 \leq h \leq 20$
	$-29 \leq k \leq 32$	$-20 \leq k \leq 21$
	$-14 \leq l \leq 13$	$-21 \leq l \leq 17$
T (K)	293(2)	293(2)
ρ_{calc} (Mg m^{-3})	2.455	1.540
λ (Mo–K$_\alpha$ Å)	0.71073	0.71073
μ (Mo–K$_\alpha$ mm^{-1})	3.671	1.519
R_1, $I > 2\sigma(I)$ (all)	0.0340 (0.0437)	0.0870 (0.1316)
wR_2, $I > 2\sigma(I)$ (all)	0.0796 (0.0833)	0.2243 (0.2568)
no. reflns collected	12804	24536
independent reflections (R_{int})	4634 (0.0216)	9492 (0.0744)
no. observed reflns, $F_o > 4\sigma(F_o)$	3950	6585

on polycrystalline samples were carried out by means of a Quantum Design SQUID magnetometer in the temperature range 1.9–300 K (**1** and **2**) under direct current (dc) fields of 1000 G ($T < 15$ K) and 1 T ($T > 15$ K) for **1** and 50 G ($T < 25$ K), 100 G ($T < 40$ K), and 1000 G ($T > 70$ K) for **2**. Alternating current magnetic susceptibility measurements for **2** were performed at various frequencies (1, 10, 100, and 1000 Hz) under an oscillating field of ±3 G and in the lack of static field. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants[23] as -297×10^{-6} (**1**) and -680×10^{-6} cm³ mol^{-1} (**2**) [per three copper(II) ions]. Corrections for the temperature-independent paramagnetism [60×10^{-6} cm³ mol^{-1} per copper(II) ion] and the magnetization of the sample holder were also applied.

Crystal Structure Determination. Single crystal X-ray diffraction data sets were collected at 293(2) K (**1** and **2**) on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation (0.71073 Å). Orientation matrix and lattice parameters were determined by least-squares refinement of the reflections obtained by a $\theta-\chi$ scan (Dirac/lsq method). Data collection and data reduction of **1** and **2** were performed with the COLLECT[24] and EVALCCD[25] programs. All the measured independent reflections were used in the analysis. The structures of **1** and **2** were solved by direct methods using the SHELXS97 computational program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares technique based on F^2 using SHELXL97.[26] The hydrogen atoms (except those of the water molecules) were positioned geometrically and refined with a riding model. The tetraphenylphosphonium cations in **2** are disordered and not all carbon-atoms of phenyl groups were located. These cations were modeled as rigid bodies with tetrahedral geometry [SAME and SADI] at P and phenyl groups with C–C and C–H bond lengths of 1.39 and 0.998 Å [AFIX 6 and AFIX 66 for P(1) and P(2), respectively]. Although the cell parameters and the (10,3)-a topology suggested the possibility to solve the structure in a different crystal system such as the cubic one $P2_13$, the solutions obtained after thoroughly testing were

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

Cu(1)–O(11)	1.949(2)	Cu(3)–O(5)	1.934(2)
Cu(1)–O(15)	1.937(2)	Cu(3)–O(15)	1.949(2)
Cu(1)–O(1w)	2.345(3)	Cu(3)–O(1w)	2.592(3)
Cu(2)–O(5)	1.909(2)		
Cu(2)–O(11)	1.920(2)		
O(15)–Cu(1)–O(11)	97.19(9)	O(5)–Cu(3)–O(15)	97.72(10)
O(15)–Cu(1)–O(1w)	84.72(10)	O(5)–Cu(3)–O(1w)	91.27(9)
O(11)–Cu(1)–O(1w)	90.34(10)	O(15)–Cu(3)–O(1w)	77.97(10)
O(5)–Cu(2)–O(11)	93.96(9)		
Cu(1)⋯Cu(2)	3.5034(6)	Cu(1)–O(11)–Cu(2)	129.75(12)
Cu(1)⋯Cu(3)	3.1974(7)	Cu(1)–O(15)–Cu(3)	110.75(11)
Cu(2)⋯Cu(3)	3.4585(7)	Cu(1)–O(1w)–Cu(3)	80.97(10)
		Cu(2)–O(5)–Cu(3)	128.30(11)

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**

Cu(1)–O(11)	1.933(8)	Cu(3)–O(5)	1.957(7)
Cu(1)–O(15)	1.937(8)	Cu(3)–O(15)	1.948(8)
Cu(1)–Cl(1)	2.701(5)	Cu(3)–Cl(1)	2.726(5)
Cu(2)–O(5)	1.949(8)		
Cu(2)–O(11)	1.962(8)		
Cu(2)–Cl(1)	2.640(5)		
O(11)–Cu(1)–O(15)	96.7(3)	O(5)–Cu(3)–O(15)	97.6(3)
O(11)–Cu(1)–Cl(1)	84.6(3)	O(5)–Cu(3)–Cl(1)	81.8(3)
O(15)–Cu(1)–Cl(1)	83.6(3)	O(15)–Cu(3)–Cl(1)	82.8(3)
O(5)–Cu(2)–O(11)	98.2(3)	Cu(1)–Cl(1)–Cu(2)	74.78(11)
O(5)–Cu(2)–Cl(1)	84.3(2)	Cu(1)–Cl(1)–Cu(3)	74.94(11)
O(11)–Cu(2)–Cl(1)	85.8(2)	Cu(2)–Cl(1)–Cu(3)	75.62(11)
Cu(1)⋯Cu(2)	3.2455(14)	Cu(1)–O(11)–Cu(2)	112.8(4)
Cu(1)⋯Cu(3)	3.3025(9)	Cu(1)–O(15)–Cu(3)	116.4(4)
Cu(2)⋯Cu(3)	3.2903(14)	Cu(2)–O(5)–Cu(3)	114.8(4)
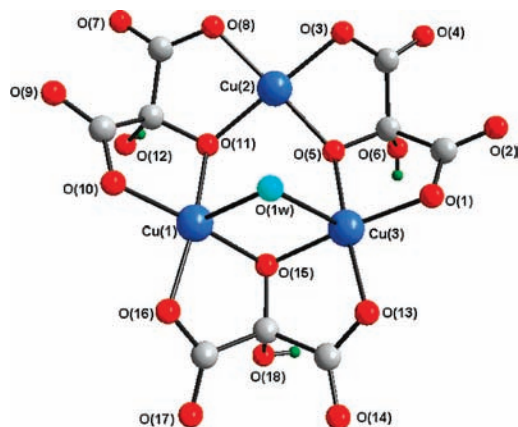
Figure 1. Molecular structure of the crystallographically independent [Cu₃(Hmesox)₃(H₂O)]³⁻ unit in **1**.

not satisfactory. Attempts to solve the structure with synchrotron radiation did not yield better results; hence, problems arise from intrinsic disorder and not from poor diffraction power. The final geometrical calculations and the graphical manipulations were carried out with the PARST97,[27] PLATON,[28] and DIAMOND[29] programs. Their crystallographic data and the details of the refinements have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 788030 and 788031, respectively. They are reported in a condensed form in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Tables 2 and 3 respectively.

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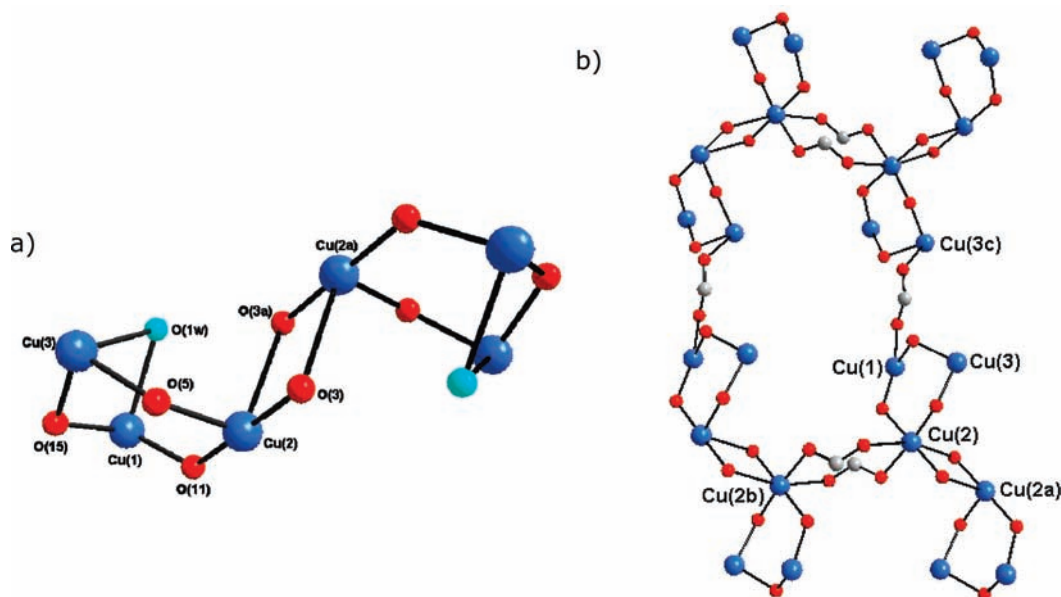
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Figure 2. Views of the core of the centrosymmetric hexacopper(II) unit of **1** (a) and of their assembling through double- and single-carboxylate bridges in the *anti-syn* conformation (b).

Results and Discussion

Description of the Structures. **K$_3$[Cu$_3$(Hmesox)$_3$(H$_2$O)]·4H$_2$O (1).** The crystal structure of **1** is made up of the crystallographically independent [Cu$_3$(Hmesox)$_3$(H$_2$O)]$^{3-}$ anions (Figure 1) and [K(H$_2$O)$_n$]$^+$ [n = 1, 2, and 3, for K(3), K(1), and K(2), respectively] cations. The tricopper(II) unit dimerizes through a double μ-oxo(carboxylate) bridge to form hexanuclear entities (Figure 2a) which are interlinked through double- (along the crystallographic a axis) and single-carboxylate (in the bc plane) bridges in the *anti-syn* conformation to afford a three-dimensional anionic network (Figures 2b and S1). The resulting channels of approximate dimensions 10×5 Å^2 are filled with aqua-bridged potassium cations as shown in Figure 3. Hydrogen-bonding among the coordinated water molecules and carboxylate-mesoxalate oxygen atoms contribute to the stabilization of the crystal structure. Oxygen atoms from the mesoxalate ligands and water molecules build distorted seven- [K(1) and K(3)] and nine-coordinated [K(2)] surroundings around the univalent potassium cations.

The three crystallographically independent copper(II) ions in **1** exhibit square pyramidal [Cu(1) with $\tau = 0.12$][30] and 4 + 2 distorted octahedral environment [Cu(3) and Cu(2) with s/h and ϕ being 1.55 and 53.3° and 1.51 and 53.4°, respectively (values to be compared to those for a ideal octahedron which are s/h = 1.22 and ϕ = 60°)].[31] The basal plane at Cu(1) is built by two alkoxo [O(11) and O(15)] and two carboxylate-oxygen atoms [O(10) and O(16)] whereas the apical position is filled by a water molecule [O(1w)]. The basal Cu(1)−O bond lengths [values varying in the range 1.923(2)−1.949(2) Å] are shorter than the apical one [Cu(1)−O(1W) = 2.345(3) Å]. Two alkoxo [O(5) and O(11) at Cu(2) and O(5) and O(15) at Cu(3)] and two carboxylate-oxygen atoms [O(3) and O(8) (Cu(2)) and O(1) and O(13) (Cu(3))] occupy the

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(31) Stiefel, E. I.; Brown, G. F. *Inorg. Chem.* **1972**, *11*, 434.

equatorial positions at the other two copper atoms whereas their axial positions are filled by two carboxylate-oxygens [O(3a) and O(7b) at Cu(2)] and a water molecule and a carboxylate-oxygen [O(1w) and O(17d) at Cu(3)]. The equatorial copper to oxygen bond distances [values in the ranges 1.909(2)−1.929(2) (Cu(2)) and 1.915(2)−1.949(2) Å (Cu(3))] are shorter than the axial ones [Cu(1)/Cu(2)−O(carboxylate) = 2.628(2)−2.689(2) Å and Cu(3)−O(1w) = 2.592(3) Å] (see Table 2). The latter axial copper to carboxylate-oxygen interactions belong to different tricopper(II) units, and they are responsible for the interlocking of these trinuclear units as above-described.

Three different hydrogenmesoxalate ligands occur in **1**, and they have in common the formation two five-membered chelates sharing the edge defined by the C−O-(alkoxo) bond carbon-edge to give an inner six-membered [Cu−O]$_3$ metallacycle with a chair conformation, very similar to that observed in tartronate and malate complexes.[17,20] The center of this metallacycle accommodates a bridging water ligand [μ-O(1w)], linking Cu(1) and Cu(3). The water molecule is 1.856(3) Å out of the plane defined by the three crystallographically independent copper atoms. The values of the copper−copper distances within the crystallographically independent tricopper(II) unit are 3.1974(7) [Cu(1)···Cu(3)], 3.4585(8) [Cu(2)···Cu(3)], and 3.5034(7) Å [Cu(1)···Cu(2)], and those of the angle at the alkoxo bridge are 129.75(12) [at O(11)], 110.75(11) [at O815)] and 128.30(11)° [at O(5)]. The values of the Cu(2)−O(3)−Cu(2a) bond angle and Cu(2)···Cu(2a) separation are 98.48(9)° and 3.5373(7) Å, respectively [symmetry code: (a) = 1−x, 1−y, −z]. Finally, the copper−copper separations through the single and double-carboxylate bridges in the *anti-syn* conformation which connect equatorial-axial positions are 5.2030(9) [Cu(2)···Cu(2b); (b) = −x, 1−y, −z]] and 5.8967(10) Å [Cu(1)···Cu(3c); (c) = x, 0.5−y, 0.5−z].

$^3_\infty${(Ph$_4$P)$_2$[CoCu$_3$(Hmesox)$_3$Cl]} (2). The crystal structure of **2** consists of PPh$_4^+$ cations and an anionic
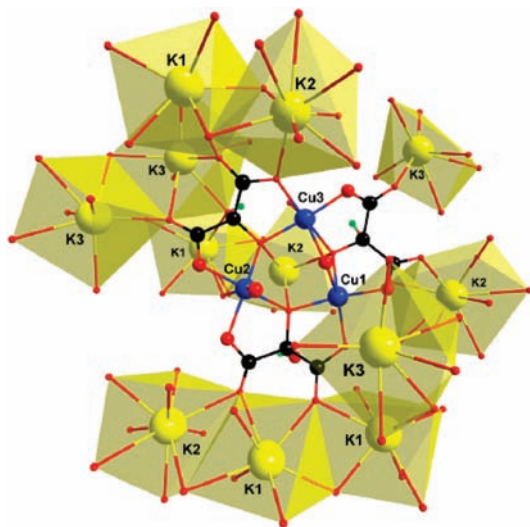
Figure 3. View of the different coordination polyhedra of the univalent potassium cations around a tricopper(II) unit in the structure of **1**.

$[CoCu_3(\mu_3\text{-Cl})(Hmesox)_3]_n^{2n-}$ three-dimensional (10,3)-a network with the cobalt(II) ions as 3-fold nodes and the $[Cu_3(Hmesox)_3(\mu_3\text{-Cl})]^{4-}$ groups as 3-fold connectors, (Figure 4) in such a way that each Co(II) is surrounded by three neighboring $[Cu_3(Hmesox)_3(\mu_3\text{-Cl})]^{4-}$ units.

The cubic (10,3)-a network is better seen in Figure 5 where the cobalt(II) ions, the $[Cu_3(\mu_3\text{-Cl})]^{5+}$ motifs and the $Hmesox^{3-}$ ligands are represented as purple spheres, green spheres, and dark blue straight lines, respectively. The anionic framework leaves chiral cavities with an available space of 4088 Å^3 per unit cell which are filled by the PPh_4^+ cations, this space corresponding to the 74% of the cell volume.[28] The phenyl groups of the cations do not display a fixed position in the network, and cannot be located. When the cations are represented only by the P atoms (yellow spheres) with P···P linkages, it results also in a (10,3)-a network which interpenetrates the anionic network (Figure 5). The P···P distance is within the 6.4218(97) to 6.6112(105) Å range. Another interesting feature of the interpenetrated anionic-cationic networks is their opposite handedness. The structural features of compound **2** are similar to other cubic (10,3)-a networks with $P2_13$ space group.[32] However, this is the first time that the tetraphenylphosphonium cation yields this type of network.

The tricopper(II) motif, $[Cu_3(\mu_3\text{-Cl})(Hmesox)_3]^{4-}$ (Figure 6), is similar to the $[Cu_3(Hmesox)_3(H_2O)]^{3-}$ entity of **1**. The $[Cu_3(Hmesox)_3(\mu_3\text{-Cl})]^{4-}$ unit shows a six-membered $[Cu-O]_3$ metallacycle with a chair conformation, the center of this metallacycle accommodating a capping Cl^- ion bridging the three Cu(II) ions. This coordination causes important structural changes in the complex-anion geometry with respect to **1**. The cyclic tricopper(II) units in **2** are centered about a pseudo-3-fold axis passing through the chloro atom, so that the three copper atoms fall at the corners of an almost equilateral triangle. The values of the Cu−Cl bond lengths and those of the Cu−Cl−Cu angles vary in the ranges 2.640(4)−2.726(5) Å and 74.78(11)−75.562(11)°, respectively. The Cu···Cu

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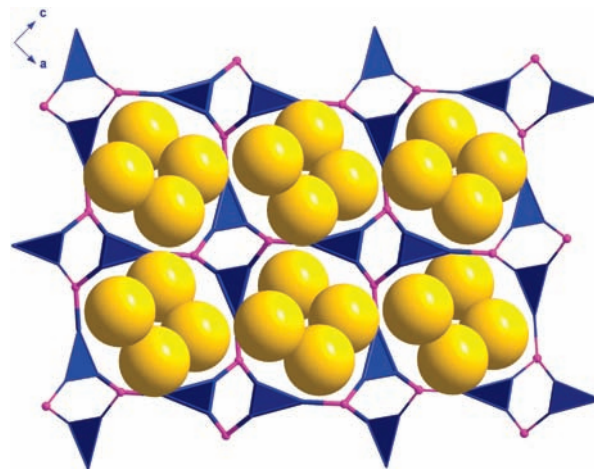

Figure 4. Perspective view of the cubic (10,3)-a anionic network with the tetraphenylphosphonium cations filling the holes in compound **2**.

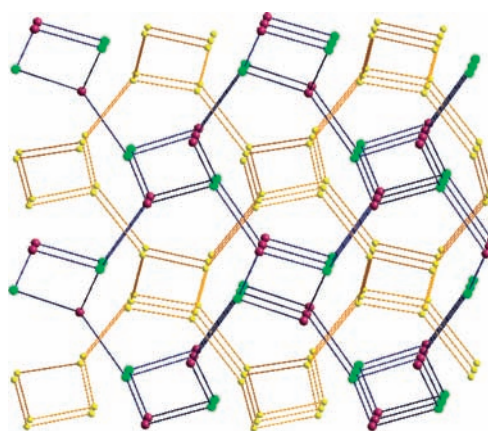**Figure 5.** Anionic and cationic interpenetrated (10,3)a networks with opposite chirality. The $[Cu_3(\mu_3\text{-Cl})]^{5+}$ motifs and the $Hmesox^{3-}$ ligands are represented as purple spheres, green spheres, and dark blue straight lines, respectively. The Ph_4P^+ cations are represented only by the P atoms (yellow spheres).

distances within the tricopper(II) unit and those of the angles at the alkoxo bridge span in the ranges 3.2455(14)−3.3025(9) Å and 112.8(4)−116.4(4)° (see Table 3)

The three crystallographically independent copper(II) ions in **2** are five-coordinated with a somewhat distorted square pyramidal environment [τ value being 0.18, 0.17, and 0.22 for Cu(1), Cu(2), and Cu(3), respectively].[30] The basal planes of the copper(II) ions are built by alkoxo- and carboxylate-hydrogenmesoxalate oxygen atoms [mean values for the Cu−O bond distances are 1.924(9) Å, 1.940(9) Å, and 1.943(9) Å for Cu(1), Cu(2), and Cu(3), respectively] whereas the apical positions are filled by a chloro atom [Cu−Cl(1) bond distance being 2.700(5), 2.641(5), and 2.727(5) Å for Cu(1), Cu(2), and Cu(3)]. In the $[Cu_3(mesox)_3Cl]^{4-}$ anionic motif, each Hmesox ligand forms two five-membered chelate rings sharing the edge defined by the carbon-alkoxo bond, as in **1**. Additionally, each hydrogenmesoxalate group of the $[Cu_3(mesox)_3(\mu_3\text{-Cl})]^{4-}$ motif acts as a bidentate ligand toward the cobalt(II) ions yielding six-membered chelate rings. The cobalt(II) ions are *tris*-chelated with a Λ-configuration in an almost perfect octahedral environment (Figure 7) [the mean Co−O bond distance and the
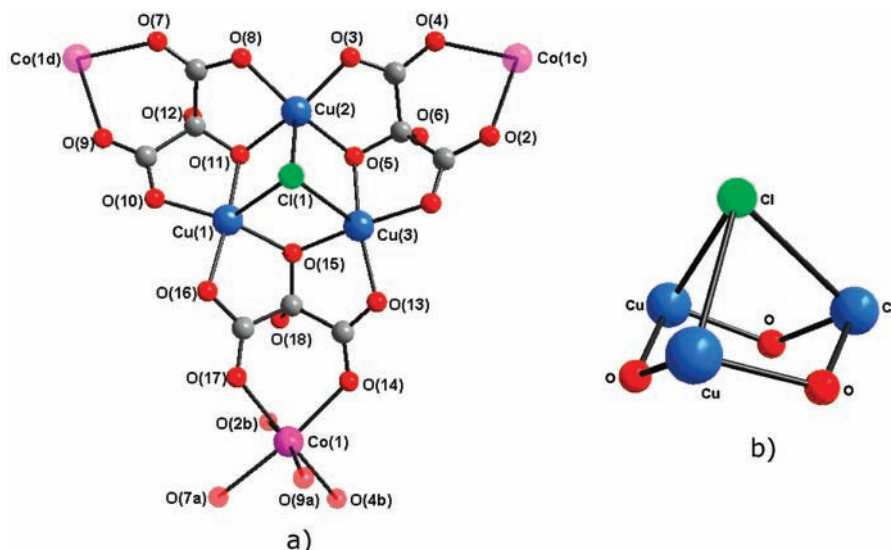
Figure 6. Perspective view of crystallographically independent unit of **2** showing the coordination modes of the Hmesox- and Cl- anions (a) and a detail of the chloro capped alkoxo-bridged six-membered $[Cu-O]_3$ metallacycle (b).
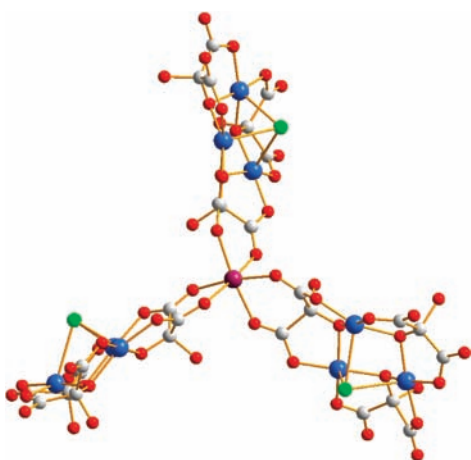

Figure 7. Chiral environment of the Co(II) ion in **2** (only one enantiomeric trischelated form at the cobalt atom occurs in **2**).
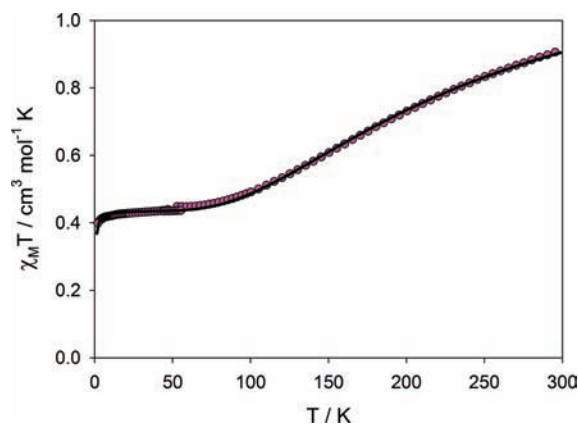

Figure 8. Thermal dependence of the $\chi_M T$ product for compound **1**. The solid line corresponds to the best fit through eq 3, see text.

O−Co−O bite angle being 2.144(10) Å and 90.1(4)°, respectively]. The particular disposition of the multidentate Hmesox ligand links two copper(II) ions with a cobalt(II) ion through two *anti-anti* carboxylate bridges, which is a very efficient magnetic exchange pathway (see the magnetic part); the shortest copper−cobalt distances are 5.733(3) [Cu(1)···Co(1)], 5.655(3) [Cu(3)···Co(1)], 5.6658(19) [Cu(2)···Co(1c)], 5.748(3) [Cu(3)···Co(1c)], 5.686(2) [Cu(1)···Co(1d)], and 5.7988(16) Å [Cu(2)···Co-(1d)] [symmetry code: (c) = 1−x, 0.5+y, 0.5−z and (d) = 0.5-x, −y, −0.5−z].

Magnetic Properties. **K₃[Cu₃(Hmesox)₃(H₂O)]·4H₂O (1).** The magnetic properties of compound **1** under the form of $\chi_M T$ versus T plot [χ_M is the magnetic susceptibility per three copper(II) ions] are shown in Figure 8. At room temperature, $\chi_M T$ is 0.92 cm³ mol⁻¹ K, a value which is lower than that expected for three magnetically isolated Cu(II) ions [$\chi_M T = 3(N\beta^2 g^2/3kT) S(S+1) = 1.24$ cm³ mol⁻¹ K with $g = 2.1$ and $S = 1/2$]. Upon cooling, $\chi_M T$ continuously decreases reaching a plateau with a value of 0.48 cm³ mol⁻¹ K in the temperature range 65−5 K. This plateau would correspond to a low-lying spin doublet from the antiferromagnetically

coupled triangular $[Cu_3(Hmesox)_3(H_2O)]^{3-}$ unit shown in Figure 1. The slight decrease of $\chi_M T$ which occurs at $T < 5$ K is most likely due to antiferromagnetic interactions among the tricopper(II) entities.

Having in mind the isosceles triangle corresponding to the tricopper(II) core of **1** (C_{2v} point-group symmetry), we propose the following isotropic spin Hamiltonian to account for its magnetic coupling pattern [eq 1]
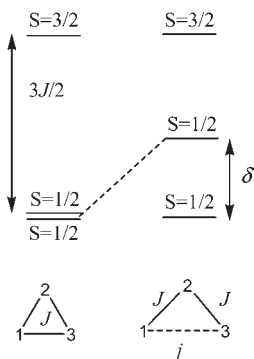
$$\hat{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3) - j(\hat{S}_1 \cdot \hat{S}_3) \qquad (1)$$

The corresponding eigenvalues are given by eq 2

$$E(S_U, S_A) = \frac{-J}{2}[S_U(S_U + 1) - \sum_{i=1}^{3} S_i(S_i + 1)]$$

$$- \frac{\delta}{2}[S_A(S_A + 1) - \sum_{i=1}^{3} S_i(S_i + 1)] \qquad (2)$$

with $S_1 = S_2 = S_3 = 1/2$, $S_A = S_1 + S_3$, $S_U = S_2 + S_A$ and $\delta = J - j$. The splitting of the energy levels and their spin states are illustrated by Scheme 3.

Scheme 3. Energy Levels for Equilateral (left) and Isosceles (right) Triangle Systems ($\delta = J - j$)
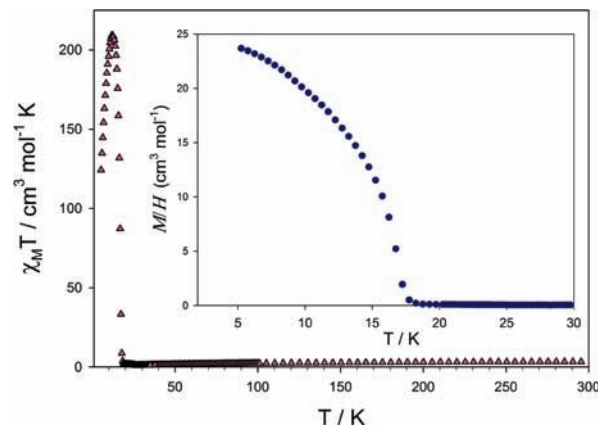

Figure 9. Thermal dependence of the $\chi_M T$ product for **2**. The inset shows the field-cooled magnetization (FCM) in the low temperature domain.

The total spin, S_U yields two spin doublets with different spin intermediate $S_A = 1$ and 0, and a spin quartet. The ground and first excited states are the spin doublets, and the energy gap between them corresponds to δ. The application of the Zeeman term and the Van Vleck's approach to these energy levels give the well-known analytical expression for the magnetic susceptibility [eq 3]:[14c,18,19]

$$\chi = \frac{N\beta^2 g^2}{4k(T - \Theta)} \left[\frac{1 + \exp\dfrac{\delta}{kT} + 10\exp\dfrac{3J}{kT}}{1 + \exp\dfrac{\delta}{kT} + 2\exp\dfrac{3J}{kT}} \right] \quad (3)$$

where N, β, and k have their usual meaning and g is the average Landé factor. At low temperatures, a magnetically isolated tricopper(II) unit would follow the Curie law for a spin doublet. However, the slight decrease of $\chi_M T$ for **1** in the very low temperature domain shows that antiferromagnetic interactions take place among the trinuclear units. Consequently, a Curie−Weiss term (Θ) was introduced in eq 3 to account for them. Most likely, the exchange pathway for these interactions is provided by the long μ-oxo bridges that connects each trinuclear unit with its symmetry-related through the inversion center, as described above. Least-squares best-fit parameters for **1** through eq 3 are as follows: $J = -194(1)$ cm^{-1}, $j = -3(4)$ cm^{-1}, $g = 2.20(1)$, $\theta = -0.20(1)$ K, and $R = 3.44 \times 10^{-4}$ (R is the agreement factor defined as $\sum_i[(\chi_M T)^{exp}_i - (\chi_M T)^{calc}_i]^2/\sum_i[(\chi_M T)^{exp}_i]^2$). The calculated curve (solid line in Figure 8) matches very well the experimental data in the whole temperature range. The isotropic model in **1** is good enough to account for its magnetic behavior in the whole temperature range, and other magnetic phenomena such as the antisymmetric exchange are not observed.

The magnitude and sign of exchange coupling in hydroxo- and alkoxo-bridged dicopper(II) complexes is strongly dependent on structural factors such as the copper−copper distance and the angle at the hydroxo/alkoxo bridgehead. Strong antiferromagnetic coupling is observed for large Cu−O−Cu angles and long Cu···Cu distances, whereas ferromagnetic coupling is favored for small Cu−O−Cu bond angles that usually imply shorter Cu···Cu distances.[33,34] In compound **1**, there are two

relatively long Cu···Cu distances [mean value 3.481(7) Å for Cu(1)−Cu(2) and Cu(2)−Cu(3)] with an average Cu−O−Cu angle of 129.03(12)°. On the basis of previous studies,[17] the strong antiferromagnetic coupling for **1** [$J = -194(1)$ cm^{-1}] would be mediated by this exchange pathway. Also in agreement with the literature data,[35,36] a weaker antiferromagnetic coupling would be expected for the exchange pathway constituted by Cu(1)−O(15)−Cu(3) and Cu(1)−O(1w)−Cu(3) with values at O(15) and O(1w) bridgeheads of 110.75(11) and 80.57(10)°, respectively.

$^3_\infty${(**Ph₄P**)₂[**CoCu₃(Hmesox)₃Cl**]} (**2**). The magnetic properties of compound **2** under the form of $\chi_M T$ versus T plot are shown in Figure 9 [χ_M is the magnetic susceptibility per Cu^{II}₃Co^{II} unit]. At room temperature, $\chi_M T$ is 3.41 cm^3 mol^{-1} K, a value which is lower than the expected for a high-spin Co(II) and three uncoupled Cu(II) ions. One can expect χT values around 2.5−3.5 cm^3 mol^{-1} K for a Co(II) ion and about 1.2 cm^3 mol^{-1} K for three magnetically non-interacting Cu(II) ions.[23,37] Then, the observed value of $\chi_M T$, already implies a certain degree of antiferromagnetic coupling between the spin carriers. It deserves to be noted that the core of the Cu(II) ions in the trinuclear unit of **2** is not identical to that of **1**. Upon cooling, $\chi_M T$ continuously decreases reaching a minimum value of 0.93 cm^3 mol^{-1} K at 26 K. This decrease is too important to be explained only in terms of a spin−orbit-coupling of the Co(II) and the magnetic interactions within the tricopper(II) unit.[37] Thus, the antiferromagnetic nature of the coupling is confirmed in the high temperature domain. $\chi_M T$ sharply increases below 26 K to reach a value of 209 cm^3 mol^{-1} K at 12 K and further it linearly decreases to 130 cm^3 mol^{-1} K at 2 K. These features suggest a predominant antiferromagnetic coupling between the Co(II) and the Cu(II) ions that leads to a long-range ferrimagnetic ordering below a critical temperature. However, χ_M does not exhibit any maximum in the whole temperature range studied, under our experimental conditions.

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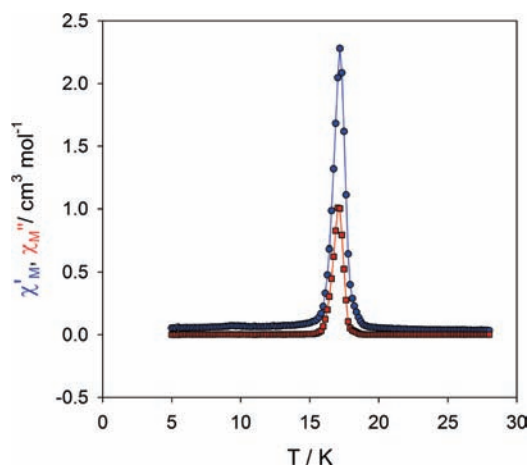
Figure 10. Thermal dependence of the in-phase and out-of-phase magnetic susceptibilities for **2**.
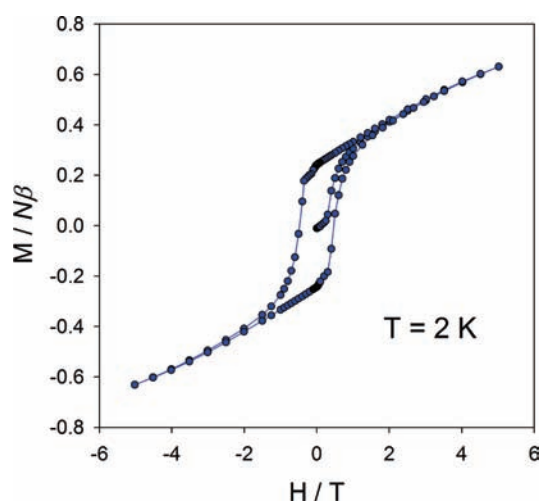

Figure 11. Field dependence of the magnetization of **2** at 2 K.

The long-range magnetic ordering is also observed from the FCM plot under an applied field of 50 G that shows an abrupt increase below 18.5 K, indicating the onset of the long-range phase transition (see inset in Figure 9). The critical temperature of the ferrimagnetic ordering is confirmed by the out-of-phase susceptibility plot that exhibits a sharp peak with a maximum value at $T = 17.2$ K (Figure 10). The fact that the alternating current (ac) susceptibility is not frequency dependent for **2** rules out the occurrence of the spin-glass behavior for this compound. The magnetization versus H plot at 2 K (Figure 11) exhibits the characteristic shape of a ferri-magnetically ordered system (sigmoidal shaped curve) and a very large coercive field [$H_c = 5000$ G].

The magnetic behavior of **2** is in agreement with the chemical nature of the paramagnetic species, the adequate orientation of the μ-oxo and carboxylate bridges of the hydrogenmesoxalate ligand and with its three-dimensional (3D) structure. At high temperatures the magnetic properties are dominated by the spin–orbit-coupling of the cobalt(II)[37a] ion and the antiferromagnetic coupling between the copper(II) ions through the μ-alkoxo group. At lower temperatures the antiferromagnetic coupling between the cobalt(II) and the copper(II) ions through the *anti-anti* carboxylate bridge are propagated along the

3D structure and lead to the long-range ferrimagnetic ordering.[38,39] The mechanism of the antiferromagnetic coupling through the *anti-anti* carboxylate bridge between cobalt(II) and copper(II) is expected to be similar to that through the oxamato bridge,[4g,40−42] which is explained in terms of the overlap between the magnetic orbitals of the spin carriers with those of the bridge. The strong covalent bonds and the configuration of the oxamate bridge favor the electronic delocalization and a relatively strong antiferromagnetic coupling takes place. However, the lower donor character of the hydrogenmesoxalate ligand and the deviations from the planarity of the trinuclear unit leads to a slightly weaker magnetic interaction, and the critical temperature is somewhat lower than those observed in the oxamato-bridged heterobimetallic Co(II)−Cu(II) compounds. The magnetic ordering is then as expected from the antiferromagnetic coupling and the 3D structure of **2**.

Conclusions

α-Hydroxycarboxylate ligands afford copper(II) trinuclear species in which the copper(II) ions are bridged by μ-oxo(carboxylate) groups. The tartronate derivatives give rise to trinuclear species in which the carboxylate groups have a very suitable configuration to join other metallic ions to yield high dimensional networks. The trinuclear unit in **1** is isolated, and this allows an accurate evaluation of the exchange coupling constants and the energy gaps between the different spin states. The magnetic coupling of the copper(II) ions in the trinuclear unit is as expected from the structural features of the Cu−O−Cu bridges. The magnetic study reveals that it has a non-zero net spin in the whole temperature range. This together with its structural properties make compound **1** a potential good precursor for molecular magnetism. The magnetic properties of compound **2** confirm this hypothesis. **2** was designed to exhibit intense magnetic coupling through the *anti-anti* carboxylate groups, and it behaves as a ferrimagnet with a T_c of 18.5 K. Compound **2** represents the first example of a series of compounds with similar structure and properties. The easy exchange of the Co(II) ion in **2** by other paramagnetic 3d M(II) cations and also the use of precipitating univalent cations would lead to a new family of rationally designed heterometallic chiral magnets to be added to previously

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reported examples of chiral hetero-[43a−c] and homometallic molecule-based magnets.[43d]

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.