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Hexanuclear Copper(II) Cages Built on a Central {μ_3−O···H···μ_3−O} Moiety, 1,3-Bis(dimethylamino)-2-propanolato and Capping R-phosphonates: Crystal Structures, Magnetic Behavior, and DFT Studies

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Supporting Information

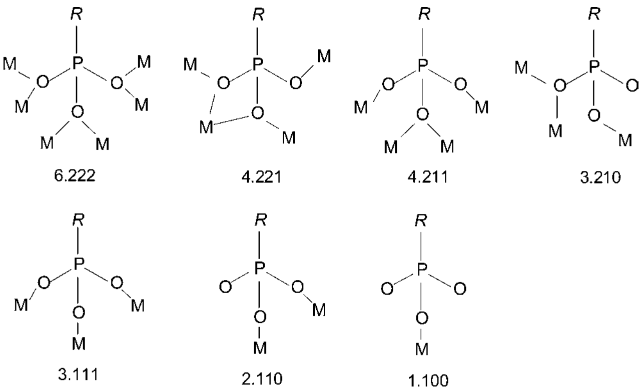
ABSTRACT: The syntheses, structural characterization, and magnetic behavior of two new hexanuclear copper(II) complexes derived from R-phosphonic acids and 1,3-bis(dimethylamino)-2-propanol (Hbdmap) with formulas [Cu_6(μ-bdmap)$_3$(μ_3-*Ph*-PO_3)$_2$(μ_3−O···H···μ_3−O)(ClO_4)$_2$(H_2O)]·5H_2O (**1**) and [Cu_6(μ-bdmap)$_3$(μ_3-*t-Bu*-PO_3)$_2$(μ_3−O···H···μ_3−O)($\mu_{1,3}$-dca)(dca)(H_2O)]·6H_2O (**2**) (*Ph*-H_2PO_3 = phenylphosphonic acid, *t-Bu*-H_2PO_3 = *tert*-butylphosphonic acid, dca = dicyanamide) are reported. Compounds **1** and **2** are hexanuclear 3.111 *R*-phosphonate(2-)/1,3-bis(dimethylamino)-2-propanolato(1-) cages including in the center the [μ_3−O···H···μ_3−O]$^{3-}$ unit. The temperature dependence of the magnetic properties of **1** and **2** clearly indicates an overall strong antiferromagnetic coupling confirmed by DFT calculations.

■ INTRODUCTION

The organophosphonate ligands, R-HPO_3^- and R-PO_3^{2-} (where R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$, C_6H_5, ...) can generate polymeric transition-metal compounds with extended layered and pillared structures. From the synthetic point of view, the described compounds are usually insoluble in the most common solvents, and to obtain single crystals suitable for the X-ray structural determination, it is often necessary to use solvatothermal reactions.[1−11] However, using organophosphonates that bear a bulky R group in combination with ancillary ligands such as pyrazoles and pyridines, it is possible to prepare discrete transition-metal organophosphonate derivatives.[11−34] A good example are the anionic derivatives of the *tert*-butylphosphonic acid, *t-Bu*-HPO_3^- and *t-Bu*-PO_3^{2-}, which have been used as ligands with transition metals to obtain several types of polynuclear compounds with different metals and variable nuclearities:[25−34] Cu_{12}, Co_{12}, Cu_{10}, Cu_4, Co_4, Mn_5, Mn_4, Fe_4, Fe_{10}, Mn_{20}. The R-HPO_3^- and R-PO_3^{2-} ligands show different coordination modes in this series of polynuclear compounds.[1−34] The common ones with Harris notation are reported in Scheme 1.[35]

On the other hand, the aminoalcohols 1,3-bis(dimethylamino)-2-propanol (Hbdmap) and 1,3-bis(amino)-2-propanol (Hbdap) can generate, after deprotonation, the anionic polytopic ligands 1,3-bis(dimethylamino)-2-propanolato (bdmap) and 1,3-bis(amino)-2-propanolato (bdap), respectively, which contain anchoring N-donor atoms and alkoxo units able to act as a bridge between two or three cations. The compounds bdmap and bdap have been widely used to generate high nuclearity compounds.[36−52] The analysis of the structures reported to date shows that bdmap and bdap can use several coordination modes.[49−52] The most common coordination mode of these ligands is shown in Scheme 2. We can suppose that this dinuclear [Cu_2L]$^{3+}$ entity (L= μ-bdmap or μ-bdap) is formed when the corresponding aminoalcohol and the copper(II) salt are mixed in basic aqueous or alcoholic media. Each dinuclear [Cu_2L]$^{3+}$ entity (*complex as metal*) has still other

Scheme 1. Different Coordination Modes with Harris Notation of Phosphonic Acid Derivatives[a]



[a]R= phenyl, *tert*-butyl.

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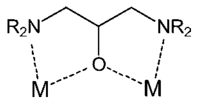
Scheme 2. Most Common Coordination Mode of 1,3-Bis(R-amino)2-propanolato (R = CH_3, H)



free coordination positions (temporally occupied by solvent or counteranion labile ligands) that can be used by means of the appropriate ligands to prepare new polynuclear compounds through the "*complex as metal approach*".[49] In several recent works,[50−52] we have used this approach to prepare large list of compounds that possess the dinuclear $[Cu_2L]^{3+}$ structural unit.

The aim of this work is to combine R-phosphonic acids and 1,3-bis(dimethylamino)-2-propanol with copper(II) salts in a basic medium in order to create synergies in the form of new polynuclear compounds in which anionic bridging derivatives of the *R*-phosphonic acids, *R*-HPO_3^{-} and *R*-PO_3^{2-}, and also anionic bridging derivatives of the polytopic ligand 1,3-bis(dimethylamino)-2-propanolato (bdmap) coexist. As a result of this synthetic strategy, we have obtained two new copper(II) complexes: the hexanuclear cages with formulas $[Cu_6(\mu\text{-bdmap})_3(\mu_3\text{-}Ph\text{-}PO_3)_2(\mu_3{-}O\cdots H\cdots\mu_3{-}O)(ClO_4)_2(H_2O)]\cdot 5H_2O$ (**1**) and $[Cu_6(\mu\text{-bdmap})_3(\mu_3\text{-}t\text{-}Bu\text{-}PO_3)_2(\mu_3{-}O\cdots H\cdots\mu_3{-}O)(\mu_{1,3}\text{-dca})(dca)(H_2O)]\cdot 6H_2O$ (**2**). (Hbdmap = 1,3-bis(dimethylamino)-2-propanol, *Ph*-H_2PO_3 = phenylphosphonic acid, *t-Bu*-H_2PO_3 = *tert*-butylphosphonic acid, dca = dicyanamide.) To the best of our knowledge, **1** and **2** are the first examples of discrete hexanuclear copper(II) cages with the $[Cu_3O\cdots H\cdots OCu_3]$ motif built from other ligands different than oximate.[53−58] Herein, we report the structural characterization, the magnetic behavior, and DFT calculations of the two compounds.

■ EXPERIMENTAL SECTION

Starting Materials. Copper(II) perchlorate hexahydrate, copper(II) hydroxide, sodium dicyanamide, 1,3-bis(dimethylamino)-2-propanol, phenylphosphonic acid, and *tert*-butylphosphonic acid (Aldrich) were used as obtained.

[***Caution***: Although no incidents were recorded in this study, perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.]

Spectral and Magnetic Measurements. Infrared spectra (4000−400 cm^{-1}) were recorded from KBr pellets on a Perkin−Elmer Model 380-B spectrophotometer. Magnetic susceptibility measurements were performed under magnetic fields of 0.1 and 0.05 T in the temperature range of 2−300 K (field of ~500 G (2−30 K) and ~1000 G (35−300 K) and magnetization measurements were performed in the field range of 0−5 T with a Quantum Design MPMS-XL SQUID magnetometer at the Magnetic Measurements Unit of the University of Barcelona. All measurements were performed on polycrystalline samples. Pascal's constants were used to estimate the diamagnetic corrections,[59] which were subtracted from the experimental susceptibilities to give the corrected molar magnetic susceptibilities.

Synthesis of $[Cu_6(\mu\text{-bdmap})_3(\mu_3\text{-}Ph\text{-}PO_3)_2(\mu_3{-}O\cdots H\cdots\mu_3{-}O)(ClO_4)_2(H_2O)]\cdot 5H_2O$ (1). To 30 mL of an aqueous solution of 1.35 mmol of $Cu(ClO_4)_2$ (502 mg) was added 0.71 mmol of Hbdmap (104 mg), 10 mL of an aqueous solution of 0.70 mmol of phenylphosphonic acid (111 mg), and 2.70 mmol of NaOH (108 mg). The resulting solution was stirred for several hours and filtered, and after a few days of slow evaporation, compound **1** was obtained as blue hexagonal crystals.

Synthesis of $[Cu_6(\mu\text{-bdmap})_3(\mu_3\text{-}t\text{-}Bu\text{-}PO_3)_2(\mu_3{-}O\cdots H\cdots\mu_3{-}O)(\mu_{1,3}\text{-dca})(dca)(H_2O)]\cdot 6H_2O$ (2). To a methanolic solution of $Cu(OH)_2$ and *tert*-butylphosphonic acid was added 0.73 mmol of Hbdmap (107 mg) in 5 mL of water and 0.69 mmol of $NaN(CN)_2$ (61 mg) in 3 mL of water. After stirring for a few hours, the resulting solution is filtered and after two weeks of slow evaporation, compound **2** was obtained as blue sheets.

Infrared (IR) Spectra and Analytical Data. In both spectra, we can observe the vibrations for the bdmap ligand; μ-bdmap (ν_{C-H} and δ_{CH_2}) between 2800 and 3000 cm^{-1} and a band close to 1470 cm^{-1}. In addition to these bands in the infrared (IR) spectra of **1**, we can also observe the band corresponding to the perchlorate anion at 1120 and 1090 cm^{-1} (ν_3) and 625 cm^{-1} (ν_4). Compound **2** exhibits a strong absorption in the 2310−2150 cm^{-1} region corresponding to the combination modes of vibration of the dca anion. These bands are characteristic of the ν_s(C−N) plus ν_{as}(C−N) and ν(C≡N) vibrations, for which the first band is diagnostic of the binding mode. In compound **2**, the first band possesses an additional satellite band at 2285 cm^{-1}. These features appear to be indicative of two different binding modes of dca anions around the Cu^{2+} ion, and are consistent with the X-ray structure in which dca was found to coordinate to copper through its cyano nitrogen atoms and also the amide nitrogen[60] and the bands corresponding to the *tert*-butylphosphonate can be observed at 2968 and 2869 cm^{-1}.

The elemental analyses (C, N, H) for the different syntheses were consistent with the product formulation: Anal.: Found for **1**: C, 28.33; H, 4.24; N, 5.84. Calcd. for $C_{33}H_{72}Cl_2Cu_6N_6O_{25}P_2$: C, 27.08; H, 4.92; N, 5.74%. Anal.: Found for **2**: C, 29.89; H, 6.13; N, 12.57. Calcd. for $C_{33}H_{81}Cu_6N_{12}O_{18}P_2$: C, 28.84; H, 5.90; N, 12.24%.

X-ray Crystallography. Data for **1** were collected on a blue block at 100 K using a single-axis HUBER diffractometer on station BM16 of the European Synchrotron Radiation Facility, Grenoble, France. Cell refinement, data reduction, and absorption corrections were done with the HKL-2000 suite.[61] The structure was solved by direct methods and the refinement and all further calculations were carried out using the SHELX-TL suite.[62] Non-hydrogen atoms were refined anisotropically, but the compound showed some strong disorder: five of the Cu atoms (Cu2, Cu3, Cu4, Cu5, and Cu6) were disordered over two positions with a 85:15 ratio, while related to this disorder, the oxygen atoms of one of the phosphonate groups (O9, O10, O11) were also disordered over two positions. In addition, most carbons of the bdmap ligands also exhibited positional disorder. For all those, displacement parameters restraints were used. Hydrogens were fixed at calculated positions on their carrier atom and refined with a riding model. Note that for the disordered C, hydrogens were thus placed only for one of the two positions, corresponding to the bdmap ligand with major occupancy. Hydrogens of the lattice water molecules and of the central hydroxo−oxo moiety were not found in difference Fourier maps and, therefore, are omitted. However, the short distances between these indicate the presence of hydrogen bonds among them.

On the other hand, to provide a structural model free of positional disorder for DFT calculations, an alternate refinement was performed; voluntarily avoiding splitting disordered atoms into partial positions. Thus, the disordered copper (Cu2, Cu3, Cu4, Cu5, and Cu6), oxygens (O9, O10, O11) and carbon atoms were simply refined with displacement parameters restraints as well as 1,2/1,3 distance restraints in the case of the bdmap central $CH_2CH(O)CH_2$ groups. The resulting alternate cif file is provided as Supporting Information.

Data for compound **2** were collected on a blue block on a Bruker APEX II CCD diffractometer on Advanced Light Source beamline 11.3.1 at Lawrence Berkeley National Laboratory, from a silicon 111 monochromator (T = 100 K, λ = 0.7749 Å). The structure was solved by direct methods and refined on F^2 using the SHELX-TL suite.[62] The crystals were found to be twinned, which was refined with TWIN/BASF. All non-hydrogen atoms were refined anisotropically. One of the ^{t}Bu groups, as well as one of the ligands, were found to be disordered over two positions, while a weakly coordinated water molecule sitting close to the Cu6 complex was also disordered over two positions (O12 and O12B). These were refined with displacement parameters restraints. Hydrogens were placed geometrically at fixed positions on their carrier atom and refined with a riding model.

Hydrogen atoms of the lattice water molecules as well as those on O12/O12B could not be found in difference maps nor fixed and are not included in the structural model. On the other hand, the hydroxyl hydrogen on the O2 atom was found in a difference Fourier map. It was refined with its thermal parameter 1.5 times that of O2 and a soft distance restraint.

Crystallographic and experimental details are summarized in Table 1. Selected bond distances and angles are given in Tables 2 and 3, while all details can be found in the supplementary crystallographic data for this paper.

Table 1. Crystal Data for Compounds (1) and (2)

property	1	2
formula	$C_{66}H_{144}Cl_4Cu_{12}N_{12}O_{50}P_4$	$C_{33}H_{81}Cu_6N_{12}O_{18}P_2$
formula weight, FW	2924.24 g/mol	1377.26 g/mol
crystal system	orthorhombic	tetragonal
space group	*Pbca*	$I4_1/a$
a	15.422(3) Å	33.4404(14) Å
b	20.250(4)	33.4404(14) Å
c	35.116(7) Å	22.3622(9) Å
α	90°	90°
β	90°	90°
γ	90°	90°
V	10967(4) $Å^3$	25007(3) $Å^3$
Z	4	16
ρ_{calc}	1.771 g/cm^3	1.462 g/cm^3
μ	2.949 mm^{-1}	2.664 mm^{-1}
T	100 K	100 K
transmission range	0.62–0.86	0.56– 0.86
unique reflections	13079	9961
parameters/restraints	790/126	735/376
$wR2\ [I > 2\sigma(I)]$	0.1606	0.1958
$R1\ [I > 2\sigma(I)]$	0.0597	0.0692
$S\ [I > 2\sigma(I)]$	1.048	1.039
*wR*2 (all data)	0.1633	0.2075
*R*1 (all data)	0.0629	0.0774
S (all data)	1.081	1.057

Table 3. Selected Bond Lengths and Bond Angles for 2

Bond Lengths (Å)			
Cu1–O3	1.932(6)	Cu4–O6	1.977(8)
Cu1–O9	1.936(6)	Cu4–N2	2.058(11)
Cu1–O1	1.950(5)	Cu5–O7	1.945(8)
Cu1–N1	2.047(9)	Cu5–O2	1.953(6)
Cu1–N7	2.450(15)	Cu5–O10	1.953(6)
Cu2–O5	1.919(7)	Cu5–N4	2.020(9)
Cu2–O1	1.938(5)	Cu5–N10	2.417(11)
Cu2–O10	1.961(6)	Cu6–O2	1.929(6)
Cu2–N3	2.041(9)	Cu6–O11	1.941(6)
Cu3–O11	1.944(6)	Cu6–O8	1.941(8)
Cu3–O1	1.946(5)	Cu6–N6	2.024(10)
Cu3–O4	1.963(6)	O1–O2	2.417(5)
Cu3–N5	2.070(11)	O1–H2	1.46(3)
Cu4–O9	1.942(6)	O2–H2	1.00(2)
Cu4–O2	1.948(6)		
Bond Angles (deg)			
∠Cu2–O1–Cu3	115.4(2)	∠Cu4–O2–Cu5	112.0(3)
∠Cu2–O1–Cu1	115.8(2)	∠Cu1–O9–Cu4	137.1(3)
∠Cu3–O1–Cu1	105.8(2)	∠Cu5–O10–Cu2	136.0(3)
∠Cu6–O2–Cu4	112.4(3)	∠Cu6–O11–Cu3	136.9(3)
∠Cu6–O2–Cu5	110.8(3)		

■ RESULTS AND DISCUSSION

Description of the Structures. *$[Cu_6(\mu\text{-}bdmap)_3(\mu_3\text{–}Ph\text{-}PO_3)_2(\mu_3\text{–}O\cdots H\cdots\mu_3\text{–}O)(ClO_4)_2(H_2O)]\cdot 5H_2O$ (**1**).* The atom numbering scheme of 1 is depicted in Figure 1, and relevant bond parameters are collected in Table 2. Compound **1** is a hexanuclear cage compound which can be considered as being built from three $[Cu_2(bdmap)]^{2+}$ units (Scheme 2) maintained together through two μ_3–*Ph*-PO_3^{2-} [3.111] bridging ligands (Scheme 1). Each μ_3-*Ph*-PO_3^{2-} ligand acts as a bridge of three Cu atoms of the three different $[Cu_2(bdmap)]^{2+}$ dinuclear units, closing the cage. In the center of the cage is placed one $[\mu_3\text{–}O\cdots H\cdots\mu_3\text{–}O]^{3-}$ unit. Each O^{2-} ligand of the $[\mu_3$–

Table 2. Selected Bond Lengths and Bond Angles for 1

Bond Lengths (Å)			
Cu1–O3	1.939(3)	Cu4–O10	1.975(3)
Cu1–O1	1.946(3)	Cu4–N4	2.025(4)
Cu1–O6	1.951(3)	Cu4–O17	2.548(5)
Cu1–N1	2.029(3)	Cu5–O1	1.934(3)
Cu1–O12	2.557(5)	Cu5–O5	1.945(3)
Cu2–O2	1.932(3)	Cu5–O8	1.973(3)
Cu2–O3	1.950(3)	Cu5–N5	2.034(4)
Cu2–O9	1.981(4)	Cu5–O17	2.604(6)
Cu2–N2	2.041(4)	Cu6–O5	1.941(3)
Cu3–O1	1.927(3)	Cu6–O2	1.952(3)
Cu3–O7	1.946(3)	Cu6–O11	1.963(3)
Cu3–O4	1.947(3)	Cu6–N6	2.029(4)
Cu3–N3	2.003(4)	Cu6–O13	2.486(5)
Cu4–O2	1.941(3)	Cu6–O6W	2.490(6)
Cu4–O4	1.971(3)	O1–O2	2.408(7)
Bond Angles (deg)			
∠Cu3–O1–Cu1	107.99(13)	∠Cu4–O2–Cu6	112.00(13)
∠Cu5–O1–Cu1	110.98(13)	∠Cu1–O3–Cu2	135.25(15)
∠Cu3–O1–Cu5	114.93(14)	∠Cu3–O4–Cu4	135.69(15)
∠Cu2–O2–Cu4	111.18(13)	∠Cu6–O5–Cu5	136.12(15)
∠Cu2–O2–Cu6	113.63(14)		

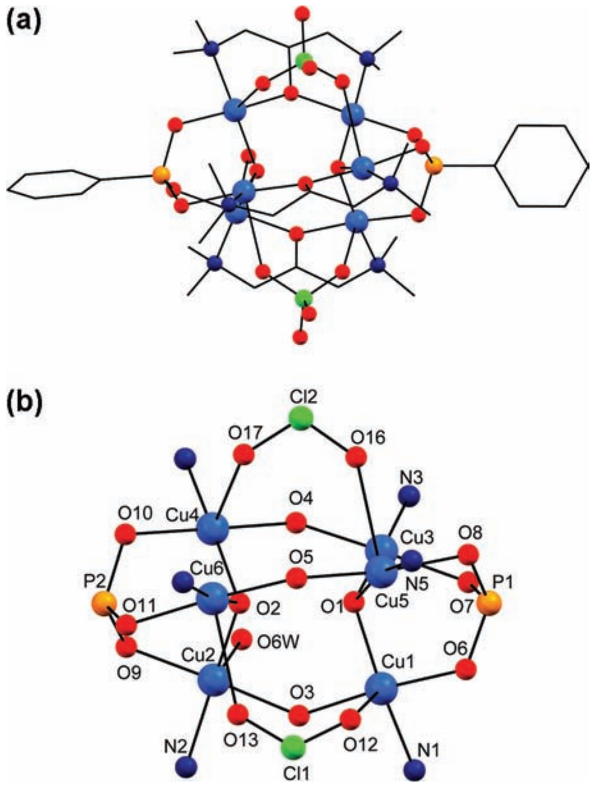


Figure 1. (a) Structural representation of complex **1**. Disordered hydrogen atoms and lattice water molecules are omitted for clarity. (b) Structural representation with atoms numbering scheme of the hexanuclear core in **1**.

$O\cdots H\cdots\mu_3–O]^{3-}$ unit acts also as a bridge between three Cu atoms of the three different $[Cu_2(bdmap)]^{2+}$ dinuclear units, forming triangular $[\mu_3–O–Cu_3]^{4+}$ entities. The cage skeleton of compound **1** is shown in Figure 1b. The distance between the central μ_3–O atoms is 2.408 Å. This distance is comparable to the O···O distances in the range of 2.428−2.517 Å found in the reported hexanuclear copper(II) cages with the $[Cu_3–O\cdots H\cdots O–Cu_3]$ motif built from oximate ligands.[53−58] Additional evidence for the existence of this bridging proton is the fact that there are two perchlorate ligands in the asymmetric unit and so to achieve charge balance the charge of the hexanuclear unit must be 2+. Each of the perchlorate anions acts as a bridging ligand between two copper atoms occuping axial positions in the distorted square-planar polyhedra of the Cu atoms. The Cu−O(perchlorate) distances are 2.557, 2.548, 2.604, and 2.486 Å for Cu1−O12, Cu4−O17, Cu5−O16, and Cu6−O13, respectively. The structure has also one water molecule coordinated to Cu2 in the axial position. The Cu2−O6(W) distance is 2.490 Å. The Cu···Cu distances in the $[Cu_2(bdmap)]^{2+}$ dinuclear units are in the 3.596−3.629 Å range. The Cu···Cu distances in the triangular $[\mu_3\text{-O-}Cu_3]^{4-}$ units are in the 3.133−3.255 Å range for the triangle formed by Cu1−Cu3−Cu5 and in the range of 3.195−3.250 Å for the triangle formed by Cu2−Cu4−Cu6. The Addison parameter (τ) values[63] for the distorted square pyramids polyhedra around Cu1, Cu2, Cu4, Cu5, and Cu6 is: 0.18, 0.06, 0.05, 0.09, and 0.02, respectively. For Cu3, the coordination can be described as distorted square-planar. The Cu−O distances are in the 1.92−2.311 Å range, and the Cu−N distances are in the 2.02−2.03 Å range. In compound **1**, there are five different Cu−O−Cu angles, ranging from 104.8° to 114.6° for the oxo μ-bdmap and varying between 135.0° and 136.9° for μ_3–O^{2-}. Taking into account the least-squares planes for each Cu_3 triangle, the bridging μ_3-oxygen atoms O1 and O2 are displaced by 0.584 and 0.552 Å from these planes. These two planes are approximately parallel, intersecting at 0.6°. The Cu_3O units are staggered (see Figure S1 in the Supporting Information). The bond distances and angles for the phenylphosphonate anion are similar to those reported in the literature. Each [Cu6] complex is connected to three neighbors through a network of intermolecular hydrogen bonds involving the phosphonate O8, O9, and O11 and the perchlorate O16 oxygens and lattice water molecules (see Figure S2 in the Supporting Information). The phenyl ring only has weak C−H···py contacts with a bdmap methyl group from a neighboring complex. The resulting shortest intercomplex Cu···Cu separations amount to 9.607, 10.742, and 11.894 Å.

$[Cu_6(\mu\text{-bdmap})_3(\mu_3\text{–}t\text{-Bu-PO}_3)_2(\mu_3\text{-O}\cdots\text{H}\cdots\mu_3\text{–O})(\mu_{1,3}\text{-dca})(\text{dca})(\text{H}_2\text{O})]\cdot 6\text{H}_2\text{O}$ (**2**). A perspective view of compound **2**, together with the atom numbering scheme, is presented in Figure 2. Selected bond distances and angles are listed in Table 3. Compound **2** is a hexanuclear cage compound with similar structure as **1**. The distance between the central μ_3 oxygen atoms is 2.417 Å, which is also shorter but comparable to the O···O distances (in the range 2.428−2.517 Å) found in the hexanuclear copper(II) cages with the $[Cu_3–O\cdots H\cdots O–Cu_3]$ motif built from oximate ligands.[53−58] Additional evidence for

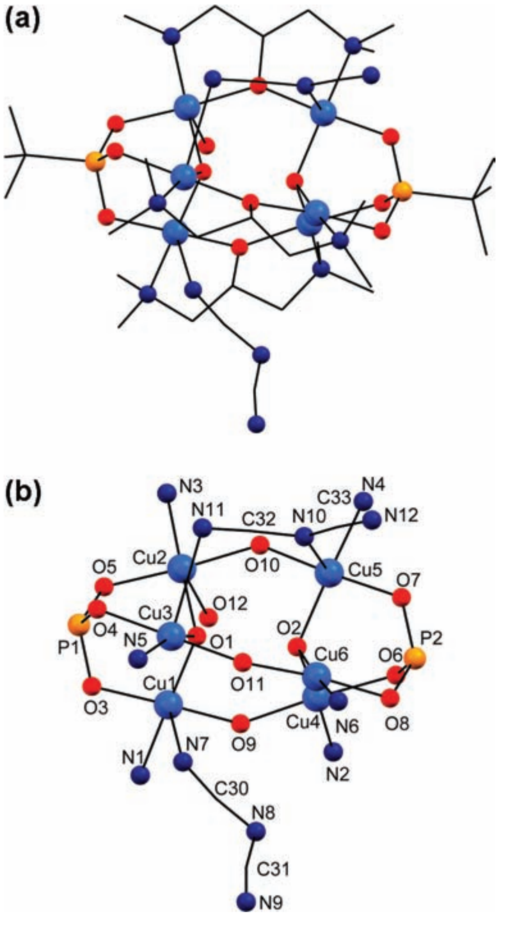


Figure 2. (a) Structural representation of complex **2**. Hydrogen atoms and lattice water molecules are omitted for clarity. (b) Structural representation with the atom numbering scheme of the hexanuclear core in **2**.

the existence of this bridging proton is the fact that there are two dicyanamide ligands in the asymmetric unit and so the charge of the hexanuclear unit must be 2+. The cage skeleton of compound **2** is shown in Figure 2b. One of the dicyanamide anions acts as bridging ligand between two copper atoms by using the $\mu_{1,3}$ coordination mode of the dicyanamide ligand occuping axial positions in the distorted square-planar polyhedra of the copper atoms Cu3 and Cu5. The other dicyanamide anion acts as a terminal ligand, occupying also the axial position in the distorted square-planar polyhedron of the Cu1 atom. The Cu−N(dicyanamide) distances are 2.450, 2.726, and 2.415 Å for Cu1−N7, Cu3−N11, and Cu5−N10, respectively. The structure has also one water molecule coordinated to Cu2 in the axial position. The Cu2−O12 distance is 2.609 Å. The Cu···Cu distances in the $[Cu_2(bdmap)]^{2+}$ dinuclear units are in the 3.610−3.630 Å range. The Cu···Cu distances in the triangular $[\mu_3{-}O{-}Cu_3]^{4-}$ units are in the 3.196−3.233 Å range for the triangle formed by Cu1−Cu2−Cu3 and in the range 3.107−3.294 Å for the triangle formed by Cu4−Cu5−Cu6. The Addison parameter (τ)[63] for the distorted square pyramide polyhedra around Cu1, Cu2, Cu3, and Cu5 is 0.12, 0.0, 0.19, and 0.13, respectively. For Cu4 and Cu6, the coordination can be described as distorted square-planar. The Cu−O distances are in the 1.922−2.311 Å range, and the Cu−N distances are in the 2.023−2.035 Å range. In compound **2**, there are five different Cu−O−Cu angles in the 104.83(10)°−114.58(9)° range for the oxo μ-bdmap and in the 135.05°−136.94° range for $\mu_3{-}O^{2-}$. Taking into account the least-squares planes for each Cu_3 triangle, the bridging μ_3−oxygen atoms O1 and O2 are displaced by 0.548 and 0.572 Å from these planes. These two planes are approximately parallel, intersecting at 1.09°. The Cu_3O units are staggered (see Figure S3 in the Supporting Information). The bond distances and angles for the *tert*-butylphosphonate anion are in accordance with the literature. Each [Cu6] complex is connected to four neighbors through a network of intermolecular hydrogen bonds involving the phosphonate O4, O5, and O6 oxygens, O12, the dicyanamide N11 and N12 nitrogens, and lattice water molecules (see Figure S4 in the Supporting Information). The resulting shortest intercomplex Cu···Cu separations amount to 8.383 and 8.796 Å.

Magnetic Study. Compounds **1** and **2** show $\chi_M T$ values for hexanuclear unit of 1.040 and 1.368 $cm^3\ mol^{-1}$ K, respectively, at 300 K, which are smaller values than that expected for six uncoupled $S = {}^1/_2$ ions with $g = 2.0$ (2.25 $cm^3\ mol^{-1}$ K). On cooling, $\chi_M T$ decreases quickly, reaching a diamagnetic plateau below ca. 100 K for **1** and ca. 85 K for **2**, indicating a very strong antiferromagnetic coupling (see Figure 3). At 300 K, the χ_M shows a maximum of 3.47 × 10^{-3} $cm^3\ mol^{-1}$ for **1** and 3.89 × 10^{-3} $cm^3\ mol^{-1}$ for **2**, then decreases, reaching a diamagnetic plateau below ca. 100 K (1.97 × 10^{-4} $cm^3\ mol^{-1}$) for **1** and ca. 85 K (1.82 × 10^{-4} $cm^3\ mol^{-1}$) for **2**.

Taking into account the similar structural topology in the two compounds, we can count 15 exchange pathways grouped into three averaged different exchange parameters, J_1, J_2 and J_3, corresponding to (i) three interactions through double-bridge bdmap ligand and hydrogen bond (between ex. Cu3···Cu6), (ii) six interactions through double bridge μ_3−O and a O−P−O fragment of the phosphonate anion (ex. Cu1···Cu3), and (iii) six intramolecular interactions through hydrogen bond (O···H−O) (ex. Cu1···Cu6) sets, respectively (see Figure 4). The possible exchange pathways through ClO_4^- anions in **1** or dca anions in **2** have not been considered since the distances

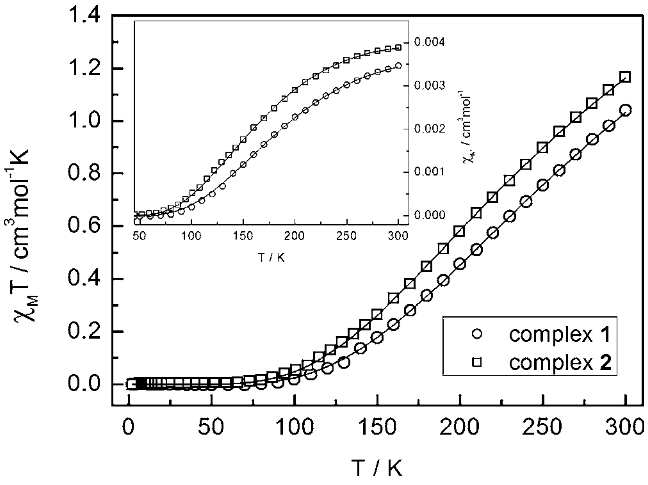


Figure 3. Plots of observed $\chi_M T$ vs T and χ_M vs T (inset) of **1** and **2**. Solid line represents the best theoretical fit (see text).

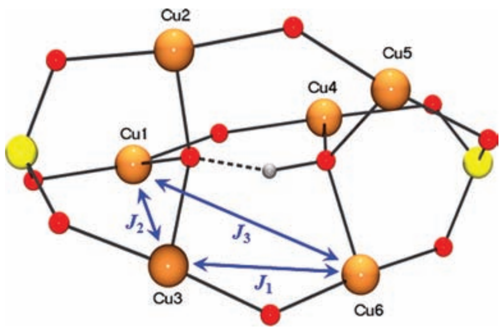


Figure 4. Schematic diagram representing three exchange interactions within complexes **1** and **2**. For clarity, only one of each three interaction types is drawn.

Cu−O(ClO_4) or Cu−N(dicyanamide), are 2.604 Å or 2.726 Å, respectively, are too long. As a consequence, a fit with the indicated scheme was performed by means of the computer program *CLUMAG*,[64] using the following Hamiltonian:

$$\begin{aligned} H = {} & -J_1(S_1{\cdot}S_4 + S_2{\cdot}S_5 + S_3{\cdot}S_6) \\ & - J_2(S_1{\cdot}S_2 + S_1{\cdot}S_3 + S_2{\cdot}S_3 + S_4{\cdot}S_5 + S_4{\cdot}S_6 + S_5{\cdot}S_6) \\ & - J_3(S_1{\cdot}S_5 + S_1{\cdot}S_6 + S_2{\cdot}S_4 + S_2{\cdot}S_6 + S_3{\cdot}S_4 + S_3{\cdot}S_5) \end{aligned}$$

where the numbering of the spins follows the numbering of the Cu atoms in Figure 4. The best fit obtained parameters were $J_1 = -424.5\ cm^{-1}$, $J_2 = +27.5\ cm^{-1}$, and $J_3 = -2.6\ cm^{-1}$ with g = 2.19 for complex **1** and $J_1 = -375.8\ cm^{-1}$, $J_2 = +32.4\ cm^{-1}$, and $J_3 = -4.3\ cm^{-1}$ with $g = 2.13$ for complex **2**.

This behavior can be related to the structural parameters, especially the large $Cu{-}O_{bdmap}{-}Cu$ angles, which are between 135.7° and 137.1°. It is well-known that the magnetic behavior of divalent copper complexes bridged by a pair of hydroxide[65−67] or alkoxide[68,69] O atoms is highly dependent on the Cu−O−Cu bridge angle. Also, it can be influenced, but in smaller measure, by the Cu−O bridge distance, the Cu···Cu separation, the geometry around the copper(II) center, and the geometry around the bridging oxygen atom. Hatfield and Hodgson[64] have found a linear correlation between the experimentally determined exchange coupling constant and the Cu−O−Cu angle (θ). An antiferromagnetic character is found for complexes with θ larger than 97.6°, while ferromagnetic character appears for values of θ smaller than 97.6°. An apparent similar linear relationship for alkoxide cases shows that, at angles of ~95.6°, the exchange integral approaches zero, the point of the "accidental orthogonality". The high $|J_1|$ values found for **1** and **2** are reasonable if one takes into account the big Cu$-$O$_{bdmap}$$-$Cu angles and similar structural cases reported in the literature.[49] While J_2 values with positive sign indicating ferromagnetic interaction between the Cu is due mainly via $\mu_3$$-$O also can been acceptable considering the Cu$-$O$-$Cu angles, which are varying between 110.6° and 114.6°. On the other side, the J_3 values can be well-compared to the recently reported value of the interaction via H-bond in a hexanuclear tricationic copper(II) cage complex, at 4.5 cm^{-1}.[58]

As shown, the magnetic response of **1** and **2** is dominated by the strong antiferromagnetic coupling through the alkoxide bridge (O$_{bdmap}$). Taking into account the relatively low $|J_3|$ value, the experimental magnetic data were fitted again using the previous Hamiltonian by fixing (i) $J_3 = 0$ and (ii) J_3 fixed at the same values as the first fitting but with opposite sign (2.6 cm^{-1} for **1** and 4.3 cm^{-1} for **2**). The best fit parameters found in the first case ($J_3 = 0$) were $J_1 = -425.9$ cm^{-1}, $J_2 = +27.5$ cm^{-1}, and $g = 2.19$ for complex **1** and $J_1 = -375.2$ cm^{-1}, $J_2 = +32.4$ cm^{-1} and g = 2.13 for complex **2**. In the second case (J_3 fixed at low ferromagnetic values), the best fit parameters found were $J_1 = -427.5$ cm^{-1}, $J_2 = +27.5$ cm^{-1}, $J_3 = 2.6$ cm^{-1} and g = 2.19 for complex **1** and $J_1 = -374.6$ cm^{-1}, $J_2 = +32.4$ cm^{-1}, $J_3 = 4.3$ cm^{-1} and g = 2.13 for complex **2**.

As we can observe, no changes are appreciated in the J and g values between the different fits; therefore, we can conclude that interaction J_3 should be very weak antiferromagnetic or ferromagnetic.

Theoretical Study Using DFT Methods. Theoretical methods based on density functional theory have been employed to study the exchange coupling in the two Cu$_6$ systems. A plot of simulated $\chi_M T$ vs T, using the exchange coupling parameter constants calculated by the B3LYP functional, is shown in Figure 5. For complex **1**, the central hydrogen atom was not detected by X-ray diffraction and we assumed that such a hydrogen atom is placed collinear and equidistant to the oxygen atoms. In the case of complex **2**, the X-ray structure indicates the hydrogen atom is not collinear in the $[\mu_3$$-$O-H$\cdots$$\mu_3$$-O]^{3-}$ entity and close to one of the O atoms, however, the case with the hydrogen atom collinear and equidistant to the oxygen atoms is more stable than the former by ~8 kcal mol^{-1}. The calculated J values are collected in Table 4. We performed the calculation for the 15 J values present in the structure and also the calculation of the mean values for each interaction type to compare with the experimental data using the notation presented in Figure 4. Theoretical and experimental data agree in the strong antiferromagnetism of the J_1-type interactions through $\mu_2$$-$OR and O$\cdots$H$\cdots$O bridging ligands, due to the large Cu$-$O$-$Cu angle of the $\mu_2$$\cdots$OR bridging ligand. The analysis of the calculated J values with the Cu$-$O$-$Cu angle seems to correlate the larger angles with the strongest ferromagnetic coupling for each complex. The J_2-type couplings through $\mu_3$$-O_3$PR and $\mu_3$$-$OH bridging ligands are moderately ferromagnetic and there is an excellent agreement between theoretical and experimental J values. At first glance, the results indicate that there is a rough correlation of the Cu$-$O$-$Cu angle (through the $\mu_3$$-$OH bridging ligands) and the strength of the ferromagnetic coupling, as expected smaller angles stronger interactions with the exceptions of the weaker J_{46} and J_{45} ferromagnetic interaction for the complexes **1** and **2**, respectively. A detailed geometrical analysis of the exchange pathways for these two interactions reveals that, in both cases, there are relatively long Cu$-$O distances (not shown), together with large Cu$-$O$-$Cu angle value. Thus, the two geometrical parameters (Cu$-$O distances and Cu$-$O$-$Cu angles with the $\mu_3$$-$OH bridging ligand) seem to be key factor that control the strength of the ferromagnetic coupling. There are no reported similar complexes containing Cu$_3$ units with only two $\mu_3$$-O_3$PR and $\mu_3$$-$OH bridging ligands. In this case, the ferromagnetic nature of the interactions can be due to the relatively small Cu$-$O$-$Cu angles caused by the higher topicity of the ligands in comparison with the equivalent dinuclear complexes with $\mu_2$$-O_2PR_2$ and $\mu_2$$-$OH bridging ligands that are antiferromagnetic.[70]

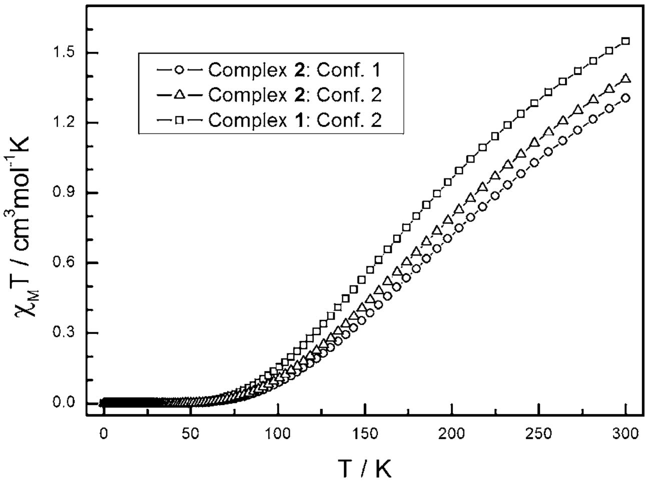


Figure 5. Plot of simulated $\chi_M T$ vs T, using the exchange coupling parameter constants calculated by the B3LYP functional. Two different positions of the central hydrogen atom were considered for complex **2**: the first corresponds to X-ray structure (circles), while, in the second one, the central hydrogen atom is collinear and equidistant to the two oxygen atoms (triangles) as in **1** (squares). In all cases, the g-value was fixed at the experimental g-values (see text).

For the last type of interactions J_3 through the central O$\cdots$H$\cdots$O bridging ligands, there are two sets of interactions those with a Cu$-$O$\cdots$O$-$Cu torsion angle close to 100° giving ferromagnetic couplings while those with this angle close to 140° are slightly antiferromagnetic or weakly ferromagnetic. It is worth mentioning comparing the results for the hydrogen positions in complex **2**, that the case with the hydrogen atom collinear and equidistant to the oxygen atoms give usually stronger couplings either ferromagnetic or antiferromagnetic that same complex with the hydrogen atom mostly coordinated to one of the oxygen atoms.

Computational Details. The spin Hamiltonian for a general polynuclear complex, if the zero-field splitting parameters are not considered, is indicated in eq 1:

$$H = -\sum_{i>j} J_{ij} S_i S_j \qquad (1)$$

where S_i and S_j are the spin of the paramagnetic centers. The J_{ij} values are the coupling constants for the different exchange pathways between all the paramagnetic centers of the molecule. The noninclusion of the spin$-$orbit terms in our calculations makes our calculated energies free of zero-field splitting contributions that can be rather small for this type of Cu^{II}

Table 4. Calculated J Values for Complexes 1 and 2[a]

		∠Cu−O−Cu [°]		d(Cu···Cu) [Å]		J [cm^{-1}]		
	bridging ligands	1	2	1	2	1	2[b]	
J_{14}	(μ_2−OR) (O···H···O)	135.7	137.1	3.590	3.610	−304.0	−449.9	(−400.7)
J_{25}	(μ_2−OR) (O···H···O)	135.6	136.1	3.625	3.630	−269.2	−310.0	(−294.3)
J_{36}	(μ_2−OR) (O···H···O)	136.4	136.9	3.599	3.614	−325.4	−312.1	(−307.6)
J_{12}	(μ_3−O_3PR) (μ_3−OH)	108.9	115.8	3.142	3.294	30.2	34.1	(22.5)
J_{13}	(μ_3−O_3PR) (μ_3−OH)	110.6	105.8	3.189	3.107	28.6	55.3	(34.4)
J_{23}	(μ_3−O_3PR) (μ_3−OH)	114.6	115.4	3.249	3.283	24.0	39.8	(31.4)
J_{45}	(μ_3−O_3PR) (μ_3−OH)	111.3	111.9	3.192	3.233	30.3	1.7	(5.3)
J_{46}	(μ_3−O_3PR) (μ_3−OH)	113.9	112.4	3.252	3.221	0.04	35.1	(27.8)
J_{56}	(μ_3−O_3PR) (μ_3−OH)	111.3	110.8	3.209	3.196	29.0	46.7	(60.5)
J_{15}	(O···H···O)[c]	139.1	147.5	4.959	5.026	1.8	1.2	(−2.0)
J_{16}	(O···H···O)[c]	102.0	93.3	4.558	4.445	5.1	8.9	(10.9)
J_{24}	(O···H···O)[c]	96.9	96.3	4.493	4.494	7.9	11.4	(20.6)
J_{26}	(O···H···O)[c]	141.2	142.8	4.971	4.997	−4.5	−3.9	(−11.9)
J_{34}	(O···H···O)[c]	138.9	139.8	4.970	4.974	−1.6	−1.4	(−1.2)
J_{35}	(O···H···O)[c]	101.9	100.3	4.586	4.558	2.0	4.2	(0.8)
J_1	(μ_2−OR) (O···H···O)	135.9	136.7	3.605	3.618	−299.5	−357.3	(−333.9)
J_2	(μ_3−O_3PR) (μ_3−OH)	111.8	112.0	3.206	3.222	23.7	35.5	(30.3)
J_3	(O···H···O)[c]	120.5	120.0	4.752	4.749	1.8	3.4	(2.9)
			Experimental Values (First Fit)					
J_1	(μ_2−OR) (O···H···O)	135.9	136.7	3.605	3.618	−424.5	−375.8	
J_2	(μ_3−O_3PR) (μ_3−OH)	111.8	112.0	3.206	3.222	27.5	32.4	
J_3	(O···H···O)[c]	120.5	120.0	4.752	4.749	−2.6	−4.3	

[a] For each system, all 15 J values are indicated, as well as the average values (Figure 4), using only three different ones (J_1−J_3). Selected Cu···Cu distances, Cu−O−Cu angles, and the experimental J values are provided for comparison. [b] For **2**, two different positions of the central hydrogen atom were considered; the first J values correspond to X-ray structure and the second one, in parentheses, with the H atom collinear and equidistant to the two oxygen atoms as in **1**. [c] The Cu−O−Cu angle for this bridging ligand correspond to the Cu−O···O−Cu torsion angle.

complexes. In this work, we will focus only on the calculation of exchange coupling values.

A more detailed description of the procedure to obtain the exchange coupling constants can be found in previous publications.[71−73] Basically, we need to calculate at least the energy of $n + 1$ spin distributions if we have a system with n different exchange coupling constants. These values will allow us to build up a system of n equations where the J values are the unknowns. If more energies values are calculated, a fitting procedure is required to extract the J values.[74,75] To obtain all the first neighbor interactions of the Cu_6 complexes (the 15 J values), we considered 18 spin distributions; the high spin $S = 3$ distribution, six $S = 2$ distributions for the spin flip of the following atoms (see Figure 4) {Cu1}, {Cu2}, {Cu3}, {Cu4}, {Cu5}, {Cu6}, 10 $S = 1$ distributions for the spin flip of {Cu1, Cu2}, {Cu1, Cu3}, {Cu1, Cu4}, {Cu1, Cu5}, {Cu2, Cu3}, {Cu2, Cu5}, {Cu3, Cu4}, {Cu3, Cu5}, {Cu4, Cu5}, {Cu5, Cu6}, and finally, one $S = 0$ spin distribution {Cu4, Cu5, Cu6}. Calculations with the B3LYP functional[76] were performed with the Gaussian 09 code[77] using a guess function generated with the Jaguar 7.5 code.[78,79] The triple-ζ all-electron Gaussian basis set proposed by Schaefer et al. was employed for all atoms.[80]

■ CONCLUSIONS

The synthetic strategy to combine in the same synthesis two ligands, R-phosphonic acid and 1,3-bis(dimethylamino)-2-propanol, individually capable to form polynuclear compounds with variable nuclearities and bridging coordination modes, has been successful employed with copper(II) salts, and we have been able to prepare and fully characterize two new hexanuclear 3.111 R-phosphonate(2-)/bis-dimethylaminopropanolate(1-) cages including in the center the $[\mu_3O\cdots H\cdots O\mu_3]^{3-}$ unit. The reported new compounds, as far as we know, are the first examples of discrete hexanuclear copper(II) cages with the $[Cu_3O\cdots H\cdots OCu_3]$ motif built with ligands different than oximate.[53−58] Currently, we are expanding this synthetic strategy with other phosphonic acids.

DFT calculation confirms the presence of predominant antiferromagnetic interactions between the Cu_3 triangles through μ_2-OR (bdmap) and O···H···O bridging ligands but it is worth noting the ferromagnetic character of the exchange interactions in the Cu_3 triangles and a weak ferromagnetic interaction theoretically predicted through an O···H··O bridging ligand.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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