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Two new tetranuclear copper(II) complexes: Structure and magnetic studies

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ABSTRACT

The syntheses, structural characterization and magnetic behaviour of two new tetranuclear copper(II) compounds with formulae $[Cu_4(\mu_2\text{-}PhCOO)_2(\mu\text{-}bdmap)_2(\mu_{1,3}\text{-}N_3)_2(N_3)_2(H_2O)_2]$ **1**, and $[Cu_4(\mu_2\text{-}PhCOO)_2(\mu\text{-}bdmap)_2(\mu_{1,3}\text{-}N_3)_2(PhCOO)_2(CH_3OH)_2]$ **2**, in which bdmap is 1,3-bis(dimethylamino)-2-propanolato are reported herein. The magnetic behaviour of the two complexes has been checked giving a bulk antiferromagnetic coupling in the two cases with *J* values of −85.4 and −89.5 cm^{-1} for **1** and **2**, respectively.

1. Introduction

The aminoalcohols 1,3-bis(dimethylamino)-2-propanol (Hbdmap) and 1,3-bis(amino)-2-propanol (Hbdap) can generate, after deprotonation, the anionic poly-topic 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. bdmap and bdap have been widely used to generate high nuclearity compounds [1–18]. The analysis of the structures reported to date shows that bdmap and bdap can use several coordination modes [15,16]. The most common coordination mode of these ligands is shown in Scheme 1.

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 aqueous or alcoholic media. Each metal ion has still other 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 (*complex as metal* approximation).

In a recent work [17], we have used the complex as metal approximation to prepare a series of four structurally related compounds possessing the dinuclear $[Cu_2L(\mu_2\text{-acetato})]^{2+}$ unit (L = μ-bdmap or μ-bdap) with the aim to study the countercomplementarity phenomenon in these compounds. The structure of the common dinuclear $[Cu_2L(\mu_2\text{-acetato})]^{2+}$ unit is shown in Scheme 2, (R = H, CH_3, R′ = CH_3). With the aim to study the influence of the carboxylato ligand in the coupling constant of related new compounds with the same skeleton shown in Scheme 2 (R = CH_3, R′ = C_6H_5), we have reacted copper(II) benzoate with Hbdmap and azide salts. We have been able to isolate two new polynuclear species with formulae $[Cu_4(\mu_2\text{-}PhCOO)_2(\mu\text{-}bdmap)_2(\mu_{1,3}\text{-}N_3)_2(N_3)_2(H_2O)_2]$ **1**, and $[Cu_4(\mu_2\text{-}PhCOO)_2(\mu\text{-}bdmap)_2(\mu_{1,3}\text{-}N_3)_2(PhCOO)_2(CH_3OH)_2]$ **2**. The compounds **1** and **2** have been structurally characterised by means of single crystal X-ray diffraction and, in the two cases, the $[Cu_2L(\mu_2\text{-benzoato})]^{2+}$ unit can be identified. In spite of the different structural patterns, the compounds **1** and **2** may be considered from the magnetic point of view as dinuclear $[Cu_2L(\mu_2\text{-benzoato})]^{2+}$ entities (L = μ-bdmap).

The found *J* values for **1** and **2** of −85.4 and −89.5 cm^{-1}, respectively, can be justified from the structural data taking into account the orbital countercomplementarity [19].

2. Experimental

2.1. Starting materials

Copper(II) benzoate trihydrate was prepared by mixing aqueous solutions of copper(II) sulfate and sodium benzoate, according to the literature method [20,21]. 1,3-Bis(dimethylamino)-2-propanol, and sodium azide (Aldrich) were used as such.

Caution: Although no incidents were recorded in this study, azido salts of metal complexes with organic ligands are potentially

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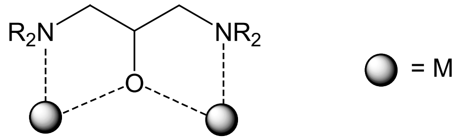
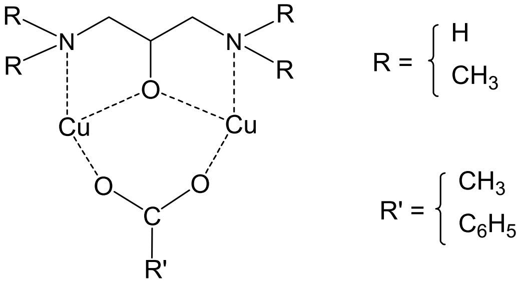


Scheme 1.



Scheme 2.

explosive. Only a small amount of material should be prepared, and it should be handled with care.

2.2. Spectral and magnetic measurements

Infrared spectra (4000–200 cm^{-1}) were recorded from KBr pellets in a Perkin Elmer 1330 IR spectrophotometer. Magnetic susceptibility measurements under magnetic fields of approximately 0.1 T, in the range 2–300 K, were performed with a Quantum Design MPMS-XL SQUID magnetometer at the Magnetochemistry Service of the University of Barcelona. All measurements were performed on polycrystalline samples. Diamagnetic corrections were estimated from Pascal Tables.

2.3. Synthesis of complexes

2.3.1. [$Cu_4(\mu_2$-$PhCOO)_2(\mu$-bdmap$)_2(\mu_{1,3}$-$N_3)_2(N_3)_2(H_2O)_2$] **1**

To a suspension of 1.08 g (3 mmol) of $Cu(PhCOO)_2 \cdot 3H_2O$ in 50 ml of water were added 0.22 g (1.5 mmol) of 1,3-bis(dimethylamino)-2-propanol in 5 ml of water: a green solution was formed. After 1/2 h of stirring, 0.195 g (3 mmol) of sodium azide were added. After air filtration, slow evaporation of the green solution gave after few days green dark crystals of compound **1** suitable for X-ray determination.

2.3.2. [$Cu_4(\mu_2$-$PhCOO)_2(\mu$-bdmap$)_2(\mu_{1,3}$-$N_3)_2(PhCOO)_2(CH_3OH)_2$] **2**

To a suspension of 1.08 (3 mmol) of $Cu(PhCOO)_2 \cdot 3\,H_2O$ in 50 ml of water/methanol 1:1 was added a solution of 0.439 (3 mmol) of 1,3-bis(dimethylamino)-2-propanol in 10 ml of water: a green solution was formed. After few minutes of stirring, a solution of 0.1 g (1.5 mmol) of sodium azide in 10 ml of water was added and a green precipitated in small amount was formed. After air filtration, slow evaporation of the green mother solution gave after few days compound **2** as green crystals suitable for X-ray determination.

2.4. IR and analytical data

The most characteristic bands are those attributable to benzoate registered as two bands centred in the ranges 1362–1405 and 1547–1595 cm^{-1} for the two complexes. The azido band appears and at 2071(s) cm^{-1} for the compound **1** and at 2057(s) cm^{-1} for the compound **2**, respectively. In the infrared spectra, the absorptions attributed to the aminoalcohol are detected in the interval 2800–3095 cm^{-1} and close to 1466 cm^{-1} corresponding to (ν_{C-H} and δ_{CH_2}).

The elemental analyses (C, N, H) for the different syntheses were consistent with the product formulation: Found for **1**: C, 34.2; H, 5.1; N, 22.6%. Calc. for $C_{28}H_{48}Cu_4N_{16}O_8$: C, 33.9; H, 4.9; N, 22.6. Found for **2**: C, 43.4; H, 5.1; N, 12.8%. Calc. for $C_{44}H_{64}Cu_4N_{10}O_{12}$: C, 44.8; H, 5.7; N, 11.8.

2.5. Crystal structure determination and refinement

Good quality crystals of complex **1** and complex **2** were selected and mounted on a MAR345 diffractometer with image plate detector. The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in Table 1. The accurate unit-cell parameters were determined from automatic centring of 2196 ($3° < \theta < 31°$) for **1**, 105 ($3° < \theta < 31°$) for **2**, refined by least-squares method. Intensities were collected with graphite monochromated Mo K_α radiation for **1** and **2**. 22291 (**1**), 30570 (**2**), reflections were measured in the $2.65° \leqslant \theta \leqslant 30.00°$, $2.55° \leqslant \theta \leqslant 32.50°$, range for **1**, and **2**, respectively. 5873 (**1**), and 16158 (**2**), reflections were non-equivalent by symmetry, R_{int} (on I) = 0.0661 (**1**) and 0.0543 (**2**). The observed reflections applying the condition $I > 2\sigma(I)$ were, 4234 for **1**, and 11926 for **2**. Lorentz polarization was made for **1**, **2** and absorption corrections were made only for **1**. The structures were solved by Patterson synthesis using the SHELXS computer program [22] and refined by full-matrix least-squares method, using the SHELX97 computer program [23] using 22291 for **1**, and 30570 for **2** reflections (very negative intensities were not assumed). The functions minimised were $\sum w\ [|F_o|^2 - |F_c|^2]^2$, where $w = [\sigma^2(I) + (0.0621 \cdot P)^2 + 2.9096 \cdot P]^{-1}$ for **1** and $w = [\sigma^2(I) + (0.0655 \cdot P)^2 + 1.429 \cdot P]^{-1}$ for **2**. $P = (|F_o|^2 + 2|F_c|^2)/3$ for **1** and **2**. f, f', and f'' were taken from international tables of X-ray crystallography [24]. 22H atoms for **1** and all H atoms for **2** were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which are linked. Final R (on F) factor was 0.0550, and 0.667, for **1** and **2**, respectively; wR (on $|F_o|^2$) was 0.1604 for **1**, and 0.1496 for **2**. The number of refined parameters was 253 and 641 for **1** and **2**, respectively. The maximum and the minimum shift/esd were 0.00 for **1** and **2**. The molecular plots were obtained using the ORTEP32 program [25].

3. Results and discussion

3.1. Description of the structure of [$Cu_4(\mu_2$-$PhCOO)_2(\mu$-bdmap$)_2(\mu_{1,3}$-$N_3)_2(N_3)_2(H_2O)_2$] **1**

The structure of the compound **1** is illustrated in Fig. 1. Selected bonds lengths and angles are listed in Table 2. The structure of compound **1** can be described as a tetranuclear compound formed by two dinuclear units of copper(II) atoms [Cu_2(bdmap/benzoate)] bridged by two azido ligands in the $\mu_{1,3}$ coordination mode. In each dinuclear unit the copper(II) atoms are bridged by the μ-bdmap ligand through one oxygen atom and by one μ-*syn-syn*-benzoate ligand. Two azide ligands in the $\mu_{1,3}$ coordination mode link two copper atoms of different dinuclear units with a long and a short distance. In the compound, the nearest-neighbour Cu···Cu distances are 3.468(4) and 4.859(4) Å, corresponding to the two sets of bdmap/benzoate and di-$\mu_{1,3}$-azide bridges, respectively. The coordination around the Cu(1) and Cu(2) centres is square pyramidal, the Addison parameter, τ is 0.08 and 0.05, respectively, [26]. The equatorial plane around Cu(1) is formed by O(1) and N(1) (bdmap ligand), O(2) (benzoato), and N(6) (bridging azide). The

Table 1
Crystal data and structure refinement for **1** and **2**

Compound	1	2
Empirical formula	$C_{28}H_{48}Cu_4N_{16}O_8$	$C_{44}H_{64}Cu_4N_{10}O_{12}$
Formula weight	990.98	1179.21
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
Unit cell dimensions		
a (Å)	8.571(4)	11.348(9)
b (Å)	10.592(3)	14.503(9)
c (Å)	22.494(7)	16.649(3)
α (°)	90.0	110.01(3)
β (°)	94.96(2)	99.63(4)
γ (°)	90.0	89.90(4)
V (Å^3)	2034.4(13)	2534(3)
Z, D_{calc} (Mg/m^3)	2, 1.618	2, 1.546
Absorption coefficient (mm^{-1})	2.128	1.725
F(000) 1016	1220	
θ Range for data collection (°)	2.65–30.00	2.55–32.50
Index ranges	$-12 \leqslant h \leqslant 11$;	$-15 \leqslant h \leqslant 16$;
	$0 \leqslant k \leqslant 14$;	$-21 \leqslant k \leqslant 20$
	$0 \leqslant l \leqslant 31$	$0 \leqslant l \leqslant 25$
Reflections collected	22291	30570
Independent reflections (R_{int})	5873 (0.0661)	16158 (0.0543)
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5873/4/253	16158/0/641
Goodness-of-fit on F^2	1.156	1.199
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0550$, $wR_2 = 0.1604$	$R_1 = 0.0667$, $wR_2 = 0.1496$
R indices (all data)	$R_1 = 0.0889$, $wR_2 = 0.1772$	$R_1 = 0.0995$, $wR_2 = 0.1601$
Largest difference in peak and hole (e Å^{-3})	0.542 and −0.508	0.723 and −0.329

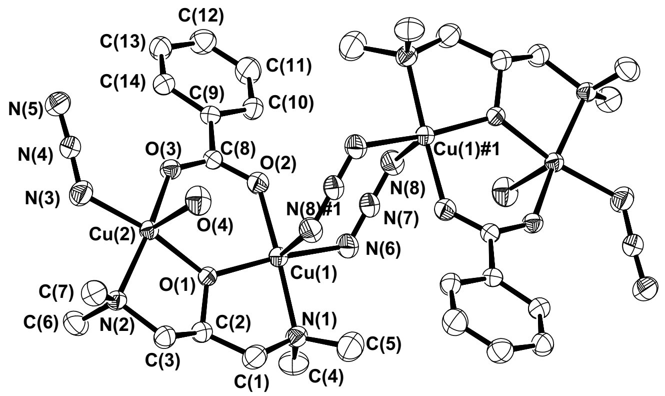


Fig. 1. ORTEP drawing of the compound **1** showing atom labelling scheme. Ellipsoids at the 50% probability level.

Table 2
Relevant bond lengths (Å) and angles (°) for **1**

Cu(1)–O(1)	1.903(3)	Cu(2)–O(1)	1.936(3)
Cu(1)–O(2)	1.947(4)	Cu(2)–N(3)	1.950(5)
Cu(1)–N(6)	1.965(4)	Cu(2)–O(3)	1.970(3)
Cu(1)–N(1)	2.030(4)	Cu(2)–N(2)	2.064(4)
Cu(1)–N(8)$^{\#1}$	2.584(4)	Cu(2)–O(4)	2.278(4)
Cu(1)···Cu(2)	3.468(4)	Cu(1)···Cu(1)$^{\#1}$	4.859(4)
O(1)–Cu(1)–O(2)	94.3(1)	O(1)–Cu(2)–N(3)	168.6(2)
O(1)–Cu(1)–N(6)	167.9(2)	O(1)–Cu(2)–O(3)	93.4(1)
O(2)–Cu(1)–N(6)	88.6(2)	N(3)–Cu(2)–O(3)	90.0(2)
O(1)–Cu(1)–N(1)	85.4(1)	O(1)–Cu(2)–N(2)	85.1(1)
O(2)–Cu(1)–N(1)	172.6(2)	N(3)–Cu(2)–N(2)	88.8(2)
N(6)–Cu(1)–N(1)	90.2(2)	O(3)–Cu(2)–N(2)	165.4(2)
O(2)–Cu(1)–N(8)$^{\#1}$	93.6(2)	O(1)–Cu(2)–O(4)	92.2(2)
O(1)–Cu(1)–N(8)$^{\#1}$	93.8(2)	N(3)–Cu(2)–O(4)	98.3(2)
N(1)–Cu(1)–N(8)$^{\#1}$	93.7(2)	O(3)–Cu(2)–O(4)	94.5(2)
N(6)–Cu(1)–N(8)$^{\#1}$	97.7(2)	N(2)–Cu(2)–O(4)	100.1(2)
Cu(1)–O(1)–Cu(2)	129.2(2)		

$^{\#1}$ $1 - x, -y, -z$.

Cu(1)–O(1), Cu(1)–N(1), Cu(1)–O(2) and Cu(1)–N(6) distances are 1.903(3), 2.030(4), 1.947(4) and 1.965(4) Å, respectively. The axial position is occupied by the N(8)#1 atom of the other $\mu_{1,3}$ azido ligand. The Cu(1)–N(8)#1 distance is 2.584(4) Å.

The equatorial plane around Cu(2) is formed by O(1) and N(2) (bdmap ligand), O(3) (carboxylato), and N(3) (terminal azide). The Cu(2)–O(1), Cu(2)–N(2), Cu(2)–O(3) and Cu(2)–N(3) distances are 1.1936(3), 2.064(4), 1.970(3) and 1.950(5) Å, respectively. The axial position of Cu(2) is occupied by the oxygen atom of one water molecule O(4). The Cu(2)–O(4) distance is 2.278(4) Å. The Cu(1)–O(1)–Cu(2), Cu(1)–N(6)–N(7) and Cu(1)#1–N(8)–N(7) angles are 129.2(2)°, 124.87(4)° and 108.76(4), respectively. The bond distances and angles related with the benzoate ligand are in good agreement with data reported in the literature.

3.2. Description of the structure of [$Cu_4(\mu_2$-PhCOO$)_2(\mu$-bdmap$)_2(\mu_{1,3}$-$N_3)_2$(PhCOO$)_2$(CH$_3$OH$)_2$] **2**

The asymmetric unit contains two independent clusters of four copper(II) atoms. The structures of the two clusters are similar with very slight differences in bonds lengths and angles; therefore only one tetranuclear molecule (A) will be discussed further. As shown in Fig. 2, the structure of the tetranuclear compound can be described as two dinuclear subunit of copper(II) atoms [Cu_2(bdmap/benzoate)] bridged by two azido ligands in the $\mu_{1,3}$ coordination mode. Selected bonds lengths and angles are listed in Table 3. In the molecule (A) of **2**, the nearest-neighbour Cu···Cu distances are 3.489(3) and 5.233(3) Å, corresponding to the two sets of bdmap/benzoate and di-$\mu_{1,3}$-azide bridges, respectively. In each dinuclear unit the copper(II) atoms are bridged by one oxygen atom from the μ-bdmap ligand and one μ-*syn-syn*-benzoate ligand. The coordination around the Cu(1) and Cu(2) centres is distorted square pyramidal, the Addison parameter, τ, is 0.26 and 0.07, respectively, [26]. Around Cu(1), the equatorial plane is formed by O(3) and N(1) (bdmap ligand), O(1) and O(4) from two benzoate ligands (bridge and terminal ones, respectively). The Cu(1)–O(3), Cu(1)–N(1), Cu(1)–O(1) and Cu(1)–O(4) distances are 1.943(3),

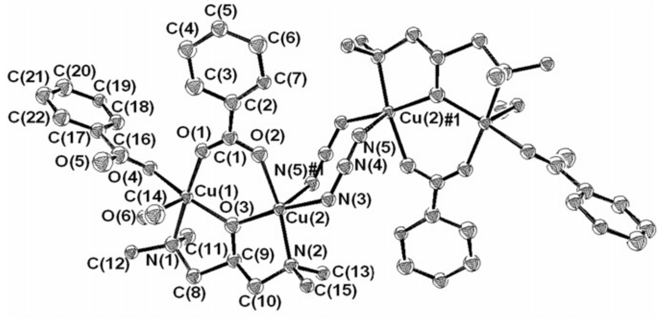


Fig. 2. ORTEP drawing of the compound **2** showing atom labelling scheme. Ellipsoids at the 50% probability level.

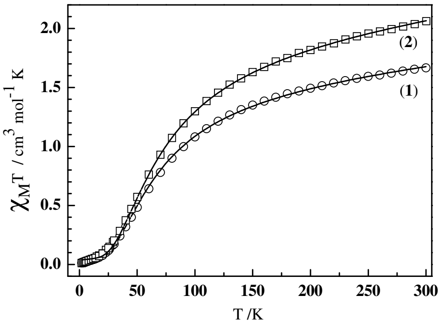


Fig. 3. Plot of observed $\chi_M T$ vs. T of (○) compound **1**, (□) compound **2**. Solid lines represent the best theoretical fit for each compound (see text).

Table 3
Relevant bond lengths (Å) and angles (°) for **2**

Molecule A		Molecule B	
Cu(1)–O(1)	1.924(3)	Cu(3)–O(7)	1.904(3)
Cu(1)–O(3)	1.943(3)	Cu(3)–O(9)	1.924(2)
Cu(1)–O(4)	1.963(2)	Cu(3)–O(10)	1.948(2)
Cu(1)–N(1)	2.023(4)	Cu(3)–N(6)	2.028(3)
Cu(1)–O(6)	2.337(3)	Cu(3)–O(12)	2.317(3)
Cu(2)–O(3)	1.890(3)	Cu(4)–O(9)	1.907(3)
Cu(2)–N(3)	1.912(3)	Cu(4)–N(8)	1.929(3)
Cu(2)–N(2)	1.984(3)	Cu(4)–N(7)	2.051(3)
Cu(2)–O(2)	2.022(3)	Cu(4)–O(8)	1.858(3)
Cu(2)–N(5)$^{\#1}$	2.572(3)	Cu(4)–N(10)$^{\#2}$	2.698(3)
Cu(1)···Cu(2)	3.489(3)	Cu(3)···Cu(4)	3.510(3)
Cu(2)···Cu(2)$^{\#1}$	5.233(3)	Cu(4)···Cu(4)$^{\#2}$	5.297(3)
O(1)–Cu(1)–O(3)	92.9(1)	O(7)–Cu(3)–O(9)	94.5(1)
O(1)–Cu(1)–O(4)	91.8(1)	O(7)–Cu(3)–O(10)	89.6(1)
O(3)–Cu(1)–O(4)	160.3(1)	O(9)–Cu(3)–O(10)	158.1(1)
O(1)–Cu(1)–N(1)	176.1(1)	O(7)–Cu(3)–N(6)	175.7(1)
O(3)–Cu(1)–N(1)	84.7(2)	O(9)–Cu(3)–N(6)	86.7(1)
O(4)–Cu(1)–N(1)	89.4(1)	O(10)–Cu(3)–N(6)	87.7(1)
O(1)–Cu(1)–O(6)	93.4(1)	O(7)–Cu(3)–O(12)	92.2(1)
O(3)–Cu(1)–O(6)	99.3(1)	O(9)–Cu(3)–O(12)	104.3(1)
O(4)–Cu(1)–O(6)	99.5(1)	O(10)–Cu(3)–O(12)	97.1(1)
N(1)–Cu(1)–O(6)	90.0(1)	N(6)–Cu(3)–O(12)	91.4(1)
O(3)–Cu(2)–N(3)	171.9(1)	O(9)–Cu(4)–N(8)	175.1(1)
O(3)–Cu(2)–N(2)	81.9(1)	O(9)–Cu(4)–N(7)	85.6(1)
N(3)–Cu(2)–N(2)	91.2(1)	N(8)–Cu(4)–N(7)	89.6(1)
O(3)–Cu(2)–O(2)	93.4(1)	O(8)–Cu(4)–O(9)	97.6(1)
N(3)–Cu(2)–O(2)	92.6(1)	O(8)–Cu(4)–N(8)	87.1(1)
N(2)–Cu(2)–O(2)	167.8(1)	O(8)–Cu(4)–N(7)	170.3(1)
N(5)$^{\#1}$–Cu(2)–O(2)	89.2(1)	N(10)$^{\#2}$–Cu(4)–O(8)	84.9(1)
N(5)$^{\#1}$–Cu(2)–O(3)	98.0(1)	N(10)$^{\#2}$–Cu(4)–O(9)	94.36(1)
N(5)$^{\#1}$–Cu(2)–N(2)	102.5(1)	N(10)$^{\#2}$–Cu(4)–N(7)	104.0(1)
N(5)$^{\#1}$–Cu(2)–N(3)	87.6(1)	N(10)$^{\#2}$–Cu(4)–N(8)	87.6(1)
Cu(1)–O(3)–Cu(2)	131.0(1)	Cu(3)–O(9)–Cu(4)	132.7(1)

$^{\#1}$ $-x, -y, -z$.
$^{\#2}$ $1-x, 1-y, z$.

2.023(4), 1.924(3) and 1.963(2) Å, respectively. The axial position is occupied by the O(6) atom of one methanol molecule. The Cu(1)–O(6) distance is 2.337(3) Å. The equatorial plane around Cu(2) is formed by O(3) and N(2) (bdmap ligand), O(2) (benzoate), and N(3) (azido bridge). The Cu(2)–O(3), Cu(2)–N(2), Cu(2)–O(2) and Cu(2)–N(3) distances are 1.890(3), 1.984(3), 1.964(3) and 2.022(3) Å, respectively. The axial position is occupied by the N(5)#1 atom of one bridging azido ligand. The Cu(2)–N(5)#1 distance is 2.572(3) Å. The Cu(1)–O(3)–Cu(2), Cu(2)–N(3)–N(4) and Cu(2)#1–N(5)–N(4) angles are 131.0(1)°, 124.5(4)° and 120.4(4), respectively.

3.3. *Magnetic study*

Magnetic measurements were carried out on polycrystalline powder samples in the 2–300 K range of temperatures. The applied field was 1 T. The compounds **1** and **2** show a similar moderate antiferromagnetic behaviour with very slight differences. In Fig. 3 we show the magnetic behaviour of **1** and **2** in the form of $\chi_M T$ versus T plots.

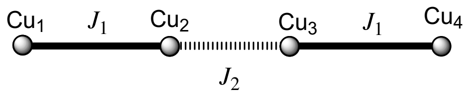
As expected, the magnetic response of the two compounds is dominated by the antiferromagnetic coupling through the bdmap/benzoate bridges with large Cu–O$_L$–Cu bond angles (129.2 for **1** and 131.0 for **2**). At room temperature, compounds **1** and **2**, show a $\chi_M T$ value of 1.667, and 2.061 cm^3 K mol^{-1}, respectively, those values are slightly high to that expected for four uncoupled $S = 1/2$ spins (1.5 cm^3 K mol^{-1}, $g = 2.0$). In the case of compound **2**, the relative high value of $\chi_M T$ is due probably to the high g value which depends mainly to the environment of copper(II) atoms. With decreasing temperature, $\chi_M T$ decreases gradually for **1** and **2** to reach the zero cm^3 K mol^{-1} value approximately at around 10 K, indicating antiferromagnetic coupling.

The structures of **1** and **2** consist of copper ions linked between them by bdmap/benzoate and double μ$_{1,3}$-azide bridges giving lineal tetramer compounds. Thus, two coupling parameters (J_1, J_2) can be considered to interpret the magnetic interactions in the complexes **1** and **2**. J_1 corresponds to the bdmap/benzoate bridges, while J_2 corresponds to the double azide in the *end-to-end* bridging mode in the two compounds (Scheme 3). As consequence of the coupling scheme the Hamiltonian to use in the two cases is $H = -J_1(S_1S_2 + S_3S_4) - J_2(S_2S_3)$. The fit on the indicated scheme was performed by means of the computer program CLUMAG [27]. The best fit parameters found were $J_1 = -85.4$ cm^{-1}, $J_2 = -5.5$ cm^{-1} and $g = 2.06$ for **1** and $J_1 = -89.5$ cm^{-1}, $J_2 = -7.0$ cm^{-1} and $g = 2.27$ for **2**. The J_1 values of -85.4 and -89.5 cm^{-1} are the mean value corresponding to the bdmap/benzoate bridges.

On the other side, taking into account the relatively low J_2 value, we can consider that in compounds **1** and **2** the magnetic coupling is mainly dominated by the relative strongest interaction, J_1, which reduces the system to two dinuclear units magnetically isolated in each compound. To prove this possibility, the experimental magnetic data were fitted again by using the Bleaney–Bowers expression, based on the following isotropic Hamiltonian: $H = -J(S_1 \cdot S_2)$

$$\chi_M = \frac{Ng^2\mu_B^2}{kT}\,\frac{2\exp(J/kT)}{1+3\exp(J/kT)} \tag{1}$$

The parameters N, μ$_B$ and k in Eq. (1) have their usual meanings, J = singlet–triplet splitting. Least-square fitting of experimental data leads to the following parameter: $J = -84.7$ cm^{-1} and $g = 2.06$ for



Scheme 3.

complex **1**; $J = -86.3\ \mathrm{cm}^{-1}$ and $g = 2.23$ for complex **2**. The J values found in **1** and **2** are close to those found above. This fact confirms that **1** and **2** behave, from the magnetic point of view, as dinuclear compounds. It is necessary to indicate here that to fit the magnetic data of **1** and **2**, we have multiplied the Eq. (1) by 2, to reach the correct number of copper atoms in each cluster. In all the calculations, the agreement factor $R = \sum[(\chi_M T)_{\mathrm{obs}} - (\chi_M T)_{\mathrm{calcd}}]^2 / \sum[(\chi_M T)^2_{\mathrm{obs}}]$ is lower than $R = 5.7 \times 10^{-6}$.

3.4. Coupling constants correlation

It seems to be that the magnetic response of compounds **1** and **2** is dominated mainly by the expected antiferromagnetic coupling trough the double bdmap/benzoate bridge. In the two compounds, the magnetic exchange is propagated principally via the $d_{x^2-y^2}$ orbitals of the Cu(II) ions which interact with the appropriate orbitals of the oxygen or nitrogen atoms of the bdmap bridging ligand ($J_1 = -85.4$ and $-89.5\ \mathrm{cm}^{-1}$ for **1** and **2**, respectively). While, the magnetic coupling between the Cu(II) atoms through the *axial* positions (long distances) should be practically negligible ($J_2 = -5.5$ and $-7.0\ \mathrm{cm}^{-1}$ for **1** and for **2**, respectively). This agree with a previous theoretical studies reported on $\mu_{1,3}$-N_3 asymmetric double bridges with one large Cu–N distance [28].

In copper(II) complexes bridged by a pair of hydroxide or alkoxide oxygen atoms the value and sign of the $|J|$ coupling is mainly dependent on the Cu–O–Cu bridge angle. In a yet classical paper Hatfield and Hodgson [29] have published a linear correlation for homobridged $[Cu(OH)_2Cu]^{2+}$ dinuclear compounds between the experimental exchange coupling constant and the Cu–O–Cu bond angle (θ). The dinuclear compounds with θ larger than 97.6° are antiferromagnetically coupled, while the coupling is ferromagnetic if θ is lower than 97.6°. For θ larger than 97.6° the $|J|$ value increases with increasing θ. The antiferromagnetic interaction in **1** and **2**, expressed as $|J|$ values of 85.4 and $89.5\ \mathrm{cm}^{-1}$, respectively, is smaller than that expected from their large Cu–O–Cu angles of 129.2 and 131.0/132.7° for which $|J|$ values around $400\ \mathrm{cm}^{-1}$ have been obtained in similar polynuclear compounds with only alkoxo bridges [15,16]. The lowering of the $|J|$ value in heterobridged dinuclear systems in which one hydroxo or alkoxo bridge is substituted by one carboxylate bridging ligand is due to the orbital countercomplementarity phenomenon. This concept was reported for the fist time by Nishia et al. [30] and by Mckee et al. [31] In a recent work [17], we have reported a series of four structurally related compounds possessing the dinuclear $[Cu_2L(\mu_2\text{-acetato})]^{2+}$ unit (L = μ-bdmap or μ-bdap) (see Scheme 2). The Cu–O–Cu angles for these compounds are in the range 130.3–133.3° with $|J|$ values in the range $109–144\ \mathrm{cm}^{-1}$. The relatively low $|J|$ values have been justified in basis to the orbital countercomplementarity. The Cu–O–Cu angles in **1** and **2** are similar [129.2 and 131.8° (mean)] but if we compare the $|J|$ values (85.4 and $89.5\ \mathrm{cm}^{-1}$) found in complexes **1** and **2** with the values reported for the four $[Cu_2L(\mu_2\text{-acetato})]^{2+}$ compounds [17], we observe that they are small: they decrease 30% approximately. This fact may indicate that the countercomplementarity phenomenon generated for the benzoate group when combines with the aminoalcohol is strongest than the combination of the acetate group with the aminoalcohol.

4. Conclusion

Here we have presented the syntheses, crystal structure and magnetic study of two new tetranuclear compounds obtained from copper(II) benzoate trihydrate, 1,3-bis(dimethylamino)-2 propanol and azido ligands with formulae $[Cu_4(\mu_2\text{-PhCOO})_2(\mu\text{-bdmap})_2(\mu_{1,3}\text{-}N_3)_2(N_3)_2(H_2O)_2]$ **1**, and $[Cu_4(\mu_2\text{-PhCOO})_2(\mu\text{-bdmap})_2(\mu_{1,3}\text{-}N_3)_2(PhCOO)_2(CH_3OH)_2]$ **2**. In compounds **1** and **2** the magnetic core is $[Cu_2(\mu\text{-}O_{\mathrm{bdmap}})(\mu\text{-}syn\text{-}syn\text{-benzoate})]^{2+}$ and the relatively small $|J|$ values (-85.4 and $-89.5\ \mathrm{cm}^{-1}$) can be explained from the orbital countercomplementarity.

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Appendix A. Supplementary material

CCDC 676412 and 676413 contain the supplementary crystallographic data for complexes **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.03.050.

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