

The templating effect of halides in the tetrameric copper(II) $[\text{Cu}_2(\text{LH})_2(\mu_4\text{-X})\text{Cu}_2(\text{LH})_2]^{3+}$ complexes ($\text{LH}_2 = \text{N}-(2\text{-pyridylmethyl})\text{-N}$, N -bis-[2'-hydroxy-5'-methyl-benzyl]-amine; $\text{X} = \text{Br}, \text{Cl}$). Synthesis and magneto-structural characterization



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ABSTRACT

The synthesis, magnetic and structural characterization of two tetrameric copper(II) complexes $\{\text{N}(\text{C}_4\text{H}_9)_4\}\text{-}[\text{Cu}_2(\text{LH})_2(\mu_4\text{-Br})\text{Cu}_2(\text{LH})_2](\text{PF}_6)_4$ (**1**) and $[\text{Cu}_2(\text{LH})_2(\mu_4\text{-Cl})\text{Cu}_2(\text{LH})_2](\text{Cl})_2(\text{PF}_6)$ (**2**) is described. LH stands for the hemi-deprotonated anion of the tripodal aminophenol ligand $\text{N}-(2\text{-pyridylmethyl})\text{-N}$, N -bis-[2'-hydroxy-5'-methyl-benzyl]-amine. The complexes are tetrametallic species formed around the central halide ion which behaves as an anion template for the formation of the tetranuclear species, by bridging two dimeric phenoxo bridged $[\text{Cu}_2(\text{LH})_2]^{2+}$ units. The magnetic behaviour is dominated by the strong antiferromagnetic exchange within the dimeric unit, mediated by the phenoxo bridges: $J = -439(4) \text{ cm}^{-1}$, $g = 2.10(2)$ for (**1**) and $J = -429(2) \text{ cm}^{-1}$, $g = 2.090(9)$ for (**2**).

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1. Introduction

Over the last decades, the templating effect of anions in the syntheses of a wide range of organic [1] and metal-organic [2] assemblies has been firmly demonstrated. Simple mono-atomic anions are able to nucleate polymetallic assemblies generating interesting structures depending on various factors, such as size, charge and nature of the nucleating atom. Halide nucleating examples include μ_3 , μ_4 , μ_5 and higher nuclearity metal clusters [3–8]. For example, Kamiyama et al. [3], reported the synthesis of the copper(II) complex $[\text{Cu}_6\text{Cl}(\text{MeO})_2(\text{pz})_9]$ via a chloride templated reaction. Within this complex two trinuclear units, $[\text{Cu}_3(\text{MeO})(\text{pz})_3]^{2+}$, are linked by three pyrazolate ligands. The six copper(II) ions form a trigonal prism, and the chloride ion occupies the centre of the cage. Paital et al. [4] described the synthesis of a new family of tetranuclear copper(II) clusters $[\text{Cu}_4(\mu_4\text{-X})\text{L}_2]\text{ClO}_4$ where $\text{X} = \text{Cl}, \text{Br}, \text{I}$, and $\text{H}_3\text{L} = 2\text{-}(2\text{-hydroxyphenyl})\text{-1,3-bis}[4\text{-}(2\text{-hydroxyphenyl})\text{-3-azabut-3-enyl}]\text{-1,3-imidazolidine}$. The X-ray crystal structure of the chloride species shows that the spherical Cl bridging anion

($\mu_4\text{-Cl}$), is responsible for the self-assembly of two $[\text{Cu}_2\text{L}]^+$ units, giving the tetrameric complex. Although synthesized, the crystal structure of the corresponding bromide analogue has not been reported to date. Another system was described by Noel et al. [5] who reported different bridging modes of the bromide anion in the nickel(II) complex (μ_6 -bromo)-bis(μ_3 -bromo)-hexakis(μ_2 -bromo)-tris(μ_2 -3,5-bis(2,6-diisopropylphenylimino-methyl)-pyrazolato)-hexa-nickel(II) chloroform solvate.

In previous works we have reported [9,10] the magneto-structural characterization of a series of copper(II) complexes with tripodal N , N -bis(pyridylalkyl)-aminophenol ligands. Bis-pyridyl-aminophenols can act as polydentate ligands, producing different polymetallic species depending on the synthetic conditions. Even though, for the preparation of the reported complexes we started from copper(II) chloride as the precursor salt, the chloride does not act as a template for the assembly of polymetallic species. In contrast, in this work the use of the pyridyl-amino-bisphenol ligand and copper(II) chloride or bromide as the metal salt leads, under the same experimental conditions, to the isolation of μ_4 -halide bridged tetranuclear copper(II) species.

In this work we describe the synthesis, the magnetic properties and the X-ray crystal structures of the new μ_4 -bromide and μ_4 -chloride bridged tetranuclear copper(II) complexes, $\{\text{N}(\text{C}_4\text{H}_9)_4\}$

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$[\text{Cu}_2(\text{LH})_2(\mu_4\text{-Br})\text{Cu}_2(\text{LH})_2](\text{PF}_6)_4$, (**1**), and $[\text{Cu}_2(\text{LH})_2(\mu_4\text{-Cl})\text{Cu}_2(\text{LH})_2(\text{Cl})_2(\text{PF}_6)_2$, (**2**), with the ligand $\text{LH}_2 = \text{N}-(2\text{-pyridylmethyl})\text{-N,N-bis-}[2'\text{-hydroxy-5'-methyl-benzyl}]\text{-amine}$.

2. Experimental

2.1. Materials and measurements

All reagents were reagent grade and used without further purification. HPLC quality solvents were freshly distilled under nitrogen before use. The ligand LH_2 , $\text{N}-(2\text{-pyridylmethyl})\text{-N,N-bis-}[2'\text{-hydroxy-5'-methyl-benzyl}]\text{-amine}$, was prepared by a Mannich reaction of bis(2-pyridylmethyl) amine, paraformaldehyde and p-cresol (Scheme 1), as described for similar ligands [10]. Elemental analyses for C, H, and N were performed at CEPEDQ (University of Chile) on a Fison-Carlo Erba EA 1108 model analyzer. Copper was determined by atomic absorption spectroscopy. ^1H NMR spectra were recorded in CDCl_3 on a Bruker AMX-300 NMR spectrometer. Chemical shifts are reported as δ values downfield of an internal Me_4Si reference.

Magnetic susceptibility measurements for (**1**) and (**2**) were carried out on polycrystalline samples, at the Servei de Magnetoquímica of the Universitat de Barcelona, with a Quantum Design SQUID MPMS-5 equipment working in the range 2–300 K under an external magnetic field of 1 Tesla. X-band EPR spectra were recorded with a Bruker ES200 spectrometer.

2.2. Synthesis of the ligand $\text{N}-(2\text{-pyridylmethyl})\text{-N,N-bis-}[2'\text{-hydroxy-5'-methyl-benzyl}]\text{-amine}$ (LH_2)

To a suspension of paraformaldehyde 1.8 g (0.06 mol) in methanol (100 mL) were added 3.2 g (0.03 moles) of 2-pyridylmethylamine [11] and 6.5 g (0.06 moles) of p-cresol. The reaction mixture was refluxed for 48 h. under nitrogen. After cooling to room temperature, the solvent was removed under vacuum and the residue crystallized from acetonitrile giving 5.1 g (49%) of a white crystalline solid. ^1H NMR (CDCl_3): δ 8.6 (1H, d, $\text{H}_\alpha\text{-Py}$), 7.7 (1H, t, $\text{H}_\beta\text{-Py}$), 7.27 (1H, t, $\text{H}_\gamma\text{-Py}$), 7.1 (1H, d, $\text{H}_\delta\text{-Py}$), 6.98 (2H, dd), 6.87 (2H, d) and 6.80 (2H, d) (phenyl protons), 3.89 (2H, s, $\text{CH}_2\text{-Py}$), 3.78 (4H, s, $\text{CH}_2\text{-Ph}$), 2.25 (6H, s, $\text{CH}_3\text{-Ph}$), 10.5 (2H, broad, OH).

2.3. Synthesis of $\{\text{N}(\text{C}_4\text{H}_9)_4\}[\text{Cu}_2(\text{LH})_2(\mu_4\text{-Br})\text{Cu}_2(\text{LH})_2](\text{PF}_6)_4$ (**1**)

A solution of CuBr_2 (0.447 g, 2 mmol) in 5 mL MeOH was added to a solution of the ligand LH_2 (0.70 g, 2 mmol) and triethylamine (280 μL , 2 mmol) in MeOH (20 mL), and the mixture was refluxed for 60 min. Addition of excess tetrabutylammonium hexafluorophosphate to the solution precipitates the crystalline product immediately (0.648 g, 51%). Recrystallization from boiling methanol affords crystals suitable for X-ray structural studies. *Anal. Calc.*

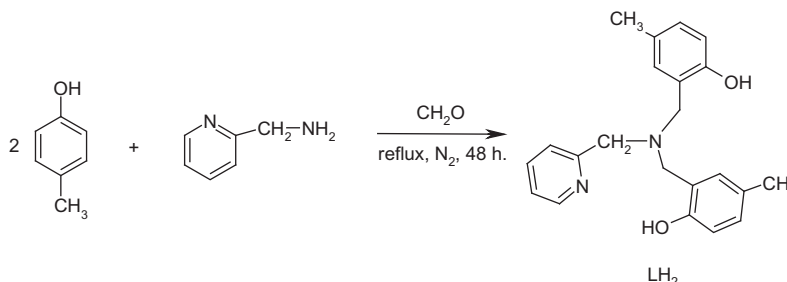
for $\text{Cu}_4\text{C}_{88}\text{H}_{92}\text{N}_8\text{O}_8 \text{Br} \cdot (\text{C}_4\text{H}_9)_4\text{N} \cdot 4(\text{PF}_6)$: C, 49.04; H, 5.07; N, 4.95; Cu, 9.98. Found: C, 50.0; H, 5.1; N, 4.8; Cu, 9.8%.

2.4. Synthesis of $[\text{Cu}_2(\text{LH})_2(\mu_4\text{-Cl})\text{Cu}_2(\text{LH})_2](\text{Cl})_2(\text{PF}_6)_2$ (**2**)

This compound was synthesized by the same procedure as the bromide, but using CuCl_2 instead CuBr_2 . *Anal. Calc.* for $\text{C}_{88}\text{H}_{92}\text{Cu}_4\text{Cl}_3\text{F}_6\text{N}_8\text{O}_8\text{P}$: C, 47.33; H, 4.16; N, 5.02; Cu, 11.38. Found: C, 48.1; H, 4.2; N, 5.2; Cu, 11.2%.

3. Crystallographic measurements

The crystal structure of $\{\text{N}(\text{C}_4\text{H}_9)_4\}[\text{Cu}_2(\text{LH})_2(\mu_4\text{-Br})\text{Cu}_2(\text{LH})_2](\text{PF}_6)_4$ was determined at 150 K by X-ray diffraction measurements on a prismatic $0.38 \times 0.30 \times 0.28 \text{ mm}^3$ single crystal. Data collection was run on a SMART CCD diffractometer, using ω -scans. Data reduction was done with SAINT [12], while the structure solution by direct methods, completion and refinement was conducted with SHELXL [13]. Multi-scan absorption correction was applied using SADABS [14]. The hydrogen atoms positions were calculated after each cycle of refinement with SHELXL, using a riding model for each structure, with C–H distance of 0.98 Å and O–H distance of 0.88 Å. $U_{\text{iso}}(\text{H})$ values were set equal to 1.2 U_{eq} of the parent carbon atom (1.5 U_{eq} for methyl) and 1.5 U_{eq} of the parent oxygen atom. During the final stages of the refinement it was clear that there was disorder on the uncoordinated charge balancing hexafluorophosphate anion. It was modelled using two disordered positions, labelled A and B, for four of the six fluorine atoms. They were then refined and finally held constant at 0.63/0.37 (A/B), while the fluorine to phosphorous distance was constrained to be 1.615 Å. During the structure completion process by difference Fourier synthesis, it was clear that some ill defined electron density were present in voids left by the cations and hexafluorophosphate anions. Efforts to model this density as molecules gave no meaningful result. The remaining and unassigned electron density was modelled using PLATON SQUEEZE [15], a method allowing a good modelling of unresolved electron density [16]. It leads to about 159 electrons for each void within the unitary cell. Taking this into account, one tetrabutylammonium cation per copper tetramer was included in the reported formulae of the compound, $\text{C}_{104}\text{H}_{128}\text{BrCu}_4\text{F}_{24}\text{N}_9\text{O}_8\text{P}_4$. The crystal structure of $[\text{Cu}_2(\text{LH})_2(\mu_4\text{-Cl})\text{Cu}_2(\text{LH})_2](\text{Cl})_2(\text{PF}_6)_2$ was determined at room temperature on a stick shaped $0.67 \times 0.19 \times 0.15 \text{ mm}^3$ single crystal. During the final stages of the refinement it became clear there was disorder on the uncoordinated charge balancing hexafluorophosphate anion. It was modelled using seven positions, subjected to add six fluorine atoms per tetrameric unit. Their occupancies were then refined and finally held constant during the last cycles of refinement. Table 1 contains data collection and structure refinement details, while selected bond distances and bond angles are given in Table 2.



Scheme 1. Synthesis of the ligand $\text{N}-(2\text{-pyridylmethyl})\text{-N,N-bis-}[2'\text{-hydroxy-5'-methyl-benzyl}]\text{-amine}$, LH_2 .

Table 1Crystal data and structure refinement details for $\{N(C_4H_9)_4\}[Cu_2(LH)_2(\mu_4-Br)Cu_2(LH)_2](PF_6)_4$ (**1**) and $[Cu_2(LH)_2(\mu_4-Cl)Cu_2(LH)_2](Cl)_2(PF_6)$ (**2**).

	(1)	(2)
Formula weight	2546.0	1859.76
T (K)	293	293
Crystal system	tetragonal	tetragonal
Space group	$P4_2/n$	$P4_2/n$
a (Å)	16.1565(9)	16.1287(2)
c (Å)	20.902(2)	21.0989(7)
V (Å ³)	5456.0(6)	5488.6(2)
Z (Z')	8(2)	8(2)
δ (g cm ⁻³)	1.384	1.116
μ (mm ⁻¹)	1.29	0.884
F (000)	2334	1910
θ range	$\theta_{\min} = 1.6^\circ, \theta_{\max} = 25.1^\circ$	$\theta_{\min} = 1.6^\circ, \theta_{\max} = 26.0^\circ$
hkl range	$h = -13 \rightarrow 13$ $k = 0 \rightarrow 19$ $l = 0 \rightarrow 24$	$h = -19 \rightarrow 14$ $k = -17 \rightarrow 14$ $l = -24 \rightarrow 24$
$N_{\text{tot}}, N_{\text{uniq}} (R_{\text{int}}), N_{\text{obs}}$	4858, 4858(0.00), 3117	19066, 5362(0.0575), 2663
Refinement parameters	298 parameter (9 restraints)	329 parameter (25 restraints)
Goodness-of-fit	0.94	1.057
R_1, wR_2 (obs)	0.077, 0.237	0.081, 0.246
R_1, wR_2 (all)	0.107, 0.262	0.175, 0.331
Maximum and minimum $\Delta\rho$	$\Delta_{\max} = 0.87$ and $\Delta_{\min} = -1.11$	$\Delta_{\max} = 1.01$ and $\Delta_{\min} = -1.30$

Table 2Selected bond distances (Å) and bond angles (°) for $\{N(C_4H_9)_4\}[Cu_2(LH)_2(\mu_4-Br)Cu_2(LH)_2](PF_6)_4$ (**1**) and $[Cu_2(LH)_2(\mu_4-Cl)Cu_2(LH)_2](Cl)_2(PF_6)$ (**2**).

	(1)	(2)
Cu–O2	1.931 (4)	1.924(4)
Cu–O2 ⁱ	1.954 (4)	1.961(4)
O2–Cu ⁱ	1.954 (4)	1.961(4)
Cu–O1	2.494(5)	2.512(6)
Cu–N1	1.977 (5)	1.982(5)
Cu–N2	2.038 (5)	2.035(5)
Cu–X1	3.1500 (8)	3.0812(9)
X1–Cu ⁱ	3.1500 (8)	3.0812(9)
X1–Cu ⁱⁱ	3.1500 (8)	3.0812(9)
Cu...Cu ⁱ	2.932 (1)	2.923(2)
O2–Cu–O2 ⁱ	75.7 (2)	76.5(2)
O2–Cu–N1	170.7 (2)	172.3(2)
O2–Cu–N2	94.6 (2)	93.9(2)
N1–Cu–N2	84.0 (2)	84.2(2)
O2 ⁱ –Cu–Br1	81.5 (1)	80.6(2)
N2–Cu–Br1	91.6 (1)	92.3(2)
Cu–O2–Cu ⁱ	98.0 (2)	97.6(2)
O2–Cu–O1	101.8(2)	96.9(2)
N1–Cu–O1	87.3(2)	90.5(2)
N2–Cu–O1	85.6(2)	85.8(2)
O2 ⁱ –Cu–N1	104.6 (2)	104.5(2)
O2 ⁱ –Cu–N2	168.8 (2)	168.8(2)
O2–Cu–Br1	81.8 (1)	80.6(2)
N1–Cu–Br1	89.1 (1)	91.5 (2)
Cu–Br1–Cu ⁱⁱⁱ	141.55 (2)	140.8(2)
Cu–Br1–Cu ⁱ	55.50 (2)	56.64(2)
Cu ⁱⁱⁱ –Br1–Cu ⁱ	141.55 (2)	140.8(2)
Cu–Br1–Cu ⁱⁱ	141.55 (2)	140.8(2)
Cu ⁱⁱ –Br1–Cu ⁱⁱⁱ	55.50 (2)	56.64(2)
Cu ⁱⁱ –Br1–Cu ⁱ	141.55 (2)	140.8(2)

Symmetry labels: *i*: $-x + 1/2, -y + 1/2, z$; *ii*: $y, -x + 1/2, -z + 3/2$; *iii*: $-y + 1/2, x, -z + 3/2$.

4. Results and discussion

4.1. Synthesis

The compounds $\{N(C_4H_9)_4\}[Cu_2(LH)_2(\mu_4-Br)Cu_2(LH)_2](PF_6)_4$ (**1**) and $[Cu_2(LH)_2(\mu_4-Cl)Cu_2(LH)_2](Cl)_2(PF_6)$ (**2**), (LH is the

hemi-deprotonated anion of the N-(2-pyridylmethyl)-N,N-bis-[2'-hydroxy-5'-methyl-benzyl]amine ligand) were obtained straightforward as dark brown polycrystalline solids from the reaction mixture of the ligand and copper(II) salt, by precipitation with $N(C_4H_9)_4PF_6$.

4.2. Structural description

4.2.1. $\{N(C_4H_9)_4\}[Cu_2(LH)_2(\mu_4-Br)Cu_2(LH)_2](PF_6)_4$ (**1**) and $[Cu_2(LH)_2(\mu_4-Cl)Cu_2(LH)_2](Cl)_2(PF_6)$ (**2**)

Both complexes display a tetrametallic $[Cu_2(LH)_2(\mu_4-X)Cu_2(LH)_2]^{3+}$ cation, formed by two dimeric $[Cu_2(LH)_2]^{2+}$ units bonded to a central halide anion, which connects them as depicted in Scheme 2. Fig. 1(a and b) show details for the $[Cu_2(LH)_2(\mu_4-Br)Cu_2(LH)_2]^{3+}$ species. Within the cation the halide is tetrahedrally surrounded by cupric centres, Fig. 1b. Although significant differences in the ionic radii between bromide and chloride exist (182 vs. 167 pm), both cations are almost isostructural.

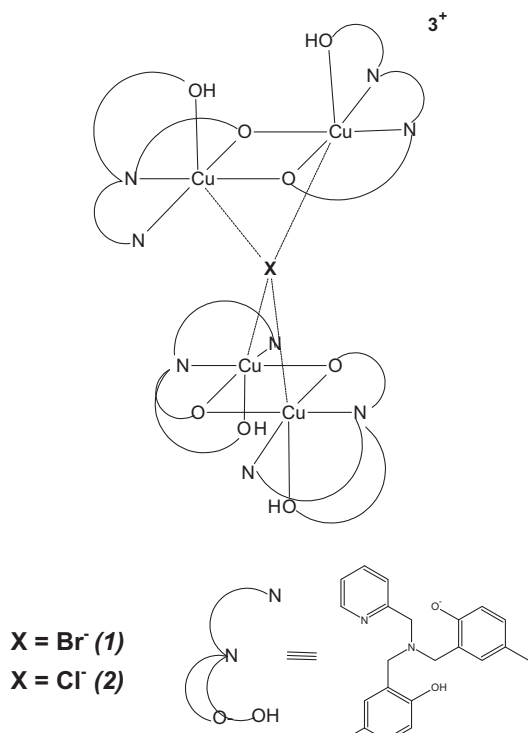
The coordination environment of each cupric centre within $[Cu_2(LH)_2(\mu_4-X)Cu_2(LH)_2]^{3+}$ is well described as an elongated octahedron along the central halide, in contrast to what is observed for $[Cu_4(\mu_4-Cl)_2ClO_4]$ [4]; ($H_3L = 2$ -(2'-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine), where the coordination of the copper(II) centre is better described as a square base pyramid. The hemi-deprotonated ligand molecule LH^- in (**1**) and (**2**), acts as a tetradentate ligand occupying four of the six coordination positions of the octahedron, while one is occupied by the bromide and the other by the phenolate oxygen bridge. Considering that the halide ion bridges the two cupric centres within the $Cu_2(LH)_2^{2+}$ unit, these are described as two fused face-sharing octahedron. A second $Cu_2(LH)_2^{2+}$ unit, rotated by 90°, is bonded to the other end of the bromide, defining an approximately tetrahedral environment for this anion between the $Cu_2(LH)_2^{2+}$ units. This conformation allows the lowest steric hindrance between the two dimeric units bonded to the halide.

For each compound, the $Cu_2(LH)_2^{2+}$ unit is composed of two crystallographically equivalent $Cu(LH)^+$ centres related by a 180° rotation. Inside the dimeric unit both metal centres are bridged through the phenolate oxygen atoms defining a central Cu_2O_2 , which is better described as a butterfly, since the dihedral angles defined by the Cu–O₂–Cuⁱ and the Cu–O₂ⁱ–Cuⁱ planes are as large as 34.2(2)° for (**1**) and 33.2(2) for (**2**) (*i*: $-x + 1/2, -y + 1/2, z$). The distance between the metal centres inside the dimer is 2.932(1) Å and 2.923(2) Å for (**1**) and (**2**), respectively. In addition to the phenolate bridges there is an halide bridge between the cupric centres, showing rather long copper to halide distances, 3.1500(8) and 3.0812(9) Å, respectively.

As depicted in Fig. 1S, the empty space available for the tetrabutylammonium cation (computed by means of Platon Squeeze [15]) has the shape of a four legged tetrahedral X (Fig. 1S), according to the expected geometry of the cation, with rather linear C_4H_9 chains.

Copper(II) dimers $Cu_2(\mu-O-L)_2$ have been described forming tetrameric units by coordination of the copper(II) centres to an anion [4], or to a cation like sodium [17] through the dimer bridging oxygen atoms. The anion encapsulation has been known for a long time for compounds like $Cu_4OX_6L_4$, where a central O^{2-} anion is tetrahedrally surrounded by copper(II) ions [18].

The encapsulation of halides within several arrangements of metal ions has been reported, including four metal ions connected in a rather square planar environment [19] or six metal neighbours in an anti-prismatic [20] or even planar hexagonal environment [21]. Paital et al. [4] reported the syntheses of a family of μ_4 -halide tetrameric copper(II) complexes, but only the X-ray structure of the chloride analogue was determined. The geometry around the encapsulated anion is highly flexible and it is determined mainly



Scheme 2. General structure of the $[\text{Cu}_2(\text{LH})_2(\mu_4\text{-X})\text{Cu}_2(\text{LH})_2]^{3+}$ cation.

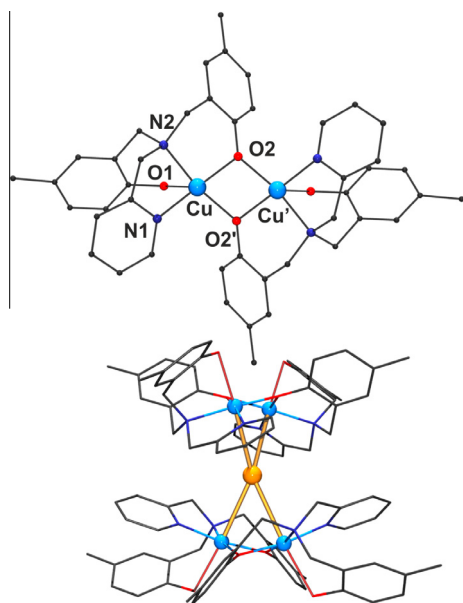


Fig. 1. Molecular structure diagram for the cationic dimeric $[\text{Cu}_2(\text{LH})_2]^{2+}$ unit (up). The tetrameric $[\text{Cu}_2(\text{LH})_2(\mu_4\text{-Br})\text{Cu}_2(\text{LH})_2]^{3+}$ cation showing the tetrahedral coordination of the bromine ion (down).

by the degree of flexibility of the encapsulating moieties and by the steric hindrance between them.

To the best of our knowledge the complex reported in this work is the first example of the encapsulation of a bromide anion within a tetrahedral arrangement of four copper centres, which is structurally characterized.

4.3. Magnetic properties

Susceptibility data for compounds (1) and (2) are depicted in Fig. 2 as a $\chi_{\text{M}}T$ vs T graph. Compounds (1) and (2) show an

elongated Oh (4+2) environment with no distortion towards a trigonal bipyramid geometry. Bond parameters (Table 2), including the Cu-(O2,O2')-Cu' dihedral angles, exhibit very close values of 33.2 and 34.2° for (1) and (2), respectively. Both compounds show very similar magnetic behaviour as can be anticipated from their structural similarities. At room temperature the $\chi_{\text{M}}T$ value is close to $0.30 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, well below the theoretical value of $0.750 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for two $1/2$ spin non coupled copper centers, with a g value of 2.0 (Fig. 2), suggesting a very strong antiferromagnetic interaction. The value of the $\chi_{\text{M}}T$ product decreases continuously until ca. zero and both compounds become diamagnetic below 80 K. The magnetic susceptibility curve does not show a maximum in the experiment temperature range, being above room temperature.

The copper(II) cations in each dinuclear subunit are linked by two O-phenolate atoms, and according to reported DFT calculations [22] the antiferromagnetic exchange for Cu-O-Cu bond angles close to 98° should be strong. In contrast, the interaction through the halogen bridge (Cu-(μ_4 -X)-Cu) between dinuclear subunits is expected to be weak, since the overlap mainly involves the non magnetic d_{z^2} copper(II) orbitals. The shape of the curve indicates a dominant antiferromagnetic coupling, which results from the interaction between the copper(II) atoms mediated by the phenoxo bridges. The parameters that determine the magnitude of the magnetic exchange in this type of systems, with two phenoxo bridges, are the geometry around the copper atoms, the Cu-O-Cu angle and the dihedral Cu-O-O-Cu angle. Therefore, if the interaction mediated by the Cu-O-Cu angle is strong, the Cu_2 fragments are fully coupled at moderated temperatures, and the evaluation of the magnetic exchange coupling constant due to the halogen bridge becomes null.

According to the above considerations the interaction mediated by the halide bridge was assumed as negligible and the experimental data was fitted with the Bleaney-Bowers equation [23] derived from the Hamiltonian $H = -J(S_1 \cdot S_2)$.

$$\chi_{\text{M}} = \frac{2Ng^2\beta^2}{kT} \left[\frac{1}{3 + \exp(-J/kT)} \right]$$

Best fit parameters were $J = -439(4) \text{ cm}^{-1}$, $g = 2.10(2)$ for the Br complex (1) and $J = -429(2) \text{ cm}^{-1}$, $g = 2.090(9)$ for the Cl complex (2). These magnetic exchange coupling constants are comparable to other reported complexes with similar structural parameters [24].

The Cu...Cu distances of 2.932(1) Å and 2.923(2) Å for (1) and (2) inside the dimeric subunits should make operative dipolar interactions, but EPR spectra (X-band) do not show evidence of splitting of the bands due to D effect (Fig. 2). The spectra for both compounds is very similar, exhibiting a main absorption at

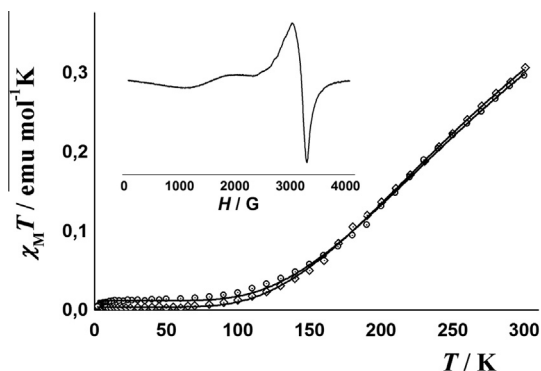


Fig. 2. $\chi_{\text{M}}T$ vs. T plot for compounds 1 (diamonds) and 2 (circles). Inset, X-band EPR spectrum for compound 2.

$g = 2.098$ (**1**) and 2.083 (**2**) in excellent agreement with susceptibility values and a broad forbidden half field signal at $g = 4.01$ (**1**) and 4.22 (**2**) (Fig. 2, inset). Hyperfine coupling with A of c.a.100 G can be observed for (**2**).

5. Concluding remarks

The reaction of the pyridyl-amino-bisphenol ligand N-(2-pyridylmethyl)-N,N-bis-[2'-hydroxy-5'-methyl-benzyl]-amine with copper(II) bromide or chloride leads to the formation of a square pyramidal dinuclear copper species with a syn configuration, which are assembled into tetranuclear complexes by a bridging μ_4 -halide ion, which serves as an anionic template. However, when N,N-bis(pyridylalkyl)-amino-monophenol ligands are used, the obtained compounds, under similar experimental conditions were dinuclear species [9]. For complexes with ligands with two pyridyl residues, the anti configuration of the two square pyramidal copper ions precludes the formation of a tetrameric species.

The magnetic behaviour of both reported complexes is dominated by the antiferromagnetic exchange through the phenoxo bridges,

The complex $\{N(C_4H_9)_4\}[\text{Cu}_2(\text{LH})_2(\mu_4\text{-Br})\text{Cu}_2(\text{LH})_2](\text{PF}_6)_4$ is the first example structurally characterized of a μ_4 -Br-copper(II) tetrameric compound, which illustrates the templating effect of the bromide anion.

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Appendix A. Supplementary data

CCDC 916507 and 970887 contains the supplementary crystallographic data for (**1**) and (**2**). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2014.03.048>.

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