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The templating effect of halides in the tetrameric copper(II) $[Cu_2(LH)_2(\mu_4\text{-}X)Cu_2(LH)_2]^{3+}$ complexes (LH_2 = N-(2-pyridylmethyl)-N, N-bis-[2′-hydroxy-5′-methyl-benzyl]-amine; X = Br, Cl). Synthesis and magneto-structural characterization

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ABSTRACT

The synthesis, magnetic and structural characterization of two tetrameric copper(II) complexes $\{N(C_4H_9)_4\}$-$[Cu_2(LH)_2(\mu_4\text{-}Br)Cu_2(LH)_2](PF_6)_4$ (**1**) and $[Cu_2(LH)_2(\mu_4\text{-}Cl)Cu_2(LH)_2](Cl)_2(PF_6)$ (**2**) is described. LH stands for the hemi-deprotonated anion of the tripodal aminophenol ligand N-(2-pyridylmethyl)-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 $[Cu_2(LH)_2]^{2+}$ units. The magnetic behaviour is dominated by the strong antiferromagnetic exchange within the dimeric unit, mediated by the phenoxo bridges: $J = -439(4)\ cm^{-1}$, $g = 2.10(2)$ for (**1**) and $J = -429(2)\ cm^{-1}$, $g = 2.090(9)$ for (**2**).

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 $[Cu_6Cl(MeO)_2(pz)_9]$ via a chloride templated reaction. Within this complex two trinuclear units, $[Cu_3(MeO)(pz)_3]^{2+}$, 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 $[Cu_4(\mu_4\text{-}X)L_2]ClO_4$ where X = Cl, Br, I, and H_3L = 2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine. The X-ray crystal structure of the chloride species shows that the spherical Cl bridging anion (μ_4-Cl), is responsible for the self-assembly of two $[Cu_2L]^+$ 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(2,6diisopropylphenylimino-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, $\{N(C_4H_9)_4\}$

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$[Cu_2(LH)_2(\mu_4\text{-}Br)Cu_2(LH)_2](PF_6)_4$, (**1**), and $[Cu_2(LH)_2(\mu_4\text{-}Cl)Cu_2(LH)_2(Cl)_2(PF_6)$, (**2**), with the ligand LH_2 = N-(2-pyridylmethyl)-N,N-bis-[2′-hydroxy-5′-methyl-benzyl]-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, N-(2-pyridylmethyl)-N, N-bis-[2′-hydroxy-5′-methyl-benzyl]-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 CEPEDEQ (University of Chile) on a Fison-Carlo Erba EA 1108 model analyzer. Copper was determined by atomic absorption spectroscopy. ^{1}H 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 Magnetoquimica 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 Brucker ES200 spectrometer.

2.2. Synthesis of the ligand N-(2-pyridylmethyl)-N,N-bis-[2′-hydroxy-5′-methyl-benzyl]-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. ^{1}H NMR ($CDCl_3$): δ 8.6 (1H, d, H_α-Py), 7.7 (1H, t, H_β-Py), 7.27 (1H, t, H_γ-Py), 7.1 (1H, d, H_δ-Py), 6.98 (2H, dd); 6.87 (2H, d) and 6.80 (2H, d) (phenyl protons), 3.89 (2H, s, CH_2-Py), 3.78 (4H, s, CH_2-Ph), 2.25 (6H, s, CH_3-Ph), 10.5 (2H, broad, OH).

2.3. Synthesis of $\{N(C_4H_9)_4\}[Cu_2(LH)_2(\mu_4\text{-}Br)Cu_2(LH)_2](PF_6)_4$ (**1**)

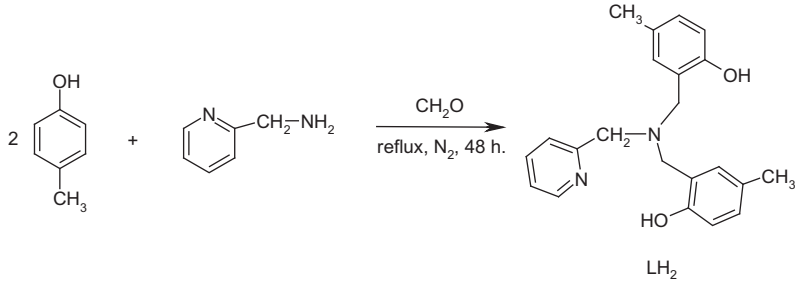
A solution of $CuBr_2$ (0.447 g, 2 mmol) in 5 mL MeOH was added to a solution of the ligand LH_2 (0.70 g, 2 mmol) and triethylamine (280 μL, 2 mmol) in MeOH (20 mL), and the mixture was refluxed for 60 min. Addition of excess tetrabutylammonium hexafluorophosphate to the solution precipitates the crystalline product immediately (0.648 g, 51%). Recrystallization from boiling methanol affords crystals suitable for X-ray structural studies. *Anal.* Calc. for $Cu_4C_{88}H_{92}N_8O_8\,Br\cdot(C_4H_9)_4N\cdot 4(PF_6)$: 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 $[Cu_2(LH)_2(\mu_4\text{-}Cl)Cu_2(LH)_2](Cl)_2(PF_6)$ (**2**)

This compound was synthesized by the same procedure as the bromide, but using $CuCl_2$ instead $CuBr_2$. *Anal.* Calc. for $C_{88}H_{92}Cu_4Cl_3F_6N_8O_8P$: 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 $\{N(C_4H_9)_4\}[Cu_2(LH)_2(\mu_4\text{-}Br)Cu_2(LH)_2](PF_6)_4$ was determined at 150 K by X-ray diffraction measurements on a prismatic $0.38 \times 0.30 \times 0.28$ 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. $U_{iso}(H)$ 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 hexafluorphosphate 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, C104H128BrCu4F24N9O8P4. The crystal structure of $[Cu_2(LH)_2(\mu_4\text{-}Cl)Cu_2(LH)_2](Cl)_2(PF_6)$ was determined at room temperature on a stick shaped $0.67 \times 0.19 \times 0.15$ mm^3 single crystal. During the final stages of the refinement it became clear there was disorder on the uncoordinated charge balancing hexafluorphosphate 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 N-(2-pyridylmethyl)-N,N-bis-[2′-hydroxy-5′-methyl-benzyl]-amine, LH_2.