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A new family of multinuclear mixed-ligand copper(II) clusters: crystal structures, magnetic properties and catecholase-like activity

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Abstract

In this work we report a family of mixed-ligand copper(II) clusters obtained with different nuclearities: $[Cu_3(\mu-OH)(\mu-dppi)_3(\mu-hfac)_3]$ (1), $[Cu_4(\mu-dppi)_4(Hdppi)_2(hfac)_4]$ (2), $[Cu_5(\mu-O)_2(\mu-dppi)(\mu-Hdppi)_2(\mu-hfac)_3(hfac)_2]$ (3) and $[Cu_6(\mu-O)_2(\mu-dppi)_2(\mu-Hdppi)(\mu-hfac)_6]$ (4) complexes, where *hfac* = hexafluoroacetylacetonate, *dppi* = diphenylphosphinate and *Hdppi* = diphenylphosphinic acid. Complexes 3 and 4 are the first examples of copper(II) clusters containing a μ -oxo oxygen atom and *hfac* as bridging ligands. The magnetic properties of all

compounds showed predominant antiferromagnetic interactions and the magnetic coupling constants were evaluated using an isotropic exchange model based on the spin topology. A spin frustration phenomena was observed for the equilateral cyclic trinuclear complex (1), thus an antisymmetric exchange term was also considered to fit the experimental magnetic data. The obtained *J* values are in the range from -89 cm⁻¹ to 1.7 cm⁻¹ and were interpreted based on structural features. The electrochemical properties and catalytic activity of complexes 1 and 2 were investigated and compared with the [Cu(hfac)₂] precursor. Catecholase-like activity of copper(II) complexes via oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) to 3,5-di-*tert*-butylquinone (3,5-DTBQ) was performed.

Keywords: copper(II) complexes, mixed-ligand complexes, magnetism, phosphinate, Catecholase-like activity

1) Introduction

Polynuclear metal complexes (PMCs) are a hot topic nowadays due to the application of some of these compounds as catalysts,[1,4] luminescence systems,[5,6] electronic devices,[7] semiconductors,[8,9] molecular-based magnetic[10-15] materials and mimics of the active site of metalloenzymes.[16-18] A large number of copper(II)-based PMCs with different architectures and nuclearities can be constructed by using this cheap and readily available metal.[1-18] However, the synthesis of polynuclear copper(II) clusters in a controllable way is challenging. Apart from the major role played by the ligand or combination of ligands selected in assembling the units leading to the coordination framework, other factors such as solvent, temperature, counter-ion and additives can be determinant for the definitive structure and properties of the complex.[19,20] An useful approach to obtain high-nuclearity copper clusters relies on the use of multiple functional bridging and/or chelating neutral or anionic ligands. The carboxylate group C(O)O⁻ is a popular component of these multinucleating agents.[21] Similar to the carboxylate

linkage, the ability of the phosphinate moiety $P(O)O^{-}$ to act as a bridging ligand have been extensively investigated. Although this kind of ligands have been widely used to prepare organic-inorganic hybrid polynuclear complexes of main group and transition metal ions such as titanium, manganese, cobalt, nickel, silver, etc,[22-28] very few copper complexes built on the exclusive basis of phosphinate ligands have been described to date. Generally, the 2.11 (II and III) coordination mode[29, 30] predominates, *i.e.*, μ -O,O'-bridges (Scheme 1),[31-37, 38] even though a 3.21 (IV) binding mode has been found in a dimethylphosphinate complex. [39]



Scheme 1. Coordination modes of phosphinate in transition metal complexes (R^1 , R^2 = alkyl,

aryl).[29, 30]

A few examples of heteroleptic copper(II) complexes containing phosphinate ligands have been previously described.[40-42] In these cases, the phosphinate groups act as a bridging ligand between copper ions, leading to chains and dinuclear compounds. In addition, some examples of mononuclear[43,44] and dinuclear[38] copper(II)-diphenylphosphinate complexes in which the ligand is bound to the metal through only one up to the two oxygen atoms are also known.

However, to the best of our knowledge, no copper(II) cluster assembled through the phosphinate group has been reported until now.

Binuclear and trinuclear copper clusters are present in multicopper oxidases (MCOs). These are a family of enzymes featuring at least four copper ions per functional unit that nature has developed for the oxidation of their substrates with concomitant four-electron reduction of O_2 to water.[45,46] Mechanistic studies suggested the participation in this process of oxygen bridged metal–dioxygen intermediates.[47,48] Due to the technological and economical relevance of the four-electron reduction of O_2 ,[49-51] intensive efforts have been devoted to the development of simpler and more accessible synthetic multicopper systems to achieve this process.[52-55] Many complexes containing several Cu–O₂ binding modes that mimic the behavior of MOCs have been described. Inspired by these works, we thought that the complexation of copper(II) hexafluoroacetylacetonate with diphenylphosphinic acid could be directed to the formation of new copper(II) coordination clusters by using dioxygen as an organizing agent of the metal centers. Hexafluoroacetylacetonate ligand is extensively used as building block in molecular magnetism area.[56-60] However, there are no precedent mixed-ligand copper(II) compounds containing *hfac* and phosphinates.

In this contribution, we report the synthesis and crystal structure of the mixed-ligand copper(II) clusters $[Cu_3(\mu-OH)(\mu-dppi)_3(\mu-hfac)_3]$ (1), $[Cu_4(\mu-dppi)_4(Hdppi)_2(hfac)_4]$ (2), $[Cu_5(\mu-O)_2(\mu-dppi)(\mu-Hdppi)_2(\mu-hfac)_3(hfac)_2]$ (3) and $[Cu_6(\mu-O)_2(\mu-dppi)_2(\mu-Hdppi)(\mu-hfac)_6]$ (4). Complexes 1-3 are obtained from the reaction of $[Cu(hfac)_2]$ with Hdppi in the presence of dioxygen while complex 4 is formed in the reaction of $[Cu(hfac)_2]$ with dppnTEMPO radical (1-piperidinyloxy-4-[(diphenylphosphinyl)amino]-2,2,6,6-tetramethyl) via hydrolysis of the P(O)-N linkage. The careful selection of the reaction conditions allowed us to obtain complexes with

different nuclearities varying from trinuclear to hexanuclear in a reproducible way. Complexes **3** and **4** are the first examples of copper(II) clusters having a μ -oxo-independent oxygen atom with *hfac* as bridging ligands. The magnetic properties of all compounds were studied, and in addition, the electrochemical properties and catalytic activity of complexes **1** and **2** in a redox reaction were investigated. Catecholase-like activity of copper(II) complexes via oxidation of 3,5-di-*tert*-buthylcatechol (3,5-DTBC) to 3,5-di-*tert*-buthylquinone (3,5-DTBQ) was performed.

2) Experimental section

2.1. General procedures

All the reagents and solvents were purchased from commercial sources and directly handled without further purification.

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2.2. Synthesis of complexes 1 and 3

[Cu(hfac)₂(H₂O)₂] (1: 117 mg, 0.23 mmol, and 3: 24 mg, 0.039 mmol) was dissolved in 50 mL of boiling n-heptane followed by continuous bubbling of oxygen gas. The solution was concentrated until *ca*. 15 mL, then a chloroform solution (2 mL) of diphenylphosphinic acid (1: 50 mg, 0.23 mmol; and 3: 10 mg, 0.046 mmol) was added. For the synthesis of 1, triethylamine (32 μ L, 0.23 mmol) was added under vigorous stirring. Addition of Ph₂P(O)OH caused solution color changes from dark-green to light green-yellow and the appearance of small amounts of a pale blue precipitate. Insoluble material was removed through filtration. After a few hours (1) or 2-3 days (3) dark-green crystals were obtained. 1: Yield 38%. *Anal. Calc.* for C₅₇H₅₂Cu₃F₁₈NO₁₄P₃ (1·Et₃NH⁺·H₂O): C, 42.77; H, 3.27; N, 0.88. Found: C, 42.28; H, 3.57;

N, 1.10. IR (ATR, v cm⁻¹): 3058, 3013 (w) (vC-H_{Ar}), 1646 (s) (vC=O), 1545 (s) (vC=C), 1260 (s) (vP=O), 1192 (s) 1131 (s), 1033 (s) (vC-F). Complex **3**: Yield 11%. *Anal. Calc.* for $C_{61}H_{37}Cu_5F_{30}O_{18}P_3$: C, 35.94 ; H, 1.83. Found: C, 36.39 ; H, 1.97. IR (ATR, v cm⁻¹): 1644 (m) (vC=O), 1433 (m) (vC=C), 1267 (s) (vP=O), 1107 (sb), 1011 (sb) (vC-F).

2.3. Synthesis of 2

The $[Cu(hfac)_2(H_2O)_2]$ (235 mg, 0.47 mmol) was dissolved in 50 mL of boiling n-heptane followed by continuous bubbling of oxygen gas. The volume of the solution was reduced to *ca*. 15 mL and then a solution of 100 mg of diphenylphosphinic acid (0.46 mol) in 2 mL of methanol was added. Bubbling of oxygen was continued during 30 min. After 2-3 days, dark green crystals were obtained. Yield 23%. *Anal. Calc.* for $C_{92}H_{66}Cu_4F_{24}O_{20}P_6$: C, 46.28 ; H, 2.70. Found: C, 46.64 ; H, 2.74. IR (ATR, v cm⁻¹): 3062 (w) (vC-H_{Ar}), 1644 (s) (vC=O), 1459 (s) (vC=C), 1243 (s) (vP=O), 1131 (sb), 1050 (m) (vC-F).

2.4. Synthesis of 4

Complex 4 was obtained from the reaction of [Cu(hfac)₂(H₂O)₂] with dppnTEMPO radical through in situ hydrolysis of the P(O)-N linkage as secondary product together with the main product already described in our previous work.[61] 26 mg (0.053 mmol) of [Cu(hfac),(H,O),] was added to 10 mL of *n*-heptane and boiled until dissolution was complete. Then, 20 mg (0.053 mmol) of the dppnTEMPO radical was dissolved in CHCl₂ and quickly added under constant stirring. After few days, dark-green crystals of а $[Cu(hfac)_{2}(dpnnTEMPO)_{2}][Cu(hfac)_{2}(dpnnTEMPO)]$ were obtained. These crystals were filtered out and the filtrated kept at 15 °C. After 2 months, dark-blue crystals formed from the filtrate solution were separated manually from the main compound. Yield 30%. Anal. Calc. for

 $C_{66}H_{37}Cu_6F_{36}O_{20}P_3 \cdot 0.5H_2O$, 34.21%; H, 1.65%. Found: C, 34.66%; H, 1.84%. IR (ATR, v cm⁻¹): 1638 (s) (vC=O), 1452 (s) (vC=C), 1217 (s) (vP=O), 1139 (sb), 991 (mb) (vC-F).

2.5. Physical Measurements

CHN elemental analyses were performed on a Perkin Elmer 2400. Infrared spectra (4000-400 cm⁻¹) were recorded on a Bruker Alpha-P FTIR spectrometer. Electronic spectra were acquired from THF solutions on a Varian 1200 spectrophotometer. The magnetic measurements were performed on a bunch of single crystals using a Cryogenic Sx-600 SQUID in the temperature range 2-280 K and field range of 0 to 6.5 T. The sample was placed in a gelatine capsule and data were corrected for the sample diamagnetism and sample holder. The magnetic data were fitted using the Magprop software, available within the DAVE package.[62]

Electrochemical studies were achieved on Metrohm Autolab potentiostat PGSTAT101 with Pt (Ø3 mm) as working and counter electrode, and Ag/AgCl as a reference electrode. All manipulations were carried out at 298 K in THF with 0.10 mol·L⁻¹ tetrabutylammonium hexafluorophosphate, Bu₄NPF₆, as supporting electrolyte. Sweep rate was 50-100 mV/s.

Single crystal X-ray data of **1-3** complexes were collected on a Bruker D8 Venture diffractometer using graphite monochromatic MoK α radiation ($\lambda = 0.71073$ Å). Data collection and cell refinement were performed with Bruker Instrument Service v4.2.2 and APEX2,[63] respectively. Data reduction was carried out using SAINT.[64] Empirical multiscan absorption correction using equivalent reflections was performed with the SADABS program.[65] For **4**, the crystallographic data were collected on an Oxford GEMINI A Ultra diffractometer using graphite monochromated Mo K α radiation. Data collection, data reduction, cell refinement and absorption corrections were performed by using the CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.32.38. The structures solution and refinement were performed with the SHELXS-

2014 and SHELXL-2014 programs.[66] All atoms except hydrogen were refined anisotropically. The H-atoms were treated using a constrained refinement. Despite of our best efforts it was not possible to achieve a good refinement for compound **1**. It is possible to say that it crystallizes in a trigonal crystal system and the molecular structure consists of a trimetallic triangular core, in which the copper(II) ions are linked by bridging *hfac*, *dppi* and one μ_3 -hydroxo ligand (see Fig. S1). Details of data collection and structure refinement for compounds **2-4** are summarized in Table 1.

	2	3	4
Chemical formula	$2(C_{46}H_{33}Cu_2F_{12}O_{10}P_3)$	$C_{61}H_{37}Cu_5F_{30}O_{18}P_3$	$C_{66}H_{37}Cu_6F_{36}O_{20}P_3.(H_2O)_{0.5}$
Formula weight	1193.71	2038.51	2316.11
Crystal system	Triclinic Monoclinic		Monoclinic
a/Å	13.6349(17)	15.15877 (13)	22.5132(6)
b/Å	13.6603(16)	21.278 (2)	14.0879(4)
c/Å	15.7376(19)	22.9840 (18)	27.5041(10)
α''^o	84.342(4)	90	90
β'^{o}	75.042(3)	98.975 (3)	106.332(3)
y/°	61.085(3)	90	90
Unit cell volume/Å ³	2477.7(5)	7322.2 (1)	8371.3(4)
Temperature/K	293(2)	293(2)	120(2)
Space group	P-1	$P2_1/n$	Сс
Z	2	4	4
Radiation type	ΜοΚα	ΜοΚα	ΜοΚα
μ/mm^{-1}	1.056	1.638	1.702
θ range /°	2.1-25.7	2.0-27.3	1.9-25.0
reflections measured	25867	65017	26074
independent reflections	9334	16368	12239
R_{int}	0.056	0.070	0.049
R_I values ($I > 2\sigma(I)$)	0.075	0.047	0.0587
$wR(F^2)$ values ($I > 2\sigma(I)$)	0.192	0.104	0.1418
R_1 values (all data)	0.120	0.083	0.0758
$wR(F^2)$ values (all data)	0.213	0.1213	0.1560
Goodness of fit on F^2	1.072	1.020	1.036
Largest diff. peak and role (e. Å ⁻³)	0.888;-0.536	1.268; -0.976	2.086; -0.640

Table 1: Summary of crystal data, collection and refinement for compounds 2-4.

2.6. Catalytic oxidation of 3,5-DTBC

Catecholase-like activity was determined using 10^{-4} mol·L⁻¹ solutions of each copper complex in THF. In order to keep the same number of Cu^{II} ions in solution, the molar

concentration of complexes 1, $[Cu(hfac)_2]$ and 2 was calculated dividing their molecular weights by three (Cu₃), one (Cu) and four (Cu₄), respectively. The UV spectra were recorded in 1 min interval following the increasing of absorption values at $\lambda = 392$ nm during 20 min at 25 °C. All experiments were carried out using air and dioxygen-saturated THF solutions. To determine the dependence of the rates and kinetic parameters such as V_{max} , K_m and k_{cat} , the kinetics measurements were performed using 3,5-DTBC in the concentration range from $5 \cdot 10^{-2}$ to $8 \cdot 10^{-4}$ 'n $\operatorname{mol} L^{-1}$.

3) Results and discussion

3.1. Syntheses

Complexes 1-3 have been prepared according to the synthetic routes shown in Scheme 2a. The complex 1 was obtained by reacting diphenylphosphinic acid and $[Cu(hfac)_2]$ in 1:1 stoichiometry in a *n*-heptane-chloroform solution, using triethylamine as a base and under continuously bubbling of dioxygen gas. The analogous reaction of [Cu(hfac)₂] with diphenylphosphinic using *n*-heptane-methanol solution provided the complex 2. Increasing to two equivalents the amount of [Cu(hfac)₂] that reacted with diphenylphosphinic acid (1:2 stoichiometry) in a *n*-heptane-chloroform solution lead to the formation of the complex 3. Complex 4 proceeds from the reaction of $[Cu(hfac)_2]$ with dppnTEMPO radical using a stoichiometric ratio [Cu(hfac)₂]:radical of 1:1 in a *n*-heptane-chloroform solution (Scheme 2b). Formation of 4 involved in situ hydrolysis of the P-N bond of the radical to give diphenylphosphinic acid that acts as bridging ligand towards copper(II) ions. Crystals of complex 4 were isolated after growing for 2 months in the reaction medium and were separated

manually from the main compound identified as the complex [Cu(hfac)₂(dpnnTEMPO)₂][Cu(hfac)₂(dpnnTEMPO)] previously reported.[61]



Scheme 2. Synthesis of the complexes 1-3 (a) and 4 (b)

3.2. Structure descriptions

The coordination modes of *dppi* in complexes **1-4** include binding types **I**, **II**, **III** shown in Scheme 1, and a new one that has not been previously reported, *syn*-3.21 (**VI**, Scheme 3).[29, 30] As for the *hfac* ligand, two coordination modes are present, the usual chelate *syn*-1.11 (**VII**) and the first example of a homonuclear copper(II) complex showing a *syn*-2.11 (**VIII**) coordination (Scheme 3).



Scheme 3. Coordination modes of the *dppi* and *hfac* ligands in complexes 1-4.

Despite extensive experimentation, good quality single crystals of complex 1 could not be obtained. Notwithstanding, the analysis of the X-ray data collected allowed to identify the molecular structure of this compound as a trimetallic equatorial triangular core, in which the copper(II) ions are joined together by three *hfac*, three *dppi* ligands and one independent hydroxo ligand (Fig. S1).

Compound 2 crystallizes in triclinic *P-1* and the molecular structure consists of a tetranuclear copper(II) cluster, in which metal ions are held together by four *dppi*, two *Hdppi* and four *hfac* ligands as seen in Fig. 1. The four copper(II) centers are pentacoordinated, and in this geometry the metal environment can be described between square-pyramidal (SP) and trigonal-bipyramidal (TBP) extremes. In terms of the parameter τ , these extremes are represented by the values $\tau = 0$ and $\tau = 1$ for the SP and TBP geometries, respectively.[67] The calculated $\tau = 0.16$ indicates a distorted square pyramidal geometry with equatorial positions occupied by two *hfac* oxygen atoms [O3, O4 for Cu1 and O1, O2 for Cu2], one *dppi* (or *Hdppi*) oxygen atom [O7 for Cu1; O1, O7 for Cu2] and in apical position by one *dppi* (or *Hdppi*) oxygen atom [O7 for Cu1 and O10 for Cu2]. All *hfac* ligands are coordinated in a chelating 1.11 mode (VII), while the *dppi* ligands are bridged coordinated in the 3.21 (VI) and 2.11 (II) modes (Scheme 2 and 3). The terminal *Hdppi* with respect to the Cu4 plane are

shown in Figure S2. Selected bond lengths and bond angles are listed in Table S1. The assignment of the protonated Hdppi or dppi ligands in the structure was made by a careful analysis on the P-O bond distances, which ranges between 1.501(5) and 1.522(6) Å. It is important to stress that the diphenylphosphinate group in compounds 2-4 is bridged coordinated to two or more metal ions in asymmetric and symmetric modes, while the diphenylphosphinic acid is coordinated also in monodentated mode through the P=O moiety. The shortest P-O bond length was attributed to the phosphinyl group (P=O), as also described for the complex $[Cu(Hdppi)(bdmpp)]_2(dppi)_2$, where Hbdmpp = 1,3-bis(3,5-dimethylpyrazol-1-yl)-propan-2ol[38]. The equatorial Cu-O_{dppi} bond lengths range from 1.887(5) to 1.971(6) Å, while the axial Cu-O_{dppi} are 2.712(5) Å for Cu1-O7 and 2.634(5) Å for Cu2-O10ⁱ (*i*=-x,-y,-z). These bond lengths are in agreement with other reported phosphinic copper(II) based complexes[36, 38-39]. The axial Cu1-O7_{dppi} bond length (2.712(5) Å) is among the longest reported for copper(II) complexes.[38] This long bond length can be attributed to steric hindrance around the metal ion associated to Jahn-Teller axial elongation.[68,69] The intermolecular O10 to O10ⁱ distance within the tetranuclear core of 2.414(8) Å is significantly longer than the O-O bonds found in peroxydiphosphate compounds $[P_2O_8]^{4-}$ (1.49 Å). [70] Based on the charge balance as well as coordination modes of Hdppi/dppi, we conclude that the bridging central ligands are deprotonated. The four copper(II) ions of the complex define a planar parallelogram with the two y,-z] and 5.653(1) (Cu2^{...}Cu2¹). These distances are close to those seen in the dimer [Cu(HdppiH)(bdmpp)]₂(dppi)₂[38] and in the chain of *bis*(dibutylphosphinato)copper(II),[33] in which the metal ions are bridged by dppi ligand in the 3.21 (IV) and 2.11 (II) modes. Other intramolecular copper-copper distances are 7.685(2) Å [Cu1^{...}Cu2ⁱ or Cu1^{i...}Cu2] and 10.571(2)

Å (Cu1^{...}Cu1ⁱ). All *dppi* ligands are in *trans* positions of the plane of the Cu₄ core (Figure S2). If the *dppi* ligands in 2.11 (II) coordination mode bind the copper(II) ions outside of the Cu₄ plane, then the 3.21 (VI) and 1.10 (I) ones are closer to the metallic core plane. Hydrogen-bonding involving terminal *Hdppi* ligands are observed between the Cu4 molecular units, leading to a supramolecular 1D chain along the *c* axis. The shortest intermolecular distance between the copper(II) ions is 5.851(1) Å [Cu1^{...}Cu1ⁱ].

Complex 3 crystallizes in the monoclinic $P2_1/n$ space group. Selected bond lengths and bond angles for 3 are listed in Table S2. As shown in Figure 1, the asymmetric unit of complex 3 consists of a discrete pentanuclear copper(II) cluster. In this compound, the copper ions are held together by one *dppi*, two *Hdppi*, five *hfac* and two independent oxo ligands. Copper ions Cu1, Cu2 and Cu3 are six-coordinated with distorted octahedral geometries, whereas the metal ions Cu4 and Cu5 are pentacoordinated with distorted square-pyramidal geometry ($\tau = 0.34$ for Cu4 and $\tau = 0.21$ for Cu5). Cu1, Cu2 and Cu3 ions are connected by two hfac ligands in the unique 2.11 mode (VIII), being O10 and O13 the bridging atoms, two 3.21 (VI) Hdppi and one independent μ_3 -oxo ligand O1. The Hdppi and dppi were assigned based on the difference observed for P-O bond length. In contrast, Cu4 and Cu5 ions are linked together by one *dppi* (O5 and O6) and a μ_2 -oxo ligand (O2). The moieties Cu1-Cu3 and Cu4-Cu5 are connected to each other by two Hdppi (O4 and O7) and one dppi (O5 O6) ligands in the coordination mode already described for 3. Due to the Jahn-Teller distortion all metal ions have short Cu-O equatorial bond lengths in the range 1.922(3)-1.985(2) Å and long axial ones [2.654(3)-2.716(3) Å for Cu1, Cu2 and Cu3 ions; 2.375(2) and 2.687(3) Å for Cu4 and Cu5, respectively]. The average Cu-O-Cu bond angles varies depending on chelate ligand

being for oxo bridge, *hfac* and *dppi* and *Hdppi* ligands in the range 111.1(1)-130.4(1)°, 86.9(1)-89.1(1)° and 92.21-98.4(1)°, 97.5(1)-105.4(1)°, respectively. The Cu···Cu distances in the plane formed by four copper ions [Cu2-Cu5] are in the range 3.2728(6)-3.5158(6) Å. The Cu1 ion is above the plane containing the other four copper(II) ions with the intramolecular distances 3.2265(6), 3.2935(6), 4.9048(6) and 4.8137(6) Å between Cu1 and the respective ions Cu2, Cu3, Cu4 and Cu5. This complex shows short intermolecular F···F interactions that contribute to stabilize the crystal packing (F3···F20 = 2.805(4) Å, \angle C17-F3···F20 = 157.1(3)°; F4···F19ⁱ = 2.794(5) Å; \angle C13-F4···F19ⁱ = 107.1(3)°; F5···F19ⁱ = 2.932(5)Å, \angle C13-F5···F19ⁱ = 100.4(2), i = -x, -y, -z; F18···F23Aⁱⁱ = 2.77(1) Å; \angle C51-F18···F23Aⁱ = 107.1(3)°, ii = 1/2+x, 1/2-y,1/2+z).

Compound 4 crystallizes in the monoclinic *Cc* space group and the molecular unit is shown in **Figure 1**. Selected bond lengths and bond angles are displayed in **Table S3**. The molecular structure consists of a discrete hexanuclear copper cluster with one crystallization water molecule. In this compound, the copper(II) ions are held together by two *dppi*, one *Hdppi*, six *hfac* ligands and two oxo-oxygen atoms (**Figure 1**). The hexanuclear core is formed by two Cu₃ triangular units connected to each other by the *dppi* and *Hdppi* ligands. For *Hdppi* and *dppi* ligands two are bridging in 4.22 mode (**V**) and one in 3.21 (**VI**) coordination mode. All *hfac* ligands are involved in 2.11 (**VIII**) coordination mode, in contrast with compound **3** in which some of the *hfac* coordinates in the 1.11 (**VII**) mode (**Scheme 3**). Five copper ions (Cu1, Cu3, Cu4-Cu6) have a distorted octahedral geometry being coordinated to two *dppi* oxygen atoms, three oxygen atoms provided by two *hfac* ligands and one independent oxo ligand. The sixth copper ion (Cu2) is pentacoordinated linked by a bridging *dppi* ligand through an oxygen atom only. The calculated τ parameter is 0.16, indicating a slightly distorted SP coordination

environment. Due to the Jahn-Teller distortion, the axial Cu-O bond lengths of six-coordinated copper ions are longer [2.531(4) - 2.788(7) Å] than equatorial ones [1.910(6) - 2.02(2) Å]. The same effect is observed for Cu2 ion. The apical Cu-O length in the square pyramid of 2.712(8) Å is significantly longer than average Cu-O bond length of 1.941(6) Å in its basal plane. The average Cu^{...}Cu distances in the triangular units formed by Cu1 to Cu3 and Cu4 to Cu6 metal ions are 3.207(6) Å (average), while the distance between two opposite copper ions of distinct triangular units is 3.500(1) Å (average). The Cu-O-Cu angles varies depending on the bridging ligands being for oxo bridge, *hfac*, and *dppi* ligands in the range 111.2(3)-114.7(3)°, 83.0(2)-86.9(3)° and 94.4(3)-101.5(2)°, respectively. Short contacts C_{sp2} -H···F, C_{sp2} -H···C_{sp2} and F···F contribute to stabilize the crystal packing (F4···F12A = 2.78(2) Å, ∠C6A-F12A···F4ⁱ = 115(1)°; i = x, -y, 1/2 + z; F13···F32 = 2.83(2) Å, ∠C26-F32····F13 = 131(1)°).



Figure 1. Molecular structures of complex 2 (a), 3 (b) and 4 (c). Crystallization solvent molecules, fluorine and hydrogen atoms were omitted for the sake of clarity. The *dppi* and *Hdppi* carbon atoms are represented in green while *hfac* ligands are represented in blue.

3.3. Magnetic Studies

The temperature dependence of the magnetic susceptibility of complex 1, represented as χ T, is shown in **Figure 2**. At 270 K, χ T is 1.16 cm³·mol⁻¹·K, smaller than the expected value

 $(1.24 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K})$ for three non-interacting copper(II) ions with g = 2.1. Upon cooling, χT decreases gradually until 140 K, followed by faster decrease down to 0.21 cm³·mol⁻¹·K at 2.0 K. This behavior indicates the presence of dominant antiferromagnetic interaction. Since the three copper(II) ions are equivalent by symmetry, the magnetic interaction was initially estimated by fitting χT considering equilateral triangle with an isotropic exchange (H_{exch}) conventional Heisenberg-Dirac-van Vleck Hamiltonian described by the $H = -J(\vec{S}_1 \bullet \vec{S}_2 + \vec{S}_2 \bullet \vec{S}_3 + \vec{S}_1 \bullet \vec{S}_3)$ where J is the magnetic exchange interaction. An intermolecular interaction (zJ) was considered using the mean-field approximation to describe the data at low temperatures, and the best fit curve was found for g = 2.12, $J_1 = -16$ cm⁻¹ and zJ = -1.9 cm⁻¹ (see Figure S3 for details). The shortest intermolecular distances between adjacent trinuclear units are large (≈ 9 Å), and the intermolecular magnetic interaction obtained is too large and cannot be considered as realistic. It is known that cyclic trinuclear copper(II) complexes can show geometric spin frustration.[71,72] In fact, the χT value at the lowest temperature is smaller than expected for a magnetically isolated copper(II) ion (0.4 $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$). In this case, to interpret the magnetic data would be necessary to go further than the isotropic exchange model and consider also an antisymmetric exchange interaction[73,74] $\sum [G_{ii}(S_i \times S_i)]$ according to the Hamiltonian described in Equation 1, where G_{ij} is the antisymmetric exchange vector, β is the Bohr Magneton and g_{\parallel} , g_{\perp} are the parallel and perpendicular component of the g value. In an equilateral triangle (D_{3h} symmetry) $\mathbf{G}_{\mathbf{x}} = \mathbf{G}_{\mathbf{y}} = 0$ and all pairs of $\mathbf{G}_{\mathbf{ij}}^{\mathbf{z}}$ are equal ($\mathbf{G}_{12} = \mathbf{G}_{23} =$ G₃₁). The effective antisymmetric exchange constant, G, is related to the sum of the components of two interacting centers, *Gij*, through the expression $\mathbf{G} = (\mathbf{G}_{\mathbf{z}}/6)\sqrt{3}$. The best fit parameters were found for: $J = -20 \text{ cm}^{-1}$, $g_{\parallel} = 2.30$, $g \perp (\text{fixed}) = 2.00$ and $\mathbf{G} = 3 \text{ cm}^{-1}$ with R =

3.5x10⁻², where $R = \sum [(\chi T_{exp.} - \chi T_{teor.})^2 / \chi T_{exp}^2]$. A Temperature Independent Paramagnetism (TIP) of $101x10^{-6}$ cm³·mol⁻¹ was considered. The *J* and **G** values found for **1** are smaller than previously reported for other trinuclear copper(II) complexes[75] since those complexes have different bridging ligands in addition to μ_3 -OH. Although, it was found some variance in the *J* and **G** values, the ratio $|\mathbf{G}/J| \sim 0.15$ found for **1** is close to the value ($|\mathbf{G}/J| \sim 0.17$ -0.19) reported for those complexes.[75]

$$H = H_{exch.} + H_{ASE} + H_{zeeman}$$
(Eq. 1)
$$H_{exch} = -J_1(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_1 \cdot \vec{S}_3 + \vec{S}_2 \cdot \vec{S}_3)$$

$$H_{ASE} = G_{z}[\vec{S}_{1} \times \vec{S}_{2} + \vec{S}_{2} \times \vec{S}_{3} + \vec{S}_{3} \times \vec{S}_{1}]$$
$$H_{zeeman} = \beta \Big\{ g_{\perp}[H_{x}(\vec{S}_{1x} + \vec{S}_{2x} + \vec{S}_{3x}) + H_{y}(\vec{S}_{1y} + \vec{S}_{2y} + \vec{S}_{3y})] + g_{\parallel}H_{z}(\vec{S}_{1z} + \vec{S}_{2z} + \vec{S}_{3z}) \Big\}$$



Figure 2. Temperature dependence of χT for 1. The black line represents a fit using the parameters described in the text (Eq. 1).

The temperature dependence of the magnetic susceptibility of 2, represented as χT is shown in Figure 3. In the temperature range 60-235 K, χT has a constant value of 1.58 $cm^3 \cdot mol^{-1} \cdot K$ which is lower than the expected one (1.65 $cm^3 \cdot mol^{-1} \cdot K$) for four non interacting copper(II) ions with g = 2.10. Below 60 K, χT decreases down to 1.23 cm³·mol⁻¹·K at 2.5 K. This behavior suggests the presence of dominant antiferromagnetic interaction. To estimate the magnetic interaction, χT curve was fitted assuming the spin topology outlined in Figure 4 using the Hamiltonian described in Eq. 2. The spin topology model for 2 was built considering the shortest distances between copper(II) ions bridged by phosphinate groups that act as magnetic exchange pathways. The magnetic interaction between Cu1 and Cu2 is represented by J_1 while the magnetic interaction between Cu²⁻Cu^{2ⁱ} is represented by J_2 . Since the distance between two Cu1 ions represented by S₁ and S₃ as well as the distances Cu1⁻⁻Cu2ⁱ (-x, -y, -z) represented by S₁, S₄ and S₂, S₃ are large, the magnetic interactions between them are expected to be weaker and were neglected to prevent overparametrization. The best fit was found for the average g = 2.05, $J_1 = -1.6$ cm⁻¹ and $J_2 = 1.7$ cm⁻¹ with R = 2.2×10^{-3} , where the negative sign indicates an antiferromagnetic interaction. We also fitted the magnetic data using a simpler model assuming $J_1 = J_2$, however it gave a poor quality fit of the data.



Figure 3. Temperature dependence of χT for 2. The black line represents a fit using the model described in the text.



Two different magnetic couplings ferro- and antiferromagnetic found for **2** are in the range observed $(J = -5.9 \text{ cm}^{-1} \text{ to } J = 2.6 \text{ cm}^{-1})$ for $bis(\mu$ -dialkylphosphinato)copper(II) complexes, coordinated by phosphinate groups in 2.11 (II) mode.[33-37] In fact, the difference in the magnetic coupling were attributed to ligand-mediated conformational variations as well as differences on metal environment. Comparing the copper(II) environment of $[Cu(R_2PO_2)_2]$ where *R* is the alkyl group, the flattenest tetrahedral environment leads to the largest O-Cu-O angle as well as the longest intrametallic distance. It is well known that these features favor the transition from ferromagnetic to antiferromagnetic coupling.[76]



Figure 5. Temperature dependence of χT for 3. The black line represents the best fit using the parameters described in the text.

The temperature dependence of χT for **3** is shown in **Figure 5**. At 290 K, χT is 1.97 cm³·mol⁻¹·K that is smaller than expected for five non-interaction copper(II) ions (2.07 cm³·mol⁻¹·K) with g = 2.1. As the temperature decreases, the χT decreases down to 0.45 cm³·mol⁻¹·K at 2.0 K. This behaviour indicates dominant intramolecular antiferromagnetic

interactions. In order to estimate the magnetic coupling constant the magnetic data was fitted using the Hamiltonian described in Eq. 3 based on spin topology shown in Figure 6. All five copper(II) ions are crystallographically independent, so it is expected to have different magnetic exchange between them. However, Cu1 and Cu2 and Cu3 have similar metal environment with similar intramolecular distances between them, and also similar Cu-O-Cu angles. Then, an approximation was made considering the magnetic couplings between these three ions (J_1) equal. Similar approximation was used to the magnetic coupling (J_2) between Cu2···Cu4, Cu3···Cu5 and Cu4···Cu5 although not all of them have the same metal environment. Due to larger distances between Cu1 and Cu4 as well as between Cu1···Cu5, Cu2···Cu5 and Cu3···Cu4, the magnetic interactions between them are expected to be weaker and were neglected to prevent overparametrization. Firstly, the simplest model was applied considering $J_1 = J_2$, but a poor quality fit was obtained indicating that not all magnetic couplings are the same. Thus, the magnetic data was fitted considering two distinct coupling constants and the best fit parameters found were g average = 2.25, $J_1 = -89 \text{ cm}^{-1}$ and $J_2 = -25 \text{ cm}^{-1}$ with R = 7.8x10⁻³. There is a good agreement between experimental data and calculated curve using this model above 20 K. We stress that a fit performed by considering the magnetic coupling constant between Cu4···Cu5 is not the same as J_2 , adding a third magnetic coupling constant (J_3). However, the quality of the fit was not improved by adding one free variable. Although pentanuclear rings can exhibit a geometric spin frustration, [77] its effect on magnetic susceptibility data is in general less evident than in cyclic trinuclear ones.

$$H = -J_1(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_1 \cdot \vec{S}_3) - J_2(\vec{S}_2 \cdot \vec{S}_4 + \vec{S}_3 \cdot \vec{S}_5 + \vec{S}_5 \cdot \vec{S}_4) + \beta g H(\vec{S}_1 + \vec{S}_2 + \vec{S}_3 + \vec{S}_4 + \vec{S}_5)$$

(Eq. 3)



Figure 6. Spin topology considered to fit magnetic data of 3.

The temperature dependence of the χ T product for compound **4** is shown in **Figure 7**. The χ T value at 280 K is 2.15 cm³·mol⁻¹·K, which is smaller to the calculated one for six non-interacting copper(II) ions with g = 2.10 (2.48 cm³·mol⁻¹·K). Upon cooling, χ T value decreases continuously to 0.29 cm³·mol⁻¹·K due to the presence of predominant antiferromagnetic interactions. In order to estimate the magnetic coupling constants between the metal ions, a careful analysis of the distances between paramagnetic centers was performed based on the mainly pathways for the interactions. As discussed previously, the crystal structure consists of two Cu₃ triangles linked by *dppi* groups. Magnetic interactions pathways should be considered between the copper(II) ions from two the Cu₃ units bridged by the *dppi* groups. In this case, the magnetic interaction via *dppi* is expected to be weaker than those ones within the Cu₃ triangles, as reported elsewhere for other phosphinate-based compounds.[78] The first model used to fit the

magnetic data consisted in a system described by two magnetic couplings, namely J_1 (within the Cu₃ triangles) and J_2 (between two Cu₃ triangular units through *dppi* bridging ligands). Nevertheless, no acceptable fit could be obtained for this model below 50 K. Since there are many possible pathways for magnetic interactions between two Cu₃ units leading to a complicated model described by different magnetic interactions (*J*), we considered a simplified model to prevent overparametrization. This model assumes magnetic interactions within each Cu₃ units (J_1), and in order to take account the magnetic interactions between Cu₃ units was obtained using a mean field approximation (J') (Eq. 4). The best fit parameters were found for the average g = 2.09, J = -38 cm⁻¹ and J' = -8 cm⁻¹ with R = 2.6x10⁻² (solid line





Figure 7. Temperature dependence of χT for 4. The black line represents the best fit using the parameters described in the text.

$$H = H_{exch.} + H_{zeeman} \qquad (Eq. 4)$$

$$H_{exch.} = -J(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_1 \cdot \vec{S}_3 + \vec{S}_4 \cdot \vec{S}_5 + \vec{S}_5 \cdot \vec{S}_6 + \vec{S}_4 \cdot \vec{S}_6)$$
$$H_{zeeman} = \beta g \vec{B} (\vec{S}_1 + \vec{S}_2 + \vec{S}_3 + \vec{S}_4 + \vec{S}_5 + \vec{S}_6)$$

It is known that the magnetic exchange is strongly influenced by the distance between copper(II) ions, Cu-ligand bond lengths since copper(II) ions can exhibit Jahn-Teller distortion as well as Cu-O-Cu bond angle. For 2, the copper(II) ions are bridged coordinated by dppi ligands in 2.11 (II) mode leading to weak ferro- and antiferromagnetic interactions in agreement with the magnetic coupling found for other complexes having the same bridging mode.[33-37] The strength of magnetic couplings found in 1, 3 and 4 are larger than the values found for 2. In fact, the former complexes have shorter Cu...Cu intramolecular distances and additional bridging ligands such as *hfac* and oxo when compared with the latter one. The shorter intramolecular distances between Cu(II) ions and additional bridging ligands favor a better pathway for magnetic interactions leading to stronger magnetic interactions in 1, 3 and 4 when compared with 2. Since the magnetic interaction through bridged-phosphinate pathway is weak, the magnetic interaction through other groups such as μ -oxo or μ -hydroxo bridge is expected to be dominant.[75,79] Although the magnetostructural correlation in copper(II) bridgedphosphinate complexes related to Cu-O and Cu-O-Cu is not well understood, such correlation has been described for other systems containing μ_3 -oxo bridge.[79] Surprisingly, practically no dependence of the magnetic exchange interaction on Cu⁻⁻Cu distance, Cu-O bond length and Cu-O-Cu bond angle was found for μ_3 -oxo copper(II) complexes. However, a strong dependence of the magnetic interaction on the distance between the oxygen atom of μ_3 -oxo and the plane containing the three copper(II) ions was observed. [79] Ferromagnetic interactions were found for

distances larger than 0.3 Å while antiferromagnetic (AFM) interactions were observed for distances smaller than 0.3 Å.

In compound **3-4**, even if the distance between the plane containing the three copper(II) ions and μ_3 -oxo atom is ~ 0.5 Å, the interaction is in contrast with expected one.[79] On the other hand, AFM interactions were observed for μ -OH bridge,[75] in agreement with the result found for compound **1**. It should also be considered that the presence of μ -*hfac* and μ_2 -oxo as bridging ligands can influence the magnetic interaction making hard the interpretation of the magnetic properties based on structural parameters.

3.4. Electrochemistry of Copper Complexes

The redox properties of complexes **1** and **2** have been compared with those of the starting reagent [Cu(hfac)₂]. In this experiment, a 10 mL three electrode cell (AglAgCl as reference electrode and a Pt wire counter electrode) filled by a 0.1 M Bu₄NPF₆ THF solution was used. Cyclic voltammograms were recorded at 25 mVs⁻¹, being given in the Supporting Information. The first CV scan on [Cu(hfac)₂] (**Figure S4**) reveals only an irreversible reduction at -0.25 V that can be assigned to the one step Cu^{II}/Cu^o reduction since copper deposition on the electrodes was observed. A reverse scan (**Figure S5**) shows an irreversible oxidation at +1.0 V that arises from the copper stripping from the electrode due to the Cu^o/Cu^I oxidation, with possible formation of [Cu(THF/H₂O)₄]⁺ species, as observed by D. Cook et *al.* for [Cu(hfac)₂] in acetonitrile solution.[80] The CV of **1** shows only two irreversible oxidation processes at +0.85 V and +1.4 V, respectively (**Figure S6**). The first oxidation can be assigned to the Cu^{II}/Cu^{III} redox couple and the second one to some decomposition of the complex due mainly to the *hfac* ligand.[81] In the voltammogram of **1**, no Cu^{II}/Cu^{II} reduction was observed leading to the

conclusion that **1** is more suitable to stabilize the Cu^{III} state when compared to $[Cu(hfac)_2]$. The value of oxidation redox potential of **1** corresponding to the Cu^{II}/Cu^{III} process is similar to other Cu_3 complexes (+0.81 V *vs.* AglAgCl normalizing against SCE values).[82] The initial CV scan of the complex **2** shows two irreversible features at +0.65 V and at -0.8 V, attributed to the Cu^{II}/Cu^{III} and Cu^{II}/Cu^{I} redox processes, respectively. No deposition of the copper on the electrodes was observed (**Figure S7**).

3.5. Catalytic Oxidation of 3,5-DTBC



Scheme 4. Catalytic oxidation of 3,5-DTBC to 3,5-DTBQ in THF.

The catecholase-like activity of polynuclear complexes **1** and **2** has been evaluated using 3,5-DTBC as a model substrate due to its easy oxidation to 3,5-di-*tert*-butylbenzoquinone (3,5-DTBQ, **Scheme 4**). The study was extended to mononuclear $[Cu(hfac)_2]$ for comparison, since it is a simpler source of Cu^{II} metal ions. Reactivity studies were performed in air and in dioxygen-saturated THF solutions (see Supporting Information). By observing the time evolution of the 392 nm absorption band characteristic of the quinone it was ascertained that the three complexes showed catecholase activity. **Figure 8** shows the UV spectral changes of the oxidation catalyzed by **2**. Complexes [Cu(hfac)₂] and **1** behave similarly (Figures S15-S16).

Next, the kinetics of the 3,5-DTBC oxidation were determined through the initial rates method. The pseudo-first-order condition was maintained by using substrate solutions ranging

between 10 times and 100 times larger than that of the Cu(II) complex. The initial rates were determined from the limiting slope of the absorbance versus time curve at t = 0 s using $\varepsilon(3,5)$ -DTBQ) = 1720 mol⁻¹·L·cm⁻¹ in THF (Figure S8). The data were analyzed by a Michaelis-Menten model with a Lineweaver-Burk (double reciprocal) plot (Figures S9-14) to calculate the kinetic parameters V_{max} , K_m and k_{cat} (**Table 5**). The catalytic activity of the complexes under both experimental conditions (air and saturated dioxygen) decreased in the order $[Cu(hfac)_2] > 2 > 1$. All complexes showed a higher catalytic activity in dioxygen-saturated solution. The dioxygen increase the catalytic activity of the complexes usually by reoxidation of the Cu^I intermediate. [83,84] [Cu(hfac)₂] (k_{cat} 190 h⁻¹) proved to be a better catalysts for 3,5-DTBC oxidation than some mono- $(k_{cat} 4.1 - 63.7 h^{-1})$ [85,86] or dinuclear copper complexes $(k_{cat} 11.6 - 95 h^{-1})$.[87-89] However, its efficiency is significantly lower than that of highly active Cu₂ catalysts (k_{cat} 32400 h^{-1}).[90] As far as we know there are no previous report on the catecholase activity of [Cu(hfac)₂] neither kinetic parameters regarding catecholase activity for copper(II)-based multinuclear systems coordinated only by oxygen donor atoms. However, when compared with other trinuclear and tetranuclear copper clusters containing mixed N/O donors coordinated to the metal ion, complexes 1 (k_{ext} 16.2 h^{-1}) and 2 (k_{ext} 19.4 h^{-1}) act as moderate catecholase-like catalyst.[91, 92] The different catecholase-like activity of the two compounds is certainly related to their structural features. Several works in the literature illustrate that a number of factors influence the efficiency of a complex as catalyst in catecholase activity, such as Cu-Cu distance, coordination geometry of the metal centers, nature of the donor groups and electronic properties of the ligands, among others.[52-55, 89, 93]



Figure 8. Increase of 3,5-DTBQ band at 392 nm (⁻) in dioxygen-saturated THF for the complex
2 (⁻) (10⁻⁴ mol·L⁻¹) using 1·10⁻² mol·L⁻¹ initial concentration of 3,5-DTBC (⁻). The spectra were recorded at 1 min interval.

It is important to note that the molecular structure of complex **1** provides a new model for multicopper oxidases having three copper active centers that catalyze 4e⁻ reduction of O_2 ,[45, 46] because it has been found that the enzymatic intermediate must have a fully oxidized Cu_3 (II) core where metal ions are mutually bridged by the oxo-independent oxygen atom obtained from cleavage of the O=O bond.[94]

air-saturated solvent THF					
Complex	V_{max} (Ms ⁻¹)	K_m (mM)	$k_{\text{cat}} (\mathbf{h}^{-1})$		
1	$2.9 \cdot 10^{-7}$	23.7	10.4		
2	$4.4 \cdot 10^{-7}$	2.59	15.8		
$Cu(hfac)_2$	$1.02 \cdot 10^{-6}$	28.2	36.0		
dioxygen-saturated solvent THF					
Complex	$V_{max} (\mathrm{Ms}^{-1})$	K_m (mM)	$k_{\rm cat} ({\rm h}^{-1})$		
1	4.6·10 ⁻⁷	58.5	16.2		
2	$5.3 \cdot 10^{-7}$	3.89	19.4		
Cu(hfac) ₂	$5.3 \cdot 10^{-6}$	126.7	190.2		

Table 5. Kinetic parameters for the complexes evaluated

4) Conclusions

A new strategy for the synthesis of polynuclear copper(II) complexes based on the unexplored combination of hfac and dppi mixed ligands has been developed. Relatively small changes in the reaction conditions related to the solvent, the stoichiometry, the addition of triethylamine as a base and the use of a dioxygen atmosphere provided a set of unique $(Cu)_n$ species (n = 3, 4, 5, and 6) containing heteroleptic ligands in a variety of coordination modes. Thus, the reaction of equimolar amounts of $[Cu(hfac)_2]$ and *Hdppi* in the presence of Et₃N under oxygen bubbling in boiling *n*-heptane-chloroform afforded the trinuclear complex $[Cu_3(\mu -$ OH) $(\mu$ -dppi)₃ $(\mu$ -hfac)₃ (1). Changing the solvent to methanol and in the absence of Et₃N a new tetranuclear complex $[Cu_4(\mu-dppi)_4(Hdppi)_2(hfac)_4]$ (2) was isolated. On the other hand, when [Cu(hfac)₂] and *Hdppi* are allowed to react in a ratio of 1:2 in the presence of oxygen in boiling *n*heptane-chloroform the pentanuclear species $[Cu_5(\mu-O)_2(\mu-dppi)(\mu-Hdppi)_2(\mu-hfac)_3(hfac)_2]$ (3) was obtained. Finally, the treatment of dppnTEMPO with $[Cu(hfac)_2]$ (ratio of 1:1) in boiling *n*heptane-chloroform serendipitously gave the hexanuclear complex $[Cu_6(\mu-O)_2(\mu-dppi)$ Hdppi) $(\mu$ -hfac)₆ (4) in a process involving the *in situ* hydrolysis of the phosphinic amide linkage of dppnTEMPO. The structures of 1 to 4 show some unique features. Except for 1, where the three phosphorus-containing ligands exist as phosphinates due to the action of the amine, all other complexes show different combinations of diphenylphosphinic acid and diphenylphosphinate ligands. Besides the unprecedented mixture of Hdppi/dppi and hfac ligands involved in the construction of these polynuclear copper(II) systems, new coordination modes of these ligands have been revealed. This is the case of the syn-3.21 coordination of dppi found in 2 and 3 and the 2.11 coordination of two hfac ligands in 3. Furthermore, complex 1 includes one

hydroxo ligand, while in complexes **3** and **4** additional coordination of some copper(II) ions to two oxo ligands were observed.

The magnetic properties of all complexes were investigated and showed dominant antiferromagnetic interactions including also the spin-frustration phenomena observed for **1**. Modeling the spin topology of these polynuclear systems provided insight into the interaction pathways. In addition, the electrochemical behavior and catecholase activity of **1** and **2** were investigated. These are the first examples of 3,5-DTBC oxidations performed on the hfac based compounds. However, the catalytic activities observed were modest with reaction rates decreasing in the order $[Cu(hfac)_2] > 2 > 1$.

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Supplementary Material

X-ray crystallographic data in cif format available at CCDC-1456345-1456347 (2-4) can be obtained free of charge via <u>www.ccdc.cam.ac.uk/data_request/cif</u>. Fig. S1 and S2 display the molecular structure of **1** and the coordination modes of dppi ligand in **2**, respectively. Selected bond length and bond angles for **2-4** are shown in Tables S1-S3. The temperature dependence of χ T for **1** is shown in Fig. S3. Cyclic voltamograms of [Cu(hfac)₂], **1** and **2** are depicted in Fig.S4-

S7. Kinetic data and UV-vis spectra are shown in Fig. S8-S16. This material can be found, in the online version, at

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A new family of mixed-ligand copper(II) clusters with different nuclearities (Cu3-Cu6) was obtained. The magnetic properties of all compounds showed predominant antiferromagnetic interactions. The electrochemical properties and catalytic activity of Cu3 and Cu4 compounds . IX were investigated. Catecholase-like activity of Cu3 and Cu4 clusters via oxidation of 3,5-di-tertbutylcatechol to 3,5-di-tert-butylquinone was performed.



Highlights

Four new mixed-ligand copper(II) clusters with different nuclearities have been synthesized.

The magnetic studies revealed predominant intramolecular antiferromagnetic interactions.

Catecholase-like activity of copper(II) complexes via oxidation of 3,5-di-tert-ACCEPTER butylcatechol to 3,5-di-tert-butylquinone was performed.