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A $[2 \times 2]$ Cu₄ molecular grid and a Mn₅ cluster derived from a 1-(2-pyridyl)pyrazole based polytopic ligand – Synthesis, structure, magnetic properties and catalytic activity in the allylic oxidation of cyclohexene



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ABSTRACT

The homoleptic $[2 \times 2]$ tetranuclear compound $[Cu_4(PyPzCAP)_4](NO_3)_4\cdot 8H_2O$ (1) and the pentanuclear Mn(II) cluster $[Mn_5(PyPzCAP)_6](ClO_4)_4\cdot 4C_6H_6$ (2) are self-assembled from the ditopic pro-ligand HPyPz-CAP [(5-methyl-1-(pyridin-2-yl)-N'-[1-(pyridin-2-yl)ethylidene]-1H-pyrazole-3-carbohydrazide)]. Complex **1** is almost a square grid, and all the Cu(II) centers show a distorted octahedral environment with an N₄O₂ chromophore. Complex **2** has a pentanuclear core with a trigonal bipyramidal arrangement of the Mn(II) atoms. The axial Mn centers bear an N₃O₃ chromophore and the equatorial centers have an N₄O₂ distorted octahedral arrangement. Complex **1** shows a ferromagnetic exchange interaction ($J = +4.62 \text{ cm}^{-1}$ and g = 2.05), whereas **2** shows weak an antiferromagnetic interaction ($J = -2.73 \text{ cm}^{-1}$ and g = 2.02). Both complexes **1** and **2** catalyze the allylic oxidation of cyclohexene to cyclohex-2-ene-1-one with good selectivity and an excellent overall turnover number.

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1. Introduction

A variety of aesthetical architectures, like clusters [1], grids [2–5], helicates [6], cages [7], ladders [8] and racks [9], have been synthesized through self-assembly processes. Researchers are becoming more enthusiastic towards the synthesis of these structures because of their enormous range of applications in different challenging fields due to their electronic, redox, magnetic, photophysical and catalytic properties [10–13]. The self-assembly of transition metals with multifunctional organic ligands represents a successful domain for the single step synthesis of new clusters of well-defined and predesigned architectures. A major challenging goal in this area is the design and synthesis of new polytopic ligands which can be used for the synthesis of molecular metal grids and clusters. Hence, with the proper choice of paramagnetic metal ions which interact with these polytopic ligands, the magnetic coupling can be fine-tuned. In these self-assembled grids and clusters, spin

exchange interactions can occur between the paramagnetic metal ions through the direct bridging (e.g. μ -O, μ -N–N) functionalities of the ligands. Moreover, depending on the packing, such assemblages have the unique potential to exhibit either long-range order or single molecule magnetic behavior. Transition metal ions templated cyclizations have produced many tetranuclear $[2 \times 2]$ Mn₄, Co_4 , Ni_4 , Cu_4 and Zn_4 grid complexes [14–16], in which the bridging arrays among the metal ions involve oxygen donor groups. Most of the so far reported alkoxo-bridged polynuclear grids [Mn(II), Co(II) and Ni(II)] show anti-ferromagnetic coupling, while the ferromagnetic interaction prevails only in Cu(II) grids. Manganese is suitable for self-assembling high-nuclearity clusters primarily based on ligands with oxygen donors due to its oxophilicity. The easy availability of at least three oxidation states, +II (d⁵),+III (d⁴),+IV (d³), with the highest number of unpaired electrons possible in the 3d orbital of the coordinated metal center, makes the study of selfassembled Mn clusters interesting. The study of these Mn clusters has helped us gain knowledge about the structure and function of manganese-containing biological systems [17], as well as supplying



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a wealth of data for species that are able to function as "single molecule magnets" (SMMs).

Immense applications of α,β -unsaturated ketones are found in different fields, for example as building blocks and products of pharmaceutical interest [18-19], chemo sensors for metal ions [20-21], intermediates of many natural products and bioactive compounds [22–28]. Conventionally, they are prepared by the aldol condensation of aldehydes and ketones [29-30] or elimination reactions of precursors such as α -halide ketones [31–32]. Some α , β -unsaturated ketones prepared through a C–C bond forming reaction between primary alcohols and ketones in the presence of gold nanoparticles [33] have been reported by Kim et al. Yadav et al. have reported a one-pot process for the synthesis of α,β unsaturated ketones with a cation exchange resin-promoted coupling reaction of aldehydes with alkynes [34]. The technique for the preparation of cyclohex-2-ene-1-one, an α . β -unsaturated ketone, by the transition metal catalyzed selective oxidation of cyclohexene has being studied for a long time [35-43]. Copper(II) and Mn(II) complexes have featured as catalysts in a few of these methods. However, the use of multinuclear complexes is still little explored and deserves further attention.

In this work, we report the use of a new non-linear unsymmetrical polytopic ligand, PyPzCAP (Scheme 1) to prepare a $[2 \times 2]$ Cu₄ molecular grid and a Mn₅ cluster. The Schiff base ligand precursor HPyPzCAP has been prepared by the condensation of 5-methyl 1-(2-pyridyl) 3-pyrazole carbohydrazide and 2-acetyl pyridine. The magnetic studies reveal that the Cu₄ grid is ferromagnetically coupled and the Mn₅ cluster is anti-ferromagnetically coupled. Apart from the magnetic properties, we have explored the catalytic properties of these multinuclear complexes towards the allylic oxidation of cyclohexene. This is our first attempt in studying the catalytic properties of a Cu₄ grid and a Mn₅ cluster. It has been found that these two complexes catalyze the allylic oxidation of cyclohexene to cyclohex-2-ene-1-one with good selectivity and a remarkable turnover number (TON).

2. Experimental

2.1. Materials

2-Acetyl pyridine was purchased from Aldrich. Other commercially available chemicals and solvents were used and purified by standard procedures. *Caution*! Although we have not encountered any problems, it should be kept in mind that only small amounts of the perchlorate compound should be prepared and it should be handled with care.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) of the proligand PyPzCAP and the metal complexes 1 and 2 were carried out with a Perkin Elmer CHNS/O analyzer 2400. The electronic spectra of **1** in purified CH₃OH solution were recorded on a Hitachi model U-3501 spectrophotometer. IR spectra (KBr pellet, 4000-400 cm⁻¹) were recorded on a Perkin Elmer model 883 infrared spectrophotometer. The mass spectrum of the ligand was performed at the Indian Institute for Chemical Biology, Kolkata with a JEOL JMS-AX 500 mass spectrometer. Room temperature magnetic susceptibility was measured with a PAR 155 vibrating sample magnetometer. Magnetic susceptibility measurements were carried out on polycrystalline samples, at the Servei de Magnetoquímica of the Universitat de Barcelona, with a Quantum Design SQUID MPMS-XL susceptometer apparatus working in the range 2-300 K under a magnetic field of approximately 500 G (2-30 K) and 1000 G (35-300 K). Diamagnetic corrections were estimated from Pascal Tables.

2.3. Synthesis of the ligand

5-Methyl-1-(2-pyridyl) pyrazole-3-carbohydrazide was prepared following an established method. The ligand HPyPzCAP was synthesized by refluxing an ethanolic solution (30 mL) of 5methyl-1-(2-pyridyl) pyrazole-3-carbohydrazide (2.17 g, 10 mmol) with 1-(pyridin-2-yl) ethanone (1.21 g, 10 mmol), also taken in ethanol (10 mL). Refluxing was continued for ca. 30 min at water bath temperature. After slow solvent evaporation of the reaction mixture, a solid microcrystalline compound separated. It was filtered off, washed several times with cold ethanol and dried in a vacuum over fused CaCl₂.

HPyPzCAP Yield: 2.37 g (70%); m.p. 232 °C. Anal. Calc. for $C_{16}H_{16}N_6O$: C, 62.34; H, 5.19; N, 27.27. Found: C, 62.29; H, 5.13; N, 27.20%. IR/cm⁻¹: vNH 3360; vCO 1650(s); vCN 1555(s); vN-Npz 1062(s); vpy 1015(s).



Scheme 1. Preparation of complexes 1 and 2.

2.4. Synthesis of the complexes

2.4.1. Preparation of the complex $[Cu_4(PyPzCAP)_4](NO_3)_4 \cdot 8H_2O(1)$

The ligand HPyPzCAP (0.122 g, 1 mmol) was added to a hot solution of Cu(NO₃)₂·6H₂O (0.148 g, 1 mmol) in CH₃OH (30 mL). The resulting suspension was stirred with heating (~60 °C) until complete dissolution of the ligand occurred. The resulting deep green solution was filtered to remove any undissolved ligand and left at room temperature. Dark green crystals suitable for X-ray diffraction were isolated from the filtrate after standing for several days. Yield: 40%. *Anal.* Calc. for C₆₈H₇₆Cu₄N₂₈O₂₄: C, 42.46; H, 3.98; N, 20.39. Found: C, 42.47; H, 3.95; N, 20.41%. IR/cm⁻¹: vNH/H₂O 3379; 3179; vCO 1670(s); 15429(s); vCN 1542(s); vN-Npz 1053(s); vpy 1027(s). UV–Vis (λ_{max}/nm): 675.

2.4.2. Preparation of the complex $[Mn_5(PyPzCAP)_6](ClO_4)_4 \cdot 4(C_6H_6)$ (2)

The ligand HPyPzCAP (0.122 g, 1 mmol) was dissolved in methanol. Mn(ClO₄)₂·6H₂O (0.361 g, 1 mmol) dissolved in methanol was added to this solution. Then it was stirred for 5 min. The pH of the solution was kept at 7–8 by adding a few drops of a methanolic solution of NEt₃. The solution was stirred for additional half an hour and its color was reddish. The resulting solution was filtered and kept for slow evaporation at room temperature. A red crystalline compound was isolated from the filtrate after standing for several days. Crystals suitable for X-ray diffraction were grown by slow diffusion of benzene into an acetonitrile solution of the complex. Yield: 60%. Anal. Calc. for C₁₁₄H₁₀₀C₁₄Mn₅N₃₆O₂₂: C, 54.97; H, 4.05; N, 10.12. Found: C, 54.92; H, 4.09; N, 10.13%. IR/cm⁻¹: vNH 3365; vCO 1660(s); vCN 1540(s); vN-Npz 1080(s); vpy 1030(s). UV–Vis (λ_{max} /nm): 670. vRT 3.42 B.M.

2.5. Single crystal X-ray crystallography

Selected crystal data of 1 and 2 are given in Table 1. Data of complexes 1 and 2 were collected on a Bruker APEX II CCD system with Cu radiation and corrected for absorption with sadabs. The structures were solved by direct methods and all non-hydrogen atoms of the cation were refined as anisotropic by Fourier full matrix least squares on F^2 . SHELXS-97 and SHELXL-97 [44] programs were used for structure solution and refinement respectively. In 1, three of the four nitrate ions were disordered and were treated using the two part model (56.1/43.9 ratio). Atoms of two of the nitrate anions were refined isotropically and EADP constraints were used for each pair of atoms of the anions. In addition, unrefined electron density was treated by using Platon SQUEEZE. This program found a void of 893 cubic angstroms with 334 electrons and was treated as 32 water molecules, which were added to the chemical formula to account for the molecular mass, density and F000 value. In 2, the perchlorate anions were disordered and one was refined as anisotropic, the other as isotropic and both anions had their (29.5/70.5 and 51.2/49.8 ratio) distances and angles fixed using DFIX and DANG commands, and their amplitudes were matched using EADP commands. A disordered benzene molecule (59.9/40.1) was located and refined isotropically as a fixed hexagonal ring and with a common EADP command. The Platon program SQUEEZE was then used to adjust for unrefined solvent. The program found a void of 1120 cubic angstroms and 320 electrons - associated with eight benzene molecules, which were added to the unit card to adjust the molecular mass, density and F000 value.

2.6. Catalytic method

2.6.1. Oxidation of cyclohexene

Compounds **1** and **2** were investigated as catalyst precursors for the oxidation of cyclohexene to 2-cyclohexen-1-ol and 2-

Table 1

Experimental data for crystallographic analysis of 1 and 2.

Compound	1	2
Empirical formula Formula weight	C ₁₂₆ H ₁₁₂ C ₁₄ Mn ₅ N ₃₆ O ₂₂ 2899.02	C ₆₈ H ₇₆ Cu ₄ N ₂₈ O ₂₄ 1923.73
I (K)	100	100
Wavelength (A)	1.54178	0.71073
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2(1)/c
Unit cell dimensions		
a (A)	29.0264(10)	13.7957(12)
b (Å)	18.9144(10)	40.881(3)
c (Å)	22.8805(9)	14.2670(12)
α (°)	90.00	90.00
β (°)	95.520(3)	93.610(2)
γ (°)	90.00	90.00
V (Å ³)	12503.5(9)	8030.4(12)
Ζ	4	4
D_{calc} (Mg m ⁻³)	1.457	1.472
Absorption coefficient (mm ⁻¹)	5.511	1.140
F(000)	5956	3952
θ Range (°) for data collection	2.50-24.50	1.51-27.90
Index ranges	$-33 \leqslant h \leqslant 34$	$-17 \leq h \leq 17$
-	$-22 \leqslant k \leqslant 21$	$-51 \leq k \leq 53$
	$-26 \leq l \leq 26$	$-18 \leq l \leq 18$
Goodness-of-fit (GOF) on F^2	1.035	1.056
Independent reflections [R _{int}]	10465(0.044)	18085[0.075]
Absorption correction	multi-scan	multi-scan
Refinement method	full-matrix least	full-matrix least
	squares on F^2	squares on F^2
Data/restraints/parameters	10465/40/770	18085/36/1054
Reflections collected	46720	120313
Final R indices $[I > 2\sigma(I)]$	R = 0.0690	R = 0.0729
	$wR_2 = 0.2016$	$wR_2 = 0.1848$
Largest difference peak and hole (e $Å^{-3}$)	-1.64, 1.61	-0.90, 3.31
more (err)		

cvclohexen-1-one using aqueous *tert*-butvl hvdroperoxide (TBHP) under mild conditions (Scheme 3). Cyclohexene has been studied as a model substrate in view of the importance of the products (i.e., α,β -unsaturated allylic oxidation products used for further additive reactions) [18-19]. The reaction mixtures were prepared as follows: to 0.5–20 µmol (preferably 10 µmol) of complex 1 or 2, contained in a reaction flask, were added 3 mL of MeCN, 5.0 mmol cyclohexene and 1-10.0 mmol TBHP (70% aqueous solution), in this order. The reaction mixture was stirred for 10 h at the desired temperature (ca. 30-60 °C) under an air (atmospheric pressure), then 50 µL of cyclopentanone (as an internal standard) and 9.5 mL of diethyl ether (to extract the substrate and the products from the reaction mixture) were added. The resulting mixture was stirred for 15 min, and then a sample taken from the organic phase was analyzed by GC. The GC analyses showed the presence of only traces (less than 3%) of oxidation products. The reaction under pressurized dioxygen was carried out in a 13.0 mL stainless steel autoclave, equipped with a Teflon-coated magnetic stirring bar. The autoclave was closed and flushed with dioxygen three times to remove the air, and finally pressurized with 5 atm of dioxygen. The reaction mixture was stirred for 10 h at 50 °C using a magnetic stirrer and an oil bath, whereupon it was cooled in an ice bath, degassed, opened and transferred to a flask. Diethy ether (9.5 mL) and 50 µL of cyclopentanone (GC internal standard) were added. The obtained mixture was vigorously stirred for 10 min, and the organic layer was analyzed by gas chromatography (internal standard method). Blank experiments were performed and confirmed that no cyclohexene oxidation products (or only traces, below 0.5%) were obtained in the absence of the metal catalyst.



Fig. 1. Structural representation and atom numbering scheme of the cationic complex 1.

3. Results and discussion

3.1. Description of the structure of [Cu₄(PyPzCAP)₄](NO₃)₄·8H₂O (1)

The structure of the cation in **1** is illustrated in Fig. 1 and important bond distances and angles are listed in Table 2. The lattice is monoclinic with *P*21/*C* symmetry and the unit cell consists of four molecules. The complex **1** is a homoleptic $Cu_4(II)$ [2 × 2] almost square grid. The ligand PyPzCAP has two coordination pockets. It can in principle, adopt two different geometries, (a) and (b) (Scheme 2) [2], but only conformation (a) is present in 1. The overall structural arrangement shows a tetranuclear cation, four nitrate anions and eight water molecules (the nitrates and water molecules are uncoordinated). The grid consists of four six coordinate copper centers arranged in a square with alkoxide bridges connecting the Cu(II) ions. Four ligands are arranged in parallel pairs in an opposite arrangement above and below the mean Cu₄ plane. The head-to-tail arrangement of the ligand strands lead to the formation of only one type of chromophore, N₄O₂, around each Cu(II) ion, which consists of four nitrogen atoms (two nitrogens from pyridyl-pyrazole, one imine nitrogen, one pyridine nitrogen and two alkoxide ions). The coordination sphere around each Cu(II) is distorted octahedral. The Cu-O and Cu-N bond lengths and N-Cu-N, O-Cu-N and O-Cu-O bond angles (Table 2) are very similar to those previously reported for octahedral Cu^{2+} complexes with amide and pyridine containing ligands [3]. The Cu₄ square is unsymmetrical with four unequal axial contacts from copper to the oxygen bridges. The Cu-Cu distances fall in the range 4.115-4.412 Å. All the Cu–O bond distances are different, consistent with a distorted octahedral geometry. The Cu-O-Cu angles fall in the range 137.96(14)-144.31(14)°. Cu2 and Cu3 are below, while Cu1 and Cu4 are above the mean plane defined by the four copper atoms. The deviation of the Cu ions from their mean plane range between 0.414 (for Cu4) and 0.426 Å (for Cu1). The Jahn-Teller axes of Cu1, Cu2, Cu3 and Cu4 are defined as N3-Cu1-N17, N5-Cu2-N21, N9-Cu4-N23 and N11-Cu3-N15. The tetranuclear core structure is shown in Fig. 2.

3.2. Description of the structure of $[Mn_5(PyPzCAP)_6](ClO_4)_4 + 4(C_6H_6)(2)$

The structure of the pentanuclear cation cluster of **2** is illustrated in Fig. 3, and important bond distances and angles are listed in Table 2. The pentanuclear Mn(II) core is best described as a trigonal bipyramid. The lattice is monoclinic in nature with C2/c symmetry. The Mn₅ cluster consists of six ligands, four perchlorate anions and four benzene molecules. The pentanuclear core structure is shown in Fig. 4. The Mn2, Mn3 and Mn3_a centers are situated in the equatorial plane of the trigonal bypyramid, while the Mn1 and Mn1_a centers occupy the axial positions. All the angles in the Mn2-Mn3-Mn3_a equatorial triangle fall within the range 59.23–60.38°. The coordination sphere of Mn1 and Mn1_a consists of an N₃O₃ chromophore (three nitrogen atoms from pyrazole and three alkoxide oxygens), whereas for Mn2, Mn3 and Mn3_a it consists of an N₄O₂ chromophore (two imine nitrogens, two pyrazole nitrogens and two alkoxide oxygens). It is noteworthy that all the pyridine nitrogens from the pyridyl-pyrazole part remain uncoordinated. The distance between the Mn1 and Mn1_a atoms is 5.311 Å and the distances between the three equatorial atoms fall in the range 5.010-5.06 Å. The distance of the two axial Mn atoms from equatorial plane is 2.656 Å. All the Mn atoms are in a distorted octahedral environment. The metal-oxygen bond distances fall within the range 2.199–2.167 Å. The Mn–O–Mn bridge angles are in the range 128.22-128.74°.

3.3. Magnetic properties

3.3.1. Complex 1

The variable temperature magnetic susceptibility data for the compound were recorded between 300 and 2 K. A plot of $\chi_M T$

Table 2		
Selected bond distances	Å) and angles (°) for complexes 1 a	and 2

Complex	Bonds	Distances (Å)	Bond angles	Values(⁰)
complex	bonds			
1	Mn1-01	2.205(3)	01-Mn1-02	90.81(11)
	Mn1_02	2.107(3)	01 - 10111 - 03	89.71(11)
	Mr.1 N2	2.193(3)	OI-MEINS	74.93(12)
	IVIIII-IN3	2.215(4)	OI-MEI NIA	88.55(12)
	IVIIII-IN9	2.248(4)	O1-WIIII-N14	104.09(13)
	Miiii - N14	2.247(4)	02-Will-03	91.63(11)
	Mn2-02	2.180(3)	02-Mn1-N3	165.70(12)
	IVIIIZ-INTT	2.179(4)	$O_2 = W_{111} = W_9$	/5.43(12)
	IVIIIZ-INIZ	2.295(4)	O_2 Mr1 N2	88.92(13)
	Mn2-O2_a	2.180(3)	03-Min1-N3	89.38(12)
	Mn2-N11_a	2.179(4)	03-Min1-N9	166.91(12)
	$Mn2-N12_a$	2.295(4)	02-Mn2-N12	96.25(13)
	Mn3-OI	2.197(3)	02-Mn2-02_a	100.96(11)
	Mn3-N5	2.201(4)	O_2 -IVIN2-INI2_a	141.13(14)
	MIN3-N6	2.310(4)	$NII-WINZ-NII_a$	151.68(15)
	Mn3-N17	2.317(4)	O2_a-Mn2-N12	141.13(14)
	Mn3-NI8	2.192(4)	Mn1-01-Mn3	128.24(13)
	Mn3-03_a	2.199(3)	Mn1-03-Mn3_a	128.74(14)
2	Cu1-01	2.435(3)	01-Cu1-03	92.47(10)
	Cu1-03	1.986(3)	01-Cu1-N1	142.91(10)
	Cu1-N1	2.355(3)	01-Cu1-N3	71.12(11)
	Cu1-N3	1.957(3)	01-Cu1-N17	111.64(11)
	Cu1-N17	1.916(3)	01-Cu1-N18	88.81(11)
	Cu1-N18	2.028(3)	03-Cu1-N1	90.70(11)
	Cu2-01	1.971(3)	03-Cu1-N3	96.92(12)
	Cu2-04	2.639(3)	03-Cu1-N17	80.09(12)
	Cu2-N5	1.940(4)	O3-Cu1-N18	159.27(13)
	Cu2-N6	2.011(3)	N1-Cu1-N3	71.81(12)
	Cu2-N19	2.384(3)	N1-Cu1-N17	105.32(12)
	Cu2-N21	1.974(3)	N1-Cu1-N18	100.69(11)
	Cu3-02	1.980(3)	N3-Cu1-N17	175.92(12)
	Cu3-N11	1.926(3)	N3-Cu1-N18	103.05(13)
	Cu3-N12	2.018(3)	N17-Cu1-N18	80.21(13)
	Cu3-N13	2.380(3)	01-Cu2-04	89.32(10)
	Cu3-N15	1.959(3)	01-Cu2-N5	78.97(12)
	Cu4-02	2.434(3)	03-Cu3-N11	109.75(11)
	Cu4-04	1.992(3)	03-Cu3-N12	93.28(10)
	Cu4-N7	2.350(4)	02-Cu4-04	90.73(10)
	Cu4-N9	1.954(4)	02-Cu4-N7	143.78(11)
	Cu4-N23	1.927(4)	04-Cu4-N24	159.09(13)
	Cu4-N24	2.039(3)	N7-Cu4-N9	72.48(13)









Fig. 2. Structural representation and atom numbering scheme of the tetranuclear core in 1.



Scheme 3. Oxidation of cyclohexene into 2-cyclohexene-1-ol and 2-cyclohexen-1-one.

versus *T* in Fig. 5 shows ferromagnetic behavior. The $\chi_M T$ value is 1.597 cm³ mol⁻¹ K at 300 K, being close to that expected for four uncoupled *S* = 1/2 spins (with *g* = 2.1). $\chi_M T$ increases slightly when the temperature is lowered and reaches a maximum value of 2.950 cm³ mol⁻¹ K at 2 K. This maximum is consistent with that expected for ferromagnetically coupled copper(II) ions. The structure of **1** consists of copper ions linked by the ligand PyPzCAP, giving a tetranuclear compound. Taking into account the compound topology (a slight distortion from a square array, see crystallographic data), three coupling parameters J_1 , J_2 and J_3 (Fig. 6) can be considered to interpret the magnetic interactions in the complex using the Hamiltonian:

$$H = -J_1(S_1 \cdot S_2 + S_3 \cdot S_4) - J_2(S_1 \cdot S_4 + S_2 \cdot S_3) - J_3(S_1 \cdot S_3 + S_2 \cdot S_4)$$
(1)

Based on the structural data of the $[Cu_4-O_4]$ core, we have considered that $J_1 = J_2 = J$ and $J_3 = 0$ (no cross-coupling connection). For this square disposition, the E_n value can be obtained by using the Kambe method [45] from the Hamiltonian:

$$H = -J_1(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_1 \cdot S_4)$$
(2)

Analysis of the experimental susceptibility data has been performed by the use of the expression:

$$\chi_{\rm m}T = 0.125g^2 f(J,T) \tag{3}$$

where

$$f(J,T) = \frac{6\exp(J/KT) + 12\exp(2J/KT) + 30\exp(3J/KT)}{1 + 3\exp(J/KT) + 7\exp(2J/KT) + 5\exp(3J/KT)}$$



Fig. 3. Structural representation and atom numbering scheme of the cationic complex 2.



Fig. 4. Structural representation and atom numbering scheme of the pentanuclear core in 2.

The best fit parameters found are: $J = +4.62 \text{ cm}^{-1}$ and g = 2.05 with an error $R = 4.7 \times 10^{-5}$, where $R = \sum \left[(\chi_M T)_{obs} - (\chi_M T)_{calc} \right]^2 / \sum (\chi_M T)_{obs}^2$. The field dependence of the magnetization (0–5 T) measured at 2 K, shown in Fig. 7 (inset) in the form of M/Nv β (per Cu₄ entity) verus *H*, suggests that the magnetization tends to 4 N β (experimental value = 4.16 M/N β). This feature agrees with the global weak ferromagnetic coupling within the four copper(II) atoms (fit of the experimental data: *T* = 2, *S* = 2 and *g* = 2.08). The value of the superexchange parameter $J = +4.62 \text{ cm}^{-1}$ for

compound **1** should be considered as normal, taking into account the structural and magnetic data reported recently in our works [4,5].

3.3.2. Complex 2

The variable temperature magnetic susceptibility data for complex **2** were recorded between 300 and 2 K. The plot of $\chi_{M}T$ versus *T* of Fig. 7 shows typical antiferromagnetic behavior, decreasing from 20.378 cm³ K mol⁻¹ at 300 K, which is slightly lower than



Fig. 5. Plots of the $\chi_M T$ vs. *T* and M/N β vs. *H* at *T* = 2 K (inset) for **1**. Solid line corresponds to the best fit.



Fig. 6. Structural representation of the $[{\rm Cu}_4{\rm O}_4]$ core and exchange coupling constants in 1.

that expected for five uncoupled S = 5/2 spin centers (21.9 with g = 2.0), to 4.538 cm³ K mol⁻¹ at 2 K, which corresponds to one uncoupled S = 5/2 spin center (4.38 with g = 2.0) due to the odd number of spin centers in the complex. The magnetization measurements at 2 K up to an external field of 5 T in form M/N β versus H show the saturation of the complex **2** tending to 4.96 N β (electrons), corresponding to a one uncoupled S = 5/2 system (Fig. 7, inset).

As shown in the crystallographic part, compound **2** is made up of six ligands bonded in parallel pairs around the $Mn_5(\mu-O)_6$ core, with the ligands opposed (anti) in each pair, similar to the Mn_5 compounds reported by Thompson et al. [16] Thus, six of one kind of coupling parameter *J* must be considered between two neighbor manganese ions to interpret the magnetic properties of **2**. We have not considered the slight differences observed between the angles and bond lengths of two neighbor manganese ions. On the basis of this assumption, the experimental magnetic data have been fitted using the isotropic Heisenberg Hamiltonian:

$$H = -J(S_1S_2 + S_1S_3 + S_1S_5 + S_2S_4 + S_3S_4 + S_4S_5)$$
(4)

The best fit parameters obtained values are $J = -2.73 \text{ cm}^{-1}$ and g = 2.02 with an error $R = 2.6 \times 10^{-6}$ ($R = \sum \left[(\chi_M T)_{exp} - (\chi_M T)_{calc} \right]^2 / \sum [(\chi_M T)_{exp}]^2$). The series of calculations were made using the computer program clumag that uses the irreducible tensor operator formalism (ITO) [46].

3.4. Catalytic activity

Compounds **1** and **2** were investigated as catalytic precursors for the oxidation of cyclohexene into 2-cyclohexene-1-ol and 2cyclohexen-1-one (Scheme 3) under mild conditions with aqueous *tert*-butyl hydroperoxide (TBHP). Cyclohexene has been studied as the model substrate in view of the importance of the products (i.e., the allylic oxidation products, α , β -unsaturated fuctionalized substrates, are used for further additive reactions) [18– 28].



Fig. 7. $\chi_M T$ vs. T and M/N β vs. H (inset) for complex **2**.

Table 3

Peroxidative oxidation of c	vclohexene to 2-c	vclohexene-1-one and 2-c	vclohexene-2-ol cata	lyzed by complexes	1 and 2 . ^a
		J · · · · · · · · · · ·	J · · · · · · · · · · · · · · · · · · ·	J	

(a) Variat	tion of oxidant							
Entry	Entry Catalyst Oxidant		Oxidant/substrate	Selectivity of product ^b (%)		Total conv. ^c (%)	Ketone/alcohol ^d	TON ^e
			Ketone	Alcohol				
01	1	TBHP	2.0	86	12	67	7.1	1675
02	2	TBHP	2.0	70	26	66	2.6	1650
03	1	H_2O_2	2.0	-	-	-	-	-
04	2	H_2O_2	2.0	-	-	-	-	-
(b) Variat	tion of temperat	ure						
Entry	Catalyst	Temp (°C)	Oxidant/substrate	Selectivity of	product ^b (%)	Total conv. ^c (%)	Ketone/alcohol ^d	TON ^e
				Ketone	Alcohol			
05	1	30	2.0	80	17	19	4.7	475
06	1	40	2.0	82	17	53	4.8	1325
07	1	50	2.0	86	12	67	7.1	1675
08	1	60	2.0	67	30	71	2.2	1775
09	2	30	2.0	75	22	12	3.4	300
10	2	40	2.0	74	24	48	3.0	1200
11	2	50	2.0	75	20	66	3.7	1650
12	2	60	2.0	70	26	68	2.6	1700
(c) Variat	tion of catalyst a	imount						
Entry	Catalyst	n(Catalyst) µmol	Oxidant/substrate	Selectivity	of product ^b (%)	Total conv. ^c (%)	Ketone/alcohol ^d	TON ^e
				Ketone	Alcohol			
13	1	0.0	2.0	-	-	03	-	-
14	1	0.5	2.0	86	11	08	7.8	4000
15	1	1.0	2.0	82	13	29	6.3	7250
16	1	2.5	2.0	79	12	48	6.5	4800
17	1	5.0	2.0	81	10	56	8.1	2800
18	1	7.5	2.0	86	11	61	7.8	2033
19	1	10.0	2.0	86	12	67	7.1	1675
20	1	15.0	2.0	88	11	66	8.0	1116
21	1	20.0	2.0	87	09	62	9.6	775
(d) Variat	tion of oxidant a	amount						
Entry	Catalyst	n(TBHP) mmol	Oxidant/substrate	Selectivity (of product ^b (%)	Total conv. ^c (%)	Ketone/alcohol ^d	TON ^e
				Ketone	Alcohol			
22	1	1.0	0.1	80	14	55	5.7	1375
23	1	2.5	0.5	80	15	56	5.3	1400
24	1	5.0	1.0	80	15	56	5.3	1400
25	1	7.5	1.5	81	15	57	5.4	1425
26	1	10.0	2.0	86	12	67	7.1	1675
27	2	2.0	0.4	68	25	33	2.7	825
28	2	5.0	1.0	70	23	52	3.0	1300
29	2	10.0	2.0	70	24	66	2.9	1650
30	2	12.0	2.4	68	20	59	3.0	1475
(e) Variat	tion of reaction of	conditions						
Entry	Catalyst	Condition	Oxidant/substrate	Selectivity of	product ^b (%)	Total conv. ^c (%)	Ketone/alcohol ^d	TON ^e
				Ketone	Alcohol			
31	1	N ₂	2.0	80	15	18	5.3	450
32	1	N ₂	0.1	80	17	05	4.7	125
33	1	O_2^t	0.0	-	-	-	-	-
34	1	Air	0.1	83	12	56	6.9	1400
35	1	02 ¹	0.1	89	10	72	8.9	1800
36	2	N ₂	2.0	68	24	64	2.8	1600
37	1	Ph ₂ NH	2.0	72	12	13	6.0	325
38	1	CBrCla	2.0	67	11	22	60	550

^a Effects of oxidant (a), temperature (b), amount of catalyst (c), amount of oxidant (d) and other conditions (e). Reaction conditions (unless stated otherwise): catalyst precursor (0.01 mmol), MeCN (3 mL), cyclohexene (5 mmol), oxidant (10 mmol), temperature (50 °C), reaction time 8 h, under air.
 ^b (Moles of product/mole of reacted cyclohexene) × 100.
 ^c (Initial substrate-final substrate/initial substrate) × 100, amounts in moles.
 ^d Ketone (2-cyclohexene-1-one)/Alcohol (2-cyclohexene-1-ol) molar ratio.
 ^e Oursell TON unline (moles of product/mole of metal complex)

^e Overall TON values (moles of products/mole of metal complex).
 ^f Pressurised O₂ at 5 atm.

The reactions were carried out in acetonitrile medium under air or pressurized dioxygen and the effects of various factors, such as relative amounts of catalyst, oxidant and temperature on the catalytic activity, have been studied. The obtained results are presented in Table 3. No oxidation products (or only traces) are obtained in the absence of any component of the catalytic system, namely the metal catalyst or TBHP.

Both the pre-catalysts **1** and **2** are inactive with hydrogen peroxide (Table 3a, entries 3, 4) but they are quite active with *tert*-butyl hydroperoxide. The ketone (2-cyclohexen-1-one) is always the main product and the ketone/alcohol molar ratio can reach values up to ca. 10 (Table 3c, entry 21). Overall conversions of cyclohexene up to 67% can be achieved at 50 °C (e.g. for TBHP/catalyst **1** and TBHP/substrate molar ratios of 1000 and 2.0, respectively, Table 3a entry 1). Increasing the temperature to 60 °C leads to a higher conversion (71%, Table 3b, entry 8), but with a decrease in selectivity (the ketone/alcohol molar ratio lowers to 2.2). Similar behaviors are observed for both pre-catalysts **1** and **2**.

The above high conversions (67–71%) also correspond to good turnover numbers (TON, moles of products/mole of catalyst precursor) of 1.7×10^3 (Table 3a, entries 1, 2; Table 3b, entries 7, 8). Furthermore, higher TON values (up to 7.3×10^3 , Table 3c, entry 15) can be obtained for lower catalyst loadings, but with a decrease of the conversion (29% for 1 µmol 1 versus 67% for 10 µmol 1, Table 3c, entry 15 versus 19, respectively). Hence, in order to operate with good conversions, the latter amount of catalyst precursor (10 µmol, i.e. a catalyst /substrate molar ratio of 1:500) was selected for the typical reactions (Table 3, footnote a).

The effect of the amount of oxidant was also investigated (Table 3d) and commonly an increase tends to lead to a higher conversion, without a substantial change in selectivity. This is followed clearly with the precatalyst 2 (range of 0.4-2.0 for the oxidant/substrate molar ratio, Table 3d, entries 27-29), but a further increase in the oxidant amount resulted in a lowering of the conversion (entry 30), which may be due to the enhancement of the water content in the reaction mixture [47–48]. However, with the pre-catalyst 1 the increase in conversion is only observed for an oxidant/substrate molar ratio above 1.5 (Table 3e, entries 22–26). When the reaction was carried out with the absence of TBHP, the conversion was negligible (Table 3e, entry 33), but for the TBHP/ cyclohexene molar ratio of only 0.1, the conversion was already 56% (Table 3e, entry 34). The reaction was also carried out in a dioxygen atmosphere (5 atmospheric pressure), both in the presence (Table 3e, entry 35) and absence (Table 3e, entry 33) of TBHP, and the catalytic activity was found only when TBHP was present.

Although the detailed mechanism of the catalytic activity has not been studied, we observed that in the presence of a radical trap, a remarkable fall of the catalytic activity occurred for complex 1 (Table 3e, entries 37, 38). This concerns either an O-centered radical trap (Ph₂NH) [49] or a C-centered radical scavenger (CBrCl₃) [50], implying that the reaction proceeds mainly via radical paths involving both C- and O-centered radicals, as with other multi-copper systems [51–53]. In case of complex 1, the reaction did not proceed well in a dinitrogen atmosphere (Table 3e, entries 31, 32), thus suggesting the involvement of dissolved dioxygen. Hence, H-abstraction from cyclohexene conceivably by the tert-butyl peroxo radical TbOO. or the hydroxyl radical HO. (formed by metal-assisted decomposition of TBHP) leads to the cyclohexenyl radical which, as suggested in other cases [54], can react with dissolved O₂ to give the 3-cyclohexenyl peroxy radical, or with a metalhydroperoxo species to give tert-butyl peroxy-2-cyclohexene (found as a trace by GC-MS). The conversions of the 3-cyclohexenyl peroxy radical and tert-butyl peroxy-2-cyclohexene into the products can also be metal-assisted, conceivably involving dismutation of the 3-cyclohexenenyl peroxy radical to both 2-cyclohexene-1-ol and 2-cyclohexene-1-one [55].

In presence of CBrCl₃, 3-bromo cyclohexene is formed, confirming the allylic C-centered radical formation. The stability of this radical is enhanced by the presence of the conjugated double bond, which preferably helps in forming the allylic oxidation products (trace amounts of 2-cyclohexene-1,4-dione and 2-cyclohexene-1,4-diol are also identified by GC-MS) without affecting the olefinic bond. These observations justify the absence of epoxide in the product mixture, the reaction proceeding selectively toward the allylic oxidation products.

Recently, Lashanizadegan et. al. [56] reported that homogenous (and the heterogeneous analogues) azo based Schiff-base complexes of copper and manganese show high conversions of cyclohexene with good selectivity but with low TON values (105–149 range). A similar allylic oxidation of cyclohexene was carried out with a Schiff-base copper complex as a soluble or immobilized catalyst [37], where the product selectivity was quite low, along with a low TON of 47 or 146, respectively.

4. Conclusion

The two new polynuclear complexes reported herein, a tetranuclear $Cu_4 [2 \times 2]$ grid (1) and a pentanuclear Mn(II) cluster (2), are produced by a well known self-assembly technique using a new polytopic ligand, PyPzCAP. They provide important new additions to an already rich family of such compounds reported by our group and others. The ligand shows different binding modes to the metal ions. Thus, Cu(II) directs four ligand moieties to assemble and form a square grid while Mn(II) directs six ligand moieties to assemble a pentanuclear metal cluster with a trigonal bipyramidal core. The square copper grid (1) exhibits intramolecular ferromagnetic spin exchange which is associated with the orthogonal alkoxide bridging arrangement and the close proximity of the Cu(II) centers. The pentanuclear Mn(II) cluster, on the other hand, shows antiferromagnetic behavior.

The catalytic properties of these complexes were investigated to open up a new applicability for this class of self-assembled clusters. The complexes were found to be rather active catalyst precursors for the selective allylic oxidation of cyclohexene, leading to a high overall TON value up to 7.3×10^3 and a yield of up to 71%, which disclose a higher activity than those reported earlier for other copper(II) catalysts. It was shown that the allylic oxidation proceeds via a C- and O-centered radical mechanism, where both TBHP and dioxygen are shown to play relevant roles.

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Appendix A. Supplementary data

CCDC 863686 and 863687 contains the supplementary crystallographic data for complexes **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.

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