

The Goldilocks principle in action: synthesis and structural characterization of a novel $\{\text{Cu}_4(\mu_3\text{-OH})_4\}$ cubane stabilized by monodentate ligand†

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A $\{\text{Cu}_4(\mu_3\text{-OH})_4\}$ compound, where four copper(II) and four μ_3 -bridging oxygen atoms occupy alternate corners of a slightly distorted cube, has been prepared and structurally characterized. This species, formulated as $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4 \cdot 1.5\text{Et}_2\text{O}$ (Htmpz = 3,4,5-1*H*-trimethyl pyrazole), can be classified as belonging to type I Cu_4O_4 cubane complexes, and is better described as two $\text{Cu}^{\text{II}}-(\mu\text{-OH})_2\text{-Cu}^{\text{II}}$ units held together by four long Cu–O bonds. The central distorted cubane core is stabilized by neutral monodentate ligands (Htmpz) and perchlorate anions, as demonstrated by single-crystal X-ray structure analysis. The title compound was obtained by hydrolysis of a dinuclear methoxy-bridged species, $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2](\text{ClO}_4)_2$, which was prepared by reaction of $[\text{Cu}(\text{Htmpz})_4(\text{ClO}_4)_2]$ with methanol. All these reactions represent a nice example of the Goldilocks principle in action in coordination chemistry, since each single actor (solvent, counteranion, and ligand) has the “just right” electronic, steric or coordinative properties which determine the fate of the final products.

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Introduction

Polynuclear transition-metal complexes have received much attention in the recent past due to their magnetic potentialities¹ and their ability to mimic metalloprotein active sites.² In particular, M_4X_4 cubane clusters (where M = Cu, Ni, Co, Fe, Mn, Mo; X = O, S)³ have been widely studied for their application as single molecule magnets (SMMs),⁴ in bioinorganic chemistry⁵ or in catalysis.⁶ Focusing the discussion on copper(II) high-nuclearity systems, they showed interesting magnetostructural properties relevant to the field of multinuclear copper oxidases⁷ and especially to molecular magnetism.⁸ In the case of Cu_4O_4 systems, the $\text{Cu}^{\text{II}}\text{-O-Cu}^{\text{II}}$ angle has been identified as being responsible for magnetic exchange, together with the out-of-plane angle of the substituents of the bridging oxygens.⁹ Although numerous alkoxo-bridged Cu_4O_4

(O = OR) systems are known,¹⁰ fewer examples of cubane compounds having a $\text{Cu}_4(\text{OH})_4$ core have been structurally characterized.¹¹ These species have been prepared either starting from a copper(II) salt or by aerobic oxidation of a Cu(I) precursor and in most cases the coordination sphere of copper(II) was completed by bi- or tridentate ligands. Actually, there are a very limited number of examples where the $\text{Cu}_4(\text{OH})_4$ core is stabilized by monodentate ancillary ligands.^{11a,e,l,n,12}

In the past, we widely explored the coordination chemistry of nitrogen-based multidentate ligands,¹³ with special attention to pyrazole and its analogues (imidazole and triazole) both in their neutral¹⁴ and anionic azolate forms.¹⁵ The corresponding transition-metal complexes have found applications in catalysis, material science or in the synthesis of polynuclear systems. Continuing the investigation on pyrazole systems, herein we report the preparation of a copper(II) polynuclear compound with a cubane skeleton bearing 3,4,5-1*H*-trimethyl pyrazole (Htmpz) as an ancillary ligand. The latter is coordinated to copper in a monodentate fashion *via* its pyridine-like nitrogen atom. The synthesis and structural characterization of the title compound, $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4 \cdot 1.5\text{Et}_2\text{O}$ ($3 \cdot 1.5\text{Et}_2\text{O}$) and its precursors, $[\text{Cu}(\text{Htmpz})_4](\text{ClO}_4)_2$ (**1**) and $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2](\text{ClO}_4)_2$ (**2**), are described. In our opinion, the reactions discussed here represent a nice example of the Goldilocks principle applied to coordination chemistry: actually, like in the fairy tale of Goldilocks and the Three Bears,¹⁶ the solvent (methanol), the

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counteranion (ClO_4^-) and the ancillary ligand (Htmpz) each possesses “just right” properties (*i.e.*, perchlorate showing a semi-bonding coordination, neither too strongly nor too poorly coordinated to Cu^{II}) to generate complexes 1–3. The effects of the Goldilocks principle operating here are detailed in the text.

Results and discussion

Syntheses of complexes

The reaction of $[\text{Cu}(\text{ClO}_4)_2] \cdot 6\text{H}_2\text{O}$ with 3,4,5-trimethyl-1H-pyrazole (Htmpz) in THF, at 20 °C, leads to the formation of $[\text{Cu}(\text{Htmpz})_4(\text{ClO}_4)_2]$ (1) (Scheme 1).

The same reaction can be performed in other solvents besides THF (*i.e.* H_2O , ethanol) and compound 1 is always isolated in high yields. A particular behavior was noticed in methanol, where the crude product resulted in a mixture of the expected violet $[\text{Cu}(\text{Htmpz})_4(\text{ClO}_4)_2]$ compound and a blue solid. To better understand this behavior, the reaction of 1 with methanol was investigated. $[\text{Cu}(\text{Htmpz})_4(\text{ClO}_4)_2]$ readily dissolves in anhydrous methanol at room temperature to give a dark green solution, from which soon precipitates a blue solid formulated as $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2(\text{ClO}_4)_2]$ (2) (Scheme 2). Reasonably, but surprisingly enough, in the course of the reaction, methanol is deprotonated by the perchlorate anion and two moles of perchloric acid are formed. The acids are eliminated as pyrazolium salt $[(\text{H}_2\text{tmpz}^+)(\text{ClO}_4^-)]$ after protonation of free 3,4,5-trimethyl-1H-pyrazole, present in the bulk as a consequence of dissociation of two molecules of Htmpz from the Cu^{II} centre. Concurrently, the methoxido anions coordinate to the copper atoms and the stable dinuclear di- μ -methoxy-bridged $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2(\text{ClO}_4)_2]$ is formed.

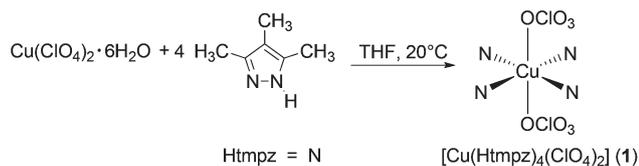
As is known, methoxy-bridged Cu(II) compounds are often closely related to hydroxo-bridged Cu(II) species,¹⁷ and then the hydrolysis of compound 2 was investigated, aiming at isolating a $\text{Cu}^{\text{II}}-(\mu\text{-OH})_x\text{-Cu}^{\text{II}}$ system. A solution of 2 in wet

CH_2Cl_2 was then stirred at room temperature for 6 hours. After removal of the solvent and recrystallization of the crude product, a light blue compound was isolated in high yields. By slow diffusion of diethylether in a CH_2Cl_2 solution of the complex, it was possible to grow single crystals suitable for X-ray diffraction analysis. Surprisingly the compound deriving from the hydrolysis of 2 is characterized by a Cu_4O_4 cubane core and can be formulated as $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4 \cdot 1.5\text{Et}_2\text{O}$ ($3 \cdot 1.5\text{Et}_2\text{O}$). It is supposed that a transient $[\text{Cu}^{\text{II}}-(\mu\text{-OH})_2\text{-Cu}^{\text{II}}]$ dihydroxo bridged system, formed by hydrolysis of the corresponding methoxy complex, self-assembles into a cubane cluster. This is somehow corroborated by the crystal structure of cubane 3 itself (*vide infra*) composed of two dimeric $[\text{Cu}^{\text{II}}-(\mu\text{-OH})_2\text{-Cu}^{\text{II}}]$ units brought together by four parallel, long Cu–O bonds. Moreover, when $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2(\text{ClO}_4)_2]$ is dissolved in dry CH_2Cl_2 in the absence of exogenous water and stirred at room temperature for a prolonged period, no reaction takes place. Then, the hydrolysis of $\mu\text{-OCH}_3$ is the first step of the reaction converting the methoxy-bridged complex 2 into cubane 3, the self-assembly process being very fast.

When $3 \cdot 1.5\text{Et}_2\text{O}$ is heated at 40 °C under vacuum for three hours, a change in color of the solid from the original light blue into green is observed, associated with the loss of diethylether. The resulting species showed spectroscopic features (IR, see ESI[†]) similar to $3 \cdot 1.5\text{Et}_2\text{O}$ and analyzed as $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4$ (3). It was easily re-converted into $3 \cdot 1.5\text{Et}_2\text{O}$ after short exposure at room temperature to diethylether vapors; thus the loss of Et_2O from $3 \cdot 1.5\text{Et}_2\text{O}$ is reversible and does not affect the stability of the Cu_4O_4 cubane core.

Infrared and electronic spectra

Together with the expected broad band at about 1100 cm^{-1} due to the ν_3 mode of ClO_4^- anions of the T_d symmetry, the infrared spectrum of 1 recorded in hexachlorobutadiene (Fig. S1, ESI[†]) is characterized by intense absorptions at 3330 cm^{-1} (N–H of Htmpz) and in the region $2870\text{--}2927\text{ cm}^{-1}$ (C–H stretching, methyl substituents in Htmpz). A similar pattern is observed in the spectrum of 2, which shows the N–H peak at 3345 cm^{-1} and the CH_3 groups (Htmpz) at $2883\text{--}2927\text{ cm}^{-1}$ (Fig. S2, ESI[†]). The N–H of the Htmpz molecules in 2 are not involved in H-bonding interactions with other atoms, thus leading to a slight increase in $\nu_{\text{N-H}}$ of 2 compared to 1 (3345 vs. 3330 cm^{-1}). The additional sharp vibration at 2809 cm^{-1} is clearly attributable to C–H stretching of the $\mu\text{-OCH}_3$ groups. By treatment of $[\text{Cu}(\text{Htmpz})_4(\text{ClO}_4)_2]$ with CD_3OD it has been possible to isolate the deuterated μ -methoxy dinuclear compound $[\text{Cu}(\mu\text{-OCD}_3)(\text{Dttmpz})_2(\text{ClO}_4)_2]$ (2-D₄). In its infrared spectrum (Fig. S3, ESI[†]), the isotopic shifts of N–D and CD_3 stretching respectively to 2492 cm^{-1} and 2051 cm^{-1} are detected. Finally, species $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4 \cdot 1.5\text{Et}_2\text{O}$ ($3 \cdot 1.5\text{Et}_2\text{O}$) shows N–H and CH_3 peaks of the Htmpz ligand respectively at 3313 and $2866\text{--}2927\text{ cm}^{-1}$ (Fig. S4, ESI[†]) and the disappearance of the sharp stretching at 2809 cm^{-1} ($\mu\text{-OCH}_3$) due to the hydrolysis of the methoxy groups. The broad band at 3551 cm^{-1} is



Scheme 1 Synthesis of $[\text{Cu}(\text{Htmpz})_4(\text{ClO}_4)_2]$ (1).



Scheme 2 Formation of $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2(\text{ClO}_4)_2]$ (2) in the reaction of (1) with methanol.

assigned to ν_{OH} of the triply-bridged hydroxyl groups. The latter are involved in weak $\text{O-H}\cdots\text{O}_{(\text{perchlorato})}$ contacts (see the crystal structure description below) and the ν_{OH} recorded for cubane 3-1.5Et₂O appears at higher wavenumbers with respect to other previously reported systems.^{8d}

The electronic spectra of complexes **2** and **3** recorded in dichloromethane display a single unstructured absorption band at 579 (**2**) and 566 nm (**3**) typical of copper(II) centers.¹⁸

Crystal structures

Selected bond distances and angles for [Cu(Htmpz)₄(ClO₄)₂] (**1**), [Cu(μ -OCH₃)(Htmpz)₂(ClO₄)₂] (**2**) and [Cu₄(μ -OH)₄(Htmpz)₈](ClO₄)₄ (**3**) are presented in Tables 1 and 2. The crystal structure of **1** (Fig. 1) shows the copper(II) centre in a distorted octahedral geometry, with the equatorial positions occupied by four N_{pyridine} atoms of four monodentate Htmpz ligands and one oxygen atoms of the two perchlorato anion at the axial sites. Bond distances found for **1** are in accordance with the literature data for similar compounds like

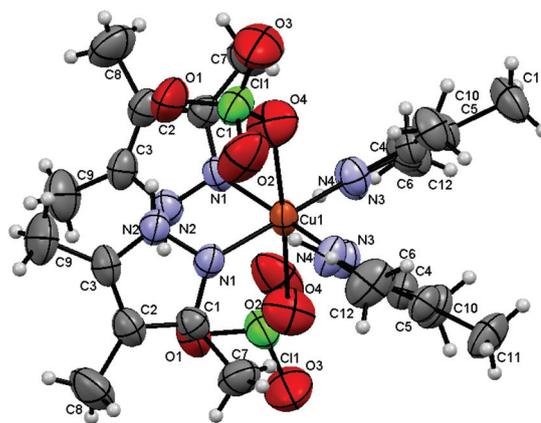


Fig. 1 Crystal structure of **1** at 35% probability level ellipsoids.²¹

Table 1 Selected bond distances (Å) and angles (°) in **1** and **2**

Distances (Å)		Angles (°)	
[Cu(Htmpz)₄(ClO₄)₂] (1)			
Cu(1)–N(1)	2.014(4)	N(1)–Cu(1)–N(3) (<i>trans</i>)	176.12(2)
Cu(1)–N(3)	1.978(4)	N(1)–Cu(1)–N(3) (<i>cis</i>)	89.31(1)
Cu(1)–O(4)	2.714(3)	N(1)–Cu(1)–N(1) (<i>cis</i>)	87.88(1)
O(4)–Cl(1)	1.433(4)	N(1)–Cu(1)–O(4)	91.89(1)
		N(3)–Cu(1)–O(4)	85.24(1)
		O(4)–Cu(1)–O(4)	176.99(1)
[Cu(μ-OCH₃)(Htmpz)₂(ClO₄)₂] (2)			
Cu(1)–N(1)	1.956(5)	Cu(1)–O(1)–Cu(1)	99.60(2)
Cu(1)–N(2)	1.964(5)	O(1)–Cu(1)–O(1)	80.40(2)
Cu(1)–O(2)	2.657(6)	N(1)–Cu(1)–N(2)	94.76(2)
O(2)–Cl(1)	1.438(6)	N(1)–Cu(1)–O(1) (<i>trans</i>)	165.29(2)
O(1)–C(1)	1.400(1)	N(2)–Cu(1)–O(1) (<i>trans</i>)	173.51(2)
Cu(1)⋯Cu(1)'	2.941(1)	N(1)–Cu(1)–O(1) (<i>cis</i>)	91.51(2)
		N(2)–Cu(1)–O(1) (<i>cis</i>)	93.82(2)
		N(1)–Cu(1)–O(2)	102.87(2)
		N(2)–Cu(1)–O(2)	86.49(2)

Table 2 Selected bond distances (Å) and angles (°) in **3**

Distances (Å)		Angles (°)					
Cu(1)–N(1)	1.986(5)	Cu(3)–O(2)	1.983(4)	N(1)–Cu(1)–O(1)	172.1(2)	O(1)–Cu(3)–O(4)	82.5(2)
Cu(1)–N(3)	1.959(6)	Cu(3)–O(4)	2.312(4)	N(3)–Cu(1)–O(2)	166.6(2)	O(1)–Cu(3)–O(2)	77.5(2)
Cu(1)–O(1)	1.968(4)	Cu(4)–N(13)	1.997(5)	Cu(1)–O(1)–Cu(2)	97.1(2)	O(3)–Cu(4)–O(4)	78.0(2)
Cu(1)–O(2)	1.964(4)	Cu(4)–N(15)	1.965(5)	Cu(1)–O(3)–Cu(2)	98.6(2)	O(2)–Cu(4)–O(4)	82.3(2)
Cu(1)–O(3)	2.296(5)	Cu(4)–O(3)	1.973(4)	N(5)–Cu(2)–O(4)	171.5(2)	O(1)–Cu(1)–O(3)	81.8(2)
Cu(2)–N(5)	1.982(7)	Cu(4)–O(4)	1.968(4)	N(7)–Cu(2)–O(3)	163.9(2)	O(2)–Cu(1)–O(3)	82.5(2)
Cu(2)–N(7)	1.966(6)	Cu(4)–O(2)	2.319(4)	O(1)–Cu(1)–O(3)	81.8(2)	O(1)–Cu(2)–O(4)	81.3(2)
Cu(2)–O(1)	2.346(4)	Cu(1)⋯Cu(2)	3.243(1)	O(1)–Cu(2)–O(3)	80.4(2)	O(1)–Cu(2)–O(3)	80.4(2)
Cu(2)–O(3)	1.973(4)	Cu(1)⋯Cu(3)	3.064(1)	N(9)–Cu(3)–O(2)	166.7(2)	Cu(1)–O(3)–Cu(2)	98.6(2)
Cu(2)–O(4)	1.968(5)	Cu(1)⋯Cu(4)	3.205(1)	N(11)–Cu(3)–O(1)	170.4(2)	Cu(2)–O(1)–Cu(1)	97.1(2)
Cu(3)–N(9)	1.987(5)	Cu(2)⋯Cu(3)	3.220(1)	Cu(3)–O(2)–Cu(4)	96.5(2)	Cu(1)–O(2)–Cu(4)	96.6(2)
Cu(3)–N(11)	1.971(5)	Cu(2)⋯Cu(4)	3.056(1)	Cu(3)–O(4)–Cu(4)	97.1(2)	Cu(2)–O(4)–Cu(3)	97.2(2)
Cu(3)–O(1)	1.952(4)	Cu(3)⋯Cu(4)	3.216(1)	N(13)–Cu(4)–O(3)	170.0(2)	Cu(3)–O(2)–Cu(4)	96.5(2)
				N(15)–Cu(4)–O(4)	168.4(2)	Cu(4)–O(4)–Cu(3)	97.1(2)
				O(2)–Cu(3)–O(4)	82.2(2)	Cu(3)–O(1)–Cu(2)	96.6(2)
				O(2)–Cu(4)–O(4)	82.3(2)	Cu(4)–O(3)–Cu(1)	97.1(2)

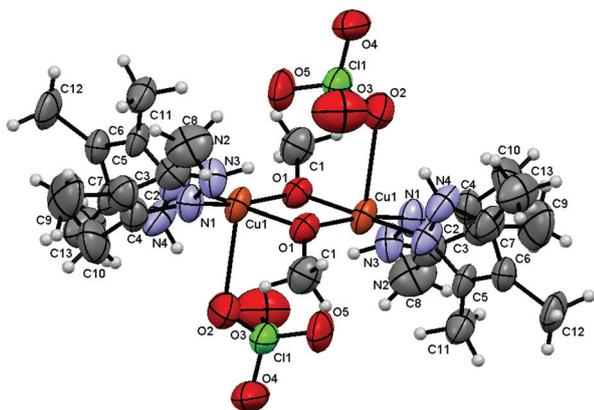


Fig. 2 Crystal structure of **2** at 35% probability level ellipsoids.

Cu...Cu distance (2.941(1) Å) is in accordance with the literature data for related $\text{Cu}^{\text{II}}-(\mu\text{-OCH}_3)_2\text{-Cu}^{\text{II}}$ systems.^{7b} The values of O–Cu–O and Cu–O–Cu angles found for $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2(\text{ClO}_4)]_2$ fall in the ranges expected for dinuclear $\text{Cu}^{\text{II}}(\text{OMe})\text{-Cu}^{\text{II}}$ compounds, Cu–O–Cu and O–Cu–O measuring respectively 99.60(2)° and 80.40(2)°. This value for the Cu–O–Cu angle suggests an antiferromagnetic behavior for $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2(\text{ClO}_4)]_2$, in conformity with what is expected for symmetrically di-bridged dinuclear copper(II) complexes.²⁴ Finally, out-of-plane angles of the methyl in bridging methoxy groups is 32.54° (see Fig. S7, ESI†).

Compound **3** represents the fifth example of a structurally characterized copper(II) tetranuclear compound where the $\{\text{Cu}_4(\mu_3\text{-OH})_4\}$ single-core is stabilized by monodentate ancillary ligands (Htmpz).^{11a,e,l,n} The four copper atoms and the four oxygens of the bridging hydroxo groups in **3** occupy alternate corners of a slightly distorted cube (Fig. 3). Each copper centre has an N_2O_3 surrounding in a square-pyramidal geometry (Addison parameter values ranging between 0.023 and

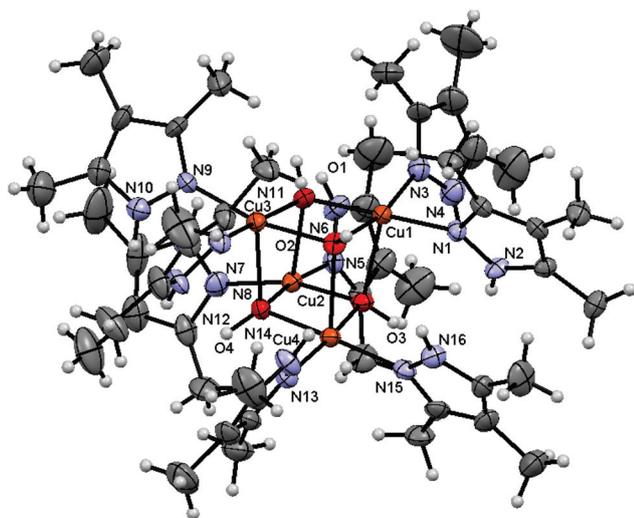


Fig. 3 Crystal structure of **3** at 35% probability level ellipsoids with ClO_4^- anions omitted for clarity.

0.127),²² the equatorial sites being occupied by one nitrogen atom of two monodentate Htmpz molecules and two $\mu_3\text{-OH}$ groups, whereas the third oxygen bound to copper occupies the apical position. Analysis of bond distances reveals that the Cu–O_{apical} distances are elongated (2.296(4) to 2.346(4) Å) compared to the Cu–O_{equatorial} distances (1.952(4) to 1.983(4) Å).

Thus, $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4$ is better described as being composed of two dimeric $\text{Cu}_2(\mu\text{-OH})_2(\text{Htmpz})_4$ units which self-assemble in a tetrameric cubane of type I.^{11b} According to the classification of Cu_4O_4 based on Cu...Cu distances proposed by Alvarez,²⁵ type I cubane is classified as (4 + 2), showing four long inter-dimeric distances and two shorter intra-dimeric distances between the copper centers. Analysis of the Cu...Cu distances in **3** confirms this trend, with four long inter-dimeric Cu...Cu distances (3.205(1), 3.216(1), 3.220(1), 3.243(1) Å) and two shorter intra-dimeric distances (3.056(1), 3.064(1) Å) (Fig. 4).

Within the dimers, the Cu–O–Cu angles range from 101.5(2)° to 102.8(2)°, whereas the O–Cu–O span ranges from 77.5(2)° to 78.0(2)°. Hatfield described a correlation between Cu–O–Cu angles and the magnetic properties of μ -hydroxo bridged dinuclear compounds,²⁶ the ferromagnetic behavior being associated with species having Cu(OH)–Cu angles smaller than 97.6°. For compounds showing bridging Cu–O–Cu angles of copper centers higher than 97.6°, the sign of the magnetic interactions among copper(II) is negative, thus leading to antiferromagnetic behavior. This is also the case for $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4$, as corroborated by low-temperature NMR measurements (see below). External Cu–O–Cu angles in the Cu_4O_4 core of **3** range from 96.5(2)° to 102.8(2)°, whereas O–Cu–O external angles span between 80.4(2)° and 82.5(2)°, in accordance with the literature data for the previous $\{\text{Cu}_4(\mu_3\text{-OH})_4\}$ species.¹¹ The crystal structure of **3** is completed by four perchlorate anions in the second coordination sphere of the cubane core. As already observed for other $\{\text{Cu}_4(\text{OH})_4\}$ cores,^{11b} the structure of **3** is further stabilized by the presence of H-bonding between the cluster itself and the four counteranions. Indeed, the oxygen atoms of the ClO_4^- form hydrogen bonding both with Htmpz ligands and the bridging OH groups (Fig. S8, ESI†). Generally, $\text{O}\cdots\text{H-N}_{\text{pz}}$ are longer than $\text{O}\cdots\text{H-O}_{\text{hydroxo}}$ interactions, ranging respectively between 2.820(1) and 3.000(9) Å ($\text{O}\cdots\text{H-N}_{\text{pz}}$) and between 2.819(6) and 2.932(6) Å ($\text{O}\cdots\text{H-O}_{\text{hydroxo}}$). In $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4$, three ClO_4^- are triply-connected to the cubane cluster, with two $\text{O}\cdots\text{H-N}_{\text{pz}}$ and one $\text{O}\cdots\text{H-O}_{\text{hydroxo}}$, while the fourth ClO_4^- anion shows only two H-bonding interactions (one $\text{O}\cdots\text{H-N}_{\text{pz}}$ and one $\text{O}\cdots\text{H-O}_{\text{hydroxo}}$). In particular, H-bonding interactions in triply-bridged perchlorate ions are longer than the corresponding ones in doubly-bridged ClO_4^- , the lengths being respectively 2.890(1)–3.000(9) Å ($\text{O}\cdots\text{H-N}_{\text{pz}}$) and 2.829(7)–2.932(6) Å ($\text{O}\cdots\text{H-O}_{\text{hydroxo}}$) in $\mu_3\text{-ClO}_4^-$ and 2.820(1) Å ($\text{O}\cdots\text{H-N}_{\text{pz}}$) and 2.819(6) Å ($\text{O}\cdots\text{H-O}_{\text{hydroxo}}$) for $\mu_2\text{-ClO}_4^-$. As magneto-structural correlations suggest an antiferromagnetic behaviour for compounds **2** and **3**, we attempted to perform an NMR investigation. Actually, species **2** and **3** show quite resolved signals in their ¹H NMR spectrum (CD_2Cl_2 , 20 °C,

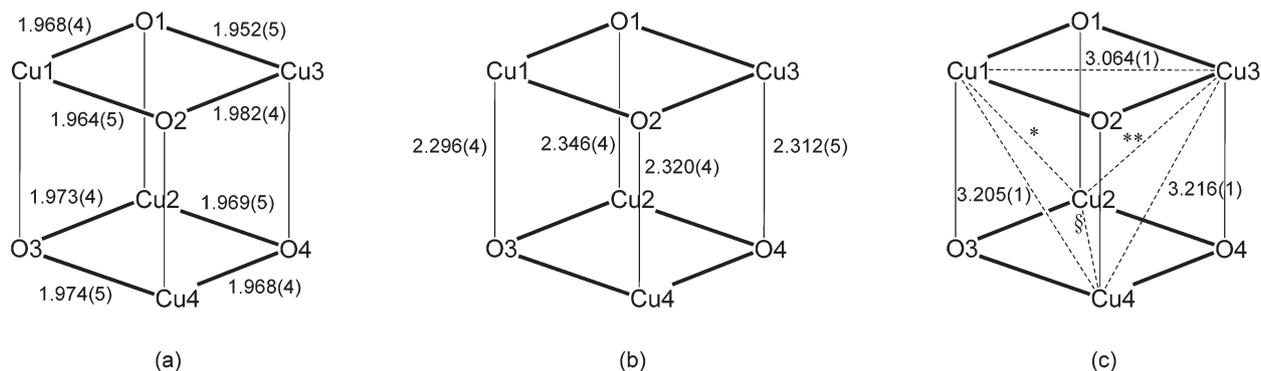


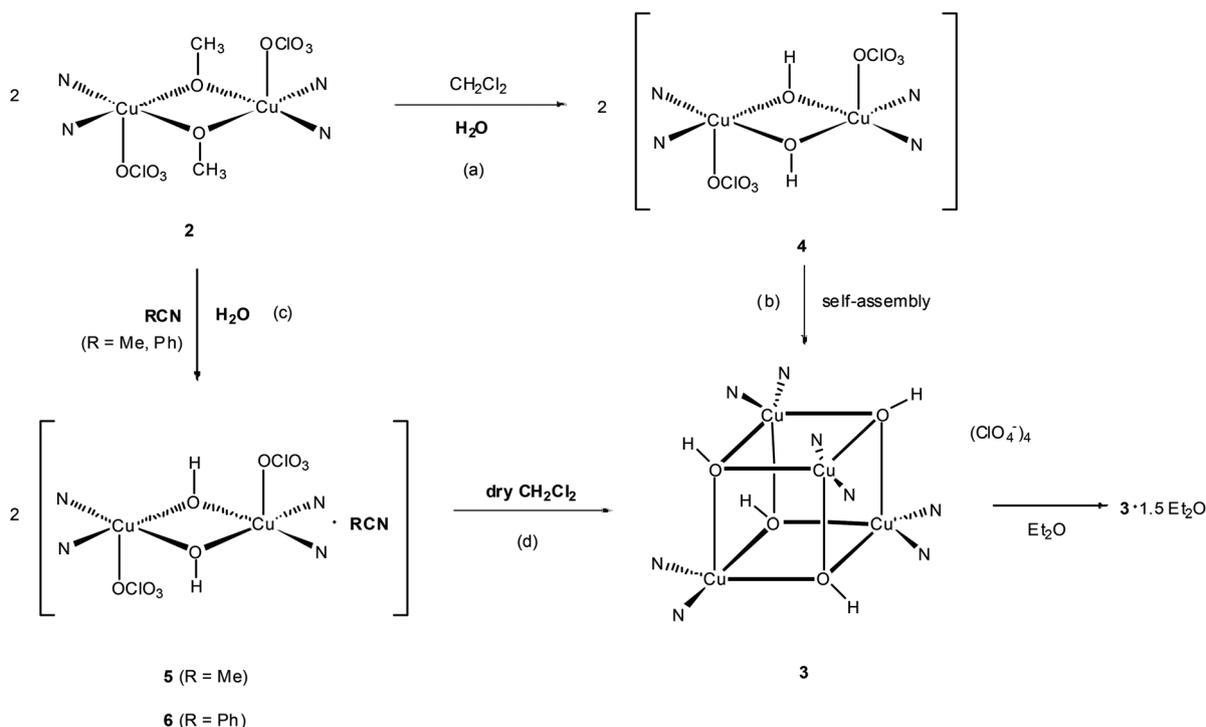
Fig. 4 Cu–O intra-dimeric (a), Cu–O inter-dimeric (b) and Cu...Cu (c) bond distances in cubane **3** (*: Cu(1)–Cu(2), 3.243(1) Å; **: Cu(2)–Cu(3), 3.220(1) Å; §: Cu(2)–Cu(4), 3.056(2) Å).

Fig. S10–S12, ESI[†]), thus confirming somehow the existence of antiferromagnetic coupling between the copper(II) centres in these complexes. This coupling is maintained in a wide range of temperatures, as illustrated by low temperature NMR experiments performed on the two samples (down to -60 °C, ESI[†]).

Mechanism of hydrolysis of **2**

Moreover, the structural analysis reveals a noticeable analogy of bond distances and angles in the $(\text{Cu}^{\text{II}}\text{--O--Cu}^{\text{II}})_x$ skeleton of $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2(\text{ClO}_4)]_2$ and $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4$. Thus, one can assume that the formation of compound **2** is crucial for leading to the title cubane *via* hydrolysis of the methoxy-bridges (Scheme 3). In Scheme 3, we assumed

that two neighboring molecules of $[\text{Cu}(\text{Htmpz})_2(\mu\text{-OH})(\text{ClO}_4)]_2$ (**4**), generated by hydrolysis of **2**, rapidly undergo a self-assembly process, yielding the tetranuclear cluster $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4$ (Scheme 3, step b). This green species, when exposed to diethylether vapors, quickly converts into a light blue compound, showing spectroscopic features identical to $3 \cdot 1.5\text{Et}_2\text{O}$ (Fig. S14, ESI[†]). Unfortunately, various attempts to intercept pure intermediate **4** were unsuccessful, due to its tendency to rapidly self-assemble into the cubane structure, as reported by Cronin *et al.* for an analogous $\{\text{Cu}_4(\mu_3\text{-OH})_4\}$ system.^{11g} Noticeably, in that case the hydrolysis of methoxy-bridged dinuclear copper(II) species to give Cu_4O_4 moieties occurred in the presence of a large amount of water (13% to 20% volume). Such a quantity was postulated to prevent weak



Scheme 3 Pathways leading to the formation of **3** by hydrolysis of **2**.

apical ClO_4^- coordination, thus ultimately favoring the association of dimers into the cubane. In the present case, a lesser amount of water (<2% vol.) was needed to perform hydrolysis of the methoxo bridges, and the semi-bonding apical coordination of ClO_4^- is fundamental to obtain the cubane (*vide infra*).

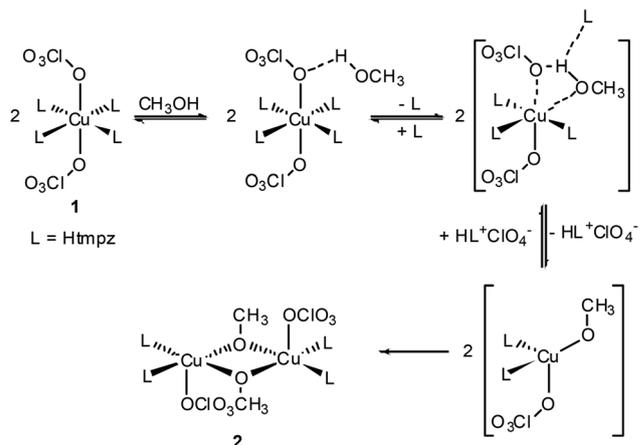
The hydrolysis of **2** was also performed in a coordinating solvent, namely acetonitrile or benzonitrile, aiming at stabilizing an intermediate species. The methoxo $[\text{Cu}(\text{Htmpz})_2(\mu\text{-OCH}_3)(\text{ClO}_4)]_2$ complex, when stirred at room temperature for 6 h in CH_3CN or PhCN , in the presence of water converts into a dark green compound, postulated as $[\text{Cu}(\mu\text{-OH})(\text{Htmpz})_2(\text{ClO}_4)]_2\text{RCN}$ ($\text{R} = \text{CH}_3$, **5**; $\text{R} = \text{Ph}$, **6**) according to elemental analyses and infrared evidence (Scheme 3, step c). In the IR spectrum of compounds **5** and **6** (Fig. S13, ESI[†]) the expected $\nu_{\text{N-H}}$ (3303 cm^{-1}), $\nu_{\text{C-H}}$ ($2863\text{--}2925\text{ cm}^{-1}$) and $\nu_{\text{Cl-O}}$ (broad band at 1103 cm^{-1}) are observed. Additionally, a small shoulder at 3550 cm^{-1} representative of OH groups is detected. The weak stretching at about 2265 cm^{-1} indicates the presence of RCN in the molecular structure of **5** and **6**, which stabilizes the dinuclear system. Actually, when compounds **5** or **6** are stirred at room temperature in dry CH_2Cl_2 for a few minutes, a change in the color of the solution from dark green to light green is observed (Scheme 3, step d). Again, the spectroscopic and analytical features of the product isolated after exposure to diethylether vapors were identical to those of cubane $3\cdot 1.5\text{Et}_2\text{O}$. Then, we suppose that the CH_3CN (or PhCN) molecule in **5** (or **6**) is easily lost in CH_2Cl_2 solution, leaving the $[\text{Cu}(\mu\text{-OH})(\text{Htmpz})_2(\text{ClO}_4)]_2$ (**4**) dinuclear system which readily undergoes self-assembly into **3**. Unfortunately, this prompt loss of RCN from **5** or **6** in solution prevented the growth of single crystals of $[\text{Cu}(\text{Htmpz})_2(\mu\text{-OH})(\text{ClO}_4)]_2\text{RCN}$ and all attempts resulted in the isolation of light-blue crystals of cubane $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4\cdot 1.5\text{Et}_2\text{O}$.

The Goldilocks principle leading to **3**

As discussed above, the hydrolysis reaction of complex **2** plays a matchless role in the genesis of cubane **3**. Hence, we decided to better explore the formation of the crucial methoxo-bridged species. Initially, to check the possibility to obtain a dinuclear $\text{Cu}^{\text{II}}\text{-(OR)}_2\text{-Cu}^{\text{II}}$ system employing a different alcohol ($\text{R} = \text{Et}$, $i\text{Pr}$) we treated compound $[\text{Cu}(\text{Htmpz})_4(\text{ClO}_4)_2]$ (**1**) with ethanol or propan-2-ol. Even after a prolonged stirring, no reaction takes place and the violet compound **1** is wholly recovered after removal of the solvent, without showing formation of an alkoxo-bridged compound. Yet, as predictable, performing the same reaction in water does not lead to the title cubane, and again $[\text{Cu}(\text{Htmpz})_4(\text{ClO}_4)_2]$ is isolated as the only product. Then, we first assume that methanol exclusively leads to the formation of the desired alkoxo-bridged dinuclear intermediate.

This may be due to the “just right” acidity of methanol, which is neither “too acid” (as water) nor “too poorly acid” (like ethanol or propan-2-ol).²⁷ Moreover, also the right steric hindrance of methanol allows it to take part in the pathway proposed in Scheme 4.

We postulate that methanol is first involved in a $\text{H}\cdots\text{O}$ interaction with a perchlorate anion, and then, after dissociation of



Scheme 4 Proposed mechanism for the generation of $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2(\text{ClO}_4)]_2$ (**2**).

one molecule of 3,4,5-trimethyl-1H-pyrazole (L), it loosely coordinates to copper(II) *via* oxygen. The reaction evolves with a four-centered $\text{Cu-O}(\text{ClO}_3)\text{-H-O}(\text{CH}_3)$ concerted hydrogen-transfer from methanol to the coordinated ClO_4^- . The generated perchloric acid is eliminated as 3,4,5-trimethyl-1H-pyrazolium salt ($\text{HL}^+\text{ClO}_4^-$), while the resulting four-coordinated methoxo species dimerize to the more stable complex **2**. Although it is quite unusual to see methanol protonate ClO_4^- , we believe that this equilibrium is favored by two factors: (i) the poor solubility of compound **2**, which precipitates off, thus progressively moving the final step forward and consequently the whole system towards the formation of **2**, and (ii) the assistance of Htmpz that, after dissociation, is however in close proximity to the coordination sphere of the copper centre and favors the final proton transfer.

In this process, also ClO_4^- plays a key role. To prove this, we prepared $[\text{Cu}(\text{Htmpz})_4(\text{NO}_3)_2]$ (**7**) and $[\text{Cu}(\text{Htmpz})_4(\text{BF}_4)_2]$ (**8**) by following a similar procedure to that for the synthesis of **1** and then we reacted them with methanol. In the course of the reaction, a color change from violet to blue is observed, but no precipitation takes place. When the solvent is removed under reduced pressure, the starting complexes are always quantitatively recovered. It should not be excluded that analogous to the reported copper(II) complexes bearing 3,5-dimethylpyrazole (Hdmpz) as a ligand¹⁸ ($[\text{Cu}(\text{Hdmpz})_4(\text{NO}_3)_2]$ and $[\text{Cu}(\text{Hdmpz})_4(\text{BF}_4)_2]$), also compounds **7** and **8** can evolve, in solution, to species with different stoichiometries. Then, only the octahedral $[\text{Cu}(\text{Htmpz})_4(\text{ClO}_4)_2]$ (**1**) bearing perchlorate in a semi-bonding range leads to the dinuclear methoxo-bridged compound **2** by reaction with methanol. This is due to the “just right” coordinating properties of ClO_4^- , which is neither too weakly nor too strongly coordinated to Cu^{II} : this allows $\text{H}\cdots\text{O}$ interaction with methanol to take place, with the consequent elimination of $(\text{HL}^+)\text{ClO}_4^-$ (Scheme 4) and generation of complex **2**.

Finally, also 3,4,5-trimethyl-1H-pyrazole plays a key role in the genesis of cubane $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4$ (**3**).

Indeed, when the more sterically crowded 3,5-di-*tert*-butyl-1*H*-pyrazole or the more acidic 3,5-dimethyl-4-nitro-1*H*-pyrazole are employed in the reaction, the stability of the methoxy-bridged compound markedly drops and neither isolation of this intermediate nor the formation of cubane species occurred. Additional experiments using 3,5-dimethyl-1*H*-pyrazole (Hdmpz), which has similar steric hindrance and basicity properties with respect to Htmpz,²⁸ were then performed. The complex $[\text{Cu}(\text{Hdmpz})_4(\text{ClO}_4)_2]$ ¹⁸ was treated with dry methanol, leading to the compound $[\text{Cu}(\mu\text{-OCH}_3)(\text{Hdmpz})_2(\text{ClO}_4)_2]$ (**9**) in good yields, as established by analytical and spectroscopic data. In particular, in the infrared spectrum of **9** (in hexachlorobutadiene), a sharp band at 2819 cm^{-1} can be undoubtedly assigned to the C–H stretching mode of the methoxy groups (Fig. S14, ESI[†]). Addition of water to a suspension of species **9** in CH_2Cl_2 resulted in a mixture of two compounds, a violet solution containing the octahedral $[\text{Cu}(\text{Hdmpz})_4(\text{ClO}_4)_2]$ and a light blue precipitate identified as $\text{Cu}(\text{OH})_2$ (see the Experimental section). Then, hydrolysis of $\mu\text{-OCH}_3$ moieties in **9** did not allow either to isolate the corresponding hydroxo-bridged dinuclear $[\text{Cu}(\mu\text{-OH})(\text{Hdmpz})_2(\text{ClO}_4)_2]$ (**10**) or the generation of cubane $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Hdmpz})_8](\text{ClO}_4)_4$ (**11**) (Scheme 5).

Such a dissimilar behavior between Htmpz and Hdmpz has to be searched in the only difference between them: the methyl substituent in position 4 of the heterocyclic ring. The single-crystal X-ray structure analysis of $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2(\text{ClO}_4)_2]$ shows that the hydrogen atoms of the methyl groups of the pyrazole ligands are involved in numerous C–H...O contacts with neighboring perchlorate anions (Fig. 5). In solution, these weak (but strong enough) interactions may persist for a time sufficiently long to maintain two transient dinuclear $\{\text{Cu}(\mu\text{-OH})(\text{Htmpz})_2(\text{ClO}_4)_2\}_2$ units close enough to favor the self-assembly to the cubane moiety.

A similar behavior was reported by Shultz and co-authors,^{16c} who showed how C–H...O lattice hydrogen bonding

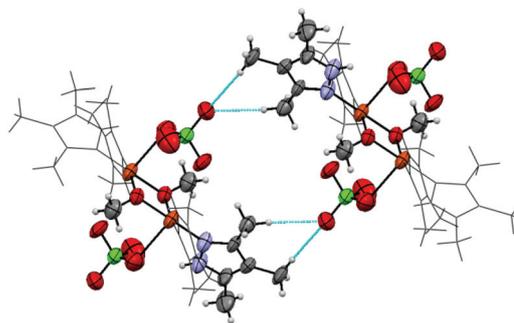


Fig. 5 The main C–H...O contacts between Htmpz and ClO_4^- of two neighboring molecules of compound **2**, responsible for the self-assembly process.

strongly influences the magnetic properties of cobalt(II) dioxolene compounds. In our case, in Hdmpz, the lack of the 4- CH_3 substituent hampers these C–H...O contacts, ultimately preventing the self-assembly of two dinuclear hydroxo units. These convert partly into octahedral $[\text{Cu}(\text{Hdmpz})_4(\text{ClO}_4)_2]$ and partly into $\text{Cu}(\text{OH})_2$.

Conclusions

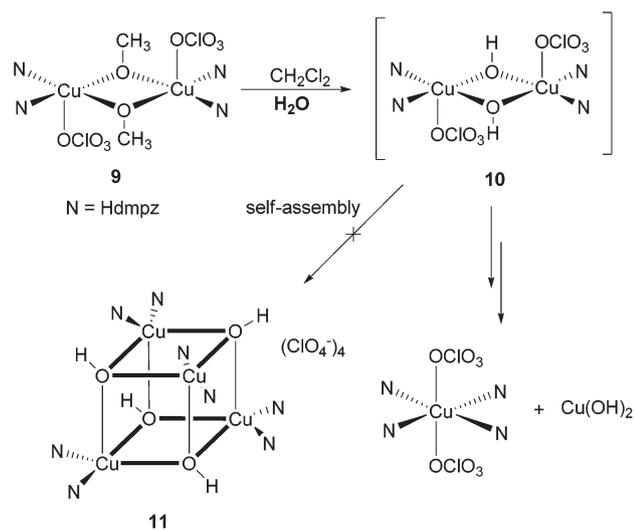
A novel copper(II) tetranuclear compound, $[\text{Cu}_4(\mu_3\text{-OH})_4(\text{Htmpz})_8](\text{ClO}_4)_4 \cdot \text{Et}_2\text{O}$, where the Cu(II) centers are stabilized by monodentate ligands, has been synthesized. This compound was obtained by hydrolysis of a dinuclear methoxy-bridged species, $[\text{Cu}(\mu\text{-OCH}_3)(\text{Htmpz})_2(\text{ClO}_4)_2]$, derived from the treatment of $[\text{Cu}(\text{Htmpz})_4(\text{ClO}_4)_2]$ with methanol. The formation of the cubane compound is the effect of a Goldilocks principle which controls the reactivity of these complexes. As illustrated in the text, changing one single factor (solvent, counteranion or ligand) would prevent the obtainment of the cubane species. This is due to the “just right” properties owned by each element: ClO_4^- shows well-balanced coordinating properties toward Cu^{II} , stabilizing intermediate species and allowing them to evolve to products; methanol has the right acidity and steric hindrance to give the dinuclear methoxy-bridged intermediate; in the latter, the methyl groups of Htmpz give C–H...O(ClO_4^-) contacts with the right strength to maintain two transient $\{\text{Cu}(\mu\text{-OH})(\text{Htmpz})_2(\text{ClO}_4)_2\}_2$ units close enough to assemble into the cubane.

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