Polyhedron 52 (2013) 370–376

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

New μ-hydroxido-bridged copper nitrate dimer and μ_4-oxido-bridged copper phenylacetate quasi-tetrahedron: Direct synthesis and uphill conversion

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ARTICLE INFO

Article history:
Available online 14 September 2012

Keywords:
Schiff base
Imine-alcohol
Phenoxido bridge
Oxido
Hydroxido
Dinuclear
Crystal structure

ABSTRACT

Dinuclear $[Cu_2(\mu\text{-OH})]$ fragment and its self-assembled tetranuclear part $[Cu_2(\mu_4\text{-O})Cu_2]$ are found in two copper(II) complexes of ligand H_3bpmp: $[Cu_2(\mu_2\text{-OH})(\mu\text{-}H_2bpmp)(\mu_{1,3}\text{-}NO_3)][Cu_2(\mu_2\text{-OH})(\mu\text{-}H_2bpmp)(NO_3)(H_2O)](NO_3)_2\cdot 2H_2O$ ($\mathbf{1}\cdot 2H_2O$) and $[Cu_4(\mu_4\text{-O})(\mu\text{-}H_2bpmp)_2(\mu_{1,3}\text{-}O_2CCH_2Ph)_4]$ (**2**) [H_3bpmp = 2,6-*bis*-[(3-hydroxy-propylimino)-methyl]-4-methylphenol]. These complexes have been synthesized and characterized by single crystal X-ray crystallography. Complex **1** showed unique reactivity with phenylacetate anions to provide **2** in which two $[Cu_2(\mu_2\text{-OH})]$ units available within same crystal lattice collapsed to give $[Cu_4(\mu_4\text{-O})]$ hub. Formation of the $[Cu_4]$ compound is also achieved from individual components and phenylacetate ligands, which allows an effective tuning of the self-assembly of two ligand bound $[Cu_2]$ fragments and removal of H^+ from hydroxido bridges to provide oxido nucleus.

1. Introduction

The design and synthesis of new family of dinuclear complexes of copper(II) and their controlled aggregation *via* self-assembly using ancillary clips to form tetranuclear complexes of varying architecture is of recent interest [1a–f]. The choice of the ligand and fine-tuning of reaction conditions with co-ligands are decisive to control the aggregation process. Understanding of such aggregation reactions is crucial in developing tetra- and higher nuclearity complexes from $[Cu_2]$ building units, which are useful model compounds to get insight into the mechanism of complex biological systems (such as in metalloenzymes) and their catalytic activity [2]. Dinucleating ligands with central phenoxido bridging functionality (Scheme 1) have been used to construct structural and Functional model of several metalloenzymes: HL [3], H_3L [4], PD′OH [5], and HL1 [6]. They can also be useful to examine interesting magnetic exchange interactions [7–9] and electron transfer behavior due to the synergism between the adjacent metal ions [10,11]. These are also useful in studying DNA binding and cleavage [12], oxidation of different catechol molecules [8,1d,13] and building motifs for the higher order complexes of [14–19]. For systematic studies on such self-assembly process, our current research focused on newer $[Cu_2]$ based aggregates. Depending on the nature and number of secondary bridges the assembly of two $[Cu_2]$ fragments leads to four types of $[Cu_4]$ aggregates: the stepped cubane, the fused defective cubane, the cubane and the tetrahedron (Scheme 2) [1a,b]. Among the ancillary ligands used, nitrato and carboxylato groups have been examined because of their versatile bridging modes.

The bridging carboxylato groups from *basal* or *apical* positions around Cu^{II} ions mediate a large diversity of magnetic exchange interactions [20–23]. Base promoted and water-derived hydroxido and oxido groups are most readily available connectors in the construction and /or stabilization of $[Cu_2]$ and $[Cu_4]$ moieties [12,18,24–28]. Out of these possibilities, the tetrahedral $[Cu_4O]$ cores are important for several reasons, such as in industrial catalytic oxidation of 2,3,6-trimethyl phenol to corresponding quinone and bio-catalytic reduction of N_2O to N_2 [29,30]. Unlike tetrahedral tetracoordinate oxygen (ttO) in $[Cu_4]$ chemistry, the corresponding planar tetracoordinate oxygen (ptO) in $[Cu_4]$ compound is only known very recently [31]. In trying to isolate and study new form of tetrahedral aggregate and the role of the secondary connectors, we have been engrossed in exploring the reactivity of H_3bpmp ligand (Chart 1, left; 2,6-*bis*-[(3-hydroxypropylimino)-methyl]-4-methylphenol) [32] with copper(II) ions. It is worth noting that the use of similar ligand H_3bemp (Chart 1, right, 2,6-*bis*-[(2-hydroxyethylimino)-methyl]-4-methylphenol) leads to systems, consisting of $[Co_4]$ [33], $[Ni_6]$ [34], $[Cu_{18}]$ [35] complexes and a heterobimetallic $[Mn_6Cu_{10}]$ [36] aggregate. Herein, $[Cu_2]$ and $[Cu_4]$ complexes of H_2bpmp^- are reported: $[Cu_2(\mu_2\text{-OH})(\mu\text{-}H_2bpmp)(\mu_{1,3}\text{-}NO_3)][Cu_2(\mu_2\text{-OH})(\mu\text{-}H_2bpmp)(NO_3)(H_2O)](NO_3)_2\cdot 2H_2O$ ($\mathbf{1}\cdot 2H_2O$) and $[Cu_4(\mu_4\text{-O})(\mu\text{-}H_2bpmp)_2(\mu_{1,3}\text{-}O_2CCH_2Ph)_4]$ (**2**). These two compounds are new examples of copper(II) complexes where Cu(II) ions are connected by two types of water-derived ligands: oxide and hydroxide. Compound 2 contains a central μ_4-oxido nucleating group and has been obtained, apart from its direct synthesis, by converting complex 1 bearing μ-hydroxido bridges by reacting with phenylacetate

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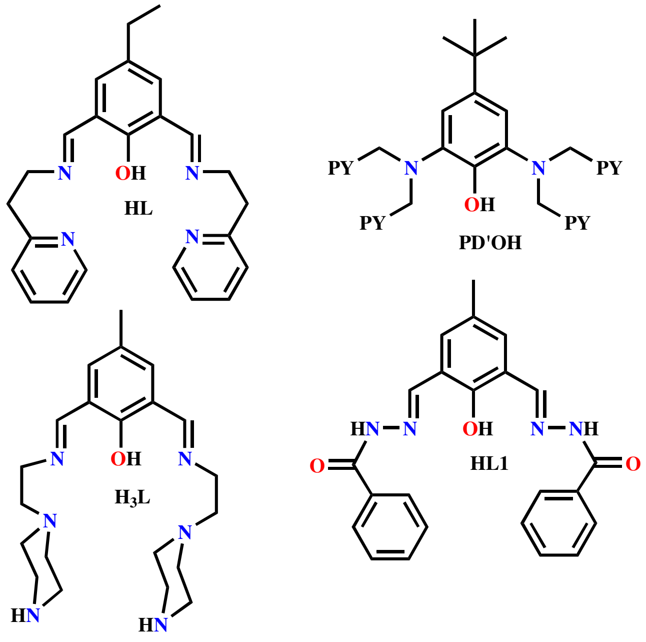
http://dx.doi.org/10.1016/j.poly.2012.08.064



Scheme 1. Some phenoxido-bridging dinucleating ligands.

ligands. These complexes have been isolated and crystallographically characterized, and the reactivity of 1 with phenylacetate examined.

2. Experimental

2.1. Materials and physical methods

2,6-Diformyl-4-methylphenol was prepared following a literature procedure [37]. The other chemicals used were obtained from the following sources: 3-amino-1-propanol from Aldrich Chemical Co. Inc., copper nitrate trihydrate, triethylamine, phenyl acetic acid, from S. D. Fine Chemicals (India). All the chemicals and solvents used in this work were of reagent grade materials and used as received without further purification. The elemental analyses (C, H, N) were performed with a Perkin–Elmer model 240 C elemental analyzer. FT-IR spectra were recorded on a Perkin–Elmer RX1 infra-red spectrometer. Solution electrical conductivity measurements and electronic spectra were carried out using a Unitech type U131C digital conductivity meter with a solute concentration of about 10^{-3} M and a Shimadzu 1601 UV–Vis–NIR spectrophotometer using 1 cm quartz cell pairs.

2.2. Syntheses

2.2.1. H_3bpmp ligand

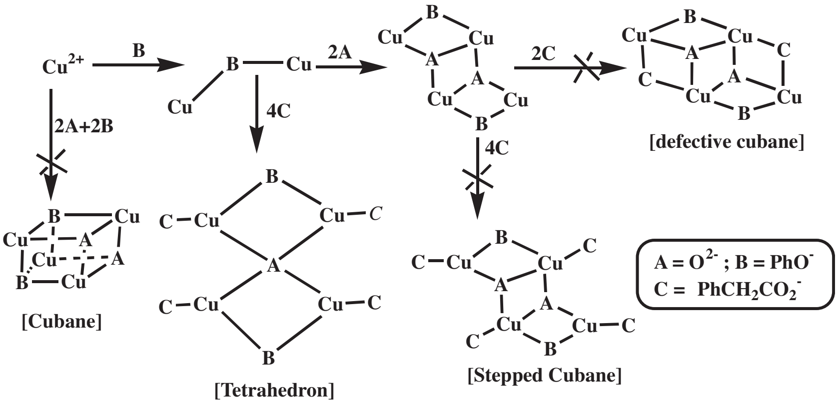
To a MeOH solution (20 mL) of 2,6-diformyl-4-methylphenol (1.0 g, 6.1 mmol), 3-amino-1-propanol (0.91 g, 12.2 mmol) was added in air at room temperature (28 °C) and stirred for 2 h to give an orange colored semi-solid product after complete evaporation of solvent in air for 12 h. The semi-solid product 2,6-*bis*-[(3-hydroxy-propylimino)-methyl]-4-methylphenol thus obtained was washed with water and used directly without further purification. Yield: 1.32 g (78%).

2.2.2. $[Cu_2(\mu_2\text{-}OH)(\mu\text{-}H_2bpmp)(\mu_{1,3}\text{-}NO_3)][Cu_2(\mu_2\text{-}OH)(\mu\text{-}H_2bpmp)(\mu\text{-}NO_3)(H_2O)](NO_3)_2\cdot 2H_2O$ (**1**·2H$_2$O)

To the yellow MeOH solution (20 mL) of H_3bpmp (0.278 g, 1.00 mmol) a MeOH solution (10 mL) of $Cu(NO_3)_2\cdot 3H_2O$ (0.482 g, 2.0 mmol) was added slowly followed by NEt_3 (0.139 mL, 0.101 g, 1.00 mmol) and stirred for 2 h at room temperature. The solvent was evaporated in air to give a green solid, which was isolated, washed with cold methanol and water, and finally dried, under vacuum over P_4O_{10}. Yield: 0.423 g, 74%. The green prismatic-shaped crystals suitable for X-ray analysis were obtained from a saturated MeOH solution after two weeks. *Anal.* Calc. for $C_{30}H_{50}Cu_4N_8O_{23}$ (1144.94 g mol^{-1}): C, 31.47; H, 4.40; N, 9.79. Found: C, 31.22; H, 4.32; N, 9.71%. Selected FT-IR bands: (KBr, cm^{-1}; s = strong, vs = very strong, m = medium, br = broad) 3401(br), 1636(s), 1560(s), 1383(vs), 1062(vs), 826(m), 615(m), Molar conductance, Λ_M: (MeOH solution) 108.1 Ω^{-1} cm^2 mol^{-1}. UV–Vis spectra [λ_{max}, nm (ε, L mol^{-1} cm^{-1})]: (MeOH solution) 677 (538), 373 (2446), 258 (12432).

2.2.3. $[Cu_4(\mu_4\text{-}O)(\mu\text{-}H_2bpmp)_2(\mu_{1,3}\text{-}O_2CCH_2Ph)_4]$ (**2**). Method A via direct route

To the yellow MeOH solution (20 mL) of H_3bpmp (0.278 g, 1.00 mmol) a MeOH solution (10 mL) of $Cu(PhCH_2CO_2)_2\cdot H_2O$ (1.068 g, 2.0 mmol) was added slowly followed by NEt_3 (0.139 mL, 0.101 g, 1.00 mmol) and stirred for 2 h at room temperature. The green solid, which was isolated, washed with cold methanol and water, and finally dried, under vacuum over P_4O_{10}. The green needle-like crystals suitable for X-ray analysis were obtained from a saturated DMF solution after three weeks. Yield: 0.532 g, 78%. *Anal.* Calc. for $C_{62}H_{70}Cu_4N_4O_{15}$ (1365.38 g mol^{-1}): C, 54.54; H, 5.16; N, 4.10. Found: C, 54.43; H, 5.02; N, 3.88%. Selected FT-IR bands: (KBr, cm^{-1}; s = strong, vs = very strong, m = medium, br = broad) 3313(br), 2924(s), 2964(s), 1604(s), 1578(s), 1457(s), 1384(vs), 1343(s), 1087(vs), 836(m), 730(m), 696(m), 632(m). Molar conductance, Λ_M: (MeOH solution) 6.5 Ω^{-1} cm^2 mol^{-1}. UV–Vis spectra [λ_{max}, nm (ε, L mol^{-1} cm^{-1})]: (MeOH solution) 637 (387), 368 (1545), 259 (65101).



Scheme 2. The possible topologies of $[Cu_4]$ aggregates.

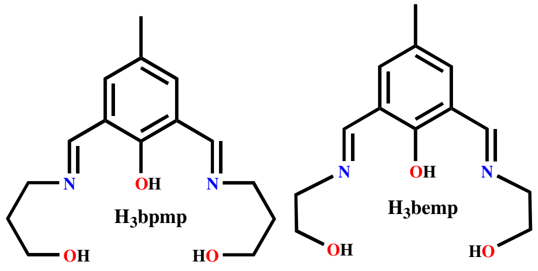


Chart 1. Ligands.

2.2.4. Method B via conversion of **1**

Addition of $PhCH_2CO_2Na$ (0.158 g, 1.0 mmol) to a green solution of **1** (0.286 g, 0.25 mmol) in MeOH (25 mL) resulted darkening of green solution followed by separation of a green solid within 15 min which was collected by filtration, washed with cold methanol and dried under vacuum over P_4O_{10}. Green needle-like crystals suitable for X-ray analysis were obtained from DMF after three weeks. Yield: 0.484 g, 71%.

2.3. X-ray crystallography

The diffraction data of **1**·$2H_2O$ and **2** were collected on a Bruker APEX-II CCD X-ray diffractometer using single crystals that uses graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by ω-scan method at 293 K. Information concerning X-ray data collection and structure refinement of the compound is summarized in Table 1. For **1**·$2H_2O$, a total of 6154 reflections were recorded with Miller indices $h_{min} = -8$, $h_{max} = 8$, $k_{min} = -22$, $k_{max} = 22$, $l_{min} = -29$, $l_{max} = 29$. For complex **2**, a total of 2116 reflections were recorded with Miller indices $h_{min} = -12$, $h_{max} = 12$, $k_{min} = -11$, $k_{max} = 12$, $l_{min} = -25$, $l_{max} = 25$. In the final cycles of refinement of full-matrix least squares on F^2, all non-hydrogen atoms were assigned anisotropically. The structure was solved using the SHELX-97 [38] program system.

Table 1
Crystallographic data.

Compound	**1**·$2H_2O$	**2**
Formula	$C_{30}H_{50}N_8O_{23}Cu_4$	$C_{62}H_{70}N_4O_{15}Cu_4$
M	1144.94	1365.38
Space group	$P2_1/n$	P-421c
Crystal system	monoclinic	tetragonal
a (Å)	8.1397(10)	11.3774(12)
b (Å)	20.401(2)	11.3774(12)
c (Å)	26.751(3)	23.437(3)
α (°)	90.00	90.0
β (°)	92.632(4)	90.0
γ (°)	90.00	90.0
U (Å^3)	4437.6(9)	3033.8(6)
T (K)	293	293
Z	4	2
D_{calc} (g cm^{-3})	1.714	1.495
F(000)	2344	1412
Crystal size (mm)	0.41 x 0.34 x 0.19	0.43 x 0.31 x 0.18
μ (Mo Kα) (cm^{-1})	19.83	14.53
Measured reflections	43006	29431
Unique reflections	6154	2116
R_{int}	0.0729	0.1706
Observed reflections $I \geqslant 2\sigma(I)$]	4207	1575
θ_{min}–θ_{max} (°)	2.14–23.00	1.74–23.00
hkl ranges	-8,8; -22,22; -29,29	-12,12; -11,12; -25,25
R (F^2) (observed reflection)	0.0578	0.0447
$wR(F^2)$ (all reflections)	0.0949	0.0762
No. variables	632	195
Goodness of fit	1.067	1.026
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^{-3})	0.999; -0.521	0.339;- 0.324

3. Results and discussion

3.1. Synthetic considerations

H_3bpmp was prepared (Scheme S1 in the Supporting Information) following a reported procedure, [32] and its reactions with copper(II) salts have been investigated (Scheme 3). Reaction of $Cu(NO_3)_2{\cdot}3H_2O$ with H_3bpmp in MeOH and NEt_3 gave $[Cu_2(\mu_2\text{-}OH)(\mu\text{-}H_2bpmp)(\mu\text{-}NO_3)(H_2O)](NO_3)_2$.

The elemental analysis, molar conductivity and X-ray diffraction data confirm the formation of $[Cu_2(\mu_2\text{-}OH)(\mu\text{-}H_2bpmp)(\mu_{1,3}\text{-}NO_3)][Cu_2(\mu_2\text{-}OH)(\mu\text{-}H_2bpmp)(\mu\text{-}NO_3)(H_2O)](NO_3)_2{\cdot}2H_2O$ (**1**·$2H_2O$) (*vide infra*). At room temperature and in air, a mixture of H_3bpmp, $Cu(NO_3)_2{\cdot}3H_2O$, and NEt_3 in a 1:2:2 M ratio in MeOH when stirred for 2 h, provided complex **1** in ~74% yield (Eq. (1)).

$$\begin{aligned}&2H_3bpmp + 4Cu(NO_3)_2\cdot 3H_2O + 4NEt_3\\&\quad\rightarrow [Cu_2(\mu_2-OH)(\mu-H_2bpmp)(\mu_{1,3}-NO_3)][Cu_2(\mu_2-OH)\\&\qquad\times(\mu-H_2bpmp)(\mu-NO_3)(H_2O)](NO_3)_2\cdot 2H_2O\\&\qquad+4(NHEt_3)(NO_3)+7H_2O\end{aligned}\tag{1}$$

Use of $Cu(PhCH_2CO_2)_2{\cdot}H_2O$ in place of $Cu(NO_3)_2{\cdot}3H_2O$ provided **2** as green solid in ~78% yield (Scheme 3). Use of NaOH or KOH in lieu of NEt_3 provided same oxido bridge in presence of bridging phenyl acetato ligands. The stronger bases were ineffective to deprotonate the alcohol arms. The preparation of **2** (Eq. (2)) accounts the formation of the oxido bridge from a molecule of water.

$$\begin{aligned}&2H_3bpmp + 4Cu(PhCH_2CO_2)_2\cdot H_2O + 4NEt_3\\&\quad\rightarrow [Cu_4(\mu_4-O)(\mu-H_2bpmp)_2(\mu_{1,3}-O_2CCH_2Ph)_4]\\&\qquad+4(NHEt_3)(PhCH_2CO_2)+3H_2O\end{aligned}\tag{2}$$

Complex **2** can also be obtained from a reaction of $Cu(NO_3)_2{\cdot}3H_2O$ with H_3bpmp in presence of NEt_3 and $PhCH_2CO_2Na$ as summarized in Eq. (3).

$$\begin{aligned}&2H_3bpmp + 4Cu(NO_3)_2\cdot 3H_2O + 4NEt_3 + 4PhCH_2CO_2Na\\&\quad\rightarrow [Cu_4(\mu_4-O)(\mu-H_2bpmp)_2(\mu_{1,3}-O_2CCH_2Ph)_4]\\&\qquad+4HNO_3+4NaNO_3+11H_2O\end{aligned}\tag{3}$$

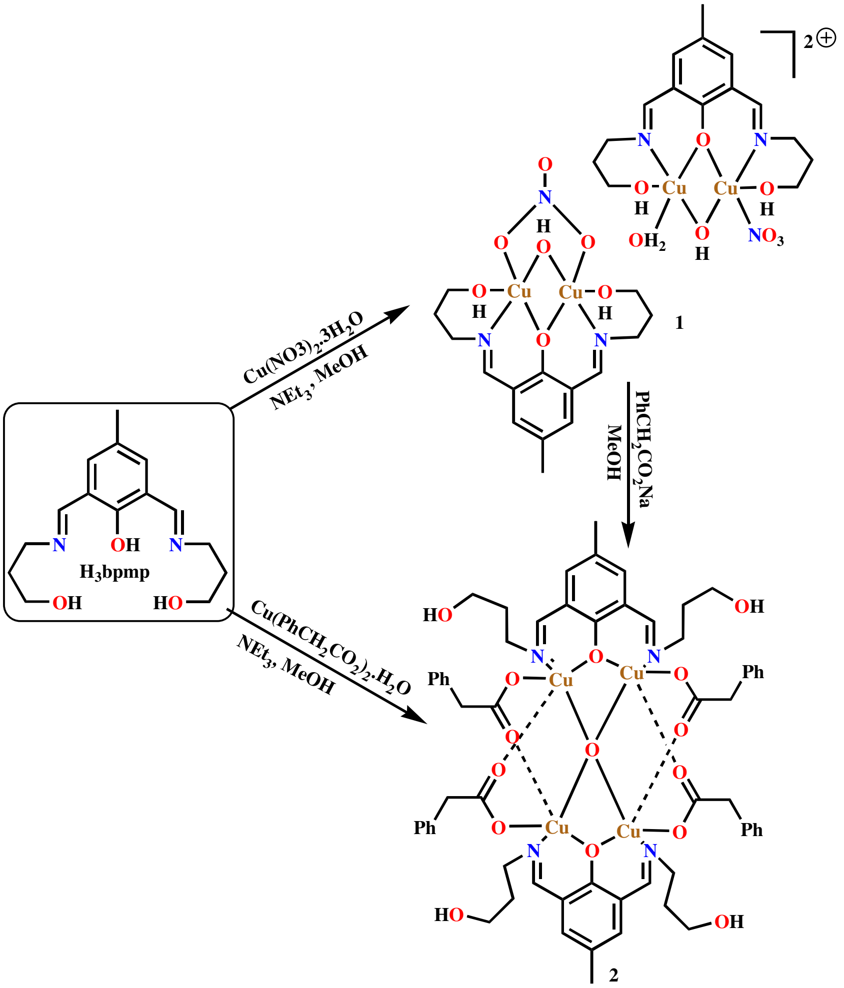
Analytical and X-ray diffraction establish the coordination of three water based ligands H_2O, HO^- and O^{2-}. Weakly coordinating NO_3^- anions support the μ-OH-bridged $[Cu_2]$ units in **1**. Whereas bridging coordination of $PhCH_2CO_2^-$ supports the μ_4-O-bridged $[Cu_4]$ core in **2**.

3.1.1. Ancillary ligand-exchange reactivity studies on complex 1

Treatment of a green solution of **1** in MeOH by sodium phenylacetate shifts the reaction equilibrium in favor of **2** with noticeable color change followed by precipitation of **2** within 15 min (Eq. (4)). From a DMF solution green crystals of **2** grew slowly over three weeks.

$$\begin{aligned}&[Cu_2(\mu_2-OH)(\mu-H_2bpmp)(\mu_{1,3}-NO_3)][Cu_2(\mu_2-OH)\\&\quad(\mu-H_2bpmp)(\mu-NO_3)(H_2O)](NO_3)_2\cdot 2H_2O\\&\quad+4PhCH_2CO_2Na\rightarrow [Cu_4(\mu_4-O)(\mu-H_2bpmp)_2\\&\quad(\mu_{1,3}-O_2CCH_2Ph)_4]+4NaNO_3+4H_2O\end{aligned}\tag{4}$$

The tentative mechanism of conversion of **1**–**2** is relatively straightforward. In presence of phenylacetate ligands the bound neutral alcohol OH functions in **1** transformed to non-coordinating pendant ones and the *basal* coordinating sited are occupied by the oxygen atoms of the phenylacetate groups replacing nitrato groups. The other end of the phenyl acetate ligand occupies the *apical* site of the adjacent *square-pyramidal* Cu centre and four such phenylacetate ligands alternately occupy *equatorial-apical* sites in a



Scheme 3. Schematic representation for the two different reaction pathways and the transformation of **1** to **2**.

cyclic fashion to bring two hydroxide bridges close to each other to form relatively basic μ_4-oxido bridge from two hydroxido bridges with liberation of one molecule of water (Fig. S1 in supporting information). Considering the quantitative and spontaneous conversion of **1**–**2** (Eq. (4)), the relative binding strength of the two ancillary anionic ligands can be recognized as: $PhCH_2CO_2^- > NO_3^-$.

The ligand exchange and core-conversion reaction has been identified by FTIR spectral measurement, observing solubility differences, checking of unit cell parameters and crystal system of grown single crystals from powder samples (Fig. S2).

3.2. Description of the crystal structures

*3.2.1. [$Cu_2(\mu_2$-OH)(μ-H_2bpmp)($\mu_{1,3}$-NO_3)][$Cu_2(\mu_2$-OH)(μ-H_2bpmp)(NO_3)(H_2O)](NO_3)$_2$·2H_2O (**1**·2H_2O)*

The green block-like single crystals of complex **1**·2H_2O obtained by the slow evaporation of the MeOH solution of the complex. Compound **1**·2H_2O crystallizes in the monoclinic, $P2_1/n$ space group with two molecule in the unit cell with three interstitial water molecules. The molecular structure of **1**·2H_2O is shown in Fig. 1, and important bond lengths and angles are given in Table 2.

Within the crystal unit-cell, one [$Cu_2(\mu_2$-OH)(μ-H_2bpmp)(NO_3)(H_2O)] fragment is packed with another [$Cu_2(\mu_2$-OH)(μ-H_2bpmp)($\mu_{1,3}$-NO_3)] part along with three molecules of water of crystallization. These two fragments differ from the water coordination and mode of binding of the nitrate anions. In the former case the doubly bridged Cu1···Cu2 provide longer inter-metallic separation 2.979 Å than the triply bridged one in the later part with Cu3···Cu4 at 2.964 Å. The *basal* positions Cu1 and Cu2 are occupied by the imine N1 (for Cu1) or N2 (for Cu2), phenoxido O1 atoms and O2(H) (for Cu1) or O3(H) (for Cu2) from the H_2bpmp$^-$ ligand, a hydroxido O4 group, [39]. In the *basal* plane the Cu-N and Cu–O distances and Cu···Cu separations within normal range [40]. From difference Fourier maps the bridging OH groups (H4 and H8A) were identified at 0.930 and 0.931 Å. The *apical* Cu–O bonds are longer at 2.38–2.41 Å for the Jahn–Teller effect, with elongations by 0.4–0.5 Å. The competitive binding of nitrato anions with water lead to monodentate and bridging $\mu_{1,3}$ coordination (Fig. 2). The Cu–O_{Ph}–Cu angles around 99° are similar Cu–O_{OH}–Cu angles (Fig. S3) [41]. The calculated Addison parameters [42] ($\tau = 0.035$, 0.036, 0.035 and 0.027) indicate the amount of distortions. Packing diagrams emphasize the intra and intermolecular hydrogen-bonds near the [Cu_2] complex (Fig. S4) and the network of hydrogen-bonds within the structure (Fig. S5).

3.2.2. [$Cu_4(\mu_4$-O)(μ-H_2bpmp)$_2$($\mu_{1,3}$-O_2CCH_2Ph)$_4$] (2)

Single crystal X-ray diffraction reveals that compound **2**, which crystallizes in tetragonal space group *P-421c* is a tetranuclear copper(II) complex. The molecular structure of **2** is shown in Fig. 3 and selected bond lengths and angles are given in Table 3. The [Cu_4] complex consists of two deprotonated H_2bpmp$^-$ ligands, each of them providing a N_2O set of donor atoms to the [Cu_4] core assembled around a tetrahedral μ_4-O group. Four phenylacetato groups complete the coordination environment (Figs. 3 and 4) with

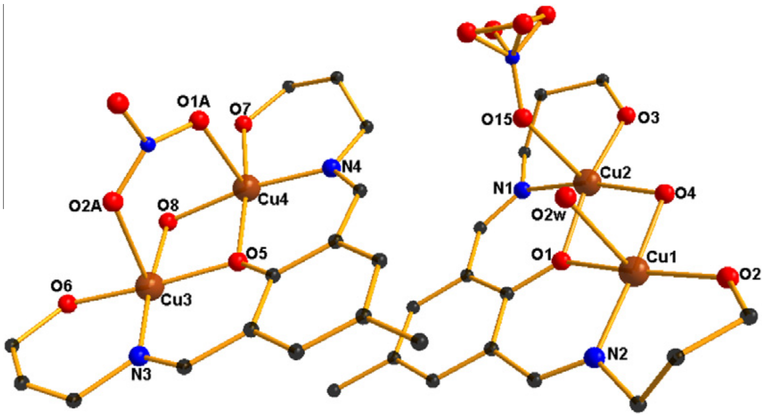


Fig. 1. Molecular structure of **1**·$2H_2O$ with atom-numbering scheme. H atoms are omitted for clarity. Color code: Cu, brown; N, blue; O, red; C, black. (Colour online.)

Table 2
Selected interatomic distances (Å) and angles (°) for complex **1**·$2H_2O$.

Distances			
Cu(1)–N(1)	1.935(7)	Cu(3)–O(5)	1.939(5)
Cu(1)–O(4)	1.945(5)	Cu(3)–O(6)	1.939(5)
Cu(1)–O(2)	1.947(5)	Cu(3)–N(3)	1.941(7)
Cu(1)–O(1)	1.947(5)	Cu(3)–O(8)	1.947(5)
Cu(1)–O(2W)	2.391(6)	Cu(3)–O(2A)	2.400(10)
Cu(1)···Cu(2)	2.9796(14)	Cu(3)–Cu(4)	2.9642(14)
Cu(2)–O(3)	1.929(6)	Cu(4)–N(4)	1.936(7)
Cu(2)–O(1)	1.943(5)	Cu(4)–O(7)	1.959(6)
Cu(2)–N(2)	1.951(6)	Cu(4)–O(8)	1.960(5)
Cu(2)–O(4)	1.954(5)	Cu(4)–O(5)	1.962(5)
Cu(2)–O(15)	2.417(7)	Cu(4)–O(1A)	2.379(8)
Angles			
N(1)–Cu(1)–O(4)	171.7(3)	O(5)–Cu(3)–O(6)	171.2(2)
N(1)–Cu(1)–O(2)	94.9(3)	O(5)-–Cu(3)–N(3)	92.4(3)
O(4)–Cu(1)–O(2)	91.8(2)	O(6)–Cu(3)–N(3)	96.1(3)
N(1)–Cu(1)–O(1)	93.0(2)	O(5)–Cu(3)–O(8)	81.0(2)
O(4)–Cu(1)–O(1)	79.8(2)	O(6)–Cu(3)–O(8)	90.5(2)
O(2)–Cu(1)–O(1)	169.5(3)	N(3)–Cu(3)–O(8)	173.4(3)
N(1)–Cu(1)–O(2W)	91.8(3)	O5–Cu3–O2A	82.7(4)
O(4)–Cu(1)–O(2W)	92.2(2)	O(6)–Cu(3)–O(2A)	100.0(4)
O(2)–Cu(1)–O(2W)	98.3(3)	N(3)–Cu(3)–O(2A)	88.0(4)
O(1)–Cu(1)–O(2W)	88.5(2)	O8–Cu3–O2A	90.3(3)
N(1)–Cu(1)–Cu(2)	132.86(19)	O(5)–Cu(3)–Cu(4)	40.83(16)
O(4)–Cu(1)–Cu(2)	40.28(14)	O(6)–Cu(3)–Cu(4)	131.08(17)
O(2)–Cu(1)–Cu(2)	132.08(18)	N(3)–Cu(3)–Cu(4).	132.6(2)
O(1)–Cu(1)–Cu(2)	39.94(15)	O(8)–Cu(3)–Cu(4)	40.81(15)
O(2W)–Cu(1)–Cu(2)	86.13(16)	O2A–Cu3–Cu4	79.9(3)
O(3)–Cu(2)–O(1)	169.8(3)	N(4)–Cu(4)–O(7)	94.9(3)
O(3)–Cu(2)–N(2)	94.3(3)	N(4)–Cu(4)–O(8)	170.6(3)
O(1)–Cu(2)–N(2)	92.6(2)	O(7)–Cu(4)–O(8)	92.2(2)
O(3)–Cu(2)–O(4)	92.2(2)	N(4)–Cu(4)–O(5)	92.9(3)
O(1)–Cu(2)–O(4)	79.7(2)	O(7)–Cu(4)–O(5)	172.2(2)
N(2)–Cu(2)–O(4)	167.6(3)	O(8)–Cu(4)–O(5)	80.1(2)
O(3)–Cu(2)–O(15)	97.4(3)	N(4)–Cu(4)–O(1A)	90.2(3)
O(1)–Cu(2)–O(15)	89.6(2)	O(7)–Cu(4)–O(1A)	93.3(3)
N(2)–Cu(2)–O(15)	94.3(3)	O(8)–Cu(4)–O(1A)	95.5(3)
O(4)–Cu(2)–O(15)	95.3(2)	O(5)–Cu(4)–O(1A)	86.3(3)
O(3)–Cu(2)–Cu(1)	132.22(18)	N(4)–Cu(4)–Cu(3)	133.1(2)
O(1)–Cu(2)–Cu(1)	40.06(14)	O(7)–Cu(4)–Cu(3)	131.98(18)
N(2)–Cu(2)–Cu(1)	132.6(2)	O(8)–Cu(4)–Cu(3)	40.49(16)
O(4)–Cu(2)–Cu(1)	40.07(15)	O(5)–Cu(4)–Cu(3)	40.26(16)
O(15)–Cu(2)–Cu(1)	88.91(17)	O(1A)–Cu(4)–Cu(3)	85.8(2)

two types of Cu···Cu distances of 3.029 and 3.175 Å, which are significantly longer than other dimers (*av.* 2.645 Å) (Fig. S6) [43]. The NO_4 coordination sphere around each Cu(II), consisting of two O atoms from the bridging phenylacetato groups, one phenoxido O and imine N atoms from the H_2bpmp^- ligand, and one central O^{2-} anion, adopts distorted *square-pyramid* geometry due to the Jahn–Teller effect expected for $3d^9$ copper(II) ion (Fig. S7).

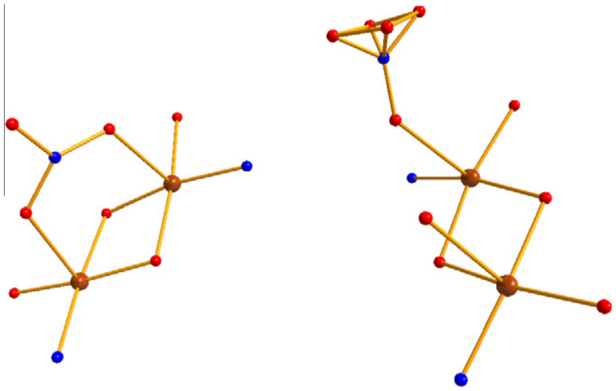


Fig. 2. Atom connectivity within the two Cu_2 fragments showing the *apical–apical* bridging from the NO_3^- group in one unit.

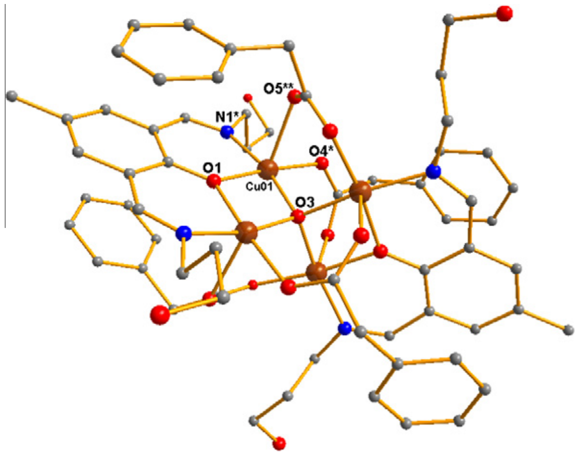


Fig. 3. Molecular structure of **2** with atom-numbering scheme. H atoms are omitted for clarity. Color code: Cu, brown; N, blue; O, red; C, grow: (*=−y, x, −z; **=−y, x, −z). (Colour online.)

The *apical* Cu–O_{pa} (pa = phenylacetate) distance at 2.31 Å is longer that the *basal* distance of 1.95 Å, and all four coordinate uniformly *via apical–basal* sequence (Figs. 3 and S8). The latter is longer than the Cu-(μ_4-O) distance (1.91 Å) but close to the Cu–O_{Ph} (O_{Ph} = ligand phenoxido O) (1.97 Å) length. The *apical–basal* sequence is complementary in nature. (Fig. S9) The Cu–O–C–O/O–C–O–Cu torsion angles (6.89°/40.82°) indicate that the pheny-

Table 3
Selected inter-atomic distances (Å) and angles (°) for complex **2**.

Distances			
Cu(01)–O(3)	1.9149(8)	O(1)**–Cu(01)	1.971(4)
Cu(01)–O(4)	1.957(4)	O(3)–Cu(01)*	1.9149(8)
Cu(01)–N(1)	1.963(6)	O(3)–Cu(01)**	1.9149(8)
Cu(01)–O(1)	1.971(4)	O(3)–Cu(01)***	1.9149(8)
Cu(01)–O(5)***	2.316(4)	O(5)–Cu(01)	2.316(4)
Cu(01)···Cu(01)***	3.0291(15)		
Angles			
O(3)–Cu(01)–O(4)	95.53(14)	N(1)–Cu(01)–O(5)***	88.37(19)
O(3)–Cu(01)–N(1)	167.71(17)	O(1)–Cu(01)–O(5)***	94.05(13)
O(4)–Cu(01)–N(1)	95.0(2)	O(3)–Cu(01)–Cu(01)*	37.73(2)
O(3)–Cu(01)–O(1)	77.52(14)	O(4)–Cu(01)–Cu(01)*	133.24(13)
O(4)–Cu(01)–O(1)	172.95(19)	N(1)–Cu(01)–Cu(01)*	131.55(18)
N(1)–Cu(01)–O(1)	92.1(2)	O(1)–Cu(01)–Cu(01)*	39.80(14)
O(3)–Cu(01)–O(5)***	98.78(12)	O(5)***–Cu(01)–Cu(01)*	98.30(11)
O(4)–Cu(01)–O(5)***	85.80(18)		

* =(−x, −y, z).
** =(−y, x, −z).
*** =(y, −x, −z).

lacetato groups bridge in a *syn–syn* arrangement in *out-of-plane* mode. The coordination geometry about the metal ions is very close to a *square pyramid* (Addison parameter τ is 0.087) [42]. The four phenylacetato bridges connect the Cu(II) ions along the four edges of the $[Cu_4O]$ tetrahedron while the ligand PhO^- groups bridge along the other two edges (Figs. 3 and S9). The *basal–apical* and *apical–basal* binding combination for four carboxylate groups is responsible for the formation of an interdimer cavity between $[Cu_2(\mu\text{-}H_2bpmp)]^{3+}$ halves which nicely traps the O^{2-} ion formed from the condensation of two HO^- bridges in **1**. The *basal–basal* phenoxido O bridge squeeze the Cu–(μ_4–O)–Cu to 104.5° (*av*) than the other angles at 112° (*av*). The crystal packing along the *c*-axis showed regular placement of the tetra-nuclear units () and phenyl rings of the bridging phenylacetate groups remain quite far to show any kind of π–π interactions (Figs. S10 and S11 in supporting information).

3.3. FT-IR Spectroscopy

The $\bar{\nu}_{C=N}$ stretching frequencies are observed at 1604–1637 cm^{-1} for **1**·3H_2O, **2** and the transformed **2** from **1**·3H_2O. For **2**, the $\bar{\nu}_{as(COO)}$ and $\bar{\nu}_{s(COO)}$ stretching vibrations are detected at 1578 and 1384 cm^{-1}, respectively. The difference, $\Delta\bar{\nu}$ = 194 cm^{-1}, is in accord with the presence of $\mu_{1,3}$-bridging carboxylates. For non-bridging carboxylato coordination, this $\Delta\bar{\nu}$ separation is usually larger (*ca.* 350 cm^{-1}) [44]. For **2,** the band at 632 is assigned for $\bar{\nu}_{Cu-O}$ vibration of $[Cu_4O]$ core [24,45,46]. In **1**, the broad band near 3401 cm^{-1} is observed for $\bar{\nu}_{OH}$ stretching mode [47]. The stretching frequencies at 1383 and 826 cm^{-1} are observed for $\bar{\nu}_{sym(N-O)}$ and $\bar{\nu}_{as(N-O)}$ modes [48]. The conversion of **1**·2H_2O to **2** in solution has been well monitored using FT-IR spectroscopy (Fig. S2).

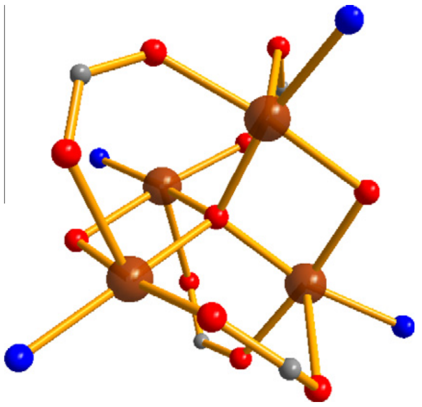


Fig. 4. Partial molecular structure of **2** highlighting the polynuclear assembly around the oxido core.

3.4. Electronic UV–Vis spectra

The ligand field spectra of the complexes show broad absorption bands (λ), with maxima at 677 nm (ε = 535 L mol^{-1} cm^{-1}) and 637 nm (ε = 387 L mol^{-1} cm^{-1}) for **1**·3H_2O and **2**, respectively. The intense absorptions below 400 nm at 258 nm (ε = 12432 L mol^{-1} cm^{-1}) and 259 nm (ε = 65101 L mol^{-1} cm^{-1}) are dominated by metal–ligand charge transfer transitions for **1**·3H_2O and **2**, respectively. Spectra of these complexes also show shoulders at 373 nm (ε = 2446 L mol^{-1} cm^{-1}) and 368 nm (ε = 1545 L mol^{-1} cm^{-1}) respectively, due to weak $HO^- \rightarrow Cu^{II}$ and $PhO^- \rightarrow Cu^{II}$ ligand-to-metal charge transfer (LMCT) transitions [49] (Fig. S12).

4. Concluding remarks

The coordination chemistry of the H_2bpmp^- ligand to Cu(II) ions has been examined in this work which establishes crucial role of the phenylacetate co-ligands for the clean and straightforward transformation of two unit-cell packed hydroxido-bridged Cu_2 complexes into a μ_4-oxido-bridged Cu_4 cluster. The nature of the water derived bridging co-ligands (HO^- or O^{2-}) seems to dictate the final structure of the complexes. The dinucleating ligand H_2-bpmp$^-$ bearing alcoholic pendant arms facilitates the binding of two Cu(II) ions by phenoxido and hydroxido bridges and left behind *apical* sites open per metal ion for binding of phenylacetate co-ligands, which displace the coordinated water and nitrate ligands, to facilitates the collapse of two Cu(OH)Cu units into $Cu_2(O)Cu_2$ core**.**

Acknowledgements

AKG is thankful to the Council of Scientific and Industrial Research, New Delhi for the financial support. The authors also thank to DST, New Delhi, for providing the Single Crystal X-ray Diffractometer facility to the Department of Chemistry, IIT Kharagpur under its FIST program.

Appendix A. Supplementary data

CCDC 868328 and 868327 contain the supplementary crystallographic data for **1**·2H_2O and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.08.064.

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