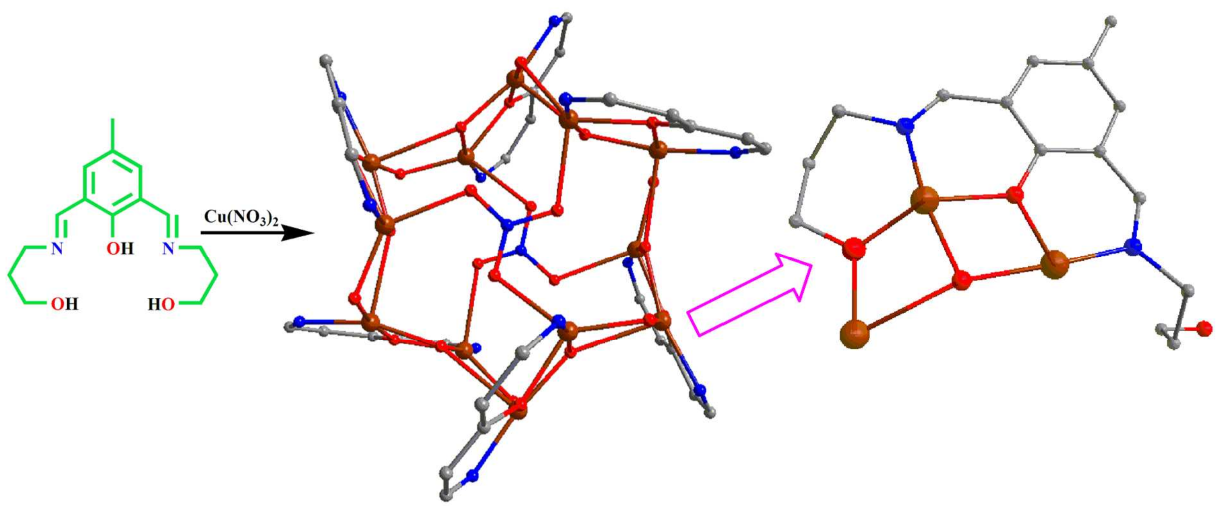
Graphical Abstract

A Dodecanuclear Copper(II) Cage Self-Assembled from Six Dicopper Building Units

Aloke Kumar Ghosh,[a] Moumita Pait,[a] Rodolphe Clérac,[b,c] Corine Mathonière,[d,e] Valerio Bertolasi,[f] Antonio Bauzá,[g] Antonio Frontera,[g] Kausikisankar Pramanik,[h] and Debashis Ray[*,a]

Sandwich capping of two $\{Cu_3(\mu_3\text{-}NO_3)\}^{5-}$ triangles over a hydroxido $\{Cu_6\}$ hexagon, cross-wise supported by six face capping forms of H_3bpmp^{2-}, resulted in a novel copper(II) cage $\{Cu_6(\mu_3\text{-}OH)_3(\mu_3\text{-}Hbpmp)_3(\mu_3\text{-}NO_3)\}_2(NO_3)_2(OH)_2\cdot 2H_2O\cdot 2MeOH$ $\{H_3bpmp$ = 2,6-bis-[(3-hydroxy-propylimino)-methyl]-4-methyl-phenol$\}$ bearing twelve Cu metal ions in a flattened cuboctahedral topology.



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Abstract

Reaction of the dinucleating phenol-based ligand,H_3bpmp (2,6-bis-[(3-hydroxy-propylimino)-methyl]-4-methyl-phenol), with Cu^{2+} ions in presence of a hybrid base (NEt_3 and NaN_3), necessary for the *in-situ* generation of required numbers of hydroxido ions, results in the formation of a novel NO_3^- capped and HO^- supported $\{Cu_{12}\}$ coordination complex $\{Cu_6(\mu_3\text{-OH})_3(\mu_3\text{-Hbpmp})_3(\mu_3\text{-NO}_3)\}_2(NO_3)_2(OH)_2\cdot 2H_2O\cdot 2MeOH$ (**1**). When the components are combined in right proportions (metal:ligand:NEt_3:NaN_3 = 2:1:3:2) in MeOH, twelve Cu^{2+} ions assemble in a cuboctahedral geometry, containing six square and eight triangular faces around a considerable void space. Six of the eight $[Cu_3]$ triangular faces are bound by the six $Hbpmp^{2-}$ ligands with six free pendant propanol arms around the central hexagonal plane. X-ray structure determination indicates new geometrical features for the core formation and reveals the face-capping potential of H_3bpmp ligand for the growth of a cuboctahedral coordination cage with the support of anions like HO^- and NO_3^-. The experimentally observed (J/k_B= –173 K)

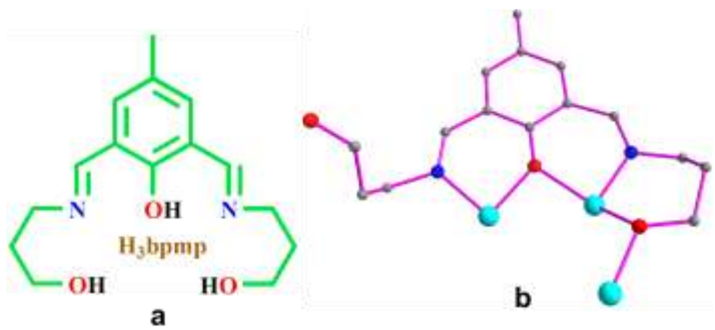
strong antiferromagnetic coupling within the Cu_{12} complex have been justified by the DFT calculations.

Introduction

Paramagnetic polyhedral coordination cages of 3d metal ions are an attractive goal in the areas of coordination induced metal-ligand aggregates,[1] hydroxido and oxido bridged multicomponent assembly,[2]and molecular magnetism.[3] These cages can be formed from self-assembly of appropriate combination of metal ions with coordinating ligands and small bridging groups.[4]Although many of these structures are obtained from serendipity, new examples can only provide the rules to control the self-aggregation processes for cage like structures from simple and known coordinating multidentate ligand system. In the recent decades, the role of non-coordinating or weakly-coordinating anions in self-assembly processes has been the topic of active research for cage-like structures and supramolecular coordination complexes.[5,6] The multi-component assembly of paramagnetic metal ions, ligands and anions by coordination bonds have been used for many metal-based cage structures.[6] To achieve the controlled synthesis of a single cage-like structure in high yield, their self-assembly can be promoted by the use of preformed dinuclear complexes with available donor or acceptor coordination sites on the ligands or on the metal ions (for example by replacing small ancillary groups). Such reactions are strongly dependent on a large range of experimental parameters, such as the stoichiometry of the reactants, the nature of the solvents, their polarity, the presence of basic or acidic medium and temperature. In many instances such reactions of preformed simple metal ligand systems are often interact with the small inorganic ions from the metal salt. Their key role is obvious in the complex formation but it is still a challenge to exploit their nucleating/bridging properties in a chosen direction.[7] In the field of molecule-based magnetism, the design and construction of high-nuclearity coordination complexes of first row magnetic transition metals has been the subject of intense work. In particular, cage-like structures with tunable magnetic properties are of importance in the development of new magnetic material with potential application.[8] In the past few years, a considerable interest has been concentrated on high-nuclearity complexes like planar polygons,[9] metallacrowns,[10] helicates,[11] catenanes,[12] rotaxanes,[13] and metallo-macrocycles.[14] Up till now, only a few copper coordination cages based on phenol-based dinucleating ligand[15] system are known, even if some dinuclear,[16] tetranuclear,[17] pentanuclear, hexanuclear,[18] and cuboctahedral[19] complexes has been reported.

In this perspective, the reactivity of H_3bpmp[20] ligand {2,6-bis-[(3-hydroxy-propylimino)-methyl]-4-methylphenol}(Chart 1a)with copper(II) nitrate in the presence triethylamine and sodium azide, as a combined base, have been explored which revealed an unprecedented binding mode (Chart 1b) of three metal ions by a doubly deprotonated ligand. The use of this H_3bpmp ligand in transition-metal chemistry is relatively new, the only compound known is a hydroxido-bridged dinuclear copper(II) complex.[21,22]

Chart 1



In this paper, we report the synthesis, X-ray characterization and magnetic properties of a unique high-symmetry dodecanuclear copper(II) coordination cage which combine face-capping hexadentate ligand components, united with six-coordinate metal-ions in an unusual 12-nuclear cubooctahedral array. This Cu_{12}aggregate is assembled from Hbpmp^{2-} ligands assisted by *in-situ* generated hydroxido ions and templating NO_3^- anions of the precursor metal ion salt. The long imine-propanol arms of the potentially binucleating ligands are responsible for their face-capping trinucleating binding mode which has not been observed earlier.

Experimental Section

Materials and Physical methods

The reagents used for the syntheses were purchased commercially from the following sources: copper nitrate and sodium azide from S.D. Fine Chem (India), triethylamine from Merck (India), 3-amino-1-propanol from Aldrich Chemical Co. Inc. 2,6-Diformyl-4-methylphenol (2-hydroxy-5-methyl-benzene-1,3-dicarbaldehyde) was prepared following a literature procedure.[23] All other chemicals and solvents were reagent grade materials and were used as received without further purification.

The microanalytical data were obtained with a Perkin-Elmer model 240 C elemental analyzer. FTIR spectra were recorded on a Perkin-Elmer RX1 spectrometer. Solution electrical conductivity values and electronic spectra were obtained using a Unitech type U131C digital conductivity meter and a Shimadzu UV 3100 UV-vis-NIR spectrophotometer, respectively.

Magnetic susceptibility measurements were obtained using a Quantum Design SQUID (superconducting quantum interference device) MPMS-XL susceptometer. This magnetometer works between 1.8 and 300 K for direct current (dc) applied fields ranging from -7 to 7 T. Measurements were performed on polycrystalline sample of **1** (27.53 mg). The magnetic data were corrected for the sample holder and the diamagnetic contributions.

For DFT-based wave functions, a reasonable estimate of the exchange coupling constants can be obtained from the energy difference between the state with highest spin, E_{HS} and the low spin wave function, E_{BS} (namely broken-symmetry solution) obtained by just flipping one of the spins, as described in the literature[24]. The hybrid M06-2X functional has been used in all calculations as implemented in Gaussian-09[25], using the 6-31+G* basis set for all atoms. For the dinuclear model of complex **1**, we have used a methanol molecule to occupy the coordination position that is available in fragment B (see Figure 2a and 2b)

Synthesis

H_3bpmp Ligands. 3-Amino-1-propanol (0.91 g, 12.2 mmol) was added to a MeOH solution (20 mL) of 2,6-diformyl-4-methylphenol (1.0 g, 6.1 mmol) in air atmosphere 28 °C and stirred for 2 h to give an orange solution which on evaporation of solvent in air for 12 h yielded orange solid. The product was thoroughly washed with water and used directly without further purification. Yield: 1.32 g (78%).

$\{Cu_6(\mu_3\text{-}OH)_3(\mu_3\text{-}Hbpmp)_3(\mu_3\text{-}NO_3)\}_2(NO_3)_2(OH)_2\cdot 2H_2O\cdot 2MeOH$(1).$Cu(NO_3)_2\cdot 3H_2O$ (0.482 g, 2.0 mmol) in a MeOH solution (10 mL) was added drop wise to another MeOH solution (20 mL) of H_3bpmp (0.278 g, 1.00 mmol) followed by a MeOH solution (10 mL) of NEt_3 (417 mL, 0.303 g, 3.00 mmol) and NaN_3 (0.130 g, 2.00 mmol). The mixture was stirred for 2 h at ambient temperature and solvent was evaporated in air for 6 h to get a green solid. This was isolated, washed with cold MeOH and dried under vacuum over P_4O_{10}. About 50 mg solid was dissolved in 15mL MeOH and green needle like crystals suitable for X-ray structure analysis were obtained after slow evaporation of the solution at room temperature after 15 d. Yield: 1.031 g, 71%. Anal. calcd. for $C_{92}H_{140}Cu_{12}N_{16}O_{42}$ (2904.6g mol^{-1}): C, 38.04; H, 4.85; N, 7.71. Found: C, 37.92; H, 4.73; N, 7.62. Selected FTIR bands: (KBr, cm^{-1}; s = strong, vs = very strong, m = medium, br = broad) 3410(br), 1637(s), 1559(s), 1384(vs), 1328(s), 1239(s), 1058(vs), 826(s), 762(m), 507(m). Molar conductance, Λ_M: (MeOH solution) 6.0Ω^{-1}cm^{2}mol^{-1}. UV-vis spectra [λ_{max}, nm (ε, M^{-1} cm^{-1})]: (MeOH solution) 676 (369), 375 (1441), 260 (75914).

Results and Discussion

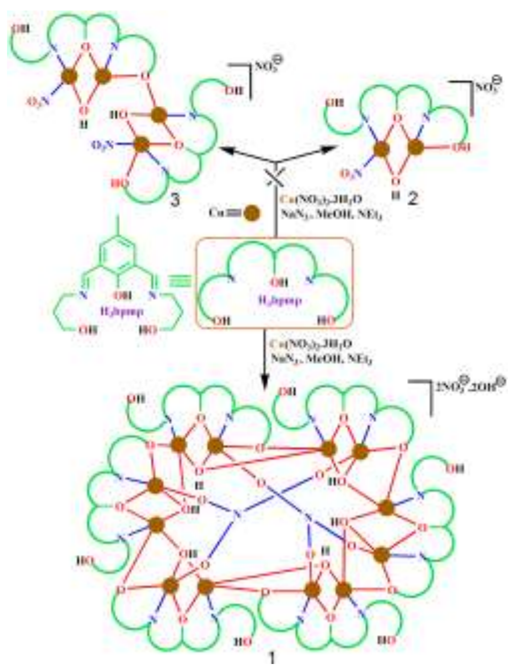
Synthesis and Characterization. The Schiff base ligand used in this work was prepared as reported earlier (Scheme S1 in the Supporting Information).[20] H_3bpmp is a *bis*-tridentate ligand with two bidentate imine-phenol arms elaborated on either side of a 4-methyl phenol spacer. The flexibility of the ligand system and the known reaction with metal salts precludes any attempts to foresee the three dimensional structure of the resultant complexes in the present reaction protocol. Combination of copper(II) nitrate with H_3bpmp in MeOH in presence of a blend of triethylamine and sodium azide (3:2) (Scheme 1)afforded a green clear solution from which green prismatic crystals of **1**grew after slow evaporation of the solution for two weeks at room-temperature. Initially, other stoichiometric ratios of the precursors were tried but only the reported ratio is leading to the isolation of pure crystalline samples of **1** in high yield in MeOH medium as summarized in eq 1. The presence of NaN_3 is crucial as in its absence, only dinuclear

$$6H_3\text{bpmp} + 12Cu(NO_3)_2\cdot 3H_2O + 20NEt_3 + 2MeOH \xrightarrow{NaN_3}$$
$$\{Cu_6(\mu_3\text{-}OH)_3(\mu_3\text{-}Hbpmp)_3(\mu_3\text{-}NO_3)\}_2(NO_3)_2(OH)_2\cdot 2H_2O\cdot 2MeOH$$

$$+ 26H_2O + 20(HNEt_3)NO_3 \qquad \ldots (1)$$

nitrato bound and bridged copper complex is obtained.[26] The dodecanuclear coordination cage**1** contains six doubly deprotonated $Hbpmp^{2-}$ ligands (Chart 1) and six hydroxido anions along with two NO_3^- anions. The generation of six hydroxido bridges during the formation of **1** clearly originates from water molecules present in the organic solvents used in the synthesis. The elemental analysis, molar conductivity and single-crystal X-ray diffraction (*vide infra*) data confirm the molecular formula for **1**.

Scheme 1. Schematic representation of the formation of**1**from a sub-component-assembly and the non-formation of the Cu_2 (**2**) and Cu_4 (**3**) species.



Single crystal X-ray diffraction study revealed the formation of nitrato capped and hydroxido bridged dodecanuclear cage $\{Cu_6(\mu_3\text{-}OH)_3(\mu_3\text{-}Hbpmp)_3(\mu_3\text{-}NO_3)\}_2(NO_3)_2(OH)_2\cdot 2H_2O\cdot 2MeOH$(**1**) supported by six ligands. However no sign of formation of phenoxido-bridged Cu(II) dinuclear complex **2** or tetranuclear species **3** (Scheme 1) were observed, possibly because of the better stability, low solubility and crystallinity of **1**, compared to **2** and **3**. The complex cage (Figure 2b) has an approximately cuboctahedral framework of 12 copper(II) ions, containing six square and eight triangular faces to assemble. The eight corners of a regular cube have been truncated to generate eight triangular faces and four ligands alternately bind these triangular faces. From eq 1 we can rationalize the stoichiometry of the complex where six deprotonated ligands $Hbpmp^{2-}$ provide twelve nitrogen and twelve oxygen donor atoms; nitrogen atoms bind in monodentate fashion and oxygen donors coordinate in bridging mode providing 36 binding sites. Two nitrate groups provide six more and six hydroxido groups in $\mu_3$mode give another 18 binding atoms. Thus altogether 60 donor groups are obtained which are exactly required for 12 five-coordinate copper(II) ions.

Description of the Crystal Structure

Single crystals suitable for X-ray structure determination were obtained by slow evaporation of a saturated MeOH solution of **1**after two weeks. A perspective view of **1** with the atom-numbering scheme is shown in Figure 1 and important bond lengths and angles are given in Table 1.The crystallographic data are summarized in Table 2.The single crystal X-ray diffraction study of green crystals of **1** revealed the formation of a unique dodecanuclear cage, which crystallizes in trigonal crystal system and P-3 space group. The asymmetric unit contains one tetranuclear A^{2+} cation (containing Cu1, Cu2, Cu3 and Cu4 sites) (Figure 2a), one dinuclear B^{+} cation (containing Cu5 and Cu6 sites),(Figure 2b), a NO_3^- anion, two OH^- groups, and a neutral solvent molecule of MeOH. Overall the crystal structure symmetries generate two structurally different, but very similar, dodecanuclear cages shown in shown in Figures 3a and 3b. In both aggregates, twelve Cu(II) ions form the twelve vertices of a cuboctahedron making eight triangular and six square faces.

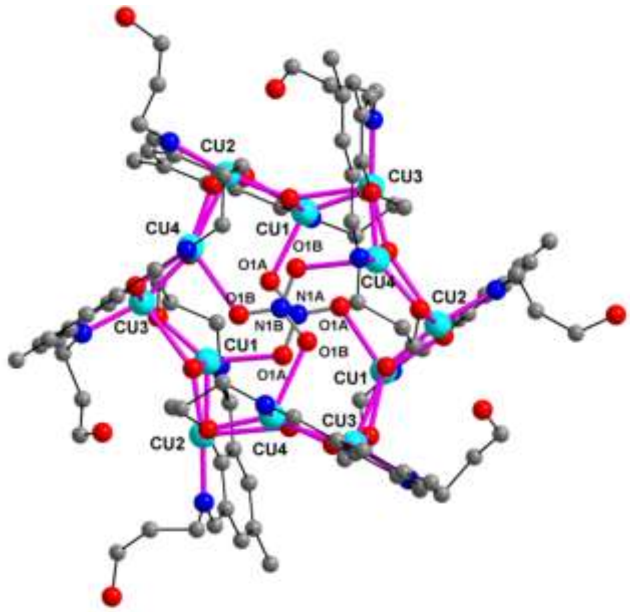


Figure 1. Molecular view the dodecanuclear cage in **1**.

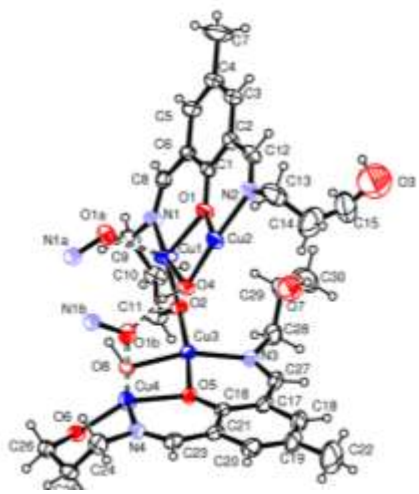


Figure 2a. ORTEP[1] view of A: the independent tetranuclear cation $[Cu_4(\mu\text{-}OH)_2(\mu\text{-}Hbpmp)_2]^{2+}$ (Cu1 to Cu4) of the asymmetric unit $\{[Cu_4(\mu\text{-}OH)_2(\mu\text{-}Hbpmp)_2]^{2+}\cdot[Cu_2(\mu\text{-}OH)(\mu\text{-}Hbpmp)]^{+}\}\cdot NO_3^{-}\cdot 2OH^{-}\cdot CH_3OH$ in **1**; The Figure includes also the fragment N1a-O1a and N1b-O1b belonging to two nitrate anions, both in special positions (1/3, 2/3, z), on a threefold axis. Blue, light blue, red and black ellipsoids (shown at 30% probability) represent the Cu, N, O and C atoms respectively.

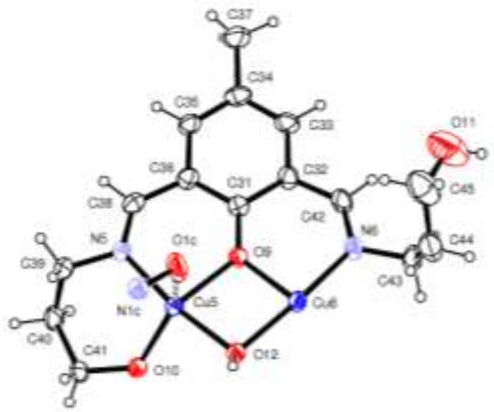


Figure 2b. ORTEP[1] view of B: the independent dinuclear cation $[Cu_2(\mu\text{-}OH)(\mu\text{-}Hbpmp)]^+$ (Cu5 and Cu6) of the asymmetric unit. The Figure includes also the fragment N1c-O1c belonging to a nitrate anion in special position (0,0,z) on a threefold axis. Blue, light blue, red and black ellipsoids (shown at 30% probability) represent the Cu, N, O and C atoms respectively.

Two of these eight triangular faces localized at extreme opposite faces are assembled around nitrate anions, which seem to help the cage formation during the conventional solvent-based room temperature synthesis. This unique cage structure suggests that the formation of **1** is controlled by a two nitrate and six hydroxido anions as 'structure controlling' groups, in which the latter ions were generated *in-situ* in required proportion in a composite (NEt_3 plus NaN_3) basic condition from water molecules.

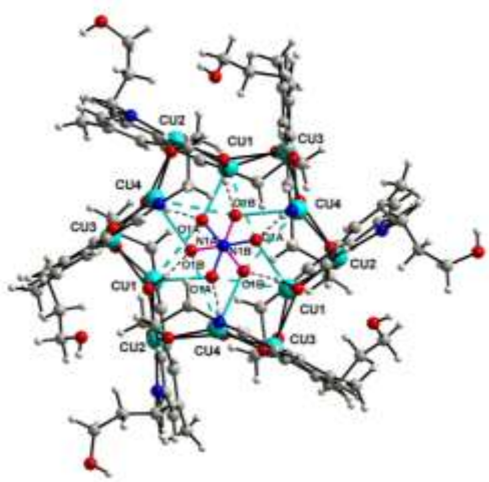


Figure 3a. The dodecanuclear independent Cu(II) complex $[Cu_{12}(\mu\text{-}OH)_6(\mu\text{-}Hbpmp)_6](NO_3)_2$ built up around a three-fold axis by means of three tetranuclear cations A and two NO_3^- anions, projected along the c axis

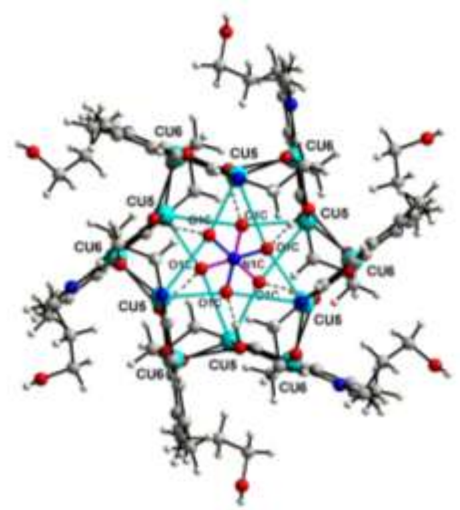
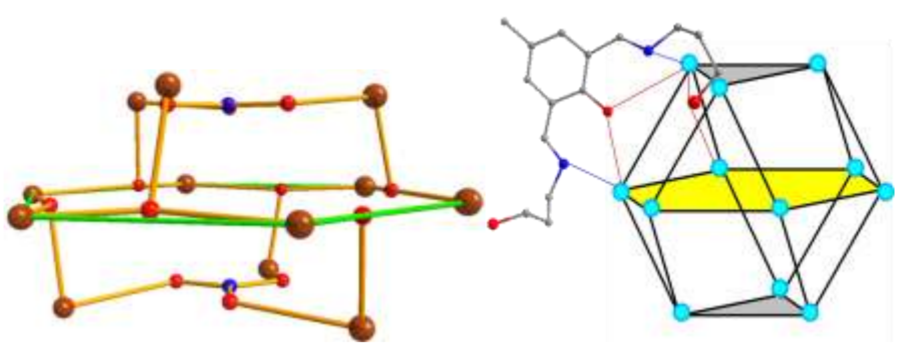


Figure 3b. The dodecanuclear independent Cu(II) complex $[Cu_{12}(\mu\text{-}OH)_6(\mu\text{-}Hbpmp)_6](NO_3)_2$ built up around a $\bar{3}$ axis by means of six binuclear cations B and two NO_3^- anions, , projected along the c axis

The Cu_{12} cage can also be described as a sandwich-like structure with a Cu_6 hexagon ring sandwiched between two capping $[Cu_3(\mu_3\text{-}NO_3)]^-$triangles as shown in Figure 4. The *in-situ* generated six hydroxido groups in μ_3 mode (Figure 4a) are coplanar with the sandwiched hexacopper ring with links to top and bottom $[Cu_3(\mu_3\text{-}NO_3)]^-$ triangles. The six bridging $Hbpmp^{2-}$ ligands are organized around this sandwiched structure in a propeller-like arrangement, each binding two Cu(II) metal ions from the hexagon ring and alternatively one of the two neighboring $[Cu_3(\mu_3\text{-}NO_3)]^{5-}$ triangles. The cuboctahedral structure has six oblique triangular faces capped by six functionally hexadentate $Hbpmp^{2-}$ ligands. The remaining top and bottom triangular faces are capped by nitrato anions. In order to comply with the hexagonal topology, the $Hbpmp^{2-}$ ligands are bent, stacked on top of each other, and mutually shifted by angles of about 118.6º, forming the six blades of this propeller-like structure. The A^{2+} fragment is centered on a 3-fold axis forming the twelve membered metallacrown C (Figure 3a) that includes two

NO_3^- anions also positioned on a three-fold axis (it is worth noting that disordered ethyl hydroxy OH groups of A^{2+} were refined over two positions). On the other hand, the B^+ fragment occupies a $\overline{3}$ symmetry site (a three-fold axis + an inversion centre) and accordingly forms a similar twelve-membered metallacrown ring D (Figure 3b) with two equivalent NO_3^- anions. The point symmetry of the Cu_{12} A cage is *C3*, approximately *C3i*, while the point symmetry of the Cu_{12} B cage is perfectly *C3i*. If the molecular structure of **1** is viewed as a wheel (Figure S1), the nitrogen atoms of nitrate group visualize the wheel's axis (with a N···N distance of 3.545 Å), the Cu–N bonds (*av*. 2.355 Å) materialize the Cu_{12} wheel spokes (Figure S2). The two central NO_3^-anions are roughly in a *gauche* conformation (Figure S3). The crystal packing projected down along the *c* axis reveal the side-by-side placement of the hexagonal faces of the Cu_{12} cage (Figure S4).

The NO_3^- anions bind the Cu(II) ions in $\mu_{1,2,3}$ coordination mode with the Cu–O bond distances range from 2.26 to 2.41 Å (Table 1). The coordination geometries of four unique copper(II) sites are in distorted geometries (τ = 0.639, Cu1; 0.006, Cu2; 0.180, Cu3 and 0.444, Cu4)[27] with NO_4 coordination spheres having *apical* O-atoms (Figure S5). These parameters range from a typical square pyramidal (0.006) to intermediate between square pyramidal and trigonal bipyramidal (0.639) geometries and point toward the role of coordination plasticity of these metal ions centers for the 12-metal cage formation. Within the sandwiched Cu_6 hexagon by two Cu_3 triangles in cuboctahedron cage structure the Cu1 and Cu4 atoms exclusively for the two triangles and the hexagon is made from Cu2 and Cu3(Figure S6).



a b

Figure 4.(a) Polyhedral view of the core of complex **1** with a [Cu_6] ring sandwiched by two [$Cu_3(\mu_3\text{-}NO_3)$] triangles. Color code: Cu, brown; O, red; N, blue. (b) The cuboctahedral Cu_{12} core, with one face-capping ligand ($Hbpmp^{2-}$) on one of the oblique triangular faces.

The Cu-N bond distances are in the range of1.94-1.98Å and Cu-O (four types) in the range of 1.92-2.57Å.The $Hbpmp^{2-}$ ligands provide an N_2O_2 set of donor atoms connecting pair wise the Cu(II) sites by the phenoxido, one of the alkoxido and the two imino donor atoms to provide $[Cu_2(Hbpmp)]^{3+}$ as building units. The Cu–O distances to the phenoxido or alkoxido oxygen atoms of the $Hbpmp^{2-}$ ligands range from 1.934 to 2.043 Å. Interestingly, the Cu–O–Cu angles span in a range 8.53º wide (151.34 - 159.87º) whereas the O–Cu–O angles are much more regular between 94.4 and 97.6º. Six μ_3-OH bridges are also stabilizing the dodecanuclear complex by connecting two Cu(II) centers from the central hexagonal wheel with alternatively one Cu(II) ions of the $[Cu_3(\mu_3\text{-}NO_3)]^{5-}$ moieties (Figure S1). Six facially capping ligands are responsible for the basic support of the three-layer cage where the Cu^{II} bearing hexagonal ring is sandwiched by two other Cu^{II} containing triangular units (Figure 5).Within the central Cu(II) hexagon ring, spanned by hydroxido bridges, the distances between adjacent Cu^{II} ions are between 4.269 to 4.463 Å, while in triangular $[Cu_3(\mu_3\text{-}NO_3)]^{-}$ moieties, they range between 5.197 and 5.484 Å. The inter plane distances between adjacent Cu^{II} ions, one from triangular plane and the other from the hexagonal plane, are between 2.996 to 3.070 Å. Six such inter planar clips originating from the binding of the six ligands are the main supports for the cage formation. The T-shaped unique binding modes of the hydroxido bridges are responsible for keeping the Cu^{II} ions > 4 Å apart. It is worth mentioning that the observed arrangement of a hexagonal ring of 3d metal ions sandwiched by two trinuclear triangular units as observed in complex **1** is unprecedented with the Cu-O-Cu bridging modes seen here. Indeed the Cu_{12}coordination cage, **1**, can also be viewed as a cyclic arrangement of six *fused* dinuclear [Cu_2(Hbpmp)] moieties, which are quite surprisingly not detected, independently of this cage self-assembly (Scheme 1) from other reactions in solution attempted so far.

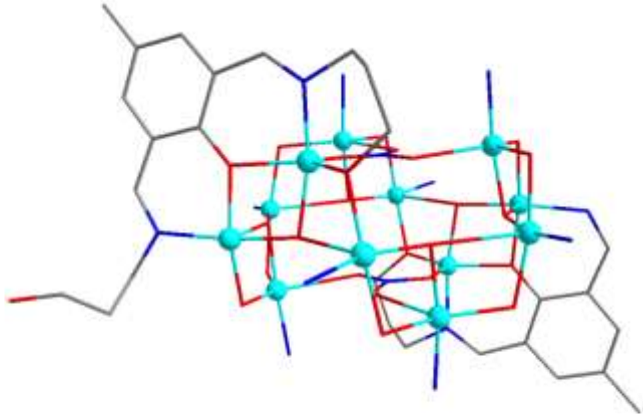


Figure 5. Orientation of two (out of six) facially capping of ligands responsible for the support of the three-layer cage.

Table 1. Selected inter-atomic distances (Å) and angles (º) for complex **1.**

Distances			
Cu(1)-O(4)	1.923(4)	Cu(4)-O(8)	1.934(4)
Cu(1)-O(2)	1.946(4)	Cu(4)-N(4)	1.945(5)
Cu(1)-N(1)	1.947(5)	Cu(4)-O(5)	1.975(4)
Cu(1)-O(1)	2.043(4)	Cu(4)-O(1B)	2.414(6)
Cu(1)-O(1A)	2.260(5)	Cu(5)-O(10)	1.930(4)
Cu(1)···Cu(2)	2.9961(12)	Cu(5)-O(12)	1.935(4)
Cu(1)···Cu(3)	3.0513(11)	Cu(5)-N(5)	1.943(5)
Cu(2)-O(6)*	1.922(4)	Cu(5)-O(9)	2.010(4)
Cu(2)-O(1)	1.934(4)	Cu(5)-O(1C)	2.390(6)
Cu(2)-O(4)	1.959(4)	Cu(5)···Cu(6)	3.0066(11)
Cu(2)-N(2)	1.980(6)	Cu(5)···Cu(6)	3.0297(11)
O(2)-Cu(3)	1.925(4)	Cu(6)-O(10)**	1.935(4)
Cu(3)-O(8)	1.954(4)	Cu(6)-O(9)	1.945(4)
Cu(3)-O(5)	1.958(4)	Cu(6)-O(12)	1.948(4)
Cu(3)-N(3)	1.974(5)	Cu(6)-N(6)	1.977(5)
Cu(3)···Cu(4)	2.9962(11)	Cu(6)···Cu(5)***	3.0297(11)
Cu(4)-O(6)	1.931(4)		
Angles			
O(4)-Cu(1)-O(2)	89.66(17)	O(6)-Cu(4)-O(8)	93.30(17)
O(4)-Cu(1)-N(1)	169.5(2)	O(6)-Cu(4)-N(4)	96.3(2)
O(2)-Cu(1)-N(1)	95.8(2)	O(8)-Cu(4)-N(4)	170.2(2)
O(4)-Cu(1)-O(1)	78.85(17)	O(6)-Cu(4)-O(5)	143.56(19)
O(2)-Cu(1)-O(1)	131.14(19)	O(8)-Cu(4)-O(5)	79.11(17)
N(1)-Cu(1)-O(1)	90.9(2)	N(4)-Cu(4)-O(5)	92.0(2)
O(4)-Cu(1)-O(1A)	90.76(18)	O(6)-Cu(4)-(O1B)	125.26(17)
O92)-Cu(1)-O(1A)	133.75(18)	O(8)-Cu(4)-O(1B)	87.72(18)
N(1)-Cu(1)-O(1A)	91.9(2)	N(4)-Cu(4)-O(1B)	88.2(2)
O(1)-Cu(1)-O(1A)	94.11(18)	O(5)-Cu(4)-O(1B)	90.31(17)
O(4)-Cu(1)-Cu(2)	39.91(12)	O(6)-Cu(4)-Cu(3)	128.28(13)
O(2)-Cu(1)-Cu(2)	120.03(13)	O(8)-Cu(4)-Cu(3)	39.83(12)
N(1)-Cu(1)-Cu(2)	130.18(16)	N(4)-Cu(4)-Cu(3)	130.68(17)
O(1)-Cu(1)-Cu(2)	39.76(12)	O(5)-Cu(4)-Cu(3)	40.16(12)
O(1A)-Cu(1)-Cu(2)	86.94(12)	O(1B)-Cu(4)-Cu(3)	82.27(12)
O(4)-Cu(1)-Cu(3)	53.22(12)	O(10)-Cu(5)-O(12)	91.32(17)

O(2)-Cu(1)-Cu(3)	37.73(12)	O(10)-Cu(5)-N(5)	94.74(19)
N(1)-Cu(1)-Cu(3)	133.31(17)	O(12)-Cu(5)-N(5)	170.2(2)
O(1)-Cu(1)-Cu(3)	120.67(13)	O(10)-Cu(5)-O(9)	135.29(19)
O(1A)-Cu(1)-Cu(3)	116.49(13)	O(12)-Cu(5)-O(9)	78.50(17)
Cu(2)-Cu(1)-Cu(3)	89.80(3)	N(5)-Cu(5)-O(9)	91.8(2)
O(6)-Cu(2)-O(1)	169.04(18)	O(10)-Cu(5)-O(1C)	135.75(18)
O(6)-Cu(2)-O(4)	92.94(18)	O(12)-Cu(5)-O(1C)	88.84(18)
O(1)-Cu(2)-O(4)	80.71(18)	N(5)-Cu(5)-O(1C)	92.2(2)
O(6)-Cu(2)-N(2)	96.3(2)	O(9)-Cu(5)-O(1C)	87.96(18)
O(1)-Cu(2)-N(2)	91.1(2)	O(10)-Cu(5)-Cu(6)	122.44(13)
O(4)-Cu(2)-N(2)	168.7(2)	O(12)-Cu(5)-Cu(6)	39.41(12)
O(6)-Cu(2)-Cu(1)	129.33(13)	N(5)-Cu(5)-Cu(6)	131.11(16)
O(1)-Cu(2)-Cu(1)	42.52(12)	O(9)-Cu(5)-Cu(6)	39.73(12)
O(4)-Cu(2)-Cu(1)	39.03(12)	O(1C)-Cu(5)-Cu(6)	82.44(12)
N(2)-Cu(2)-Cu(1)	133.64(19)	O(10)-Cu(5)-Cu(6)	38.44(12)
O(2)-Cu(3)-O(8)	94.74(17)	O(12)-Cu(5)-Cu(6)	54.08(12)
O(2)-Cu(3)-O(5)	171.74(17)	N(5)-Cu(5)-Cu(6)	132.95(16)
O(8)-Cu(3)-O(5)	79.08(17)	O(9)-Cu(5)-Cu(6)	122.92(13)
O(2)-Cu(3)-N(3)	97.1(2)	O(1C)-Cu(5)-Cu(6)	117.30(14)
O(8)-Cu(3)-N(3)	160.9(2)	Cu(6)-Cu(5)-Cu(6)***	90.73(2)
O(5)-Cu(3)-N(3)	90.3(2)	O(10)-Cu(6)-O(9)	171.71(18)
O(2)-Cu(3)-Cu(4)	132.24(13)	O(10)-Cu(6)-O(12)	92.75(17)
O(8)-Cu(3)-Cu(4)	39.35(12)	O(9)-Cu(6)-O(12)	79.80(17)
O(5)-Cu(3)-Cu(4)	40.60(12)	O(10)-Cu(6)-N(6)	96.7(2)
N(3)-Cu(3)-Cu(4)	130.64(17)	O(9)-Cu(6)-N(6)	91.3(2)
O(2)-Cu(3)-Cu(1)	38.21(13)	O(12)-Cu(6)-N(6)	166.4(2)
O(8)-Cu(3)-Cu(1)	90.90(12)	O(10)-Cu(6)-Cu(5)	130.71(13)
O(1)-Cu(6)-Cu(5)	87.97(12)	O(9)-Cu(6)-Cu(5)	41.34(12)
N(6)-Cu(6)-Cu(5)	105.45(17)	O(12)-Cu(6)-Cu(5)	39.11(12)
O(9)-Cu(6)-Cu(5)	136.75(13)	N(6)-Cu(6)-Cu(5)	132.61(17)
O(5)-Cu(3)-Cu(1)	135.56(13)	O(10)-Cu(6)-Cu(5)	38.32(12)
N(3)-Cu(3)-Cu(1)	107.64(17)	Cu(5)-Cu(6)-Cu(5)*****	111.88(4)
Cu(4)-Cu(3)-Cu(1)	112.75(4)		
* = 1-y, 1+x-y, z; ** = -x+y, 1-x, z; *** = y, -x+y, 2-z; ***** = -y, x-y, z;			

FTIR Spectroscopy. The broad and sharp peaks in the FTIR spectrum of **1**at 3410 and 1637 cm^{-1} are due to the stretching modes characteristic of the dangling alcohol O–H arms of the ligand and the bound C=N functionalities of the ligand, respectively. The $\bar{n}$ O-N-O$_{sym}$ and $\bar{n}$O-N-O$_{antisym}$ stretching vibrations for two capping nitrato groups are found at 1384 and 826 cm^{-1}.[28]

Absorption Spectroscopy. In MeOH solution complex **1** shows multiple bands in 900-200 nm wavelength range. The free ligand H$_3$bpmp shows a characteristic absorption band at 430 nm in HEPES buffer.[20a] A broad absorption band with maximum at 676 nm (ε = 369 M^{-1} cm^{-1}), is observed due to the Hbpmp^{2-} bound copper(II) centered d-d transition. A shoulder at 375 nm (ε = 1441 M^{-1} cm^{-1}) is most probably due to the

$HO^{-} \rightarrow Cu^{II}$ and $PhO^{-} \rightarrow Cu^{II}$ ligand-to-metal charge transfer (LMCT) transitions.[29] The intense single absorption at 260 nm (ε = 75914 M^{-1} cm^{-1}) may be associated with a π→π* transition originating mainly in the azomethine chromophore (imine π→π* transition).[16a]

Magnetic Properties

The solid-state magnetic properties of **1** have been investigated by dc susceptibility measurements down to 1.8 K at 0.1 T (Figure 6).At room temperature, the χT product normalized per Cu_{12} cage is around 3 cm^3 K mol^{-1} that is significantly lower in comparison to the theoretical value of 4.5 cm^3 K mol^{-1} expected for twelve isolated paramagnetic Cu^{2+} ions (d^9, S = 1/2 with g = 2 gives a Curie constant of0.375 cm^3 K mol^{-1}). Upon cooling, the χT products continuously decrease to almost vanish to a residual value of 0.08 cm^3 K mol^{-1}. This thermal behavior indicates the presence of dominant and strong antiferromagnetic interactions between the Cu^{2+} magnetic centers in the complex leading to a diamagnetic ground state for the [Cu_{12}] cage. As shown by the crystal structure, the compound may be viewed as an assembly of six dinuclear units with double oxygen-bridge linked together by single hydroxido groups. In a first hypothesis, only the most efficient pathways involving the doubly bridged Cu(II) dinuclear units have been considered in the magnetic model. In this frame, the dodecanuclear complex can be described as six independent S = 1/2 dinuclear moieties. The magnetic data have been thus approximately modeled using the following theoretical susceptibility:

$$\chi T = 6(1-x) \times \frac{2N\mu_B^2 g_{Cu}^2}{k_B} \frac{1}{3+e^{-\frac{2J}{k_B T}}} + 6x\frac{N\mu_B^2 g_{Cu}^2}{3k_B}\frac{3}{4}$$

where J is the exchange interaction within the dinuclear Cu(II) units (using the Hamiltonian $H = -2JS_{CuA}.S_{CuB}$), g_{Cu} is the average g factor of the Cu sites, and x the amount of residual paramagnetic impurities per Cu dinuclear unit. The best fit of the experimental χT product leads to the following set of parameters: g_{Cu}=2.07(5), J/k_B= -173(1) (K), and 2% of an S = ½ spin impurities per Cu centers. The obtained J/k_B value is lower than the other known dinuclear phenoxido-hydroxido-bridged dicopper complexes for which, the Cu-O_{ph}-Cu and Cu-O_{hy}-Cu angles are close to 100°.[17,30] Unfortunately, this type of double monoatomic bridge is very uncommon especially when only equatorial positions are involved. Nevertheless, this situation is always mediating strong antiferromagnetic interactions between spins in the d_{x2-y2} magnetic orbitals of Cu(II) ions with a magnitude that is strongly dependent of the Cu–O–Cu angle.

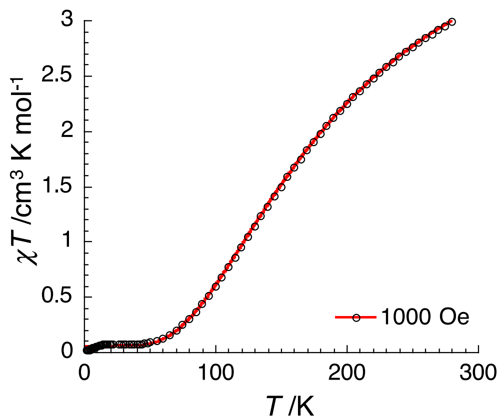


Figure 6. Temperature dependence of the χT product for **1** at 1000 Oe (χ being the magnetic susceptibility defined as M/H per Cu_{12} complex). Open circles indicate measured data points and the red line represents the best fit as described in the text.

DFT Calculations

A theoretical study of the electronic structure and magnetic properties of complex **1** was performed at the M06-2X/6-31+G* level of theory using the magnetic model explained above (six independent S = 1/2 dinuclear moieties). We have computed the J value for each Cu dinuclear unit and then obtained the average value to compare with the experimental estimation obtained from the magnetic measurements (*vide infra*). The average J has been computed using $J = (3 \text{ x } J_{Cu1\text{-}Cu2} + 3 \text{ x } J_{Cu3\text{-}Cu4} + 6 \text{ x } J_{Cu5\text{-}C6})/12$ where the three different types of Cu dinuclear unit have been taken into account. The calculated J values using the broken-symmetry approach are $J_{Cu1\text{-}Cu2}/k_B$ = –171 K, $J_{Cu3\text{-}Cu4}/k_B$ = –218 K and $J_{Cu5\text{-}C6}/k_B$ = –214 K, which gives an average value of –204 K, which is in relative good agreement with the experimental value (–173 K), and confirms the presence of strong antiferromagnetic coupling within the Cu_{12} complex. In order to further study the magnetic coupling mechanism, the spin density distribution and single-occupied molecular orbitals (SOMO) have been computed and represented in Figure 7 for the Cu5-Cu6 moiety as a representative model. Both Cu(II) ions have similar absolute values of spin density but opposite signs. The spin densities are –0.70 on Cu5 and +0.77

on Cu6, revealing that they are indeed the magnetic centers, however some of the spin density delocalizes onto the ligands. The spin delocalization is strong enough that ~26.5 % of the spin for the unpaired electrons on the Cu(II) centers are delocalized onto the ligand atoms. The spin population of the bridging oxygen atoms is small; they are 0.1 and 0.07 for phenoxido and hydroxido, respectively. The SOMO diagrams clearly show that the $d_{x^2-y^2}$ orbitals of the Cu(II) centers combine with the *p* orbitals of the bridging ligands playing an important role to the magnetic coupling (Figure 7) and consequently contributing to the antiferromagnetic interaction between the metal centers. The magnetic coupling through the single alkoxido bridge has also been calculated (J/k_B = -0.28 K [-0.2 cm^{-1}]) and is, as expected, negligible in comparison to the phenoxido-hydroxido mediated interaction.

Figure 7. Spin density map and SOMOs of a dinuclear Cu5-Cu6 unit of complex **1** computed at the M06-2X/6-31+G* level of theory.

X-ray Crystallography. The intensity data were collected on a Bruker-APEX-2 X-ray diffractometer with graphite-monochromated Mo-Kα radiation (λ =0.71073 Å), at room temperature T = 295 K. The structure was solved by direct methods using SIR97[31] system of programs and refined using full-matrix least-squares with all non-hydrogen atoms anisotropically and hydrogen atoms included on calculated positions, riding on their carrier atoms. The asymmetric unit contains one tetranuclear A^{2+} cation $(Cu_4C_{30}N_4O_8H_{42})^{++}$(containing Cu1, Cu2, Cu3 and Cu4 sites), one dinuclear B^+ cation $(Cu_2C_{15}N_2O_4H_{21})^{++}$ (containing Cu5 and Cu6 sites), a NO_3^- anion (built up by two anions in special positions 1/3,2/3,z linked to the A^{2+} cation and an anion in special position 0,0,z linked to B^+ cation, each anion having occupancy of 1/3) two OH^- groups to balance the charges, and a MeOH neutral molecule The A^{2+} cation contains two disordered O3H and O7H hydroxyl groups which were refined isotropically over two sites. An OH^- group and the molecule of MeOH are disordered and were refined isotropically over two sites. Because of the presence of an ill-defined region of residual density, the refinement was far from satisfactory. For this reason the program SQUEEZE was used to cancel out the effects of the disordered solvent. SQUEEZE is part of the PLATON program system[32] and attempts to remove mathematically the effects of disordered solvent.The crystal parameters and other experimental details of the data collections are summarized in Table 2. All calculations were performed using SHELXL-97[33] and PARST[34] implemented in WINGX[35] system of programs. ORTEP[36] views of both the independent cations of the asymmetric unit are given in Figures 2a and 2b. The corresponding dodecanuclear Cu_{12} cage complexes formed around the crystallographic 3 and $\bar{3}$ axis are shown in Figures 3a and 3b.

Table 2. Crystal Data and Structure Refinement Details for Compound 1

Compound	**1**
Asymmetric unit	$\{[(Cu_4C_{30}N_4O_8H_{42})^{++}]\cdot[(Cu_2C_{15}N_2O_4H \cdot NO_3^- \cdot 2OH^- \cdot CH_3OH\}$;
Chemical formula	$C_{46}H_{69}Cu_6N_7O_{18}$
M (g mol^{-1})	1389.32
Crystal system	Trigonal
Space group	$P\bar{3}$
a/Å	24.6656(14)
b/Å	24.6656(14)
c/Å	16.6985(9)
α/°	90.00
β/°	90.00
γ/°	120.00
Unit cell volume/Å^3	8798.1(9)
Z	6
Temperature/K	295
D_c/g cm^{-3}	1.573
F(000)	4272
μ(Mo-Kα)/mm^{-1}	2.208
Unique Reflections	10338
R_{int}	0.0810
Obs. Refl.ns [I≥2σ(I)]	7121
θ_{min}- θ_{max}/°	1.55 – 25.00
hkl ranges	-29,29;-29,29;-19,19
R(F^2) (Obs.Refl.ns)	0.0600
*w*R(F^2) (All Refl.ns)	0.1764

No. Variables	687
Goodness of fit on F^2	1.043
$\Delta\rho_{max}$; $\Delta\rho_{min}$ /e Å^{-3}	0.820; -0.631
CCDC No.	891869

$R_1 = \Sigma(\ ||F_o|–|F_c||\ )/\Sigma|F_o|$. $wR_2 = [\ \Sigma w(|F_o|–|F_c|)^2/\Sigma w(F_o)^2]^{1/2}$. $w = 0.75/(\sigma^2(F_o) +0.0010F_o^2)$.

Conclusions

A large copper phenoxido/hydroxido/nitrato complex with a novel cuboctahedral structure has been synthesized from the assembly of six ligand bound dinuclear building units. The formation of the product is dependent on the choice of solvent system and the condition of the reaction medium for the generation of required numbers of hydroxido groups needed for the self-assembly of the preformed dinuclear fragments. Combination of *bis*-propanol arm bearing face-capping phenol-based ligands, Cu(II)salt derived nitrates and solvent generated hydroxides with Cu^{2+} cations having preference for highly distorted and elongated pentagonal coordination geometries results in formation of the cage complex. The synthesis, characterization and magnetic properties of theCu_{12}cage have been described highlighting the key roles of (i) the templating anions, in particular nitrates, and (ii) the favorable coordination ability of the dinucleating ligand with long terminal alcohol arms for self-assembly aggregation. Further work is currently under progress in our laboratory to assemble larger cages supported by the *in-situ* generated and metal salt supplied anions.

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Notes and References. CCDC numbers for **1** is 891869. For crystallographic data in CIF, Schemes S1 and Figures S1 to S6 syntheses and characterization of ligand H_3pbmp. see ESI DOI: xxxx.

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