

Rhomboidal [Cu₄] coordination cluster from self-assembly of two asymmetric phenoxido-bridged Cu₂ units: Role of $\mu_{1,1}$ -azido clips

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Abstract. The coordination cluster [Cu₂(μ -OMe)($\mu_{1,1}$ -N₃)(μ -bcp)(N₃)₂ (**1**; Hbcp = 2,6-bis(2-benzoyl-4-chloro-phenylimino)-methyl)-4-methylphenol, forming a new member within the rapidly growing family of Cu₄ cluster complexes, has been synthesized and structurally characterized by X-ray crystallography. The complex crystallizes in the monoclinic system, space group P2₁/c, with unit cell parameters a = 14.620(7) Å, b = 17.923(8) Å, c = 15.008(7) Å, β = 115.815(14)° and Z = 2. It is the first example of a rhomboidal [Cu₄] compound formed from $\mu_{1,1}$ -azido clipping of two methoxido bridged [Cu₂] complexes showing asymmetric coordination from benzophenone oxygen atoms and terminal azido groups.

Keywords. Tetranuclear copper(II); azido; methoxido; phenoxido; X-ray structure; rhomboidal.

1. Introduction

In recent years, the utilization of new ligand systems have been critically examined for the gram-scale synthesis of tetranuclear transition metal aggregates following the discovery of their involvement in bioinorganic structural and functional model compounds, paramagnetic materials and catalysis.^{1–3} Phenoxido-bridged dinuclear copper(II) complexes having vacant coordination sites on both the metal ions are useful building units for the construction of tetra- and polynuclear complexes.^{4–9} In this context, the phenoxido-methoxido double bridged Cu₂ complexes are important for possible co-ligand driven controlled aggregation process. In coordinatively unsaturated condition, the ability of both the copper(II) ions to accept fourth and fifth coordinating groups from basal and apical sites leads to the association of the two such dimeric units.

The final outcome of such association is fully dependent on the number and nature of the ancillary coordinating groups added after the initial reaction of the metal salts with the phenol bearing ligands. Thus, different tetranuclear copper(II) assemblies are possible depending on the ligand precursors and ancillary coordinating ligands. Among the various aggregation possibilities, cubane, tetrahedron, stepped-cubane and

double-cubane geometries have seen in the literature. Compared to these the rhomboidal geometry is not common in the synthetic world. Among the ancillary coordinating groups, azido has been chosen for its versatility in showing a range of connecting modes as metal ion connector. The azido group can adopt numerous bridging conformations to bind two or more metal ions such as μ -1,1 (end-on, EO) or the μ -1,3 (end-to-end, EE), μ_3 -1,1,1, μ_3 -1,1,3, μ_4 -1,1,1,1 and μ_4 -1,1,3,3. (scheme 1). All these bridging conformations possible when two different binding positions (*basal* or *apical*) around copper(II) are occupied. Synthesis and characterization of these sorts of multinuclear complexes are of contemporary interest because of their involvement in the superexchange mechanism. It has now been well established that symmetric μ -1,3-copper(II) azide complexes are strongly antiferromagnetic, whereas copper(II) complexes with double-symmetric μ -1,1 azide bridges are strongly ferromagnetic when the Cu-N_{azide}-Cu angle is less than 108°. While exploring to synthesize and study newer forms of [Cu₄] aggregates, we have been attracted in exploring the coordination behaviour of the phenoxido bridging hexadentate Schiff-base ligand 2,6-(2-benzoyl-4-chloro-phenylimino)-methyl)-4-methylphenol, abbreviated as Hbcp (chart 1) with Cu(NO₃)₂·3H₂O in the presence of clipping ligand N₃⁻. It is important to note that the use of one closely related ligand of Hbcp, named Hbip (chart 1, right, 2,6-bis(benzyliminomethyl)-4-methylphenol) led to system

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Scheme 1. Different bridging modes of azido anions.

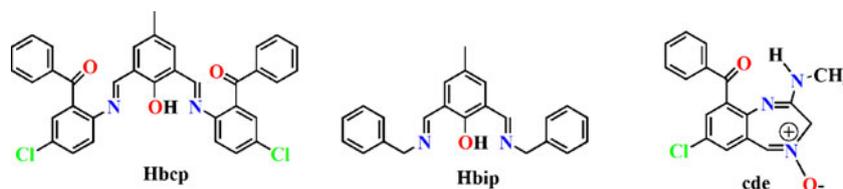


Chart 1. Synthesis of the complex.

consisting of $[\text{Cu}_4\text{O}]$ and $[\text{Cu}_4(\text{OH})_2]$.¹⁰ Here, the new $[\text{Cu}_4]$ complex based on the bcp^- anionic ligand containing a bis- N_3^- bridged rhomboid structure has been isolated and crystallographically characterized. Here, the aniline part of Hbcp, 2-amino-5-chlorobenzophenone a pro-ligand is same as that present in chloridiazepoxide (cde), the first benzodiazepine drug marketed in 1960.

2. Experimental

2.1 Reagents and materials

All the chemicals and solvents were reagent-grade materials and used as received without further purification. The chemicals were obtained from the following sources: copper nitrate trihydrate, and sodium azide, from SD Fine Chemicals (India) and 2-amino-5-chlorobenzophenone from Sisco Research Laboratory (India). 2,6-Diformyl-4-methylphenol was prepared from 4-methylphenol following a known procedure with little modification.¹¹

Caution! Azide complexes of metal ions involving organic ligands are potentially explosive. Only small quantities of the complexes should be prepared, and these should be handled with care.

2.2 Syntheses

Hbcp Ligand—the Schiff-base was prepared from a single-step condensation of 2,6-diformyl-4-methylphenol (1.64 g, 10 mmol) and 2-amino-5-chlorobenzophenone (4.63 g, 20 mmol) in MeOH (40 mL)

under reflux for 1 h by following a modified reported procedure.¹²

2.3 $[\text{Cu}_2(\mu\text{-OMe})(\mu_{1,1}\text{-N}_3)(\mu\text{-bcp})(\text{N}_3)]_2$ (**I**)

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.483 g, 2.00 mmol) dissolved in MeOH (25 mL) was added drop-wise with stirring to a yellow MeOH solution (15 mL) of Hbcp (0.59 g, 1 mmol). After about 10 min of stirring, solid NaN_3 (0.260 g, 4.0 mmol) was added to the reaction mixture. The green colour of the solution changed to brown and the reaction mixture was stirred for 2 h during which a brown precipitate appeared. The obtained brown precipitate was collected by filtration, washed with cold MeOH followed by water, and dried under vacuum over P_4O_{10} . Brown single crystals suitable for X-ray analysis were obtained from MeOH after 7 days. Yield: 0.566 g, 68%. Anal. Calcd for $\text{C}_{72}\text{H}_{52}\text{N}_{16}\text{O}_8\text{Cl}_4\text{Cu}_4$ (1665.25 g mol^{-1}): C, 51.93; H, 3.14; N, 13.45. Found: C, 51.87; H, 3.06; N, 13.36. Selected FTIR bands: (KBr, cm^{-1} , vs = very strong, s = strong, m = medium, w = weak): 3447 (vs) 2371 (vs), 1635 (vs), 1458(s), 1313 (s), 1049 (m), 775 (m), 625 (w). Molar conductance, Λ_M (MeOH solution): $6.0 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. UV-vis spectra [λ_{max} , nm (ϵ , $\text{L mol}^{-1} \text{cm}^{-1}$): (MeOH solution) 600 (410), 397 (24160), 358 (26460).

2.4 Physical measurements

The elemental analyses (C, H, N) were performed with a Perkin-Elmer model 240C elemental analyzer. FTIR spectra were recorded on a Perkin-Elmer Spectrum RX1 spectrometer. The solution electrical conductivity and

electronic spectra were obtained using a Unitech type U131C digital conductivity meter with a solute concentration of about 10⁻³ M and a Shimadzu UV 2450 UV-vis spectrophotometer respectively.

2.5 X-ray crystallography

Information concerning the X-ray data collection and structure refinement of the compound **1** is summarized in table 1. Single crystal data of the complex was collected on a Bruker APEX II CCD single crystal X-ray diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$). Data were collected at 293 K. For complex **1**, a total of 6546 reflections were recorded with Miller indices $h_{\min} = -17$, $h_{\max} = 17$, $k_{\min} = -20$, $k_{\max} = 21$, $l_{\min} = -15$, $l_{\max} = 18$. The refinement was performed using full-matrix least-squares and for all three cases, non-hydrogen atoms were refined anisotropically. All calculations were performed using SHELXL-97¹³ in the WINGX system of programs.¹⁴ The hydrogen atoms were geometrically fixed on calculated positions, riding on their carrier atoms. The

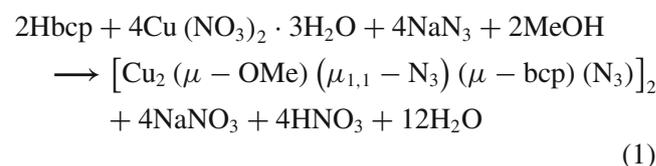
graphics were generated using Diamond 3.1e software. The structure is recognizable from the viewpoint of tetranuclearity but the crystal data are very poor and the refinement is unstable. Unfortunately, the R values are very high as well as the estimated standard deviations.

3. Results and discussion

3.1 Synthetic considerations

The Schiff base 2,6-bis(2-benzoyl-4-chlorophenylimino)-methyl-4-methylphenol (Hbcp) has been prepared (scheme 2) following a modified literature procedure,¹¹ and its reaction with copper(II) nitrate has been examined (scheme 3).

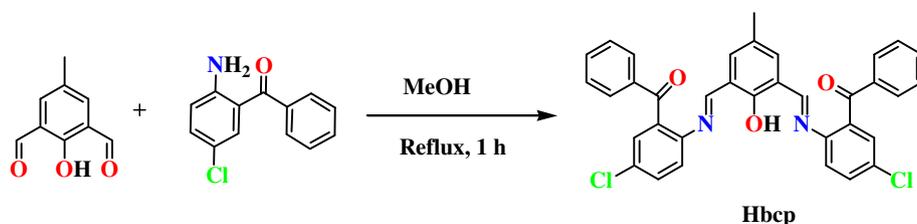
At room temperature, the reaction of Cu(NO₃)₂·3H₂O was carried out with Hbcp and NaN₃ in MeOH, [Cu₂(μ -OMe)($\mu_{1,1}$ -N₃)(μ -bcp)(N₃)₂] (**1**, scheme 2) was obtained as brown powder in ~65% yield from the reaction mixture. Several Cu/Hbcp/N₃ ratios were explored, and we report here only the optimized molar ratio (2:1:1) which gave the best yield and clean product. Same reactions in the presence of a stoichiometric addition of either NEt₃ or NaOH gave the same product, confirming the formation of hydroxide bridges independently of the type and nature of the bases added. The preparation of compound **1** is summarized in eq 1, accounting for the formation of the methoxido bridges from the methanol molecule and their incorporation as inter-dimeric bridges. Azido groups from sodium azide next simultaneously bind two copper(II) ions and clip



two dimeric fragments. Addition of excess of NaN₃ was not helpful in replacing the methoxido bridges by N₃⁻ in **1** to yield [Cu₂($\mu_{1,1}$ -N₃)₂(μ -bcp)(N₃)₂] (same as **2** in scheme 2), indicating the strong affinity and stability of the methoxido bridges in this system. The elemental analysis and solution molar conductivity data in MeOH are consistent with the formula [Cu₂(μ -OMe)($\mu_{1,1}$ -N₃)(μ -bcp)(N₃)₂] for **1**. However, no sign of formation of only phenoxido bridged Cu(II) dinuclear species (**3** in scheme 2) was observed, perhaps because of the better stability of **1**, which crystallizes with *bis*-methoxo intra-dimer bridges and *bis*-azido inter-dimer clips.

Table 1. Crystallographic data for **1**.

Compound	1
Formula	C ₇₂ H ₅₂ N ₁₆ O ₈ Cl ₄ Cu ₄
M	1665.25
Space group	<i>P</i> 2 ₁ / <i>c</i>
Cryst syst	Monoclinic
<i>a</i> / \AA	14.620(7)
<i>b</i> / \AA	17.923(8)
<i>c</i> / \AA	15.008(2)
α /deg	90.0
β /deg	115.815(14)
γ /deg	90
<i>V</i> / \AA^3	3539.94
<i>T</i> /K	293
<i>Z</i>	2
<i>D</i> _c /g cm ⁻³	1.562
<i>F</i> (000)	1688
μ (Mo-K α)/cm ⁻¹	14.05
Measd reflns	38537
Unique reflns	6546
<i>R</i> _{int}	0.5145
obsd reflns [<i>I</i> \geq 2 σ (<i>I</i>)]	2400
$\theta_{\min} - \theta_{\max}$ / $^\circ$	1.55–26.06
<i>H</i> , <i>k</i> , <i>l</i> ranges	–17, 17; –20, 21; –15, 18
<i>R</i> (<i>F</i> ²) (obsd reflns)	0.4294
<i>wR</i> (<i>F</i> ²) (all reflns)	1.062
No. of variables	469
GOF	1.062
$\Delta\rho_{\max}$; $\Delta\rho_{\min}$ (e \AA^{-3})	1.820; –1.680



Scheme 2. Preparation of the ligand.

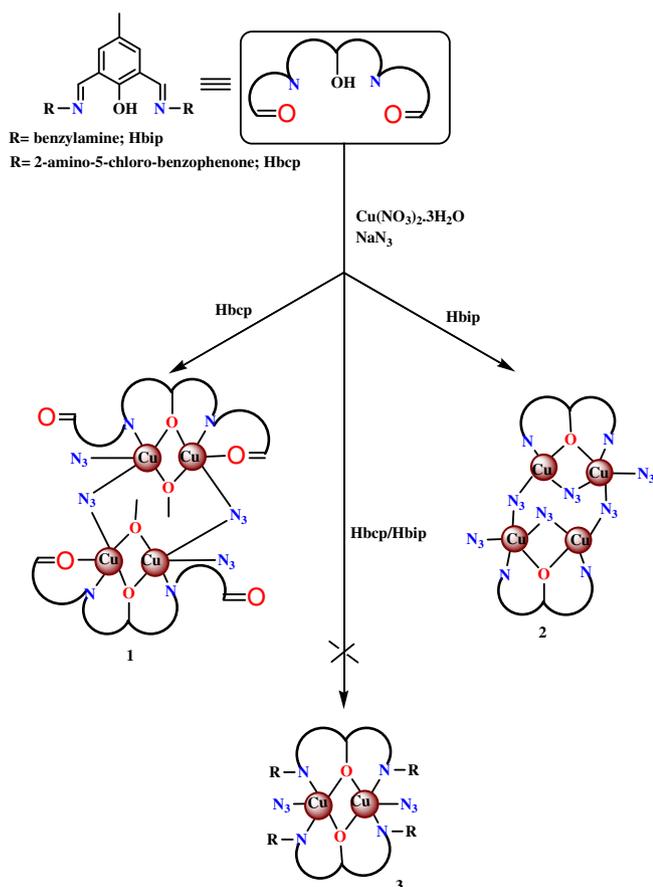
3.2 Description of the crystal structure.

$[Cu_2(\mu-Ome)(\mu_{1,1}-N_3)(\mu-bcp)(N_3)]_2$ (**1**)

The molecular structure of compound **1** is shown in figure 1, and important bond lengths and bond angles are given in table 2. Compound **1** crystallizes from a MeOH solution in the monoclinic $P2_1/c$ space group, and the asymmetric unit contains one-half of the tetranuclear unit (the second half is generated by the $(-x, 1-y, -z)$ symmetry operator). **1** is composed of neutral molecules consisting of two deprotonated bcp^- ligands, each providing an asymmetric N_2O_2 set of donor atoms consisting of phenoxido O bridge, imine N and

carbonyl O atoms to the $[Cu_4]$ core. This sort of azido-, methoxido- and phenoxido bridged $[Cu_4]$ rhomboidal core structure is not known in the literature.

Within the cluster molecule Cu1 adopts a square-pyramidal coordination sphere consisting of one O atom from a bridging methoxido anion, one phenoxido O, benzoyl O and imine N atoms of the bcp^- ligand, and one N atom from a bridging azido anion. In a similar coordination environment, Cu2 binds to one terminal azido N atom in *basal* site in lieu of the benzoyl O atom coordination to Cu1. The $[Cu_4]$ compound results from the azido clipped assembly of two $[Cu_2(\mu-Ome)(\mu-N_3)(\mu-bcp)(N_3)]$ fragments through two azido groups



Scheme 3. Schematic representation for the formation of **1**.

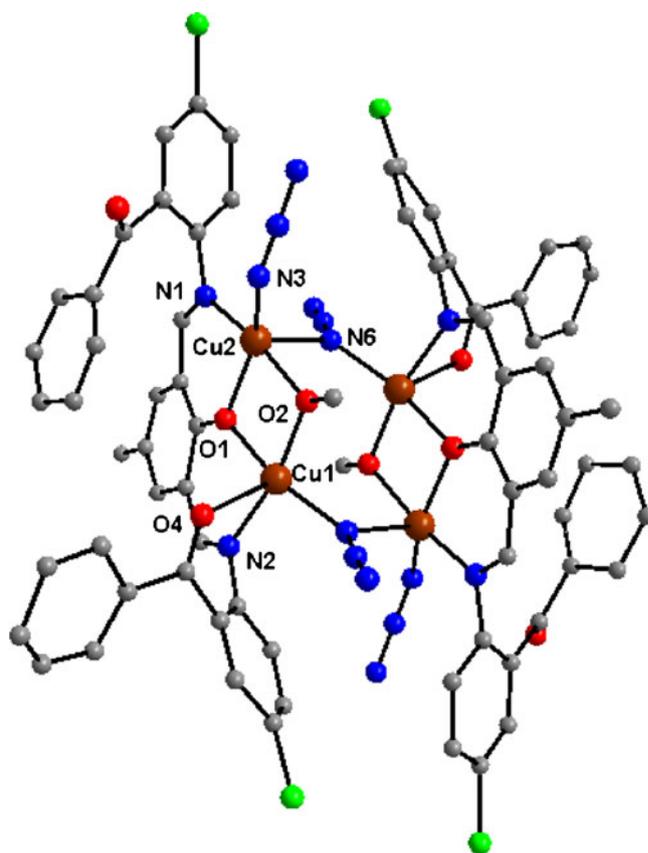


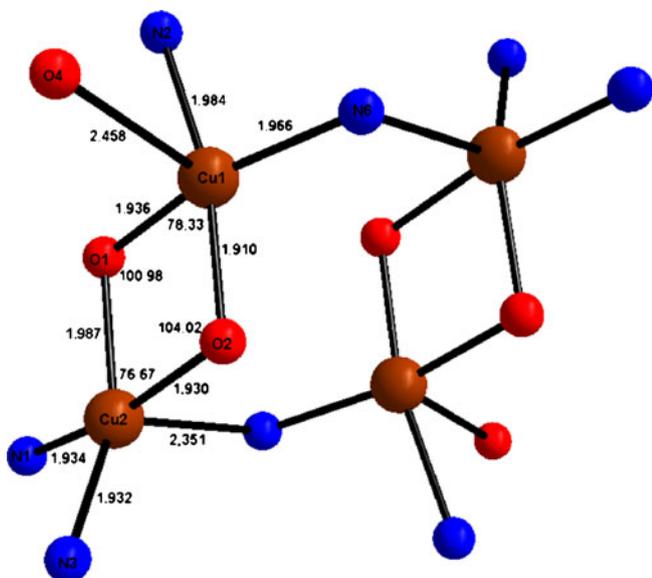
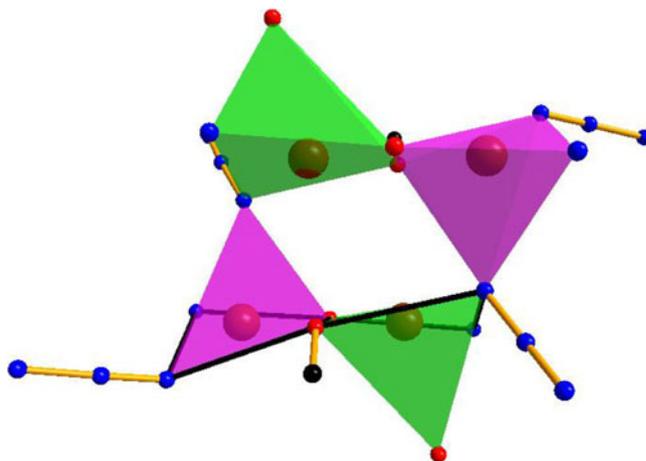
Figure 1. View of the molecular tetranuclear unit $[Cu_2(\mu-Ome)(\mu_{1,1}-N_3)(\mu-bcp)(N_3)]_2$ in **1** with atom numbering scheme and H atoms are omitted for clarity. Colour code: Cu^{II} brown, N blue, O red, C grey, Cl green.

Table 2. Selected interatomic distances (Å) and angles (°) for **1**.

Distances			
N6–Cu1	1.96(3)	Cu2–O2	1.930(19)
N1–Cu2	2.35(2)	Cu2–N3	1.93(3)
Cu1–O2	1.910(18)	Cu2–N1	1.93(2)
Cu1–O1	1.937(18)	Cu2–O1	1.986(16)
Cu1–N2	1.98(2)	Cu2–N6	2.35(2)
Cu1···Cu2	3.027(5)		
Angles			
O2–Cu1–O1	78.3(7)	N3–Cu2–N1	98.0(10)
O2–Cu1–N6	96.7(8)	O2–Cu2–O1	76.7(7)
O1–Cu1–N6	164.3(9)	N3–Cu2–O1	149.5(10)
O2–Cu1–N2	167.3(9)	N1–Cu2–O1	91.3(8)
O1–Cu1–N2	90.0(9)	O2–Cu2–N6	86.8(9)
N6–Cu1–N2	95.8(9)	N3–Cu2–N6	119.4(10)
O2–Cu2–N3	95.1(10)	N1–Cu2–N6	87.8(9)
O2–Cu2–N1	166.8(8)	O1–Cu2–N6	89.8(7)

(N6 and N6*) that bridge pentacoordinated square-based pyramidal Cu^{II} ions (Cu2 and Cu2*). In case of Cu2 and Cu2* the *apical* directions are occupied by N6 and N6* (figure 2). The same N6 and N6* atoms occupy *basal* positions and carbonyl O4 and O4* atoms *apical* positions around Cu1 and Cu1*. Among these two types of *apical* coordination, the Cu–O distances are longer than Cu–N distances. The coordination sphere of Cu1 and Cu2 are very close to the just right square-pyramidal geometry and the distortion around Cu2 is higher than that observed in Cu1 with Addison parameter of 0.051 (Cu1) and 0.288 (Cu2) (figure 3). The Jahn–Teller effect induces a significant elongation of the *apical* bonds by 0.4–0.5 Å (Cu1–O4, 2.458 and Cu2–N6, 2.351 Å). The in-plane Cu–O_{me}

(me = methoxido) bond distances fall in 1.910–1.930 Å range, which are comparable to those reported for other μ-Ome-bridged tetranuclear copper(II) complexes.^{15,16} On the other hand, the in-plane phenoxido binding is asymmetric with two Cu–O_{ph} (ph = phenoxido) distances of 1.936 (Cu1) and 1.987 (Cu2) Å, respectively. In their square-pyramidal coordination environment, the Cu1 and Cu2 are displaced by 0.098 and 0.229 Å, respectively, from the N₂O₂ mean basal planes. The C=N, C–O and C=O distances of the dialdimine, phenoxide and benzoyl fragments are consistent with the coordination of these functionalities.^{17,18} The copper bound C=O distance (1.204 Å) is longer than the dangling one (1.138 Å). For monodentate N₃[−] coordination the metal ion side N–N distance (1.143 Å) is shorter than the corresponding one (1.248 Å) in case of μ_{1,1} bridging.

**Figure 2.** View of the rhomboidal [Cu₄] core showing coordination sphere with bond distances.**Figure 3.** Perspective view of the rhomboid core from basal-apical N₃[−] clips in **1**.

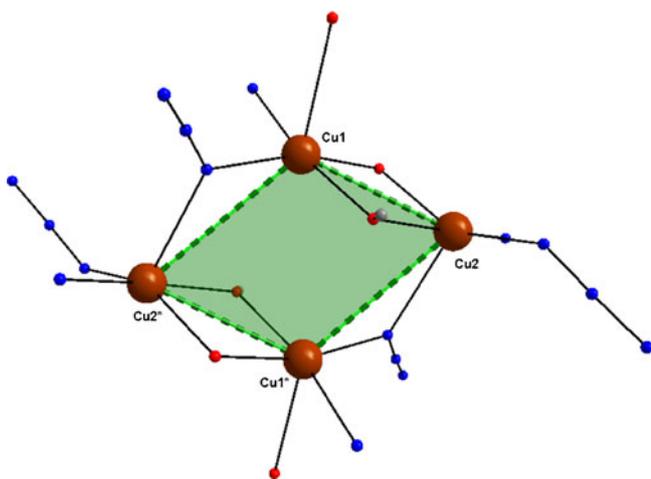


Figure 4. Placement of four Cu^{II} ions within Cu₄(N₃)₄ rhomboidal structure in **1**.

The tetranuclear assembly results from the azido-clipping of [Cu₂O₂] dinuclear cores (O are phenoxido and methoxido oxygen atoms). Within this phenoxido-methoxido-bridged fragment, the Cu(II) ions are separated by 3.027 Å. The Cu···Cu distance (3.492 Å) is longer for the azido only clipped Cu motif, which implies *apical* positions. Within the [Cu₄] rhombus the short and long Cu···Cu diagonal distances are 3.570 and 5.475 Å, respectively (figure 4). Two monodentate azide anions are coordinated to Cu2 and Cu2*. The azido terminal group is almost linear, with an N–N–N angle of ~177°, but they show a nonlinear monodentate mode on the Cu(II) ions, having an average Cu–N–N angle of ~136° and Cu–N separation of 1.932 Å. This Cu–N bond distance is short in comparison to the *basal–apical* bridging azides (1.966 and 2.351 Å).¹⁹ Packing of complex **1** along crystallographic *c*-axis

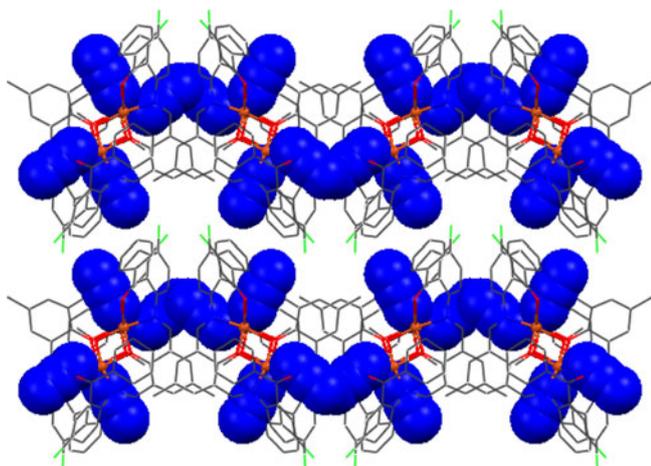


Figure 5. Ordered packing of azide groups in space fill model along *c*-axis.

shows regular layered arrangement of tetranuclear units and azide groups (figure 5).

3.3 IR spectroscopy

In compound **1**, the characteristic bands of the bcp⁻ ligand appear clearly on the FT-IR spectra. The $\bar{\nu}_{\text{C=N}}$ stretching frequency is observed at 1625 cm⁻¹. Compound **1** shows strong absorption bands at 2054 and 1365 cm⁻¹ corresponding to the $\bar{\nu}_{\text{as}}$ and $\bar{\nu}_{\text{s}}$ stretching vibrations of the $\mu_{1,1}\text{-N}_3^-$ groups. Free azide ion in NaN₃ shows single strong absorption centred at 2133 cm⁻¹.²⁰ The shift to lower wave numbers indicates the coordination of azide ion to copper(II) in complexes.

3.4 Electronic spectra

The compound in MeOH solution shows multiple bands in the 200–900 nm region. The ligand-field spectra show a broad absorption band (λ), with maxima at 600 nm ($\epsilon = 410 \text{ L mol}^{-1} \text{ cm}^{-1}$). The intense absorption below 400 nm at 397 nm ($\epsilon = 24160 \text{ L mol}^{-1} \text{ cm}^{-1}$) is dominated by the metal ion bound ligand-based absorptions. Spectra of this compound also shows shoulder at 358 nm ($\epsilon = 26460 \text{ L mol}^{-1} \text{ cm}^{-1}$), due to MeO⁻ → Cu(II) and or PhO⁻ → Cu(II) ligand-to-metal charge transfer (LMCT) transitions.

4. Conclusion

The metal ion binding potential of the bcp⁻ ligand has been scrutinized and identified the vital role played by the ancillary ligands in the synthesis of a new tetranuclear copper(II) complex. Azide ligands along with solvent derived methoxide bridges have been utilized to control the topology of the final [Cu₄] product. The pentadentate bcp⁻ ligands facilitate the trapping of two Cu^{II} pairs, leaving behind coordination sites for the binding of methoxido and azido anions which help the assembly of two pairs of Cu^{II} pairs in rhomboidal molecular topology.

Acknowledgements

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