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Novel tetranuclear copper |2 + 4| cubanes resulting from unprecedented C–O bond formation *cum* dearomatization†

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Novel tetranuclear copper |2 + 4| cubanes **1** and **2** have been synthesized from the reaction of hydrated copper salts/precursors with N,O chelating β -ketoamino ligands. Creation of **1** and **2** occurs by *in situ* generation of the tridentate chelating species HL1O^{2-} via copper mediated C–O bond formation and dearomatization of $\text{H}_3\text{L1}$, while anhydrous salts afforded mononuclear complex **3**.

Polynuclear complexes and clusters have attracted substantial current interest owing to their unusual properties and potential applications in diverse areas.^{1,2} Among these tetranuclear copper clusters exhibiting a variety of structures like butterfly, cyclic, roof-shaped dimers, Cu_4O_4 rings and cubanes have drawn particular attention.² Furthermore, Cu_4O_4 cubanes have been attractive due to their intermediate size and magnetic properties.^{2,3} Based on Cu–O bond distances, ‘Mergehenn’ and ‘Haase’ classified Cu_4O_4 cubanes into two categories: those having four long bond distances between two pseudo-dimeric units as type I and those in the same unit as type II.⁴ On the basis of Cu...Cu distances these have further been classified as: (i) |2 + 4|, containing two short and four long distances, (ii) |4 + 2|, with four short and two long distances, and (iii) |6 + 0|, with all the six Cu...Cu distances similar. The |2 + 4| and |4 + 2| cubanes are similar to types I and II. Usually, M_4L_n cubanes are formed by involvement of oxo, azido, sulfido, or iminato groups as bridging ligands.^{3,5} Numerous oxo-bridged copper cubanes derived from NNO/NOO– donor and β -ketoiminato ligands having terminal oxygen as the bridging group have been extensively studied.^{6,7}

Furthermore, dearomatizations are not feasible because these lead to disruption of the aromatic π -system. However, it

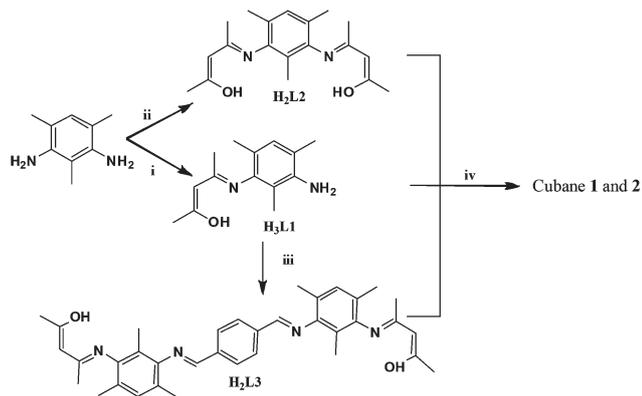
can be achieved *via* interaction of the π -electron systems of arene rings with the metal center which makes it electron deficient and favours nucleophilic attack followed by C–heteroatom bond formation.⁸ The conversion of M–R into the M–OR functionality is rather limited and occurs in the presence of O_2 following a free radical mechanism⁹ or redox process.¹⁰ Copper is a metal often used in many important biological reactions and is known as a good catalyst/reagent for C–O bond formation reactions.^{8–11} Reactions involving C–O bond formation at the aromatic carbon centre through –CH activation with retention of aromaticity have been extensively studied,¹² however such a reaction at an aromatic carbon having the methyl group has not been explored. Furthermore, numerous Cu_4O_4 cubanes derived from multidentate NOO/NOO– donor ligands with bridging oxygen have been synthesized and extensively studied.¹ In contrast, to the best of our knowledge formation of cubanes by *in situ* conversion of the bidentate NO– into the tridentate NOO– donor moiety has not been described. Through this contribution we describe the synthesis and thorough characterization of bidentate N,O chelating mono- and di- β -ketoamino ligands $\text{H}_3\text{L1}$, $\text{H}_2\text{L2}$ and $\text{H}_2\text{L3}$ and unprecedented creation of tetranuclear Cu_4O_4 cubanes derived from these ligands *via* C–O bond formation *cum* dearomatization.

Synthesis of $\text{H}_3\text{L1}$ and $\text{H}_2\text{L2}$ has been achieved by condensation of 2,4,6-trimethylbenzene-1,3-diamine with acetyl acetone in 1 : 1 and 1 : 2 molar ratios in methanol under refluxing conditions (Scheme 1).¹³ On the other hand, $\text{H}_2\text{L3}$ has been prepared by condensation of $\text{H}_3\text{L1}$ with terephthaldehyde (2 : 1) under similar conditions (Scheme 1). The deprotonated ligands reacted with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in methanol to afford cubane **1**, while their reactions with $\text{Cu}(\text{acac})_2 \cdot \text{H}_2\text{O}$ (acac = acetylacetonato) gave cubane **2** in a reasonably good yield (Scheme 2). In contrast, $\text{H}_3\text{L1}$ reacted with anhydrous $\text{Cu}(\text{CH}_3\text{COO})_2$ to afford mononuclear complex **3** (Scheme 2).

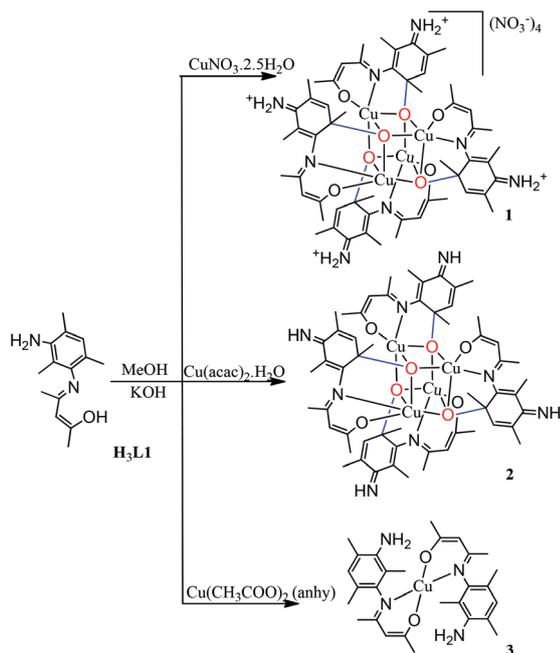
The ligands ($\text{H}_3\text{L1}$, $\text{H}_2\text{L2}$ and $\text{H}_2\text{L3}$) and complexes (**1–3**) have been thoroughly characterized by satisfactory elemental analyses, spectral (IR, NMR, UV/vis, emission, ESI-MS) and electrochemical studies (detailed discussion is given in ESI

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† Electronic supplementary information (ESI) available: Experimental sections, NMR, ESI-MS, UV/vis, fluorescence, electrochemical studies, figures and tables. CCDC 885770 ($\text{H}_3\text{L1}$), 876109 (**1a**), 876108 (**1b**), 876112 (**1c**), 876111 (**2**) and 876110 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt01887g



Scheme 1 Scheme showing the synthesis of ligands ($\text{H}_3\text{L1}$, $\text{H}_2\text{L2}$ and $\text{H}_2\text{L3}$) and cubanes (**1** and **2**). (i) Acetyl acetone (1 equiv.), refluxed in MeOH, 6 h, (ii) acetyl acetone (2 equiv.), refluxed in MeOH, 24 h, (iii) terephthalaldehyde (0.5 equiv.), refluxed in MeOH, 12 h, (iv) hydrated copper salts/precursors [$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{Cu}(\text{acac})_2 \cdot \text{H}_2\text{O}$] stirred in MeOH with KOH at RT. Structures of the cubanes **1** and **2** are presented in Scheme 2.



Scheme 2 Synthesis of cubanes **1** and **2** and mononuclear complex **3** from $\text{H}_3\text{L1}$ upon treatment with hydrated and anhydrous copper(II) salts.

Fig. S1–S21[†]). Structures of $\text{H}_3\text{L1}$ and **1–3** have been authenticated by X-ray single crystal analyses. It is noteworthy to mention that reaction of all the three ligands with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ under analogous conditions afforded cubane **1** as the sole product whose identity has been confirmed by analytical and various spectral techniques and crystal structure parameters (please see the CIF, **1a–1c**). Likewise, reaction with $\text{Cu}(\text{acac})_2 \cdot \text{H}_2\text{O}$ afforded cubane **2**, and a mononuclear complex **3** has been obtained using anhydrous copper acetate (Scheme 2). It has also been observed that in the presence of

hydrated copper salt/precursors the di- β -ketoamino ($\text{H}_2\text{L2}/\text{H}_2\text{L3}$) ligands get cleaved and form cubanes **1** and **2**.

Characterization data for **1** and **2** revealed some structural disparity which has further been supported by X-ray single crystal analyses. $\text{H}_3\text{L1}$ crystallizes in the monoclinic system with the $P2_1/c$ space group and revealed the linkage of one amine from mesitylene diamine to the β -ketoamino group through the azomethine moiety, while other amine remains free (Fig. 1a). Cubane **1** crystallizes in the monoclinic system with the $P2/n$ space group and the asymmetric unit contains two units of each of the $\text{H}_2\text{L1O}^-$, Cu^{2+} , NO_3^- and one H_2O molecule (Fig. 1b). Unexpectedly, the crystal structure of **1** exhibited formation of the new C–O bond *ortho*- to ketamine and *para*- to the amino group through oxidation of $\text{H}_3\text{L1}$ to $\text{H}_2\text{L1O}^-$. The presence of four substituents and a range of bite angles (104.53 – 113.13°) suggested sp^3 hybridization and tetrahedral geometry about the C1* and C15* and creation of a chiral centre at these carbons. Loss of the conjugation and dearomatization can be clearly understood from unequal C–C bond distances within the mesitylene ring (Table S2[†]). Shortening of the C4–N2/C18–N4 ($1.290/1.315$ Å) distances in **1** relative to $\text{H}_3\text{L1}$ (1.398 Å) clearly suggested conversion of $-\text{NH}_2$ to $=\text{NH}_2^+$ and strongly supported the formation of **1**. The copper centres are in the +2 oxidation state and additional positive charge is generated on $=\text{NH}_2^+$ leads to net 4 positive charges on the cubane core, which are compensated by four NO_3^- as counter anions. Each copper centre in **1** is pentacoordinated (NO4 environment) and immediate coordination geometry about the metal centre is distorted square pyramidal (SP). It is completed by the N,O from β -ketoamino and three bridging oxygen atoms (O1/O3) from newly generated alkoxo groups (Fig. 1b). The basal plane is formed by β -ketoamino NO- and two alkoxo oxygen atoms, while other alkoxo oxygen atoms assumed the apical position. The Cu1...Cu1/Cu2...Cu2 and Cu1...Cu2 distances [$2.979/2.983$ (two short) and $3.328/3.331$ Å (four long)] lie in the range for $|2 + 4|$ cubanes, while Cu–O distances [Cu1/Cu2–O1/O3 ($2.377/2.370$ and $1.984/2.005$ Å)]

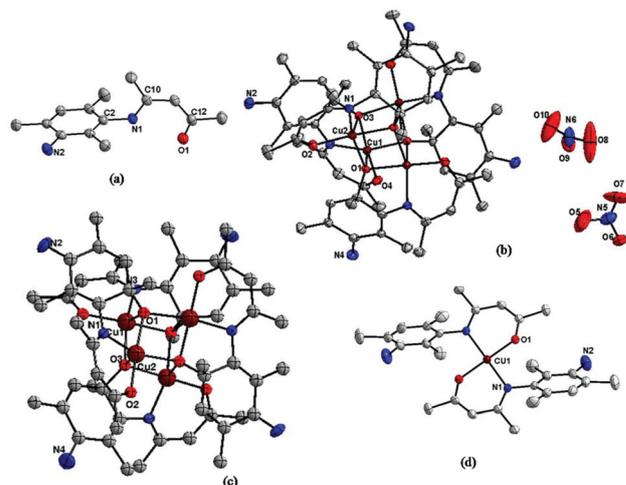


Fig. 1 Crystal structures of $\text{H}_3\text{L1}$ (a), **1** (b), **2** (c) and **3** (d).

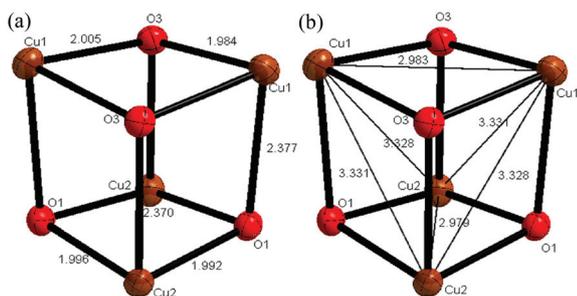


Fig. 2 Cu_4O_4 core in **1** showing Cu–O (a) and Cu–Cu (b) distances.

suggested that this molecule falls in the type I cubane category (Fig. 2).⁴

The structure of **2** closely resembles that of **1** and likewise involves C–O bond formation. It crystallizes in the monoclinic system with the 'C2/c' space group. The asymmetric unit comprises of two molecules each of the HL1O^{2-} , Cu^{2+} and H_2O , while the cubane structure has been completed by four units of each (Fig. 1c). The overall arrangement of cubane **2** is analogous to that for **1** except that only exocyclic imine ($=\text{NH}$) is present instead of the $=\text{NH}_2^+$ group. The copper centres are in the +2 oxidation state (Cu^{2+}) and in the presence of the exocyclic $=\text{NH}$ group lead to the formation of a charge neutral species **2**. The Cu...Cu and Cu–O distances are comparable to **1** (Table S2, Fig. S22, ESI[†]) and lies in the range for $|2 + 4|$ cubanes.⁴

The Addison distortion index (τ) for pentacoordinated metal complexes has been calculated using the formula ' $\tau = (\alpha - \beta)/60$ ' where α and β are two major bond angles at the metal centre. The τ value should be zero for an ideal square pyramidal and one for trigonal bipyramidal systems.¹⁴ It has been found to be 0.285/0.246 (Cu1/Cu2) for **1** and 0.307/0.308 (Cu1/Cu2) for **2** suggesting distorted square pyramidal geometry around the copper centre.

The crystallographic parameters suggested that the central cubane core is analogous for both **1** and **2**, but these differ by the presence of the exocyclic $=\text{NH}_2^+$ group in **1** leading to a tetra cationic species, while $=\text{NH}$ in **2** leads to a charge neutral cubane. In **1**, one of the terminal $=\text{NH}_2^+$ interacts with oxygen from two nitrates ($\text{N4-H4A/4B}\cdots\text{O9}$; 2.872/3.004) *via* intermolecular hydrogen bonding and forms a rectangular cavity while others ($\text{N2-H2A}\cdots\text{O11}$; 2.826) interacted with one water molecule (Fig. S23–S25, ESI[†]). Conversely, in **2** each of the $=\text{NH}$ groups interacted with water molecules ($\text{N2-H2}\cdots\text{O11/N4-H4}\cdots\text{O12}$; 2.701/3.048 Å) through intermolecular hydrogen bonding (Fig. S26, ESI[†]). Differences in weak interactions supported the presence of the $=\text{NH}_2^+$ in **1**, and $=\text{NH}$ in **2**. Unit cell packing in **1** creates a helical structure through nitrate, while water molecules are arranged in a helical manner in **2** (Fig. S27 and S28, ESI[†]). Both the cubanes are symmetric in nature and possess the C2 axis along the cubane centre (Fig. S29, ESI[†]).

The mononuclear complex **3** crystallizes in the monoclinic system with the 'C2/c' space group. In this molecule copper is

bonded to N,O donor sites of two ligands disposed *trans* to each other and adopted distorted square planar geometry (Fig. 1d). The extent of distortion from square planar geometry (34.46°) has been estimated from the interplanar angle between N1-Cu1-O1 and N2-Cu1-O2 planes. The interplanar angle between *trans* disposed N1-Cu1-N1 and O1-Cu1-O1 is 89.94° . The Cu–O (1.898 Å), Cu–N (1.968 Å) bond distances and bite angles about the copper centre (O-Cu-N ; $92.54/-92.65^\circ$) are normal and lie in the range of the ideal square planar system.

The crystallographic parameters and crystal structures revealed formation of the cubanes **1** and **2** *via* oxidation and dearomatization of $\text{H}_3\text{L1}$. It is specifically copper(II) catalyzed reaction and initiated only when hydrated copper(II) salts/pre-cursors were used, not with the other metal salts. The reaction of $\text{H}_3\text{L1}$ with other metal salts [Zn(II) , Ni(II) , Co(II) and Mn(II)] yielded different products relative to **1** under similar conditions (please see ESI Fig. S30–S33[†]). Formation of the diverse products relative to **1** has also been supported by ^1H NMR spectra of Zn complexes [$\text{Zn}(\text{H}_2\text{L1})_2$] and [ZnL2]₂ derived from $\text{H}_3\text{L1}$ and $\text{H}_2\text{L2}$ (Fig. S34, ESI[†]) suggesting that transformation of ligands has not been achieved in the presence of the Zn(II) salts. IR and ^1H NMR spectral data indicated that oxidation of $\text{H}_3\text{L1}$ to $\text{H}_3\text{L1O}$ and hydrolysis of di- β -keto-aminato ligands are induced only by hydrated Cu(II) not by other metal salts.

To gain deep insight into oxidized species ($\text{H}_3\text{L1O}$) being generated during the formation of cubanes and whether it exists freely in the reaction mixture or only in the complexed form, HRMS of the reaction mixture has been acquired. It showed a feeble peak at m/z 249.1571 assignable to $\text{H}_3\text{L1O}$ (almost negligible compared to the molecular ion peak for **1**) (Fig. S35–S36, ESI[†]) and clearly suggested that the said species exists only in the complexed form. It has further been supported by ^1H NMR titration studies involving $\text{H}_3\text{L1}$ in CD_3OD with Cu(II) in D_2O . A downfield shift for the aromatic protons and greater disruption for methyl protons suggested oxidation and dearomatization of the $\text{H}_3\text{L1}$ and broadening of signals due to various protons which substantiated immediate coordination of $\text{H}_3\text{L1O}$ with copper (Fig. S37, ESI[†]). Above results clearly suggested that $\text{H}_3\text{L1O}$ does not exist freely in the reaction mixture.

As pointed out, formation of cubanes takes place in deprotonated methanolic solution of the ligands. The deprotonation of hydroxyl groups with KOH in methanol liberates water in the reaction medium. Now, the question arises that whether coordinated or solvent water molecules play significant role in the creation of cubanes *via in situ* generation of $\text{H}_3\text{L1O}$ involving oxidation and dearomatization of $\text{H}_3\text{L1}$. To affirm this, a reaction has been carried out in an anhydrous solvent (acetonitrile) using sodium hydride (NaH) as a base which is generally used for deprotonation of the alcoholic/phenolic –OH in polar aprotic solvents.¹⁵ The reaction of $\text{H}_3\text{L1}$ with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in dry acetonitrile in the presence of NaH yielded a product analogous to **1** (Fig. S38, ESI[†]), which clearly indicated a significant role of the coordinated water in oxi-

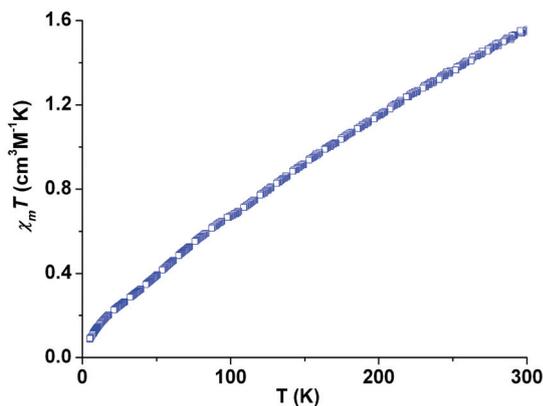


Fig. 3 Temperature dependent $\chi_M T$ data of **1** measured in an applied magnetic field of 0.3 T.

dation of **H₃L1**. To explore the role of atmospheric oxygen/moisture another reaction has been performed under a nitrogen atmosphere which also gave a product similar to **1**. This undoubtedly suggested that the reaction is unaffected by the atmospheric oxygen/moisture and ruled out their role in transformation of the ligands (Fig. S38, ESI[†]). Furthermore, if these play any role in oxidation and dearomatization of the ligands, then a cubane structure must also result from anhydrous Cu(II) salts under aerobic conditions not the mononuclear complex **3**. On the other hand, reaction of **H₃L1** with anhydrous Cu(CH₃COO)₂ in dry acetonitrile in the presence of NaH gave mononuclear complex **3** (Fig. S39, ESI[†]). Overall observations unquestionably suggested that cubanes **1** and **2** have been obtained from hydrated Cu(II) salts/precursors, while anhydrous salts gave mononuclear complex **3**.

The variable temperature (4–300 K) magnetic susceptibility of tetranuclear Cu(II) cubane (**1**) has been investigated with an applied field of 0.3 T and temperature dependent molar magnetic susceptibility for **1** (Fig. 3). At 300 K, the $\chi_M T$ value for this complex came out to be 1.57 cm³ K mol⁻¹ which is in good agreement with the theoretical value of 1.50 cm³ K mol⁻¹ for four uncoupled Cu(II) centres ($S = 1/2$, $g = 2$). As the temperature decreases the $\chi_M T$ product decreases, indicating antiferromagnetic coupling within the Cu(II) ions through oxo bridges.¹⁶

Conclusions

Through this work we have presented the synthesis of tetranuclear $|2 + 4|$ copper cubanes derived from the NOO⁻ chelating moiety by *in situ* conversion of a simple NO⁻ chelating ligand **H₃L1**. Cationic and charge neutral cubanes **1** and **2** with four exocyclic =NH₂⁺ and =NH groups, respectively, have been prepared from Cu(NO₃)₂·2.5H₂O and Cu(acac)₂·H₂O as the copper source. Formation of cubanes takes place by creation of tridentate chelating species **HL1O**²⁻ via copper mediated C–O bond formation and dearomatization of **H₃L1**. The cubanes **1**

and **2** were obtained using hydrated copper(II) salts/precursors whereas anhydrous salts gave the mononuclear complex **3**.

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