

Synthesis and structural characterization of the formate bridged Cu(II) cubane: Crystallographic evidence of atmospheric CO₂ fixation as formate in a tertranuclear Cu(II) cluster

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ABSTRACT

Fixation of atmospheric carbon-di-oxide (CO₂) by metal complexes continuously receives a great deal of attention from the viewpoint of environmental concerns. Herein, a novel tetranuclear copper (II) cluster [Cu₄ μ₃-(mhp)₄ μ₂-(HCO₂)₂] (ClO₄)₂.CH₂Cl₂ (**1**), synthesized using Methyl(6-hydroxymethyl)picolinate ligand (Hmhp) and Cu(ClO₄)₂.6H₂O in the presence of triethylamine base, is reported where atmospheric CO₂ is serendipitously trapped in the form of formate-bridging ligand. The single X-ray structural elucidation of the complex **1** reveals a Cu₄O₄ cubane cluster stabilized by four peripheral mhp ligands, all of which display μ₃-η¹: η¹: η³ binding mode (each bridging ligand link three Cu (II) ions). Moreover, the cubane core was supported by two bridging formate groups, resulted from the reduction of atmospheric CO₂. The two formate ions exhibit μ₂-η¹: η¹ binding mode, bridges two Cu(II) atoms. All the Cu(II) ions in the cubane core possess distorted octahedral coordination geometry (CuN1O5). Based on the observed Cu...Cu interactions in the Cu₄O₄ cubane core, **1** can be categorized under [2+2+2] type of classification. In addition to the synthesis and characterization of **1**, a mechanistic hypothesis for the reduction of atmospheric CO₂ to formate is also proposed to highlight the future potential of similar complexes in CO₂ fixation/conversion.

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1. Introduction

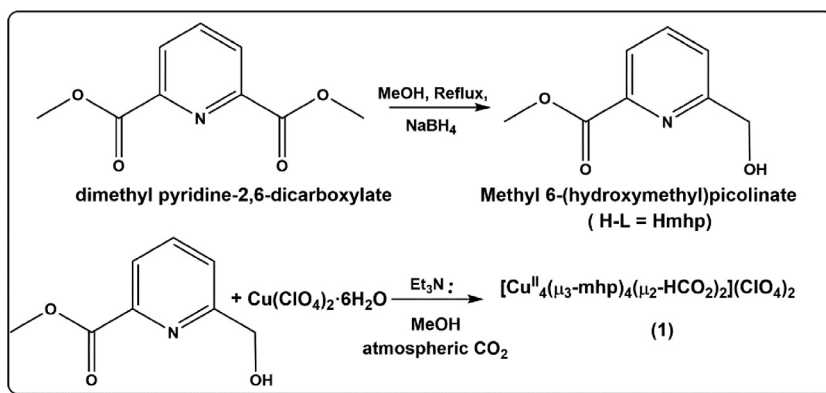
Anthropogenic carbon-dioxide (CO₂) is the largest contributor of greenhouse gases, responsible for global warming and disastrous climatic change [1]. The present average global concentration of CO₂ reaches the highest recorded levels of (> 400 ppm), posing imminent and alarming threat to environment [1,2]. To tackle this serious issue, “development of efficient methods to reduce the quantity of CO₂ produced, via storage and utilization of CO₂ [3–5]” are urgently required. However, the CO₂ activation/reduction/conversion process is not an easy task to accomplish since CO₂ is a thermodynamically stable and kinetically inert molecule. Despite the challenges related to this, chemical [6–11], photochemical [12], electrochemical [12–14] and enzymatic methods [15] methods for CO₂ fixation and/or conversion to other environmentally-benign products have been reported as sustain-

able approaches for mitigating the present situation. In that context, over the past few decades, the investigations related to the activation/incorporation of atmospheric CO₂ into several transition metal complexes have attracted significant interest [16–19]. Similarly, spontaneous activation/fixation of atmospheric CO₂ in 4f [20,21] and 3d-4f [22,23] molecular clusters were also actively investigated. Additionally, metal-organic frameworks with good CO₂ uptake capabilities have also been reported in the literature [24].

Meanwhile the trapping of CO₂ by several copper(II) complexes/clusters (dinuclear, trinuclear, and tetranuclear) [25] have received significant attention because the study of model complexes of these systems not only provide better understanding of the biological molecules [25,26] but also assist in the development of new types of materials [27,28]. Usually polydentate N-donor ligands bearing an array of suitably organized coordination pockets, are employed in conjunction with the appropriate metal-precursors for the synthesis of these clusters as these ligands offer specific geometric arrangements to the metal centres which allow to effectively capture the atmospheric CO₂ through

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Scheme 1. Synthetic route of ligand Hmhp and complex 1.

various bridging CO_2 connections [29,30]. In developing such CO_2 capturing system, the choice of copper as metal is prevalent in literature and not completely arbitrary as this inexpensive earth-abundant metal candidate provides better control the metal-ligand interaction (including CO_2) through fine-tuning of its redox property and geometrical constraints as compared to its other counterparts. Interestingly, most of previous studies demonstrated that by employing this particular type of ligands, fixation of atmospheric CO_2 takes place either as in the form of carbonate (CO_3^{2-}) or oxalate ($\text{C}_2\text{O}_4^{2-}$) or carbonate monoester ($\text{O}_2\text{COH/R}$) [29]. On the other hand, electroreduction of CO_2 to formate carried out by numerous metal-based electro-catalysts has previously been reported in the literature [31]. However, to the best of our knowledge, there are no reports on structurally characterized copper(II) clusters that fixes atmospheric CO_2 as formate reported so far regardless of the (any) ligand systems used. Lately formate is proved to be one of the valuable fuels and its applications in energy storage is well documented [31]. In regard to the importance of CO_2 activation/reduction/fixation by transition metal clusters along with poorly explored mechanistic understanding, the synthesis of molecular clusters capturing atmospheric CO_2 as formate especially based on Cu(II) as metal ions with the use of new or less developed ligands, is still desirable.

Herein, the use of methyl(6-hydroxy methyl) picolinate ligand (Scheme 1) for the synthesis of cubane shaped tetranuclear copper(II) cluster $[\text{Cu}_4 \mu_3\text{-}(\text{mhp})_4 \mu_2\text{-}(\text{HCO}_2)_2] (\text{ClO}_4)_2 \cdot \text{CH}_2\text{Cl}_2$ (**1**) is reported. The atmospheric CO_2 was trapped as formate in the complex **1** in the form of a rare formate-bridged Cu(II) cubane cluster. To best of our knowledge **1** constitutes the first crystallographic evidence of atmospheric CO_2 fixation as formate in a tetranuclear Cu(II) cluster

2. Experimental section

All Materials chemicals and solvents used for the synthesis were of analytical grade. Dimethyl pyridine-2,6-dicarboxylate, NaBH_4 , $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, triethylamine, common solvents such as methanol, dichloromethane etc. were purchased from Aldrich Chemical Co. and used as received without further purification.

2.1. Syntheses

2.1.1. Synthesis of the ligand (Hmhp)

To dimethyl pyridine-2,6-dicarboxylate (1.000 g, 5.1237 mmol) was added methanol (50 ml). To this, NaBH_4 (0.193 g, 5.1237 mmol) was added slowly over 10 min at room temperature (0°C). The mixture was then stirred for 30 min at RT, followed by reflux for 10 h. The reaction mixture was allowed to come to RT, the solvent was removed under reduced pressure. To the residue, ace-

tone was added (20 ml) and the mixture was refluxed for 1 h. Later aqueous K_2CO_3 (20 ml) was added and the mixture was re-fluxed for 1 h. The mixture was then allowed to stand at RT for 15 minutes and extracted with EtOAc (10×10 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo to yield the crude product. The crude product was then purified by column chromatography (50% EtOAc/n-hexane) to afford the title compound as a colourless solid. The compound is structurally characterized by single crystal X-ray analysis (*vide infra*). Yield: 0.650 g (82.2%). ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, 1H, pyr-H), 7.79 (t, 1H, pyr-H), 7.53 (d, 1H, pyr-H), 4.83 (s, 2H, methylene-H), 4.31 (s, 1H, -OH), 3.90 (s, 3H, methyl-H). FT-IR (cm^{-1}): 3368(w), 3099(m), 2955(m), 2898(m), 1730(s), 1677(m), 1601(s), 1521(s), 1471(w), 1446(w), 1371(s), 1222(m), 1161(m), 988(s), 788(m), 675(m). Anal. Calc. for $[\text{C}_8\text{H}_9\text{NO}_3]$: C, 57.48; H, 5.43; N, 8.38%. Found: C, 57.64; H, 5.72; N, 8.68%.

2.1.2. Synthesis of $[\text{Cu}_4 \mu_3\text{-}(\text{mhp})_4 \mu_2\text{-}(\text{HCO}_2)_2] (\text{ClO}_4)_2 \cdot \text{CH}_2\text{Cl}_2$ (**1**)

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Although we did not suffer any explosion, only a small amount of compound should be prepared, and it should be handled with caution.

To a solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.110 g, 0.299 mmol) and Hmhp (0.05 g, 0.299 mol) in 50 mL of methanol, Et_3N (0.037 g, 0.373 mmol) was added and the mixture was stirred for 1 h under refluxing condition. The solution was cooled and filtered. The precipitate was separated, dried and recrystallized from dichloromethane. Blue block-shaped single crystals of **1** suitable for X-ray analysis was obtained from crude gummy mass after 15 days. Yield: 0.040 g (41.7%, based on Cu), M.P. 154°C . FT-IR (cm^{-1}): 3400(w), 3214(m), 3060(s), 2852(m), 1723(m), 1620(w), 1562(s), 1382(s), 1161(w), 986 (s), 796(m), 674(m), 482(w), 396(m). Anal. Calc. for $[\text{C}_{35}\text{H}_{36}\text{Cl}_4\text{Cu}_4\text{N}_4\text{O}_{24}]$: C, 32.52; H, 2.81; N, 4.33. Found: C, 32.70; H, 2.97; N, 4.76.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Flash EA Series 1112 CHNS Analyzer. Fourier-Transformed Infrared spectra (FT-IR) were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. The ^1H solution NMR spectra were recorded on a Bruker DRX 400 instrument. Melting points were measured by using a Fargo MP-2D melting point apparatus.

2.3. X-ray crystallography

Single crystal X-ray data collection was carried out at 298 (2) K (**1**) and 100 (2) K (**2**) on a Bruker Smart Apex CCD area detector system (λ (Mo $K\alpha$) = 0.71073 Å), with a graphite monochromator.

Table 1
Crystal structure parameters corresponding to Hmhp and Cu(II)-complex (1).

Compound	Hmhp (H-L)	Cu(II)-complex (1)
Chemical formula	C ₈ H ₉ NO ₃	C ₃₅ H ₃₆ Cl ₄ Cu ₄ N ₄ O ₂₄
Formula weight	167.16	1292.64
Temperature	298(2) K	100(2) K
Crystal system	Monoclinic	Orthorhombic,
Space group	P2(1)/c	P2(1)2(1)2(1)
a (Å)	7.0423(11)	13.3088(10)
b (Å)	13.215(2)	16.2797(13)
c (Å)	9.1440(14)	20.6098(16)
α (°)	90	90
β (°)	112.062(2)	90
γ (°)	90	90
V (Å³)	788.7(2)	4465.4(6)
Z	4	4
ρ (calc.) mg m⁻³	1.408	1.923
μ (Mo Kα) mm⁻¹	0.109	2.214
2θ_{max} (°)	24.95	25.05
R(int)	0.0350	0.0817
Completeness to θ	99.6 %	99.8 %
Data / param.	1372 / 112	7879 / 644
GOF	1.084	1.114
R1 [F > 4σ(F)]	0.0469	0.0482
wR2 (all data)	0.1171	0.1030
max. peak/hole (e.Å⁻³)	0.147 / -0.135	0.814/-0.519

The data were reduced using SAINT PLUS [32] and the structures were solved using SHELXS-97 [33] and refined using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Selected crystal parameters for 1–2 are given in Table 1.

3. Results and discussions

3.1. Fourier transform infrared spectra (FT-IR)

In the FT-IR spectra of complex **1**, the absorption bands found in the region of 3060 cm⁻¹ indicates the presence of C–H stretching frequencies of the mhp ligand. Further characteristic peaks observed in the range of 1382–1723 cm⁻¹ which can be assigned to ν(O–C=O) stretching frequencies of mhp ligand and formate group present in the Cu(II) cluster [34,35]. The bands corresponding to Cu–N and Cu–O bonds are observed at 482 and 396 cm⁻¹ respectively. The FT-IR frequencies of the complex are consistent with the earlier reports [36].

3.2. Description of crystal structures

The crystals of methyl 6-(hydroxymethyl) picolinate (Hmhp) were grown from slow evaporation of ethyl acetate. The crystals were solved in monoclinic, P2(1)/c space group. The X-ray crystal structure of the ligand (Hmhp, H-L) along with atom numbering is shown in Fig. 1. A strong O–H...N interaction (Fig. 2) with d_{H...N}, 2.095 Å, and <OHN 162.15° Å (symmetry operator x,1.5-y,-0.5+z) exists between the CH₂OH group and pyridine nitrogen atom of adjacent ligand molecules along the crystallographic c-axis to form 1D supramolecular chain.

The single X-ray structural elucidation of the complex **1** reveals a Cu₄O₄ distorted cubane like structural motif. The complex **1** crystallizes in triclinic P-1 space group along with two perchlorate anions and one dichloromethane molecule in the crystal lattice, therefore confirming the molecular formula [Cu₄(μ₃-mhp)₄(μ₂-HCO₂)₂](ClO₄)₂.CH₂Cl₂. The overall charge on the cluster is neutralized and obeys the electric neutrality principle. Molecular structure together with the atom labelling around the metal centres for the complex **1** are depicted in Fig. 3. Crystal data and refinement parameters are given in Table 1. The tetranuclear cluster

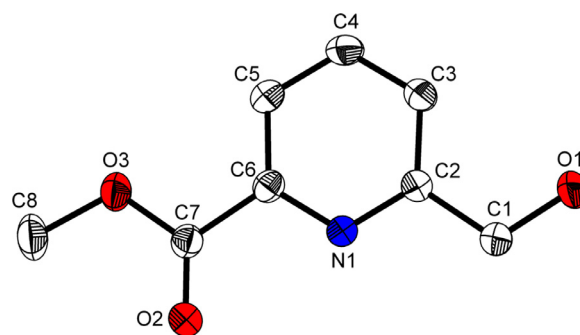


Fig. 1. ORTEP plot of the Hmhp (30% probability thermal ellipsoids). For the sake of clarity, all hydrogen atoms have been omitted.

featuring a cubane core (Fig. 3) comprised of four copper atoms and four (μ₃-O) alkoxide bridges occupying the alternating corners of a cube respectively. Alternatively, structure **1** can be visualized as two interpenetrated Cu₄ and O₄ tetrahedrons. Similar structures on tetranuclear oxo-bridged Cu(II) cubane clusters stabilized by variety of bridging ligands have previously been reported in the literature [37–40]. The periphery of the cubane core was stabilized by four μ₃-mhp ligands and two μ₂-formate groups. The four mhp ligands exhibit both chelating as well as bridging mode connectivity (μ₃-η1: η1: η3) towards the metal centers, each bridging three three Cu (II) ions of the cubane. The two formate ion (HCOO⁻) is produced in situ from CO₂ (*vide infra*), behaves as a deprotonated bidentate ligand. Each formate ion displays μ₂-η1:η1 binding mode and bridges a pair of Cu(II) atoms (Cu1,Cu4 and Cu2,Cu3) that resides on faces of the cube. This kind of bridging mode by formate ions was previously established in some copper formate paddle-wheel compounds and formate supported homometallic and heterometallic molecular assemblies [41–44]. All the Cu(II) ions in the cubane core possess same coordination environments (CuN1O5) with distorted octahedral shape, Cu1 is subjected for discussion here. The octahedral geometry around the Cu1 is achieved by one nitrogen atom (N1), four oxygen atoms (O1, O2, O3 and O9) all of which belong to mhp ligand and sixth coordination centre is occupied by the oxygen atom (O6) of the formate ligand. The Cu–O bond lengths and Cu–O–Cu bond angles in Cu₄O₄ cubane core are shown in Fig. 4. Similarly, Cu–N and Cu–O (other than core) bond distances are in the order of 1.991–2.003 Å and 1.931–2.380 Å, all the bond metric values are in good agreement with a relevant report that was published earlier [45].

Further, molecular self-assembly in the presence of bridging ligands resulted in the formation of two fused five-membered chelate rings at each copper centre. The dihedral angles between these various five membered ring mean planes ranges from 2.85 to 8.90 Å (Fig. 5). Similarly, the torsion angles between these chelate rings were in the range ±173.7–179.8° confirming that these two five membered rings were slightly deviated from planarity.

Based on the available literature, Cu₄O₄ cubane clusters can be classified into type I (2+4 class), type II (4+2 class) and type III (6+0 class) depending on Cu...Cu inter-atomic distances (by Ruiz [46,47] in the Cu₄O₄ cubane core (Fig. 6). According to Ruiz et al. [47,48], compounds of type I (2+4 class) exhibit 2 short and 4 long Cu...Cu distances while the complexes of type II (4+2 class) display 4 short and 2 long Cu...Cu distances and the compounds of type III (6+0 class) contain six equivalent Cu...Cu distances. However type III (6+0 class) compounds are scarce and are very limited when compared with the others [48]. However, in the present case, close inspection of the Cu...Cu interactions of Cu₄O₄ cubane core in our case reveals that there are two short (Cu1...Cu4 and Cu2...Cu3), two medium (Cu1...Cu3 and Cu2...Cu4), and two long

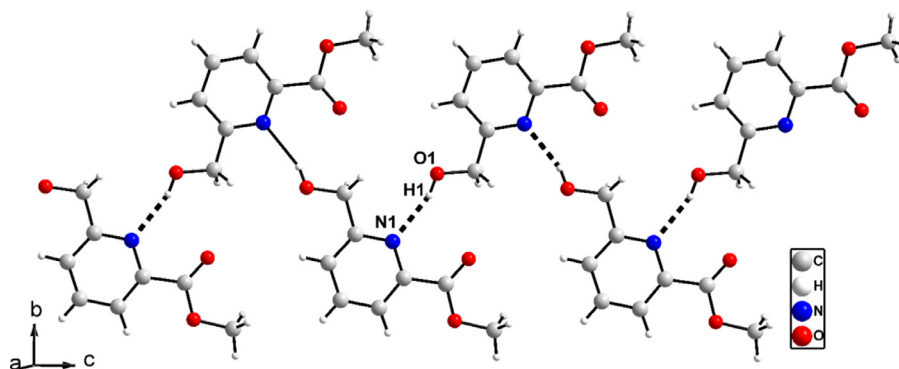


Fig. 2. Inter molecular hydrogen bonding interactions in Hmhp.

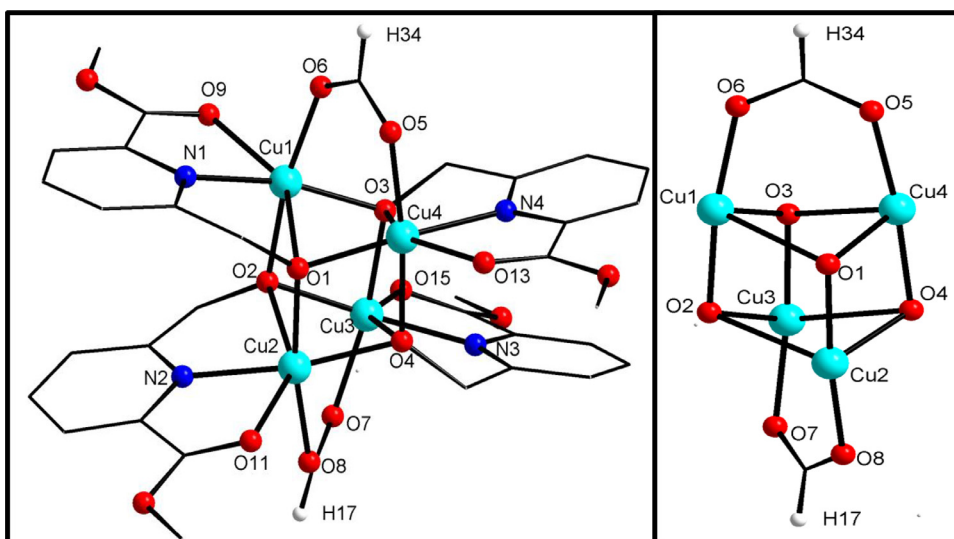


Fig. 3. Molecular structure of **1** (left) and the perspective view of cubane core with bridging formate ligands (right).

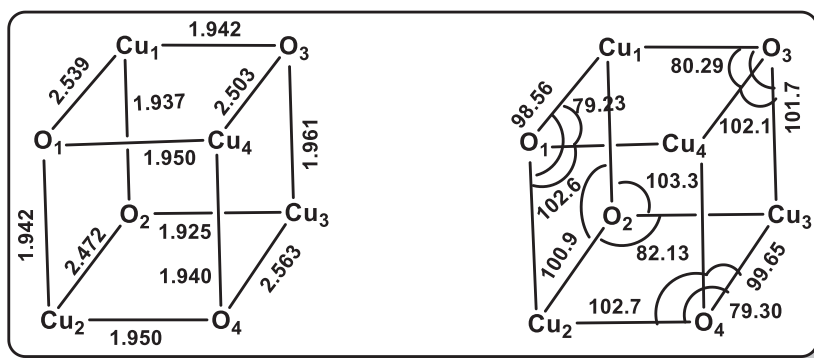


Fig. 4. Schematic Cu-O bond lengths and Cu-O-Cu bond angles of the cubane Cu_4O_4 core for **1**.

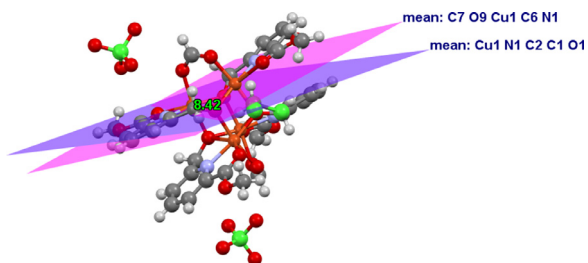


Fig. 5. Dihedral angles between two five membered ring mean planes.

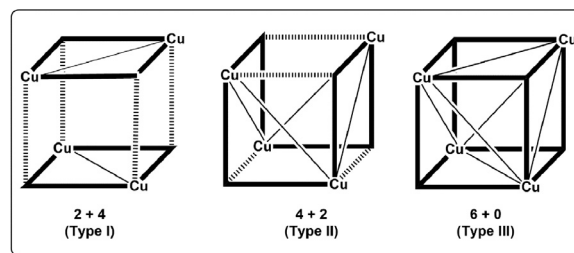


Fig. 6. Classification of cubane core based on Ruiz's model of classification.

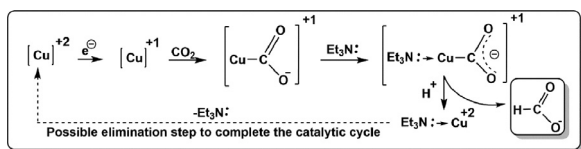


Fig. 7. Proposed mechanism for CO₂ reduction by **1**.

Table 2

Non-bonding Cu...Cu interactions (Å) in the Cu₄O₄ cubane core.

Non-bonding Cu—Cu interactions	Bond-length (Å)
Cu1...Cu2	3.419
Cu1...Cu3	3.029
Cu1...Cu4	2.897
Cu2...Cu3	2.918
Cu2...Cu4	3.039
Cu3...Cu4	3.464

(Cu1...Cu2 and Cu3...Cu4) intermetallic distances (Table 2) which, therefore, can be attributed as [2+2+2] Cu₄O₄ cubane. Though this is not unprecedented [49,50], this shows of the possibility of various cubane structures beyond Ruiz's classification via judicious selection of ligands and their interplay with the metal ions.

3.3. Proposed mechanism

During the synthesis of complex, the incorporation of CO₂ into the complex in the form of formate ion has made the complex unique when compared to other CO₂ fixation complexes/clusters (29). While in most of the cases, CO₂ was trapped as carbonate and oxalate into the metal complex, the metal-complex catalyzed electroreduction of CO₂ to formate [51] offers some idea regarding the underlying mechanism. We hypothesized that initially the Cu(II) metal centre is reduced to Cu(I) in the presence of redox-active ligand [52]. The reduced metal centre activates CO₂ via electron transfer and forms Cu-CO₂ adduct. In the next step, the base (in this case excess triethylamine used in reaction to synthesize the complex) assists to generate metal carboxylate intermediate. The intermediate is then converted to the formate ion (Fig. 7) by accepting the proton from the solvent and releases triethylamine bound Cu(II). Under the reaction condition, triethylamine bound Cu(II) may liberate the triethyl amine to form Cu(II) to continue the catalytic cycle. The released formate ions spontaneously fixes on to the copper centers of the cube to yield [Cu₄(μ₃-mph)₄(μ₂-HCO₂)₂](ClO₄)₂. Though details mechanistic investigation is still due, the present hypothesis is strongly supported by some recent reports on CO₂ activation/reduction by Fe(porphyrin) [51], Pd(triphosphine) [53], Ni(cyclam) [54] and Co(tetrapyrroline) [55] complexes, where in the experimental finding suggests that an appropriate combination of Lewis acid and Lewis base plays an important role in promoting electron transfer from the reduced metal center to CO₂.

4. Conclusion

In this paper a serendipitous discovery of a self-assembly comprising of tetranuclear formate-bridged copper(II) cluster [Cu₄(μ₃-mph)₄(μ₂-HCO₂)₂](ClO₄)₂ supported by mph ligands and formate anions is reported. Single crystal X-ray diffraction analysis reveals that the complex **1** contains Cu₄O₄ cubane-like scaffold and belongs to "cubane [2+2+2] class" of Cu₄O₄ structure. We anticipated that the formate anion is generated from atmospheric CO₂ during the synthesis of the complex in the presence of triethylamine base. To best of our knowledge this result represents the first example where atmospheric CO₂ is suc-

cessfully trapped as formate in tetranuclear Cu(II) cluster. Our current research is focussed on developing methods for the removal of formate groups and experimenting with modified 6-(hydroxymethyl)picolinate (Hmph) ligands to investigate whether the complexes can be made more reactive with CO₂. We expect that the present as well as the ongoing research activities will help making **1** (or it's modified derivatives) suitable as catalytic candidates for conversion of CO₂ to other valuable products, thus making a significant contribution towards addressing the present challenges related to CO₂ fixation/conversion.

Credit author statement

P.V.V.N. Kishore and J.A. Kumar: Synthesis, structural characterization and writing the manuscript, contributed equally. A. Goswami: Analysing the data, writing and revising of the manuscript. B.K. Tripuramallu, R. Kishore and Jajula Kashanna: X ray diffraction analyses for ligand and cluster.

Supplementary data

CCDC 2005914 and 2005915 contain the supplementary crystallographic data for ligand and complex respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223336033.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2020.129064](https://doi.org/10.1016/j.molstruc.2020.129064).

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