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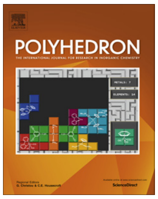

Ligand exchange reaction in open-face $[Cu_4(\mu_3\text{-}OH)_2]$ cubane aggregates: Synthesis, structural change and difference in magnetic interactions

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ABSTRACT

Distorted $[Cu_4(\mu_3\text{-}OH)_2]$ cubane type arrangements, one tetracationic and one neutral, have been achieved as $[Cu_2(\mu\text{-}H_2bpmp)(\mu_3\text{-}OH)(H_2O)]_2(SO_4)_2\cdot 3H_2O\cdot CH_3OH$ (**1**) and $[Cu_2(\mu\text{-}Hbpmp)(\mu_3\text{-}OH)(\mu_{1,3}\text{-}O_2CCF_3)]_2\cdot H_2O\cdot 2CF_3CO_2H$ (**2**) [H_3bpmp = 2,6-bis-[(3-hydroxypropylimino)methyl]-4-methylphenol] from the reactions of H_3bpmp with $CuSO_4\cdot 5H_2O$ and $Cu(CF_3CO_2)_2\cdot xH_2O$ in the presence of NEt_3 in MeOH medium. Two types of apical interactions of the Cu^{II} ion with H_2O and $CF_3CO_2^-$ induced hydroxido-bridge supported aggregation of $\{Cu_2\}$ precursors. In MeOH solution, the reaction of **1** with $CF_3CO_2^-$ resulted in **2**, showing a ligand-exchange reaction, leading to different Cu···O separations in the space on the open faces of the cubane structure. Magnetic susceptibility measurements (1.8–350 K) revealed stronger antiferromagnetic interactions in **1**, where the average in plane Cu–O–Cu angle is 100.4°, than for **2**, having a smaller Cu–O–Cu angle of 97.2°.

1. Introduction

Use of *in situ* generated and externally added auxiliary bridges to control self-aggregation synthesis has gained interest in recent years, wherein the initially formed metal ion-ligand units undergo aggregation reactions in solution to provide unique structures in the solid state and further reactivity in solution [1,2]. In this regard, the exchange of ligands on any aggregate without degrading the basic structure would be of interest. The reaction outcome of phenoxido-bridged $\{Cu_2\}$ fragments around *in situ* generated hydroxido groups for aggregated product formation would be of current interest. The reaction conditions, choice of primary ligand and use of other groups, solvent medium and added bases can play determining roles for the process [3–6]. Ligand bound multimetallic coordination compounds, partly designed and partly obtained by serendipity, can display interesting structures, properties and functions such as single-molecule magnet behavior [7–10], catalysts for organic reactions [11,12], and, in several instances, show structural and functional connection to several metalloenzymes [12–14]. Thus, we have focused our attention on new $\{Cu_2\text{-ligand}\}$ precursors having several vacant coordination sites buried by counter anions or solvent molecules for the assembly reactions of these preformed species. The number and nature of the auxiliary ligands control the aggregation process for five different structures in $[Cu_4]$ aggregates. These are stepped cubane, fused partial dicubane, cubane, open cubane and tetrahedron. In the literature, examples of open face $[Cu_4]$ cubane topology having irregular structures are rare [15,16]. In this work two such aggregates and the conversion to a new aggregate through a ligand displacement reaction have been reported (1 and 2 in Scheme S1).

The hydroxido group is known to function as a unique bridge to connect several metal ions (Scheme S2) [17–19] and can clip two or more $\{Cu_2\text{-ligand}\}$ fragments. The carboxylate groups show a variety of coordination modes, while satisfying the coordination demands of the metal ions and charge neutralization with the complexes (Scheme S2) [20–25]. Depending upon the availability of the *basal* or *apical* sites around these Cu^{II} ions, different modes of coordination of the carboxylate anions show a variety of magnetic exchange interactions by modulating the Cu···Cu distance and Cu–O–Cu bridge head angle.

During the last two decades, numerous $[Cu_4]$ complexes bound to ligands of different types and numbers have been reported [15,26–29]. In trying (i) to establish the role of the phenoxido

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groups of the ligand of choice in stabilizing the $\{Cu_2\}$ entity, (ii) to assemble such fragments by hydroxido groups, (iii) to assist the aggregation reaction and (iv) to prepare and study new forms of $[Cu_4]$ aggregates, we explored the reactivity 2,6-bis-[(2-hydroxypropylimino)methyl]-4-methylphenol (H_3bpmp) (Chart 1) [30] towards $CuSO_4·5H_2O$ and $Cu(CF_3CO_2)_2·xH_2O$.

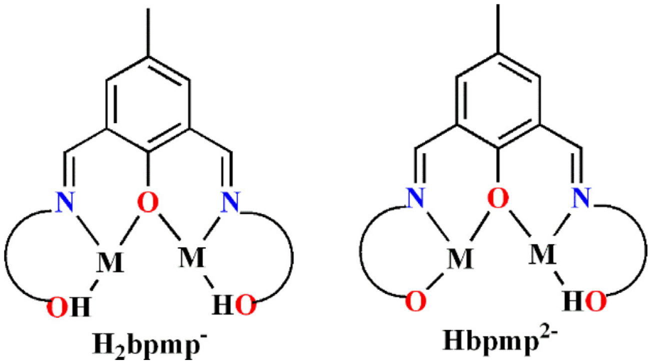
The alcohol donor bearing side arms play an important role in the reaction by blocking the available coordination sites in solution. Use of the closely related ligand H_3bemp (Chart 1, right, 2,6-bis-[(2-hydroxyethylimino)methyl]-4-methylphenol) having one carbon shorter alcohol arms, gave $[Cu_8]$ [31], $[Cu_2]_\alpha$ [32], $[Na_2Cu_4]$ [33] and $[Mn_{12}Cu_8]$ [34] complexes. In this work two forms of the ligand, H_2bpmp^- and $Hbpmp^{2-}$, were utilized for two $[Cu_4]$ complexes (Scheme 1).

The formation of $[Cu_4]$ complexes is reported for $[Cu_2(\mu\text{-}H_2bpmp)(\mu_3\text{-}OH)(H_2O)]_2(SO_4)_2·3H_2O·CH_3OH$ (**1**) and $[Cu_2(\mu\text{-}Hbpmp)(\mu_3\text{-}OH)(\mu_{1,3}\text{-}O_2CCF_3)]_2·H_2O·2CF_3CO_2H$ (**2**). Coordination of solvent water derived μ_3-OH anions at the corners of the two open-face cubane structures stabilizes the product. From **1** generation of **2** was induced by a facile ligand substitution reaction. Herein *apically* bound H_2O molecules were replaced by $CF_3CO_2^-$ groups with compaction of the open face causing a change in the Cu–OH–Cu angles and magnetic interactions. Earlier we have shown that coordination of H_2bpmp^- to two copper(II) centers resulted in a $(\mu_4\text{-}O)(\mu\text{-}PhCH_2CO_2)$ motif in a $[Cu_4]$ complex [35], whereas use of AcO^- anions resulted in a different type of aggregation for a $[Cu_5]$ complex [36].

2. Experimental

2.1. Materials

The chemicals used were obtained from the following sources: 3-amino propan-1-ol from Aldrich Chemical Co. Inc., copper(II) sulfate from S.D. Fine Chem. (India), and triethylamine from Merck (India). 2,6-Diformyl-4-methylphenol (2-hydroxy-5-methyl-benzene-1,3-dicarbaldehyde) was prepared following a literature procedure with appropriate modification [37]. Hydrated copper(II) trifluoroacetate, $Cu(CF_3CO_2)_2·xH_2O$ was prepared from the reaction of basic copper(II) carbonate, $CuCO_3·Cu(OH)_2$ (AR grade, E. Merck, India) with 60% trifluoroacetic acid (AR grade, E. Merck, India), followed by slow evaporation on a steam bath. It was then filtered through a fine glass frit and stored in a $CaCl_2$ desiccator. All other chemicals and solvents were reagent grade materials and were used as received without further purification.



Scheme 1. Observed binding modes of H_2bpmp^- and $Hbpmp^{2-}$.

2.2. Synthesis

2.2.1. The ligand H_3bpmp

To a CH_3OH solution (20 mL) of prepared 2,6-diformyl-4-methylphenol (1.0 g, 6.1 mmol), 3-amino-1-propanol (0.91 g, 12.2 mmol) was added in air at room temperature (28 °C) and stirred for 2 h to give an orange colored gummy product after complete evaporation of the reaction solvent in air for 12 h. The gummy mass of H_3bpmp was washed copiously with water and dried over P_4O_{10} in a $CaCl_2$ charged desiccator. The product was later used directly without undergoing further purification steps. Yield: 1.32 g (78%).

*2.2.1.1. $[Cu_4(\mu\text{-}H_2bpmp)_2(\mu_3\text{-}OH)_2(H_2O)_2](SO_4)_2·3H_2O·CH_3OH$ (**1**).* To a CH_3OH solution (20 mL) of H_3bpmp (0.278 g, 1.00 mmol) a CH_3OH solution (10 mL) of $CuSO_4·5H_2O$ (0.500 g, 2.00 mmol) was added slowly, followed by dropwise addition of NEt_3 (0.139 mL, 0.101 g, 1.00 mmol) and the resultant mixture was stirred for 2 h at room temperature. The solvent was evaporated in air to give a green solid, which was isolated, washed with cold methanol and dried under vacuum over P_4O_{10}. It was redissolved in MeOH and slow evaporation of the solvent gave nice green crystals suitable for X-ray structure analysis after two weeks. Yield: 0.428 g, 74%. *Anal.* Calc. for $C_{31}H_{58}Cu_4N_4O_{22}S_2$ (1157.05 g mol^{-1}): C, 32.18; H, 5.05; N 4.84. Found: C, 32.02; H, 5.11; N, 4.72%. Selected FT-IR bands (KBr, cm^{-1}; s = strong, vs = very strong, m = medium, w = weak, br = broad): 3383(br), 2924(m), 1639(vs), 1560(s), 1458 (m), 1339(m), 1236(w), 1118(vs), 984(w), 829(w), 767(w). Molar conductance, Λ_M (CH_3OH solution, Ω^{-1} cm^2 mol^{-1}): 165. UV–Vis

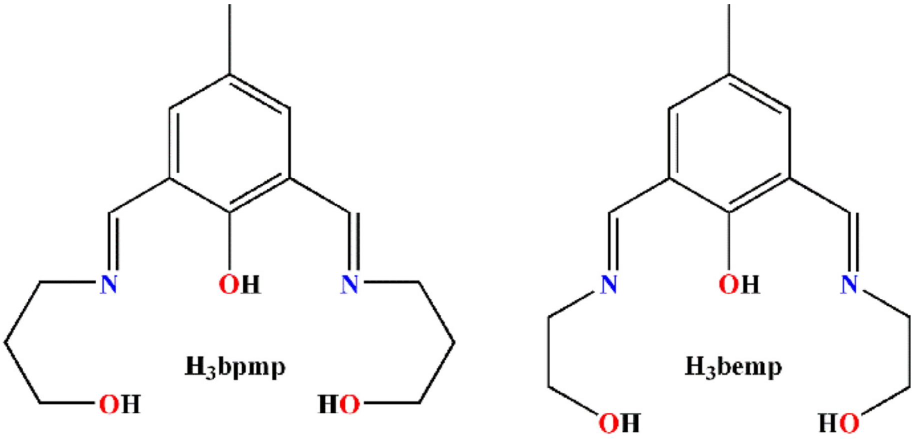


Chart 1. H_3bpmp and H_3bemp.