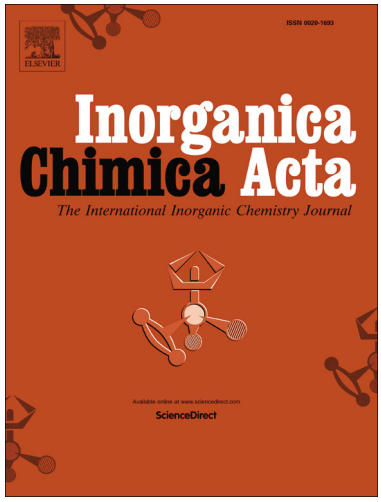

Trinuclear Cu(II) complexes from the classic $[Cu_2(RCOO)_4(H_2O)_2]$ lantern complex and pyrazole: a DFT modelling of the reaction path

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Trinuclear Cu(II) complexes from the classic $[Cu_2(RCOO)_4(H_2O)_2]$ lantern complex and pyrazole: a DFT modelling of the reaction path.

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Abstract

A plausible path for the $Cu_3(\mu_3\text{-}OH)(\mu\text{-}Pz)_3$ core formation is herein proposed by theoretically modelling the reaction in water between $[Cu_2(RCOO)_4]_n$, (R = $CH_3(CH_2)_2$) and HPz, which yields the hexanuclear species $[\{Cu_3(\mu_3\text{-}OH)(\mu\text{-}Pz)_3(RCOO)_2(CH_3OH)(H_2O)\}_2]$. We focused on the **A** → **B** reaction (**A** = $[Cu_2(RCOO)_4(H_2O)_2]$; **B** = $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}Pz)_3(RCOO)_2(CH_3OH)(H_2O)]$) with the final goal of pinpointing stable intermediates, tightened by experimental conditions, by exploiting the outcomes of numerical experiments carried out in the habit of the density functional theory.

Keywords: trinuclear copper complexes, DFT calculations, reactivity

1. Introduction

Copper is an essential bioelement usually present as polynuclear assemblies in some metallo-enzymes responsible for catalytic processes in living organisms [1],[2]. Among them, trinuclear triangular Cu(II) arrays are present in some multicopper oxidases [3] as laccase or ascorbate oxidases, which catalyse the four-electron reduction of O_2 to H_2O [4]. As such, biomimetic inorganic chemistry methodologies have shown promise in synthesizing active sites' structural and/or functional analogues [5]; i.e., molecular models [6] able to "approach or duplicate the biological unit in terms of composition, ligand types, structure, and oxidation level(s)" [7]. These analogues are particularly useful to look into active sites' structural parameters and electronic properties [1],[5], both of them of paramount importance to elucidate the structure/reactivity relationships. Besides bioinspired applications, the Cu(II) coordinative flexibility coupled to the conceivable presence of carboxylates [8], may lead to the generation of different assemblies, ranging from mononuclear complexes to supramolecular coordination polymers or Metal Organic Frameworks (MOFs) [9].

In the last two decades several triangular Trinuclear Cu(II) Complexes (hereafter, TCCs) containing the $Cu_3(\mu_3\text{-}OH)(\mu\text{-}Pz)_3$ core (Pz = pyrazolate anion) have been reported and structurally

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