



Anion dependent supramolecular architectures in Cu(II) complexes containing N₂O-donor Schiff-base and 4,4'-bipyridine ligands: Structural analyses and theoretical studies



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ABSTRACT

Three new copper(II) complexes, [Cu₂L₂Cl₂(4,4'-bpy)]·2.7H₂O (**1**), [CuL(4,4'-bpy)(H₂O)]NO₃ (**2**) and [CuL(4,4'-bpy)(H₂O)]ClO₄ (**3**), where HL = 1-[1-(2-Dimethylamino-ethylimino)-ethyl]-naphthalen-2-ol, have been synthesized and characterized by elemental analysis, IR, UV-Vis spectroscopy and single crystal X-ray diffraction studies. Complex **1** is a centrosymmetric dinuclear species in which 4,4'-bipyridine acts as bridging bidentate linker between the two copper(II) ions whereas, complexes **2–3** are rare mononuclear complexes in which the 4,4'-bpy ligand shows monodentate coordination mode stabilized by H-bonding interactions through its electronegative non-coordinated N-atom. These interactions involve imine and methylene hydrogen atoms of the Schiff-base ligand for **2**, whereas a single H-bond with one of the hydrogen atoms of the coordinated water is established in **3**. In addition, several non-covalent interactions like hydrogen bonding and π -based interactions (C–H/ π , anion– π and π – π stacking) are also observed in crystal packing of all three complexes. These interactions have been investigated by means of DFT calculations and assigned with discrete interaction energies. The strong influence of the coordination of the 4,4'-bpy ligand to the copper(II) centers upon the binding strength of the π -based interactions has also been demonstrated.

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1. Introduction

Non-covalent interactions between molecules are weak intermolecular contacts that play an important role in biological systems and govern the physicochemical properties of molecular systems in the condensed phase [1–10]. Conventional X–H...Y and non-conventional C–H...X (X or Y = F, Cl, O, N, S) hydrogen bonding, C–H/ π , cation– π , anion– π and π ... π stacking interactions are very well known non-covalent interactions. H-bonds play a central role in the structure, function, and dynamics of chemical and biological systems [11]. Cation... π interactions are supposed to be decisive in the ion selectivity of potassium channels [12–13] whereas anion... π interactions support the theoretical

prediction and promising proposal for use of anion receptors in molecular recognition [14–19]. π ... π interactions are responsible in the folding of proteins [20–21] in the structure of DNA. Thus, these interactions are crucial in crystal engineering for the design of functional materials [22].

The formation of a given supramolecular assembly can be affected by many factors, such as the choice of ligand system [23–28], counter anions [29–30], metal ions [31–34], solvent [35–37], temperature [38], etc. Among them, the choice of ligand system and the counter anions are two important factors. If the ligand contains either electron rich or electron deficient π -electron system and quite a few electronegative atoms then the resulting assembly can be stabilized in solid state through various non-covalent forces like H-bonds, π ... π stacking, anion– π and C–H/ π interactions [39–44]. The Schiff base ligand derived from a naphthalene moiety that contains an extended π -system and an electron deficient 4,4'-bipyridine (4,4'-bpy) moiety that contains neutral and

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rigid N-donor sites are excellent candidates to construct supramolecular architectures as the aromatic hydrogen atoms of 4,4'-bpy moiety could participate in C–H... π interactions with π -system of a naphthalene moiety. Besides, the electron deficient pyridine ring of the 4,4'-bpy ligand is well suited for interacting with an electron rich entities to furnish well known anion- π , lone-pair- π and π - π interactions. It is important to mention that the 4,4'-bpy moiety commonly acts as a bridging linker but its monodentate coordination is also well known. The monodentate coordination of the 4,4'-bpy can usually be effected if its non-coordinated N-atom is (i) protonated [39–40,45–46] or (ii) participates in H-bond formation [47–48]. On the other hand, the rational selection of counter anions is very important because the coordinating ability/involvement in non-covalent interactions of anions can control the final supramolecular assembly.

In the present work, we report syntheses, characterizations, X-ray structures and theoretical calculations of three copper(II) complexes using a tridentate N₂O donor Schiff base ligand derived from naphthalene moiety and 4,4'-bpy as co-ligand by changing the counter anions (Cl⁻, NO₃⁻ and ClO₄⁻). Complex [Cu₂L₂Cl₂(4,4'-bpy)]·2.7H₂O (**1**) is a 4,4'-bpy bridged dimer with coordinated chloride anions and Schiff base ligands, whereas complexes [CuL(4,4'-bpy)(H₂O)]NO₃ (**2**) and [CuL(4,4'-bpy)(H₂O)] ClO₄ (**3**) are discrete mononuclear compounds in which 4,4'-bpy acts as monodentate ligand (Scheme 1). The assemblies observed in the solid state architectures of compounds **1–3** show different types of non-covalent interactions. We have performed theoretical DFT calculations at the BP86-D3/def2-TZVP level of theory in order to analyze the various non-covalent interactions observed in the crystal packing (like hydrogen bonds, anion- π , C–H/ π and π - π interactions), as well as the influence the coordination of the 4,4'-bpy ligand to the copper(II) centers on the π -based interactions.

2. Experimental

2.1. Starting materials

All the chemicals including N,N-dimethylethylenediamine, *o*-hydroxynaphthaldehyde and 4,4'-bipyridine were purchased from Lancaster and were of reagent grade. They were used without further purification.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

2.2. Synthesis of Schiff base (HL) 1-[1-(2-Dimethylamino-ethylimino)-ethyl]-naphthalen-2-ol

The tridentate Schiff base ligand (HL) was prepared by the condensation of *o*-hydroxynaphthaldehyde (1.720 g, 10 mmol) and N,N-dimethylethylenediamine (1.09 mL, 10 mmol) in methanol (20 mL) under reflux for 1 h following the literature method [49]. The resulting dark yellow solution was then used directly for formation of the title complexes.

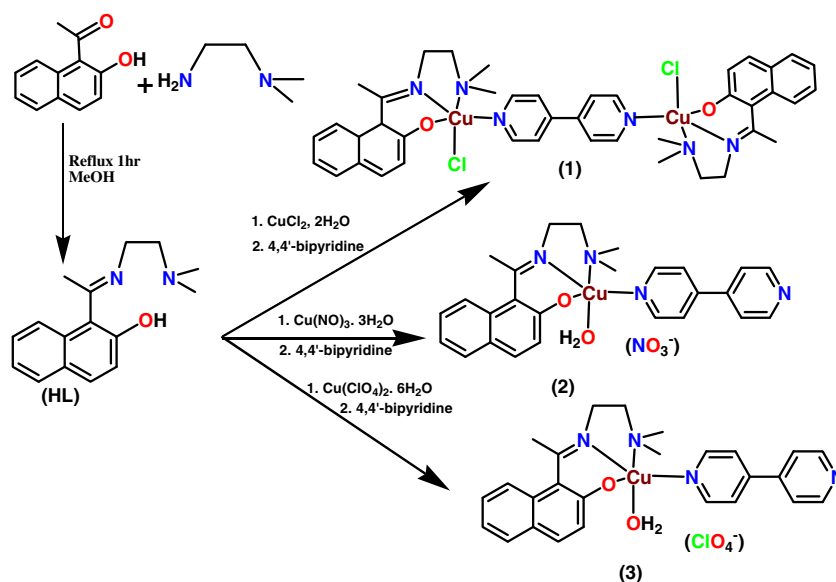
2.3. Synthesis of [Cu₂L₂Cl₂(4,4'-bpy)]·2.7H₂O (**1**)

A methanolic solution (20 mL) of CuCl₂·2H₂O (0.34 g, 2 mmol) was added to a methanolic solution of HL (2 mmol, 5 ml) with constant stirring. Then a methanolic solution (1 mL) of 4,4'-bipyridine (0.156 g, 1 mmol) was added to the mixture. The deep green colored mixture was stirred for 1 h at room temperature. It was then filtered and allowed to stand overnight at open atmosphere. Deep green needle of complex **1** suitable for X-ray diffraction were obtained by slow evaporation of solvent after 1 day at room temperature. The compound was washed with diethyl ether and dried in a desiccator containing anhydrous CaCl₂, then characterized by elemental analysis, spectroscopic methods and X-ray diffraction.

Compound **1**: Yield: 782 mg. (86 %). *Anal.* Calc. for C₄₀H₄₂Cl₂Cu₂N₆O_{4.7} (879.36): C, 54.59; H, 4.81; N, 9.55. Found: C, 54.48; H, 4.93; N, 9.52%. IR (KBr, cm⁻¹) bands: 2862w, 1623s, 1410m, 1358m, 828m and 749w. UV-Vis, λ_{\max} (nm) in acetonitrile: 596, 365, 298 and 271.

2.4. Syntheses of [CuL(4,4'-bpy)(H₂O)]NO₃ (**2**) and [CuL(4,4'-bpy)(H₂O)] ClO₄ (**3**)

Complexes **2** and **3** were synthesized by following a procedure similar to that of **1**, but varying counter anions and the stoichiometric ratios of reactants. The Cu(NO₃)₂·3H₂O (480 mg, 2 mmol) precursor was dissolved in methanol (20 mL) and then a methanolic solution (2 mL) of HL (2 mmol) followed by the methanolic



Scheme 1. Formation of the complexes (**1–3**).

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