



## Synthesis, structure, solution and DFT studies of a pyrazine-bridged binuclear Cu(II) complex: On the importance of noncovalent interactions in the formation of crystalline network



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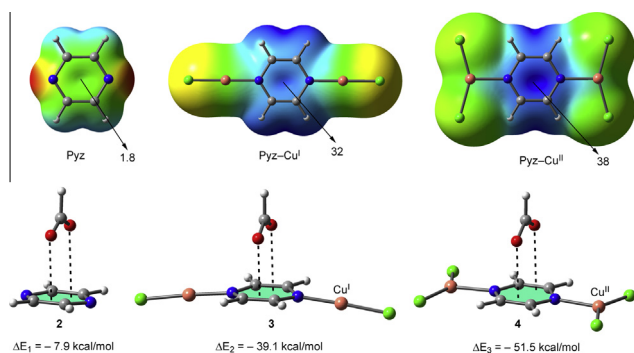
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### GRAPHICAL ABSTRACT

A new pyrazine-bridged binuclear Cu(II) complexes with formulae of  $[\text{Cu}_2(\text{chel})_2(\text{pyz})(\text{H}_2\text{O})_4]$ , (**1**, pyz = pyrazine,  $\text{H}_2\text{chel}$  = chelidamic acid), has been synthesized and characterized by elemental analyses, IR spectroscopy and solution studies. Hydrogen bonding and  $\text{C}-\text{O} \cdots \pi$  interactions link the binuclear Cu(II) complex generating the 3D infinite network. These assemblies are described and analyzed by means of density functional theory (DFT) calculations since they play an important role in the construction of three-dimensional supramolecular frameworks. A comparison between the stoichiometry of the crystalline compounds and the most abundant species of that detected in solution phase clearly reveals that the most abundant species existing in aqueous solution possesses a stoichiometry similar to these compounds obtained in the single crystal X-ray diffraction studies.



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### ABSTRACT

A pyrazine-bridged binuclear Cu(II) complexes with formulae of  $[\text{Cu}_2(\text{chel})_2(\text{pyz})(\text{H}_2\text{O})_4]$ , (**1**, pyz = pyrazine,  $\text{H}_2\text{chel}$  = chelidamic acid), has been synthesized and characterized by elemental analyses, IR spectroscopy and solution studies. The crystal structure of the binuclear Cu(II) complex has been determined by X-ray single-crystal diffraction technique. Both copper(II) metal centers are bridged by pyrazine. The coordination environment around each copper(II) atom can be described as a distorted octahedral geometry. The axial positions of each Cu(II) complex are occupied by two water molecules and equatorial positions are occupied by a tridentate chelidamic acid dianion and a pyrazine molecule that functions as a linear bidentate ligand bridging two Cu(II) complexes to form a dimer. Hydrogen bonding and  $\text{C}-\text{O} \cdots \pi$  interactions link the binuclear Cu(II) complex generating the 3D infinite network.

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These assemblies are described and analyzed by means of density functional theory (DFT) calculations since they play an important role in the construction of three-dimensional supramolecular frameworks. The protonation constants of pyrazine and chelidamic acid as the building blocks of the proton transfer systems ( $H_2chel-pyz$ ) and their corresponding stability constants were determined by potentiometric studies. The stoichiometry and stability constants of  $H_2chel-pyz$  complex with  $Cu^{2+}$  was investigated by potentiometric technique in aqueous solution. The results from solution studies were compared with the solid state data, in details.

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## Introduction

Considerable effort has been devoted to the syntheses and characterizations of metal–organic frameworks (MOFs) composed of transition metal ions and organic ligands because of their unmatched structural versatilities and potential applications such as gas storage, separation, absorption chemistry, luminescence, catalysis, sensors and magnetism [1–11]. Binuclear and polynuclear complexes containing monoatomic and multidentate bridging ligands are of considerable interest from the standpoint of inorganic and bioinorganic chemistry. In particular, the coordination chemistry of copper(II) complexes containing carboxylates is interesting from structural and magnetic points of view [12–19]. The synthesis and characterization of mono, di, tri and polynuclear copper complexes using bridging molecules like pyrazine, 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethane, etc. are also well documented [20–29]. The chemistry of dinuclear copper complexes with ligands of biological relevance where the metal centers are located at close proximity is of continuous interest because they have greater cleaving efficiency and DNA interaction ability than mononuclear complexes [30–33].

Noncovalent interactions, such as hydrogen bonds,  $\sigma$ -hole bonds, electrostatic as well as metal ion coordination, represent the backbone of self-assembly processes and supramolecular architectures [34–37]. Hydrogen bonding still remains the most important interaction to control organization in the solid state. Moreover, supramolecular interactions with  $\pi$  aromatic clouds, such as  $C-H \cdots \pi$ ,  $cation \cdots \pi$ ,  $\pi \cdots \pi$  stacking, lone pair  $\cdots \pi$  and anion  $\cdots \pi$  have enriched our knowledge to a great extent [38] and contributed tremendously in exploring and understanding the solid state architecture in small synthetic inorganic–organic hybrid crystals.

In this work, we present a synthesis, spectral properties, solution studies, and the X-ray single-crystal analysis of a copper(II) compound formulae of  $[Cu_2(chel)_2(pyz)(H_2O)_4]$  (**1**) combined with a DFT theoretical analysis of the interesting supramolecular assemblies observed in its solid state architecture.

## Experimental

### Chemicals and methods

Chelidamic acid (97%), pyrazine (97%) and  $Cu^{II}$  nitrate trihydrate (99%), were purchased from merck and Alfa Aesar companies and used without further purification. Infrared spectra were recorded in the region  $4000-400\text{ cm}^{-1}$  on a Buck500 IR spectrometer. Elemental analyses (C, H and N contents) were carried out on a Thermo Finning Flash-1112EA microanalyzer. The X-ray data were obtained with STOE IPDS 2T diffractometers. Melting points were determined using an Electro thermal IA-9300 apparatus and without being corrected. All pH measurements were carried out with a model 686 digital pH meter equipped with a combined glass–calomel electrode (Metrohm).

### Synthesis of $[Cu_2(chel)_2(pyz)(H_2O)_4]$

An aqueous solution of pyrazine (0.30 mmol, 24 mg) is added dropwise to an aqueous solution of chelidamic acid (0.15 mmol, 30 mg) and stirred at  $70\text{ }^\circ\text{C}$  for 15 min. Then, an aqueous solution of  $Cu(NO_3)_2 \cdot 6H_2O$  (0.07 mmol, 18 mg) is added to the reaction mixture and the stirring is continued for 3 h. By slow evaporation of the solvent at room temperature, blue needle crystals are obtained after 2 weeks. (m.p.  $>300\text{ }^\circ\text{C}$ ). Yield ca. 55%. Anal. Calcd. for  $C_{18}H_{18}Cu_2N_4O_{14}$ : C, 33.70; H, 2.83; N, 8.73. Found: C, 35.17; H, 2.78; N, 9.77%. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3492(br), 3074(br), 2586(w), 2482(w), 1614(s), 1410(s), 1312(w), 1242(w), 1124(m), 1066(m), 856(s), 804(s), 747(s).

### Crystal structure determination and refinement

The X-ray diffraction measurements were made on a STOE IPDS-2T diffractometer with graphite monochromated  $Mo\ K\alpha$  radiation. For complex  $[Cu_2(chel)_2(pyz)(H_2O)_4]$ , blue needle shape crystal was chosen using a polarizing microscope and was mounted on a glass fiber which was used for data collection. Cell constants and orientation matrices for data collection were obtained by least-squares refinement of diffraction data from 2920 unique reflections. Data were collected to a maximum  $2\theta$  value of  $58.34^\circ$  in a series of  $\omega$  scans in  $1^\circ$  oscillations and integrated using the Stoe X-Area [39] software package. A numerical absorption correction was applied using X-RED [40] and X-SHAPE [41] software. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods [42] and subsequent difference Fourier maps and then refined on  $F^2$  by a full-matrix least-squares procedure using anisotropic displacement parameters [43]. The atomic factors were taken from the International Tables for X-ray Crystallography [44]. All refinements were performed using the X-STEP32 crystallographic software package [45].

### Theoretical methods

The energies of all complexes included in this study were computed at the BP86-D3/def2-TZVP level of theory. The geometries have been obtained from the crystallographic coordinates. The calculations have been performed by using the program TURBOMOLE version 6.5 [46]. The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys-Bernardi counterpoise technique [47]. For the calculations we have used the BP86 functional with the latest available correction for dispersion (D3). The “atoms-in-molecules” (AIM) [48] analysis was performed at the BP86/def2-TZVP level of theory. The calculation of AIM properties was done using the AIMAll program [49].

### Solution studies procedure

All pH measurements were carried out with a model 686 digital pH meter equipped with a combined glass–calomel electrode

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