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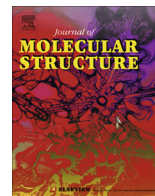


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Synthesis, structure and DFT study of a chelidamic acid based Cu coordination polymer: On the importance of π – π interactions and hexameric water clusters

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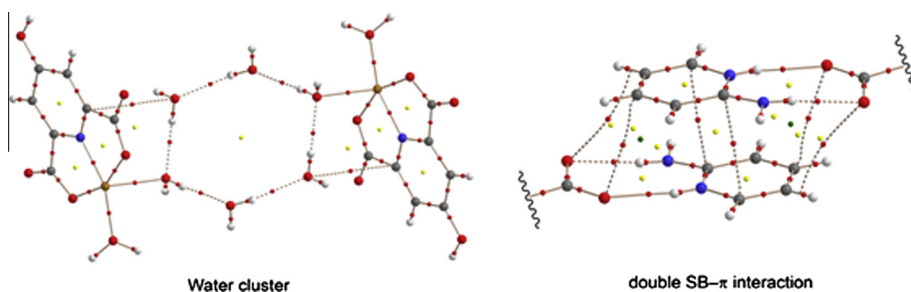
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HIGHLIGHTS

- One dimensional coordination polymer of Cu(II) with aminopyridine and chelidamic acid is X-ray characterized.
- We report a density functional study of the energetic features of several noncovalent interactions.
- We perform an “atoms-in-molecules” analysis to investigate the close intermolecular contacts.

GRAPHICAL ABSTRACT

Interplay of weak forces like hydrogen bonding, salt bridge $\cdots \pi$, and π – π stacking interactions leading to the formation of supramolecular network in a $\{(\text{C}_6\text{H}_9\text{N}_2)[\text{Cu}(\text{C}_7\text{H}_5\text{NO}_5)(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$ polymer.



ARTICLE INFO

Article history:

Received 10 July 2014

Received in revised form 13 August 2014

Accepted 18 September 2014

Available online 28 September 2014

Keywords:

DFT

Chelidamic acid

2-Amino-6-methylpyridine

Coordination polymer

π – π interactions

Water clusters

ABSTRACT

One-dimensional coordination polymer, i.e., $\{(\text{Hampy})[\text{Cu}(\text{chel})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$ (**1**, ampy = 2-amino-6-methylpyridine, H_3chel = chelidamic acid), has been synthesized and characterized by elemental analysis, IR spectroscopy, solution studies and X-ray single-crystal diffraction. In the monomeric unit of compound **1** the metal center exhibits a distorted square–pyramidal coordination sphere. The Cu(II) ion is coordinated to chelidamic acid and water. These monomers are interlinked generating a 1D polymer by means of the *para* hydroxyl group of the ligand. Protonated 2-amino-6-methylpyridine rings act as counter cations. The crystal lattice is aggregated through intermolecular interactions, such as electrostatic attraction, $\text{N}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding and aromatic π stacking interactions. Hydrogen bond interactions between the water molecules led to formation of six-membered rings with chair conformation. 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.

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Introduction

In the past decade, coordination polymers have been intensively studied, in particular those compounds constructed from metal ions and organic bridging ligands that are considered to form a new fam-

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ily of polymeric “metal–organic frameworks” [1–6]. The selection of appropriate ligands to link metal ions facilitates the design and construction of coordination polymers of different shapes and properties. The versatility of carboxylate ligands for connecting metal centers has led to extensive research on the structures and properties of polymeric carboxylate complexes. Chelidamic acid is a polydentate ligand that has attracted great interest and has been used in many areas of science, such as biochemistry, organic chemistry, medical chemistry and even in HIV investigation [7–12]. In addition, it has been extensively used in coordination chemistry [13–15].

Metal–organic coordination networks with carboxylate ligands usually provide void spaces that are adequate for incorporating hydrophilic guests. For instance, water clusters can be encapsulated with the help of hydrogen bonds [16]. A variety of finite and infinite water clusters have been trapped in the crystal hosts in the solid state [17–19]. Moreover, several water-clusters with different topologies have been reported in the context of crystal engineering [20–22]. Among the different water clusters, the structure of the hexamer (H_2O)₆ represents a transition from cyclic to three-dimensional geometries, and it has been extensively studied theoretically [23–26] and experimentally [27–30]. Although some of *ab initio* calculations suggested that the cyclic and the prismatic structures are the most stable, a large number of alternative three-dimensional structures, such as chair, boat, and cage, are also thermodynamically stable and energetically comparable [31].

As a part of our continuous interest in the syntheses of metal–organic frameworks including polycarboxylic acid ligands in the solid state and solution phase [32], herein we report the synthesis and X-ray characterization of a new coordination polymer $\{(\text{Hampy})[\text{Cu}(\text{chel})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$ obtained from the reaction of chelidamic acid (H_3chel) and 2-amino-6-methylpyridine (ampy) in the presence of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$. Interestingly, hexameric water clusters were observed in the crystal structure where two water molecules are coordinated to two different Cu metal centers. Taking into consideration that the cooperative behavior of water molecules leading to the formation of cluster networks is a prerequisite for unveiling the properties of water, the study and analysis of these assemblies is of especial interest. In particular, we have studied by means of DFT calculations the influence of the Cu-coordinated water molecules in the stability of the assembly. The coordinated water molecules participate in hydrogen bond donor–acceptor interactions with the uncoordinated water molecules and have a crucial role in the generation and stability of the water clusters observed in compound **1**.

Experimental

Chemicals and methods

All reagents for synthesis and analysis were obtained commercially with analytical grade and used without further purification and all manipulation was carried out in the laboratory atmosphere. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Buck 500 IR spectrometer. Elemental analysis (C, H and N contents) was carried out on a Thermo Finning Flash-1112EA microanalyzer. The X-ray data was obtained with STOE IPDS 2T diffractometer. Melting point was determined using an Electro thermal IA-9300 apparatus and without being corrected. The thermogravimetric (TG) runs were taken on a TGA-50/50H standard type thermal analysis system. The compound was heated to 1000 °C in nitrogen at a heating rate of 10 K min^{-1} .

Synthesis of $\{(\text{Hampy})[\text{Cu}(\text{chel})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$

An aqueous solution of $\text{Cu}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.07 mmol, 18 mg) in water (10 ml) was added to a solution of chelidamic acid

(0.15 mmol, 30 mg) in water (20 ml) and 2-amino-6-methylpyridine (0.30 mmol, 32 mg) in water (7 ml) under stirring at room temperature in a 1:2:4 M ratio for 3 h. After 5 weeks, green crystals of the complex were obtained by slow evaporation of the solvent at room temperature. (m.p. >310 °C). Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{CuN}_3\text{O}_8$: C, 38.38; H, 4.21; N, 10.33. Found: C, 39.18; H, 4.39; N, 10.45%. IR (KBr pellet, cm^{-1}): 3267, 3095, 2778, 1678, 1600, 1544, 1486, 1396, 1318, 1270, 1174, 1121, 1068, 933, 876, 804, 741.

Crystal structure determination and refinement

The X-ray diffraction measurements were made on a STOE IPDS-2T diffractometer with graphite monochromated Mo K α radiation. For complex $\{(\text{Hampy})[\text{Cu}(\text{chel})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$, green plate 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 4033 unique reflections. Data were collected to a maximum 2θ value of 58.3° in a series of ω scans in 1° oscillations and integrated using the Stoe X-Area [33] software package. A numerical absorption correction was applied using X-RED [34] and X-SHAPE [35] software. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods [36] and subsequent difference Fourier maps and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [37]. The atomic factors were taken from the International Tables for X-ray Crystallography [38]. All refinements were performed using the X-STEP32 crystallographic software package [39].

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 [40]. The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise technique [41]. For the calculations we have used the BP86 functional with the latest available correction for dispersion (D3). The “atoms-in-molecules” (AIM) [42] analysis was performed at the BP86/def2-TZVP level of theory. The calculation of AIM properties was done using the AIMAll program [43].

Results and discussions

Spectroscopic studies

Besides elemental analysis, compound **1** was initially characterized by its IR spectrum and Thermogravimetric analysis. Infrared spectroscopy of compound **1** is in consistent with its structure characteristics as determined by single-crystal X-ray diffraction. Absorptions in the range 3400–3000 cm^{-1} correspond to the N–H stretching vibrations of the amine and ammonium groups, water molecules and different hydrogen bonds such as O–H \cdots O, N–H \cdots O, and C–H \cdots O. The band associated to the asymmetric stretching vibrational mode, ν_{asym} ($-\text{COO}^-$), appears at 1678 cm^{-1} , while the band associated to symmetric stretching vibrational mode, ν_{sym} ($-\text{COO}^-$), appears at 1396 cm^{-1} . The absence of the characteristic band at around 1700 cm^{-1} attributed to $-\text{COOH}$ groups indicates that complete deprotonation of all carboxyl groups has occurred upon reaction with metal ions. Additional evidence for the formation of 2-amino-6-

methylpyridinium, confirming the presence of $(\text{NH})^+$ group, can be achieved from the presence of band at 3267 cm^{-1} . Broad band in 3094 cm^{-1} is due to stretching vibrations of aromatic C–H's of 2-amino-6-methylpyridinium and 4-hydroxypyridine-2,6-dicarboxylate ions. Moreover, the sharp bands in $933\text{--}741\text{ cm}^{-1}$ are due to out-of-plane aromatic C–H.

Thermogravimetric study

Thermogravimetric analysis for **1** was performed from $5\text{ }^\circ\text{C}$ to $1000\text{ }^\circ\text{C}$ (see Fig. S1) and four decomposition stages are observed. In the first stage, the graph shows a weight loss that corresponds to the removal of both uncoordinated and one coordinated water molecules that occurs at $98\text{ }^\circ\text{C}$. In the second and third stages, the chelidamate and 2-amino-6-methylpyridinium ions decomposed at the temperature ranges $285\text{--}331\text{ }^\circ\text{C}$ (found: 60.80%, calcd. 71.07%). From the remaining weight it could be confirmed that only CuO remained in the system at temperatures above $500\text{ }^\circ\text{C}$ (found: 17.25%, calcd. 19.55%).

Crystal structure

Crystallographic data and parameters for complex are summarized in Table 1. The structure of title compound can be described as one anionic complex, $[\text{Cu}(\text{chel})(\text{H}_2\text{O})]^-$, one $(\text{Hampy})^+$ cation, and two uncoordinated water molecules (see Fig. 1). The anionic complex extends via coordination bonds to form an infinite polymeric chain along the b axis. Each Cu(II) atom is coordinated to one N atom and two O atoms from the tridentate chelidamic ligand, one oxygen atom from the adjacent p -hydroxy group of the chelidamic acid and a water molecule, giving a slightly distorted square-pyramidal geometry. Selected bond lengths and angles with their standard deviations for title complex is given in Table 2. The axial position is occupied by the water molecule (O6), with Cu1–O6 bond length of $2.303(19)\text{ \AA}$, while the equatorial plane is formed by three oxygen atoms, O1, O3 and O5, with Cu–O

Table 1
Crystal data and structure refinement for $\{(\text{H}_2\text{a-6mpy})[\text{Cu}(\text{hypydc})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$.

Empirical formula	$\text{C}_{13}\text{H}_{17}\text{CuN}_3\text{O}_8$
Formula weight	406.85
Temperature (K)	120
Wavelength (\AA)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (\AA)	10.089(2)
b (\AA)	14.902(3)
c (\AA)	10.296(2)
β ($^\circ$)	103.00(3)
Volume (\AA^3)	1508.3(5)
Z	4
Density _{calc} (g cm^{-3})	1.792
Absorption coefficient (mm^{-1})	1.501
$F(000)$	836
Crystal size (mm^3)	$0.50 \times 0.30 \times 0.20$
θ Ranges for data collection ($^\circ$)	$2.48\text{--}29.15$
Index ranges	$-13 \leq h \leq 13$ $-19 \leq k \leq 20$ $-10 \leq l \leq 14$
Reflections collected	10,514
Unique data, (R_{int})	4033, (0.0653)
Refinement method	Least-squares matrix: full on F^2
Parameters/restraints	248/4
Final R_1/wR_2^a ($I > 2\sigma(I)$)	$R_1 = 0.0392$, $wR_2 = 0.0899$
Final R_1/wR_2^a (all data)	$R_1 = 0.0518$, $wR_2 = 0.0941$
Goodness-of-fit on F^2 (S)	1.050
Largest diff. peak and hole (e \AA^{-3})	0.757, -0.456

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$.

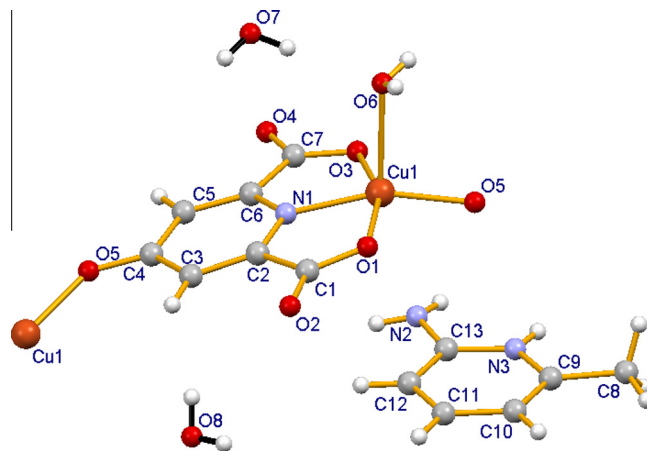


Fig. 1. Perspective view of asymmetric units of **1** showing the atom labeling schemes.

Table 2
Selected bond lengths (\AA) and bond angles ($^\circ$) for $\{(\text{H}_2\text{a-6mpy})[\text{Cu}(\text{hypydc})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$.

Cu(1)–O(1)	2.028(16)	N(3)–C(13)	1.356(3)
Cu(1)–O(3)	2.118(17)	O(4)–C(7)	1.249(3)
Cu(1)–O(5)	1.896(15)	O(5)–C(4)	1.292(2)
Cu(1)–O(6)	2.303(19)	N(1)–C(2)	1.337(3)
Cu(1)–N(1)	1.903(18)	N(1)–C(6)	1.332(3)
O(1)–C(1)	1.278(3)	N(2)–C(13)	1.340(3)
O(2)–C(1)	1.241(3)	N(3)–C(9)	1.368(3)
O(3)–C(7)	1.285(3)		
O(1)–Cu(1)–O(3)	158.50(6)	C(13)–N(3)–C(9)	123.40(2)
O(1)–Cu(1)–O(6)	100.89(7)	O(1)–C(1)–C(2)	114.38(19)
O(3)–Cu(1)–O(6)	88.53(7)	O(2)–C(1)–O(1)	124.70(2)
O(5)–Cu(1)–O(1)	85.57(7)	O(2)–C(1)–C(2)	120.88(19)
O(5)–Cu(1)–O(3)	113.84(6)	N(1)–C(2)–C(1)	111.40(18)
O(5)–Cu(1)–O(6)	90.76(7)	N(1)–C(2)–C(3)	122.00(2)
O(5)–Cu(1)–N(1)	160.68(7)	O(5)–C(4)–C(5)	118.67(19)
N(1)–Cu(1)–O(1)	79.89(7)	N(1)–C(6)–C(5)	121.30(19)
N(1)–Cu(1)–O(3)	79.05(7)	N(1)–C(6)–C(7)	112.72(18)
N(1)–Cu(1)–O(6)	104.36(7)	O(3)–C(7)–C(6)	115.01(18)
C(1)–O(1)–Cu(1)	115.28(14)	O(4)–C(7)–C(6)	119.47(18)
C(7)–O(3)–Cu(1)	113.04(13)	N(3)–C(9)–C(8)	116.43(19)
C(4)–O(5)–Cu(1)	137.29(14)	C(10)–C(9)–N(3)	118.50(2)
C(2)–N(1)–Cu(1)	118.89(15)	N(2)–C(13)–N(3)	118.40(2)
C(6)–N(1)–Cu(1)	119.97(14)	N(2)–C(13)–C(12)	123.30(2)
C(6)–N(1)–C(2)	120.86(18)	N(3)–C(13)–C(12)	118.30(2)

Symmetry codes:

i $-x + 1, y - 1/2, -z + 3/2$.

ii $-x + 1, y + 1/2, -z + 3/2$.

bond distances Cu1–O1 = $2.028(16)\text{ \AA}$, Cu1–O3 = $2.118(17)\text{ \AA}$ and Cu1–O5 = $1.896(15)\text{ \AA}$, and a nitrogen atom with Cu1–N1 bond length of $1.903(18)\text{ \AA}$.

The 3D architecture of compound **1** is dominated by strong hydrogen bonding ($\text{O} \cdots \text{O}$) and weak hydrogen bonding ($\text{C} \cdots \text{H} \cdots \text{O}$ and $\text{C} \cdots \text{H} \cdots \text{N}$) aromatic π stacking interactions. Moreover less directional electrostatic attractions between the anionic coordinated chelidamic ligand and the protonated aminopyridine ring are also very important. The D \cdots A distances of the $\text{O} \cdots \text{H} \cdots \text{O}$, $\text{N} \cdots \text{H} \cdots \text{O}$ and $\text{C} \cdots \text{H} \cdots \text{O}$ hydrogen bonds (see Table 3) range from $2.780(3)$ to $3.413(3)\text{ \AA}$. The polymeric chains are connected to water molecules and cationic Hampy moieties, via $\text{O} \cdots \text{H} \cdots \text{O}$, $\text{N} \cdots \text{H} \cdots \text{O}$ and $\text{C} \cdots \text{H} \cdots \text{O}$ interactions creating hetero synthons that can be described as $R_2^2(8)$, $R_2^2(11)$, $R_2^2(7)$ and $R_2^2(6)$ which increase the stability of the crystalline network (see Fig. 2).

The water molecules play a significant role in the expansion of the three-dimensional network of title compound. As it is shown in

Table 3
Hydrogen-bond geometry (Å, °).

D–H...A	d(D–H)	d(H...A)	d(D...A)	<DHA
N(2)–H(2A)...O(3 ^{vi})	0.84(2)	2.11(2)	2.943(3)	174(3)
N(3)–H(3A)...O(4 ^v)	0.80(3)	1.99(3)	2.780(3)	171(3)
N(2)–H(2B)...O(2 ^{viii})	0.81(3)	2.02(3)	2.831(3)	172(3)
O(6)–H(6A)...O(8 ^{vi})	0.77(3)	2.03(3)	2.795(3)	173(3)
O(7)–H(7A)...O(4 ^{vii})	0.80(2)	2.23(2)	3.035(2)	178(3)
O(6)–H(6B)...O(1 ^{ix})	0.80(3)	2.42(3)	2.953(2)	125(3)
O(6)–H(6B)...O(5 ^{vii})	0.80(3)	2.18(4)	2.951(3)	162(3)
O(7)–H(7B)...O(6)	0.79(2)	2.00(2)	2.790(2)	176(3)
O(8)–H(8D)...O(7 [*])	0.77(2)	2.09(2)	2.860(3)	171(3)
O(8)–H(8E)...O(2 ^{xi})	0.77(3)	2.03(3)	2.804(2)	177(3)
C(8)–H(8C)...O(8 ⁱⁱⁱ)	0.98	2.56	3.413(3)	146
C(10)–H(10)...O(8 ⁱⁱⁱ)	0.95	2.56	3.385(3)	146
C(11)–H(11)...O(7 ^{iv})	0.95	2.55	3.353(3)	143

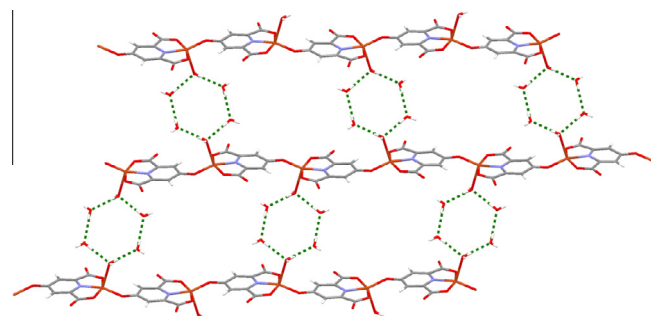
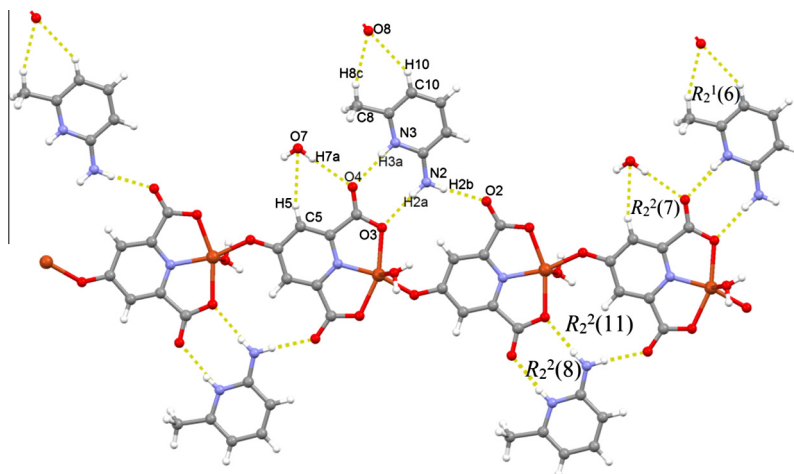
Symmetry codes:

- ⁱⁱⁱ $x + 1, y, z$.
- ^{iv} $x + 1, y - 1, z$.
- ^v $-x + 1, -y, -z + 2$.
- ^{vi} $x, y - 1, z$.
- ^{vii} $x, -y + 1/2, z - 1/2$.
- ^{viii} $x, -y + 1/2, z + 1/2$.
- ^{ix} $-x + 1, -y, -z + 1$.
- ^x $-x, -y + 1, -z + 1$.
- ^{xi} $-x + 1, -y + 1, -z + 1$.

Fig. 3. four uncoordinated and two coordinated water molecules are linked together via hydrogen bonding interactions (O–H...O hydrogen bonds, ranging from 2.790 to 2.859 Å) and facilitate the formation of six-membered ring water cluster that adopts a chair conformation. These water clusters act as a stabilizing factor, linking the polymeric chains along the *a* axis. The crystal packing of compound **1** along the *b* axis (see Fig. 4) clearly shows the alternating anionic polymeric layers and cationic layers formed by π -stacked Humpy cations. This π – π stacking interaction is characterized by a centroid–centroid distance of 3.700 Å between the pyridine rings of the (Humpy)⁺ cation.

Theoretical DFT study

We have focused our theoretical study to analyze the energetic features of the interesting supramolecular assemblies described above. Particularly, one relevant feature of compound **1** is the presence of hexameric water clusters, which significantly stabilize the structure. Two water molecules of the cluster are coordinated to two Cu metal centers. We have studied the influence of this coordination upon the water cluster stability. We have evaluated how the presence of the Cu ions influences the strength of the hydrogen bonds established between the coordinated and uncoordinated water molecules to form the water hexamer and vice versa. To achieve this we have used the equations shown in Fig. 5. It should be mentioned that due to the polymeric nature of compound **1**, we have used a mono-nuclear monomeric model for the calculation (see Fig. 5, bottom) and we have used the crystallographic coordinates for the calculations because the final objective of this study is to gain insight into the importance of the water cluster as it is in the solid state of **1**. We have evaluated the influence of the Cu ions by computing the formation energy of the hexameric cluster without and with the presence of the Cu ions. In the absence of Cu, we have denoted the formation energy as ΔE_1 and, for the calculation, we have considered that a water tetramer has been previously formed and that two water molecules are added to complete the assembly. As a result the interaction energy is $\Delta E_1 = -16.6$ kcal/mol that accounts for four hydrogen bonds where each water participates as an H-bond donor/acceptor simultaneously. Consequently, the interaction energy of each H-bond is approximately -4.15 kcal/mol. Moreover, we have also evaluated the formation energy of the cluster coordinated to the Cu ions using the same methodology: the computation of the interaction energy is done considering the tetramer previously formed that interacts with two water molecules coordinated to the Cu (denoted as ΔE_2). Accordingly to the values gathered in Fig. 5, the ΔE_2 energy is 2.4 kcal/mol more favorable (negative) than ΔE_1 , suggesting that the presence of the Cu ions coordinated to the water molecules reinforces the hydrogen bonds and consequently the cluster formation.

**Fig. 3.** View of hydrogen bond interactions between the water molecules and formation of six membered rings.**Fig. 2.** View of O–H...O, N–H...O and C–H...O hydrogen bonds interactions of compound **1** between water molecules, polymeric chain and cations.

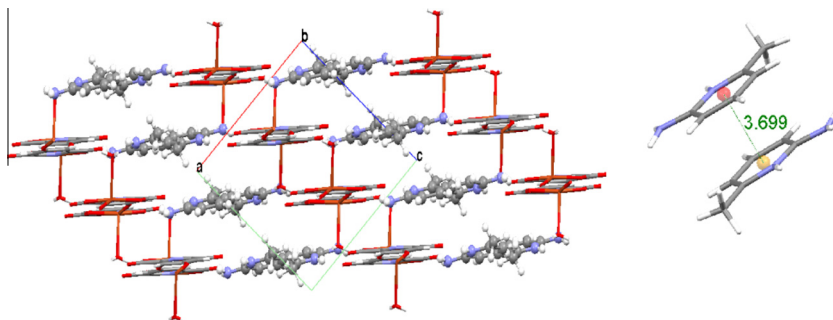


Fig. 4. Packing arrangement of $\{[(\text{H}2\text{a-6mpy})][\text{Cu}(\text{hypydc})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$ when viewed along the b axis and schematic image of $\pi\cdots\pi$ stacking interactions between cationic moieties.

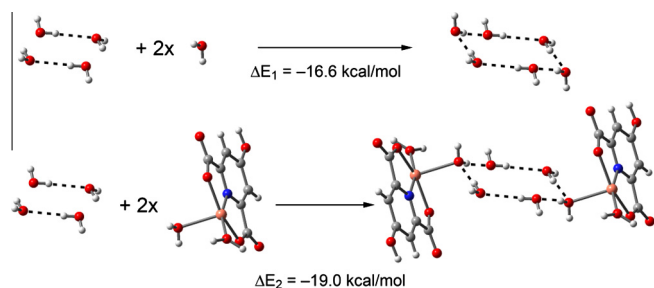


Fig. 5. Equations used to evaluate cooperativity effects in the water cluster present in compound **1**.

We have also examined the Cambridge Structural Database [44], which is a big depot of geometrical information, to learn whether the hexameric water cluster observed in compound **1** is common in X-ray structures. We have found several compounds presenting the same assembly where two water molecules are coordinated to Cu ions. In some cases (like AQAQEO [45]) the hexameric cluster of water molecules (considering the oxygen atoms) resembles a cyclohexane-like chair. In others like EKEHEI [46] the oxygen atoms are coplanar (resembling a benzene ring). Compound **1** exhibits an intermediate geometry, where the oxygen atoms are disposed in an almost planar disposition. Using the reactions abovementioned in Fig. 5, we have computed the formation energies of the clusters in the absence and presence of Cu and we have included them in Fig. 6. Interestingly the planar cluster is energetically favored compared to the other two conformations that are very similar. In addition the synergistic effect of the Cu coordination to the formation energies is higher in the planar cluster.

We have expanded our study to the $\pi\cdots\pi$ stacking [47] noncovalent interactions observed in the solid state of compound **1** (see Fig. 4). Obviously the counterions are very important to stabilize the assembly, since the 2-amino-6-methylpyridine moieties are

protonated and consequently a strong electrostatic repulsion is expected. The theoretical models used are shown in Fig. 7, with are retrieved from the crystallographic coordinates. It can be observed that each protonated aminopyridine ring forms a salt bridge interaction with the anionic counterpart that has been simplified (only a monomer of the polymeric chain is used). Therefore the interaction can be also viewed as a double salt-bridge(SB)- π interaction that has been recently described in related systems [48]. We have also observed that one hydrogen atom of the methyl group is close to one carbon atom of the ring (2.73 Å, see Fig. 7, left), thus a weak C-H/ π interaction [49] also contributes to the formation of the $\pi\cdots\pi$ stacked dimer. We have computed the interaction energy of the complete assembly that is large and negative ($\Delta E_7 = -18.0$ kcal/mol) and the interaction energy of a model where the methyl groups have been replaced by hydrogen atoms. As a result the interaction energy is reduced to $\Delta E_8 = -15.7$ kcal/mol. Therefore the contribution of this double C-H/ π interaction is $\Delta E_7 - \Delta E_8 = -2.3$ kcal/mol.

Finally, we have used the Bader's theory of "atoms in molecules", which provides an unambiguous definition of chemical bonding, to further describe the aforementioned noncovalent interactions. The AIM theory has been successfully used to characterize and understand a great variety of interactions; therefore it is adequate to analyze the interactions described above. In Fig. 8 we show the AIM analysis of the SB/ π - π /SB assembly and the water cluster of compound **1**. As it can be observed for the assembly is characterized by several bond critical point that connect the oxygen atoms of the carboxylate groups with the aminopyridine moieties. In addition additional bond critical points interconnect both aromatic rings characterizing the $\pi\cdots\pi$ stacking interaction. The assembly is further characterized by the presence of several ring critical points (yellow spheres) and two cage critical points (green spheres). The water cluster is characterized by the presence of six bond critical points that corresponds to the hydrogen bonding interactions. The cluster is further characterized by the presence of one ring critical points (yellow sphere) as a consequence of

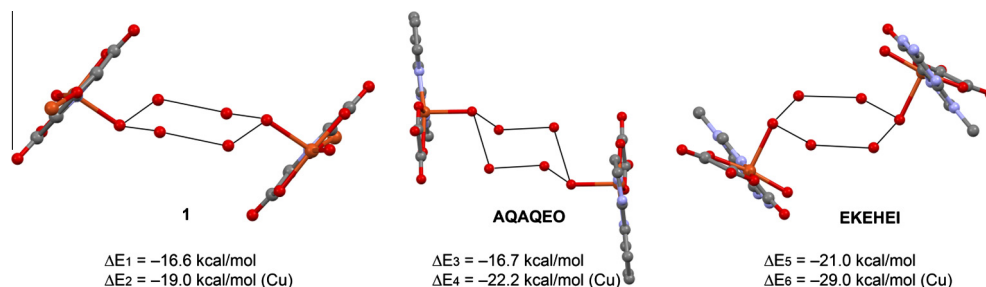


Fig. 6. Partial views of the water clusters observed in two X-ray structures retrieved from the CSD and compound **1**. For clarity, the hydrogen atoms have been omitted.

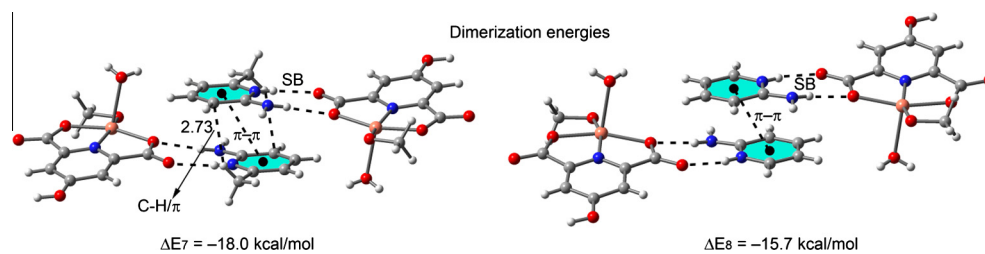


Fig. 7. Dimerization energies computed at the BP86-D3/def2-TZVP level of theory. Distance in Å.

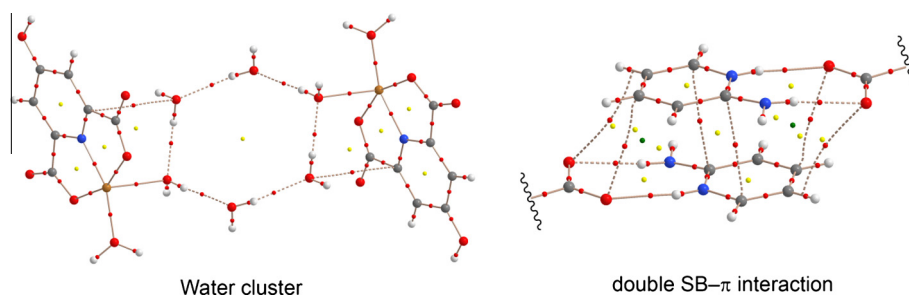


Fig. 8. AIM analysis of the water cluster (left) and SB/π-π/SB assembly (right) of compound **1**. Bond, ring and cage critical points are represented by red, yellow and green spheres, respectively. The bond paths connecting bond critical points are also represented by dashed lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the formation of the cluster. The value of the Laplacian of the charge density computed at the bond critical points in both complexes is positive, as is common in closed-shell interactions.

Conclusion

We have synthesized and structurally characterized a new 1D copper coordination polymer based on 2-amino-6-methylpyridine and chelidamic acid. The structural analyses show that there are a wide range of intermolecular hydrogen bonds in this crystal structure which play important role in its stabilization, including a double salt-bridge- π interaction. Hydrogen bond interactions between the water molecules led to formation of six-membered water clusters that generate the 3D architecture of the compound by linking the polymeric chains. In the theoretical study we have estimated the contribution of each interaction to the formation of the assembly (C-H/ π and π - π interactions). Moreover the influence of the coordination of two water molecules to the Cu metal centers on the stability of the water cluster has been demonstrated computationally. The assignment of the contribution of each interaction and its mutual influence is certainly important to gain general knowledge in the intricate mechanism that governs the molecular recognition and crystal packing since it could be useful to the crystal engineering community. Finally, the AIM analysis and representation of critical points and bond paths are useful to characterize and validate the interactions that influence the crystal packing.

Acknowledgements

MM and HEH wish to thank to the Ferdowsi University of Mashhad for financial support of this article (Grant No. 19042/3). This work was supported by the DGICYT of Spain (projects CTQ2011-27512/BQU and CONSOLIDER INGENIO 2010 CSD2010-00065, FEDER funds) and the Direcció General de Recerca i Innovació del Govern Balear (project 23/2011, FEDER funds). We thank the CTI (UIB) for free allocation of computer time.

Appendix A. Supplementary material

CCDC 1011636 contains the supplementary crystallographic data for compound $\{(\text{Hampy})[\text{Cu}(\text{chel})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}\}_n$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/contents/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molstruc.2014.09.053>.

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