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27th October 2021

Jointly Organized by

Department of Biological Science, Physical Science and Computational Science

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A nations's growth is in proportion to education and intelligence spread among the masses. Having this idealistic vision, two great philanthropists late. S.P. Nallamuthu Gounder and Late. Arutchelver Padmabhushan Dr.N.Mahalingam formed an organization called Pollachi Kalvi Kazhagam, which started NGM College in 1957, to impart holistic education with an objective to cater to the higher educational needs of those who wish to aspire for excellence in knowledge and values. The College has achieved greater academic distinctions with the introduction of autonomous system from the academic year 1987-88. The college has been Re-Accredited by NAAC and it is ISO 9001 : 2015 Certified Institution. The total student strength is around 6000. Having celebrated its Diamond Jubilee in 2017, the college has blossomed into a premier Post-Graduate and Research Institution, offering 26 UG, 12 PG, 13 M.Phil and 10 Ph.D Programmes, apart from Diploma and Certificate Courses. The college has been ranked within Top 100 (72nd Rank) in India by NIRF 2021.

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Coordination of Metal (M=Ni, Cu) with Triazolopyrimidine and Auxillary Ligands and Formation of Hydrogen Bond Network: A Theoretical Study

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ABSTRACT: The coordination of metal with triazolopyrimidine and auxillary ligands has been studied using density functional theory. The plane of the triazolopyrimidine ligand is almost perpendicular to the plane defined by the auxiliary ligands and the metal centre. As the atomic radius of the metal cation increases, the coordination distances with the ligands are also found to be increased in the order. The binding energy, metal ion affinity and vibrational frequency have been examined. The highest binding energy and metal ion affinity allows effective charge transfer of electron density from the lone pair of electronegative atoms of the ligands to the metal cation. The geometrical parameters and vibrational frequencies agree well with the crystallographic results. A detailed knowledge of the hydrogen bonding patterns is important for understanding the influence of the metal moiety on the ligands. From the optimized structures of $[Ni(dmax)_2(en)_2].3H_2O$ and $[Cu(dmax)_2(en)2].2H_2O$ complexes, hydrogen bonding network has been built which is found to increase the dimensionality of the solids.

Keywords: Triazolopyrimidine, Auxillary ligand, Metal ion affinity, Binding Energy, Hydrogen bond

1. INTRODUCTION

The study of the interaction of metal ions with nucleic acids, their constituents and their analogues have important biochemical implications in nucleotide biochemistry, genetic information storage and control of gene expression [1]. The main interest in this study is due to the direct bonds formed between cation and ligand called the first co-ordination sphere, relegating the weakestinteractions to a secondary role. Among these interactions, hydrogen bonding is more than ever a topic of vital scientific research as it plays a key role in a vast number of chemical systems, which range from inorganic to biological chemistry [2, 3]. Hydrogen bonds could in principle be used as the way of joining the building blocks in the rational design of supramolecular structures [4].

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The research on triazolopyrimidines (tp), including their coordination to transition metals, has resulted in a significant number of new compounds with interesting structural and biological properties [5-11]. More than 50 metal binding patterns to nucleosides and nucleotides of the common bases guanine, adenine, cytosine, thymine and uracil have now been established [12]. The interaction of transition metal ions with 1,2,3-triazolo-[4,5- d]pyrimidines has been the focus of relatively few chemical, spectroscopic and crystallographic studies [13-15]. Subsequent studies employing pyridine as auxiliary ligand [16,17] have revealed that for Ni(II) and Cu(II), the dimethylated derivative is monodentately linked to the metal centre through the N2 endocyclic atom while the heterocycle is not directly linked to the metal atom in Mn(II), Co(II), Zn(II) and Cd(II) compounds. In the present study, the coordination of metal with triazolopyrimidine and auxillary ligands have been studied using quantum chemical methods, in order to explore the coordination of divalent metals with ligands.

2. COMPUTATIONAL DETAILS

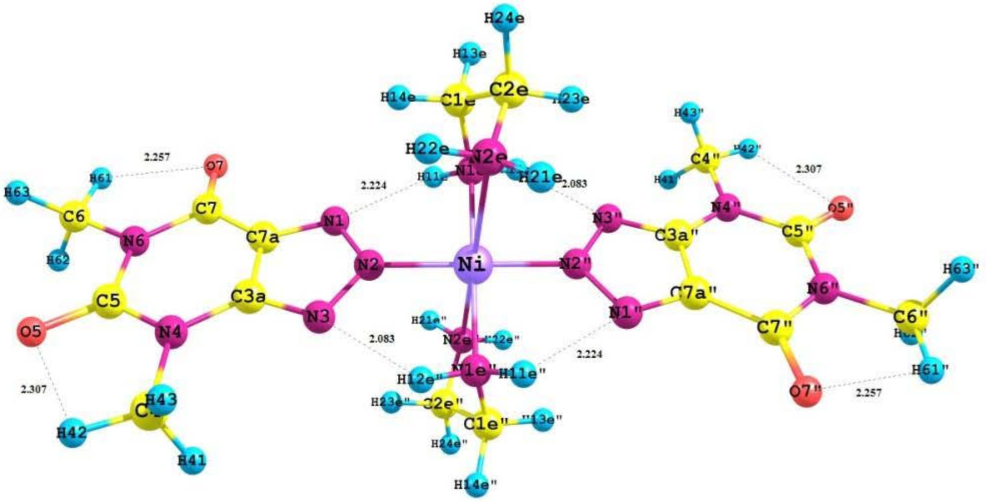
Density functional theory method has been applied to study the interaction of triazolopyrimidine and auxillary ligands with the metal cations. The equilibrium geometries of isolated and hydrated complexes have been determined by B3LYP method which includes Becke's three parameter exchange functional (B3) [18, 19] along with Lee- Yang-Parr (LYP) [20] type nonlocal correlation functional using LANL2DZ and 6-311G** basis sets. The choice of functional and basis set have been made based on the previous results obtained for metal-ligand interactions [21-23]. The energy minimizations followed by harmonic vibrational frequency calculations have been performed at B3LYP/LANL2DZ and B3LYP/6-311G** levels of theory to characterize all the stationary points on the potential energy surface as local minima. The interaction energies have been corrected for the basis set superposition error (BSSE), using the counterpoise method of Boys and Bernardi [24]. The metal ion affinity (MIA) has been computed as

$$\mathrm{MIA} = - [E_{el}\,(BM) - E_{el}(B) - E_{el}(M) + (E_{vib}(BM) – E_{vib}(B)]$$

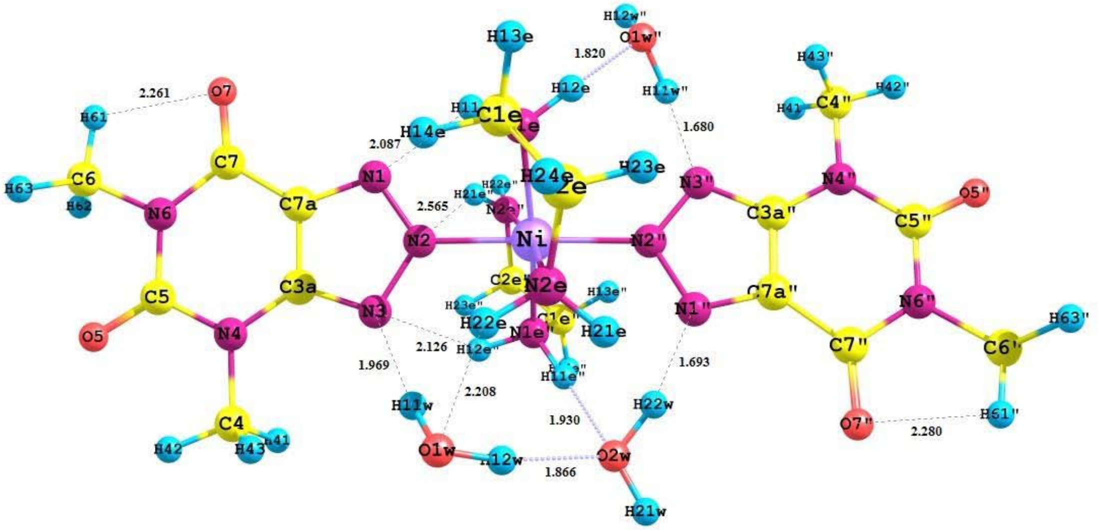
where, B and M are the monomers of ligands and metal cation; BM is the ligand-metal complexes, E_{el} is the electronic energy obtained from the SCF computation and E_{vib} includes the zero point energy and temperature corrections from 0 to 298 K [25,26] calculated by thermochemical analysis of vibrational frequencies. The optimized structures of Ni^{2+} and Cu^{2+} complexes are made to further interact among themselves to generate the hydrogen bond network. All the computations have been performed using Gaussian 03W computational package [27].

3. RESULTS AND DISCUSSION

The ground state geometry of $Ni(dmax)_2(en)_2$, $[Ni(dmax)_2(en)_2].3H_2O$, $Cu(dmax)_2(en)_2$, $[Cu(dmax)_2(en)_2].2H_2O$ and anhydrous $Cu(dmax)_2(bapa)$ complex have been optimized at B3LYP/LANL2DZ and B3LYP/6-311G** levels of theory. The structures are displayed in Figs. 1, 2 and 3. The co-ordination of metal with ethylenediamine (en) and 4,6-dimethyl-1,2,3-triazolo-[4,5-d]-pyrimidin-5,7-dione (dmax) anions are almost perpendicular to each other in (Figs. 1 and 2). The complex $[Ni(dmax)_2(en)_2].3H_2O$ has simultaneous coordination with three water molecules forming a seven and nine-membered ring structure. The third water molecule observed in the experimental structure is slightly twisted during geometry optimization. In [Cu(dmax)$_2$(en)$_2$].2H$_2$O, simultaneous coordination of two water molecules form a seven-membered ring structure. The coordination distance has been found to be increased as moving from Ni^{2+} to Cu^{2+}.



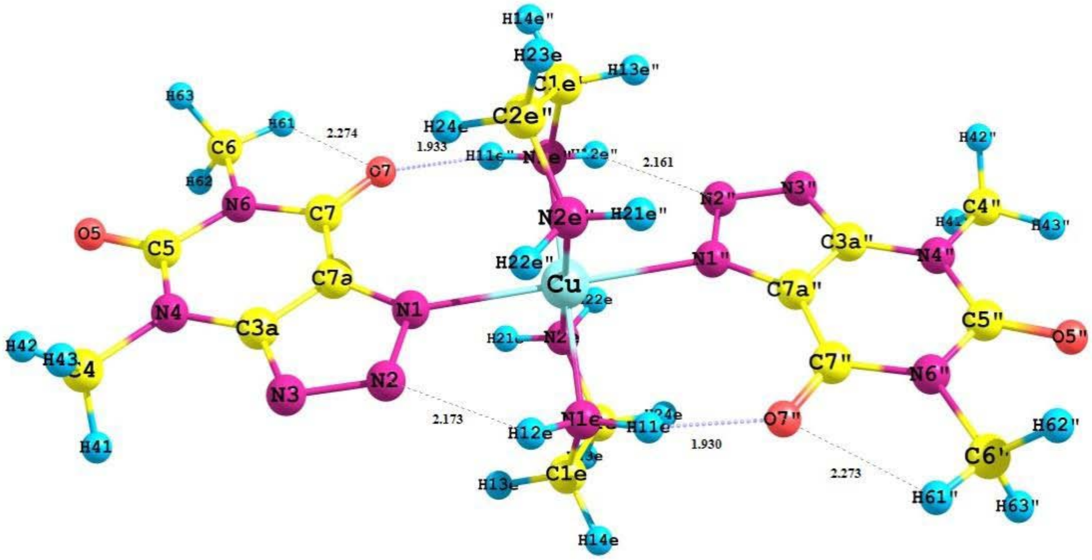
Ni(dmax)$_2$(en)$_2$



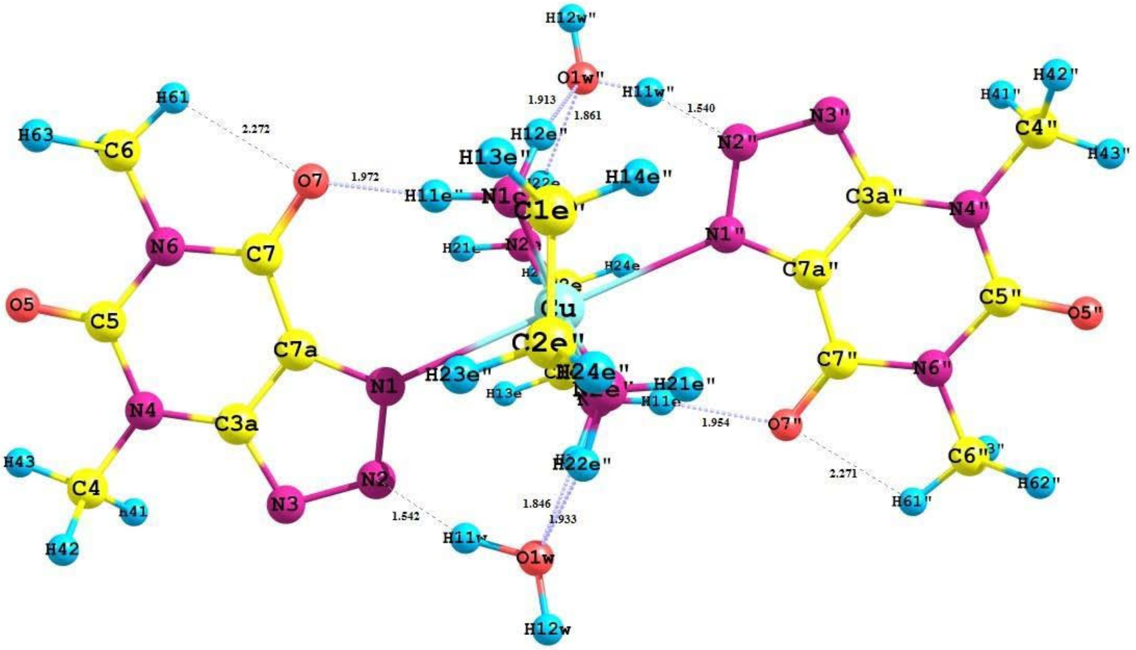
[Ni(dmax)$_2$(en)$_2$].3H$_2$O

Fig. 1. The optimized structures of Ni(dmax)$_2$(en)$_2$ and [Ni(dmax)$_2$(en)$_2$].3H$_2$O

In Cu(dmax)$_2$(bapa), dmax is almost perpendicular to auxiliary ligand (1,3-bis-(3- aminopropyl)-amine(bapa)). The complex Cu(dmax)$_2$(bapa) is anhydrous, as a result the available hydrogen bond donors are the amine N-H of the bapa and C-H bonds of the dmax ligand. Four of these ligands are involved in intramolecular hydrogen bonds (Fig. 3). The dmax coordinate through N2 atom as observed for Ni(dmax)$_2$(en)$_2$ [17].

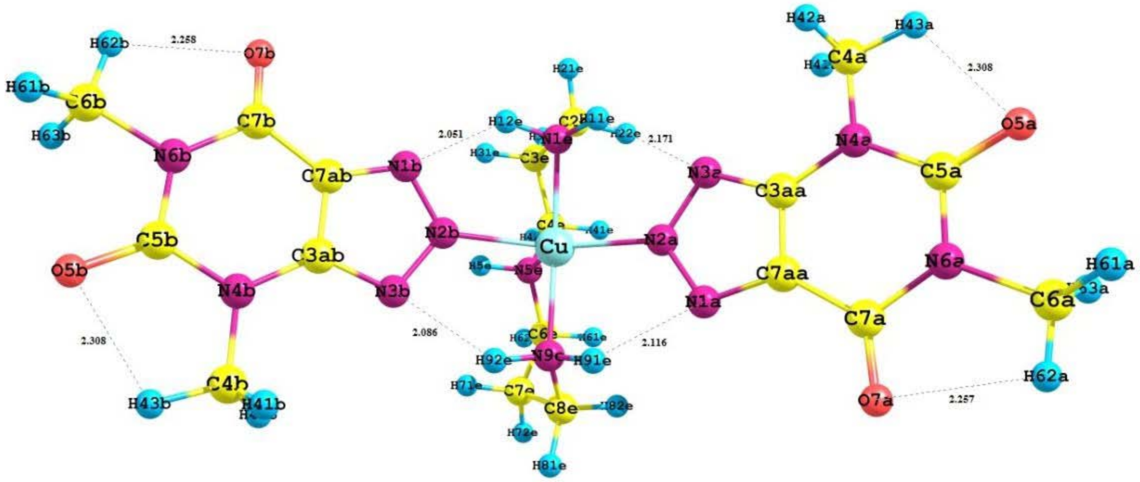


$Cu(dmax)_2(en)_2$



$Cu(dmax)_2(en)_2].2H_2O$

Fig. 2. The optimized structures of $Cu(dmax)_2(en)_2$ and $[Cu(dmax)_2(en)_2].2H_2O$



$Cu(dmax)_2(bapa)$

Fig. 3. The optimized structure of $Cu(dmax)_2(bapa)$

As the atomic number increases with the same group of elements, the coordination distance has been found to be increased as moving from Ni^{2+} to Cu^{2+}. Thus, the computing trends regarding the change of the coordination distance is in accordance with the generally known properties of the periodic table. As the ionic radius increases from nickel to copper complexes, the electronic affinity decreases and the corresponding coordination distance increases. However, as the ionic radius decreases, the electronegativity increases but the coordination distances decreases.

4. BINDING ENERGY AND METAL ION AFFINITY

To obtain an in-depth knowledge of the coordination of metal with the ligand in the complexes, binding energy has been calculated at B3LYP/LANL2DZ level of theory and the results are summarized in Table 1. The previous studies [28-30] have reported B3LYP functional as the most suitable method for calculating the MIA values. The highest binding energy of 278.80 kcal/mol has been observed for $Ni(dmax)_2(en)_2$ with the corresponding MIA value of 738.82 kcal/mol. The highest binding energy and MIA values are due to small ionic radius of Ni^{2+} coordinated mutually with electronegative atoms of the ligands. With increasing ionic radius, this process becomes less effective for Cu^{2+} complexes.

Table 1: BSSE corrected binding energy ΔE_{int} (kcal/mol) and metal ion affinity MIA (kcal/mol) of $Ni(dmax)_2(en)_2$, $[Ni(dmax)_2(en)_2].3H_2O$, $Cu(dmax)_2(en)_2$ $[Cu(dmax)_2(en)_2].2H_2O$ and $Cu(dmax)_2(bapa)$ calculated at B3LYP/LANL2DZ level of theory.

Complex	ΔEint	MIA
Ni(dmax)2(en)2	-278.80	738.82
[Ni(dmax)2(en)2].3H2O	-271.59	727.93
Cu(dmax)2(en)2	-133.85	700.68
[Cu(dmax)2(en)2].2H2O	-146.46	694.99
Cu(dmax)2(bapa)	-105.36	706.16

5. HARMONIC VIBRATIONAL FREQUENCY ANALYSIS

A harmonic vibrational frequency analysis of the metal complexes has been performed to characterize the molecular interaction and the corresponding stretching frequencies are summarized in Table 2. The vibrational frequencies of the above complexes agree with the experimental results [17]. The stretching frequency of Na-H, Ca-H, C=O and CH_3 bonds do not show a significant variation from neutral complex.

Table 2: Harmonic vibrational frequency (cm^{-1}) of $Ni(dmax)_2(en)_2$, $[Ni(dmax)_2(en)_2].3H_2O$, $Cu(dmax)_2(en)_2$, $[Cu(dmax)_2(en)_2].2H_2O$ and $Cu(dmax)_2(bapa)$ calculated at B3LYP/LANL2DZ and B3LYP/6-311G** levels of theory.

	Ni(dmax)2(en)2		**Cu(dmax)2(en)2**		**Cu(dmax)2(bapa)**		
	LANL2DZ	**6-311G****	**LANL2DZ**	**6-311G****	**LANL2DZ**	**6-311G****	**Expt^a**
Na-H	3388-3674	3408-3586	3312-3596	3342-3567	3324-3451	3380-3521	3200-3400
Ca-H	2987-3136	2972-3098	3052-3147	3033-3110	2996-3116	2957-3092	2850-3000
C=O	1642-1697	1743-1787	1587-1668	1696-1760	1641-1697	1743-1788	-
CH3	3064-3211	3040-3176	3071-3212	3049-3178	3063-3212	3041-3177	-
	[Ni(dmax)2(en)2].3H2O				**[Cu(dmax)2(en)2].2H2O**		
	LANL2DZ	**6-311G****	**Expt^a**		**LANL2DZ**	**6-311G****	**Expt^a**
O-H	3480-3811	3461-3868	3400-3600		2544-3808	3352-3883	3400-3600
Na-H	3272-3679	3376-3439	3200-3400		3226-3540	3328-3530	3200-3400
Ca-H	2957-3152	2970-3054	2850-3000		3046-3141	3031-3100	2850-3000
C=O	1647-1695	1746-1788	-		1635-1682	1697-1762	-
CH3	3064-3213	3035-3177	-		3071-3213	3048-3179	-

Na,Ca = terminal N and C atom of en and bapa.
[a] Taken from Maldonado et al.[17]

6. HYDROGEN BONDING NETWORK

The presence of potential acceptor in triazolopyrimidine ligand and donor sites in auxiliary ligand generates hydrogen bonded networks that increase the dimensionality of the solids [17]. Interstitial water molecules in $[Ni(dmax)_2(en)_2].3H_2O$ and $[Cu(dmax)_2(en)_2]$. $2H_2O$ are actively involved in forming the network (Figs. 6 and 7). In $[Ni(dmax)_2(en)_2].3H_2O$ complex, three water molecules form a chain to build the network. In the copper complex $[Cu(dmax)_2(en)_2].2H_2O$, the water molecule alone is responsible for building the supramolecular structure. In both the compounds $[Ni(dmax)_2(en)_2].3H_2O$ and $[Cu(dmax)_2(en)_2].2H_2O$, the hydrogen bonds interact more weakly with each other through C-H groups of ethylenediamine with carbonyl oxygen atoms. However, the hydrogen bond lengths of the metal complexes in hydrogen bond network are significantly stronger than the experimental values.

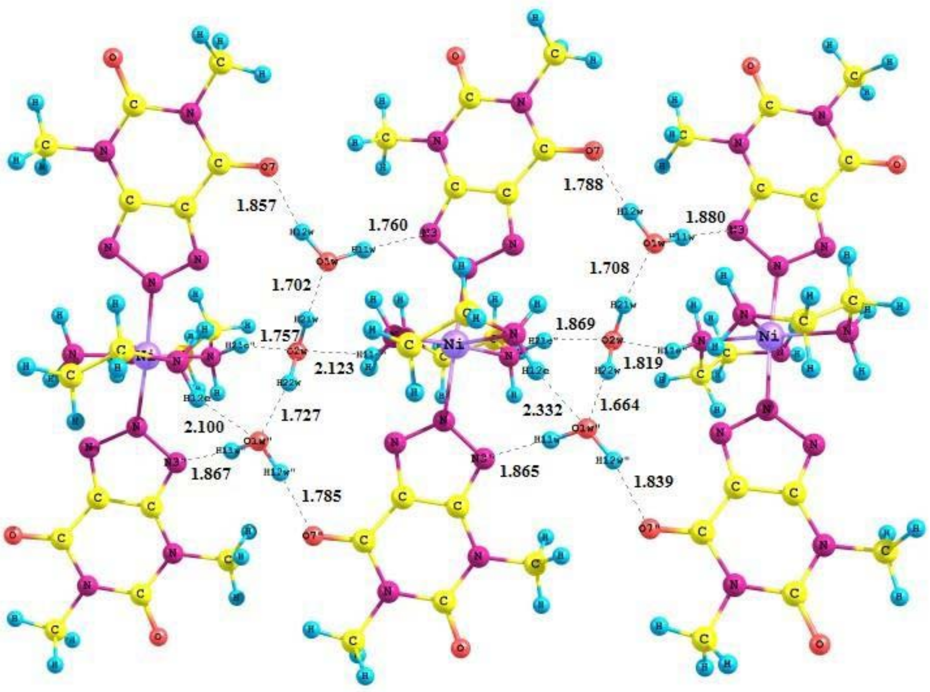


Fig. 4. The tape built by the hydrogen bond network in $[Ni(dmax)_2(en)_2].3H_2O$

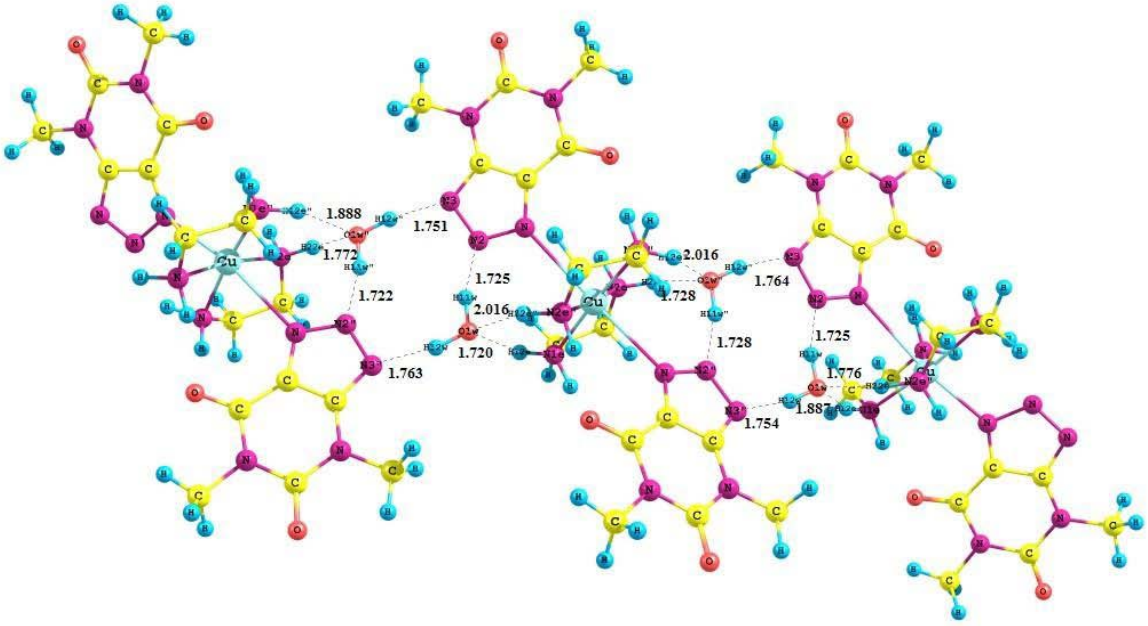


Fig. 5. The tape built by the hydrogen bond network in $[Cu(dmax)_2(en)_2].2H_2O$

7. CONCLUSIONS

The metal cation coordinates with ligands in the first coordination sphere of the complexes. The coordination distances of metal with the ligands calculated at B3LYP/LANL2DZ and B3LYP/6-311G** levels of theory agree well with the X-ray crystallographic data. As the atomic radius of the metal cation increases, the metal coordination distances with the ligands are also found to be increased in the order. The highest binding energy and metal ion affinity has been observed for Ni^{2+} complexes than Cu^{2+} complexes due to small ionic radius of Ni^{2+} coordinated mutually with electronegative atoms of the ligands and allow effective charge transfer from the lone pair of electronegative atoms of the ligands to the metal cation. The IR stretching frequencies corresponding to N-H, C-H, C=O and CH_3 of triazolopyrimidine and auxillary ligands agree well with the previous experimental results. The hydrogen bond lengths of the metal complexes in hydrogen bond network are significantly stronger than the experimental values. The research in metal-ligand framework has profound applications in solar energy; gas separation and storage. An in-depth knowledge on how molecules interact with each other will help the researchers in the design of successful materials or devices.

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