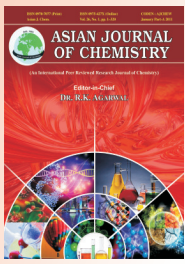
Asian Journal of Chemistry; Vol. 26, No. 12 (2014), 3643-3648

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16836



Chloride Assisted Supramolecular Self-Assembly of Square-Pyramidal $[Cu(imidazole)_4(Cl)]^+$ Unit Involving C-H···Cl, N-H···Cl, π···π, C-H···π Interactions : A Structural, Spectral and Theoretical Investigation

B. DEY[1,*], P. MUKHERJEE[1], R.K. MONDAL[1] and M. FLECK[2]

[1]Department of Chemistry, Visva-Bharati University, Santiniketan-731 235, India
[2]Institut für Mineralogie und Kristallographie, Universität Wien, Althanstr. 9, A-1090 Wien, Austria

*Corresponding author: E-mail: bdeychem@gmail.com

Received: 7 December 2013; *Accepted*: 4 February 2014; *Published online*: 5 June 2014; AJC-15310

A proposed crystal engineering principle, *i.e.*, the anion directed association of molecular complexes driven by the formation of hydrogen bonding patterns and by C-H···π and π···π interactions among π-systems involving suitable aromatic organic heterocyclic ligands have been examined through this work where we report the supramolecular self-assembly of $[Cu(imidazole)_4(Cl)]^+$ units in a water soluble fluorescent molecular complex with formula {[Cu(imidazole)$_4$(Cl)](Cl)}(1). The free chlorine atom (Cl2) and the metal bound chlorine atom (Cl1) in complex **1** act as hydrogen bonding acceptors while the metal coordinated imidazole groups directs the self-assembling pattern of complex **1** *via* self-complementary hydrogen-bonding interactions (C-H···Cl, N-H···Cl) along with π···π stacking and C-H···π interactions between metal coordinated aromatic imidazole moieties. The experimental work is completed with a computational analysis of complex **1**.

Keywords: Supramolecule, DFT, Fluorescence, Cu(II).

INTRODUCTION

The significance of supramolecular phenomena has increased day by day, particularly from the discovery of single crystal X-Ray diffractometer[1-3]. Self-assembly[4] and molecular recognition, being the primary parts of supramolecular chemistry, not only direct crystal nucleation and growth, but also these are very essential in many biological processes like protein folding[5], DNA replication[6], and correspondingly for other scientific routes like chemo-sensors[7], nanotechnology[8] and crystal engineering[9].

In the past decades, extensive studies on different supramolecular interactions[10] including π-π[11], X-H···π (X = C, N, O)[12], anion···π[13], lone pair···π[14], cation···π[15] have been employed for molecular self-assemblies of organic and inorganic materials, nanomaterials and biomolecules[16]. Recently, the control of hydrogen bonding interactions by transition metals has become a hot topic[17]. Strategic complexation of metals with suitable organic ligands may direct hydrogen bonding patterns which are significant towards bio-inorganic[18], medicinal[19], organometallic[20], solid state[14] chemistry and in different supramolecular self-assemblies[21]. Interestingly, the chloride ion, directly coordinated to metal centre, facilitates the hydrogen-bonding pattern for the development of novel metallo-supramolecular building blocks[22,23].

In this contribution, we report the synthesis, structural, spectral characterization as well as a theoretical investigation of a water soluble square pyramidal Cu(II) complex, {[Cu(imidazole)$_4$(Cl)](Cl)}(**1**), where the interplay of some supramolecular non-covalent interactions (including C-H···Cl, N-H···Cl, π···π, C-H···π) plays a critical role to the formation of crystal structure in the solid-state.

EXPERIMENTAL

All reactions were carried out under aerobic conditions. Copper(II) chloride hexahydrate and imidazole were purchased from Sigma-Aldrich and used as received. Double distilled water was used as the solvent throughout the present work.

Elemental analysis (C, H, N) was carried out using a Perkin-Elmer 240C elemental analyzer. IR spectroscopy was measured on Shimadzu FTIR-8400S spectrometer between 400 and 4000 cm^{-1}, using the KBr pellet method. Absorption and fluorescence spectra of the aqueous solutions of complex **1** were measured in a Shimadzu UVPC-3200 spectro-photometer and a Perkin-Elmer LS55 fluorimeter, respectively.

Synthesis of Complex 1: To a 75 mL beaker $CuCl_2.6H_2O$ (0.170 g, 1 mmol) and imidazole (0.272 g, 4 mmol) are dissolved in 40 mL of distilled water and the resulting blue colour solution was heated at ~70 °C and stirred continuously for about 2 h. Then the solution was allowed to cool. It was filtered

off and kept for crystallization. Deep blue block shaped single crystals suitable for X-ray analysis were separated after several days from the mother liquid by slow evaporation at room temperature. The crystals were filtered off, washed with cold water and dried in air. The yield was 60 % based on Cu. Anal. Calcd. (Found, %) for $C_{12}H_{16}N_8Cl_2Cu$: C, 35.40 (35.37); H, 3.93 (3.89); N, 27.53 (27.51).

Spectral studies: Main IR absorption bands observed for **1** (KBr pellet/cm^{-1}) are: 3479 cm^{-1} (s), 3436 cm^{-1} (s), 2939 cm^{-1} (b), 1583 cm^{-1} (b). The electronic spectra of the dilute aqueous solution of complex **1** ([complex **1**] = 3.4×10^{-4} M) exhibits distinct absorption bands at 280 nm (λ_{max}), due to n-π^* or π-π^* transitions. There is an intense peak at 357.5 nm in the fluorescence emission spectra of the same aqueous solution of complex **1**, where, $\lambda_{excitation}$ = 280 nm, which implies that the complex **1** is highly fluorophore.

X-ray crystal structure determination of 1: X-ray diffraction data were collected at ambient conditions on a Bruker APEX-II diffractometer, equipped with CCD area detector and graphite-monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å) using suitable single crystals of the title compound with the dimensions of 0.10 mm × 0.07 mm × 0.06 mm. In the measurements, multiple sets of ϕ- and ω-scans were used. The intensity data were processed with the Bruker-Nonius program suite Saint-Plus[24] and corrected for Lorentz, polarization, background and absorption effects[24,25]. The crystal structure was determined by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements[26] on F^2. Scattering factors for neutral atoms were employed in the refinements. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms isotropically. The final R1-value of the refinement was 0.075. A summary of the crystallographic data, structural parameters and refinement details are presented in Table-1.

Computational details: All calculations were performed with the Gaussian09 package[27], employing the M06-2X DFT functional[28] together with the 6-311++G(d,p) basis set, a level that has been shown to well reproduce stacking interactions between aromatic molecules. Two models were extracted from the X-ray structure: model **1**, containing 5 molecules of **1** arranged in a cluster similar to that of Fig. 4; model 2, containing 5 molecules of 1, arranged as in Fig. 5. On both models single-point calculations were performed at the M06-2X/6-311++G(d,p) level of theory in order to carry out an Atoms in Molecules (AIM) analysis[29]. The AIM analysis was used to quantify the intermolecular interactions present in the crystal. AIM is based upon those critical points (CPs) where the gradient of the density vanishes. Such points are classified by the curvature of the electron density, for example bond or (3, 1) CPs have one positive curvature (in the internuclear direction) and two negative (perpendicular to the bond). Properties evaluated at such points characterize the bonding interactions present. In particular electron density at the bond critical points (ρ^{BCP}) roughly correlates with the strength of the interaction.

RESULTS AND DISCUSSION

Single crystal structural analysis indicates that complex **1** crystallizes in the monoclinic space group $P2_1/c$ (Table-1)

TABLE-1
CRYSTALLOGRAPHIC DATA OF **1**

CCDC No.	928301
Formula	$C_{12}H_{16}N_8Cl_2Cu$
Formula weight	406.77
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.8683(9)
b (Å)	13.3193(13)
c (Å)	16.4907(15)
α (°)	90
β (°)	122.532(4)
γ (°)	90
V (Å^3)	1642.2(3)
Z	4
D(calc) (g/cm^3)	1.645
μ(MoKα) (mm)	1.666
F(000)	828
Temperature (K)	293
Radiation (Å)	MoK$_\alpha$ 0.71073
Theta Min-Max (°)	2.72, 32.04
h/k/l	-12,13/-18,18/-17,11
Tot.	9022
Uniq. Data	3804
R(int)	0.120
Observed data [I > 2.0 σ(I)]	2143
Nref	3804
Npar	209
R1	0.0757
wR2	0.1507
Goodness of fit	1.096
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Å^3]	-1.320, 0.894

w = 1/[Σ(Fo^2) + (0.1637P)^2 + 13.5711P] where P = (Fo^2 + 2Fc^2)

and forms a three-dimensional hydrogen-bonded supramolecular network of Cu(II). Each asymmetric unit of complex **1** contains a square-pyramidal geometry where the four imidazole rings, connected with the Cu(II) centre *via* nitrogen atoms (*i.e.* N1,N2, N3, N4 of four different imidazole rings), form the basal plane of the square pyramid, with a chlorine atom (Cl1) in apical position, while another chlorine atom (Cl2) remains free. The ORTEP diagram of the asymmetric unit is shown in Fig. 1. In the basal plane, the Cu-N distances are 2.013(4) Å, 1.995(5) Å, 2.008(4) Å and 1.999(5) Å for N1, N2, N3 and N4 of four different coordinated imidazole rings, respectively. The axial Cu-Cl1 bond distance, 2.6220(14) Å, is significantly elongated which is attributed by the Jahn-Teller effect, typically expected for a d^9 system of Cu(II). Four other imidazolium nitrogen atoms (N1A, N2A, N3A and N4A) whose lone-pair are involved in the aromatic resonance of each imidazole ligand remain inert from coordination with metal ions. Distortion from perfect square pyramidal geometry is indicated by the 'τ' value, which is 0.28 for Cu1[30]. The bond distances and angles (Table-2) fall within the usual range, observed in similar square pyramidal environments of Cu(II) complexes[22,31].

The one dimensional hydrogen-bonded polymeric chain of successive [Cu(imidazole)$_4$(Cl)]$^+$ units is formed by the self-complementary N3A-H3A···Cl1 hydrogen bonding pattern between one of the imidazole ligand of one square-pyramidal cationic unit of Cu(II) and the apical Cl1 atom of the another

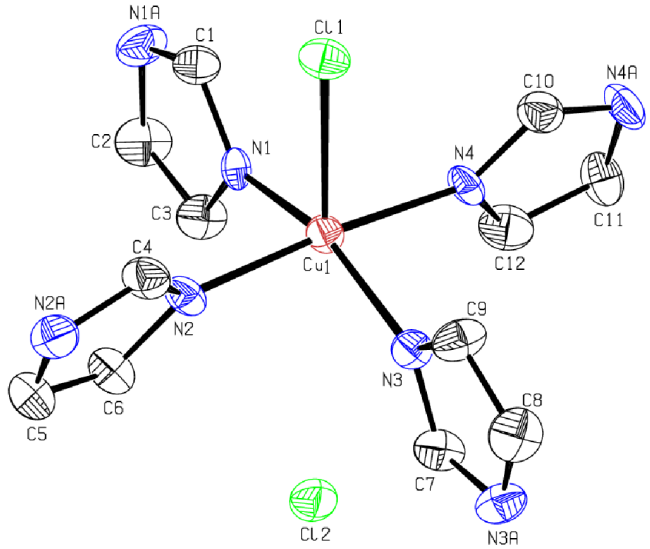


Fig. 1. An ORTEP representation of complex **1** with atom numbering scheme and 50 % ellipsoid probability for all non-hydrogen atoms

TABLE-2
SELECTED BOND DISTANCES (Å)
AND BOND ANGLES (°) FOR COMPLEX **1**

Bond distances		Bond angles	
Cu1-N1	2.013(4)	Cl1-Cu1-N1	98.33(1)
Cu1-N2	1.995(5)	Cl1-Cu1-N2	93.24(1)
Cu1-N3	2.008(4)	Cl1-Cu1-N3	104.05(1)
Cu1-N4	1.999(5)	Cl1-Cu1-N4	92.09(1)
Cu1-Cl1	2.6220(1)	N1-Cu1-N2	89.7(2)
		N1-Cu1-N3	157.62(2)
		N1-Cu1-N4	90.3(2)
		N2-Cu1-N3	88.9(2)
		N2-Cu1-N4	174.61(2)
		N3-Cu1-N4	89.0(2)

adjacent square pyramidal [Cu(imidazole)$_4$(Cl)]$^+$ unit, where the H3A···Cl1 distance is 2.43Å. The electron density at the bond critical point, ρ^{BCP}, equal to 0.0173 au (Table-3). 1D self-assembled hydrogen-bonded chain of [Cu(imidazole)$_4$(Cl)]$^+$ propagates along the crystallographic a-axis (Fig. 2).

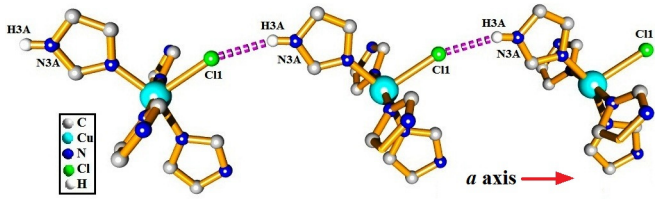


Fig. 2. One-dimensional chain structure of [Cu(imidazole)$_4$(Cl)]$^+$ in 1 propagated along crystallographic a-axis *via* N3A-H3A···Cl1 hydrogen bond

These self-assembled 1D hydrogen-bonded chains are further bridged by C-H···Cl and N-H···Cl hydrogen bonding interactions, linking [Cu(imidazole)$_4$(Cl)]$^+$ units and free Cl2 atoms, leading to the formation of two dimensional supramolecular sheets parallel to crystallographic *ac*-plane (Figs. 2 and 3). The apical chlorine atom (Cl1) of the [Cu(imidazole)$_4$(Cl)]$^+$ unit connects two adjacent self-assembling cationic units from either side *via* C11-H11···Cl1 and C5-H5···Cl1 self-complimentary hydrogen bonds. The free chlorine atom (Cl2) assembles three contiguous [Cu(imidazole)$_4$(Cl)]$^+$ units through C3-H3···Cl2, C7-H7···Cl2, N1A-H1A···Cl2, N2A-H2A···Cl2 and N4A-H4A···Cl2 hydrogen bonds. The aromatic systems of imidazole rings connected with the Cu(II) centre are engaged to build-up another type of supramolecular sheet parallel to crystallographic (100) plane *via* non-covalent interactions such as C-H···π and π···π between nearby [Cu(imidazole)$_4$(Cl)]$^+$ units (Fig. 4).

The H2 atom from Cg(1) of one self-complementary [Cu(imidazole)$_4$(Cl)]$^+$ unit is linked *via* C-H···π interaction with Cg(4), C2-H2···Cg(4) distance being 2.80Å. The electron density, ρ^{BCP}, is equal to 0.0033 au, which confirms that the interaction exists but it is rather weak (Table-3). Cg(1) of one [Cu(imidazole)$_4$(Cl)]$^+$ unit stacks between Cg(1) and Cg(3) from another two [Cu(imidazole)$_4$(Cl)]$^+$ units *via* π···π interactions propagated along bottom to top direction, whereas, Cg(3), formed by N(3), C(7), N(3A), C(8), C(9) atoms of one [Cu(imidazole)$_4$(Cl)]$^+$ unit, also stacks within Cg(3) and Cg(1) of another two neighboring [Cu(imidazole)$_4$(Cl)]$^+$ units *via*

TABLE-3
SUPRAMOLECULAR INTERACTION PARAMETERS IN **1**

Selective Hydrogen bond donor/acceptor scheme (Å, °) and electron density at the bond critical points, ρ^{BCP} (au)						
D-H···A	D-H	H···A	D···A	D-H···A	ρ^{BCP} (au)	Symmetry code
N1A-H1A···Cl2	0.86	2.53	3.179(7)	133	0.0080	-1 + x, y, z
N2A-H2A···Cl2	0.86	2.4100	3.252(6)	168	0.0193	x,1/2-y, 1/2 + z
N3A-H3A···Cl1	0.86	2.4300	3.256(7)	160	0.0173	1 + x, y, z
N4A-H4A···Cl2	0.86	2.4000	3.246(6)	168	0.0195	-1 + x, 1/2-y, -1/2 + z
C3-H3···Cl2	0.93	2.7700	3.640(8)	155	0.0083	
C4-H4···Cl1	0.93	2.7700	3.535(7)	140	0.0080	1-x,1-y,1-z
C7-H7···Cl2	0.93	2.7800	3.664(7)	160	0.0084	
C-H···π interactions (Å, °)						
D-H···Cg	D-H	H···Cg	D···Cg	D-H···Cg	ρ^{BCP} (au)	Symmetry code
C2-H2···Cg(4)	0.93	2.80	3.524(7)	135	0.0033	1-x,-1/2+y,1/2-z
π··· π interactions (Å, °)						
Cg-Cg	Cg-Cg distance	Dihedral angle (i,j)	Perpendicular distances between baricentres (i,j)	Slippage		Symmetry code
Cg(1)···Cg(1)	4.069(4)	0	3.549(3)	1.988	--	1-x, -y, 1-z
Cg(1)···Cg(3)	3.918(4)	4.6(4)	3.491(3)		0.0098	1-x, -1/2 + y, 1/2-z
Cg(3)···Cg(1)	3.918(4)	4.6(4)	3.523(3)		0.0095	1-x, 1/2 + y,1/2-z
Cg(3)···Cg(3)	3.783(4)	0	3.379(3)	1.702	0.0132	2-x, 1-y, 1-z

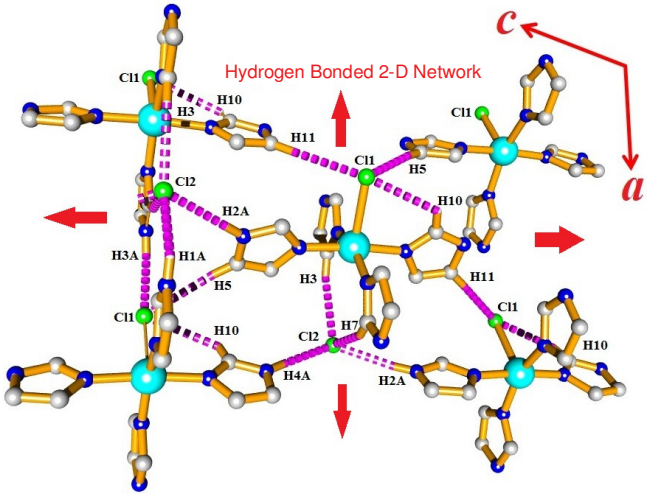


Fig. 3. Two-dimensional network structure in **1** formed through N-H···Cl and C-H···Cl hydrogen bonds parallel to crystallographic (010) plane

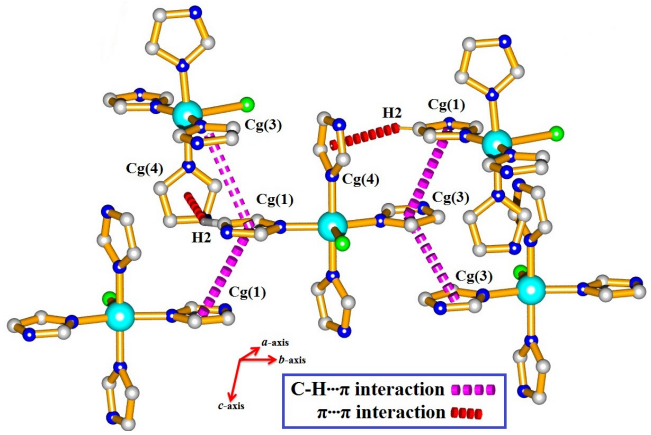


Fig. 4 Interplay of C-H···π (indicated red broken line) and π···π interactions (indicated deep yellow broken line) in **1** towards the formation of supramolecular architecture parallel to crystallographic *bc*-plane

π···π interactions propagated along bottom to top direction, respectively (Table-3). These non-covalent interactions, which involve C-H···π and π···π, play a crucial role towards the formation of the three dimensional self-assembled supramolecular structure of complex **1**.

The electron density analysis confirms the existence of the Cg(1) ··Cg(3), Cg(3) ··Cg(1) π···π interactions, with an electron density at the bond critical point of 0.0108 au on average, the Cg(3)···Cg(3) interaction being the strongest, with a ρ^{BCP} = 0.0132 au. Despite the potentially favorable geometry (distance equal to 4.069 Å) no interaction was found between Cg(1) and Cg(1). These interactions are comparable to or weaker than those found in the π-stacked benzene dimer, which is characterized by an electron density of 0.0141 au, calculated at the BhandH/6-311++G(d,p) level[32].

A cluster of each monomeric [Cu(imidazole)$_4$(Cl)]$^+$ unit along with free chlorine atom (Cl2) is self-assembled *via* a network of supramolecular cyclic hydrogen-bonded motifs (*i.e.* supramolecular synthons) (Figs. 5 and 6).

The two apical chlorine atoms (Cl1) from two adjacent [Cu(imidazole)$_4$(Cl)]$^+$ units combine *via* R_2^2 (10) cyclic motif generated by self-complementary C4-H4···Cl1 interactions

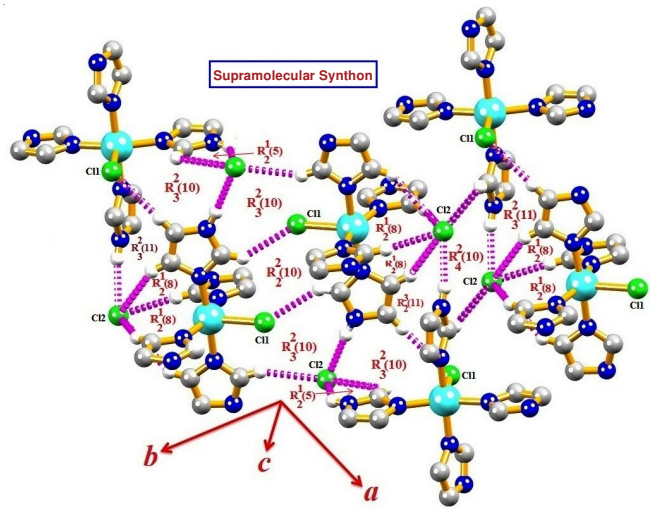


Fig. 5. Hydrogen-bonded network involving several supramolecular synthons including different cyclic motifs R12(5), R12(8), R22(10), R23(10), R23(11) and R24(10) in Etter's graph set notation

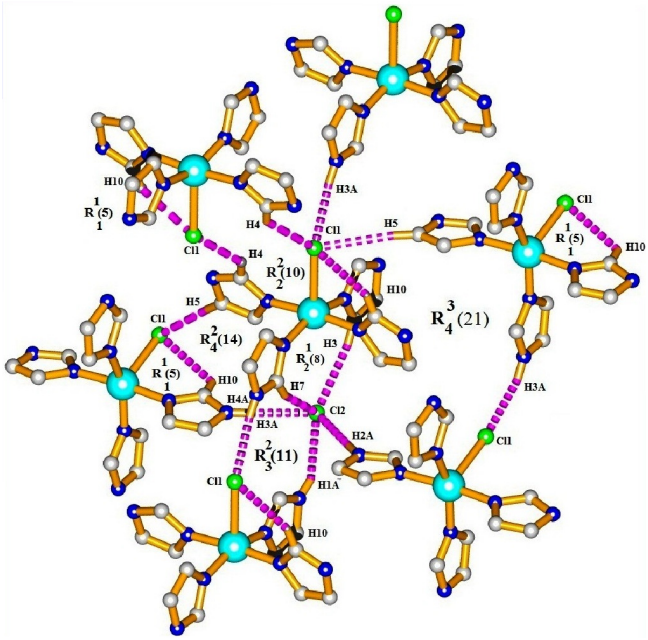


Fig. 6. Supramolecular synthons including different cyclic motifs of R^1_1(5), R^2_2(10), R^2_3(11), R^2_4(14) and an unusual R^3_4(21) due the hydrogen bonding patterns of two different chlorine atoms

from each cationic unit (Figs. 5 and 6). The connection of these two [Cu(imidazole)$_4$(Cl)]$^+$ units are being further strengthened by two R_3^2 (10) cyclic motifs (up and down of R_2^2 (10) cyclic motif) constructed by another self-complementary N2A-H2A···Cl2, C10-H10···Cl2 and C4-H4···Cl1 hydrogen bonding pattern through the involvement of free chlorine atom (Cl2) and two cationic units of Cu(II). Each free chlorine atom (Cl2) promotes R_2^1 (5) cyclic motifs through N1A-H1A···Cl2 and C1-H1···Cl2 hydrogen bonds and another interesting four R_2^1 (8) cyclic motifs with one monomeric [Cu(imidazole)$_4$(Cl)]$^+$ unit *via* four C-H···Cl hydrogen bonds, C3-H3···Cl2, C6-H6···Cl2, C7-H7···Cl2 and C12-H12···Cl2 (Figs. 4 and 5). Another R_3^2(10) cyclic motif connects two cationic units and

one of the free chlorine atoms (Cl2) through C1-H1···Cl2, C5-H5···Cl1 and N2A-H2A···Cl2 hydrogen bonds. Two cationic units of Cu(II) and one of the free chlorine atoms (Cl2) also forms a $R_3^2(11)$ cyclic motif through C6-H6···Cl2, C5-H5···Cl1 and N4A-H4A···Cl2 hydrogen bonds.

Two adjacent [Cu(imidazole)$_4$(Cl)]$^+$ units along with two different free chlorine atoms (Cl2) assemble to form $R_4^2(10)$ cyclic motifs through two self-complementary C10-H10···Cl2 and N4A-H4A···Cl2 hydrogen bonds. The apical chlorine atom (Cl1) forms intramolecular hydrogen-bonding patterns with H10 atom leading to the formation of $R_1^1(5)$ cyclic motif (Fig. 5). Both of the chlorine atoms (Cl1 and Cl2) produce two more hydrogen bonded cyclic motifs like $R_4^2(14)$ (*via* C3-H3···Cl2, C5-H5···Cl1, C10-H10···Cl1, N4A-H4A···Cl2) and $R_3^2(11)$ (*via* N3A- H3A···Cl1, N1A-H1A···Cl2, C7-H7···Cl2). A hydrogen-bonded cyclic motif of $R_4^3(21)$ is also found in the solid-state architecture of complex **1** and it is placed in between three bordering [Cu(imidazole)$_4$(Cl)]$^+$ units linked by means of C5-H5···Cl1, C3-H3···Cl2, N2A-H2A···Cl2, N3A-H3A···Cl1 interactions (Fig. 6). These different cyclic recognition motifs ensure the donor acceptor balance within the solid-state architecture of complex **1**.

The metal bound chlorine atom (Cl1), placed at the apical position of the square pyramidal geometry of each [Cu(imidazole)$_4$(Cl)]$^+$, connects three more adjacent monomeric units of Cu(II) by exploiting different self-complementary C-H···Cl (C4-H4···Cl1 and C5-H5···Cl1) and N3A-H3A···Cl1 hydrogen-bonding interactions shaping the self-assembly of square-pyramidal Cu(II) monomeric units (Fig. 7).

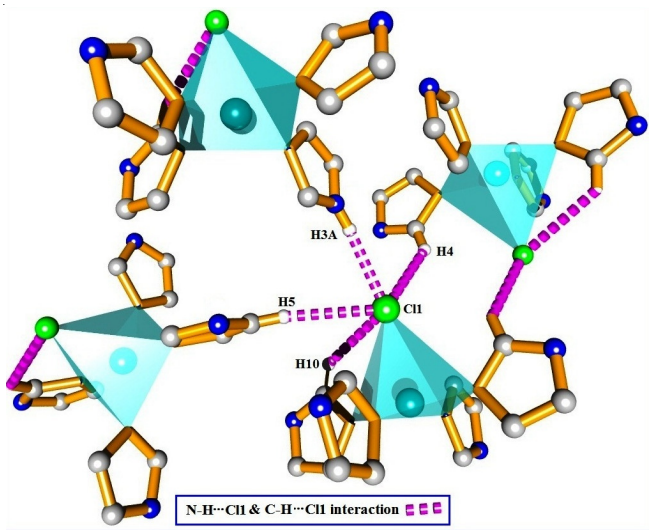


Fig. 7. Role of metal bound Cl1 atom towards the crystal packing of complex **1**. Here, blue coloured polyhedral represent the square-pyramidal geometry of each Cu(II) monomer (*i.e.* CuN$_4$Cl core)

Interestingly, each free chloride atom (Cl2) adopts a pseudo-square pyramidal hydrogen-bonded motif through C3-H3···Cl2, C7-H7···Cl2, N2A-H2A···Cl2, N1A-H1A···Cl2 and N4A-H4A···Cl2 interactions (shown by light green coloured polyhedra containing Cl2 atom in Fig. 8) among four surrounding [Cu(imidazole)$_4$(Cl)]$^+$ units. This specific orientation favours the donor acceptor balance, thereby directing the three dimensional self-assembled supramolecular network of complex **1**.

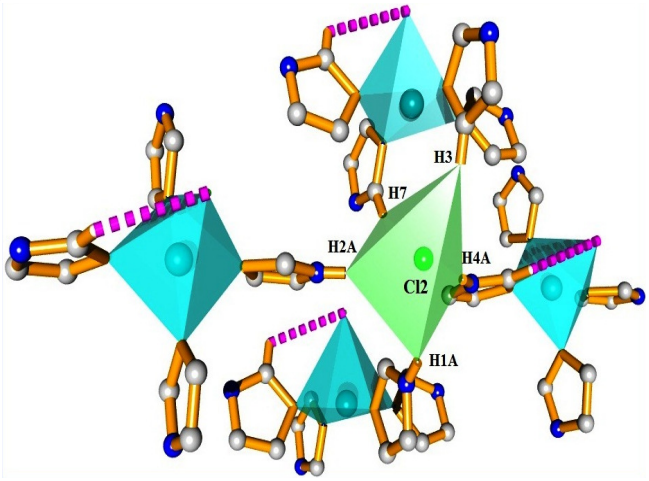


Fig. 8. Impact of free chlorine atom (Cl2) towards the crystal packing of complex **1**. Here, four blue coloured polyhedra represents the square-pyramidal geometry of each Cu(II) monomer (*i.e.* CuN$_4$Cl core) and middle light green coloured polyhedra with Cl2 atom centre depicts a pseudo square pyramidal type hydrogen-bonded motif

Conclusion

In this contribution, we have proposed the design, synthesis, structural and theoretical characterizations of a water soluble luminescent Cu(II) complex which adopts a supramolecular architecture in solid-state. A specific crystal engineering principle *i.e.* the chloride directed self-assembling tendency of monomeric Cu(II) units *via* the formation of self-complementary N-H···Cl and C-H···Cl hydrogen-bonding interactions which promote the π···π and C-H···π interactions among aromatic imidazole moieties was followed for the design of the three dimensional supramolecular network.

The electron density analysis performed on two models of five {[Cu(imidazole)$_4$(Cl)] (Cl)} arranged as in Figs. 2 and 3 confirm the existence of the non-covalent interactions suggested by the experimental structure. In particular, the electron density at the hydrogen bonds ranges between 0.0080 and 0.0193 au, that of the C-H···π is somewhat weaker, ρ^{BCP} = 0.0033 au and that of the π···π interactions is comparable to or slightly weaker than those found in the benzene dimer. In addition, the fluorescence property of the complex **1** in water medium was also assessed in this work.

ACKNOWLEDGEMENTS

One of the authors, B.D. thankfully acknowledges Visva-Bharati authority for a special financial supports. B.D. is also thankful to Dr. Arturo Robertazzi, Department of Biology, Chemistry and Pharmacy, Institute of Chemistry and Biochemistry, Freie Universität Berlin, Fabeckstrasse 36a, D-14195 Berlin, Germany, for his kind support in the computational part.

REFERENCES

1. G.R. Desiraju, *Nature*, **412**, 397 (2001).
2. J.-M. Lehn, Supramolecular Chemistry–Concepts and Perspectives, VCH: Weinheim, Germany (1995).
3. C.B. Aakeröy, N.R. Champness and C. Janiak, *Cryst. Eng. Comm*., **12**, 22 (2009).
4. G.M. Whitesides and B. Grzybowski, *Science*, **295**, 2418 (2002).
5. C.L. Kielkopf, N.A. Rodionova, M.R. Green and S.K. Burley, *Cell*, **106**, 595 (2001).
6. P. Selenko, G. Gregorovic, R. Sprangers, G. Stier, Z. Rhani, A. Kramer and M. Sattler, *Mol. Cell*, **11**, 965 (2003).
7. B. Dey, R. Saha and P. Mukherjee, *Chem. Commun.*, **49**, 7064 (2013).
8. A. Langner, S.L. Tait, N. Lin, R. Chandrasekar, M. Ruben and K. Kern, *Angew. Chem. Int. Ed*., **47**, 8835 (2008).
9. G.R. Desiraju and T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, Oxford University Press: Oxford (1999).
10. G.R. Desiraju, *Chem. Res*., **35**, 565 (2002).
11. C. Janiak, *J. Chem. Soc., Dalton Trans*., 3885 (2000).
12. C.M. Reddy, A. Nangia, C.-K. Lam and T.C.W. Mak, *Cryst Eng Comm*, **4**, 323 (2002).
13. A.L. Cresswell, M.O.M. Piepenbrock and J.W. Steed, *Chem. Commun. (Camb.)*, **46**, 2787 (2010).
14. S.R. Choudhury, B. Dey, S. Das, P. Gamez, A. Robertazzi, K.T. Chan, H.M. Lee and S. Mukhopadhyay, *J. Phys. Chem. A*, **113**, 1623 (2009).
15. J.C. Ma and D.A. Dougherty, *Chem. Rev*., **97**, 1303 (1997).
16. S.K. Burley and G.A. Petsko, *Science*, **229**, 23 (1985).
17. A.S. Borovik, *Acc. Chem. Res*., **38**, 54 (2005).
18. S. Das, C.D. Incarvito, R.H. Crabtree and G.W. Brudwig, *Science*, **312**, 1941 (2006).
19. S. Aime, A. Barge, A.S. Batsanov, M. Botta, D.D. Castelli, F. Fedeli, A. Mortillaro, D. Parker and H. Puschmann, *Chem. Commun. (Camb.)*, 1120 (2002).
20. M. Yamakawa, I. Yamada and R. Noyori, *Angew. Chem. Int. Ed*., **40**, 2818 (2001).
21. D. Braga and F. Grepioni, *Acc. Chem. Res*., **33**, 601 (2000).; M.W. Hosseini, *Acc. Chem. Res*., **38**, 313 (2005).
22. B. Dey, S.R. Choudhury, S. Das, A.D. Jana, L.-P. Lu, M.-L. Zhu, A. Dutta and S. Mukhopadhyay, *Polyhedron*, **27**, 2899 (2008).
23. P.J. Davies, D.M. Grove, G. van Koten, N. Veldman, A.L. Spek and B.T.G. Lutz, *Angew. Chem. Int. Ed. Engl*., **35**, 1959 (1996).
24. Bruker-Nonius, Apex-II and Saint-Plus (Version 7.06a), Bruker AXS Inc., Madison, Wisconsin, USA (2004).
25. Z. Otwinowski and W. Minor, *Methods Enzymol*., **276**, 307 (1997).
26. G.M. Sheldrick, *Acta Crystallogr. A*, **64**, 112 (2008).
27. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, Gaussian, Inc., Pittsburgh PA (2009).
28. Y. Zhao and D. Truhlar, *Theor. Chem. Acc*., **120**, 215 (2008).
29. R.F.W. Bader, *Chem. Rev*., **91**, 893 (1991).
30. A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn and G.C. Verschoor, *J. Chem. Soc., Dalton Trans*., 1349 (1984).
31. C.P. Pradeep and S.K. Das, *Polyhedron*, **28**, 630 (2009).
32. M.P. Waller, A. Robertazzi, J.A. Platts, D.E. Hibbs and P.A. Williams, *J. Comput. Chem*., **27**, 491 (2006).