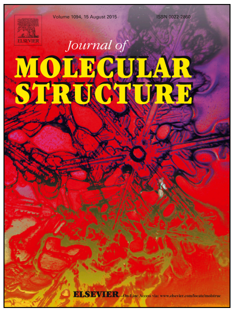


Synthesis, characterization and electrochemical investigations of mixed-ligand copper(II)-organic supramolecular frameworks

Sandeep K. Singh, Ashish Kumar Srivastava, Krishna Srivastava, Rahul Banerjee, Jagdish Prasad

PII: S0022-2860(17)30909-2

DOI: 10.1016/j.molstruc.2017.06.128

Reference: MOLSTR 24014

To appear in: *Journal of Molecular Structure*

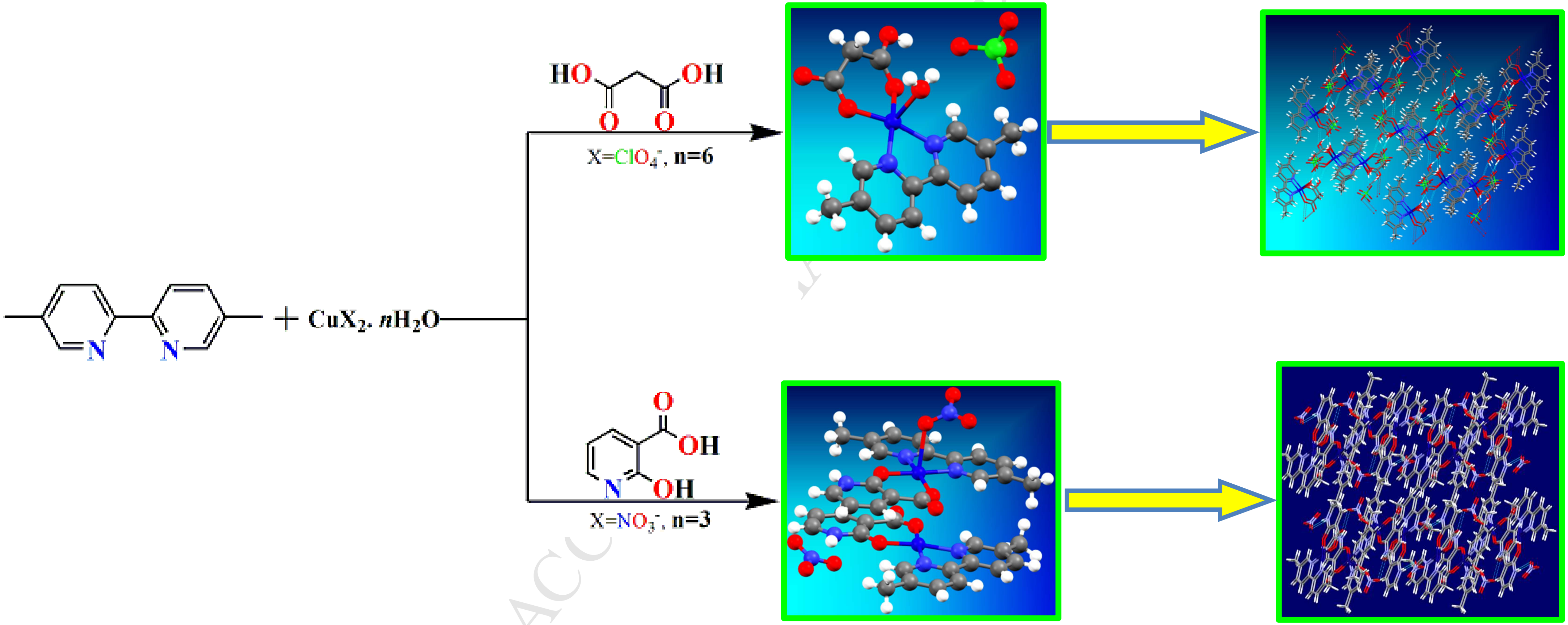
Received Date: 25 April 2017

Revised Date: 17 June 2017

Accepted Date: 28 June 2017

Please cite this article as: S.K. Singh, A.K. Srivastava, K. Srivastava, R. Banerjee, J. Prasad, Synthesis, characterization and electrochemical investigations of mixed-ligand copper(II)-organic supramolecular frameworks, *Journal of Molecular Structure* (2017), doi: 10.1016/j.molstruc.2017.06.128.

Graphical abstract



Synthesis, characterization and electrochemical investigations of mixed-ligand copper(II)-organic supramolecular frameworks

Sandeep K. Singh*[a,b], Ashish Kumar Srivastava[b], Krishna Srivastava[b], Rahul Banerjee[c] and Jagdish Prasad[b]

*Author to whom all correspondence should be made.
*[a]Regional Water Analysis & Research Laboratory, U. P. Jal Nigam, Lanka, Varanasi-221005 (U.P.), India
Tel: +91-9450750601; E-mail: skssrinet@gmail.com
[b]Nanoscience and Electrochemical Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad-211002 (U.P.), India
Fax: +91-532-2462241; Tel: +91-9415247536; E-mail: dr_jagdish_p@yahoo.co.in
[c]Physical Chemistry Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008 (Maharashtra), India
Fax: +91-20-25902636; Tel: +91-020-2590-2535; E-mail: r.banerjee@ncl.res.in

Abstract: Two mixed-ligand copper(II)-organic coordination compounds with 5,5'-dimethyl-2,2'-bipyridine (5,5'-Me_2bpy) as a primary ligand while aliphatic malonate (Hmal) and aromatic 2-hydroxynicotinate (2-OHNA) as secondary ligands, were synthesized. These complexes are formulated as: [Cu(Hmal)(5,5'-Me_2bpy)(H_2O)](ClO_4) **1** and [Cu_2(2-OHNA)$_2$(5,5'-Me_2bpy)$_2$(NO_3)](NO_3) **2.** These two complexes were structurally characterized by single crystal X-ray diffraction analysis. Characterization was further supported by powder X-ray diffraction analysis, elemental analyses, FT-IR, FAB-MASS and TGA, DSC studies. Cyclic voltammetric and UV-visible spectral studies of these two complexes have also been done. The electrochemical studies of complex **1** in DMSO and DMF have shown that this complex undergoes quasi-reversible diffusion-controlled one-electron transfer reaction without any chemical complication while complex **2** in DMSO undergoes quasi-reversible diffusion-controlled one electron transfer reaction, following EC mechanism. The electrochemical behaviour of complex **2** in DMF is complicated probably due to presence of more than one species in solution phase.

Keywords: Mixed-ligand complex; Supramolecular framework; X-ray diffraction; Cyclic voltammetry; 5,5'-dimethyl-2,2'-bipyridine; π-π stacking interaction.

1. Introduction

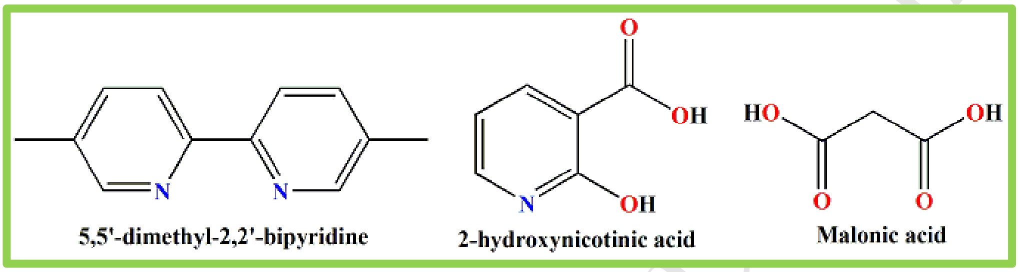
Recent years have witnessed rapid progress in the construction of metallosupramolecular frameworks due to their variety of architectures, enchanting topology [1-7], and the potential applications as functional materials [8-14]. Early reports have shown that carboxylate compounds and nitrogen heterocyclic ligands have been successfully employed in the generation of many novel structures [15]. Cui and his co-workers have extensively studied the application of nitrogen-heterocyclic ligand based metal-organic coordination compounds in the field of photo-catalysis, electrochemistry, luminescence, fluorescence and dye adsorption [16-21]. Further, it has also been recognized for many years that mixed-ligand copper(II) complexes containing an aromatic amine or its derivatives and an anionic auxiliary ligand are much more stable than would be expected on statistical grounds [22]. Earlier studies have also demonstrated that the aromatic ligand receives π-electron density from the metal ions and that this process is augmented by the binding of anionic auxiliary ligands to the metal ions [23]. These electronic effects have been suggested to lead to the enhanced stability of the complex species. In contrast to this, the stability of mixed-ligand copper(II) complexes, containing neutral donor ligands as a moiety, are of the order expected on statistical ground [24].

Moreover, copper(II)-organic frameworks possess enormous structural diversity due to its flexible coordination sphere around the copper(II) ion, in combination with steric and packing forces [25]. Copper(II) is one of the most important transition metal ions, not only because of its relevance as the active-site structure of metalloproteins [26], but also due to its magnetochemistry [27].

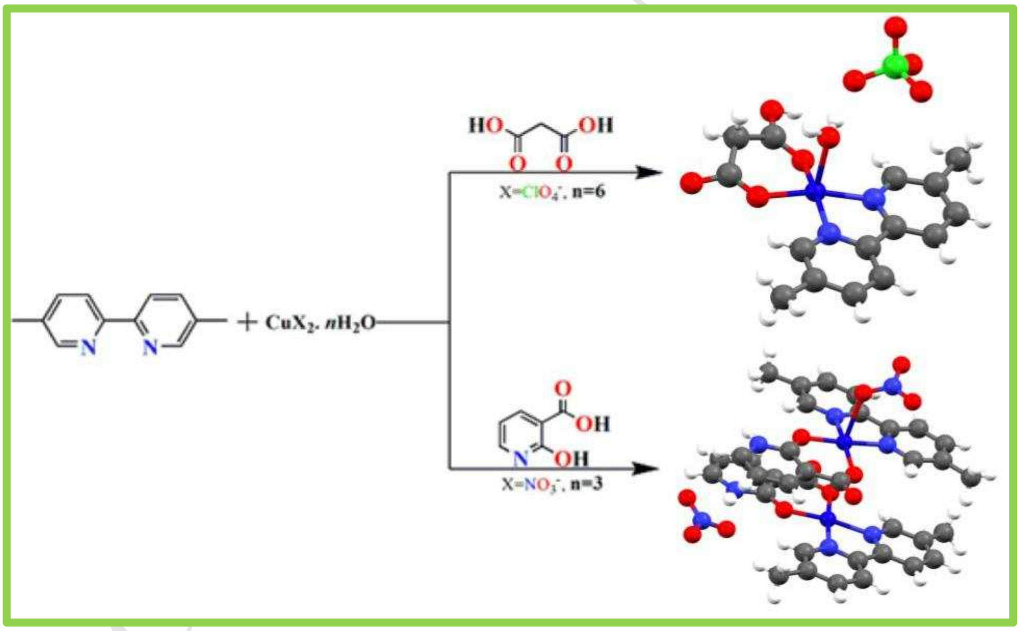
In this respect polycarboxylates along with copper(II) ions are widely used in the construction of supramolecular architectures organised through coordination bonds, π-π stacking interaction and/or hydrogen bondings. For this purpose dicarboxylate ligands are frequently used as bridging and chelating linkers. Among these malonate is a dicarboxylate with singular behaviour different from the other dicarboxylates. It shows a number of coordination modes with transition metal ions [28]. It also acts as a blocking agent through bidentate chelation and produces an isolated structure which is further extended by supramolecular interactions [29]. Mono-deprotonated malonate frequently enhances the structures with low dimensionality to supramolecular architectures via the assembly of hydrogen bonding [30]. Further, functionalized carboxylates can easily be applied to construct functionalized metal-organic coordination compounds with supramolecular architectures.

Functional groups like –OH, $-NH_2$ are frequently used for this purpose [31]. 2-hydroxynicotinic acid (2-OHNAH) is one of the most successful functionalized carboxylates used for the purpose due to its versatile modes of coordination [32,33].

A fascinating supramolecular architecture can easily be achieved via the combination of carboxylate ligands with other ligands having N-donor chelating bipyridine moiety. 2,2'-bipyridine and its derivatives are frequently used for the synthesis of low dimensional molecular architectures [34-38], which can be further extended to high dimensional supramolecular architectures via supramolecular interactions.



Scheme 1. Ligands used for the synthesis of mixed-ligand complexes.



Scheme 2. General synthetic routes for the complexes $[Cu(Hmal)(5,5'-Me_2bpy)(H_2O)](ClO_4)$ **1** and $[Cu_2(2-OHNA)_2(5,5'-Me_2bpy)_2(NO_3)](NO_3)$ **2.**

Thus keeping in mind the above mentioned importance and properties a successful attempt has been made for synthesizing two mixed-ligand copper(II)-organic coordination compounds, taking 5,5'-dimethyl-2,2'-bipyridine ($5,5'-Me_2bpy$) as a primary ligand while aliphatic malonate (Hmal) and aromatic 2-hydroxynicotinate (2-OHNA) as secondary ligands (Scheme 1). These complexes are formulated as: $[Cu(Hmal)(5,5'-Me_2bpy)(H_2O)](ClO_4)$ **1** and $[Cu_2(2-OHNA)_2(5,5'-Me_2bpy)_2(NO_3)](NO_3)$ **2.** These two complexes were procured by traditional room temperature synthesis (Scheme 2) and were structurally characterized by single crystal X-ray diffraction analysis. Characterization was further supported by powder X-ray diffraction, elemental analyses, FT-IR, FAB-MASS, UV-Visible spectral analyses, TGA, DSC and cyclic voltammetric (CV) studies.

2. Experimental

2.1. Materials and physical measurements

All the chemicals used in the synthesis were purchased from vendors and were used as such. Metal salts, i.e., $Cu(NO_3)_2.3H_2O$, $Cu(ClO_4)_2.6H_2O$ and organic ligands 5,5'-dimethyl-2,2'-bipyridine (5,5'-Me_2bpy), malonic acid (H_2mal) and 2-chloronicotinic acid (2-ClNAH) were purchased from Sigma Aldrich Chemicals Pvt. Ltd., New Delhi. Ethanol was purchased from Bengal Chemicals, Kolkata, India and methanol, dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were procured from Merck Specialities Pvt. Ltd. All experimental operations were performed in air. FT-IR spectra were taken on a Bruker Optics ALPHA-E spectrometer with a Universal Zn-Se ATR accessory in the 600–4000 cm^{-1} region. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANalytical diffractometer for Cu-Kα radiation (λ = 1.5406 Å), with a scan speed of 2^o min^{-1} and a step size of 0.02^o in 2θ. Elemental (C, H, N) analyses were done on Elemental Analyzers Elementar Vario EL III Carlo Erba 1108. FAB-MASS spectra were recorded on a Jeol SX 102/Da-600 mass spectrometer/Data System using Argon/Xenon (6kv, 10mA) as the FAB gas. The accelerating voltage was 10 kv and spectra were recorded at room temperature. UV-Visible spectra were recorded at Perkin-Elmer UV-Visible spectrophotometer model Lambda-35. Cyclic voltammetric studies were carried out at BAS electrochemical system model EPSILON at room temperature. Thermo-gravimetric analyses (TGA) and DSC experiments were carried out in the temperature range of 50-400^oC on a SDT Q600 TG-DTA analyzer under N_2 atmosphere at a heating rate of 10 ^{o}C min^{-1}.

2.2. Synthesis of Cu(II)-mixed-ligand complexes

2.2.1. Synthesis of $[Cu(Hmal)(5,5'\text{-}Me_2bpy)(H_2O)](ClO_4)$, 1

40 mL aqueous solution of malonic acid (2 mM, 0.208 g) was added to another 20 mL aqueous solution of $Cu(ClO_4)_2.6H_2O$ (2 mM, 0.741 g), followed by 30 mL ethanolic solution of 5,5'-dimethyl-2,2'-bipyridine (2 mM, 0.368 g) with constant stirring. Initially deep blue coloured solution was obtained. After continuous stirring (30 min.) green coloured precipitate with blue coloured supernatant solution was obtained. Precipitate turned blue after 3h continuous stirring. Filtered the content and kept the turquoise coloured solution for

evaporation at room temperature. Blue coloured shining single crystals of [Cu(Hmal)(5,5'-Me_2bpy)(H_2O)](ClO_4), suitable for X-ray diffraction were obtained after two days. Resulting crystals were washed with water followed by ether and dried at room temperature (yield: 289 mg, 39% based on Cu). FTIR (KBr 4000–600 cm^{-1}): 3482m(b), 3221w, 3051w, 1627s, 1479s, 1391m, 1095s, 846m, 722m, 625m. Anal. Calcd for $C_{15}H_{17}CuN_2O_9Cl$ (%): C, 38.44; H, 3.63; N, 5.98. Found: C, 38.32; H, 3.49; N, 6.07.

2.2.2. Synthesis of [Cu_2(2-OHNA)$_2$(5,5'-Me_2bpy)$_2$(NO_3)](NO_3), 2

50 mL methanolic solution of 2-chloronicotinic acid (6.67 mM, 1.039 g) was slowly added to 20 mL aqueous solution of $Cu(NO_3)_2.3H_2O$ (3.33 mM, 0.805 g) with continuous stirring. After 20 min. of continuous stirring another 20 mL aqueous-methanolic (1:1) solution of 5,5'-dimethyl-2,2'-bipyridine (3.33 mM, 0.615 g) was added to the above mixed solution, resulting in a deep blue coloured solution. Whole content was stirred for another 1h with constant heating at water bath. Now cooled the solution and raised the pH from 1.85 to 4.5 and heated over water bath for 1h. Filtered the content and kept the blue coloured solution for evaporation. Blue coloured shining crystals of [Cu_2(2-OHNA)$_2$(5,5'-Me_2bpy)$_2$(NO_3)](NO_3), were obtained after three days. Resulting crystals were washed with 1:1 aqueous-methanol solution followed by ether and dried at room temperature (yield: 459 mg, 57% based on Cu). FTIR (KBr 4000–600 cm^{-1}): 3454m(sh), 3064w, 2922w, 2758w, 2474m(br), 1875m(sh), 1717m(sh), 901m, 774s, 667s. Anal. Calcd for $C_{36}H_{32}Cu_2N_8O_{12}$ (%): C, 48.23; H, 3.57; N, 12.50. Found: C, 48.16; H, 3.52; N, 12.52.

2.3. Instrumentation

2.3.1. Single crystal X-ray diffraction data collection of 1 and 2

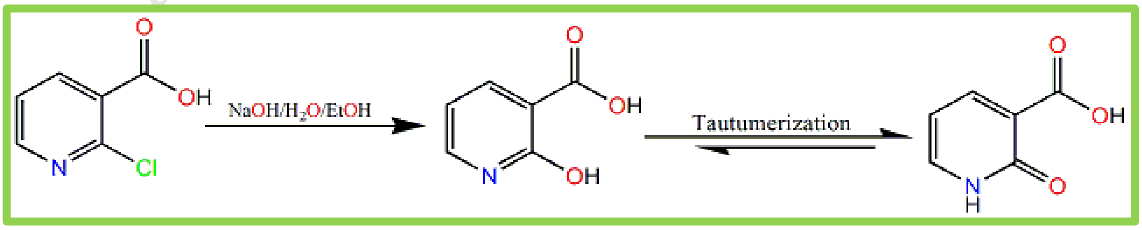
All single crystal data were collected on a Bruker SMART APEX three circle diffractometer equipped with a CCD area detector (Bruker Systems Inc., 1999a) [39] and operated at 1500W power (50kV, 30 mA) to generate Mo-Kα radiation (λ = 0.71073Å). Crystals of the coordination compounds reported herein were mounted on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). Data were integrated using Bruker SAINT Software [40]. Data were subsequently corrected for absorption by the program SADABS [41]. The space group determinations and tests for merohedral twinning were carried out using XPREP [42]. All structures were solved by direct methods and refined using the SHELXTL 97 software suite [42]. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times Ueq of the attached C atoms. Data were collected at 150(2) K for $[Cu(Hmal)(5,5'\text{-}Me_2bpy)(H_2O)](ClO_4)$ **1**, and $[Cu_2(2\text{-}OHNA)_2(5,5'\text{-}Me_2bpy)_2(NO_3)](NO_3)$ **2.** All structures were examined using the ADDSYM subroutine of PLATON [43] to ensure that no additional symmetry could be applied to the models. Crystallographic data of all these complexes are summarized in Table 1. CCDC 756584 and 756654 contains the supplementary crystallographic data (excluding structure factors) for complexes **1** and **2**, respectively. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk).

2.3.2. Electrochemical measurements

Cyclic voltammetric experiments were carried out with a Bio-Analytical Systems (BAS) model EPSILON (Bioanalytical Systems, Inc, USA). Ag/AgCl in saturated KCl (E^0 = +0.199V vs NHE) was used as reference electrode. The working electrode was a platinum microelectrode (MF-2013), platinum wire was used as an auxiliary electrode. All the cyclic voltammetric experiments were done in an inert atmosphere achieved by purging the cell solution with nitrogen (99.999% pure) for about 20 minutes at 20±0.5°C. An inert atmosphere of nitrogen was also maintained over the cell solution during the recording of the voltammograms. Great care was taken in the electrode pre-treatment. Mechanical polishing of the working electrode (GCE) was done over a velvet micro-cloth with an alumina suspension.

3. Results and discussion

As mentioned earlier, these two complexes were synthesized by using traditional or solvent evaporation method. Blue coloured shining crystals of complex **1** were obtained by mixing $Cu(ClO_4)_2.6H_2O$:H_2mal:5,5'-Me_2bpy in 1:1:1 molar ratio into 2:1 water-ethanol mixture. Interestingly, in this complex malonic acid is monodeprotonated being only one carboxylic group dissociated. Crystals for complex **2** were obtained by mixing $Cu(NO_3)_2.3H_2O$:2-ClNAH:5,5'-Me_2bpy in 1:2:1 molar ratio into 1:2 water-methanol mixture under basic condition. In this complex the original 2-ClNAH ligand underwent to a base hydrolysis reaction followed by *keto-enol* tautomerization (Scheme 3).



Scheme 3. Hydrolysis of 2-chloronicotinic acid in presence of base and successive *keto-enol* tautomerization.

3.1. *Crystal structure of 1*

Mixed-ligand complex **1** crystallizes in monoclinic crystal system with space group $P2_1/n$. The structure of this complex consists of $[Cu(Hmal)(5,5'-Me_2bpy)(H_2O)]^+$, monocation unit and a non-coordinating ClO_4^- anion. The metal ion in this complex is penta-coordinated with distorted square-pyramidal geometry. The base of square-pyramid is built by the N-atoms of the chelating 5,5'-Me_2bpy ligand and two O-atoms of the chelating mono-deprotonated H_2mal ligand, while the apical position is occupied by the O-atom of a coordinated water molecule. The ORTEP diagram with 50% probability and atom numbering scheme of the crystallographic independent unit is depicted in fig. 1. The two Cu-N bond distances present same value (1.980(3) Ǻ) with a chelating angle of 81.60(11)^o. The two oxygen atoms from Hmal ligand are at 1.937(2) and 1.926(2) Ǻ, with a O-Cu-O bond angle of 91.11(10)^o, while the Cu-O5 distance for the axially coordinated water is significantly longer, being 2.239(3) Ǻ.

Table 1. Crystallographic data and structure refinement for complexes **1** and **2**

Compounds	**Complex 1**	**Complex 2**
CCDC No.	**756584**	**756654**
Formula	$C_{15}H_{17}CuN_2O_5ClO_4$	$C_{36}H_{32}Cu_2N_8O_{12}$
Mr	468.30	895.80
Crystal system	Monoclinic	Triclinic
Space group	P 21/n	P-1
a (Å)	8.1563(10)	10.590(2)
b (Å)	17.7192(17)	12.0717(17)
c (Å)	12.892(2)	15.056(3)
α (^{o})	90.00	70.614(16)
β (^{o})	105.584(15)	80.063(18)
γ (^{o})	90.00	76.954(16)
V (Å^3)	1794.7(4)	1758.8(6)
Z	4	2
Crystal size	0.30x0.20x0.10 mm	0.23x0.18x0.15 mm
F(000)	956	916
D_c (g cm^{-3})	1.733	1.691
μ (mm^{-1})	1.420	1.290
Reflections collected	12026	22472
Unique reflections	5899	12742
R_{int}	0.0901	0.0724
GOF on F^2	1.080	0.766
R_I [I>2σ(*I*)]	0.0601	0.0503
wR_2 (all data)	0.1612	0.1381

All these bond lengths fall in the common range observed for penta-coordinated copper(II) ion [44]. Selected bond lengths and bond angles are given in table 2.

The lattice structure is further stabilized and extends to a 3D supramolecular framework by weak π-π stacking interactions and hydrogen bonding. The π-π stacking interactions occur between symmetry related pyridine rings of the 5,5'-Me_2bpy ligand, with centroid distance in the range 3.94 - 4.35 Ǻ. The intermolecular hydrogen bonds occur between the coordinated water with the oxygen atoms of symmetry related perchlorate anions (O···O distances of 2.829(4) and 2.953(5) Ǻ). Further a strong interaction is observed between the carboxylic O(2)-H with carboxylate oxygen O(4) (at ½+x, ½-y, ½+z) of another complex. The O···O donor-acceptor distances is 2.475(3) Ǻ. Selected hydrogen bond geometry is listed in table 3. The hydrogen bondings lead the structure to a one dimensional linear polymeric chain. This supramolecular 1D chain is expanded to 2D and further expanded to 3D supramolecular network by the combination of π-π stacking interactions. 1D, 2D and 3D supramolecular network structures of complex **1** are given in figure 2.

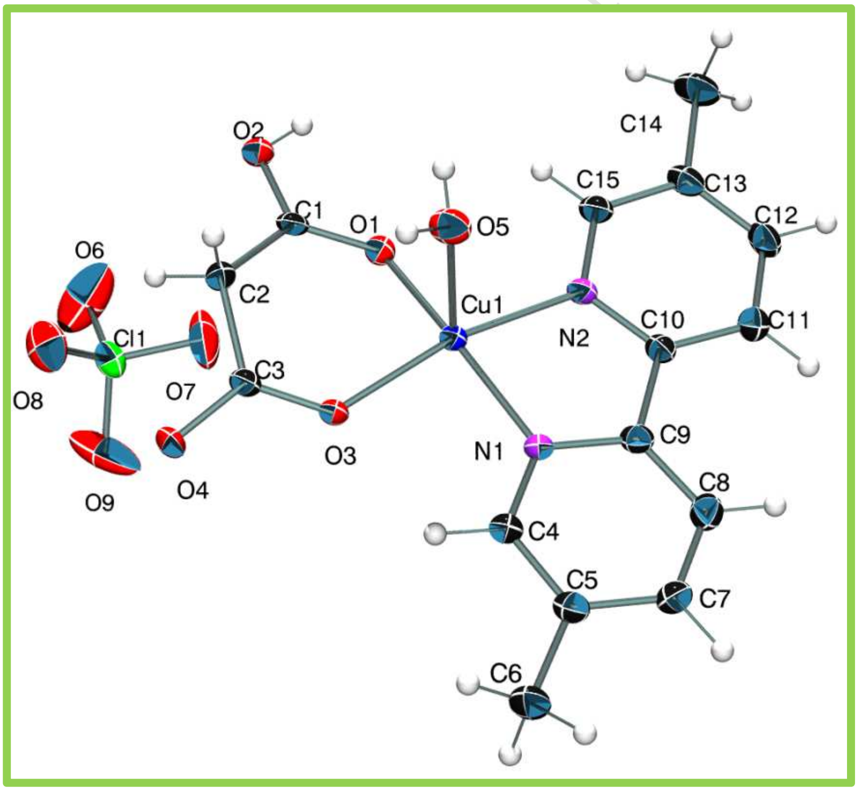


Fig. 1. ORTEP diagram (50% probability) of [Cu(Hmal)(5,5'- Me_2bpy)(H_2O)](ClO_4) **1**, with atom numbering.

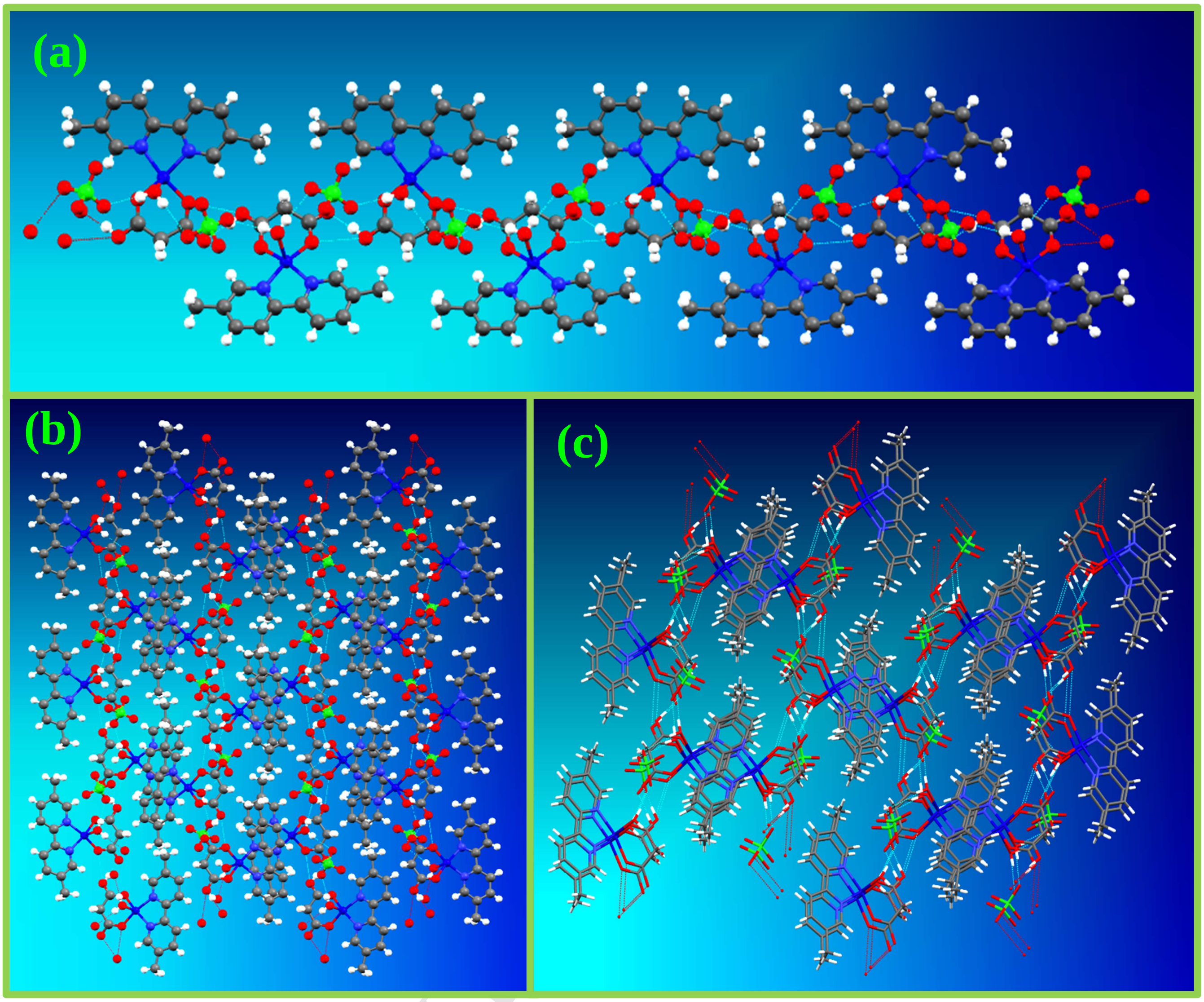


Fig. 2. Supramolecular network structure of complex **1, (a)** 1D chain along *b-axis*; **(b)** 2D sheet viewed down *a-axis*; and **(c)** 3D network structure showing π-π stacking interactions and H-bondings.

3.2. Crystal structure of 2

Mixed-ligand complex **2** crystallizes in triclinic crystal system with space group *P-1*. The crystal structure of this complex consists of $[Cu_2(2\text{-}OHNA)_2(5,5'\text{-}Me_2bpy)_2(NO_3)]^+$ and a non-coordinated NO_3^- anion. It should be noted that in complex **2** the asymmetric unit comprises two copper complexes. Out of these the first complex is neutral where the copper(II) ion is penta-coordinated with distorted square-pyramidal geometry. The coordination set of the copper(II) ion is satisfied by the two N-atoms from bidentate chelating 5,5'-Me_2bpy ligand, two O-atoms from 2-OHNA ligand, these four coordinate bonds are lying in one plane and constitute the base of square-pyramid, and one O-atom from axially coordinated nitrate anion (Fig. 3).

Table 2. Selected bond lengths and bond angles in complexes **1** and **2**

Complex 1			
Cu1-O3	1.926(2)	O3-Cu1-N1	90.85(10)
Cu1-O1	1.937(2)	O1-Cu1-N1	166.30(10)
Cu1-N2	1.980(3)	N2-Cu1-N1	81.60(11)
Cu1-N1	1.980(3)	O3-Cu1-O5	98.19(10)
Cu1-O5	2.239(3)	O1-Cu1-O5	92.31(10)
O3-Cu1-O1	91.11(10)	N2-Cu1-O5	93.77(10)
O3-Cu1-N2	166.88(10)	N1-Cu1-O5	100.83(11)
O1-Cu1-N2	93.77(10)		
Complex 2			
Cu1-O1A	1.910(2)	O2A Cu1 N2A	166.66(11)
Cu1-O2A	1.912(2)	N1A Cu1 N2A	81.83(10)
Cu1-N1A	1.982(2)	O1A Cu1 O13	93.23(10)
Cu1-N2A	1.985(3)	O2A Cu1 O13	107.35(11)
Cu1-O13	2.487(3)	N1A Cu1 O13	86.83(10)
Cu2-O1B	1.889(2)	N2A Cu1 O13	84.83(11)
Cu2-O2B	1.901(2)	O1B Cu2 O2B	93.39(9)
Cu2-N1B	1.969(2)	O1B Cu2 N1B	171.62(9)
Cu2-N2B	1.982(2)	O2B Cu2 N1B	94.14(10)
O1A-Cu1-O2A	93.13(9)	O1B Cu2 N2B	90.96(10)
O1A Cu1 N1A	173.35(10)	O2B Cu2 N2B	175.65(9)
O2A Cu1 N1A	93.20(10)	N1B Cu2 N2B	81.53(10)
O1A Cu1 N2A	91.55(9)		

The second complex is mono-cationic, in which the copper(II) ion is in square planar geometry. Four coordination around the central metal ion are satisfied by the two N-atoms from chelating 5,5'-Me$_2$bpy and two O-atoms from 2-OHNA ligands. These four coordinate bonds lie in the same plane and constitute the square-plane. The extra cationic charge of this unit is balanced by the counter nitrate anion. ORTEP diagram with 50% probability and atom numbering scheme of crystallographic independent unit of complex 2, is depicted in figure 3. In this complex, ligand 2-OHNA exists in *keto* form and bidentately coordinates to the metal centre in O,O'-salicylate manner. In this way the ligand 2-OHNA constituting a six membered rings with the central metal ion. Cu-N bond distances in this complex lie in the range 1.969 to 1.985 Ǻ, while Cu-O bond distances are in the range 1.889 to 2.487 Ǻ. All these bond lengths fall in the common range observed for the square-pyramidal and square planar copper(II) complexes [44]. In addition to these, weak bonding interactions are also observed between the Cu1-O2b (3.082(3) Å) and Cu2-O2a (2.856(3) Å). Selected bond lengths and bond angles are listed in table 2.

Further, the weak supramolecular interactions such as hydrogen bonding, π-π stacking interaction etc. stabilize the lattice structure. The π-π stacking interaction is observed between the pyridine rings of the 5,5'-Me$_2$bpy and 2-OHNA ligands. The shortest π-π stacking interacting distances between centroids are between pyridine rings N(2a) and N(3) (at 1-x, 1-y, 1-z) of 3.706 Å and between pyridine rings N(2b) and N(4) at (1-x, 1-y, -z) of 3.859 Å. Hydrogen bondings are observed between the oxygens of nitrate ions and the pyridine N-H of the 2-OHNA ligand. First type of intermolecular hydrogen bonding is observed between O(12) of the coordinated nitrate ion and pyridyl N(3)-H of 2-OHNA ligand associated with square-pyramidal complex. N···O donor-acceptor distances is 2.940(4) Å (at 1-x, 1-y, 1-z). Second type of hydrogen bonding is observed between O(23) of free nitrate ion and pyridyl N(4)-H of 2-OHNA ligand associated with square-planar complex. In this case N···O donor-acceptor distances is 2.838(4) Å (at x, y, z). Selected hydrogen bond geometry is shown in table 3. These weak interactions produce 3D supramolecular architectures as shown in figure 4.

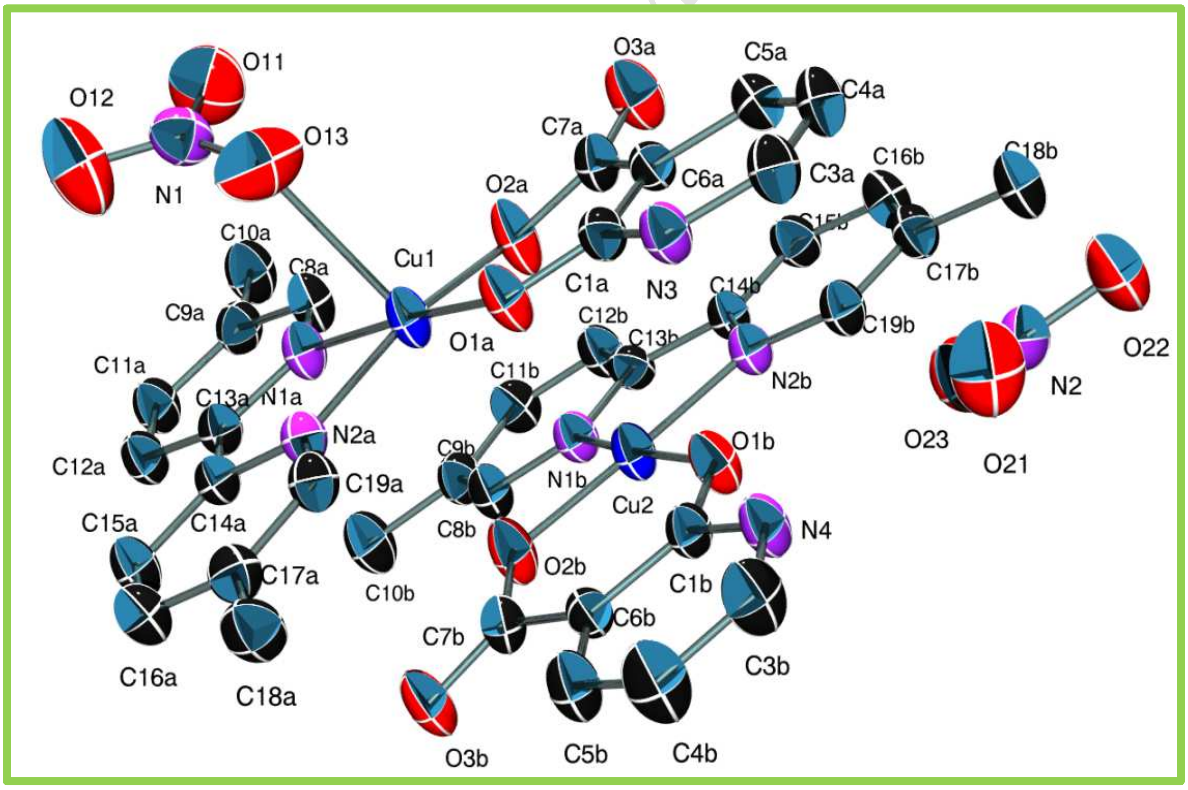


Fig. 3. ORTEP diagram (50% probability) of [Cu$_2$(2-OHNA)$_2$(5,5'-Me$_2$bpy)$_2$(NO$_3$)](NO$_3$) **2**, with atom numbering (Hs are omitted due to clarity).

Table 3. Selected hydrogen bonds geometry (Å, °) in complexes **1** and **2**

D-H····A	D····H	H····A	∟DHA	D····A
Complex 1				
O2-H2····O4	0.84	1.64	170.24	2.475(3)
O2-H2····O3	0.84	2.53	119.34	3.035(3)
O5-H101····O9	0.82(3)	2.02(3)	170.0(3)	2.829(4)
O5-H102····O6	0.80(3)	2.19(3)	160.0(4)	2.953(5)
Complex 2				
N3-H3····O12	0.88	2.17	145.3	2.940(4)
N3-H3····O13	0.88	2.42	158.6	3.251(4)
N4-H4····O21	0.88	2.44	140.0	3.164(4)
N4-H4····O23	0.88	1.99	162.9	2.838(4)

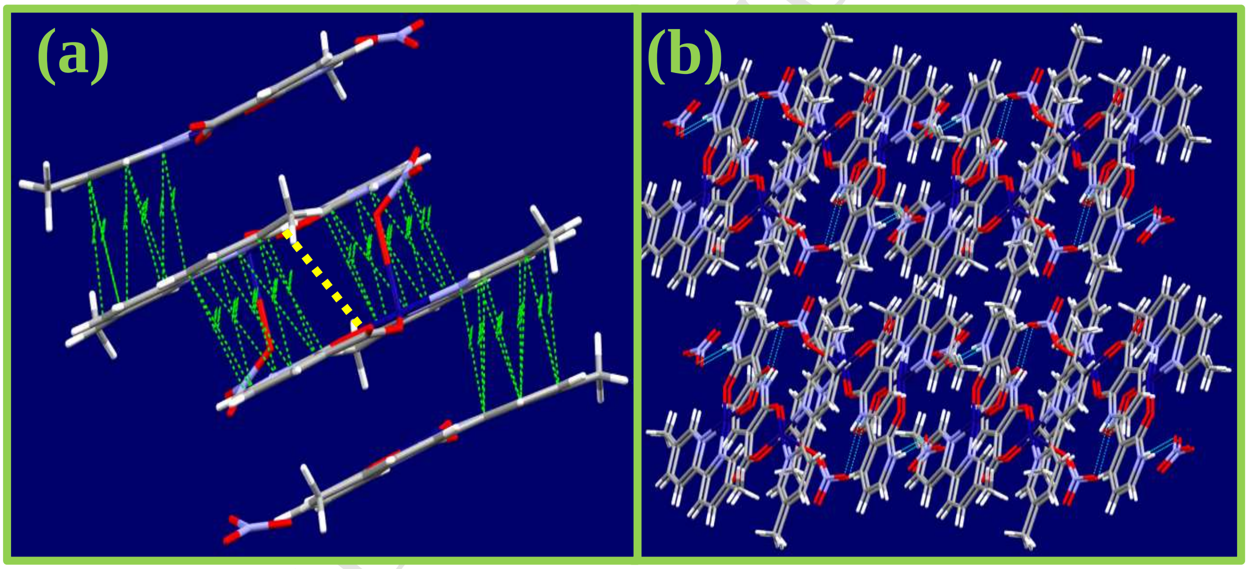


Fig. 4. Supramolecular interactions in complex **2, (a)** π-π stacking interactions (centroid distances shown in bold yellow dotted line); **(b)** 3D network structure showing π-π stacking interaction and H-bonding.

3.3. Vibrational studies

Vibrational study of complex **1** reveals a broad band at 3482 cm^{-1}, which simply indicates the presence of hydrogen bonded water molecule. Presence of water in coordination is further supported by the bands at 846 and 772 cm^{-1} [45]. Further, weak bands at 3221 and 3051 cm^{-1}, correspond to the hydrogen bonded carboxylic O-H stretching and aromatic C-H stretching, respectively. The presence of a sharp band at 1479 cm^{-1} may be designated for the C=N stretching of the pyridine ring. Finally, the presence of bands at 1627 and 1391 cm^{-1} are assigned to asymmetric and symmetric C=O stretching of the carboxylate group. Their difference is above 200 cm^{-1}, i.e., 236 cm^{-1} confirms the monodentate coordination of the carboxylate group in this complex [46].

In the FT-IR spectrum of complex **2** a sharp medium band at 3454 cm^{-1} is assigned to the aromatic N-H stretching frequency. Two successive bands at 3064 and 2922 cm^{-1} are assigned to the aromatic (pyridine ring) and aliphatic C-H (-CH_3) stretching, respectively. Further, the presence of pyridine rings are also confirmed by the weak bands at 1477 and 1450 cm^{-1}, which are assigned to C=N and C=C stretching, respectively. Two sharp bands at 1651 and 1378 cm^{-1}, respectively, assigned for the asymmetric and symmetric stretching of the carboxylate group. Their difference is above 200 cm^{-1}, i.e., 273 cm^{-1} confirms the monodentate coordination of the carboxylate group [46]. Presence of another strong band at 1579 cm^{-1} indicates the availability of C=O group directly associated with the aromatic ring. Moreover, the strong and sharp bands at 1259 and 1153 cm^{-1} are assigned for asymmetric and symmetric stretching frequency of coordinated nitrate ion. Difference of asymmetric to symmetric stretching frequency comes out to be around 106 cm^{-1} confirms the monodentate coordination of nitrate ion [45]. Again a sharp band at 1062 cm^{-1} is assigned for the coordinated nitrate ion [47]**.**

Finally, the presence of un-coordinated nitrate ion represents the bands at 1875, 1717 and 838 cm^{-1} in this complex [45]. FT-IR spectra of the complexes **1** and **2** are given in supplementary information (SI) as figures **S1** and **S2**.

3.4. FAB-MASS studies

FAB-MASS spectra of the complexes **1** and **2** are given in SI as figures **S3** and **S4**, respectively. MASS spectral study of complex **1,** shows a peak at m/z 467 assigned for molecular ion peak (Calc. 468). Another peak is observed after the expulsion of perchlorate radical ion at m/z 369 (Calc. 368.5). Further successive fragmentation produces a number of peaks at m/z 355 (Calc. 350.5), 307 (Calc. 306.5), 247 (Calc. 247.5), 221 (Calc. 217.5) and 136 (Calc. 140) assigned for radical ions [$C_{15}H_{15}CuN_2O_4$], [$C_{14}H_{15}CuN_2O_2$], [$C_{12}H_{12}CuN_2$], [$C_{10}H_6CuN_2$] and [C_5H_3CuN] obtained after the expulsion of a water, CO_2, CH_2COOH, two CH_3 and a pyridine radical ions, respectively. The peak at m/z 136 is assigned as base peak. Moreover, a peak at 154 (Calc. 154), shows the presence of bipyridine radical ion which is obtained by the combination of two pyridine radical ions.

In the MASS spectrum of complex **2,** the molecular ion peak appears at m/z 893 (Calc. 895.8). Two other successive peaks appeared at m/z 845 (Calc. 833.8) and 764 (Calc.

771.8) obtained after the two successive expulsion of two nitrate ion. Further, successive fragmentation of the radical ion produces a number of peaks at m/z 744 (Calc. 741.8), 700 (Calc. 697.8), 663 (Calc. 667.8), 577 (Calc. 573.8), 523 (Calc. 529.8), 431 (Calc. 435.8), 358 (Calc. 369.8), 307 (Calc. 308.8), 289 (Calc. 280.8), 247 (Calc. 247.8) and 137 (Calc. 140.8) assigned for [$C_{34}H_{26}Cu_2N_6O_6$], [$C_{33}H_{26}Cu_2N_6O_4$], [$C_{31}H_{20}Cu_2N_6O_4$], [$C_{26}H_{16}Cu_2N_5O_3$], [$C_{25}H_{16}Cu_2N_5O$], [$C_{20}H_{12}Cu_2N_4$], [$C_{15}H_9Cu_2N_3$], [$C_{20}H_{12}N_4$], [$C_{10}H_6Cu_2N_2$], [$C_{12}H_{12}CuN_4$] and [C_5H_3CuN] radical ions, respectively. Moreover, a peak with 100% abundance is observed at m/z 154 assigned for bipyridine radical ions obtained after the combination of two pyridine radical ions.

3.5. Electrochemical studies

The electrochemical behaviours of mixed-ligand copper(II) complexes [Cu(Hmal)(5,5'-Me_2bpy)(H_2O)](ClO_4) **1**, and [Cu_2(2-OHNA)$_2$(5,5'-Me_2bpy)$_2$(NO_3)] (NO_3) **2,** have been studied in dimethylsulfoxide (DMSO) and dimethylformamide (DMF) containing 0.2M $NaClO_4$ as the supporting electrolyte at a glassy carbon working electrode (GCE) using cyclic voltammetry. CV data for complexes **1** and **2** in DMSO and DMF are given in SI as Table **S1** and **S2**, and the representative cyclic voltammograms are displayed in figures **S5** and **S6**.

Cyclic voltammogram of complex **1** in DMSO showed a single well defined quasi-reversible one electron reduction couple (c/a) associated with $Cu^{2+/+}$ change, with Epc = 26 mV, Epa = 108 mV, $E^{0'}$ = 67 mV vs Ag/AgCl and ΔEp = 82 mV at 100 mVs^{-1}. The peak current ratio Ipa/Ipc is equal to unity, clearly indicating that the reduction process is reversible. Further, the plot of Ipc or Ipa vs square root of scan rate ($\upsilon^{1/2}$) gives a straight line passing through the origin, indicating that the redox process is diffusion controlled (Fig. 5(a)).

This complex shows almost similar behaviour in DMF also, with Epc = 79 mV, Epa = 163 mV, $E^{0'}$ = 120 vs Ag/AgCl and ΔEp = 84 mV at 100 mVs^{-1}. Here again, the peak current ratio (Ipa/Ipc) is equal to unity, and the plot of Ipc or Ipa vs square root of scan rate ($\upsilon^{1/2}$) gives a straight line without any intercept, showing that the redox process is reversible and diffusion controlled (Fig. 5(b)).

The cyclic voltammogram of complex **2,** in DMSO showed a well-defined quasi-reversible one electron redox couple associated with $Cu^{2+/+}$ change, with Epc_1 = 41 mV, Epa_1 = 157 mV, $E_1^{0'}$= 99 mV vs Ag/AgCl and ΔEp_1 = 116 mV. The plot of Ipc_1 vs square root of scan rate ($\upsilon^{1/2}$) gives a straight line passing through origin, indicating that the redox process is diffusion controlled (Fig. 5(c)). Further, the peak current ratio (Ipa_1/Ipc_1) is below unity ($Ipa_1/Ipc_1<1$), suggesting that the redox process follows EC mechanism [48]**.** The electrochemical behaviour of complex **2** appears to be different in DMF as evident from the cyclic voltammogram (Figure **S6(b)** in SI). The cyclic voltammogram shows two cathodic waves (c_1 and c_2) in the forward negative scan while the reverse anodic scan exhibited two ill-defined anodic peaks (a_2 and a_1). It must be noted that a_1 is not the corresponding peak of c_1. This may be due to the presence of two complex species in equilibrium in DMF solution.

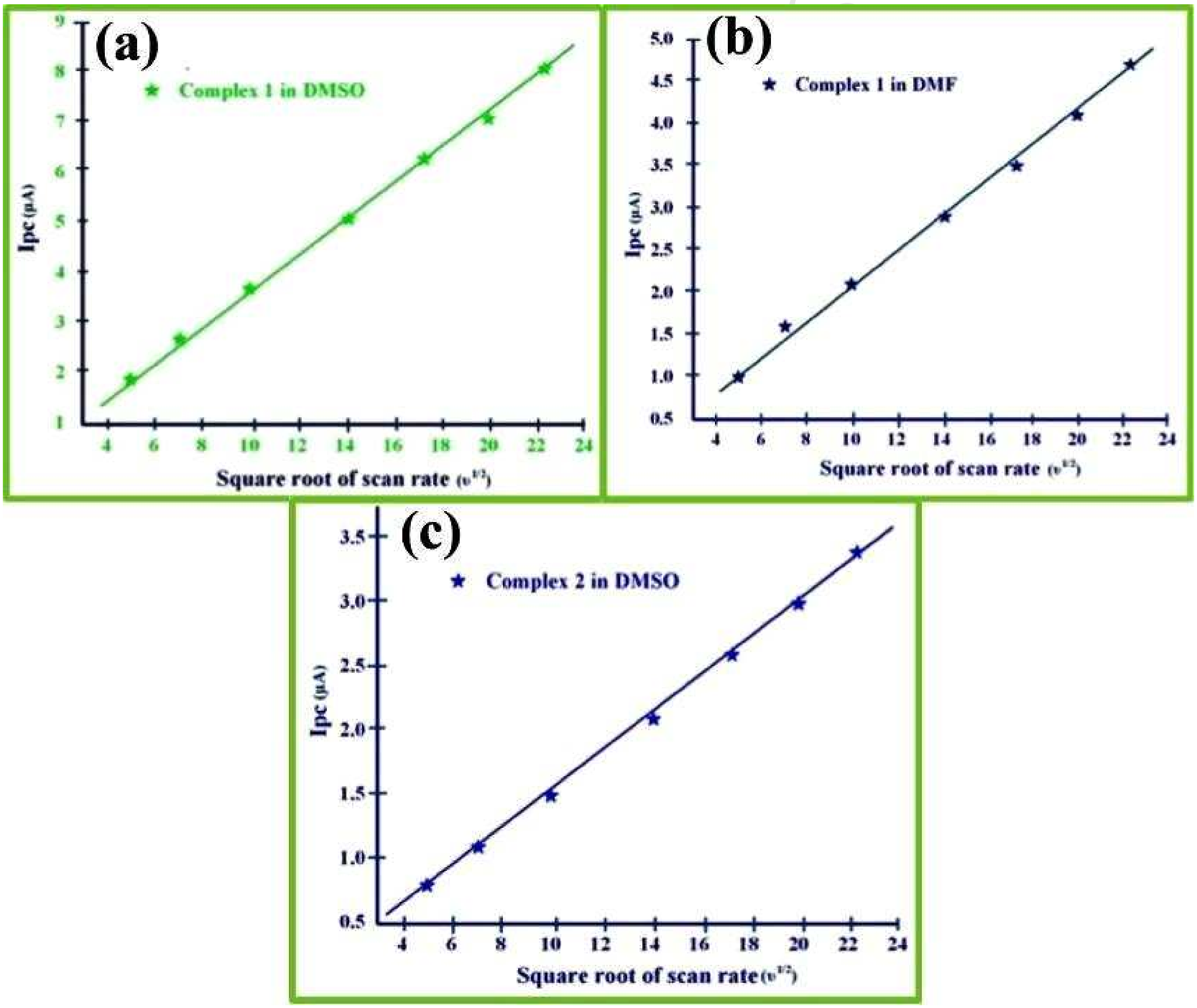


Fig. 5. Plot of Ipc (μA) vs square root of scan rate ($\upsilon^{1/2}$) **(a)** complex **1** in DMSO, **(b)** complex **1** in DMF and **(c)** complex **2** in DMSO**.**

3.6. UV-Visible spectral studies

UV-Visible spectra of complexes **1** and **2** have also been recorded in DMSO and DMF. For complex **1**, a weak band is observed at 663 and 649 nm in DMSO and DMF, respectively. Complex **2** also exhibited a weak band at 698 and 676 nm in DMSO and DMF, respectively (Table **S3**, Figures **S7** and **S8** in SI). All these bands are due to d-d transitions. This type of spectra is typical for tetragonally distorted octahedral copper(II) complexes [49-51]. This indicates the coordination of the solvent molecule to the metal centre.

3.7. Thermal studies

Thermal study of complex **1** shows two steps degradations in the range 30-400 ^{o}C, one related to the water and other related to the rest of the compound. The first one between 80-120 ^{o}C related to the expulsion of coordinated water molecule and other between 190-350 ^{o}C. The overall loss of weight is around 75 percent at the temperature of 400 ^{o}C. There is still a residue equivalent to 25 percent which has not degraded even upto 400 ^{o}C. Likewise complex **1,** complex **2** also shows two steps degradation. The first one is very sharp between 185-190 ^{o}C. There is very strong indication of phase change at around 188 ^{o}C and loss of matter is around 18 percent. The second degradation starts at 190 ^{o}C and ends around 390 ^{o}C but there could be one smaller step in this complex as we can see a clear phase change at 240 ^{o}C. The weight loss between 190-245 ^{o}C is being around 33 percent. The total weight loss at 240 ^{o}C is 50 percent (half of the sample). If we reject the in between phase then the complex undergoes a total weight loss equal to around 75 percent. This is akin to the complex **1**, which shows similar loss at 400^{o}C.

Another interesting observation about complexes **1** and **2** is that the phase change is observed in both these complexes. Phase change is endothermic for complex **1** and exothermic for complex **2,** and is accompanied by a heat flow of 15 and 1 watt per gram, respectively. TGA profiles of these two complexes are given in SI as figures **S9** and **S10.**

3.8. Powder X-ray diffraction patterns

A comparison of the experimental X-ray powder pattern of both complexes with respective simulated X-ray powder pattern shows the similarity in the major peaks. It also confirms the phase purity and crystallinity of the complexes in bulk. Powder X-ray patterns of these complexes are given as supplementary material (Figs. **S11** and **S12**).

4. Conclusion

In summary, synthesized mixed-ligand complexes viz.; [Cu(Hmal)(5,5'-Me$_2$bpy)(H$_2$O)] (ClO$_4$) **1** and [Cu$_2$(2-OHNA)$_2$(5,5'-Me$_2$bpy)$_2$(NO$_3$)](NO$_3$) **2** were structurally characterized by single crystal X-ray diffraction analysis and different spectral techniques such as FT-IR, UV-Visible and FAB-MASS analyses. The electrochemical studies of complex **1** in DMSO and DMF containing 0.2M $NaClO_4$ have shown that this complex undergoes quasi-reversible diffusion-controlled one-electron transfer reaction ($Cu^{2+/+}$) without any chemical complication while complex **2** in DMSO undergoes quasi-reversible diffusion-controlled one electron transfer reaction, following EC mechanism. The electrochemical behaviour of complex **2** in DMF is complicated probably due to presence of more than one species in solution.

Appendix A. Supplementary data

CCDC Nos. 756584 and 756654 contain the supplementary crystallographic data (excluding structure factors) for complexes **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail:deposite@ccdc.cam.ac.uk.

Acknowledgements

The author (SKS) is thankful to University Grant Commission, New Delhi for providing financial support as SRF. We are also thankful to Director, NCL, Pune & Head, Department of Chemistry, Panjab University, Chandigarh, Panjab for their outstanding support in providing facilities for characterization of complexes.

†Supporting Information

Supplementary information contains figures, including IR spectra, FAB-MASS, Cyclic Voltammetry, UV-Visible, TGA profiles and PXRD patterns, tables of Cyclic Voltammetric data and UV-Visible data.

References

[1] B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629.

[2] Q. Fang, G. Zhu, M. Xue, J.S. Sun, Y. Wei, S.L. Qiu, R.R. Xu, Angew. Chem., Int. Ed. 44 (2005) 3845.

[3] M. Eddaoudi, D.B. Moler, H. Li, B.L. Chen, T.M. Reineke, M. O’Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319.

[4] X. Zhao, B. Xiao, A.J. Fletcher, K.M. Thomas, D. Bradshaw, M.J. Rosseinsky, Science 306 (2004) 1012.

[5] S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem., Int. Ed. 43 (2004) 2334.

[6] C. Janiak, J. Chem. Soc., Dalton Trans. (2003) 2781.

[7] S.R. Batten, R. Robson, Angew. Chem., Int. Ed. 37 (1998) 1460.

[8] D. Maspoch, D. Ruiz-Molina, J. Veciana, Chem. Soc. Rev. 36 (2007) 770.

[9] N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keefee, O.M. Yaghi, Acc. Chem. Res. 38 (2005) 176.

[10] B.L. Chen, C.D. Liang, J. Yang, D.S. Contreras, Y.L. Clancy, E.B. Lobkovsky, O.M. Yaghi, S. Dai, Angew. Chem., Int. Ed. 45 **(**2006) 1390.

[11] J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, Nature 404 (2000) 982.

[12] S.L. James, Chem. Soc. Rev. 32 (2003) 276.

[13] Q. Fang, G. Zhu, M. Xue, Q.L. Zhang, J.Y. Sun, X.D. Guo, S.L. Qiu, S.T. Xu, P. Wang, D.J. Wang, Y. Wei, Chem. Eur. J. 12 **(**2006) 3754.

[14] J.L.C. Rowsell, O.M. Yaghi, Angew. Chem., Int. Ed. 44 (2005) 4670.

[15] S.-Q. Zang, Y.-J. Fan, R.Liang, H.-W. Hou, T.C.W. Mak, Cryst. Growth & Des. 11 (2011) 3395.

[16] J.-M. Hu, V.A. Blatov, B. Yu, K.V. Hecke, G.-H Cui, Dalton Trans. 45 (2016) 2426.

[17] J.-W Cui, W.-J. An, K.V. Hecke, G.-H Cui, Dalton Trans. 45 (2016) 17474.

[18] X.X. Wang, B. Yu, K.V. Hecke, G.-H. Cui, RSC Adv. 4 (2014) 61281.

[19] J.-M. Hao, B. Yu, K.V. Hecke, G.-H. Cui, Cryst. Eng. Comm. 17 (2015) 2279.

[20] X.X. Wang, Z.X. Li, B. Yu, K.V. Hecke, G.-H Cui, Inorg. Chem. Commun. 54 (2015) 9.

[21] G.-H. Cui, J.-R. Li, T.-L. Hu, X.-H. Bu, J. Mol. Struct. 738 (2005) 183.

[22] (a) G.A. L'Heureux, A.E. Martell, J . Inorg. Nucl. Chem. 28 (1966) 481; (b) H. Sigel, Chimia 21 (1967) 489; (c) H. Sigel, R. Grimser, Helv. Chim. Acta 50 (1967) 1842; (d) G.F. Condike, A.E. Martell, J. Inorg. Nucl. Chem. 31 (1969) 2455.

[23] F.A. Walker, H. Sigel, D.B. McCormick, Inorg. Chem. 11 (1972) 2756.

[24] H. Sigel, Metal Ions in Biological Systems, **Vol. 2**, Marcel Dekker, New York, Chapter 2 (1973).

[25] (a) M. Melnik, M. Kabesova, L. Macaskova, C.E. Holloway, J. Coord. Chem. 45 (1998) 31; (b) M. Melnik, M. Kabesova, M. Koman, L. Macaskova, J. Garaj, C.E. Holloway, A. Valent, J. Coord. Chem. 45 (1998) 147; (c) M. Melnik, M. Kabesova, M. Koman, L. Macaskova, C.E. Holloway, J. Coord. Chem. 48 (1999) 271; (d) M. Melnik, M. Kabesova, M. Koman, L. Macaskova, C.E. Holloway, J. Coord. Chem. 50 (2000) 177; (e) B.P. Murphy, Coord. Chem. Rev. 124 (1993) 63.

[26] (a) K.D. Karlin, J. Zubieta, Copper Coordination Chemistry, Adenine Press, New York (1983); (b) P. Comba, R. Remenyi, Coord. Chem. Rev. 238 (2003) 9 and references cited therein; (c) E.I. Solomon, D.W. Randall, T. Glaser, Coord. Chem. Rev. 200 (2000) 595 and references cited therein.

[27] (a) O. Kahn, Molecular Magnetism, VCH Publishers, New York (1993); (b) E. Garribba, G. Micera, D. Sanna, L. Strinna-Erre, Inorg. Chim. Acta 299 (2000) 253; (c) J. Cernak, M. Orendac, I. Potocnak, J. Chomic, A. Orendacova, J. Skorsepa, A. Feher, Coord. Chem. Rev. 224 (2002) 51; (d) J.G. Haasnoot, Coord. Chem. Rev. 200 (2000) 131; (e) R. Mukherjee, Coord. Chem. Rev. 203 (2000) 151.

[28] Y. Rodriguez-Martin, M. Hernandez-Molina, F.S. Delgado, J. Pasan, C. Ruiz-Parez, J. Sanchiz, F. Lloret, M. Julve, Cryst. Eng. Comm. 4 **(**2002) 522.

[29] Y. Rodriguez-Martin, J. Sanchiz, C. Ruiz-Parez, F. Lloret, M. Julve, Inorg. Chim. Acta. 326 (2001) 20.

[30] R. Chakrabarty, P.S. Mukherjee, P.J. Stang, Chem. Rev. 111 (2011) 6810.

[31] M. Ma, H. Noei, B. Mienert, J. Niesel, E. Bill, M. Muhler, R.A. Fischer, Y. Wang, U. Schatzschneider, N. Metzler-Nolte, Chem. Eur. J. 19 (2013) 6785.

[32] L. Yu-Mei, C. Yun-Xia, Z. Ji-Min, Chinese J. Struct. Chem. 25 (2006) 572.

[33] W. De-Cai, L. Shi-Xiong, Chinese J. Struct. Chem. 26 (2007) 1281.

[34] M.J. Plater, M.R.S.J. Foreman, E. Coronado, C.J. Comez-Garcia, J. Chem. Soc., Dalton Trans. (1999) 4209.

[35] (a) H. Oshio, H. Ichida, J. Phys. Chem. 99 (1995) 3294; (b) F.A. Cotton, L.M. Daniels, C. Lin, C.A. Murillo, Inorg. Chem. Comm. 4 (2001) 130; (c) M.J. Plater, M.R.S.J. Foreman, R.A. Howie, J.M.S. Skakle, M.B. Hursthouse, Inorg. Chim. Acta 319 (2001) 159.

[36] G.A. van Albada, A. Mohamadou, I. Mutikainen, U. Turpeinen, J. Reedijk, Eur. J. Inorg. Chem. (2004) 3733.

[37] K.J. Catalan, S. Jackson, J.D. Zubkowski, D.L. Perry, E.J. Valente, L.A. Feliu, A. Polanco, Polyhedron 14 (1995) 2165.

[38] H. Kooijman, A.L. Spek, G.A. van Albada, J. Reedijk, Acta Cryst. C58 (2002) m124.

[39] SMART (Version 5.05). Bruker AXS, Inc., Madison, Wisconsin (1998).

[40] Bruker. SAINT-Plus (Version 7.03). Bruker AXS Inc., Madison, Wisconsin, USA (2004).

[41] G.M. Sheldrick, SADABS (Version 2.03) and TWINABS (Version 1.02), University of Gottingen, Germany (2002).

[42] G.M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, University of Gottingen, Germany (1997).

[43] L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands (2005).

[44] A.F. Wells, Structural Inorganic Chemistry, 5th Edn, Oxford University Press, Oxford (1984).

[45] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B, 5th Edn, Willey, New York (1997).

[46] W. Lewandowski, B. Dasiewicz, P. Koczon, J. Skiersky, K. Dobrosz-Teperek, R. Swislocka, L. Fuks, W. Priebe, A.P. Mazurek, J. Mol. Struct. 604 (2002) 189.

[47] K.R.K. Reddy, P. Suneetha, C.S. Karigar, N.H. Manjunath, K.N. Mahendra, J. Chil. Chem. Soc. 53(4) (2008) 1653.

[48] K. Srivastava, A.K. Srivastava, S.K. Singh, J. Prasad, J. Indian Chem. Soc. 89 (2012) 1135.

[49] J. Moncol, M. Korabic, P. Segla , M. Koman, D. Milkos, J. Jaskova, T. Gloviak, M. Melnik, J. Mrozinsky, M.R. Sundberg, Z. Anorg. Allg. Chem. 633 (2007) 298.

[50] A.B.P. Lever (Ed.), Inorganic Electronic Spectroscopy, 2nd Ed., Elsevier, Amsterdam, Oxford, New York (1984).

[51] B.N. Figgis, M.A. Hitchman, Ligand Field Theory and its Applications, Wiley-VCH, New York (2000).

Highlights:

- Two new mixed-ligand complexes were synthesized.
- Electrochemical studies of these complexes have been done.
- These complexes involve supramolecular interactions.
- FAB-MASS studies have also been carried out.