

**Hybrid inorganic-organic complexes: Synthesis, spectroscopic characterization, single crystal X-ray structure determination and antimicrobial activities of three copper(II)–diethylenetriamine–p-nitrobenzoate compounds**

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**Abstract:**

Three new hybrid inorganic-organic complexes:  $[\text{Cu}(\text{dien})(\text{pnb})_2]\cdot\text{H}_2\text{O}$ , **1**;  $[\text{Cu}(\text{dien})_2](\text{pnb})_2$ , **2**; **and**  $[\text{Cu}(\text{dien})(\text{pnb})(\text{H}_2\text{O})](\text{pnb})(\text{H-pnb})$ , **3** (where *pnb* = *p*-nitrobenzoate, *dien* = diethylenetriamine, tridentate N-donor ligand), have been synthesized and characterized by spectroscopic (FT-IR, UV-Vis, EPR) methods. The structures of all newly synthesized compounds **1-3** have been unambiguously established by single crystal X-ray structure determination. All the compounds **1-3** showed variation in the coordination environment around copper(II) metal center obtained under slightly different reaction conditions by using same reactants but different synthetic routes at room temperature. Crystal lattices of coordination compounds **1-3** are stabilized by various non-covalent interactions such as N-H...O, C-H...O, O-H...O etc. All the three copper(II) complexes **1-3** show significant antimicrobial resistance against gram positive bacteria.

**Keywords:** copper (II) complex; *p*-nitrobenzoate; X-ray crystallography; EPR spectroscopy; diethylenetriamine; antimicrobial activity

## 1. Introduction:

Hybrid inorganic–organic compounds [1] that incorporate different metal centres (Cu, Cd, Ni etc.) and multifunctional ligands are a class of complexes that receive much attention due to their potential applications in magnetism, photoluminescence, sorption, catalysis, ion exchange and storage [2, 3]. Among this class, copper(II) complexes are distinct for their importance in many research areas and applications as luminescent devices [4], anticancer agents [5], and so on. This distinction may stem from the intriguing feature of copper based on its variable oxidation state (0, +1, +2, +3) and associated different geometries (such as linear, trigonal planar, square planar, tetrahedral, square pyramidal, octahedral). Additionally, in its complexes the nature and the chemical structure of the organic ligands, besides the synthetic modalities (sequence of reagent addition, variation in stoichiometry, reaction temperature and concentration *etc.*), can strongly affect the coordination modes and/or the dimensionality of the crystalline frameworks besides the overall chemical properties [6]. As a result, the synthesis of low molecular weight copper(II) complexes with precise reaction sequences and conditions employed and their structural characterization to the extent of molecular level (coordination mode, structural architecture *etc.*) become important to understand structure-property relationships especially in context of copper-protein interaction in biological systems [5-17].

In this contest, the p-nitrobenzoate ligand, derived from p-nitrobenzoic acid, proved to be a widely used versatile ligand as it showed diversity of coordination modes (monodentate, bidentate, bidentate bridging, ionic) through carboxylate and nitro group towards metal ion, which resulted in coordination complexes with different properties [18-20]. It has previously shown that *pnb* is not coordinated to copper(II) in presence of nitrogen donor ligands ethylene diamine and diethylenetriamine, thereby forming complex salts  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2](\text{pnb})_2$  and  $[\text{Cu}(\text{Hdien})_2(\text{H}_2\text{O})_2](\text{pnb})_4 \cdot 4\text{H}_2\text{O}$  [18], while it is coordinated to Cu(II) in presence of

hexamethylenetetramine (hmt)  $[\text{Cu}_3(\text{pnb})_6(\text{hmt})]_n$  [20], N,N-diethylnicotinamide  $[\text{Cu}(\text{pnb})_2(\text{N,N-diethylnicotinamide})_2(\text{H}_2\text{O})_2]$  (monomeric) [21], ammine;  $[\text{Cu}(\text{pnb})_2(\text{NH}_3)_4]$  (monomeric) [22] and triethanolamine ( $\text{H}_3\text{tea}$ );  $[\text{Cu}_2(\text{pnb})_2(\text{H}_2\text{tea})](\text{pnb}) \cdot 0.5 \text{ H}_2\text{O}$  (dimeric) [23a], diethylnicotinamide,  $[\text{Cu}_2(\text{pnb})_4(\text{nicotinamide})](\text{toluene})$  (dimeric) [23b]. Further exploration of copper(II) compounds containing both the ligands (dien and pnb) led to the isolation of three new hybrid inorganic-organic compounds *i.e.*  $[\text{Cu}(\text{dien})(\text{pnb})_2] \cdot \text{H}_2\text{O}$ , **1**;  $[\text{Cu}(\text{dien})_2](\text{pnb})_2$ , **2** and  $[\text{Cu}(\text{dien})(\text{pnb})(\text{H}_2\text{O})](\text{pnb})(\text{Hpnb})$ , **3** showing coordination features and packing modes which is worth investigating. Thus, in continuation of our interest in copper(II) complexes with various nitrogen donor ligands [24], these three new copper(II) complexes were synthesized and fully characterized by various physico-chemical techniques and single crystal X-ray crystallography. Moreover, since the synthesis of new cheap and effective anti-bacterial metal complexes is becoming a challenging task due to increasing multi-drug-resistant (MDR) of micro-organisms [25], their antibacterial potential has been also tested.

## **2. Experimental**

### **2.1 Materials**

Analytical grade reagents were used throughout this work without any further purification.

### **2.2 Instruments and measurements**

Carbon, hydrogen and nitrogen were determined micro-analytically by automatic Perkin Elmer 2400 CHN elemental analyzer and copper was determined by standard literature method [26]. FT-IR spectra were recorded using Thermo-scientific Nicolet iS50 FT-IR. Electronic spectra were recorded in methanol-water mixture using HITACHI 330 SPECTROPHOTOMETER. Conductance measurements were performed on Pico Conductivity Meter (Model CNO4091201, Lab India) in aqueous medium at 25°C by using double distilled water. The EPR spectra of all

complexes **1-3** were recorded at ~9.6 GHz (X-band) and 34 GHz (Q-band) frequencies using a Bruker Elexsys E500 spectrometer equipped with a NMR teslameter and a frequency counter. The X-band spectra were recorded at 77 K and the Q-band spectra at 298 K. The simulations of the experimental spectra were performed using a computer program employing full diagonalization of the spin Hamiltonian matrix, written by A. Ozarowski (National High Magnetic Field Laboratory, Florida State University).

The crystallographic data for complexes **1** and **3** were collected on a Nonius Kappa CCD diffractometer at room temperature using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data sets were integrated with the Denzo-SMN package [27] and corrected for Lorentz-polarization and absorption effects [28]. The structures were solved by direct methods (SIR97) [29] and refined by full-matrix least-squares methods with all non-hydrogen atoms anisotropic. In both structures the hydrogens bound to O and N atoms were located in the difference Fourier map and refined isotropically, while those bound to C atoms were included on calculated positions, riding on their carrier atoms. In spite of the good shape of crystals of complex **1**, it was only possible to reach a data completeness of 0.95. All calculations were performed using SHELXL-2014/7 [30] implemented in the WINGX system of programs [31].

For complex **3**, data were collected at 296 K on a Bruker X8 APEXII Kappa CCD area-detector diffractometer using graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data processing including integration, reduction together with absorption correction, and merging was carried out using SAINT, SADABS, and XPREP, respectively in the APEX2 program suite [32]. The structure was solved by intrinsic phasing method with SHELXTL XT [33] and was refined anisotropically by full matrix least-squares on  $F^2$  with SHELXTL XLMP [34]. The H atoms of NH and NH<sub>2</sub> groups were located from difference Fourier maps and refined with  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{N})$ , while those bound to C atoms

were included on calculated positions, riding on their carrier atoms. Crystal data and refinement statistics of complexes **1–3** are given in Table 1.

### **2.3. Synthesis:**

#### **2.3.1. [Cu(*dien*)(*pnb*)<sub>2</sub>].H<sub>2</sub>O, **1**:**

1 g (0.0060 mol) of p-nitrobenzoic acid was dissolved in 20 mL of methanol:water (4:1), 0.6 mL of diethylenetriamine and 10 mL methanolic solution of CuSO<sub>4</sub>.5H<sub>2</sub>O (0.75 g, 0.0030 mol) was added to it and aqueous solution of sodium p-nitrobenzoate (*in situ* by dissolving 1g (0.0060 mol) of p-nitrobenzoic acid and 0.24 g (0.0060 mol) of NaOH in 10 mL of water) was also added. The reaction mixture was stirred for 20 minutes and a clear dark blue solution was obtained. When it was put aside for slow evaporation at room temperature, dark blue crystals started appearing in few hours. They were removed and dried in air. Newly synthesized complex **1** is soluble in methanol and other organic solvents but partially soluble in water. The complex **1** decomposed at 180 °C. Anal. Calcd. for [C<sub>18</sub>H<sub>21</sub>CuN<sub>5</sub>O<sub>8</sub>·H<sub>2</sub>O Cu] Cu 12.28, C 41.78, H .4.44, N 13.54%; Found: Cu 12.50, C 41.52, H 4.62, N 13.36%.

#### **2.3.2. [Cu(*dien*)<sub>2</sub>](*pnb*)<sub>2</sub>; **2**:**

Sodium salt of p-nitrobenzoic acid was prepared by dissolving 1 g (0.0060 mol) of p-nitrobenzoic acid and 0.24 g (0.0060 mol) of sodium hydroxide in 20 mL of water. In another beaker 0.75 g (0.0030 mol) of CuSO<sub>4</sub>.5H<sub>2</sub>O was dissolved in minimum amount of water (10 mL). Sky blue colored precipitate appeared immediately on mixing both solutions. The precipitated product was filtered through fine filter paper, washed with water and dried in air. The above sky blue colored copper(II) complex was suspended in methanol : water mixture (4 : 2 v/v) and *dien* was added dropwise (in excess). On addition of *dien*, a clear dark blue solution was obtained. Upon slow evaporation blue colored crystals started appearing after two days which were removed and air

dried. Complex **2** is soluble in water and methanol but insoluble in other organic solvents. The complex **2** decomposed at 172 °C. Anal. Calcd. for [C<sub>22</sub> H<sub>34</sub> Cu N<sub>8</sub> O<sub>8</sub>Cu] Cu 10.54, C 43.84, H 5.64, N 18.60%; Found: Cu 10.68, C 44.02, H 5.52, N 18.43%.

### **2.3.3. [Cu(*dien*)(*pnb*)(H<sub>2</sub>O)](*pnb*)(H-*pnb*); **3**:**

Crystals of [Cu(*dien*)<sub>2</sub>](*pnb*)<sub>2</sub> (**2**) were powdered and dissolved in methanol: water mixture (4:1 v/v) and p-nitrobenzoic acid was added to it in 1:2 stoichiometry. The solution was stirred for 20 minutes at room temperature that resulted in a clear dark blue solution. When it was put aside for slow evaporation at room temperature, crystals started appearing slowly. After a day, these crystals were separated and dried in air. The complex was soluble in methanol and other organic solvents but partially soluble in water. The complex **3** decomposed at 197 °C. Anal. Calcd. for [C<sub>14</sub>H<sub>9</sub>N<sub>2</sub>O<sub>8</sub>·C<sub>11</sub>H<sub>19</sub>CuN<sub>4</sub>O<sub>5</sub>Cu] Cu 9.28, C 43.85, H 4.09, N 12.27%; Found: Cu 9.53, C 43.62, H 4.20, N 12.48%.

## **2.4. Antimicrobial activities:**

### **2.4.1. Well diffusion assay:**

Well diffusion assay was performed to assess the antimicrobial activity of the three synthesized copper(II) complexes. Autoclaved nutrient agar was poured into sterile 90 mm petriplates and allowed to cool down. 100 µl of bacterial culture (0.5 OD<sub>600</sub>) of standard strains of *Escherichia coli* or *Pseudomonas aeruginosa* or Methicillin resistant *Staphylococcus aureus* or *Klebsiella pneumoniae* was spread plated on separate nutrient agar plates. Copper(II) complexes were dissolved in DMSO at a concentration of 30 mg/ml. Wells in agar plates were prepared and 50 µl of either of solvent control *i.e.*, DMSO or copper(II) complexes were filled in different wells. The plates were left for an hour in laminar flow hood to allow diffusion of solvent as well as copper(II)

complexes. The plates were incubated for 18-24 hours at 37°C and zone of inhibition was observed around the wells.

#### **2.4.2. Minimum inhibitory concentration (MIC) and Minimum bactericidal (MBC) assay:**

MIC and MBC of synthesized copper complexes was also determined by micro broth dilution method. A stock solution in a concentration of 30 mg/ml of each of three copper(II) complexes in DMSO was prepared to form a homogenous solution. To determine MIC and MBC, the test concentration was kept in the range of 15mg/ml to 0.058mg/ml with DMSO as solvent control. Using sterilized tips, 50µL of copper(II) complexes at varying concentration were added to each well containing 50µL sterile nutrient broth and another well loaded with similar volume of solvent control *i.e.*, DMSO. Then 50µL of fresh nutrient broth containing bacteria, (0.5 OD<sub>600</sub>) of each organism was added to wells in separate rows and incubated overnight at 37 °C. After 24 hours of incubation, for MIC determination, visible turbidity in the wells was considered and for MBC determination, the contents from each well were plated on nutrient agar plates, incubated overnight at 37 °C and observed for growth of viable bacterial cells

### **3. Results and Discussion**

#### **3.1. Syntheses:**

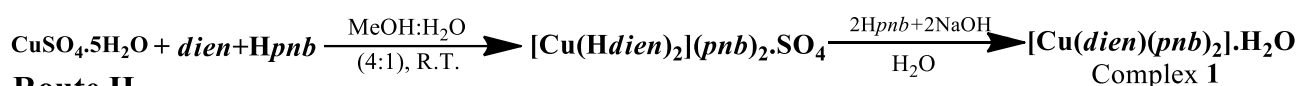
While investigating the reactions of copper(II) with ligands diethylenetriamine and *pnb*, but following different synthetic routes (Scheme 1) at room temperature, we have succeeded in isolating three Cu-*dien-pnb* complexes.

The reaction between sodium hydroxide, copper(II) sulfate pentahydrate and p-nitrobenzoic acid in appropriate stoichiometries in aqueous medium resulted in the formation of desired Cu(*pnb*)<sub>2</sub>.xH<sub>2</sub>O. This sky blue compound was insoluble in common organic solvents. When

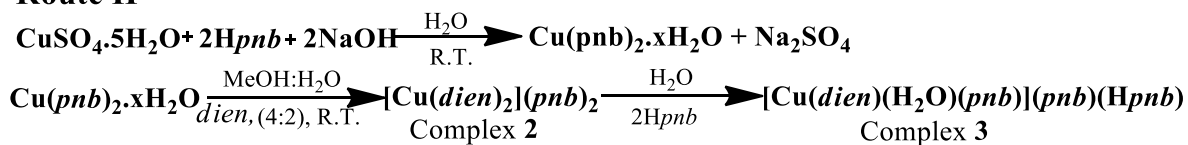


diethylenetriamine was added to the suspension of  $\text{Cu}(\text{pnb})_2 \cdot x\text{H}_2\text{O}$  in methanol-water (4:2) mixture until a clear blue solution was obtained, which on slow evaporation at room temperature gave respective crystalline product (complex **2**) as shown in Scheme 1. With excess addition of p-nitrobenzoic acid to the methanol:water solution of complex **2**, complex **3** was obtained from reaction mixture after 2 days. Complex **1** was synthesized using synthetic route I as shown in Scheme 1.

### Route 1



### Route II



**Scheme 1:** Schematic representation of synthesis of complexes **1-3**

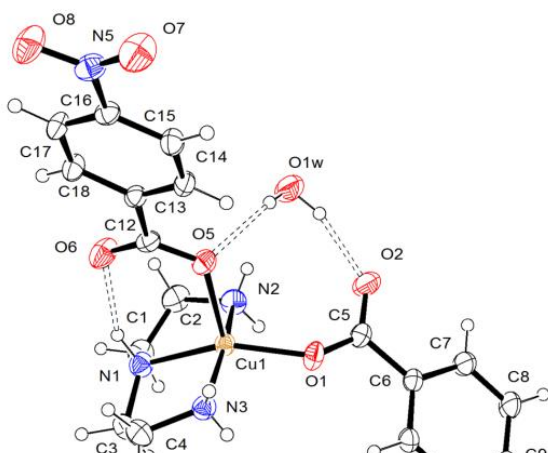
The ionic nature of complex **3** was indicated by molar conductance measurement performed at room temperature. The value of molar conductance measured ( $\Lambda_m=250$ ) is closer to the range observed for 1:2 electrolytes (235-273) [35]. The elemental analyses of all three compounds are consistent with the observed composition of the compounds which was subsequently confirmed by single crystal X-ray diffraction analysis.

## 3.2. X-ray Crystallography

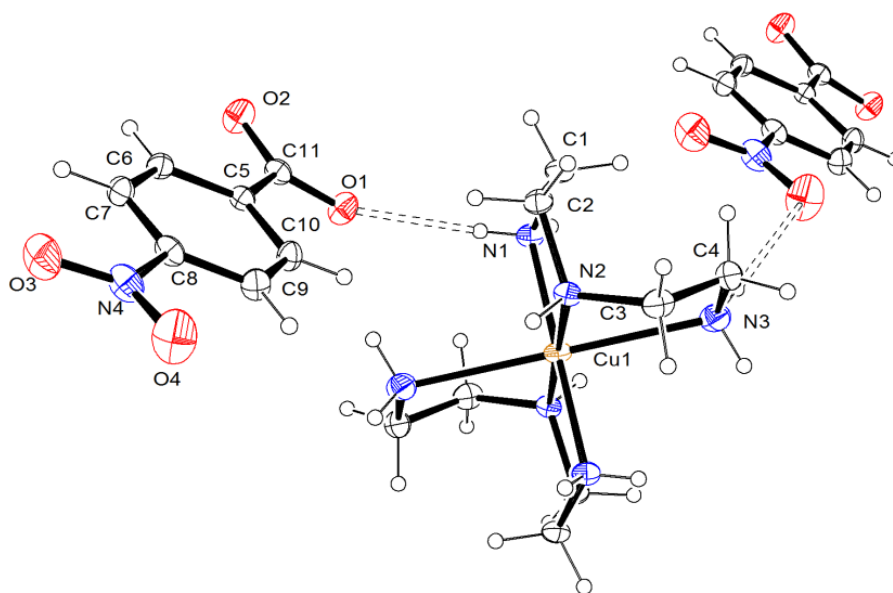
*Distinction of Cu(II) coordination geometry.* Single crystal X-ray structure determination of complexes **1-3** revealed that the complexes possess different coordination environments around the copper(II) centre. The ORTEPIII [36] view of complexes **1-3** are shown in Figs. 1-3, respectively. The ORTEPIII [36] view of complexes **1-3** are shown in Figs. 1-3, respectively.

The molecular entities constituting the asymmetric unit of **1**, i.e. one neutral  $[\text{Cu}(\text{dien})(\text{pnb})_2]$  complex and one co-crystallized water molecule, are shown in Fig. 1. The coordination around the central copper metal can be described as square pyramidal (*vide infra*), with both the *pnb* anions acting as monodentate ligands. The Cu(II) atom is located 0.32 Å above the least-squares equatorial plane formed by O1, N1-N3 atoms, while the apical position is occupied by the O5 atom belonging to a *pnb* ligand located almost perpendicularly to the Cu-N1 bond through the formation of an intra-molecular N-H...O hydrogen bond involving the free carboxylic oxygen O6 and N1 atom of the *dien* molecule. The co-crystallized water molecule is in turn involved in two O<sub>w</sub>-H...O interactions with O2 and O5 atoms of the same molecule (Fig. 1).

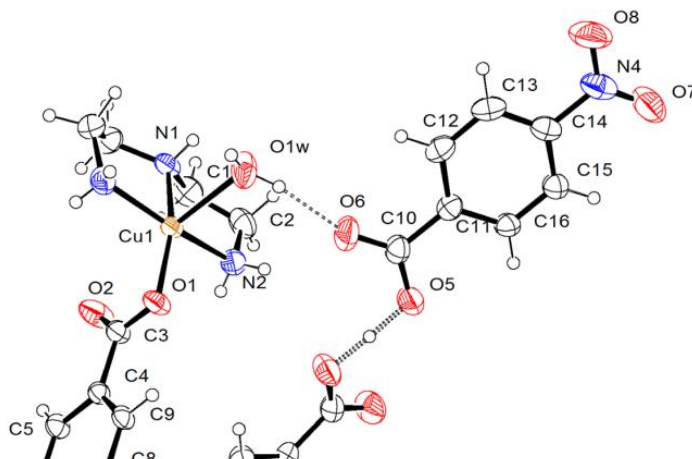
The basal N-Cu-N bite angles are smaller than 90° due to the tridentate nature of the *dien* ligand. As for the Cu-N/O distances, they are perfectly in line with those reported in literature. From a CSD search on Cu-dien complexes (irrespective of the coordination geometry), mean Cu-N distances of 2.01(2) and 2.04(4) Å have been obtained for central and side N atoms, respectively (105 hits). As usual, the apical Cu-O5 distance is longer than the basal Cu-O1 one.



**Fig.1.** ORTEPIII view and atom numbering scheme of complex **1**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen bonds are drawn as dashed lines.



**Fig 2:** ORTEPIII view and atom numbering scheme of complex **2**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen bonds are drawn as dashed lines.



**Fig. 3.** ORTEPIII view and atom numbering scheme of complex **3**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen bonds are drawn as dashed lines.

Complex **3** exhibits a similar type of coordination sphere around copper center, i.e similar CuN3O2 chromophore, with the difference that the apical site is occupied by a coordinated water molecule instead of a *pnb* ligand. Even in this case the *pnb* ligand can be considered as monodentate, due to the long Cu-O2 distance (2.699(2) Å). The Cu(II) atom is located 0.314(1) Å above the least-squares equatorial plane. The central Cu metal, N1, O1w and all atoms of the coordinated benzoate ligand lie on a mirror; a second *pnb* anion, outside the first coordination sphere, guarantees the overall electroneutrality carrying a 0.5 charge since the hydrogen formally linked to the O5 carboxylic oxygen is located on a two-fold axis and is shared with a symmetrical molecule. Consequently, a dimeric nitrobenzoic unit (*pnb.Hpnb*) is observed, where the constituting molecules are linked through a very strong O-H...O hydrogen bond (O...O distance= 2.459(2) Å). Cu-N/O bond distances and angles around Cu are very similar to those reported for complex **1**.

The distortion of the coordination polyhedra in **1** and **3** can be quantified by the value of the geometrical index  $\tau$  [37], calculated as  $\tau = (\varphi_1 - \varphi_2)/60$ , where  $\varphi_1$  and  $\varphi_2$  are the largest and second largest X1-Cu-X2 angles. The value of  $\tau = 1$  corresponds to trigonal bipyramidal, while  $\tau$

= 0 to square pyramidal geometry. For the structures **1** and **3** reported here (see Table 2), the  $\tau$  values are 0.12 and 0.11, respectively, which are close to the square pyramidal limit.

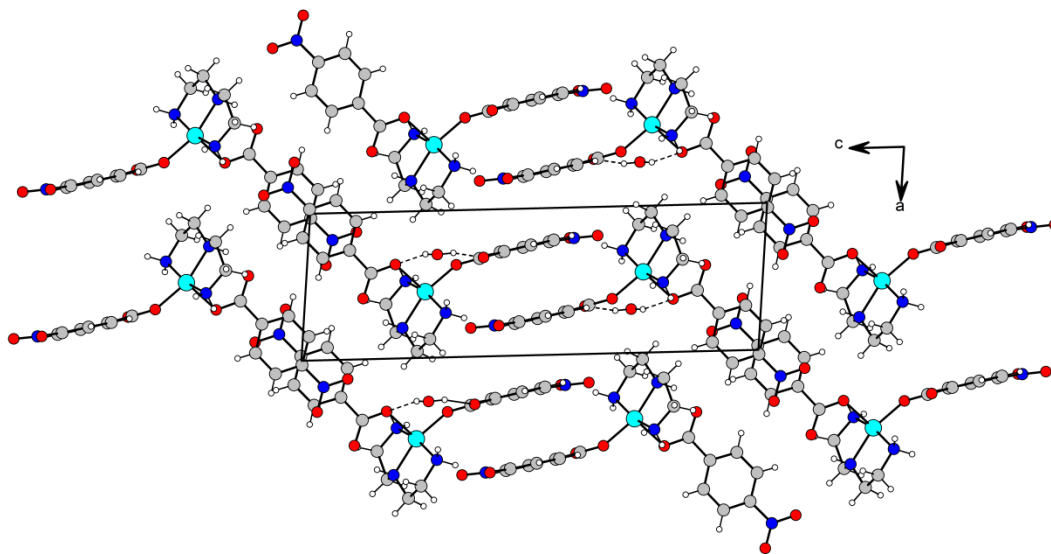
Conversely, complex **2**, that crystallized in triclinic crystal system, shows an axially elongated octahedral arrangement around copper (II) atom residing on a centre of symmetry. The octahedral geometry is satisfied by two chelating tridentate nitrogen donor ligand diethylenetriamine forming  $[\text{Cu}(\text{dien})_2]^{2+}$  coordinating cationic species and counter balanced by two *pnb* moieties. The ORTEPIII [36] view of complex **2** is shown in Fig. 2.

With the aim of better understanding the role played by the ligand as far as the final coordination geometry is concerned, CSD searches of Cu complexes containing *pnb* ligands was performed. Nitrobenzoate ligand shows a significant tendency to bridge two adjacent copper atoms through the carboxylate group to give polynuclear complexes (13 structures out of 34 total hits) but, in the majority of cases, it acts as a monodentate ligand like in **1** and **3** and the observed geometries are octahedral or pyramidal depending mainly on the steric encumbrance of the other ligands. Besides the already mentioned structure of ref. 18, in only other two structures the *pnb* molecule is outside the first coordination sphere and in both cases the bound molecules are chelating ligands (ethylenediamine and phenanthroline) [38]. As mentioned above, a discrete number (105 hits) of copper complexes containing the *dien* ligand has been found, but only 17  $\text{Cu}(\text{dien})_2$  structures have been reported so far; in 5 cases, the *dien* molecule is monoprotonated and act as a bidentate ligand. In all the other 12 cases but one (a Re/Se clustered structure, where Cu is coordinated in a square-pyramidal manner [39]) the coordination around the copper is octahedral, with the anions residing outside the first coordination sphere like in **3**.

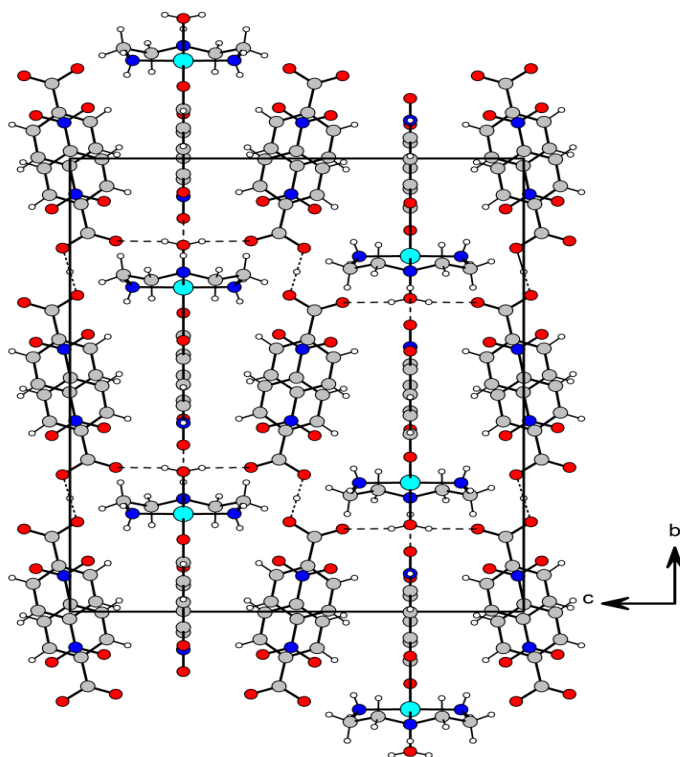
*3-D arrangement for complexes 1–3*. The observed different coordination modes lead to different interaction patterns and crystal architectures. As described above, in complex **1** the Cu complex

and the co-crystallized water molecule are tightly bound in a single unit by two O-H...O hydrogen bonds. The different units are packed in such a way that rows of stacked Cu atoms alternating with layers constituted by the organic part are easily recognizable (Fig.4). The different layers are linked in turn by weaker N-H...O hydrogen bonds or interactions of C-H...O type (Table 3).

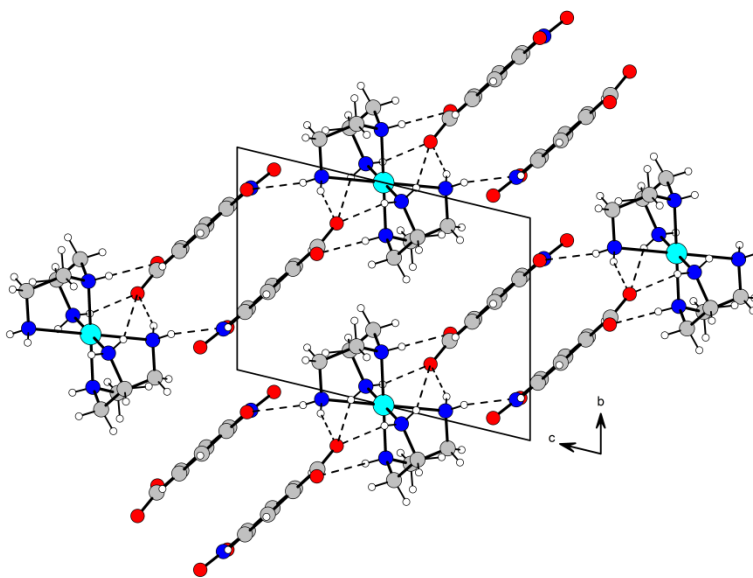
The packing architecture of complex **3** is characterized by the formation of a zig-zag O-H...O hydrogen bonded chain running along the *c* direction and involving the carboxylic group of the counter anion and the coordinated water molecule (Fig. 5). These interactions, significantly stronger than the other formed in the crystal, can be classified as positively charge-assisted hydrogen bonds and their formation presumably drives the packing mode of the molecules. Other N-H...O and C-H...O interactions, listed in Table 3, contribute to make the lattice more robust.



**Fig.4.** Packing diagram of complex **1** (viewed down *b* axis). O-H...O hydrogen bonds are drawn as dashed lines



**Fig.5.** Packing diagram of complex **3** (viewed down *a* axis). Main O-H...O hydrogen bonds are drawn as dashes



**Fig.6.** Packing diagram of complex **2** (viewed down *a* axis). Main O-H...O hydrogen bonds are drawn as dashes

In contrast to complexes **1** and **3**, complex **2** showed a layered arrangement of cationic and anionic layers. Anionic layers are constituted by *pnb* moieties oriented in alternate fashion and cationic layers are formed by  $[\text{Cu}(\textit{dien})_2]$  units. The crystal lattice of complex **3** was stabilized by mutual interplay of various non-covalent interactions, i.e. ‘classical’ N-H...O and O-H...O hydrogen bonding and weaker C-H...O intermolecular interactions. Packing diagram of complex **2** is shown in Fig. 6.



**Table 1.** Crystal data and refinement details of complexes **1-3**

	Complex 1	Complex 2	Complex 3
Chemical formula	C <sub>18</sub> H <sub>21</sub> CuN <sub>5</sub> O <sub>8</sub> ·H <sub>2</sub> O	C <sub>22</sub> H <sub>34</sub> CuN <sub>8</sub> O <sub>8</sub>	C <sub>14</sub> H <sub>9</sub> N <sub>2</sub> O <sub>8</sub> ·C <sub>11</sub> H <sub>19</sub> CuN <sub>4</sub> O <sub>5</sub>
<i>M<sub>r</sub></i>	516.95	602.12	684.07
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Orthorhombic, <i>Pbcm</i>
<i>a</i> (Å)	6.9986(2)	7.0433(5)	7.0949(1)
<i>b</i> (Å)	7.1975(2)	8.7772(6)	22.9896(5)
<i>c</i> (Å)	21.3652(5)	11.3557(8)	17.8629(6)
$\alpha$ (°)	88.546(2)	74.287(2)	90
$\beta$ (°)	85.023(2)	80.973(2)	90
$\gamma$ (°)	79.245(2)	70.463(2)	90
<i>V</i> (Å <sup>3</sup> )	1053.28(5)	635.17(8)	2913.60(12)
<i>Z</i>	2	1	4
Radiation type	Mo- <i>K</i> $\alpha$	Mo- <i>K</i> $\alpha$	Mo- <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.10	0.92	0.83
Crystal size (mm)	0.44 × 0.29 × 0.15	0.06 × 0.20 × 0.20	0.52 × 0.23 × 0.06
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	10333, 4364, 4068	17968, 3902, 3239	17613, 4342, 3164
<i>R</i> <sub>int</sub>	0.036	0.046	0.051
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.031, 0.087, 1.06	0.039, 0.082, 1.04	0.039, 0.110, 1.04
No. of reflections	4364	3902	4342
No. of parameters	326	193	243
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.50, -0.58	0.37, -0.34	0.47, -0.67
CCDC no.	1536134	1504834	1536135

**Table 2.** Selected bond distances and angles (Å, °) of complexes **1-3****Complex 1**

Cu1 - N1	2.010(2)	Cu1 - N2	2.015(2)
Cu1 - N3	2.019(2)	Cu1 - O1	1.959(2)
Cu1 - O5	2.230(1)		
N1 - Cu1 - N2	84.25(8)	N2 - Cu1 - O1	95.66(7)
N1 - Cu1 - N3	84.08(8)	N2 - Cu1 - O5	100.55(7)
N1 - Cu1 - O1	156.92(7)	N3 - Cu1 - O1	91.00(7)
N1 - Cu1 - O5	101.25(7)	N3 - Cu1 - O5	91.99(7)
N2 - Cu1 - N3	164.31(8)	O1 - Cu1 - O5	101.45(5)

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**Complex 2**

Cu1-N1	2.034(1)	Cu1-N2	2.054(1)
Cu1-N3	2.541(2)		
N1-Cu1-N2	84.55(6)	C3-N2-C2	113.81(14)
N1-Cu1-N3	92.14(6)	C3-N2-Cu1	112.29(11)
N2-Cu1-N3	76.50(6)	C2-N2-Cu1	108.38(10)

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**Complex 3**

Cu1 - N1	1.999(2)	Cu1 - N2	2.014(2)
Cu1 - O1	1.978(2)	Cu1 - O1W	2.332(2)
N1 - Cu1 - N2	84.36(5)	N2 - Cu1 - O1W	91.82(5)
N1 - Cu1 - O1	161.63(8)	N1 - Cu1 - O1W	90.36(9)
N2 - Cu1 - O1	94.79(5)	O1 - Cu1 - O1W	108.01(8)
N2 - Cu1 - N2 <sup>i</sup>	168.17(11)		

Symmetry code: (i) x, y, 3/2-z

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**Table 3.** Hydrogen bonding parameters; D= donor, A= acceptor (Å, °) of complexes **1-3**

D-H...A	D-H	D...A	H...A	>D-H...A
<b>Complex 1</b>				
N1-H...O6	0.94(3)	2.902(2)	2.02(3)	156(3)
N2-H...O1W	0.82(3)	3.230(3)	2.51(3)	148(3)
O1W-H...O2	0.82(3)	2.773(3)	1.97(3)	164(3)
O1W-H...O5	0.84(3)	2.811(2)	2.00(3)	162(3)
C18-H...O7 <sup>i</sup>	0.93	3.381(3)	2.63	138
C3-H...O8 <sup>ii</sup>	0.97	3.374(3)	2.56	142
N2-H...O4 <sup>iii</sup>	0.95(4)	3.132(3)	2.22(4)	159(3)
N3-H...O8 <sup>iv</sup>	0.78(3)	3.243(2)	2.52(3)	155(3)
C4-H...O7 <sup>iv</sup>	0.97	3.476(3)	2.59	152
N3-H...O1W <sup>v</sup>	0.86(3)	3.010(3)	2.19(3)	159(3)
C10-H...O2 <sup>v</sup>	0.93	3.392(2)	2.59	144
Equivalent positions: (i) x-1,y,z; (ii) 1-x,-y,-z; (iii) 1-x,1-y,1-z; (iv) 2-x,-y,-z; (v) x,y+1,z				
<b>Complex 2</b>				
N1-H...O1	0.82(2)	3.028(3)	2.23(2)	164(2)
N3-H...O4 <sup>i</sup>	0.85(2)	3.238(3)	2.39(2)	170(2)
N2-H...O2 <sup>ii</sup>	0.84(2)	2.944(3)	2.10(2)	173(2)
C3-H...O1 <sup>ii</sup>	0.97	3.410(3)	2.63	137
C9-H...O2 <sup>ii</sup>	0.93	3.387(3)	2.64	138
N3-H...O1 <sup>iii</sup>	0.88(2)	3.006(3)	2.16(2)	161(2)
N1-H...O1 <sup>iv</sup>	0.84(2)	3.065(3)	2.29(2)	152(2)
C6-H...O4 <sup>v</sup>	0.93	3.436(3)	2.66	140
Equivalent positions : (i) x,1+y,z-1; (ii) x-1,y,z; (iii) -x,2-y,1-z; (iv) 1-x,2-y,1-z; (v) x+1,y,z				
<b>Complex 3</b>				
N2-H...O6	0.83(2)	3.074(3)	2.33(2)	148(2)
O1W-H...O6	0.85(2)	2.776(2)	1.96(2)	159(2)
O5-H...O5 <sup>i</sup>	1.230(2)	2.459(2)	1.230(2)	175.6(1)
C5-H...O3 <sup>ii</sup>	0.93	3.267(3)	2.44	148
N2-H...O8 <sup>iii</sup>	0.76(3)	3.102(3)	2.44(3)	145(2)
C8-H...O2 <sup>iv</sup>	0.93	3.206(3)	2.39	145
N1-H...O4 <sup>v</sup>	0.87(4)	2.863(3)	2.16(4)	137(3)
Equivalent positions: (i) x, 1/2-y,1- z; (ii) x-1,y,z; (iii) 1-x,y-1/2,z; (iv) x+1,y,z; (v) 1-x,y+1/2,z				

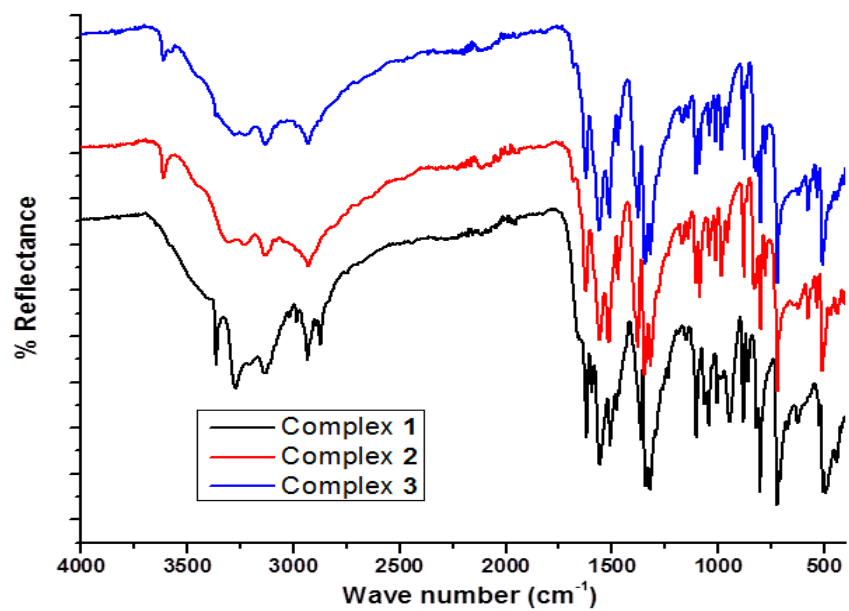
### 3.3. Spectroscopy:

#### 3.3.1. FT-IR and electronic spectroscopy

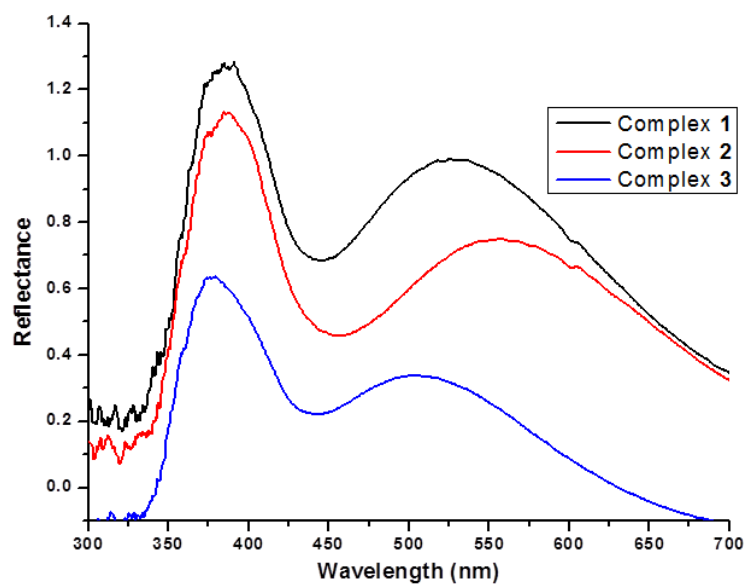
The infrared spectra of the newly synthesized complexes **1-3** have been recorded in the region 4000–400  $\text{cm}^{-1}$  (Fig.7) and tentative assignments have been made on the basis of earlier reports [40-43] in literature. The bands in the region 3500-3100  $\text{cm}^{-1}$  were attributed to O-H stretching vibration of water molecule in case of complexes **1** and **3**. The absence of broad absorption peak for complex **2** in the region 3500-3100  $\text{cm}^{-1}$  indicated absence of water molecule. The sharp bands in the region 3300-3100  $\text{cm}^{-1}$  for all complexes **1-3** have been assigned to N-H stretching vibration of the nitrogen donor ligand, diethylenetriamine. The sharp bands varying from weak to medium intensity in the region 3195–2855  $\text{cm}^{-1}$  in all the complexes **1-3** may be attributed to C-H stretching vibrations of aromatic moiety of *pnb* ligand. The sharp peaks in the region 1610-1575  $\text{cm}^{-1}$  and 1400-1360  $\text{cm}^{-1}$  were assigned to  $\nu_{\text{as}}(\text{carboxylate})$  and  $\nu_{\text{s}}(\text{carboxylate})$  stretching vibration. The different value of  $\Delta\nu = \nu_{\text{as}}(\text{carboxylate}) - \nu_{\text{sym}}(\text{carboxylate})$  in complexes **1-3** indicated different coordination mode of carboxylate ligand in all three newly synthesized complexes. The values of  $\Delta\nu$  is diagnostic to find out carboxylate coordination mode in metal carboxylates. The values  $\Delta\nu = 202, 195 \text{ cm}^{-1}$  for complex **1** and **3** respectively are in the range  $\Delta\nu = 180-220 \text{ cm}^{-1}$  which indicated monodentate coordination mode of carboxylate ligand [32,33]. The  $\Delta\nu = 235 \text{ cm}^{-1}$  for complex **2** falls in the range observed for ionic nature of carboxylate ligand ( $\Delta\nu = 180-220 \text{ cm}^{-1}$ ) [42, 43]. The sharp bands in the region 530-475  $\text{cm}^{-1}$  were assigned to Cu-N or Cu-O stretching frequency.

Although it is difficult to predict geometry of copper(II) complex on the basis of UV-Visible spectroscopy (solid or solution state) but extensive investigation on the copper(II) complexes with various geometries revealed their characteristic spectral features of 5- or 6-coordinated copper (II) complexes [44,45]. The appearance of two peaks in the visible region, i.e. one shoulder and other

intense broad band is characteristic feature of square pyramidal/trigonal-bipyramidal geometry of copper(II) complexes as found in complexes **1** and **3**. [44-49] The solid state diffuse reflectance spectra of complexes **1-3** showed significant variation in peak positions indicating different coordination geometry for complex **2** (distorted octahedral) than that for complexes **1** and **3** (square pyramidal) [46]. In square pyramidal complexes, three transitions expected are:  $d_z^2 \rightarrow d_{x^2-y^2} < d_{xy} \rightarrow d_{x^2-y^2} < d_{xz} \rightarrow d_{x^2-y^2} \cong d_{yz} \rightarrow d_{x^2-y^2}$  [45,50]. Complexes **1** and **3** showed a small shoulder at around 630 nm and intense broad bands at 530 nm for complex **1** and 560 nm in complex **2**, typical for 5-coordinated copper(II) complex [45]. As for as complex **2**, only one broad band observed at 510 nm revealed the presence of elongated octahedral geometry around copper(II) center. The sharp bands in the region 400-350 nm in all complexes **1-3** might be assigned to  $\pi \rightarrow \pi^*$  transition in aromatic moiety of *pnb* ligand [45]. In order to know stability of complexes **1-3** (coordination geometry) in solution state, electronic spectra were recorded in methanol : water (4:1) mixture. Electronic spectra of complexes **1-3** showed significant changes in the position of peaks in visible region as compared to those of the solids, which indicated that some structural modification may occur in solution state. The complexes **1-3** showed broad absorption band at 615 ( $\epsilon_{max} = 194.34$ ), 618 ( $\epsilon_{max} = 120.34$ ) nm and 608 ( $\epsilon_{max} = 140$ ) nm, typical for d-d transitions of elongated octahedral copper(II) complexes [18, 42]. The UV-Visible spectra for complexes **1-3** in solution state were given in Fig. S1(supplementary data). Diffuse reflectance spectra for complexes **1-3** have been given in Fig. 8.



**Fig.7.** FT-IR spectra of complexes **1-3**



**Fig. 8** Diffuse reflectance spectra of complexes **1-3**

### 3.3.2. EPR spectroscopy

When the geometry of a Cu(II) complex is square planar, elongated octahedral or square pyramidal, the unpaired electron occupies the  $d_{x^2-y^2}$  orbital and the two  $g$  values, the parallel ( $g_{\parallel} = g_z$ ) and perpendicular ( $g_{\perp} = g_x = g_y$ ) one, can be given as:

$$g_{\parallel} = g_z = 2.0023 \pm \frac{8\lambda}{E(d_{x^2-y^2}) - E(d_{xy})},$$

$$g_{\perp} = g_x = g_y = 2.0023 \pm \frac{2\lambda}{E(d_{x^2-y^2}) - E(d_{xz})} = 2.0023 \pm \frac{2\lambda}{E(d_{x^2-y^2}) - E(d_{yz})},$$

where  $\lambda$  is the spin-orbit coupling constant for Cu(II) and  $E$  are the orbital energies. In this case the relation  $g_{\parallel} \gg g_{\perp} > 2.0023$  is expected. Compounds  $[\text{Cu}(\beta\text{-pic})_2(\text{H}_2\text{O})_2(5\text{-chloro-2-nitrobenzoate})_2]$ ,  $[\text{Cu}(\gamma\text{-pic})_2(5\text{-chloro-2-p-nitrobenzoate})_2]$  or  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2](5\text{-chloro-2-nitrobenzoate})_2 \cdot 2\text{H}_2\text{O}$ , (where  $\beta\text{-pic} = \beta\text{-picoline}$ ,  $\gamma\text{-pic} = \gamma\text{-picoline}$  and  $\text{en} = \text{ethylenediamine}$ ) can be given as characteristic examples [51].

The  $d_{z^2}$  orbital becomes the ground state of a Cu(II) complex, if the molecular structure is compressed octahedral or trigonal bipyramidal. In such a case the perpendicular and parallel component can be described by the following equations:

$$g_{\parallel} \approx 2.0023,$$

$$g_{\perp} = g_x = g_y = 2.0023 \pm \frac{6\lambda}{E(d_{z^2}) - E(d_{xz})} = 2.0023 \pm \frac{6\lambda}{E(d_{z^2}) - E(d_{yz})},$$

and their relation is  $g_{\perp} > g_{\parallel}$ ; so-called *inversed spectrum* reported inter alia for  $[\text{Cu}_2(\mu\text{-X})(\mu\text{-L})_2](\text{ClO}_4)_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{OH}$ ,  $\text{L} = \text{m-bis}[\text{bis}(3,5\text{-dimethyl-1-pyrazolyl)methyl}] \text{benzene}$ ) [52] or the complexes with crown ethers [53,54].

In the case of intermediate situations, i.e. if the geometry is midway between the square pyramid and the trigonal bipyramid, a *rhombic spectrum*, exhibiting three different g values, is observed.

This is an indication of the ground state being a linear combination of the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals:

$$\Psi_{GS} = c_1|d_{x^2-y^2}\rangle + c_2|d_{z^2}\rangle,$$

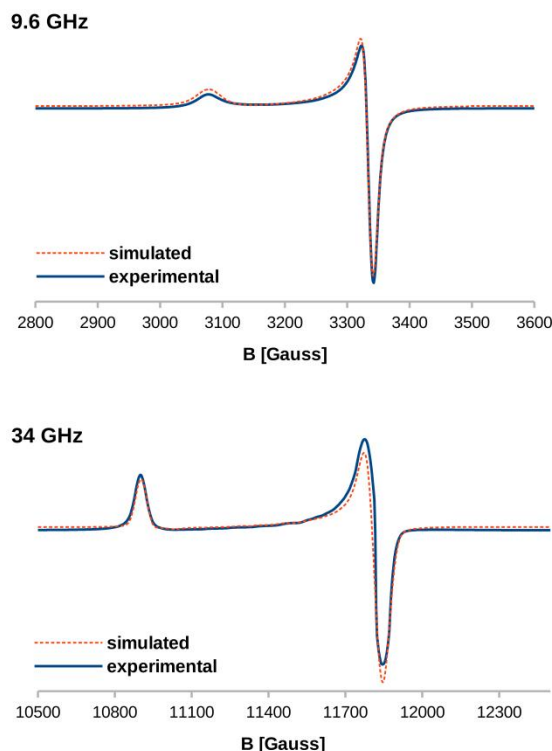
where  $c_1$  and  $c_2$  are the coefficients of linear combination. Chlorotetrakis(1H-2-isopropyl imidazole-κN<sup>3</sup>)copper(II) chloride [55], Cu(dafone)<sub>2</sub>Br<sub>2</sub> [56], Cu(NH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>COO)Br and Cu(NH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> [57] can held up as examples of such complexes. A parameter  $G$ :

$$G = \frac{g_2 - g_1}{g_3 - g_1},$$

with  $g_3 > g_2 > g_1$ , can be used as a criterion of the predominance of the  $d_{z^2}$  ( $c_1 < c_2$ ) or  $d_{x^2-y^2}$  ( $c_1 > c_2$ ) orbital in the ground state. [45] If  $G > 1$ , the predominant contribution to the ground state arises from  $d_{z^2}$ , otherwise the greater contribution arises from  $d_{x^2-y^2}$ .

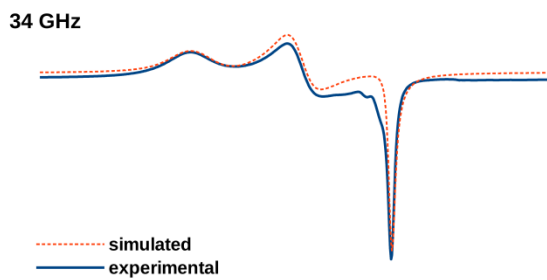
All the powdered compounds exhibited anisotropic EPR spectra. Regardless of the used frequency, the spectrum of complex **2** (Fig. 9) is well resolved due to resonance transitions corresponding to the two components of the g tensor ( $g_{||} = 2.227$ ,  $g_{\perp} = 2.053$ ). The relation  $g_{||} \gg g_{\perp} > 2.0023$  is typical for uniaxial symmetry of the coordination sphere around Cu(II), in line with an elongated octahedral geometry of the complex determined by the X-ray diffraction experiment. Therefore, the unpaired electron of Cu(II) is expected to occupy a molecular orbital with primary contribution from  $d_{x^2-y^2}$  atomic orbital.



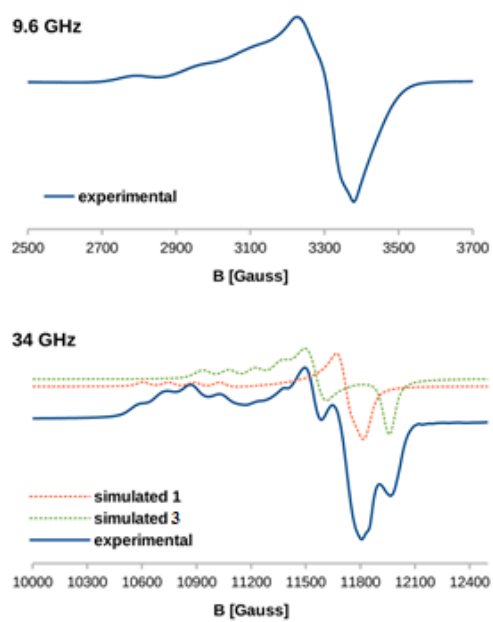


**Fig.9.** EPR spectra of powdered complex **2** recorded at 9.6 (X-band) and 34 (Q-band) GHz frequencies

In the case of complexes **1** and **3** the advantage of 34 GHz frequency (Q-band) is manifested. The EPR spectrum of complex **3** (Fig. 10) is far better resolved if the higher frequency is applied in the experiment. The  $g$  components derived from the simulation, that is  $g_3 = 2.188$ ,  $g_2 = 2.108$  and  $g_1 = 2.045$ , are a firm indication of the ground state being a mix of the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. More notably, only the EPR spectrum recorded for the powdered sample of **1** (Fig. 11) at 34 GHz clearly revealed that the observed resonance transitions stem from two forms of the Cu(II) complex. One signal was well reproduced with the three  $g$  components determined for complex **3** and hyperfine coupling constant  $A_3 = 148 \times 10^{-4} \text{ cm}^{-1}$  (simulated 3). The other signal, successfully emulated with  $g_3 = 2.245$ ,  $g_2 = 2.075$ ,  $g_1 = 2.055$  and  $A_3 = 143 \times 10^{-4} \text{ cm}^{-1}$  (simulated 1), was therefore attributed to complex **1**.



**Fig.10.** EPR spectra of powdered complex **3** recorded at 9.6 (X-band) and 34 (Q-band) GHz frequencies

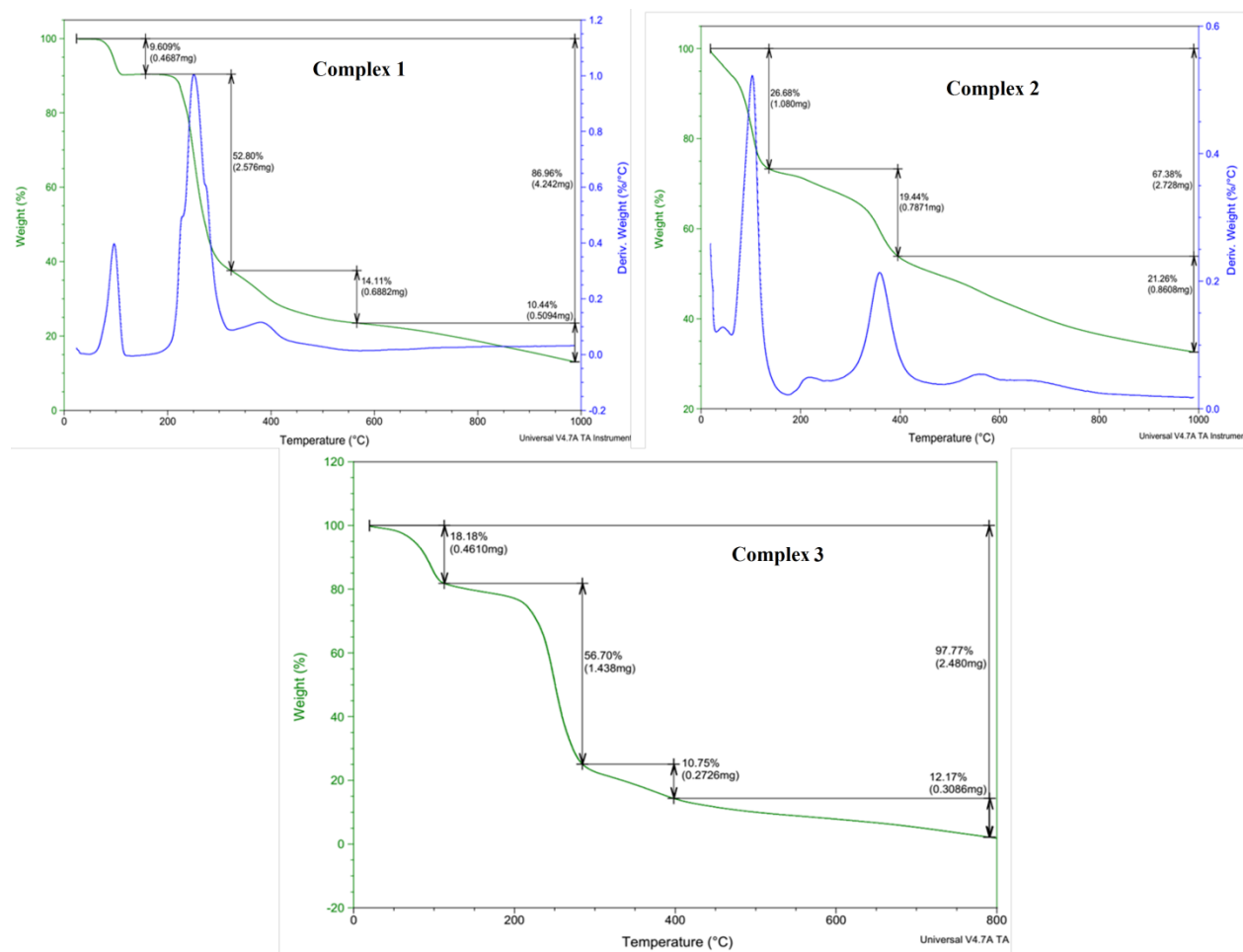


**Fig.11.** EPR spectra of powdered complex **1** recorded at 9.6 (X-band) and 34 (Q-band) GHz frequencies

Two things should be noted here. Firstly, keeping in mind the structural similarity between compounds **1** and **3** the fact that complex **1** contains an admixture of complex **3** cannot be labeled as surprising. Secondly, the  $G$  parameter calculated for compounds **1** and **3** amounts to 0.12 and 0.79, respectively. This indicated that for the both compounds the contribution from the  $d_{x^2-y^2}$  orbital predominates the ground state ( $c_1 > c_2$ ), but the contribution arising from  $d_{z^2}$  is significantly greater in the case of complex **3**. In order to understand this divergence structures of the two compounds should be inspected in details. According to X-ray diffraction experiments, they show a similar type of coordination sphere around Cu(II) center, that is distorted square pyramidal CuN3O2 chromophore, with the difference that the apical site is occupied by a *pnb* ligand in the case of complex **1** and by a water molecule in the case of complex **3**. The oxygen atom of *pnb* anion is a carrier of more significantly negative charge than the oxygen atom of water. The substantial contribution from  $d_{z^2}$  to the half-occupied molecular orbital of complex **1** would increase repulsive interaction with the O atom of *pnb* and hence is energetically more unfavorable in comparison with complex **3**.

**3.4. Thermogravimetric analyses:** Thermogravimetric curves for compounds **1-3** were recorded under nitrogen atmosphere to study the thermal stability of all newly synthesized compounds. Thermogravimetric loss in first step for compounds **1** and **3** in the temperature range 70-150 °C revealed the loss of water molecule. For complex **2** no weight loss has been observed in the temperature range 70-150 °C indicating absence of water molecule. The second step of thermogravimetric loss for compounds **1-3** corresponded to loss of *pnb* moieties in the temperature range 150-300 °C. Thereafter, 300 °C, no sharp loss was observed in all compounds **1-3** indicated slow thermogravimetric degradation of diethylenetriamine moieties and formation of stable CuO residue after 500 °C.

DTA curves have also been recorded in order to check the endothermic or exothermic nature of all the compounds with increase in temperature. DTA curves in all compounds **1-3** clearly showed endothermic nature of all thermogravimetric loses. TGA-DTA curves have been given in Fig.12.



**Fig.12.** TGA-DTA curves for complexes **1-3**

### 3.5. Antimicrobial activities

### **3.5.1. Well diffusion assay**

Well diffusion assay was performed for the three synthesized copper(II) complexes. All of the three copper(II) complexes **1-3** showed potent antibacterial activity against *E. coli*, *P. aeruginosa*, Methicillin resistant *S. aureus* and *K. pneumoniae* as a wide zone of inhibition around the wells was observed as compared to solvent control.

### **3.5.2. Minimum inhibitory concentration and minimum bactericidal assay:**

Three synthesized copper(II) complexes **1-3** and solvent control DMSO were used to calculate the MIC and MBC of *E. coli*, *P.aeruginosa*, Methicillin resistant *S. aureus* and *K. pneumoniae*. As shown in Table 4 that all three copper(II) complexes showed significant antimicrobial activity, as MIC and MBC of three of the complexes was extremely low as compared to solvent control DMSO. Copper(II) complexes showed higher antibacterial potential against gram positive Methicillin resistant *S. aureus* than other tested gram negative organisms. This might be due to the differences in the cell wall composition of gram positive and gram positive bacteria.

**Table 4. MIC of three copper(II) complexes in comparison to DMSO (control)**

	<i>E. coli</i> 25922	<i>S. aureus</i> 43300	<i>K. pneumoniae</i> B5055	<i>P. aeruginosa</i> PAO1
Solvent Control DMSO (μl)	25	25	50	50
Complex <b>1</b> (μg/ml)	1875	937	1875	1875
Complex <b>2</b> (μg/ml)	1875	937	1875	1875
Complex <b>3</b> (μg/ml)	1875	937	1875	1875

## Conclusions

Three new hybrid inorganic-organic copper (II) complexes **1-3** were isolated using same ligands but different reaction conditions at room temperature for the first time. All the complexes showed different coordination sphere around copper(II) metal center. Single crystal X-ray structure of all complexes revealed that all complexes have different geometries i.e. distorted square pyramidal for complexes **1** and **3** (neutral) but axially elongated octahedral cation  $[\text{Cu}(\text{dien})_2]^{2+}$  and *pnb* anion for complex **2** (ionic). The ligand diethylenetriamine (*dien*) acts as tridentate ligand through three N-donor sites in all three complexes and not as bidentate as reported earlier by our group [18]. Packing diagrams of complexes **1-3** clearly revealed that all complexes made a different 3-D arrangement of structural units in crystal lattice. Various non-covalent interactions such as N-H...O and O-H...O hydrogen bonding interactions play an important role in stabilization of crystal lattice. In addition EPR spectra of all three complexes clearly indicated different coordination spheres around copper(II) metal center in agreement with X-ray structure determination and revealed information about their electronic ground states. All copper(II) complexes **1-3** showed

higher antibacterial potential against gram positive Methicillin resistant *S. aureus* than other tested gram negative organisms.

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### **Supplementary data**

UV-VIS spectra and checkcif reports for **1-3**. Crystallographic data for the structural analysis of the three new complexes have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK, and are available free of charge from the Director on request quoting the deposition number CCDC **1536134**, **1504834** and **1536135** for complexes **1-3**, respectively.

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