

# Synthesis and Structural Features of Copper(II) Complexes of N,N,N',N'-tetramethylethylenediamine with 2-chlorobenzoate<sup>1-</sup> and 2-hydroxybenzoate<sup>1-</sup>

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## Abstract

Two copper(II) coordination complexes, formulated as [Cu(tmen)(ClBA)<sub>2</sub>] (**1**) and [Cu(tmen)(Hsal)<sub>2</sub>.H<sub>2</sub>O] (**2**), (where tmen = N,N,N',N'-tetramethylethylenediamine (C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>), ClBA = 2-chlorobenzoate (C<sub>7</sub>H<sub>4</sub>ClO<sub>2</sub><sup>1-</sup>) and Hsal<sup>1-</sup> (C<sub>7</sub>H<sub>5</sub>O<sub>3</sub><sup>1-</sup>) = monoanion of o-hydroxybenzoic acid (salicylic acid), have been synthesized and characterized by elemental combustion analysis, spectroscopic techniques, thermal studies and single crystal X-ray analyses. The complex (**1**) consists of two distinct monomeric units in which coordination environment around the central copper(II) ion is a distorted octahedron with CuN<sub>2</sub>O<sub>4</sub> chromophore, constituted by; a chelating tmen molecule, and two 2-chlorobenzoate<sup>1-</sup> anions coordinated through their carboxylate-O atoms in an asymmetrical bidentate fashion. The complex (**2**), is also a monomer and consists of CuN<sub>2</sub>O<sub>3</sub> chromophore, in which tmen is coordinated to Cu(II) through its two N atoms in a chelating bidentate fashion, an aqua-O and the two o-hydroxybenzoate<sup>1-</sup> (HSal<sup>1-</sup>) anions coordinated through one of their carboxylate-O atoms in a monodentate mode, forming a square pyramidal structure. Hydrogen bonding interactions especially of O–H···O, N–H···O, and C–H···Cl types interweave monomeric units and stabilize the overall crystal structures in both complexes. Thermal analysis and antibacterial activities of **1** and **2**, against various bacterial strains are also investigated.

**Keywords:** copper(II) carboxylate, N,N,N',N'-tetramethylethylenediamine, salicylate, 2-chlorobenzoate, supramolecular architectures

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## 1. Introduction

Among biologically significant d-elements, copper is one of the essential micronutrients needed by all living organism, and plays important roles in various biochemical processes [1]. Carboxylic acids constitute an important class of biologically important ligands. Benzoic acid, salicylic acid and their derivatives like acetylsalicylic acid, and chlorobenzoic acids are among such biologically relevant carboxylic acids. Salicylic acid shows antioxidant, antiseptic, anti-bacterial, anti-fungal, keratolytic, and photoprotective activities, and is used in skin ointments [2-3].

The bioactivity of copper(II)-salicylates, copper(II)-difunctional nitrogen-donor ligand complexes, and their ternary copper carboxylates seems to be further enhanced as compared to that of free ligands. The copper(II) complex of aspirin possesses antiulcer properties as opposed to aspirin alone, which tends to induce ulcers [4-5]. These complexes act as mimics of biological systems and can be applied as model systems for the study of copper(II)-containing metalloproteins, including tyrosinase, superoxide dismutase etc. Their pharmacological effects such as anticancer, anticarcinogenic, antimetastatic, and antimutagenic, antiarthritic, antiepileptic, anti-convulsant activities, and ability to prevent chemically induced skin cancers, suggest their potential use as new therapeutically administered drugs [6-9]. Some examples include the complexes  $[\text{Cu}_2(\text{sal})_2(2,2'\text{-bipy})_2] \cdot 2\text{H}_2\text{sal}$  [10], and  $[\text{Cu}(\text{sal})(2,2'\text{-bipy})] \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$  [4].  $[\text{Cu}(\text{salH})_2(\text{H}_2\text{O})]$  and  $[\text{Cu}(\text{sal})(\text{phen})]$  (Where phen = 1,10-phenanthroline, 2,2'-bipy = 2,2'-bipyridine) are potent superoxide dismutase mimetics, the former is also a moderate COX-1 inhibitor. These complexes also manifest DNA binding and cleaving properties and are potent anti cancer agents against both cisplatin sensitive and resistant cancer cell lines [7].

In the coordination chemistry perspective, aromatic acids like salicylic acid ( $\text{H}_2\text{Sal}$ ) and halogeno-benzoic acids are of interest in designing supramolecular metal-organic frameworks that are linked through weak forces like H-bonding and  $\pi$ - $\pi$  interactions [11].

The free ligand salicylic acid ( $\text{H}_2\text{Sal}$ ) has three potential sites for attachment to a metal ion, including two carboxylate-O atoms and a hydroxyl-O atom. Since it is a diprotic acid, it forms two anions;  $\text{Hsal}^{1-}$  and  $\text{sal}^{2-}$ . The carboxylate moiety of  $\text{Hsal}^{1-}$  ion can assume any of monodentate, bidentate (chelating) and bridging coordination modes.  $\text{Sal}^{2-}$  on the other hand also tends to utilize its deprotonated hydroxyl-O atom along with its carboxylate-O atoms to coordinate with metal ions [12].

Copper(II)-salicylate based complexes can assume, monomeric  $\{[\text{Cu}(\text{phen})_2(\text{Hsal})].[\text{Hsal}][\text{H}_2\text{O}]\}$ , [9], dimeric  $\{[\text{Cu}_2(\text{phen})_2(\text{sal})_2] \cdot 2\text{H}_2\text{O}\}$  [9] and polymeric forms [13] depending on the nature of ligands, and reaction conditions such as temperature, pH, solvent system etc [14-15]. The carboxylate moiety being coordinatively flexible, can assume monodentate, bidentate, or bridging coordination modes. Salicylate group can also be in outer coordination sphere acting as a mere counterion, like in the complexes;  $[\text{Cu}(\text{imzH})_5].(\text{Hsal})_2$ , and  $[\text{Cu}(\text{imzH})_6].(\text{Hsal})_2$  (where Himz = imidazole,) [16]. The monodentate mode of carboxylate moiety of  $\text{Hsal}^{1-}$  is reported in the complex  $[\text{Cu}(\text{imz})_2(\text{Hsal})_2]$  [16].

In the dimeric complexes like  $[\text{Cu}_2(\text{sal})_2(2,2'\text{-bipy})_2] \cdot 2\text{H}_2\text{sal}$  [10], the  $\text{sal}^{2-}$  ion coordinates to copper(II) through one of its carboxylate-O atom and its phenolato-O atom forming a chelate. The phenolato-O is also linked to second Cu(II) center and acts as a bridging moiety. Some examples of complexes exist in which the carboxyl group (-COOH) of salicylic acid coordinates with copper(II) ion, without losing its proton [12].

Metal-chlorobenzoates have garnered reasonable interest not only due to their biological [17], and magnetic properties [18], but also as important constituents, in the design of new metal-organic frameworks [19-20]. The structural variety in coordination modes of their carboxylate moiety and possibility of varying nuclearities, leads to the formation of monomeric to polymeric [19] complexes. For instance the carboxylate moiety of  $\text{Clba}^{1-}$  is; monodentately coordinating in the monomeric complex  $[\text{Mn}(\text{Clba})_2(\text{DENA})_2(\text{H}_2\text{O})_2]$ , (DENA= diethylnicotinamide) [21], bidentately chelating in dimeric  $[\text{Pb}_2(\text{Clba})_4(4,4'\text{-bipy})]$ , (4,4'-bipy= 4,4'-bipyridine) complex [22], monoatomic bridging in dimeric  $[\text{Cu}(\text{ClBA})_2(2,2'\text{-bipy})_2]$  (2,2'-bipy=2,2'-bipyridine) complex [23], syn-anti bridging in dimeric 2,2'-bipyridine  $[\text{Mn}_2(\text{bipy})_4(\text{ClBA})_2](\text{ClO}_4)_2 \cdot 2\text{EtOH}$  complex [24]. Halogenated aromatic carboxylates containing chloro, and fluoro groups are also potent, nucleolytic, cytotoxic and antibacterial agents [25].

Ethylenediamine and its derivative N,N,N',N'-tetramethylethylenediamine (tmen) are both bidentately chelating ligands with suitably placed two nitrogen atoms that can form stable, metal containing 5-membered rings. The metal complexes of such diamines, especially those of platinum and palladium with cis- structures are antihypoxic, radioprotective and exhibit resistance to malignant tumors [26].

The aspiration of our work is to gain insight into the coordination chemistry of copper(II)-diamine-carboxylates [27-28]. Herein, we report structures, characterization and antibacterial studies of two copper(II)-tmen adducts with salicylate and 2-chlorobenzoate.

## 2. Experimental

### 2.1. Materials and methods

CuCl<sub>2</sub>.2H<sub>2</sub>O was purchased from Merck chemical company Germany, while N,N,N',N'-tetramethylethylenediamine, 2-chlorobenzoic acid, 2-acetylsalicylic acid, methanol and NaOH were purchased from Sigma-Aldrich, chemical company, and are used in the same condition as received. The melting points were observed, using a Gallenkamp serial number C040281, U.K, electro-thermal melting point apparatus. Elemental analyses for C, H and N were performed using a Perkin-Elmer 2400 II elemental analyzer. The thermogravimetric analysis (TGA) was recorded on TGA instrument Q500, USA, in N<sub>2</sub> atmosphere at the rate 10 °C per minute and a flow rate of 20 ml per minute pure nitrogen atmosphere. Uv-Visible spectra of **1** and **2** dissolved in DMSO were recorded in 1cm quartz cells, using Mega-2100 Double Beam Uv-Visible spectrophotometer. FT-IR absorption spectra were recorded as KBr pellets with FT/IR-4100TypeA spectrometer in the range of 4000–400 cm<sup>-1</sup>, with the resolution of 4 cm<sup>-1</sup>, number of scans 32, and TGS detector.

### 2.2 Syntheses of Complexes (1) and (2)

Both complexes were synthesized by a similar reported method [28].

#### 2.2.1. Preparation of bis(2-Chlorobenzoato-O,O')-(N,N,N',N'-tetramethylethylenediamine)-copper(II) (1)

To aqueous CuCl<sub>2</sub>.2H<sub>2</sub>O (1.00 mmol= 0.170 g/15 cm<sup>3</sup>), a methanolic solution of 2-chlorobenzoic acid (0.313 g= 2 mmol/ 15 cm<sup>3</sup>) containing 20 drops of NaOH solution (1M), was added slowly in a drop wise manner with constant stirring, which was continued for an hour at 50°C. After cooling to room temperature and followed by the addition of methanolic solution of 4 mmols of N,N,N',N'-tetramethylethylenediamine (tmen) to the reaction mixture, the stirring of the resulting blue solution was continued for an hour. The solution was filtered and left for slow evaporation. Blue crystals of [Cu(tmen)(ClBA)<sub>2</sub>] (**1**) for single crystal x-ray diffraction were collected, after concentration of solution for a few days. Yield (0.245 g = 50%) m. p. =212 °C. Anal. Calc. for C<sub>20</sub>H<sub>24</sub>Cl<sub>2</sub>CuN<sub>2</sub>O<sub>4</sub> (%): C, 48.94; H, 4.93; N, 5.71. Found: C, 48.93; H, 4.95; N, 5.73. IR: ν<sub>max</sub>/cm<sup>-1</sup> 3074.94, 3058.73 ν(=C–H); 2960.60 ν<sub>as</sub>(C–H) of CH<sub>3</sub>; 2920.65 ν<sub>as</sub>(C–H) of CH<sub>2</sub>; 2847.69 ν<sub>s</sub>(C–H) of CH<sub>2</sub>; 1685.29, 1602.19 ν<sub>as</sub>(C=C); 1550.10 ν<sub>as</sub>(OCO); 1465.94 ν(C–H) of

CH<sub>3</sub>; 1435.06  $\nu_s(\text{OCO})$ ; 1428  $\nu_s(\text{C}=\text{C})$ ; 1121.56  $\nu(\text{C}-\text{N})$ ; 762.33  $\nu(\text{C}-\text{Cl})$ ; 546.56  $\nu(\text{Cu}-\text{O})$ ; 427.03  $\nu(\text{Cu}-\text{N}) \text{ cm}^{-1}$ . Solubility: Slightly soluble in water; soluble in DMSO, ethanol, methanol, and acetone.  $\lambda_{\text{d-d}}$  (DMSO) = 653 nm.

### 2.2.2. Preparation of bis(2-Hydroxybenzoato-O)-(N,N,N',N'-tetramethylethylenediamine)-copper(II)-hydrate (2)

A methanolic solution (5 cm<sup>3</sup>) of 2-acetoxybenzoic acid (0.362 g = 2 mmols) containing 20 drops of NaOH solution (1M) was added while stirring, to a solution of CuCl<sub>2</sub> · 2H<sub>2</sub>O (0.170 g = 1 mmol) in 15 cm<sup>3</sup> of H<sub>2</sub>O. The solution thus obtained, was then stirred for one hour one hour at 50°C. The solution was then cooled to room temperature, after which 15 cm<sup>3</sup> of a methanolic solution of N,N,N',N'-tetramethylethylenediamine (0.464 g = 4.00 mmols) was added to it, with stirring which was continued for further one hour at room temperature. The resulting blue solution was filtered and was allowed to stand at room temperature. After partial concentration of the solution at room temperature, dark blue crystals of **2**, suitable for single crystal x-ray diffraction were collected. The crystals were washed with cold methanol and then air dried. Yield: (0.227 g = 48%). m. p. = 215 °C (decomposed). Anal. Calc for C<sub>20</sub>H<sub>28</sub>CuN<sub>2</sub>O<sub>7</sub> (%): C, 50.98; H, 5.98; N, 5.94%. Found: C, 50.95 H, 6.0; N, 5.90). IR (KBr) cm<sup>-1</sup>: 3456  $\nu(\text{O}-\text{H})$ ; 3270  $\nu(\text{ArO}-\text{H})$ ; 3044, 3025  $\nu(\text{Ar}-\text{H})$ ; 2985  $\nu_{\text{as}}(\text{C}-\text{H})$  of CH<sub>3</sub>; 2919  $\nu_{\text{as}}(\text{C}-\text{H})$  of CH<sub>2</sub>; 2850  $\nu_s(\text{C}-\text{H})$  of CH<sub>2</sub>; 1646.10  $\nu_{\text{as}}(\text{C}=\text{C})$ ; 1584  $\nu_{\text{as}}(\text{OCO})$ ; 1470  $\nu(\text{C}-\text{H})$  bend of CH<sub>3</sub>; 1446  $\nu_s(\text{C}=\text{C})$ ; 1364  $\nu_s(\text{OCO})$ ; 1297  $\delta(\text{PhO}-\text{H})$  bend; 1245  $\nu(\text{Ph}-\text{O})$ ; 895  $\delta(\text{O}-\text{H})$  bend of H<sub>2</sub>O; 756  $\delta(=\text{C}-\text{H})$  oop bend; 508  $\nu(\text{Cu}-\text{O})$ ; 446  $\nu(\text{Cu}-\text{N}) \text{ cm}^{-1}$ . Solubility: Slightly soluble in water. Soluble in DMSO, ethanol, methanol, acetone.  $\lambda_{\text{d-d}}$  (DMSO) = 719 nm.

### 2.3. X-ray crystallography

Intensity data were collected for the single crystals of (1) and (2) at 296 K, on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). SAINT was used to refine the unit-cell and for data reduction [29]; program(s) used to solve structure: SHELXS-2014 [30] molecular graphics: ORTEP-3 for Windows and PLATON [31-32]. In the salicylic acid compound, there is disorder in the tetramethylethylenediamine with occupancy ratio of 0.718(4):0.282(4). All the heavy atoms are disordered. There are 18 restraints used to stabilize the refinement using DFIX and EADP. H atoms were positioned geometrically and refined by using a riding model, with C—H = 0.93 (aromatic), C—H = 0.96 (methyl) and C—H = 0.97 (methylene) and  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5U_{\text{eq}}(\text{C})$ . Further details are given in Table 1.

**Table 1:** Crystal data for complexes **1** and **2**

	<b>1</b>	<b>2</b>
Formula	C <sub>20</sub> H <sub>24</sub> Cl <sub>2</sub> CuN <sub>2</sub> O <sub>4</sub>	C <sub>20</sub> H <sub>28</sub> CuN <sub>2</sub> O <sub>7</sub>
Formula Weight(g mol <sup>-1</sup> )	490.85	471.98
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Radiation type	MoK $\alpha$	MoK $\alpha$
Crystal system	Monoclinic	Orthorhombic
Space Group	C 2/c	P b c a
<i>a</i> (Å)	26.070(3)	16.8070(7)
<i>b</i> (Å)	7.4943(7)	11.6652(6)
<i>c</i> (Å)	33.390(3)	22.8878(12)
$\alpha$ (deg)	90	90
$\beta$ (deg)	100.181(3)	90
$\gamma$ (deg)	90	90
V (Å <sup>3</sup> )	6421.1(11)	4487.3(4)
Z	12	8
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.523	1.397
<i>F</i> (000)	3036	1976
$\mu$ (mm <sup>-1</sup> )	1.299	1.015
Crystal size	0.44 × 0.20 × 0.18	0.38 × 0.30 × 0.28
Limiting indices; <i>h</i> , <i>k</i> , <i>l</i>	-33 ≤ <i>h</i> ≤ 33 -9 ≤ <i>k</i> ≤ 7 -42 ≤ <i>l</i> ≤ 42	-21 ≤ <i>h</i> ≤ 12 -14 ≤ <i>k</i> ≤ 14 -29 ≤ <i>l</i> ≤ 27
Reflections: collected.	26148	20729
Independent reflections	7017	4875
R <sub>int</sub>	0.0406	0.0305
$\theta_{\text{min}}$ , $\theta_{\text{max}}$ (°)	1.587, 27.0	2.153, 26.999
Data/restraints/parameters	7017/0/399	4875 / 18 / 342
<i>RI</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>	0.0500, 0.1105, 1.11	0.0378, 0.1910, 1.04
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.078, -0.505	0.293, -0.394

#### 2.4. Antimicrobial activity

The in-vitro antibacterial screening of copper(II) chloride dihydrate, the free ligands, and of synthesized complexes **1** and **2** against the bacterial was investigated by agar well diffusion method [33]. The strains utilized were *Bacillus spizizenii* (ATCC No: 6633<sup>TM</sup>), *Staphylococcus aureus* (ATCC No: 25923<sup>TM</sup>), *Klebsiella pneumonia* (ATCC No: 13882<sup>TM</sup>), and *Escherichia coli* (ATCC No: 8739<sup>TM</sup>). The procedure adopted was identical to that of already reported [28]. The glass wares were sterilized for 1 h at 170°C. The nutrient agar medium was prepared by the addition of nutrient agar (25 g in 1000 mL water (distilled) in a 1 dm<sup>3</sup> conical flask. The homogeneous mixture was boiled for half an hour, followed by cooling and adjusting pH to 7.00. The conical flasks containing

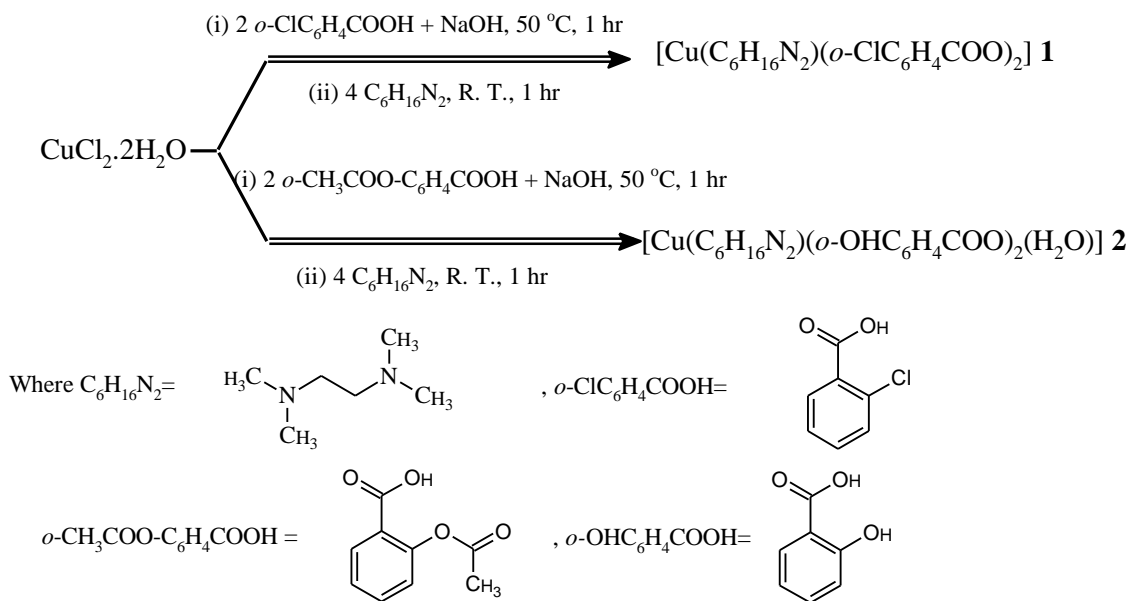
agar medium was plugged with cotton wool and was covered with aluminum foil and was sterilized in an auto-clave for 15 minutes at 121°C. The over-night culture was prepared as follows: The fresh sterile nutrient broths (Merck) were separately inoculated with bacterial strains, with the help of an inoculate wire loop from slant cultures of respective microbes (*Bacillus spizizenii*, *Escherichia coli*, *Klebsiella pneumonia* and *Staphylococcus aureus*). After incubation at 37°C for 18 hrs, the overnight culture was adjusted to  $10^6$  CFU (colony forming units). Then 100  $\mu$ L of the bacterial inoculums containing  $10^6$  CFU (colony forming units) were separately introduced into respective sterile petri dishes at 45 °C, immediately followed by the addition of 20 mL nutrient agar in each of the petridishes. The resulting mixture in the petridish was mixed well. These petridishes were then kept at 5 °C for 1h and were allowed to solidify. The wells were dug in the media with a metallic sterile borer of 8 mm diameter.

The solution of complexes **1**, **2**,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and of free ligands were prepared in three different concentrations (1000  $\mu\text{g/ml}$ , 500  $\mu\text{g/ml}$ , 250  $\mu\text{g/ml}$ ) by dissolving in pure DMSO. These solutions (90  $\mu\text{L}$  each), were separately introduced in to the wells. Cefixime, which is a standard antibacterial drug, was used as positive control. Its three different concentrations (1000  $\mu\text{g/ml}$ , 500  $\mu\text{g/ml}$ , 250  $\mu\text{g/ml}$ ) were used for comparison. A given amount of DMSO (90  $\mu\text{L}$ ) under the same conditions was also taken as a standard for all bacterial strains. Pure DMSO showed no antimicrobial activity and was used as a negative control. Petri dishes prepared in triplicates. Antimicrobial activity was evaluated by measuring the diameter of the inhibition zone around the well in mm. Since the assay was repeated thrice, results were recorded as mean  $\pm$  standard deviation ( $\pm\text{SD}$ ) (Table S1 of ESI).

### **3. Results and discussion**

The two complexes **1** and **2** have been prepared through the procedure illustrated in **scheme 1**





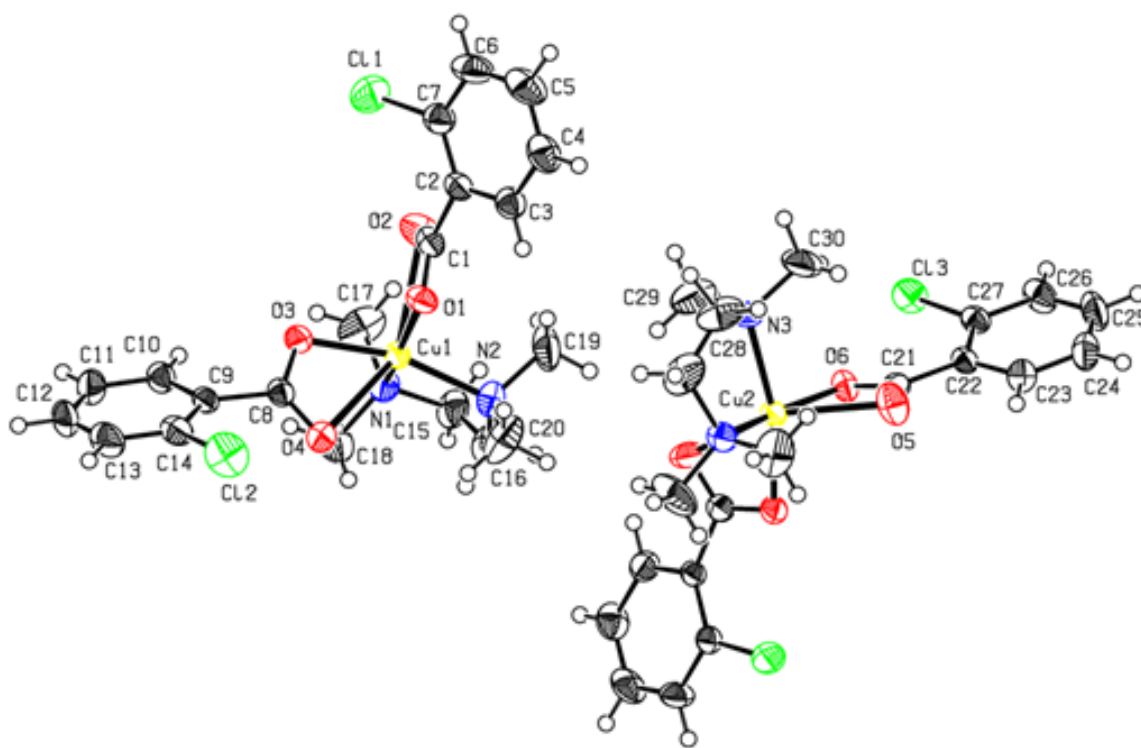
**Scheme 1.** Schematic sketch of synthetic procedure for complexes **1** and **2**

### 3.1. X-ray structure description of complexes **1** and **2**

The molecular structure of complex **1**, together with atomic labeling, is shown in figure 1. Selected bond lengths and angles are presented in table 2 and details regarding hydrogen bonds are shown in table 3. Single-crystal X-ray diffraction analysis shows that the complex (**1**) crystallizes in monoclinic,  $C2/c$  space group. The ternary complex **1** is neutral and consists of two discrete enantiomeric, monomeric entities, having essentially similar bond lengths and bond angles. Both monomeric units are centrosymmetric, with the copper(II) ion is six-coordinate and resides at the center of symmetry. Both 2-chlorobenzoate<sup>1-</sup> groups are mono-deprotonated.

As anticipated by the  $\Delta\nu$  value in FTIR spectral studies, the carboxylate moiety of 2-chlorobenzoate<sup>1-</sup> group is attached to Cu(II) ion through bidentate coordination mode. Each monomeric unit is coordinated to two 2-chlorobenzoate<sup>1-</sup> moieties, which behave as mono-deprotonated bidentate ligands and N,N,N',N'-tetramethylethylenediamine (tmen) which also acts as a bidentate (chelating) ligand. Hence, in each mononuclear entity, the central Cu(II) ion is coordinated by six donor atoms, forming a CuN<sub>2</sub>O<sub>4</sub> chromophore, in which two N atoms of tmen, and two O atoms, one from each 2-chlorobenzoate<sup>1-</sup> anions, coordinate to copper(II) to define the basal square plane, while the two axial carboxylato-O atoms, one from each Clba<sup>1-</sup> complete a distorted octahedron. The bond distances between copper(II) ion and the coordinated carboxylate

oxygen atoms (Cu–O), in the equatorial plane range from 1.975(2) to 1.993(2) with O atoms, closer to Cu(II) ion, than the tmen nitrogen atoms. The (Cu–N) distance ranges from 2.019(3) to 2.051(3). The axial Cu–O distances are elongated (Cu–O= 2.421(3)) owing to tetragonal distortion. The diamine ligand (tmen) coordinates with the Cu(II) ion to form a five-membered chelate ring in which tmen has usual gauche configuration, also the N–Cu–N bite angle and other bond angles and bond lengths are also similar to other such reported copper(II)-N-donor-carboxylate systems [34–37].



**Figure 1:** ORTEP diagram (50 % ellipsoid probability) of the molecular structure of **1**

The weak type of C–H...Cl hydrogen bonding interactions between electronegative Cl present in aromatic ring of carboxylates (CIBA<sup>1-</sup>) and hydrogens of tmen C15—H15B...Cl1 and C30—H30A...Cl3 can also be found operational in crystal structure of complex **1**

**Table 2:** Selected geometric parameters (Å, °) for **1** and **2**

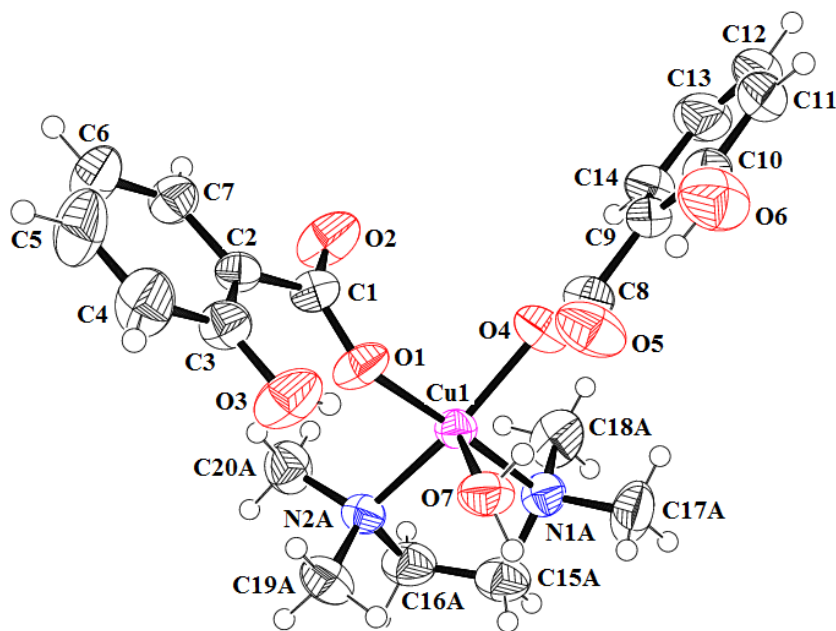
Bond Lengths(Å)			
Complex 1		Complex 2	
Cu(1)-O(3)	1.975(2)	Cu(1)-O(4)	1.9434(16)
Cu(1)-O(1)	1.979(2)	Cu(1)-O(1)	1.9547(16)
Cu(1)-O(2)	2.478(3)	Cu(1)-N(1A)	2.017(7)
Cu(1)-O(4)	2.506(2)	Cu(1)-N(2A)	2.034(13)
Cu(1)-N(2)	2.019(3)	Cu(1)-N(2B)	2.12(4)
Cu(1)-N(1)	2.034(3)	Cu(1)-N(1B)	2.13(2)
Cu(2)-O(6)	1.993(2)	Cu(1)-O(7)	2.3167(19)
Cu(2)-O(6) <sup>i</sup>	1.993(2)		
Cu(2)-O(5)	2.421(3)		
Cu(2)-O(5) <sup>i</sup>	2.421(3)		
Cu(2)-N(3)	2.051(3)		
Cu(2)-N(3) <sup>i</sup>	2.051(3)		
Bond Angles (°)			
Complex 1		Complex 2	
O(3)-Cu(1)-O(1)	92.93(10)	O(4)-Cu(1)-O(1)	93.85(8)
O(3)-Cu(1)-N(2)	163.91(11)	O(4)-Cu(1)-N(1A)	89.13(18)
O(1)-Cu(1)-N(2)	93.06(11)	O(1)-Cu(1)-N(1A)	176.91(17)
O(3)-Cu(1)-N(1)	92.39(11)	O(4)-Cu(1)-N(2A)	161.5(2)
O(1)-Cu(1)-N(1)	161.55(11)	O(1)-Cu(1)-N(2A)	90.4(2)
N(2)-Cu(1)-N(1)	86.58(12)	N(1A)-Cu(1)-N(2A)	86.5(3)
O(3)-Cu(1)-O(2)	91.95(9)	O(4)-Cu(1)-N(2B)	168.9(7)
O(1)-Cu(1)-O(2)	57.79(9)	O(1)-Cu(1)-N(2B)	90.8(5)
N(2)-Cu(1)-O(2)	103.87(11)	O(4)-Cu(1)-N(1B)	90.9(5)
N(1)-Cu(1)-O(2)	104.39(10)	O(1)-Cu(1)-N(1B)	167.4(4)
O(3)-Cu(1)-O(4)	57.45(8)	N(2B)-Cu(1)-N(1B)	82.6(7)
O(1)-Cu(1)-O(4)	95.85(9)	O(4)-Cu(1)-O(7)	96.88(7)
N(2)-Cu(1)-O(4)	107.05(10)	O(1)-Cu(1)-O(7)	79.63(7)
N(1)-Cu(1)-O(4)	101.90(10)	N(1A)-Cu(1)-O(7)	100.86(14)
O(2)-Cu(1)-O(4)	140.20(9)	N(2A)-Cu(1)-O(7)	101.6(2)
		N(2B)-Cu(1)-O(7)	93.9(7)
		N(1B)-Cu(1)-O(7)	111.4(5)

**Table 3:** Bond separations (Å) and bond angles (°) in the complex (**1**)

Donor-H ..... Acceptor	D-H (Å)	H...A (Å)	D-H...A (Å)	D-H...A (°)
C15—H15B...C11	0.97	2.98	3.900(4)	159.7
C30—H30A...C13	0.96	2.99	3.894(4)	158.2

Symmetry transformations used to generate equivalent atoms in **1**: #1 -x,y,-z+1/2 #2 x,y-1,z #3 x,y+1,z

A perspective view together with the atom labeling scheme for  $[\text{Cu}(\text{tmen})(\text{salH})_2(\text{H}_2\text{O})]$  (**2**) is given in figure 3 and its unit cell with hydrogen bonding details is given in figure 4. Selected bond parameters are given in table 2, and hydrogen bonding parameters are presented table 3. The neutral complex is monomeric in which  $\text{CuN}_2\text{O}_3$  chromophore has a distorted square pyramidal geometry (Fig. 3). The central copper(II) ion is five-coordinated by two N-atoms of chelating N,N,N',N'-tetramethylethylenediamine (tmen), and two O-atoms of carboxylate groups of two monodentate salicylate ions, forming a basal square plane and by an apical O atom of water, forming a distorted square pyramidal structure. N,N,N',N'-tetramethylethylenediamine ligand adopts its usual gauche conformation [37].



**Figure 2:** Complex **2**: The thermal ellipsoids are drawn at 50 % probability level. The H-atoms are shown as small circles of arbitrary radii. The minor part of disordered group is not shown for clarity

In the complex **2**, the Cu1–O7 bond length of 2.317(2) for apical copper–aqua–O bond, is relatively longer. Tau ( $\tau$ ) is an important parameter to decide whether the 5-coordinate polyhedron

is square pyramidal or trigonal bipyramidal ( $\tau = (\beta - \alpha)/60$ ), its value of  $\tau = 0.13$  for complex **2** proves its square pyramidal geometry. The *o*-hydroxybenzoate<sup>1-</sup> groups are different geometrically as well as in hydrogen bonding. In the first *o*-hydroxybenzoate<sup>1-</sup> (Hsal<sup>1-</sup>), the carboxylate A (C1/O1/O2) and the phenol moiety B (C2-C7/O3) (r. m. s. deviation 0.0071 Å) are oriented at a dihedral angle of 10.4 (4)°. The second *o*-hydroxybenzoate<sup>1-</sup> is almost planar and has r. m. s. deviation of only 0.0159 Å.

The [Cu(tmen)(salH)<sub>2</sub>(H<sub>2</sub>O)] (complex **2**) when compared with its anhydrous form [Cu(tmen)(salH)<sub>2</sub>] [37], was found to be very much different. In contrast to our reported square pyramidal complex **2**, the coordination geometry around copper(II) in [Cu(tmen)(salH)<sub>2</sub>] complex is octahedral. The coordination mode of carboxylate moiety in complex **2** is monodentate, while for [Cu(tmen)(salH)<sub>2</sub>], the coordination mode is bidentate. The equatorial bond lengths for [Cu(tmen)(salH)<sub>2</sub>], are Cu-O(1) = 1.975 (8) Å, Cu-O(5) = 2.001 (8) Å and for **2** are (Cu(1)-O(1) = 1.9547(16) Cu(1)-O(4) = 1.9434(16)), respectively. Since the complex [Cu(tmen)(salH)<sub>2</sub>] is octahedral, like other Cu(II) octahedral complexes, it exhibits Jahn-Teller effect and hence two axial Cu-O carboxylato-Cu(II) bonds are elongated (Cu-O(4) = 2.520 (8) Å, Cu-O(2) = 2.596 (9) Å). Though complex **2** has a water molecule at apical position, the CuO bond is also elongated Cu(1)-O(7) = 2.3167(19), thus exhibiting tetragonal distortion. The Cu-N bond lengths for bidentate tmen in [Cu(tmen)(salH)<sub>2</sub>] (Cu-N(2) = 2.020 (9), Cu-N(1) = 2.040 (10) Å), and Cu(1)-N(1A) 2.017(7) and Cu(1)-N(2A) = 2.034(13) Å for **2** are comparable. The bite angles (N(I)-Cu-N(2)) 86.9 (4)° for [37] and N(1A)-Cu(1)-N(2A) = 86.5(3) for **2** are also similar in both complexes.

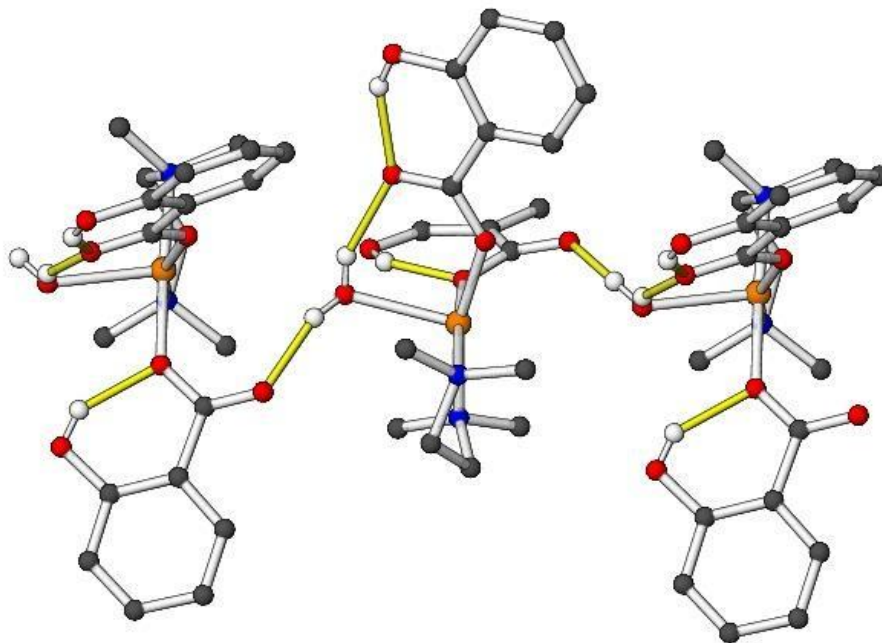
**Table 4:** Bond separations (Å) and bond angles (°) in the complex (**2**)

Donor-H ..... Acceptor	D-H (Å)	H...A (Å)	D-H...A (Å)	D-H...A (°)
O3-H3.....O1	0.79(4)	1.84(4)	2.542(2)	147(4)
O3-H3.....O7	0.79(4)	2.62(4)	3.260(3)	139(3)
O6-H6A...O5	0.81(4)	1.84(4)	2.549(3)	146(4)
O7-H7A...O2	0.86(4)	1.84(3)	2.660(3)	158(3)
O7-H7B...O5	0.80(3)	1.99(3)	2.728(3)	152(3)

Another square pyramidal polymeric complex {[Cu(l-pzdc)(tmen)] H<sub>2</sub>O}<sub>n</sub> (l-pzdc = pyrazine-2,3-dicarboxylate) also has bidentately coordinating tmen with similar bond lengths N3-Cu1 = 2.046 (4) Å, N4-Cu1 = 2.255 (5) Å and similar bite angle (N3-Cu1-N4 = 84.6 (2)°). The bond lengths

(O1–Cu1= 1.976 (3) Å, O3–Cu1= 1.969 (3) Å) for monodentately coordinating 1-pzdc<sup>2-</sup> carboxylate groups are similar to that of complex **2** [38]

The square planar complex [Cu(BZDH)<sub>2</sub>(salH)<sub>2</sub>] (BZDH= benzimidazole) [39], has also similar Cu-O bond lengths for Hsal<sup>1-</sup> carboxylate oxygen atoms (Cu(1)–O(1)= 1.9601(9) Å, Cu(1)–O(4)= 2.0115(9) Å)

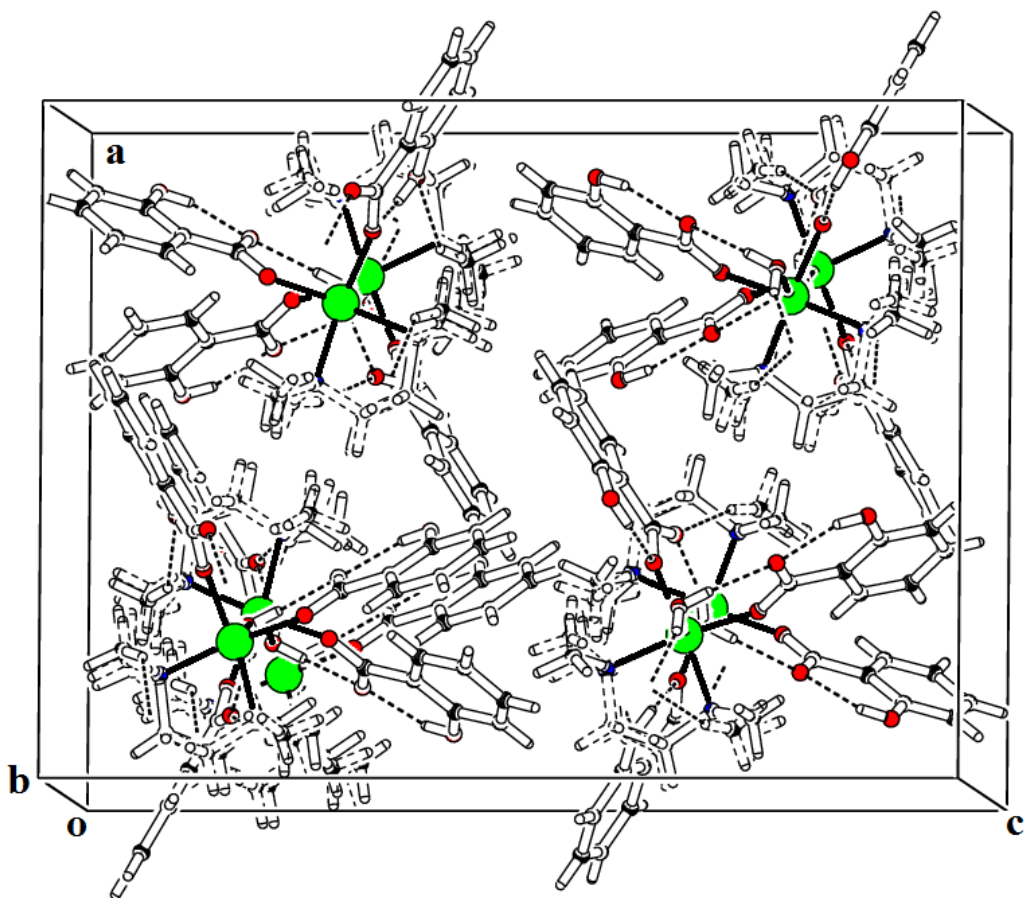


**Fig. 3:** Fragment of the chain formed by complex **2**. Hydrogen atoms of the ligands, not involved in hydrogen bonding are omitted for clarity.

Both intramolecular and intermolecular hydrogen bonding interactions of the type O–H...O and C–H...O are operational among N,N,N',N'-tetramethylethylenediamine, apical water molecule and *o*-hydroxybenzoate<sup>1-</sup> (Hsal<sup>1-</sup>) moieties. For example, in one Hsal<sup>1-</sup> group the un-coordinated carboxylate-O atom forms two intramolecular O–H...O bonds; one with the H atom of the apical water molecule, and second with the H atom of its own hydroxyl group. The second *o*-hydroxybenzoate<sup>1-</sup> moiety shows different H-bonding pattern. Its uncoordinated carboxylate-O atom forms an intermolecular H-bond with the aqua-H atom of neighboring monomer, while its coordinated carboxylate-O atom forms two O–H...O hydrogen bonds and one C–H...O bond; one with the H atom of its own hydroxyl group, and second one with the H-aqua atom nearby

monomeric unit, and third one (C-H...O), with methyl-H atom of tmen, belonging to another monomeric unit thus forming infinite 1D-chains with the base vector [010].

H atoms were positioned geometrically and refined by using a riding model, with C—H = 0.93 (aromatic), C—H = 0.96 (methyl) and C—H = 0.97 (methylene) and  $U_{iso}(H) = 1.2$  or  $1.5U_{eq}(C)$ . In each *o*-hydroxybenzoate<sup>1-</sup>, there is a S(6) loop due to O-H...O bonding (Fig. 4). The bond lengths and the bond angles are similar to those reported in literature [40-42].



**Figure 4:** Packing diagram of **2** with hydrogen bonding interactions

### 3.2. FTIR Spectroscopic Studies

The selected FT-IR frequencies of the free ligands and their copper(II) complexes, **1** and **2** are given in Table and their FTIR spectra are presented in figures S1 and S2 of ESI. In the complexes **1** and **2**, the aromatic  $\nu(\text{C-H})$  stretching vibrations range from  $3088\text{-}3025\text{ cm}^{-1}$ . The stretching

absorptions due to  $\nu_{as}(C-H)$  of  $-CH_3$  and  $\nu_{as}(C-H)$  and  $\nu_s(C-H)$  stretches of  $-CH_2$  groups appear at  $2983\text{ cm}^{-1}$ ,  $2921\text{ cm}^{-1}$ , and  $2848\text{ cm}^{-1}$  for complex **1**, and at  $2985\text{ cm}^{-1}$ ,  $2919\text{ cm}^{-1}$ , and  $2850\text{ cm}^{-1}$ , for complex **2**, respectively. The  $\delta(C-H)$  bending absorption of  $-CH_2$  groups appear at  $1466\text{ cm}^{-1}$  and at  $1470\text{ cm}^{-1}$  for complexes **1** and **2** respectively. All these peaks show a shift from equivalent values of  $2970\text{ cm}^{-1}$ ,  $2943\text{ cm}^{-1}$ ,  $2860\text{ cm}^{-1}$  and  $1467\text{ cm}^{-1}$  for free tmen [28], respectively. The  $\nu(C-N)$  absorption occur at  $1122\text{ cm}^{-1}$  in both **1** and **2**. IR spectroscopy is indicative of the binding modes of carboxylate moiety. Absence of a strong absorption band at  $1698\text{ cm}^{-1}$  for **1** and at  $1660\text{ cm}^{-1}$  for **2**, due to  $\nu(C=O)$  stretch of its  $CO_2H$  group, along with appearance of new  $\nu_{as}(OCO)$  and  $\nu_s(OCO)$  frequencies, due to asymmetric and symmetric vibrations of coordinated carboxylate groups and especially their difference ( $\Delta\nu$ ) suggests that the coordination mode for **1** is bidentate ( $\Delta\nu = 115\text{ cm}^{-1}$ ), while for **2**, it is monodentate ( $\Delta\nu = 201\text{ cm}^{-1}$ ). Some characteristic bands for **2** include: the absorption band at  $3456\text{ cm}^{-1}$  due to  $\nu(O-H)$  showing presence of coordinated/lattice water molecule [43], and at  $1245\text{ cm}^{-1}$  due to  $[\nu(Ph-O)]$  stretching vibrations, while for **1**, the  $\nu(C-Cl)$  stretching vibration appears at  $762\text{ cm}^{-1}$ . The low energy peaks, in the region  $546\text{ cm}^{-1}$  -  $428\text{ cm}^{-1}$  can be assigned to  $\nu(Cu-O)$ , and  $\nu(Cu-N)$  stretching modes. The values are also similar to other such copper(II)-carboxylate complexes [45-49]. This is further confirmed by single crystal analysis results.

**Table 5:** Selected IR frequencies ( $\text{cm}^{-1}$ ) of free N,N,N',N'-tetramethylethylenediamine (tmen), carboxylic acids, complexes **1** and **2**

Complex <b>1</b> ( $\text{cm}^{-1}$ )	Complex <b>2</b> ( $\text{cm}^{-1}$ )	tmen ( $\text{cm}^{-1}$ )	<i>o</i> -chlorobenzoic acid ( $\text{cm}^{-1}$ ) [45-47]	Salicylic acid ( $\text{cm}^{-1}$ )	FTIR Assignments
	3456				$\nu(O-H)$ , $H_2O$
	3270			3233	$\nu(PhO-H)$
			3100-2900	3365-2850	$\nu(OCO-H)$
3075	3044		3088		$\nu(C-H)_{ar}$
2983	2985	2970			$\nu_{as}(C-H)$ , $CH_3$
2921	2919	2943			$\nu_{as}(C-H)$ , $CH_2$
2848	2850	2860			$\nu_s(C-H)$ , $CH_2$
			1698	1653	$\nu(OC=O)$
1602	1646		1593		$\nu(C=C)$
1550	1584				$\nu_{as}(OCO)$
1466	1470	1467			$\nu(C-H)_{bend}$ , $CH_2$
1435	1383				$\nu_s(OCO)$



115	201				$\Delta\nu$
			1327	1235	$\nu(\text{OC-O})$
	1297			1296	$\delta(\text{PhO-H})\text{bend}$
1122	1122	1138			$\nu(\text{C-N})$
1021	1018		1050	1030	$\delta(\text{CCC})$
953	953		921		$\gamma(\text{C-H})\text{def, oop}$
706, 723	707		704	699	$\gamma(\text{CCC})$
762			710-505		$\nu(\text{C-Cl})$
546	508				$\nu(\text{Cu-O})$
428	446				$\nu(\text{Cu-N})$

### 3.3. Uv-Vis Spectroscopy

Uv-Visible spectra of complexes **1** (Fig. S3), and **2** (Fig. S4) are recorded in DMSO solution. In the Uv-Visible spectra of complexes, three absorption bands are observed. The absorption band at 273 nm, and at 275 nm for **1** and **2**, respectively, is assigned to  $\pi \rightarrow \pi^*$  transitions. For **1** and **2**, an intraligand band at 310 nm, and 309 nm, respectively, is attributable to  $n \rightarrow \pi^*$  or LMCT transitions in these complexes. The appearance of a broad band in the complexes **1**, **2** at 653 nm, and 719 nm, is related to  $d \rightarrow d$  electronic transitions originating at Cu(II) ion. The spectra resemble those reported for similar copper(II) complexes with 5-coordinate [50] and six coordinate [51] complexes' chromophores [52].

### 3.4. Thermal studies of complexes 1 and 2

The thermogram of  $[\text{Cu}(\text{tmen})(\text{ClBA})_2]$  (**1**) (Fig. S5) shows that the complex is thermally stable up to 175°C, indicated by the horizontal plateau. TG curve shows that the thermal decomposition of complex (**1**) is a two stage process. The first stage of decomposition is seen starting at 175 °C and progressing till 367 °C. The weight loss during this stage amounts to 60.90%, indicating the loss of two moles of *o*-chlorobenzoate ligands (calculated value: 60.12%). The second stage of decomposition starts immediately at 367 °C and ends at 925 °C. During this stage, the loss of 1 mole of N,N,N',N'-tetramethylethylenediamine takes place. The calculated weight loss (23.68%) agrees with the observed value (23.80%). The final product is CuO having observed residual weight of 15.30% (calc. = 16.20%).

The complex **2** is found to be thermally stable up to 195 °C (Fig. S6). The complex undergoes a three stage thermal decomposition. The first stage of decomposition starts with the

elimination of one coordinated water molecule. The removal of water starts at 88 °C and progresses till 127 °C. The weight loss during this stage amounts to 3.86% which is in good agreement with the calculated value of 3.83%. In the second stage of decomposition (127-227 °C) the weight loss amounts to 56.05%, which is in agreement with the theoretical value of 55.57% for the loss of two molecules of  $\text{salH}^{1-}$  ligands. In the third stage of decomposition (227-642 °C) the weight loss of 23.75% could be attributed to the decomposition of tmen which is in agreement with the calculated value (23.75%). The end product is CuO which is 16.34% and agrees well with the theoretical value of 16.85%.

### **3.5. Antimicrobial Studies**

Antimicrobial studies of complexes **1** and **2** (Table S1 of ESI) manifest, that complex **2** is more biologically active than complex **1**. The complex **2** was found to be the most effective against *Bacillus spizizenii*, and has shown antimicrobial activity to a lesser extent against the remaining strains. For complex **1**, a low activity was observed for *Bacillus spizizenii*, and *Staphylococcus aureus*, while other strains showed no zone of inhibition. The synthesized complexes exhibited enhanced antibacterial activities as compared to the activities of their free ligands, which may be correlated to their structural symmetry or structural features as explained by Tweedy's chelation theory and Searl's concept. An increased electron delocalization within the metal complex, that occurs due to electron donation by ligands, often reduces the positive charge of the metal ion. This may cause an increase in the hydrophobic and lipophilic character of the metal complex. Which inturn facilitates the complex to penetrate the lipid layer of the microbes and thereby killing them more efficiently. Cu(II)-complexes of the ligands containing electron withdrawing groups, especially those with N and O atoms, on the aromatic ring systems can retard enzymatic activities of bacteria [53-56]. A comparison of biological activity of complexes **1** and **2** incorporating an aliphatic diamine (tmen) with no restricted rotation of C-C bonds with the similar copper(II)-diimine-carboxylate complexes reveals that **1** and **2** are lesser active [28].

## **5. Supplementary material**

CCDC 1561305 and 1561304 contain the supplementary crystallographic data for **1** and **2**. 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 CB21EZ, UK; fax

## **Conclusion**

The reaction of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  with tmen ( $\text{C}_6\text{H}_{16}\text{N}_2$ ), and 2-chlorobenzoic acid/ acetylsalicylic acid in mole ratios of 1:1:2, in the presence of NaOH, resulted in the formation of two monomeric ternary copper(II) coordination complexes,  $[\text{Cu}(\text{tmen})(\text{CIBA})_2]$  (**1**) and  $[\text{Cu}(\text{tmen})(\text{Hsal})_2 \cdot \text{H}_2\text{O}]$  (**2**). The former (**1**), had two monomeric units in the same crystal. Its octahedral geometry resulted from coordination of copper(II) ion with four carboxylate-O atoms coming from two 2-chlorobenzoate<sup>1-</sup> moieties and two N atoms coming from tmen. In a way, the octahedral complex  $[\text{Cu}(\text{tmen})(\text{salH})_2]$  [37] resembles complex **1** more, since in both complexes the coordination behavior of carboxylate moiety is the same. Tmen being bidentately coordinating occupies equatorial position. The carboxylate-O atoms of 2-chlorobenzoate<sup>1-</sup> groups choose to occupy one of the equatorial sites and one of the axial sites. In this way, each carboxylate group forms a shorter equatorial bond and a longer axial Cu-O bond, owing to Jahn-Teller distortion.

The second complex **2**, is square pyramidal and is defined by the coordination of Cu(II) with two N atoms from tmen, two carboxylate-O atoms from a chelating salicylate<sup>1-</sup> group and one apical aqua-O atom. The Cu-O bond length for axial water molecule is longer than other equatorial carboxylate Cu-O bond lengths. In an attempt to get copper(II)-acetylsalicylate adduct with tmen, a mononuclear complex with coordinated salicylate ( $\text{Hsal}^{1-}$ ) has been obtained. The first indication of hydrolysis of acetoxybenzoate<sup>1-</sup> group into salicylate<sup>1-</sup> group came from the absence of stretching vibration of acetoxy-carbonyl group, which usually appears at nearly 1750  $\text{cm}^{-1}$  in FTIR spectrum [16], which is confirmed by single crystal structure of complex **2**. FTIR analysis has shown that the differences between asymmetric  $\nu_{\text{as}}(\text{OCO})$  and symmetric  $\nu_{\text{s}}(\text{OCO})$  stretching vibrations ( $\Delta\nu$ ) in complexes **1** and **2** was 115  $\text{cm}^{-1}$  and 201  $\text{cm}^{-1}$ , these values suggest chelating (bidentate) and monodentate coordination mode of the carboxylate moieties in the respective complexes. Thermal studies and antibacterial studies against various strains have also been investigated. The results of the preliminary antimicrobial screening against four pathogenic bacteria indicate that the complex **2** is more active than those of complex **1** and of corresponding ligands.

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