

**Coordination complexes of copper(II) with herbicide-trichlorophenoxyacetate: Syntheses, characterization, single crystal X-ray structure and packing analyses of monomeric  $[\text{Cu}(\gamma\text{-pic})_3(2,4,5\text{-trichlorophenoxyacetate})]\cdot\text{H}_2\text{O}$ ,  $[\text{trans-Cu}(\text{en})_2(2,4,5\text{-trichlorophenoxyacetate})_2]\cdot 2\text{H}_2\text{O}$  and dimeric  $[\text{Cu}_2(\text{H}_2\text{tea})_2(2,4,5\text{-trichlorophenoxyacetate})_2]\cdot 2(\text{H}_2\text{O})$**

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**Abstract**

Three novel coordination complexes of copper(II) with 2,4,5-trichlorophenoxyacetate  $[\text{Cu}(\gamma\text{-pic})_3(\text{L})_2]\cdot\text{H}_2\text{O}$  **1**,  $[\text{trans-Cu}(\text{en})_2(\text{L})_2]\cdot 2\text{H}_2\text{O}$  **2** and  $[\text{Cu}_2(\text{H}_2\text{tea})_2(\text{L})_2]\cdot 2\text{H}_2\text{O}$  **3**, where L = 2,4,5-trichlorophenoxyacetate,  $\gamma\text{-pic}$  =  $\gamma$ -picoline, *en* = ethylenediamine, *H<sub>2</sub>tea* = monodeprotonated triethanolamine, were synthesized by addition of  $\gamma$ -picoline/ethylenediamine/triethanolamine respectively, to the hydrated  $\text{Cu}(2,4,5\text{-trichlorophenoxyacetate})_2$  suspended in methanol-water (4:1, v/v). The newly synthesized complexes have been characterized by elemental analyses, spectroscopic techniques (UV-Vis and FT-IR), magnetic moment determination, molar conductance studies, TGA and single crystal X-ray diffraction method. The structure determination revealed neutral nature of complexes in all the three cases, with different coordination geometry around the copper(II) metal centre depending on the nature of the N- or N,O-donor ligands. Hydrogen bonding network i.e. O-H $\cdots$ O and C-H $\cdots$ O in complexes **1**, **3** and N-H $\cdots$ O, and O-H $\cdots$ O in complex **2** stabilizes crystal lattice in copper(II) complexes besides other non-covalent interactions.

**Keywords:** Copper(II) complex, 2,4,5-trichlorophenoxyacetate,  $\gamma$ -picoline, ethylenediamine, triethanolamine, X-ray crystallography.

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## 1. Introduction:

In the realm of crystal engineering, coordination framework solids containing inorganic metal ion and organic ligands have mushroomed as a new area of interest. These coordination complexes stems from the unusual structures and properties due to inclusion of both organic and inorganic components. Structural integration of such components into new novel materials affects the magnetic [1,2], optical [3,4], catalytic [5], electronic and spintronic properties [6]. An interesting feature of such compounds is optical, electrical and environmental durability of inorganic materials and mechanical flexibility as well as tunability of  $\pi$ -electron of organic components. A powerful strategy for constructing such materials aggregates is directed self-assembly of designed organic ligands and inorganic skeletons. In the self-assembly process, supramolecular interactions establish the likely connections between organic and/or inorganic molecular building blocks by exploiting non-covalent interactions [7-8]. Usually, a challenge lies in the synthesis of low molecular weight coordination complexes in which choice of appropriate metal ion, ligands, stoichiometric ratio of reactants and reaction conditions play vital role.

As far as the thrust on inorganic metal centre in coordination complexes is concerned, (especially the genesis, stability and long term survival of coordination modes) copper(II) complexes come to forefront as copper in +2 oxidation state exhibits considerable variation in coordination number and is an essential trace element pivotal for sustenance of aerobic life [9-12]. Copper(II) complexes have been known for their wide range of applications in biological processes, catalytic chemical bond activation, molecular magnets, pharmaceutical industry etc. [13-20]. Metal carboxylates constitute one such class of coordination complexes which have been extensively investigated [21] owing to: i) variety of coordination modes of carboxylate ligand such as monodentate, bidentate chelating and bidentate bridging etc; ii) natural occurrence of biologically important carboxylic acids e.g. ferulic acid and mafenamic acid and iii) their use as drugs in relieving pain and inflammation e.g. ibuprofen and aspirin. As a part of our extensive research programme to investigate copper(II) carboxylate

complexes [22-25], in this work, the complexation behaviour of copper(II) with commercially important herbicide, 2,4,5-trichlorophenoxyacetic acid as organic ligand in the presence of N- or N, O- donor ligands of variable denticity have been explored by single crystal X-ray structure determination. The structural diversity encountered in these complexes is due to versatility in coordination modes/ligation behaviour of this carboxylate (monodentate, symmetric/unsymmetric chelating, bidentate/monodentate bridging) towards copper(II) ion as shown in Fig. 1. [26-28] and different coordination environment provided by N- or N, O- donor ligands. In addition, phenoxyalkonic acids are used in the synthesis of a family of ester derivatives, fermentation of Penicillin V, synthesis of insect repellents, esters of cortical hormones and cation exchange resins whereas 2,4,5-trichlorophenoxyacetic acid is known to be commercial herbicide[29]. Complexation of these ligands with copper(II) resulted in copper(II) carboxylates which have been shown to possess more potency as drugs than their parent acids. The pharmacological activities of copper(II) complexes such as [superoxide-dismutase](#) and cytogenetic effects are enhanced in the presence of ancillary nitrogen donor ligands [30-33].

A combined stereo-electronic effect that emerges as a result of both participating organic ligands *i.e.*, the arylcarboxylate anion and ancillary N- or N, O- donor ligand would dictate the final nature and structure of the desired coordination complex formed. That is, in a nutshell, the chosen arylcarboxylate ligand may show propensity to exhibit different coordination modes depending upon the type of N-donor ligand chosen. Indeed, this can turn out to be a useful strategy for construction of various other copper(II) complexes.

This prompted us to choose three nitrogen-donor ligands namely  $\gamma$ -pic (4-methyl pyridine), *en* (ethylenediamine) and  $H_3tea$  (triethanolamine) having different molecular conformations (rigid to flexible) and propensity (monodentate, bidentate and polydentate) (Fig. 2). The ligand  $H_3tea$  after deprotonation (*i.e.*  $H_2tea$ ) will be endowed with two –OH groups which may take part in the hydrogen bonding as effective proton donors. The presence of three completely different nitrogen donor ligands

can form diverse coordination networks, copper(II) complexes generating a completely different crystal lattice packing.

In continuation of our current interest in copper(II) complexes, herein we report, the syntheses, spectroscopic characterization (UV-Vis, FT-IR) and single crystal X-ray structure determination of three such coordination complexes;  $[\text{Cu}(\gamma\text{-pic})_3(\text{L})_2]\cdot\text{H}_2\text{O}$  **1**,  $[\text{trans-Cu}(\text{en})_2(\text{L})_2]\cdot 2\text{H}_2\text{O}$  **2** and  $[\text{Cu}_2(\text{H}_2\text{Tea})_2(\text{L})_2]\cdot 2\text{H}_2\text{O}$  **3** where, L = 2,4,5-trichlorophenoxyacetate.

## 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 [34]. FT-IR spectra were recorded as KBr pellets on PERKIN ELMER SPECTRUM RXFT-IR system. 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. Thermogravimetric analyses were performed using Mettler Toledo TGA/SDTA 851<sup>e</sup> in air.

### 2.3 Crystal structure determination

X-ray diffraction data of the title compounds were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). Data sets were integrated using the DENZO-SMN package and corrected for Lorentz, polarization and absorption [35] effects. The structures were solved by direct methods [36] and refined on  $F^2$  by full-matrix least-squares methods using the SHELX-97 program [37]. All non-H atoms were refined anisotropically, apart from the C4 atom of the methyl group in complex **1**, lying on special position (0,y,0.25). In complex **1**, the size and shape of the ADP ellipsoids of the atoms belonging to the C13-C18 ring are indicative of a libration around the C13 position. In complex **2**, the C2 atom is disordered

over two non equivalent positions (occupancy factor: 0.7, 0.3). In all structures, hydrogens linked to C and N atoms were included on calculated positions, riding on their carrier atoms. Conversely, hydrogen atoms belonging to water molecules or to OH groups were found in the Difference Fourier map; their coordinates were refined with distance constraints, while their thermal parameters were fixed at a value of some 1.2 times the  $U_{eq}$  of the corresponding carrier atoms. All other calculations were accomplished using WINGX [38]. The packing diagrams of complexes **1-3** have been made using DIAMOND 3.0 software package [39]. Crystal data are given in Table 1 and a selection of bond distances and angles is reported in Table 2. ORTEPIII [39] views of the structures are shown in Figs. 3 a-c.

## 2.4. Synthesis:

**2.4.1. Synthesis of copper(II) 2,4,5-trichlorophenoxyacetate:** 0.97 g (0.0039 mol) of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was dissolved in minimum quantity of distilled water in a beaker. In another beaker 0.313 g (0.0078 mol) of sodium hydroxide was dissolved in 20 mL distilled water and 2.0 g (0.0078 mol) of 2,4,5-trichlorophenoxy acetic acid suspended in hot water was added to it with stirring. A light blue product was precipitated in a good yield immediately on mixing the two solutions. It was filtered through a fine filter paper, washed with water and dried in an oven at 50 °C.

**2.4.2 Synthesis of  $[\text{Cu}(\gamma\text{-pic})_3(\text{L})_2] \cdot \text{H}_2\text{O}$ , **1**:**  $\gamma$ -picoline was added drop-wise to the suspension of above blue coloured product  $\text{Cu}(\text{2,4,5-trichlorophenoxyacetate})_2 \cdot x\text{H}_2\text{O}$  (0.5 g) in 25 mL of water-methanol (1:4, v/v) mixture until a clear deep blue solution was obtained. The solution was allowed to evaporate at room temperature which afforded blue coloured crystals (fine needles) of complex **1** after five days. The newly synthesized complex was soluble in tetrahydrofuran and dimethylformamide but insoluble in methanol, water, and acetone. The complex **1** melted at 110 °C. Anal. Calcd. for  $[\text{Cu}(\text{Cl}_3\text{C}_8\text{H}_4\text{O}_3)_2(\text{C}_6\text{H}_7\text{N})_3](\text{H}_2\text{O})$ : Cu 7.30, C 46.92, H 3.56, N 4.83%; Found: Cu 7.03, C 46.32, H 3.29, N 4.43%. FT-IR (KBr pellet, in  $\text{cm}^{-1}$ ), 3490(mb) , 3077(w), 2968(w), 2483(w), 2364(w), 1641(s), 1613(ms), 1583(w), 1476(m), 1414(ms), 1393(ms), 1370(w), 1326(ms), 1282(ms), 1250(ms), 1209(m), 1136(m), 1081(ms), 1046(m), 1011(w), 908(mw), 866(m), 833(mw) 810(ms),

731(m), 678(m), 605(m), 550(w), 531(w) 497(m), 454(w); UV-Vis (methanol-water):  $\lambda_{\max} = 685$  nm ( $\epsilon_{\max} = 194$  L.mol<sup>-1</sup>cm<sup>-1</sup>).

**2.4.3. Synthesis of [Cu(en)<sub>2</sub>(L)<sub>2</sub>].2(H<sub>2</sub>O)<sub>2</sub>, 2:** Ethylenediamine was added drop-wise to the suspension of 0.5 g of blue coloured Cu(2,4,5 trichlorophenoxyacetate)<sub>2</sub>.xH<sub>2</sub>O in 25 mL of water-methanol (1:4,v/v) mixture till a clear purple solution was obtained. The solution was allowed to evaporate slowly at room temperature which gave purple coloured block shaped crystals after one day. The newly synthesized complex is freely soluble in water, methanol and ethanol but insoluble in acetone and chloroform. The complex **2** decomposed at 185 °C. Anal. Calcd. for [Cu(C<sub>2</sub>N<sub>2</sub>H<sub>8</sub>)<sub>2</sub>(Cl<sub>3</sub>C<sub>8</sub>H<sub>4</sub>O<sub>3</sub>)<sub>2</sub>].2H<sub>2</sub>O: Cu 8.70, C 32.97, H 3.84, N 7.69 %; Found: Cu 8.34, C 32.12, H 3.54, N 7.61%. FT-IR (KBr pellet, in cm<sup>-1</sup>), 3364(mw), 3304(m), 3215(m), 3134(mw), 2941(w), 2885(w), 2362(w), 1607(s), 1582(w), 1482(ms), 1426(ms), 1341(ms), 1281(m), 1242(m), 1164(vw), 1140(m), 1078(s), 1044(s), 975(w), 944(w), 872(m), 831(mw), 776(m), 701(mw), 683(mw), 633(mw), 525(m), 460(w); UV-Vis (methanol-water):  $\lambda_{\max} = 547$  nm ( $\epsilon_{\max} = 68$  L.mol<sup>-1</sup>cm<sup>-1</sup>).

**2.4.4 Synthesis of [Cu<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>tea)<sub>2</sub>].2H<sub>2</sub>O, 3:** Triethanolamine was added drop-wise to the suspension of 0.5 g of blue coloured Cu(2,4,5-trichlorophenoxyacetate)<sub>2</sub>.xH<sub>2</sub>O in 25 mL of water-methanol (1:4,v/v) mixture till a clear turquoise blue solution was obtained. The solution was allowed to slowly evaporate at room temperature which gave green coloured block shaped crystals after five days. The newly synthesized complex was soluble in methanol, tetrahydrofuran but insoluble in water and chloroform. The complex **3** melted at 162 °C. Anal. Calcd. for [Cu(Cl<sub>3</sub>C<sub>8</sub>H<sub>4</sub>O<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>15</sub>O<sub>3</sub>N)<sub>2</sub>].2H<sub>2</sub>O: Cu 13.12, C 34.69, H 4.13, N 2.89%; Found: Cu 12.99, C 34.22, H 4.04, N 2.71%. FT-IR (KBr pellet, in cm<sup>-1</sup>), 3536(mb), 3374(mb), 3195(sb), 2974(mw), 2927(mw), 2897(mw), 2860(mw), 1614(s), 1476(vs), 1445(s) 1409(s), 1361(ms), 1318(s), 1280(s), 1250(s), 1233(mw), 1139(ms), 1086(s), 1057(m), 1027(ms), 1006(mw), 941(w), 906(ms), 871(ms), 829(m), 754(vw), 728(ms), 716(w), 678(m), 629(s), 570(w), 501(w); UV-Vis (methanol-water):  $\lambda_{\max} = 735$  nm ( $\epsilon_{\max} = 163$  L.mol<sup>-1</sup>.cm<sup>-1</sup>).

### 3. Results and Discussion

### 3.1 Syntheses:

The reaction between sodium hydroxide, copper sulphate pentahydrate and 2,4,5-trichlorophenoxy acetic acid in appropriate stoichiometry in aqueous medium resulted in the formation of desired hydrated copper 2,4,5-trichlorophenoxyacetate according to equation (i). The above isolated bluish compound was insoluble in common organic solvents. When N-or N,O- donor ligands  $\gamma$ -picoline/ethylenediamine/triethanolamine was added to the suspension of hydrated copper(II) (2,4,5-trichlorophenoxyacetate)<sub>2</sub> in methanol-water (4:1) mixture until a clear blue solution was obtained, which on slow evaporation at room temperature gave respective crystalline products as shown in scheme 1, equation (ii), (iii) and (iv). The elemental analyses of all three complexes are consistent with the observed composition of the complexes which was subsequently confirmed by single crystal X-ray investigation.

### 3.2 Spectroscopy:

The infrared spectra of the newly synthesized complexes **1**, **2** and **3** have been recorded as KBr pellets in the region 4000–400 cm<sup>-1</sup> (as shown in Fig. 4 a, b and c ) and tentative assignments have been made on the basis of earlier reports in literature [40,41]. The bands at 3490 cm<sup>-1</sup> in **1**, and 3536 and 3373 cm<sup>-1</sup> in **3** are attributed to O-H stretching vibration of lattice water. The bands at 3364, 3304, 3215 cm<sup>-1</sup> in **2** are attributed to O-H stretching vibration of water and N-H stretching vibration of the ligand, ethylenediamine. The sharp bands varying from weak to medium intensity in the region 3195–2855 cm<sup>-1</sup> in all the complexes **1**, **2** and **3** may be attributed to C-H stretching vibrations of  $\gamma$ -picoline/ethylenediamine/triethanolamine as well as those of the anion (2,4,5-trichlorophenoxyacetate). The bands at 1641/1393cm<sup>-1</sup> in complex **1**, 1607/1341 cm<sup>-1</sup> in complex **2** and 1614/1318 in **3** may be attributed to  $\nu_{as}(\text{COO})/\nu_s(\text{COO})$ . The value of  $\Delta\nu\text{COO} = \nu_{as}(\text{COO}) - \nu_{sym}(\text{COO}^{-1})$  248, 266, 296 cm<sup>-1</sup> respectively in complexes **1,2** and **3** indicated same coordination mode of carboxylate coordination in all three newly synthesized complexes **1-3**. The C-Cl stretching vibrations for complexes **1**, **2** and **3** appear at 865, 872 and 871 cm<sup>-1</sup> respectively. The band at 531, 454 in

complex **1**, 524 and 460  $\text{cm}^{-1}$  in complex **2** and 570 and 501 in complex **3** may be ascribed to metal-oxygen and metal-nitrogen stretching vibration.

The electronic absorption spectra of complex **1** and complex **2**, **3** have been recorded in methanol-water (4:1) mixture. The complexes **1** and **3** showed strong absorption band at 685 ( $\epsilon_{\text{max}} = 194.34$ ) and 735 nm ( $\epsilon_{\text{max}} = 163$ ) due to d-d transitions. Complex **2** showed strong absorption at around 547 nm,  $\epsilon_{\text{max}}=68.7$ , typical for d-d transitions of elongated octahedral copper(II) complex,  $[\text{trans-Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  observed by us and others.[42-44]

### 3.3 Magnetic Measurements

Copper in +2 oxidation state has spin only magnetic moment values of the order of 1.73 B.M. at room temperature in general. However, higher values are observed due to spin orbital coupling. Normally, copper(II) compounds having ionic or weak covalent bonds have magnetic moments in the range of 1.9-2.2 B.M. as compared to 1.72-1.82 B.M. for those having strong covalent bonds [45-47] at room temperature. The room temperature magnetic susceptibilities for complexes **1**, **2** and **3** were 1.78, 1.84 and 1.54 B.M. respectively.

### 3.4 Molar Conductance:

Conductance measurements were carried out at 25 °C in aqueous medium and a plot of  $\Lambda$  (molar conductance) versus  $C^{1/2}$  (square root of concentration) was drawn (Fig.5). When the concentration was extrapolated to zero, it gave  $\Lambda_o = 232 \text{ S.cm}^2\text{mol}^{-1}$  for complex **2**. This value falls in the range observed for 1:2 electrolytes [48]. Therefore, conductance measurements revealed that complex **2** behave as 1:2 electrolytes in aqueous medium indicating that the weak axial bond dissociates in aqueous medium as shown in equation (v). Electronic spectrum of the complex showed a peak around 560 nm consolidate the above observation as in our earlier studies on copper(II) complexes with arylcarboxylates/sulphonates the  $\lambda_{\text{max}}$  values around  $\approx 550$  nm was observed when cationic species  $[\text{trans-Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  was present in various ionic complexes.[49]

$$[\text{Cu}(\text{en})_2(\text{Cl}_3\text{C}_6\text{H}_2\text{OCH}_2\text{COO})_2].2\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons [\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+} + 2\text{Cl}_3\text{C}_6\text{H}_2\text{OCH}_2\text{COO}^- \quad (\text{v})$$

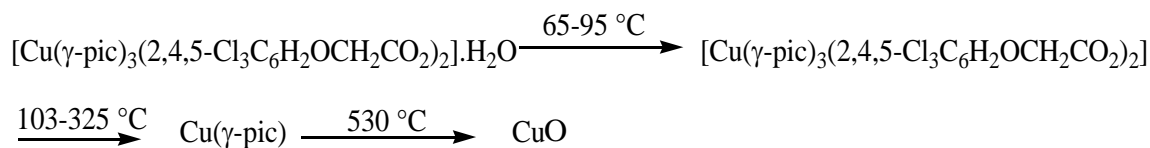




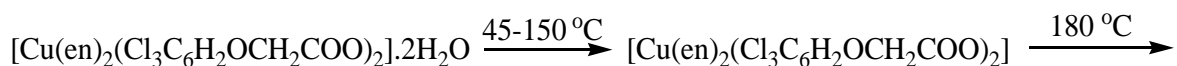
Molar conductance of complexes **1** and **3** could not be determined as they were insoluble in aqueous media.

### 3.5 Thermogravimetric Analysis:

Thermogravimetric analysis (TGA) of complexes **1**, **2** and **3** was recorded in air in temperature range of 33-800 °C in order to study the thermal stability (Fig. 6). The first step in complex **1** corresponded to the loss of one lattice water molecule (calcd. = 2.070%, obs. = 2.052%) between 65-95 °C. Horizontal portion of the TG curve from 95-102 °C corresponded to the stability of anhydrous  $[\text{Cu}(\gamma\text{-pic})_3(2,4,5\text{-Cl}_3\text{C}_6\text{H}_2\text{OCH}_2\text{COO})_2]$ . The total weight loss shown by the TG curve (calcd. = 79.03%, obs. = 78.52%) from 103-325 °C corresponded to the formation of  $\text{Cu}(\gamma\text{-pic})$  and thereafter TG curve showed continuous weight loss till 530 °C. The total weight loss corresponded to the formation of residual  $\text{CuO}$  (calcd. = 92.69 %, obs. = 92.22%). The TGA steps followed by the complex **1** are given below.



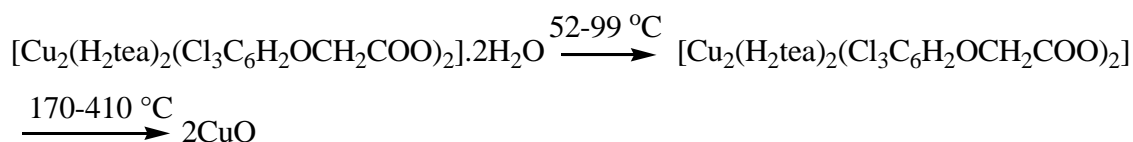
In complex **2**, the first step in the TG curve corresponded to the loss of two lattice water molecules (calcd. = 4.94%, obs. = 4.895%) from 45 to 150 °C. The horizontal portion of TG curve from 150 to 180 °C corresponded to the formation of anhydrous  $[\text{Cu}(\text{en})_2(2,4,5\text{-trichlorophenoxyacetate})_2]$ . Thereafter the complex kept on decomposing and registered weight loss due to pyrolysis of ethylenediamine and 2,4,5-trichlorophenoxyacetate. The TGA steps followed by the complex **2** are given below.



Continuous decomposition.

In complex **3**, the first step corresponded to the loss of two lattice water molecules (calcd = 3.72 %, obs = 4.231%) from 52-99 °C. The horizontal portion of TG curve from 99 to 170 °C corresponded to the stability of anhydrous  $[\text{Cu}_2(\text{H}_2\text{tea})_2(\text{Cl}_3\text{C}_6\text{H}_2\text{OCH}_2\text{COO})_2]$ . Further weight loss (calcd. =83.64 %, obs. = 84.56 %) in the TG curve corresponded to the formation of CuO.

#### 4. Crystal structure



In an effort to establish the complexes' geometry unambiguously and to investigate the non-covalent interactions in newly synthesized copper(II) 2,4,5-trichlorophenoxyacetate complexes, single crystal X-ray structural determination of complexes **1-3** were performed. The structural studies showed that copper(II) centre exhibited varied geometry ranging from square pyramidal to distorted octahedral as a consequence of the presence of different N- or N,O-donor ligands. The perspective views of complexes **1-3** are shown in Fig. 3. In all the complexes, 2,4,5-trichlorophenoxyacetate anion acts as a monodentate ligand being linked to the central copper cation through one oxygen of the carboxylate group. In complex **1**, there is a two-fold axis passing through O1w, Cu1, N1, C3 and C4 atoms; the coordination around copper center is square pyramidal since the cation is bound to three picoline molecules and two 2,4,5-trichlorophenoxyacetate anions (Fig. 3a). An interesting feature is the simultaneous presence of three  $\gamma$ -picoline molecules coordinated to Cu(II) centre, which is relatively rare; a CSD search of Cu(II) complexes having three (or more) coordinated pyridines, picolines or dimethylpyridines resulted in 161 hits, out of which only 23 entries are Cu-picoline complexes. In complex **2**, two carboxylate ligands are located at the apices of a quite elongated octahedron indicating relatively weak Cu-O<sub>carboxylate</sub> bond; actually, the mean Cu-O<sub>carboxylate</sub> distance, calculated for a sample containing more than 3000 structures, gives a value of 2.00(8) Å. The basal plane of copper(II) octahedron is formed by two chelating ethylenediamine ligands where the copper ion lies on a two-fold axis (Fig. 3 b).

Conversely, in complex **3**, a symmetry centre is positioned in between two Cu cations linked by two deprotonated oxygen atoms belonging to two different  $H_2tea$  mono anions, which in this case act as tetradentate ligands through three oxygen atoms and a nitrogen atom (Fig. 3c), as reported previously from our group [50]. The final coordination geometry around each Cu center is distorted octahedral where only one site is occupied by oxygen atom of the 2,4,5-trichlorophenoxyacetate anion. The C-O distances in the carboxylate moiety are not equal as expected in view of the delocalization of the double bond where the longer bond is always the one involving the coordinated oxygen atom. Selected bond lengths and angles are given in Table 2. The Cu-N and Cu-O bond lengths are inline with those reported in the literature for similar compounds. The structural parameters of 2,4,5-trichlorophenoxyacetate ligand are in agreement with the reported in literature. [51]

### **Packing:**

The packing pattern is mainly determined by the formation of O/C-H...O (complex **1** and **3**) and O/N-H...O (complex **2**) hydrogen bonds, which are listed in Table 3. In complex **1**, the supramolecular aggregates composed by Cu-complexes and water molecules appear to be isolated in the crystal lattice; indeed the only observed O-H...O hydrogen bonds involve the molecules belonging to the same asymmetric unit, with the formation of a  $R^2_2(10)$  motif (Fig. 3a). The unit cell contents of **1** are shown in Fig. 7. The different units are linked by weak C-H...O hydrogen bonds. No other appreciable intermolecular interaction, i.e. halogen bonds, C-H... $\pi$  or  $\pi$ ... $\pi$  interactions has been found.

In complex **2**, the units of neutral complex  $[Cu(en)_2(2,4,5\text{-trichlorophenoxybenzoate})_2]$  are held together by N/O-H...O interactions (Table 3) with the co-crystallized water molecule acting as a bridge between two adjacent complexes. Each water molecule is involved both as H-bond donor and acceptor (Fig. 8). This leads to the formation of two rings described by  $R^2_3(8)$  and  $R^2_2(8)$  graph-set motifs, from both sides of each complex molecule, resulting in the formation of a ribbon-like architecture. The packing diagram in complex **2** is also stabilized by weak  $\pi$ ... $\pi$  interaction between

2,4,5-trichlorophenoxybenzoate moieties as shown in Fig. 9 (centroid...centroid distance= 3.93Å). The unit cell contents of complex **2** are shown in Fig. 10.

In complex **3**, a strong intramolecular O-H...O hydrogen bond is formed between one OH group of the H<sub>2</sub>tea ligand (O2) and the free oxygen of the carboxylate group (O5), while the other tea hydroxyl acts as a H-bonding donor towards the non-coordinated water molecule. The connection among the different binuclear Cu complexes is provided by close contacts between Cl2 and O5 of 3.102(2) Å, which are usually called 'halogen bonds' [52] and by Cl...π interactions (3.453 Å) between chlorine of 2,4,5-trichlorophenoxy moiety of one molecule with centroid of 2,4,5-trichlorophenoxy of the adjacent one (Fig.11). In this way, ribbons running along *c*-direction are formed as shown in Fig. 11. Further the ribbons are interconnected through H-bonding interactions provided by lattice water molecule acting both as a donor and an acceptor. The O5 atom is involved in a strong intramolecular hydrogen bond with O2. Further, additional strength to the lattice is provided by weak Cl...O interactions as highlighted by blue fragmented bonds (Fig. 11).

## Conclusion

Three new copper(II) coordination complexes, monomeric [Cu(γ-pic)<sub>3</sub>(L)<sub>2</sub>].H<sub>2</sub>O (square pyramidal) **1** and [trans-Cu(en)<sub>2</sub>(L)<sub>2</sub>].2H<sub>2</sub>O (octahedral) **2** and dimeric [Cu<sub>2</sub>(H<sub>2</sub>tea)<sub>2</sub>(L)<sub>2</sub>].2H<sub>2</sub>O (distorted octahedral) **3** have been synthesized by the reaction of copper(II) 2,4,5-trichlorophenoxyacetate with N-donor ligands of different denticity in water–methanol solution. The newly synthesized complexes have been characterized by various physicochemical techniques. The analysis of the crystal structures revealed that in all cases the co-crystallized water molecules play an important role in the crystal lattice stabilization, connecting the various complexes through the formation of N/O-H...O bonds of medium/ high strength. In spite of the presence of many Cl atoms, only one significant Cl...O interaction has been observed. A set of weaker interactions like π...π, Cl...π, C-H...O *etc.* contribute to make more robust the crystal.

## Acknowledgments

The authors RPS and SK acknowledge the financial support of UGC, New Delhi (India) as a UGC Emeritus and BSR Meritorious Fellowship respectively. PV thanks DST PURSE program of PU, Chandigarh, India.

### **Supplementary data**

Crystallographic data for the structural analysis of the title compounds 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 805412, 805413 and 805411](#) for complexes **1-3** respectively.

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

	<b>1</b>	<b>2</b>	<b>3</b>
Chemical formula	C <sub>34</sub> H <sub>29</sub> Cl <sub>6</sub> CuN <sub>3</sub> O <sub>6</sub> ·H <sub>2</sub> O	C <sub>20</sub> H <sub>24</sub> Cl <sub>6</sub> CuN <sub>4</sub> O <sub>6</sub> ·2.H <sub>2</sub> O	C <sub>28</sub> H <sub>36</sub> Cl <sub>6</sub> Cu <sub>2</sub> N <sub>2</sub> O <sub>12</sub> ·2.H <sub>2</sub> O
<i>M<sub>r</sub></i>	869.86	728.70	968.40
Crystal system, space group	Monoclinic, <i>C2/c</i>	Monoclinic, <i>C2/c</i>	Triclinic, <i>P-1</i>
<i>a, b, c</i> (Å)	27.7873 (6), 13.9390 (3), 10.3170 (3)	9.5751 (2), 11.8577 (2), 25.5560 (5)	7.4697 (2), 8.0077 (2), 16.5180 (5)
$\alpha, \beta, \gamma$ (°)	90, 97.058 (1), 90	90, 90.2240 (6), 90	96.1660 (13), 90.7180 (12), 104.9610 (16)
<i>V</i> (Å <sup>3</sup> )	3965.77 (17)	2901.57 (10)	948.18 (5)
<i>Z</i>	4	4	1
$\mu$ (mm <sup>-1</sup> )	1.00	1.36	1.61
Crystal size (mm)	0.32 × 0.20 × 0.17	0.52 × 0.29 × 0.17	0.52 × 0.41 × 0.35
No. of measured, independent, observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	43661, 4773, 3517	16447, 3491, 2764	9961, 4443, 3852
<i>R</i> <sub>int</sub>	0.083	0.050	0.039
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.050, 0.131, 1.04	0.042, 0.156, 1.10	0.034, 0.114, 1.10
No. of reflections	4773	3491	4443
No. of parameters	233	196	249

**Table 2- Selected bond lengths (Å) and angles (°) for complexes 1-3**

<b>Complex 1</b>			
Cu1 - N1	2.291(3)	Cl2 - C16	1.732(4)
Cu1 - N2	2.030(2)	Cl3 - C17	1.733(4)
Cu1 - O1	1.957(2)	O1 - C11	1.257(3)
Cl1 - C14	1.727(4)	O2 - C11	1.226(3)
N1 - Cu1 - N2	95.38(6)	N2 - Cu1 - O1	89.76(8)
N1 - Cu1 - O1	90.51(5)		
<b>Complex 2</b>			
Cu1 - N1	2.011(2)	Cl2 - C9	1.735(3)
Cu1 - N2	2.018(2)	Cl3 - C6	1.730(3)
Cu1 - O2	2.655(2)	O1 - C3	1.244(3)
Cl1 - C8	1.728(3)	O2 - C3	1.257(3)
N1 - Cu1 - N2	84.32(9)	N2 - Cu1 - O2	86.99(9)
N1 - Cu1 - O2	82.96(8)		
<b>Complex 3</b>			
Cu1 - N1	2.052(2)	Cl1 - C14	1.734(2)
Cu1 - O1	1.948(1)	Cl2 - C12	1.732(2)
Cu1 - O2	2.527(2)	Cl3 - C11	1.734(3)
Cu1 - O3	2.439(2)	O4 - C7	1.255(3)
Cu1 - O4	1.970(2)	O5 - C7	1.236(3)
N1 - Cu1 - O1	84.94(8)	O1 - Cu1 - O3	98.87(7)
N1 - Cu1 - O2	79.10(7)	O2 - Cu1 - O4	88.97(7)
N1 - Cu1 - O3	77.36(7)	O3 - Cu1 - O4	80.71(7)
N1 - Cu1 - O4	97.14(7)	Cu1 - O1 - Cu1	97.10(7)
O1 - Cu1 - O2	92.35(7)		

**Table 3 -Hydrogen bonding parameters ( Å and °) for complexes 1-3.**

<b>D-H...A</b>	<b>D-H</b>	<b>D...A</b>	<b>H...A</b>	<b>D-H...A</b>
<i>Complex 1</i>				
O1W-H...O2	0.86(4)	2.814(3)	1.96(4)	172(4)
C6-H...O2 <sup>i</sup>	0.93	3.233(4)	2.51	135
C10-H...O3 <sup>ii</sup>	0.96	3.468(4)	2.69	138
<i>Complex 2</i>				
N1 -H...O1	0.89	3.152(3)	2.35	150
O1W -H...O2	0.87(2)	2.690(3)	1.86(2)	159(2)
N1 -H...O1W <sup>iii</sup>	0.89	2.889(4)	2.04	160
N2 - H...O1 <sup>iv</sup>	0.89	3.026(3)	2.21	152
O1W - H...O1 <sup>v</sup>	0.89(5)	2.752(4)	2.49(5)	102(4)
<i>Complex 3</i>				
O2-H...O5	0.86(3)	2.634(2)	1.78(3)	165(3)
O1W-H...O2	0.84(5)	2.802(3)	1.97(5)	166(4)
O1W-H...O1 <sup>vi</sup>	0.84(3)	3.181(3)	2.44(3)	145(3)
O3-H...O1W <sup>vii</sup>	0.85(4)	2.697(3)	1.89(4)	167(3)
<i>Short contact</i>				
O5...Cl2 <sup>viii</sup>	3.102(2)			

Symmetry codes: (i)  $-x, -y, 1-z$ ; (ii)  $-x, y, 3/2-z$ ; (iii)  $x+1/2, y+1/2, z$ ; (vi)  $x+1/2, y-1/2, z$ ; (v)  $1/2-x, y-1/2, 1/2-z$ ; (vi)  $-x, -y, -z$ ; (vii)  $1-x, -y, -z$ ; (viii)  $-x, y, 3/2-z$ .

## Figures Captions:

**Fig.1.** Possible binding modes of 2,4,5-trichlorophenoxyacetate towards metal ion.

**Fig.2.** Ligands used in the study (a) 2,4,5-trichlorophenoxyacetate, (b)  $\gamma$ -picoline, (c) ethylenediamine and (d) triethanolamine.

**Fig.3.** ORTEPIII view and atom numbering for (a) Complex **1**; (b) Complex **2** and (c) Complex **3**. The displacement ellipsoids are drawn at 40% probability. Hydrogen bonds are drawn as dashed bonds

**Fig.4.** FT-IR spectra of (a) complex **1**, (b) complex **2** and (c) complex **3**.

**Fig.5.** Molar conductance of complex **2**.

**Fig.6.** TG curves of complexes **1**, **2** and **3**.

**Fig.7.** Unit cell contents of complex **1** (viewed down the c axis).

**Fig.8.** Hydrogen bond interactions in complex **2** depicting  $R^2_3(8)$  and  $R^2_2(8)$  graph-set motifs.

**Fig.9.**  $\pi \dots \pi$  interaction (3.939 Å) between 2,4,5-trichlorophenoxybenzoate moieties in complex **2** as measured from the centroid of the ring.

**Fig.10.** Unit cell contents of complex **2** (viewed down the a-axis); fragmented bonds represent H-bond interactions.

**Fig.11.**  $\text{Cl} \dots \pi$  interactions in complex **3** between chlorine of 2,4,5-trichlorophenoxy of one molecule and with the centroid of 2,4,5-trichlorophenoxy of second molecule;  $\text{Cl} \dots \text{O}$  interactions and H-bond interactions are represented with blue and black fragmented bonds respectively.

**Scheme I:** Schematic representation of the synthetic procedure for complex **1-3**.