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## Synthesis and characterization of an dinuclear copper (II) complex: Stabilized at room temperature via co-crystallization.

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### Abstract:

A new Cu(II) co-crystal,  $[(CuL)_2(CuL)] \cdot CH_3OH$  (1) was synthesized and characterised by using a tetradentate di-Schiff base ligand ( $H_2L$ ) of 1,3-propanediamine and 2-hydroxyacetophenone. The X-ray structural analysis reveals that the complex contain an identical dimeric unit along with a monomeric unit of Cu(II). The dimeric unit is constructed by the combination of the two monomer of Cu(II) with help of  $\mu_1$ -phenoxido bridge. This dimer only stabilised at room temperature with co-crystal (CuL).

**Keywords:** Co-crystal / Schiff bases / Tetradentate / ligand

### Introduction

The strategy of solid-state structures is the spirit of crystal engineering [1]. Among the different types of solid compounds, there is a special class of solid compounds; those are multicomponent crystals, known as co-crystals [2]. There is currently an intense interest in the design, synthesis, and properties of such molecular co-crystals [3]. Co-crystallization of two different molecules is a possible way of deliberately prompting the position of molecules in a crystal lattice and allows for the study of newly generated properties. Certainly, studies on co-crystallization is a high opportunities for exploring the hierarchy of intermolecular interactions within a crystalline solid. Co-crystals that include of two or more molecules [4] that are solids under ambient conditions represent a well-established [4] class of compounds. Among the reported organic co-crystals, most of them are acid-base compounds [5]. However, co-crystals of metal complexes are relatively rare,[2j, 2v] because of the fact that compounds with different geometries rarely

possess similar lattice packing and display comparable crystallization kinetics. Organic co-crystals are considered in discovery and development of API (active pharmaceutical ingredients)[6] solid forms in addition to amorphous, polymorphs, solvates, and salts. However, unlike their organic counterpart, almost all the reported inorganic co-crystals are accidental products, and to the best of our knowledge, no attempts were taken to synthesize a co-crystal in which an unstable inorganic component was present at ambient condition.

In this present study, we report the synthesis, crystal structure and spectroscopic studies of the cocrystal  $[(\text{CuL})_2(\text{CuL})]\cdot\text{CH}_3\text{OH}$  (**1**) [where  $[\text{H}_2\text{L}]$  = tetradentate di-Schiff base ligand of 1,3-propanediamine and 2-hydroxyacetophenone]. The compound is previously reported but the aspect and nobility of the complex did not mentioned in the paper [7].

## Experimental section

### Starting Materials

The 2-hydroxyacetophenone and 1,3-propanediamine were purchased from Lancaster and were of reagent grade. They were used without further purification.

*Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

### Synthesis of the Schiff base ligand $\text{H}_2\text{L}$ and corresponding ligand complex $[\text{CuL}]$

The di-Schiff base ligand,  $\text{H}_2\text{L}$  was prepared by: 5 mmol of 1,3-propanediamine (0.42 mL) were mixed with 10 mmol of 2-hydroxyacetophenone (1.20 mL) in methanol (10 mL). The resulting solution was refluxed for *ca.* 2 hrs and allowed to cool. The yellow colored methanolic solution was used directly to prepare the ‘ligand complex’,  $[\text{CuL}]$  as reported earlier [8].

**Synthesis of the complex:**  $[(\text{CuL})_2(\text{CuL})]\cdot\text{CH}_3\text{OH}$  (**1**). The “ligand complex”  $[\text{CuL}]$  (0.782 g, 2 mmol) was dissolved in methanol (50 mL). Reduce the volume of the solution below 25 mL. Cooled the solution at room temperature and transferred the solution into a petri dish. The solution was stands for 3-4 days to yield brown colored X-ray quality single crystals of complex **1** at the bottom of the vessel.

Complex **1**: Yield: 0.576 g. (74 %). Anal. Calc. for  $\text{C}_{78}\text{H}_{88}\text{Cu}_4\text{N}_8\text{O}_{10}$  (1551.76): C, 60.37; H, 5.72; N, 7.22. Found: C, 60.18; H, 5.71; N, 7.28.  $\lambda_{\text{max}}$  ( $\text{CH}_3\text{CN}$ , nm): 269, 348 and 534. IR (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{N})$ , 1597.

### Physical Measurements

Elemental analysis (C, H and N) was performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets ( $4500\text{--}500\text{ cm}^{-1}$ ) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra (800–220 nm) was recorded in a Hitachi U-3501 spectrophotometer in acetonitrile solution.

### Crystallographic Data Collection and Refinement

Suitable single crystals of each complexes were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo- $\text{K}_\alpha$  ( $\lambda = 0.71073\text{ \AA}$ ) radiation. The

crystals were positioned at 60 mm from the CCD. 360 frames per scan were measured with a counting time of 10s. The structures were solved using Patterson method by using the SHELXS 97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. Successful convergence was indicated by the maximum shift / error of 0.001 for the last cycle of the least squares refinement. Absorption corrections were carried out using the SADABS program [9]. All calculations were carried out using SHELXS 97 [10], SHELXL 97 [11], PLATON 99 [12], ORTEP-32 [13] and WinGX system Ver-1.64 [14]. Data collection and structure refinement parameters and crystallographic data for the complex **1** is given in Table 1.

**Table 1.** Crystal data of the complex **1**

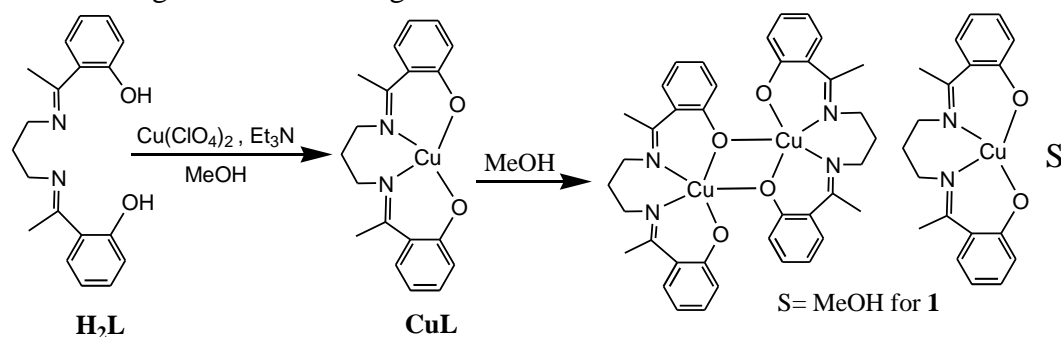
	<b>1</b>
Formula	C <sub>78</sub> H <sub>88</sub> Cu <sub>4</sub> N <sub>8</sub> O <sub>10</sub>
Formula wt.	1551.76
Space group	<i>P</i> $\bar{1}$
Crystal system	Triclinic
a / Å	9.8258(4)
b / Å	9.9105(4)
c / Å	18.8832(8)
$\alpha$ / deg	92.166(2)
$\beta$ / deg	104.147(2)
$\gamma$ / deg	95.160(2)
V / Å <sup>3</sup>	1772.42(13)
Z	1
d <sub>cal</sub> (g.cm <sup>-3</sup> )	1.454
$\mu$ (mm <sup>-1</sup> )	1.250
R <sub>int</sub>	0.0404
No. of unique data	8737
Data with I>2 $\sigma$ (I)	5953
R1 on I>2 $\sigma$ (I)	0.0519
wR2 on I>2 $\sigma$ (I)	0.1446
Gof Value	1.080

## Results and Discussion

### Syntheses, IR and UV-Vis spectra of the complexes

The Schiff-base ligand ( $H_2L$ ) and its Cu(II) complex,  $[CuL]$  were synthesized using the reported standard procedure [8]. The Cu(II) complex on dissolve in MeOH medium on a high concentration, resulted a co-crystal  $[(CuL)_2(CuL)] \cdot CH_3OH$  (**1**) was formed (see Scheme 1). The co-crystals was formed with monomer and dimer in proportion of 2:1 at room temperature. Besides elemental analysis, the complex was initially characterized by IR spectra. The spectral pattern and band positions of the complex and the 'ligand complex' are very similar. A strong and sharp band due to the azomethine  $\nu(C=N)$  group of the Schiff base appears at  $1597\text{ cm}^{-1}$  for complex **1**.

The electronic spectra of the complex (measured in acetonitrile solution) display a single absorption band at 534 nm. The positions of these bands are consistent with the observed square-based geometry around the copper centers. The intense bands at about 348 and 269 nm for complex **1** are the indicative of ligand to metal charge transfer transitions.



**Scheme 1.** Synthetic route to complex **1**.

### Description of the structures

**Complex  $[(CuL)_2(CuL)] \cdot CH_3OH$  (**1**):** The asymmetric unit of the complex contains two  $[CuL]$  units. Besides the complex part, one methanol molecule is present in the crystal lattice of complex **1**. The ORTEP view of the complex **1** is shown in Fig. 1a. The bond parameters are enlisted in Table 2. The structure determination reveals that the complex consist of a dimeric unit along with a monomer which are cocrystallised in methanol solvent. (Fig. 1b).

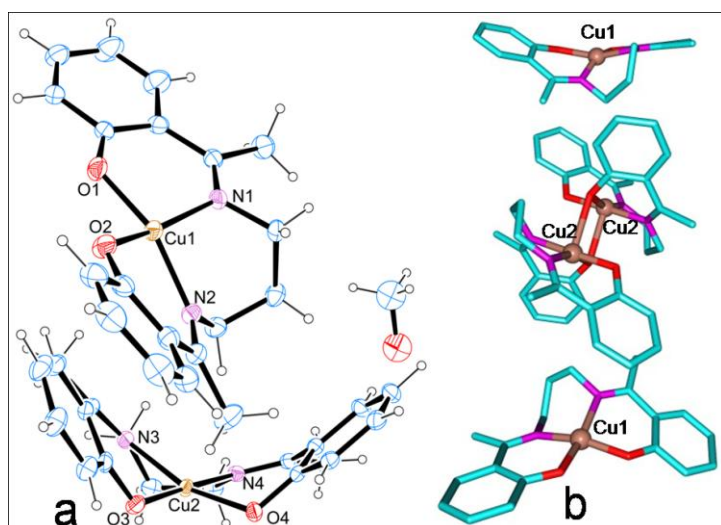


Fig. 1 (a) Asymmetric unit of complex **1** with ellipsoids at 30% probability (b) Molecular unit of the complex **1**. Hydrogen atoms and solvent molecules are omitted for clarity.

The Cu(1) atom of monomeric unit is in a square planar environment with four coordinated  $\text{N}_2\text{O}_2$  donor di-Schiff base ligand. The av. bond distances around metal center is 1.918 Å. The r.m.s. deviation of four donor atoms from their mean coordination plane of Cu(1) is 0.356 Å. The Cu(1) atoms are deviated from these plane are 0.012(1) Å for **1**, indicating a small tetrahedral distortion. This tetrahedral distortion is also verified by the so-called  $\tau_4$  index that measures the distortion between a perfect tetrahedron ( $\tau_4 = 1$ ) and a perfect square planar geometry ( $\tau_4 = 0$ ) with the formula:  $\tau_4 = [360^\circ - (\alpha + \beta)]/141^\circ$ , being  $\alpha$  and  $\beta$  (in  $^\circ$ ) the two largest angles around the central metal in the complex [14]. The  $\tau_4$  value for Cu(1) is 0.300 for complex **1**, confirming a moderate distortion towards tetrahedral geometry for this metal center of the complex. This distortion is also affirmed from the values of the range of *cis* and *trans* angles at around Cu(1) for the complex.

The Cu(2) ions of the dimeric unit in both complexes present a penta-coordinated square pyramidal geometry where the equatorial plane is formed by the two imine N atoms N(3) and N(4) and the two phenoxido O atoms, O(3) and O(4) of the dianionic di-Schiff base ligand. The two [CuL] units in the molecule are held together through the semi-coordination of one of the phenoxido groups of one unit, O(4), to the axial position of the Cu(II) ion of the other [CuL] unit with Cu(2)-O(4)<sup>a</sup> distance of 2.503(2) Å (<sup>a</sup> = 1-x, 1-y, 1-z for **1**) forming the square pyramidal geometry. This semi-coordination leads to Cu(2)···Cu(2)<sup>a</sup> distance at 3.305(1) Å for complex **1**. The r.m.s. deviation of the four basal atoms from the mean plane passing through them of Cu(2) is 0.175 Å. The metal atom is 0.154(1) Å shifted from this plane towards the axially coordinated oxygen atom. The range of *cis* angles 82.7(1)-114.3(1) and *trans* angles 160.7(1)-178.2(1) around Cu(2) indicate the distortion from the ideal square pyramidal geometry. The distortions of this geometry from square pyramid to trigonal bipyramid have been calculated by the

Addison parameter ( $\tau$ ). The Addison parameters of the Cu(2) atoms for the complex is 0.291, indicating a distorted square pyramidal geometry [14].

**Table 2.** Bond distances and angles around the metal centers in both complex **1**

<b>Complex</b>	<b>1</b>
<b>Atoms</b>	<b>Distance (Å)</b>
Cu1 - O1	1.874(2)
Cu1 - O2	1.889(3)
Cu1 - N1	1.954(3)
Cu1 - N2	1.956(3)
Cu2 - O3	1.911(3)
Cu2 - O4	1.947(2)
Cu2 - N3	1.981(3)
Cu2 - N4	1.993(3)
Cu2 - O4 <sup>a</sup>	2.503(2)

<b>Atoms</b>	<b>Angle (°)</b>
O1 - Cu1 - O2	90.3(1)
O1 - Cu1 - N1	93.3(1)
O1 - Cu1 - N2	158.0(1)
O2 - Cu1 - N1	159.7(1)
O2 - Cu1 - N2	91.6(1)
N1 - Cu1 - N2	92.6(1)
O3 - Cu2 - O4	90.2(1)
O3 - Cu2 - N3	89.2(1)
O3 - Cu2 - N4	178.2(1)
O3 - Cu2 - O4 <sup>a</sup>	95.8(1)
O4 - Cu2 - N3	160.7(1)
O4 - Cu2 - N4	88.7(1)
O4 - Cu2 - O4 <sup>a</sup>	84.9(1)
N3 - Cu2 - N4	92.3(1)
N3 - Cu2 - O4 <sup>a</sup>	114.3(1)
N4 - Cu2 - O4 <sup>a</sup>	82.7(1)

Symmetry element <sup>a</sup>= 1-x,1-y,1-z for **1**.

## Conclusions

In the present study, we have demonstrated that the dissolution of the ligand complex [CuL] (where, H<sub>2</sub>L = di-Schiff base of 1,3-propanediamine and 2-hydroxyacetophenone) at a high concentration in methanol

solvent has yielded distinct co-crystal **1** at room temperature. This synthetic technique of co-crystallization is as effective tools for stabilizing the unstable dimeric unit [CuL]<sub>2</sub> at room temperature. The dimeric unit cannot be separately synthesized at room temperature presumably its high positive Gibbs free energy. However, through co-crystallization process this energy can considerably reduce and consequently, we have found the dimer along with a monomer in the co-crystal in methanol solvent at room temperature.

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Thank you to Department of Chemistry, Sushil Kar College, Champahati, Baruipur, South 24 parganas, West Bengal, India

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