

# Synthesis and characterization of a nano Cu<sub>2</sub> cluster

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## Abstract

The synthesis and crystal structure of Cu<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>COO)<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>COOH)<sub>2</sub> (**1**) is herein reported. However, our intention was to incorporate Pb into the present system and make a new high nuclearity heteronuclear Cu-Pb cluster with magnetic or antibacterial properties. For its synthesis, first Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (2mmol) and PhCOOH (10mmol) was dissolved in a mixed solvent MeCN/EtOH (10/10, v/v); separately Pb(NO<sub>3</sub>)<sub>2</sub> (1mmol) was dissolved in EtOH/H<sub>2</sub>O (20/5, v/v) and added drop-wise to the previous mixture. The mixture was stirred vigorously for half an hour with step-wise addition of NaN<sub>3</sub> (2mmol). The heterogenous reaction mixture was filtered and the deep greenish filtrate was stored at ambient condition. In four weeks, green single crystals were generated at the bottom of the flask. Single crystal X-ray measurement shows the formation of the title compound, where Cu atoms are in +2 oxidation state that is further confirmed by BVS calculation. The Cu-Cu distance in the molecular structure is found to be 2.608 (2) Å, which indicates a Cu-Cu bond in the molecule. Each Cu atom is bonded to four oxygen atoms of two benzoate ligands and one oxygen atom of a benzoic acid molecule. The octahedral geometry of the copper(II) atoms are fulfilled by an additional copper-copper bond. The most interesting in complex **1** is both intra and intermolecular hydrogen and C-H-C bonding present in the system. The length of nano molecular size of the Cu<sub>2</sub> cluster is found to be 1.55nm. The antibacterial study of complex **1** has been checked and it has no such high antibacterial activity. Copyright © 2017 VBRI Press.

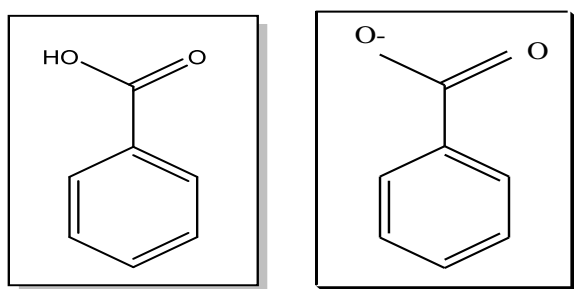
**Keywords:** Synthesis, slow evaporation, copper nano cluster, X-ray crystallography, CV, BVS calculation.

## Introduction

Carboxylates ligands coordinated copper complex is a well-known and are of interest because its different kind of structures with different mode of bonding fashions. The stability of crystal structures depends on the ligand properties (acidic or basic conditions), steric factors, hydrogen bonds and ratio of the starting materials used in the reaction solution and used solvent [1-2]. Chen *et al.* reported the possible binding modes between copper ions and carboxylates [3]. Generally monomeric Cu (II) is a d<sup>9</sup> electronic configuration and due to Jahn-Teller distortion it prefers square planar structure compared to octahedral structure. But dimeric copper (II) cluster produces octahedral structure and paramagnetic or ferromagnetic nature depends on their number of unpaired electrons coupling in syn-syn or syn-anti fashion between the two copper (II) atoms. Scientists are always interested on heterometallic clusters because of giving various properties with different applications. In the 3d transition metal series Cu has great attention in recent times and our

objective is to synthesize new Cu-Pb clusters because of the fact that they have various properties such as biological activities as well as interesting magnetic properties [4-5]. Crucial efforts in this field of work have led to the formation of high nuclearity species, which may be either homometallic or heterometallic. Though there is no such definite strategy to build high nuclearity metal clusters, but people have always tried to discover different strategies to obtain different higher nuclearity clusters [6-7]. Among this, the most frequently used strategy is the use of chelating ligands containing donor atoms such as N, O, S atoms (such as alcohols, pyrazoles, 2-pyridyl oximes etc.), which can co-ordinate metal atoms in different modesto form high nuclearity homo or heteromolecular clusters of Cu, Ni, Co etc. [7-9]. In Cu (II) cluster chemistry, Raptis and co-workers have reported Cu<sub>18</sub>, Cu<sub>27</sub>, Cu<sub>31</sub> clusters containing pyrazolato group [10] while Powell *et al.* have reported Cu<sub>36</sub> and Cu<sub>44</sub> cage like clusters using carboxyphenyliminodiacetic acid as chelating ligands [11-12] and possibly Cu<sub>44</sub> cluster is the biggest cluster of Cu atom till date.

Herein, we report the synthesis of  $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4(\text{C}_6\text{H}_5\text{COOH})_2$  (**1**) by using  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{PhCOOH}$  and  $\text{NaN}_3$  in  $\text{MeCN}/\text{EtOH}$  medium with proportion amount (1:0.5:5:1). We have chosen very simple di-coordinated benzoate ion as our ligand system and our target was to synthesize heteronuclear cluster of Cu and Pb. But the isolated product is complex **1**. The rigid nature of the metal-organic framework (MOF) architecture allows for complete thermal removal of guests including acetate type of ligands, originally bound to copper sites, of the square pyramidal clusters to yield a stable octahedral framework with periodic arrays of open copper sites. The synthesis procedure, X-ray crystal structure and other characterizations of this cluster is reported here. The structure of benzoic acid and benzoate anion is shown in **Fig. 1(a, b)**.



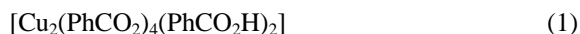
**Fig. 1.** (a) Structure of Benzoic acid and (b) benzoate anion.

## Experimental

### Chemical details

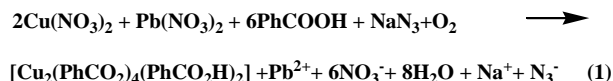
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ , Benzoic acid were of analytical grade and were purchased from Sigma Aldrich chemicals. Sodium azide ( $\text{NaN}_3$ ) was purchased from NICE chemicals. Solvents were used as received.

### Synthesis of complex



To a stirred solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.0484g, 0.2mmol) and  $\text{PhCOOH}$  (0.122 g, 1.0mmol) in  $\text{MeCN}/\text{EtOH}$  (10/10, v/v), separately dissolved  $\text{Pb}(\text{NO}_3)_2$  (0.033g, 0.1mmol) in  $\text{EtOH}/\text{H}_2\text{O}$  mixture (20/5, v/v) was added dropwise to the mixture and  $\text{NaN}_3$  (0.013g, 2mmol) is added to it and the mixture is stirred vigorously for another half an hour. The resulting solution was filtered, and the filtrate is kept in undisturbed condition in slow evaporation for crystallisation. After four weeks, high X-ray quality dark green crystals came out and were washed with  $\text{MeCN}$  and  $\text{EtOH}$  mixture (1:3, v/v) under vacuum, the yield was 0.40 g. A variety of reaction systems involving different reagent ratios and solvent media was explored to develop the procedure described here. So, in a conclusive way, reaction of  $\text{PhCOOH}$  with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{NaN}_3$  in 5:1:0.5:1 ratio in  $\text{MeCN}/\text{EtOH}$  (30/15, v/v) afforded a dark green solution from which  $[\text{Cu}_2(\text{PhCO}_2)_4(\text{PhCO}_2\text{H})_2]$  (**1**) was subsequently isolated in 65% yield. Its formation is

summarized in eq (1). Anal.Calcd (Found) for **1** ( $\text{C}_{42}\text{H}_{32}\text{Cu}_2\text{O}_{12}$ ): C, 40.39; H, 10.11; N, 0.001%. Found: C, 39.82; H, 9.61; N, 0.001%. Selected IR data ( $\text{cm}^{-1}$ ): 3458(w), 1682(s), 1570(s), 1401(s), 1286(s), 1179(m), 1025 (m), 854(m), 714(s), 685(s), 506 (m). The peak at  $3458.15\text{ cm}^{-1}$  is omitted in **Fig. SI 1** for clarity. [s=sharp, w=weak, m=medium]

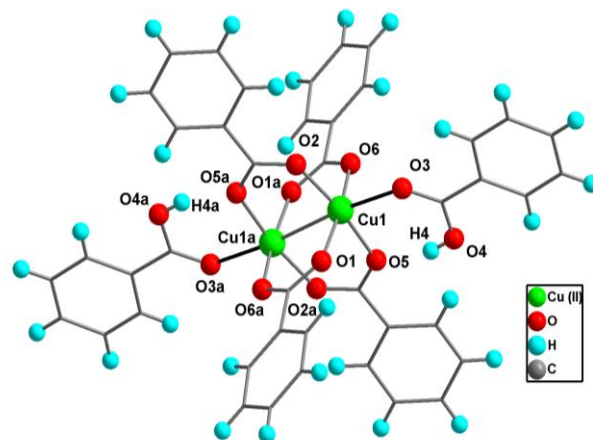


### Characterizations

The complex was characterized by Single X-ray crystallography, Elemental analysis, FTIR analysis, Cyclicvoltammetry (CV) and UV-VIS spectroscopy.

### X-ray crystallography

Single crystal X-ray data was collected for the complex **1** at 150(2)K on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software [13]. Intensity data were collected using graphite-monochromatized  $\text{Mo K}\alpha$  radiation (0.71073 Å) at 150 K. The structures were solved by direct methods using the SHELXL-2013 [14] program incorporated into WinGX [15]. Empirical absorption corrections were applied with SADABS [16]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached.



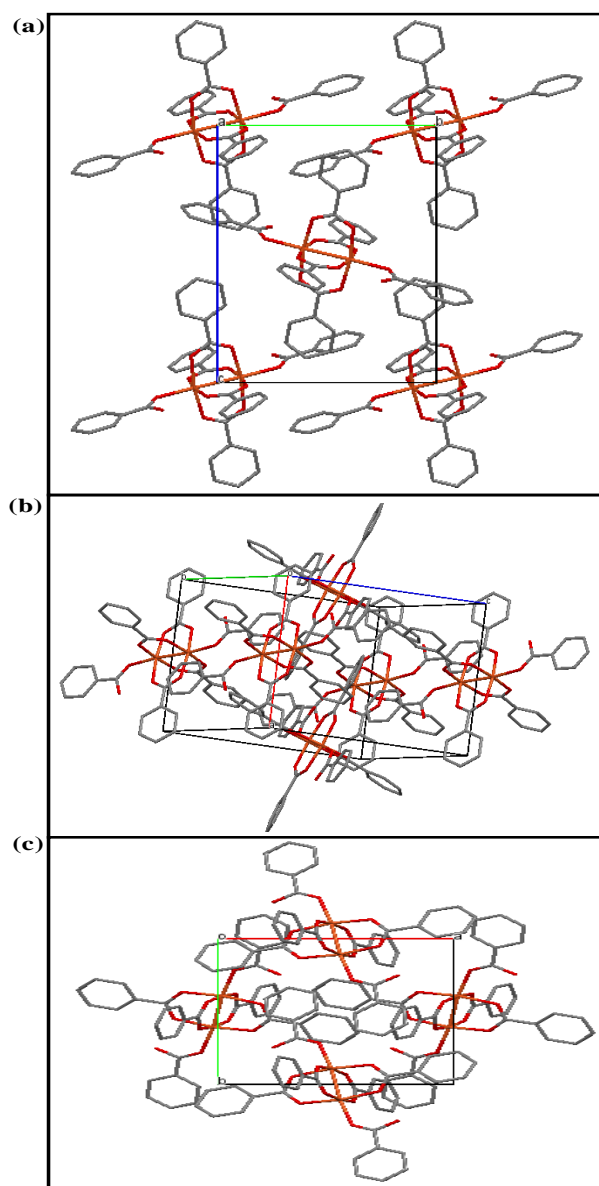
**Fig. 2.** Partially labeled structure of complex **1**. (Color code: Cu(II), green; O, red; C, gray and H, light blue).

An initial search for reciprocal space revealed monoclinic cell for **1**; space groups  $P-21/n$  is confirmed by the subsequent solution and refinement of the structures. In the final cycle of refinement, 11364 reflections (of which 7389 are observed with  $I > 2\sigma(I)$ ) were used to refine 689 parameters and the resulting  $R_1$ ,  $wR_2$  and  $S$  (goodness of fit) were 7.47%, 19.07% and 1.043, respectively. The refinement was carried out by minimizing the  $wR_2$  function using F2 rather than F

values. R1 is calculated to provide a reference to the conventional R value but its function is not minimized. Unit cell data and structure refinement details are listed in **Table 1(a)**.

### Physical measurements

Infrared spectra were recorded in the solid state (KBr pellets) on a Nicolet Nexus 670 FTIR spectrometer in the 400-4000  $\text{cm}^{-1}$  range. Elemental analyses (C, H, and N) and X-ray crystallography were performed by the Central facilities of Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032. Cyclic voltammetry and Electronic spectrum of the compound were recorded by SYNSIL (Model No. PH660) and UV-Vis spectrophotometer of PerkinElmer LAMBDA 35 from the Department of Chemistry, West Bengal State University, Barasat, Kolkata-700126.



**Fig. 3.** (a) Unit cell packing diagram of the cluster viewed along a axis, (b) Unit cell packing diagram of the cluster viewed along the b axis. (c) Unit cell packing diagram of the cluster viewed along the c axis.

**Table 1.** (a) Crystallographic Data for the complex 1, (b) Selected Interatomic Distances (Å) and Angles (deg)<sup>a</sup> for complex 1.

(a)	1
<b>Compound reference</b>	
Chemical formula	$\text{C}_{42}\text{H}_{32}\text{Cu}_2\text{O}_{12}$
Formula Mass	855.76
Crystal system	Monoclinic
a/Å	10.770(7)
b/Å	11.575(7)
c/Å	15.177(9)
$\alpha/^\circ$	90.00
$\beta/^\circ$	91.062(9)
$\gamma/^\circ$	90.00
Unit cell volume/Å <sup>3</sup>	1892(2)
Temperature/K	153(2)
Space group	P2(1)/n
No. of formula units per unit cell, Z	2
No. of reflections measured	21121
No. of independent reflections	4378
R <sub>int</sub>	0.1244
Final R <sub>1</sub> values (I > 2σ(I))	0.0528
Final wR(F <sup>2</sup> ) values (I > 2σ(I))	0.1003
Final R <sub>1</sub> values (all data)	0.1155
Final wR(F <sup>2</sup> ) values (all data)	0.1240
CCDC number	1505232

<sup>a</sup>Graphitemonochromator. <sup>b</sup>I > 2σ(I). <sup>c</sup>R<sub>1</sub> =  $\sum (|F_o| - |F_c|) / \sum |F_o|$ . <sup>d</sup>wR<sub>2</sub> =  $[\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2$ ,  $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$ , where  $p = [F_o^2 + 2F_c^2]/3$ .

(b)	Metal	Bond length (Å)	Bond type	Bond angle (deg)
	Cu(1)-O(1)	1.959(3)	O(1)-Cu(1)-O(2)	90.41(10)
	Cu(1)-O(2)	1.948(3)	O(3)-Cu(1)-O(6a)	94.60(11)
	Cu(1)-O(3)	2.189(3)	Cu(1a)-Cu(1)-O(3)	173.92(8)
	Cu(1)-O(5)	2.000(3)	O(1)-Cu(1)-O(6a)	169.55(10)
	Cu(1)-O(6a)	1.949(3)	O(1)-Cu(1)-O(3)	95.75(10)
	Cu(1)-Cu(1a)	2.608(2)	O(2)-Cu(1)-O(5)	169.15(10)
			O(2)-Cu(1)-O(6a)	89.16(12)
			O(1)-Cu(1)-O(5)	89.58(10)
			O(2)-Cu(1)-O(3)	100.33(11)
			Cu(1a)-Cu(1)-O(2)	85.73(7)
			O(3)-Cu(1)-O(5)	90.47(11)
			Cu(1)-Cu(1a)-O(1)	83.66(7)
			Cu(1a)-Cu(1)-O(6a)	85.90(8)
			O(6a)-Cu(1)-O(5)	88.89(12)

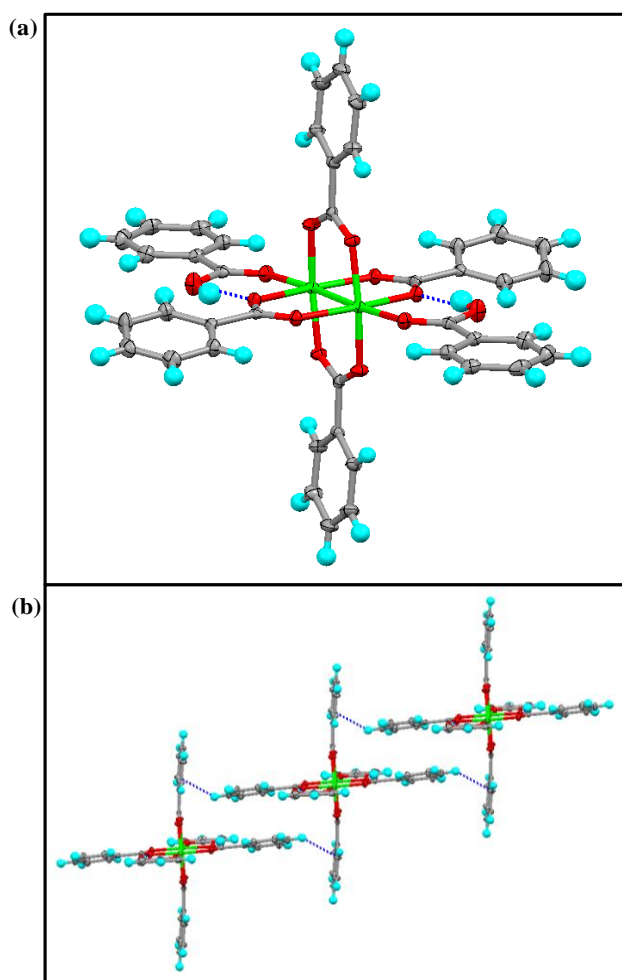
<sup>a</sup>Primed and unprimed atoms are related by symmetry.

## Results and discussion

### Description of structures

The partially labeled structure, 3D view of complex 1 is presented in **Fig. 2**; selected interatomic distances and angles are listed in **Table 1(b)**. The asymmetric molecule 1 possesses a Cu-Cu single bond and bond length has been found to be 2.608 (2) Å which may be an indication of δ bond formation by the overlap of singly filled  $d_{x^2-y^2}$  orbitals of the two Cu atoms. From the structure, we found that both the Cu atoms possess co-

ordination number 6 and they belong to an octahedral environment. The core structure of the complex 1 can be described in such a manner that four benzoate ions are attached to both the Cu atoms through chelation or common syn, syn  $\eta^1: \eta^1: \mu$  mode and the other two benzoic acid molecules are attached to both the Cu atoms axially. The most interesting thing in this cluster is the existence of intramolecular hydrogen bonding between (O5, H4) and (O5a, H4a) atoms (**Fig. 4a**) and inter molecular C-H-C bonding (**Fig. 4b**) can be confirmed from the single crystal XRD structure of the complex and bond distance is 1.82Å and 2.89 Å, respectively. The bond angle between O4-H4-O5 and O4a-H4a-O5a is found to be 164.32°. The axial bond Cu1-O3 and Cu1a-O3a is found to be 2.18Å which is much larger compared the other Cu-O bonds (Table 2) indicates existence of Jahn-Teller distortion in the molecule.



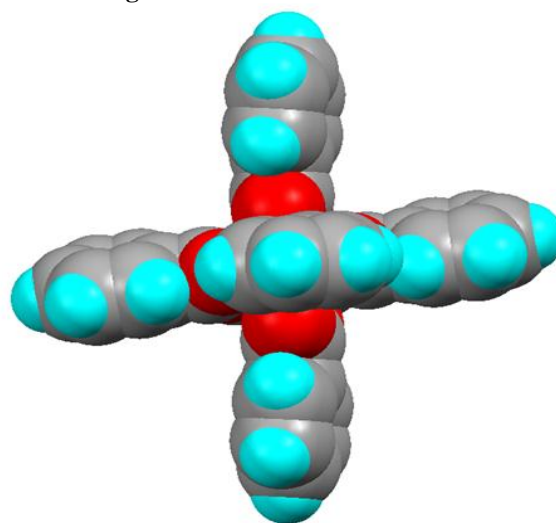
**Fig. 4.** (a) Intramolecular hydrogen bonding of Complex 1, (b) Inter molecular carbon-hydrogen-carbon bonding of Complex 1.

**Table 2.** Bond Valence Sums<sup>b</sup> for the Cu atoms of 1<sup>a</sup>

Complex	Atom	Cu(I)	Cu(II)
1	Cu 1	1.73	2.18
	Cu 1a	1.74	2.18

<sup>a</sup>The oxidation state of a particular atom is the nearest integer to the underlined value. <sup>b</sup>The underlined value is the closest to the charge for which it was calculated.

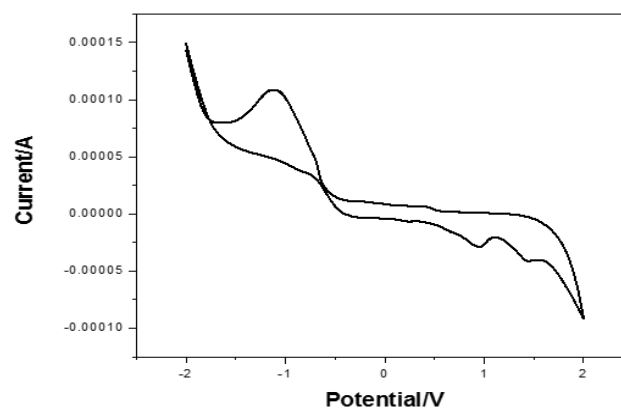
The axial bond length is 2.18Å between the Cu1-O3 and Cu1a-O3a in an octahedral geometry and because of Jahn-Teller distortion the complex has a tendency to transform its structure form an octahedral to square pyramidal structure. The nano molecular size of the complex (1) is found to be 1.55nm obtained from mercury software (distance of one molecular structure from one end to other end). From BVS calculation, it is confirmed that both the Cu atoms are in (II) oxidation state (shown in Table 2) [17-18]. **Fig. 3a, b, c** represents the unit cell packing structure of complex 1 along the a, b, c axes. Space filling model representation of the same compound is shown in **Fig. 5**.



**Fig. 5.** Space filling representation of the complex 1. (Colour Code: Cu, Green; O, Red; C, Gray; H, light blue).

#### Cyclic voltammetric study

Cyclic voltammogram (**Fig. 6**) of complex 1 indicates that two electron changes occur in the system and copper is present in +2 oxidation state in the complex. The upper portion of this voltammogram supports the reduction reaction of  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  (only one hump can be seen in that portion) but bottom portion of the voltammogram supports two oxidation steps of metal due to the appearance of two small humps in the curve. In the first step  $\text{Cu}(0)$  gets oxidised to  $\text{Cu}(I)$  and in the second step  $\text{Cu}(I)$  again gets oxidised to  $\text{Cu}(II)$  and gives the cyclic voltammogram.



**Fig. 6.** Cyclic voltammogram of the complex 1.

### Electronic absorption spectroscopy

The six coordinated Cu (II) belongs to the  $3d^9$  system. Therefore, the appearance of a single absorption band at 230.82 nm in the Fig. 7 is due to the  ${}^2E_g \rightarrow {}^2T_{2g}$  transition (d-d transition). The two small humps at 272.53 and 280.61 nm may arise because of the presence of Jahn-Teller distortion in the complex.

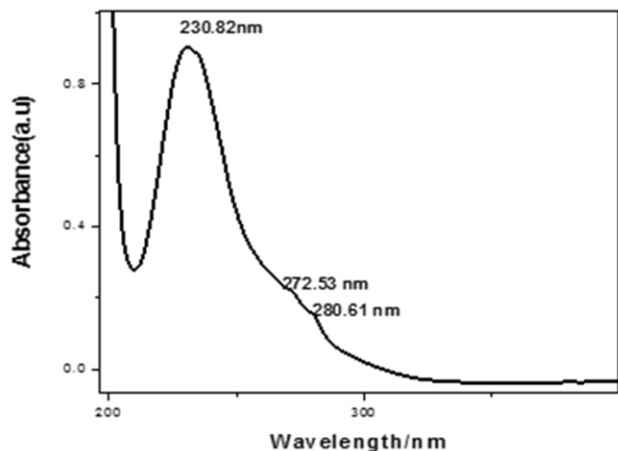


Fig. 7. UV-vis spectrum of the complex 1.

### FTIR analysis

The FTIR spectrum of the complex 1 is given in Fig. S11. The absorption band at  $3458\text{cm}^{-1}$  can be assigned as the intramolecular H-bonded O-H stretching frequency. The sharp band at  $1682\text{cm}^{-1}$  and  $1570\text{cm}^{-1}$  are C=O stretching frequency of the benzoic acid (specially of -COOH group) and of the benzoate ion (specially of COO<sup>-</sup> group) present in the molecule. The absorption band at  $1401\text{cm}^{-1}$  can be the stretching frequency of C-O-H in plane band and at  $1286\text{cm}^{-1}$  is due to C-O stretching and  $1179$  and  $1025\text{cm}^{-1}$  can be due to C-C stretching vibrations. The absorption band at  $854\text{cm}^{-1}$  can be assigned as O-H def (Out of plane). Most importantly the band at  $685$  and  $506\text{cm}^{-1}$  can be assigned as stretching frequency of Cu-O bond (O atom of the benzoic acid molecule bonded to the Cu atom axially) and stretching frequency of Cu-O bond (O atom of the benzoate anion attached to the Cu atom through chelation) respectively.

### Conclusion

In summary, we have explored the crystal structure of  $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4(\text{C}_6\text{H}_5\text{COOH})_2$  synthesized by Cu ( $\text{NO}_3$ )<sub>2</sub>·3H<sub>2</sub>O, Pb( $\text{NO}_3$ )<sub>2</sub>·PhCOOH and NaN<sub>3</sub> in exact proportion of (1:0.5:5:1) in MeCN/EtOH medium. Unfortunately, Pb is not incorporated in the cluster may be due to slight larger size of this heavy metal. The results of spectroscopic and structural studies reflect the structural stability of the complex surrounded by benzoate ion. The BVS calculation and CV support the fact that copper is in +2 oxidation state in the complex. The most interesting in complex 1 is both intra and intermolecular hydrogen (C-H-C) bonding present in the system. At present, we are exploring other reaction procedures and

conditions for the synthesis of our targeted heterometallic Cu-Pb clusters may change.

### Acknowledgements

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### Author's contributions

Conceived the plan: Tanmay K Ghorai; Performed the experiments: Sayantan Pathak; Data analysis: S. Pathak & T K Ghorai; Wrote the paper: Tanmay K Ghorai, S. Pathak (T K Ghorai are the initials of authors); X-ray crystallography analysis: Barun Jana and CV analysis: Niladri Biswas. Authors have no competing financial interests

### Supporting information

Supporting informations are available from VBRI Press.

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