

Synthesis, crystal structure and Thermogravimetry of *ortho*-phthalic acid bridged coordination polymer of Copper(II)

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Abstract. Coordination polymer of Cu(II) bridged by *o*-phthalic acid alone is not known. The reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with (2-butoxycarbonyl)benzoic acid yielded three dimensional coordination polymer bridged by *o*-phthalic acid. X-ray crystal structure shows structure with monoclinic $P2_1/c$ space group. *o*-Phthalic acid molecules act as bridge between two Cu(II), one carboxylate binds to one Cu(II) as bidentate while the other carboxylate binds to another Cu(II) as monodentate. The four planar co-ordination positions of Cu(II) are satisfied by two chelated carboxylates while fifth and sixth co-ordination positions are satisfied by monodentate carboxylates. EPR and TGA of the coordination polymer are also reported.

Keywords. *o*-Phthalic acid; coordination polymer; X-ray crystal structure; Copper(II); EPR; TGA.

1. Introduction

Coordination polymers have multifunctional properties with tremendous potential for applications in many fields like catalysis,^{1–3} separation,⁴ hydrogen storage,^{5,6} magnetic devices,⁷ non-linear optics,⁸ etc. By selecting appropriate metal ions and organic linkers, coordination polymers of different structures such as 1D chains, ladders, 2D grids and 3D networks could be designed.^{9–13}

Polycarboxylic acids have been widely used as linkers, as they can coordinate by a number of different modes, to synthesise coordination polymers of different structures.^{14,15} *o*-Phthalic acid has been widely explored as linker in synthesising coordination polymers.^{16–33} This immense popularity of *o*-phthalic acid as linker in coordination polymers is because of its ability to provide 26 different modes of coordination.³⁴ In all these reported coordination polymers, at least one other ligand is found to be present together with *o*-phthalic acid. *o*-phthalic acid in the absence of other ligands resulted in monomeric complexes when allowed to react directly with Cu(II) ion at room temperature.³⁵ There is no report of coordination polymer based on *o*-phthalic acid alone without incorporating other ligands.

We report herein for the first time, room temperature synthesis of three dimensional coordination polymer of Cu(II) with *o*-phthalic acid without incorporating any other ligand. To prevent formation of mononuclear complex, *o*-phthalic acid was not provided directly but generated *in situ* from (2-butoxycarbonyl)benzoic acid.

2. Experimental

2.1 Materials and methods

All the chemicals and solvents were purchased from Merck. The organic solvents were distilled. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was recrystallised from double distilled water before use. FTIR and UV-Visible spectra were recorded on Perkin Elmer RX1 FT-IR spectrophotometer and Shimadzu UV-1800 (with a 1.0 cm path length quartz cell) spectrophotometer, respectively. ¹H NMR spectra were recorded in Bruker ULTRASHILD 300 MHz instrument. The EPR spectra were recorded in JEOL JES-FA200. Electrochemical analysis was performed in CHI 600B Electrochemical Analyzer (USA) comprising of three electrode cell assembly. Platinum disc was used as working electrode, Ag-AgCl (3 M NaCl) as reference while a platinum wire as the counter electrode. The electrodes were cleaned as per reported procedure.³⁶

Single crystal X-ray diffraction data were recorded employing Bruker Smart APEX II (3 circle X-ray diffractometer). The intensity data for the complex were collected using Mo-K α radiation (0.71073 Å) at 293 K on a Bruker SMART APEX and Bruker KAPPA APEX II diffractometers, respectively. The SMART³⁷ program was used for collecting frames of data, indexing the reflections, and determination of lattice parameters; SAINT³⁸ program for integration of the intensity of reflections and scaling; SADABS³⁹ program for empirical absorption corrections. The structures were solved by direct methods (SHELXS-97) and standard Fourier techniques, and refined on F^2 using full matrix least

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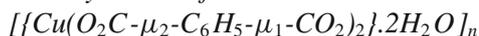
squares procedures (SHELXL-97) using the SHELX-97 package⁴⁰ incorporated in Win GX.⁴¹ All non-hydrogen atoms were refined anisotropically except for the two lattice water molecules which are in a highly disordered state. Hydrogen atoms were assigned idealized positions and given thermal parameters equivalent to either 1.5 (methyl hydrogen atoms) or 1.2 (all other hydrogen atoms) times the thermal parameter of the carbon atoms to which they are attached. Hydrogen atoms of the lattice water molecules were not found.

2.2 Synthesis of (2-butoxycarbonyl)benzoic acid (L)

1.48 g (10 mmol) phthalic anhydride and 0.91 mL (10 mmol) of 1-butanol were taken in 20 mL methanol and stirred at 60°C for 10 min; 2–3 drops of pyridine were added and stirring continued for another 2 h. An off-white product was obtained which was recrystallised from methanol. Yield: 0.304 g (85%); M.p. 178°C. FTIR (KBr, cm⁻¹): 3475 ($\nu_{\text{O-H}}$), 2962 ($\nu_{\text{C-H}}$), 1725 ($\nu_{\text{C=O}}$), 1417 ($\nu_{\text{C=C}}$), 1125 and 1293 ($\nu_{\text{C-O}}$). ¹H NMR (CDCl₃, 300 MHz, δ in ppm, TMS): 7.99–7.47 (m, 4H), 4.17 (m, 2H), 1.67–1.58 (m, 2H), 1.42–1.30 (m, 2H), 7.2 (t, 3H). Anal. Calcd. for C₁₂H₁₄O₄: C 64.86%; H 6.35%. Found: C 64.76%; H 6.48%.

The synthetic strategy for the preparation of the ligand (L) is summarized in scheme 1 below:

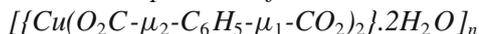
2.3 Synthesis of



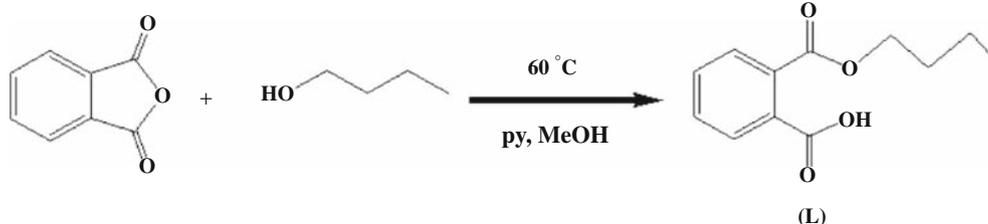
CuCl₂·2H₂O (0.170 g, 1 mmol) and L (0.358 g, 1 mmol) were stirred in 20 mL CH₃OH at room temperature for 2 h. Blue crystals were precipitated out from the reaction mixture on standing for seven days. Recrystallisation was done from 1:10 (v/v) mixture of CH₃OH: H₂O. Yield: 70%. MW 429.72.

3. Results and Discussion

3.1 FTIR spectrum of



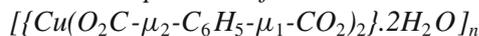
The FT-IR spectrum of the complex showed characteristic peaks due to the ligation of carboxylate.



Scheme 1. Synthetic path for L.

The peaks appearing in the region 1595–1611 cm⁻¹ can be attributed to $\nu_{\text{asym}}(\text{COO})$ vibrations while the peaks in the range 1382–1396 cm⁻¹ can be attributed to $\nu_{\text{sym}}(\text{COO})$ vibrations.

3.2 EPR spectrum of



The EPR spectrum of the complex was recorded as polycrystalline solid and has been shown in figure 1. The g_{iso} value and geometric parameter G, i.e., the measurement of exchange interaction between the copper centers were evaluated by using the following expression.^{42,43}

$$g_{\text{iso}} = (g_{\parallel} + 2g_{\perp}) / 3 \quad (1)$$

$$G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023) \quad (2)$$

The calculated value of g tensor parameter were $g_{\parallel} = 2.63$ and $g_{\perp} = 2.47$. Hence $g_{\parallel} > g_{\perp} > 2.0023$ which reveals that $d_{x^2-y^2}$ is the ground state.⁴⁴ The value of G was calculated to be 1.34 which is less than 4 indicating effective interaction between the copper centers.⁴⁵

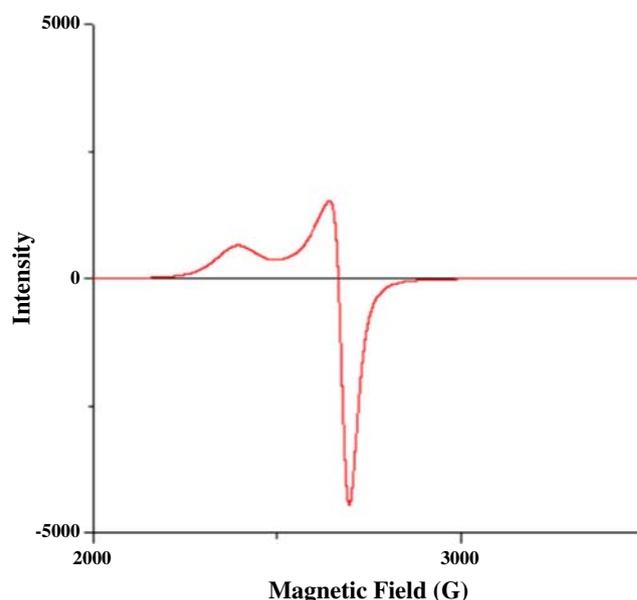


Figure 1. EPR spectrum of the coordination polymer in polycrystalline state.

3.3 Thermogravimetric analysis (TGA) of $[\{Cu(O_2C-\mu_2-C_6H_5-\mu_1-CO_2)_2\} \cdot 2H_2O]_n$

Figure 2 shows the TGA curve of the coordination polymer. The weight loss was observed from 180°C to 400°C. The first weight loss is a well-defined step with initiation temperature 180°C due to loss of guest water molecules while the second and the third weight losses are combined ones with initiation temperatures *ca.* 270°C and 340°C, respectively. The total weight loss in the three step process is 81.95% which accounts for the loss of phthalic acids from one monomeric unit

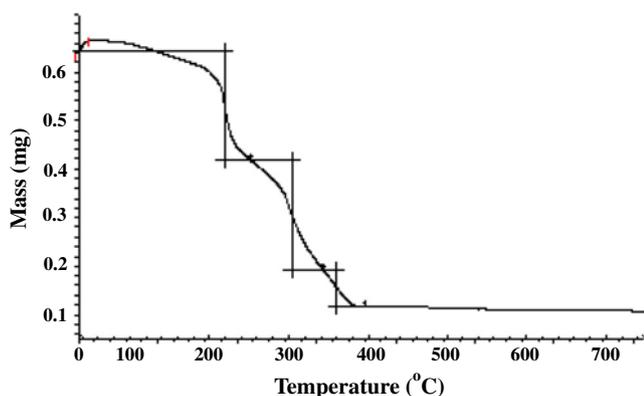


Figure 2. TGA curve of the coordination polymer.

of the coordination polymer and formation of CuO as the final residue (calculated value of weight loss is 81.49%).

3.4 Magnetic moment measurement of $[\{Cu(O_2C-\mu_2-C_6H_5-\mu_1-CO_2)_2\} \cdot 2H_2O]_n$

To investigate the spin state of Cu²⁺ in the complex, the magnetic susceptibility measurement was done at 298 K from mass susceptibility measurement. The mass susceptibility, χ_g , is calculated using the equation:

$$\chi_g = [C_{Bal} \times l \times (R - R_0)] / 109 \times m \quad (3)$$

Where l = the sample length (cm), m = the sample mass (g), R = the reading for the tube plus sample, R_0 = the empty tube reading, C_{Bal} = the balance calibration constant. Then molar susceptibility, $\chi_m = \chi_g \times$ molecular mass of the complex. The effective magnetic moment, μ_{eff} , is then calculated using the expression: $\mu_{eff} = 2.83\sqrt{(\chi_m \times 298)}$. The experimental value of magnetic moment was calculated to be 1.78 BM which is almost equal to the spin only magnetic moment value due to Cu²⁺ ion, which is 1.732 BM. Hence, the Cu(II) ions in the co-ordination polymer are magnetically independent and should be well separated.

Table 1. Crystal data and structure refinement for $[\{Cu(O_2C-\mu_2-C_6H_5-\mu_1-CO_2)_2\} \cdot 2H_2O]_n$.

CCDC Number	903426
Empirical formula	:C ₁₆ H ₁₀ Cu O ₈ · 2H ₂ O
Formula weight	:489.79
Temperature	:296(2) K
Wavelength	:0.71073 Å
Crystal system, space group	:Monoclinic, $P2_1/c$
Unit cell dimensions	:a = 11.0782(11) Å alpha = 90 deg. b = 6.6521(7) Å beta = 101.798(4) deg. c = 12.1645(12) Å gamma = 90 deg.
Volume	:877.50(15) Å ³
Z, Calculated density	:2, 1.854 Mg/m ³
Absorption coefficient	:1.328 mm ⁻¹
F(000)	:494.0
Crystal size	:0.38 × 0.32 × 0.24 mm
Theta range for data collection	:3.42 to 27.49 deg.
Limiting indices	:-14 ≤ h ≤ 14, -7 ≤ k ≤ 8, -15 ≤ l ≤ 15
Reflections collected / unique	:8917 / 2004 [R(int) = 0.0275]
Completeness to theta = 27.49	:94.7%
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	:1899 / 0 / 147
Goodness-of-fit on F ²	:1.065
Final R indices [I > 2sigma(I)]	:R1 = 0.0545, wR2 = 0.1878
R indices (all data)	:R1 = 0.0634, wR2 = 0.2144
Extinction coefficient	:0.023(6)
Shift/esd max	:0.000
Largest diff. peak and hole	:0.901 and -1.389 e.Å ⁻³

$$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2} \text{ where } w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP] \text{ with } P \text{ is } [2F_o^2 + \text{Max}(F_o^2, 0)] / 3$$

3.5 X-ray crystallography of $[Cu(O_2C-\mu_2-C_6H_5-\mu_1-CO_2)_2] \cdot 2H_2O$

Discrete single dark blue crystals of the compound suitable for X-ray studies were obtained from the concentrated reaction mixture by allowing the resulting solution to stand for seven days at room temperature. Recrystallization of the complex was done from 1:10 (v/v) mixture of $CH_3OH:H_2O$. The complex crystallizes in the monoclinic crystal system with $P2_1/c$ space group. The crystallographic data has been shown in table 1. Selected bond lengths [\AA] and bond angles [deg.] for the compound have been shown in tables 1 and 2.

The unit cell structure of the complex is shown in figure 3. The structure shows that the butoxy group from the ligand is lost during the formation of the complex and phthalic acid acts as a bridging ligand in the complex. Each Cu(II) ion is coordinated with four phthalate ligands completing an octahedral structure with six O atoms. Out of the four phthalate two coordinates to the Cu(II) through both O atoms of one carboxylate as chelate. These two chelating carboxylates are found to be in trans position to each other. Each of the

Table 2. Selected bond lengths [\AA] & bond angles [deg.] for $[Cu(O_2C-\mu_2-C_6H_5-\mu_1-CO_2)_2] \cdot 2H_2O$.

Cu(1)-O(3)	1.943(10)
Cu(1)-O(4)	1.973(11)
O(3)-Cu(1)-O(4)	91.0(5)

Symmetry transformations used to generate equivalent atoms

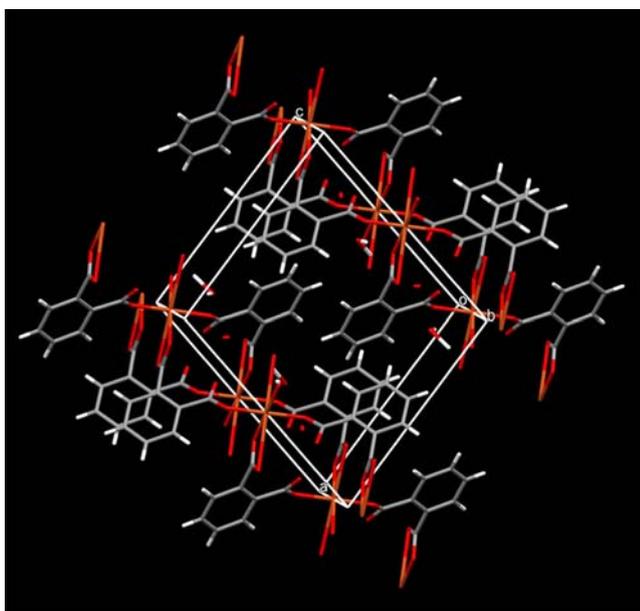


Figure 3. Packing of Cu complex showing the coordination environment around Cu along (101) plane.

other carboxylates (of these two phthalates) binds to another Cu(II) through only one O atom while the other O dangles as keto group. The other two trans coordination sites of the Cu(II) are fulfilled by carboxylate O atoms of phthalate of which the remaining carboxylates chelate to two Cu(II). In this way, a three dimensional network is generated where each phthalate acts as a bridge between two Cu(II), and coordinating to one Cu(II) by the monodentate carboxylate oxygen and to another Cu(II) by chelating carboxylate.

In the compound the two trans O-Cu(II)-O angles created each by the two O atoms of a chelating carboxylate and the Cu(II) ion were found to be equal which is 53.19° . The other two O-Cu(II)-O angles were of value 126.81° . Interestingly the axial Cu(II)-O bonds were not perfectly perpendicular to the plane of four equatorial O atoms from two chelating carboxylates. Each of the axial Cu(II)-O bonds were found to be tilted slightly towards one of the two equatorial chelating carboxylate pairs. The O-Cu(II)-O angles involving one axial O atom and the O atoms from one pair of chelating carboxylate are 92.67° and 90.99° while these angles with the other pair of carboxylate are 89.01° and 92.67° .

The distance between the two Cu(II) bound O atoms belonging to the same carboxylate is 2.216\AA while the distance between the two O atoms (on the same side of the coordination core) belonging to two different carboxylates is 4.22\AA . Hence, the equatorial O_4 core around the Cu(II) ion in the complex is rhombohedral. The asymmetric unit of the complex is shown in figure 4.

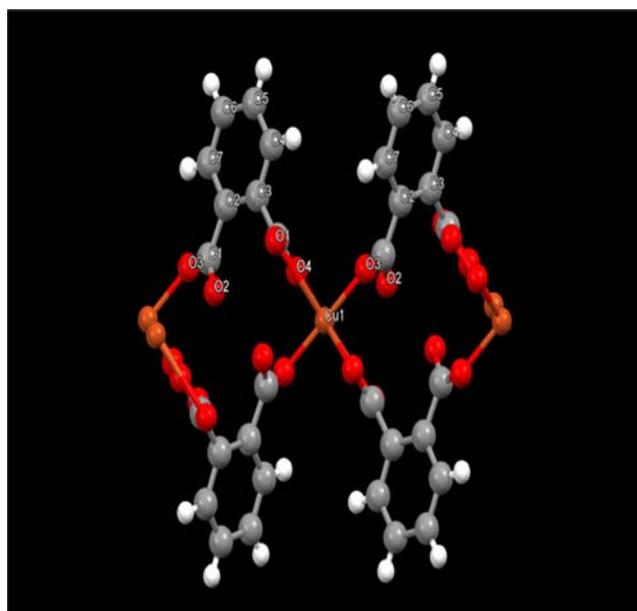


Figure 4. Phthalic acid coordinating with Cu1 through carboxylate oxygen in monodentate fashion.

The coordination of two carboxylic groups of a phthalate to two different Cu(II) finally gives rise to a polymeric structure. Figure 5 shows the two dimensional structure of the polymeric system. In the three dimensional structure shown in figure 6 specific holes are clearly visualised. It also shows van der Waals interaction ($\pi - \pi$) between the phthalate aromatic rings. The crystal packing arrangement of the compound is stabilized by the intermolecular O-H \cdots O interactions ($\sim 2.158 \text{ \AA}$) between solvent water hydrogen and carboxylate O atom.

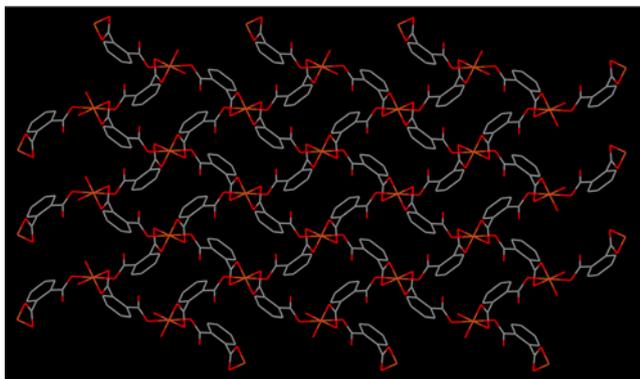


Figure 5. Two dimensional structure of the polymeric Cu(II) complex.

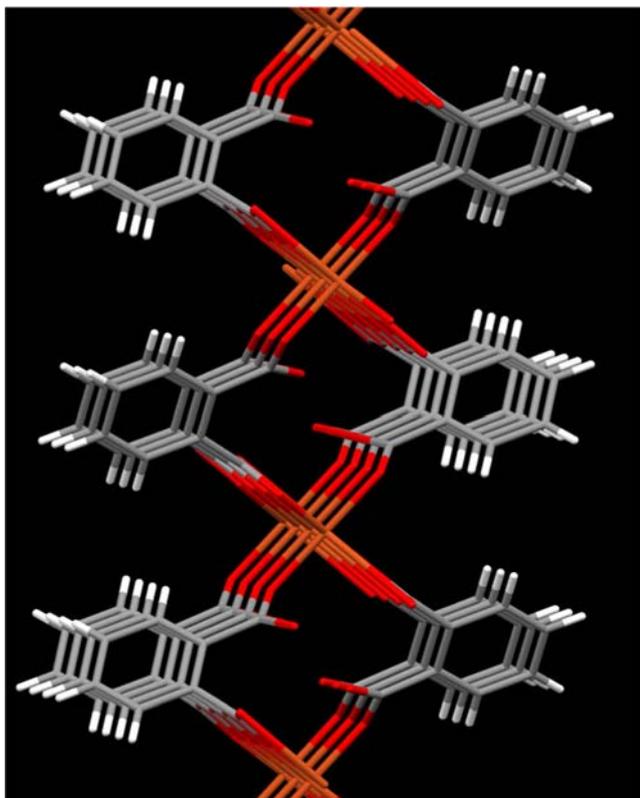


Figure 6. Three dimensional polymeric structure of the Cu(II) complex.

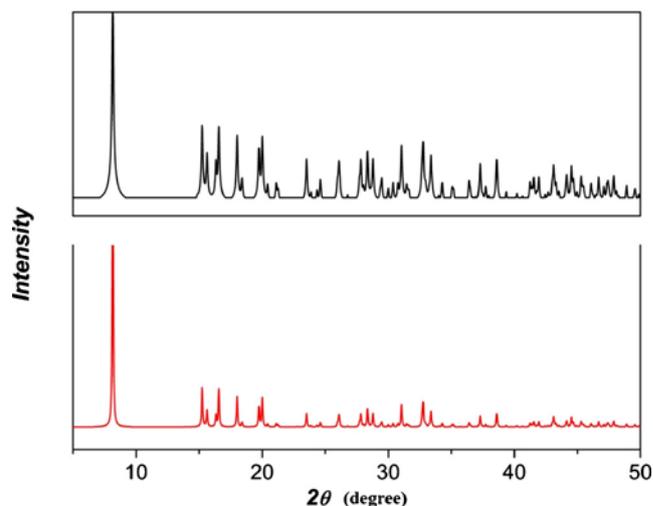


Figure 7. Observed (above) and calculated (below) powder X-ray diffraction of $\{-\text{Cu}(\mu_2\text{-O}_2\text{C-C}_6\text{H}_5\text{-CO}_2\text{-}\mu_1\text{-})_2\cdot 2\text{H}_2\text{O}\}$.

3.6 Powder X-ray diffraction study

To prove the bulk purity of the complex synthesized by us, powder X-ray diffraction data was also collected for the complex. A close similarity observed between observed and calculated X-ray diffraction patterns prove the bulk purity of the complex (figure 7).

4. Conclusions

A novel three dimensional co-ordination polymer of Cu(II) with *o*-phthalic acid was obtained on reaction of CuCl_2 and 4-(2-butoxycarbonyl)benzoic acid. X-ray crystallographic studies have shown a 3D coordination polymer with specific holes. TGA curve showed three weight losses with final composition as CuO .

Supplementary Information (SI)

All additional information pertaining to characterization of the cocrystals, namely, FT-IR spectrum (figure S1), ^1H NMR spectrum (figure S2) and CIF (pdf file) are available at www.ias.ac.in/chemsci.

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