# SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NANO-SCALE TWIN CRYSTAL OF COPPER TARTARATE

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## ABSTRACT

Twin crystal structure coordination compound [Cu (Tar)$_2$(2H$_2$O)] was synthesized using soft synthetic method by reaction of Cu (II) salt with tartaric acid after complete dissolution of the two reactants. The compound was characterized by Elemental Analysis, Infrared, UV and Visible spectroscopy and Single crystal x-ray diffraction. Elemental Analysis, Infrared, UV and Visible spectroscopy vividly showed the coordination of the deprotonated group of the tartaric acid being coordinated to the copper metal. The 3 dimensional model of the compound revealed twin compound to be found in every single crystal of the compound.The crystals display triclinic space group with $a$ = 6.7007 (8) Å, $b$ = 7.3002 (9)Å, $c$ = 8.9439 (14) Å, $α$ = 68.499 (4)$^0$, $β$ = 79.764 (6)$^0$ and $γ$ = 65.703 (4)$^0$ by exhibiting octahedral geometry. Each copper (II) ion is thus coordinated to six oxygen atoms; 2 carboxylate oxygen, two hydroxyl oxygen and two oxygen from water molecule.

**KEYWORDS:**Synthesis, characterization, x-ray christallography

## INTRODUCTION

Nano scale compounds as an important aspect of nanotechnology have engrossed much attention in the past few years due to their vast potential applications in sensory, magnetic, adsorption drug delivery, catalysisand gas storage [1].In contrast toinorganic materials like zeolite whose pores are restricted by inflexible tetrahedral oxideframework that are difficult to alter [2,3], the compositions and structures of nano-scale compounds arenumerousdue to the choice of a vast range of metal ions andorganic bridging ligands through the vital process of self-assembly at the molecular stage [4]. The resulting nano-scale materials incorporate open framework of three dimensionalstructures with vast chemical and structuraldiversity making them useful for numerous applications in different fields. This novel characteristics display by nano-materials is due to higher porosity and diversity of structural and functionality of various organic linker and metal ions [5].

Nano scale compounds embody a distinctive class of ordered porous materials that have huge potential in guest and host exchange that require pore sizes that surpass those found in zeolites[5]. This can be achieved by selecting proper building blocks during synthesis; framework with voids of predefined shapes can be formed for an anticipated application [3].

The synthesis of nano scale compounds are usually carried out at temperature higher than room temperature after complete dissolution of both the ligands and metal salt after which the two solutions are mixed and thermally treated via

refluxing or autoclave in an oven for crystallization at preferred synthetic conditions. The main factors for the synthesis of nano scale compounds are concentration, pH, temperature and time of reaction. Common polar solvents usually used during synthesis includes water, dimethyl sulfoxide dimethyl/ethyl formamides, acetone ethanol, methanolor acetonitrile[1,4].

Thousands of different nano-compounds have been synthesized and have their structure deposited in the Cambridge Structural Database (CSD) up till date. This number of nano-compounds represents only a small portion of comprehendiblenano-compounds that can still be synthesized due to the large diversity of potentialorganic linker and metal ions combinations. In lieu of this, our work focuses on synthesis and characterization of nano-scale twin crystal of copper tartarate.
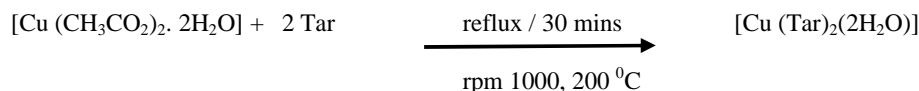
## EXPERIMENTAL

### Materials and Physical Measurements

Materials and solvents were obtained from Sigma Aldrich Company and used without distillation. Melting points were determined using a WRS-1B digital melting point apparatus. The elemental analyses were measuredon a Perkin-Elmer CHN Analyzer 2400 series II. The IR data were experimented using the SHIMADZU scientific model FTIR 8400s Spectrophometer. X-rays were spawned by an accelerating voltage of 30 kV and a current flow of 40 mA.A receiving slit of 0.6mm and a primary secondary slits of 2.5 mm were used. Samples were placed on a zero background sample holder and scanned over a range of $4^o$ to $40^o$ with a step size of 0.01 $^o\text{s}^{-1}$. X-ray Crystallographic analysis of the MOFs was carried out using a Nonious Kappa CCD diffractometer and graphite monochromated $M_oK$ radiation. Direct method was used in solving the structureand $F^2$ was refined against all reflections. Structural solution and refinement were adept using SIR97 and SHELXL97.

### Synthesis of [Cu (Tar)$_2$(2H$_2$O)]

Single crystal of copper tartarate nano-compound was synthesized by dissolving 1 mMol of Tartaric acid in water and copper acetate dihyrate [Cu(CH$_3$CO$_2$)$_2$. 2H$_2$O] of 0.5 mMolwas dissolved in methanol. The two solutions were mixed together and few drops of Triethylamine were added for deprotontion. The mixed solution was refluxed at 200 $^0$C for 30 minutes under 1000 revolution per minutes (rpm). A clear light blue solution was obtained and left standing for slow evaporation at room temperature to take place. Blue crystals were formed after 14 days. The light green crystals formed was separated out by filtration and washed with mixture of water and methanol in ratio 1:1 and dried at room temperature in a desiccator. Yield: 58 % M. wt. = 247.65 g/mol, M. pt. = 204 $^o$C, Analc. Found (Calcd) % for [C$_8$H$_{14}$O$_8$Cu]: C, 19.32 (19.38); H, 3.19 (3.23); N, <0.04 (0.00), IR (KBr, cm$^{-1}$): 2933, 1751, 1273, 761, 624. UV-Vis (DMSO) nm: 203, 220, 433.

The equation of reaction is shown below:

$$[\text{Cu (CH}_3\text{CO}_2)_2.\ 2\text{H}_2\text{O}] + 2\ \text{Tar} \xrightarrow[\text{rpm 1000, 200 }^0\text{C}]{\text{reflux / 30 mins}} [\text{Cu (Tar)}_2(2\text{H}_2\text{O})]$$

Tar = Tartaric acid

## RESULTS AND DISCUSSIONS

C, H and N for both tartaric acid and [Cu (Tar)$_2$(2H$_2$O)] were consistent with the formula units of the products as shown in Table 1.

The melting points and colours of the MOFs suggest the complexation of tartaric acid with metal ion used during synthesis.Comparison of the elemental analysis result (Table 1) and FT-IR spectra (Table 2) showed that the MOFs synthesized coordinated. The compounds were insoluble in solvent used for the dissolution of the reactants.

**Table 1: Physical and Analytical Data of Tartaric acid and its MOFs**

| Ligand/Nano-Compound | Appearance of Ligand/ MOFs | Appearance of Metal Salt | Yield (%) | Molecular Weight (g/mol) | Melting Point (°C) | Elemental analysis % Found (% Calculated) CHN | | |
|---|---|---|---|---|---|---|---|---|
| Tartaric acid | White powder | - | - | 150.09 | 172 | - (2.67) | - (3.99) | - (-) |
| [Cu(Tar)$_2$(2H$_2$O)] | Light green crystals | Deep green | 58 | 247.65 | 204 | 19.32 (19.38) | 3.19 (3.23) | <0.04 (0.00) |

### FT-IR Spectra of Tartarate Acid and its Nano-Compound

The relevant IR band frequencies of the tartarate ligand and its nano-compound are represented in Table 2. It can be seen from the table that copper tartarate has spectrum different from that of the ligand used.

**Table 2: FT-IR Data (cm$^{-1}$) of Tartaric Acid and its Copper Tartarate**

| Ligand/Nano-compound | ν(O-H) (cm$^{-1}$) | ν(C-C) (cm$^{-1}$) | ν(C=O) (cm$^{-1}$) | ν(C-O) (cm$^{-1}$) | ν(M-OH) (cm$^{-1}$) | ν(M-O) (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| Tartaric acid | 3361m | 2644m | 1751s | 1290s | | |
| [Cu(Tar)$_2$.2H$_2$O] | 2933m | 2933m | 1751s | 1273s | 748w | 624w |

m= medium, s= strong, w= weak

The infrared spectra of the MOFs in 4000 – 500 cm$^{-1}$ were compared with those of tartaric acid as shown in Table 2. Tartaric acid is a dicarboxylic acid having coordination sites at only the carboxylic acid functional groups.From table 2 above, peaks characteristics of tartaric acid are obtained in the spectra of the copper tartarate, an indication that the ligand is coordinated to the metal ion. The characteristic broad band at 3361 cm$^{-1}$ due to the ν (O-H) in the tartaric acid shifted to 2933, this indicates the existence of deprotonated form of the tartarate group in the copper tartarate and coordination through the O-H group. Also, the absorption bands of the ν(C-O) that appeared in tartaric acid at 1290 cm$^{-1}$ was observed to have shifted to 1273 cm$^{-1}$ for copper tartarate. This clearly indicates the coordination of the metal to tartarate through the carbonyl group (C-O). The coordination of water molecules to the metal ion results in the appearance of vibrational band at 748 cm$^{-1}$ for copper tartarate. The water molecules present were confirmed to be coordinated rather than lattice water by heating a known weight of copper tartarate at 100 $^0$C for 10 minutes, no weight loss was observed.

### Electronic spectra for Tartarate Acid and its Nano-Compound

The UV-Visible spectra of tartarate acid and its nano-compound as shown in Table 3 and show that the copper tartarate coordinated with the central metal and show peaks different from free tartarate acid.

**Table 3: Selected UV-Visible Spectroscopy Data of Tartaric Acid and Copper Tartarate**

| Compound /Ligand | Wavelength (nm) | Assignment |
|---|---|---|
| Tartaric acid | 240 | $\pi - \pi^*$ |
| | 317 | $n - \pi^*$ |
| [Cu(Tar)$_2$(2H$_2$O)] (**3a**) | 203 | $\pi - \pi^*$ |
| | 220 | $n - \pi^*$ |
| | 433 | $^2E_g \, ^2T_{2g}$ |

The UV-Visible spectra of tartaric acid and its complexes as shown in Table 3 show that the spectra obtained from the complexes are different from that of the free tartarate acid.

Table 3 shows that the UV-Vis spectrum of tartarate acid has bands at 240 nm and 317 nm which are assigned to $\pi$ - $\pi^*$ and $n$-$\pi^*$ respectively representing C=C and C=O bands. These bands are well represented in the copper tartarate confirming coordination of the ligand in the complex. The excitation of electron in the d orbital of $Cu^{2+}$ incopper tartarate with wavelength 433 nm show a band attributed to $^2E_g \, ^2T_{2g}$▶

**X-ray Crystallographic Analysis of [Cu (Tar)$_2$(2H$_2$O)]**

The molecular structure of the compound [Cu (Tar)$_2$(2H$_2$O)] is shown in Figure 1 with atomic numbering scheme used. Table 4 to 6 present the crystal structural data, selected bond distance and angle and inter molecular and intra molecular hydrogen bond respectively.

**Table 4: Crystal Structural Data of [Cu (Tar)$_2$(2H$_2$O)]**

| Identification Cypher | [Cu(Tar)$_2$(2H$_2$O)] |
|---|---|
| Empirical formula | C$_4$H$_8$CuO$_8$ |
| Formula weight | 247.65 |
| Cu $K\alpha$ radiation | $\lambda = 1.54180$ Å |
| Crystal system | Triclinic |
| Space group | P |
| Hall symbol | -P1 |
| Crystal shape/colour | Plate/blue |
| Unit cell dimensions | $a = 6.7007$ (8) Å <br> $b = 7.3002$ (9) Å <br> $c = 8.9439$ (14) Å <br> $\alpha = 68.499$ (4)$^0$ <br> $\beta = 79.764$ (6)$^0$ <br> $\gamma = 65.703$ (4)$^0$ |
| Cell volume (Å$^3$) | $V = 370.81$ (6) Å$^3$ |
| Z value | 2 |
| Density (calculated ) (g cm$^{-3}$) | 2.218 Mg m$^{-3}$ |
| $F$(000) | 250 |
| $\Theta$ range for data collection | 7–69$^0$ |
| Cu $K\alpha$ radiation, | 1.54180 Å |
| Cell parameters | 4287 reflections |
| Crystal size min, mid, max | $0.18 \times 0.11 \times 0.02$ mm |

**Table 5: Selected Bond Distances (Å) and Angles ($^0$) for[Cu (Tar)$_2$(2H$_2$O)]**

| Bond length (Å) | | Bond Angles ($^0$) | |
|---|---|---|---|
| Cu1—O7 | 2.3441 (12) | O7—Cu1—O3 | 93.64 (4) |
| Cu1—O3 | 1.9910 (10) | O7—Cu1—O1 | 85.45 (4) |
| Cu1—O1 | 1.9300 (10) | O3—Cu1—O1 | 82.62 (4) |
| Cu2—O4 | 2.2802 (11) | O1—Cu1—O1 | 179.994 |
| Cu2—O8 | 2.0156 (11) | O3—Cu1—O3 | 179.994 |
| Cu2—O6 | 1.9670 (11) | O4—Cu2—O8 | 89.45 (4) |
| O1—C1 | 1.2339 (19) | O4—Cu2—O6 | 77.06 |
| O2—C1 | 1.2339 (19) | O8—Cu2—O6 | 89.25 (5) |
| O3—C2 | 1.4236 (18) | O4—Cu2—O4 | 179.995 |
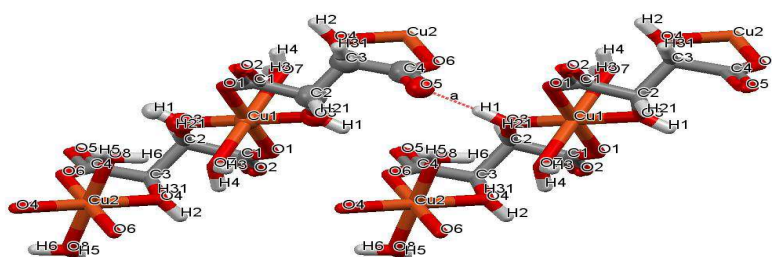


**Figure 1: 3 D Model of [Cu (Tar)$_2$(2H$_2$O)] Showing all Atoms and Numbering**

Single crystal x-ray diffraction analysis of the crystal compound revealed that the formula unit of the compound is symmetrical with 2 fold deprotonated tartarate ions, and two water molecules directly bonded to copper metal via their oxygen. The crystals are triclinic, with $a = 6.7007$ (8) Å, $b = 7.3002$ (9) Å, $c = 8.9439$ (14) Å, $\alpha = 68.499$ (4)$^0$, $\beta = 79.764$ (6)$^0$ and $\gamma = 65.703$ (4)$^0$. The complex exhibits an octahedral geometry. Each copper (II) ion is thus coordinated to six oxygen atoms (2 carboxylate oxygen, two oxygen from hydroxyl group and two oxygen from water molecule). The two tartaric acid were deprotonated prior to coordination to the copper (II) ion. The hydroxyl oxygen does not undergo deprotonation but rather coordinate to the copper ion via dative bonding.

The Cu (II) ion is octahedrally coordinated to two carboxylate oxygen with average Cu-O bond length of 1.930 Å comparing favourably with the range 1.930-1.990 Å [6] usually observed for copper complexes. The Cu-OH of 1.991 Å is very uncommon because most hydroxyl group from literature deprotonate prior to coordination, therefore, the coordination most have resulted from the lone pair of electron on the oxygen atom. This phenomenon described the special character of this compound.

Geometric distortion of a non-linear molecular system are also well observed in the octahedral coordination of this crystal complex where the two Cu-OH$_2$ axial bond are significantly longer (2.344 Å) than the Cu-O axial bonds thereby displaying Jahn-Teller distortion effect[7] a phenomenon that is very common in six-coordinate copper(II) complexes[7,8] The $d^9$ electronic configuration of the copper ion gives three electrons in the two degenerate $e_g$ orbitals, leading to a doubly degenerate electronic ground state. Such complexes distort along one of the molecular fourfold ax, which has the effect of removing the orbital and electronic degeneracies and lowering the overall energy.

The distortion normally takes the form of elongating the bonds to the ligands lying along the one of the fourfold axis, but occasionally occurs as a shortening of these bonds instead.

The crystallographic geometrical parameters are in good agreement with those reported from in the literature for compound containing Cu-O, Cu-OH and Cu-OH$_2$ bonds [6, 9, and 10]. The framework of the structure gave a neutral charge.
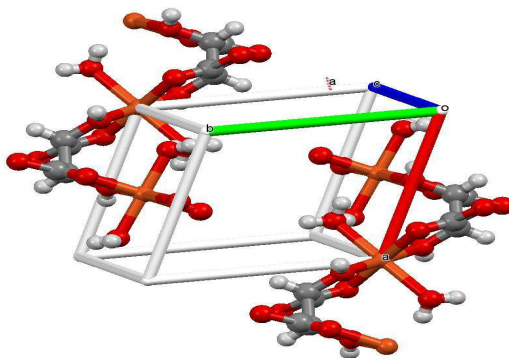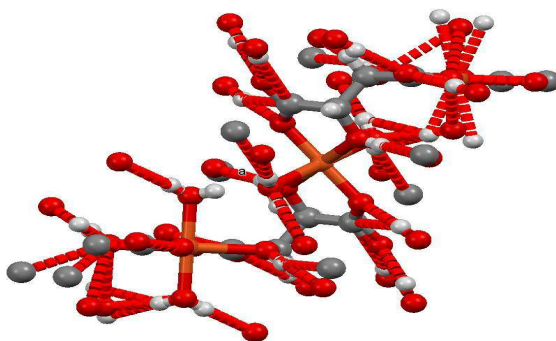


**Figure 2: 3 D Packing Mode of [Cu (Tar)$_2$(2H$_2$O)]**



**Figure 3: 3 D Short Contactof [Cu (Tar)$_2$(2H$_2$O)]**

The structure of the compound is polymeric (Figure 2 and Figure 3) based on the fact that the Copper central metal is linked to two symmetry equivalent tartarate ion which in turns can also be coordinated to another copper ion through its oxygens thereby exhibiting a coordination number of 6 (octahedral).

The crystal packing is depicted in Figure 2. The packing of the [Cu(Tar)$_2$(2H$_2$O)]in the crystal structure consist of chain parallel to the c-axis, mutually interacting through the hydrogen bonding, hence contributing the stability of the crystal structure. The H atoms were all positioned geometrically. $U_{iso}$(H) (in the range 1.2 times $U_{eq}$ of the parent atom), the positions were refined with riding constraints.

**Table 6: Intermolecular Interaction Distances (Å) for [Cu (Tar)$_2$(2H$_2$O)]**

| $D$—H···$A$ | Symm | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|---|
| O3-H1...O5 | -x,-y+1,-z+1 | 0.83 | 1.75 | 2.576 (2) | 177 (2) |
| O3-H1...C4 | -x,-y+1,-z+1 | 0.83 | 2.53 | 3.300 (2) | 154 (2) |
| O4-H2…O1 | -x+1, -y,-z+2 | 0.82 | 1.91 | 2.716 (2) | 167 (2) |
| O7-H3...O2 | -x,-y+1,-z+2 | 0.81 | 1.89 | 2.698 (2) | 176 (2) |
| O7-H4...O2 | x-1, y, z | 0.81 | 2.00 | 2.770 (2) | 160 (2) |
| O8-H5…O5 | -x+1, -y+1,-z+1 | 0.80 | 2.12 | 2.915 (2) | 170 (2) |
| O8-H6…O7 | x+1, y, z-1 | 0.82 | 1.89 | 2.701 (2) | 171 (2) |
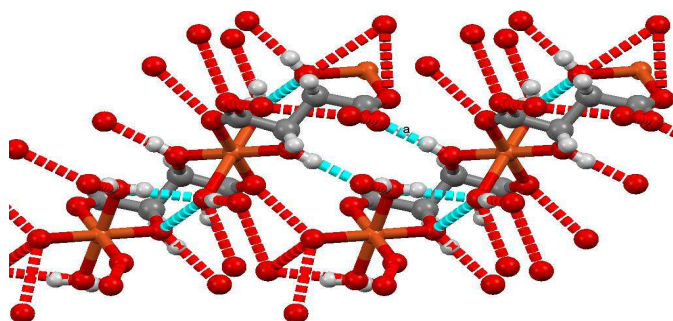


**Figure 4: Inter and Intra Molecular Hydrogen Bond of [Cu (Tar)$_2$(2H$_2$O)]**

The polymeric nature of the compound is achieved by intermolecular hydrogen of the type O-H…O through its short contact. It has been demonstrated here that hydrogen bonds play important roles in the self-assembly of the polymeric copper (II) complex of the tartarate. Hydrogen bonding turns out to be one of the dominating stabilizing contributions in the crystal packing.

## CONCLUSIONS

Twin crystal compound of [Cu (Tar)$_2$(2H$_2$O)] was synthesized via refluxing. Physicochemical parameters were characterized using different equipment and which they all concurred with the crystallographic structure of the compound,revealing that the compound exhibits an octahedral geometry. Each copper (II) ion is thus coordinated to six oxygen atoms; 2 carboxylate oxygen, two oxygen from hydroxyl and two oxygen from water molecule.

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