

Crystal structure of copper(II) citrate monohydrate solved from a mixture powder X-ray diffraction pattern

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The crystal structure of copper(II) citrate monohydrate ($C_6H_4O_7Cu_2 \cdot H_2O$) has been solved from a mixture powder diffraction pattern. Approach to indexing, structure solution and Rietveld refinement of multiphase diffraction patterns is discussed. Rietveld refinement is carried out employing free-atom refinement and rigid body refinement. © 2013 International Centre for Diffraction Data.

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Key words: powder diffraction, structure solution, X-ray diffraction, multiphase powder diffraction, Rietveld refinement

I. INTRODUCTION

In the past decade, crystal structure solution from powder diffraction data has become a viable alternative to single-crystal diffraction in obtaining accurate structural information of materials (Harris and Cheung, 2004; David and Shankland, 2008; Le Bail *et al.*, 2009; Rubčić *et al.*, 2012). Besides the fact that new materials are often prepared in the form of polycrystalline powders, structural characterization by powder diffraction experiment has another enormous benefit since it is performed on the bulk material rather than on one isolated single crystal. Moreover, materials are sometimes obtained not as a pure phase but in a mixture with other known or unknown phases (Halasz and Dinnebier, 2010). While Rietveld refinement (Rietveld, 1969) of multiphase diffraction patterns in principle presents no problem, indexing of more than one phase in a powder diffraction pattern and subsequent structure solution may be challenging. This is particularly difficult if the peaks belonging to different phases cannot be distinguished on the grounds of e.g. different peak widths (Dinnebier *et al.*, 1997).

One of the growing areas in material research is the construction and characterization of new coordination polymers, especially the porous metal-organic frameworks (Férey, 2008; Zhou *et al.*, 2012). However, the rational design of coordination polymers with desired framework and properties represents a challenge since their synthesis depends on many factors – starting chemicals, precursors, solvent, structure-directing agents, reaction temperature, or reaction time (Stock and Biswas, 2012). Copper(II) salts with citric acid have been long studied, both in solution (Dunhill *et al.*, 1966) and in the solid state (Pickering, 1912). The crystal structure of copper(II) citrate dihydrate has previously been solved from single-crystal diffraction data (Mastropaolo *et al.*, 1976; Zhang *et al.*, 2006). To the best of our knowledge, no report of the copper(II) citrate monohydrate has thus far been made. Similar reaction conditions as by Zhang *et al.* (2006) have in our experiments yielded a mixture sample of, what turned out to be, a monohydrate and the known

dihydrate. Herein we report on the crystal structure of copper(II) citrate monohydrate solved from a mixture powder diffraction pattern.

II. EXPERIMENTAL

A. Sample preparation

The clear starting solution was prepared by dissolving 8.2 mmol of $Cu(NO_3)_2 \times 3 H_2O$ (p.a., Kemika) and 6.8 mmol of citric acid monohydrate (p.a., Kemika) in 21.3 ml of demineralized water prepared in our laboratory. The solution was poured into a Teflon lined autoclave and put in a convection oven preheated to 120 °C. Intergrown small crystals were obtained after heating for 48 h and cooling in air. The ground material was turquoise in color.

B. High-resolution laboratory diffraction

High-resolution X-ray powder diffraction patterns (Bruker D8 ADVANCE in Debye-Scherrer geometry with Vântag-1 position sensitive detector with a 6° opening angle and $CuK\alpha_1$ radiation from primary Ge(111)-Johansson-type monochromator, step size of 0.00853° in 2θ) were used for indexing, structure solution, and refinement. Sample was gently crushed in an agate mortar into a fine powder and packed in 0.5 mm borosilicate glass capillary. The capillary was rotated during data collection for better particle statistics. Data were collected for 12 h in the angular range from 5 to 90° in 2θ . Herein, all the calculations were performed using the program TOPAS (Version 4.2, Bruker-AXS, 2007).

III. RESULTS AND DISCUSSION

A. Indexing, unit cell, and space group determination

Initial indexing of the powder diffraction pattern provided no solution and the pattern seemed to be unusually rich in peaks (Figure 1). Therefore, we have assumed that the pattern might correspond to a mixture sample. Inspection of the Cambridge Structural Database (CSD) revealed a known crystal structure of a copper(II) citrate dihydrate (CSD refcode

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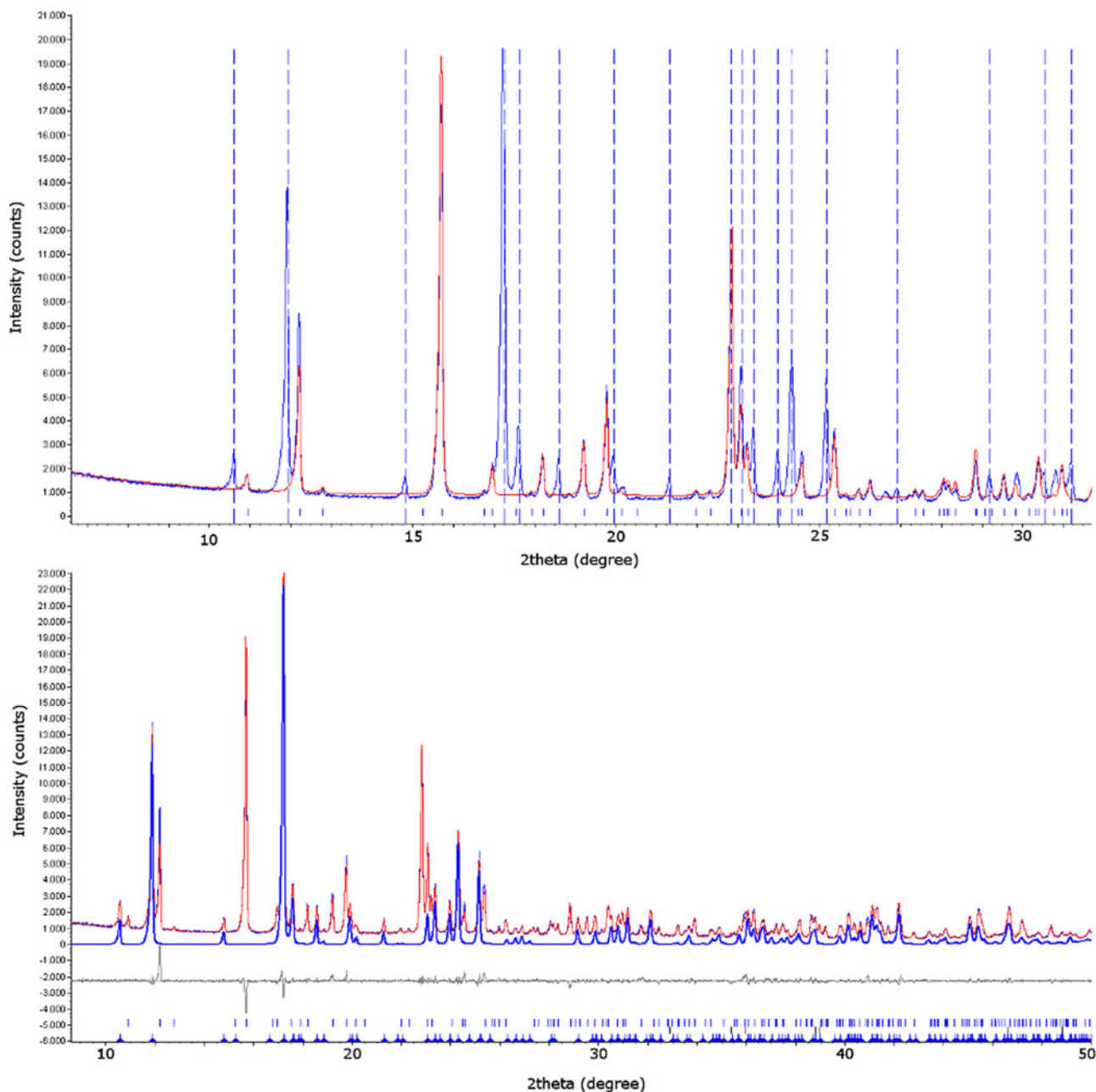


Figure 1. (Color online) (top) Low-angle peaks used for indexing of the unknown monohydrate phase are marked with vertical blue dashed lines. The experimental pattern is blue while the calculated pattern with the contribution only from the dihydrate phase is in red. Blue tick marks below the pattern designate calculated peak position of the dihydrate phase. (bottom) Pawley fit using the unit cell of Table I. The contribution of the unknown monohydrate phase is presented with the thick blue line below the pattern. The contribution of the dihydrate is included using the Rietveld method. The gray line is the difference between the calculated and measured patterns.

CUCITD01; Zhang *et al.*, 2006) which was likely to be a side product in the synthesis. Indeed, the dihydrate could fit approximately half of the peaks in the pattern. This allowed for a clear identification of unindexed peaks which could then be used to search for the unit cell of the other mixture component. The shape of unindexed peaks was described using the fundamental parameters approach (Cheary *et al.*, 2004) with finite particle size contribution to peak broadening. The refined peak positions of 18 strong reflections were subjected to indexing using singular value decomposition as implemented in TOPAS (Coelho, 2003) and yielded a unit cell with a de Wolff figure-of-merit of 40 (de Wolff, 1968). The suggested unit cell was similar to the unit cell of the dihydrate and its

volume corresponded to $Z=4$ with the assumed composition of one citrate and two copper atoms in the asymmetric unit (Table I). Such a composition is electrically neutral provided the hydroxyl group of citric acid is also deprotonated as is the case with the dihydrate. The most likely space group was determined to be $P2_1/c$ based on possible systematic extinctions. This unit cell was used in a Pawley refinement (Pawley, 1991) to determine the best peak profile parameters as well as to test both the unit cell and the assumed space group. Also, background was modeled by a Chebychev polynomial with an additional $1/2\theta$ term to describe air scattering at low angles. Since the obtained Pawley fit seemed adequate, on the next step was to proceed with structure solution.

TABLE I. Crystallographic and Rietveld refinement parameters for copper (II) citrate monohydrate. The agreement factors relate to the whole powder diffraction pattern.

Compound	Copper (II) citrate monohydrate
Molecular formula	C ₆ H ₄ O ₇ Cu ₂ ·H ₂ O
Formula weight	333.22
Space group	P2 ₁ /c
<i>a</i> (Å)	6.0191(1)
<i>b</i> (Å)	10.0670(2)
<i>c</i> (Å)	14.9436(3)
β (°)	97.154(2)
<i>V</i> (Å ³)	898.44(2)
<i>Z</i>	4
Calc. density (g cm ⁻³)	2.46
Temperature (K)	293
Wavelength (Å)	1.54056
<i>R</i> _{exp} (%)	3.39
<i>R</i> _p (%)	6.7
<i>R</i> _{wp} (%)	9.4
<i>Gof</i>	2.79
<i>R</i> (<i>F</i> ²) (%)	3.1
Starting angle (°2 θ)	6
Final angle (°2 θ)	90
Step width (°2 θ)	0.00853
Scan time (h)	12
No. of variables	78

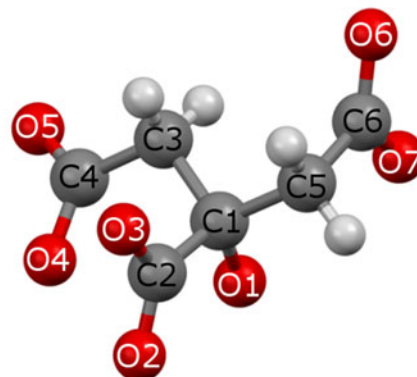
B. Crystal structure solution

The parameters contributing to peak shape, position, and background were fixed at the values obtained in the Pawley refinement. Also, the contribution of the dihydrate was included using the Rietveld method with its previously refined scale factor kept fixed. Crystal structure of the monohydrate was solved by simulated annealing in direct space taking advantage of the known connectivity between atoms of the citrate anion. The geometry of the citrate was described in the form of a Z-matrix. TOPAS allows for the geometry parameters in the Z-matrix to be defined as adjustable variables. The torsion angles defining the orientation of the three carboxylic moieties were therefore included in simulated annealing along with the rotation and translation of the whole rigid body. Two copper atoms were included independently, each with three translational degrees of freedom, into simulated annealing runs. Such a definition assumes no coordination modes of citrate toward the copper atoms. In total, 17 degrees of freedom were optimized. The simulated annealing runs yielded the solution which was recognized after the likely coordination to copper atoms was established and the structure model gave a reasonable fit to the experimental pattern. At this point it became evident that there is room in the crystal structure for one additional water molecule which was included and found by simulated annealing to be coordinated to a copper atom. Such a structure model was complete as it left no free space in the crystal and exhibited no too short contacts. This model was then introduced into Rietveld refinement.

C. Rietveld refinement

A powder diffraction pattern generally does not contain enough information to allow for a free refinement of each atomic position independently. Such refinements would lead to distorted geometries at the very least but also often to non-

interpretable structure models. The common approach is to refine atomic coordinates with restraints on bond distances and valence angles set to their expected values as well as planarity restraints imposed on atoms expected to lie in one plane. Another option is to treat structure fragments for which the geometry can be fairly well assumed as rigid bodies where they retain the geometry that is input (Figure 2). Here, we have treated the citrate moiety as a rigid body, however with torsion angles treated as variables. Copper atoms being much heavier than other atoms have a stronger scattering contribution. The coordinates of two copper atoms were thus freely refined with no restraints on any geometrical parameters. Finally, the water molecule was also treated as a rigid body with no restraints on its position or orientation. It is noteworthy that its orientation was stable during refinement to form two hydrogen bonds toward neighboring oxygen atoms. The heavier copper atoms were assigned one common isotropic temperature factor which converged to $\sim 1/3$ of the value of the common temperature factor assigned to all other atoms. The other main mixture component in the patterns is the known dihydrate which was included in the refinement using the Rietveld method with the unit cell, the scale



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prm tor1 5
prm tor2 19
prm tor3 115
prm tor4 187
prm tor5 298

rigid
z_matrix C1
z_matrix C2 C1 1.54
z_matrix O1 C1 1.42 C2 109
z_matrix O2 C2 1.22 C1 120 O1 = tor1;
z_matrix O3 C2 1.29 C1 120 O1 = tor1 + 180;
z_matrix C3 C1 1.55 C2 109 O2 120
z_matrix C5 C1 1.55 C2 109 O2 240
z_matrix C4 C3 1.51 C1 109 C2 = tor5;
z_matrix C6 C5 1.51 C1 109 C2 = tor4;
z_matrix O4 C4 1.28 C3 120 C1 = tor2;
z_matrix O5 C4 1.28 C3 120 C1 = tor2 + 180;
z_matrix O6 C6 1.28 C5 120 C1 = tor3;
z_matrix O7 C6 1.28 C5 120 C1 = tor3 + 180;
z_matrix H3a C3 0.97 C1 109 C2 = tor5 + 120;
z_matrix H3b C3 0.97 C1 109 C2 = tor5 + 240;
z_matrix H5a C5 0.97 C1 109 C2 = tor4 + 120;
z_matrix H5b C5 0.97 C1 109 C2 = tor4 + 240;

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Figure 2. (Color online) Z-matrix representation of the citrate anion in TOPAS. The torsion angles defining the allowed rotations around single carbon-carbon bonds are defined as free variables named “tor1” to “tor5”.

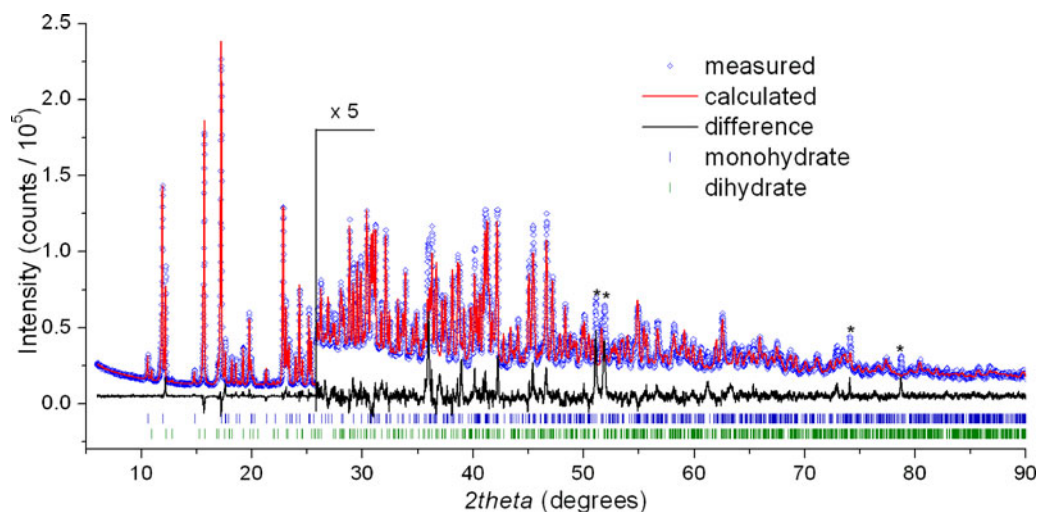


Figure 3. (Color online) Final Rietveld refinement plot for the mixture powder diffraction pattern of the monohydrate and the dihydrate. The corresponding weight fractions are 56 and 44%, respectively. The previously known crystal structure of the dihydrate was not refined. The high-angle region is enlarged to reveal more detail. Tick marks represent calculated peak positions: monohydrate-upper row, dihydrate-lower row. The unaccounted peak intensities arising from unidentified impurities are marked with asterisks.

factor, and the overall temperature factor refined but the structure model was kept fixed. The final Rietveld refinement plot is given in Figure 3, and crystallographic and refinement details in Table I.

D. Crystal structure description

The monohydrate crystal structure is a three-dimensional coordination polymer similar to the dihydrate (Figure 4). The hydroxyl group, along with all three carboxylic groups, is deprotonated rendering the formal charge of the citrate to -4 . All the oxygen atoms of the citrate coordinate to copper atoms both of which are pentacoordinated in distorted square pyramids. The coordination of the citrate to two copper atoms is essentially the same as in the known crystal structure of the dihydrate (Figure 5). The hydroxide moiety of the citrate bridges two copper atoms, which are also chelated by carboxylate moieties forming the core (Zhang *et al.*, 2006). In the dihydrate, two water molecules are coordinated to the same

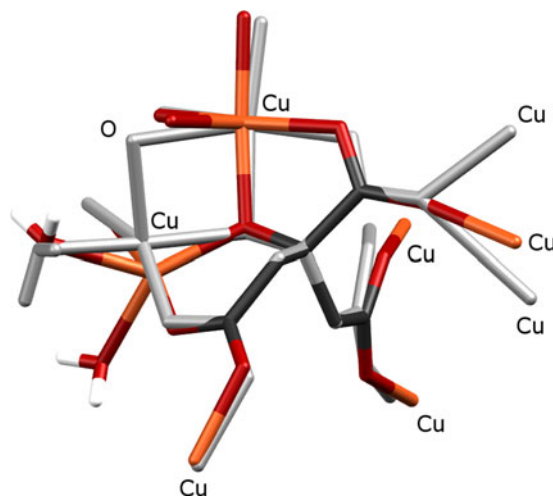


Figure 5. (Color online) Overlay of fragments of the monohydrate (light gray) and the dihydrate crystal structures demonstrating the similarities in coordination of the citrate to two copper atoms (atoms color-coded: copper-orange, oxygen-red, carbon-dark gray, and hydrogen-white). Methylene hydrogens are omitted for clarity.

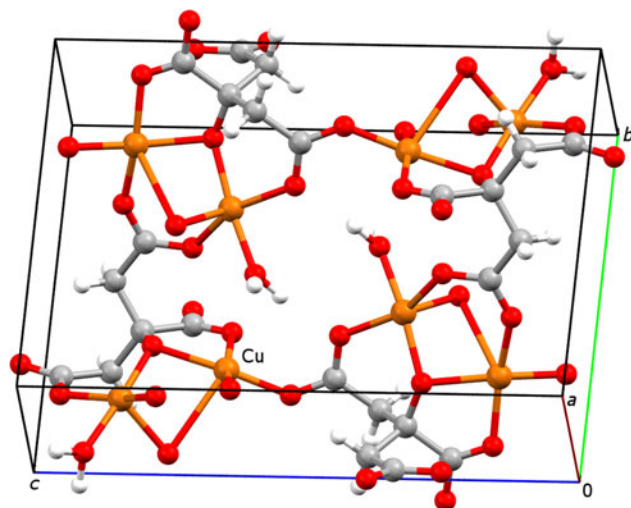


Figure 4. (Color online) Packing in the copper(II) citrate monohydrate (atoms color-coded: copper-orange, oxygen-red, and carbon-gray).

copper atom, while in the monohydrate one water molecule is replaced by the carboxylate oxygen in the coordination sphere of copper. Thus, in the dihydrate the citrate anion is octadentate, while in the monohydrate it is nonadentate. It would be interesting to examine physical properties of the monohydrate but we were unable to prepare it in a pure form.

IV. CONCLUSION

Crystal structure solution from powder diffraction data yielded the crystal structure of copper(II) citrate monohydrate. The structure was solved and refined against a laboratory high-resolution powder diffraction pattern. The fact that the powder diffraction pattern corresponded to a mixture of two copper citrates presented no problem at the structure solution or Rietveld refinement stage. However, as noted previously (Halasz and Dinnebier, 2010), in such cases indexing and

finding the unit cell may be the bottle-neck for successful structural characterization. The structure of the monohydrate and the dihydrate differ in formation of three-dimensional coordination networks while the coordination of citrate anions to copper atoms is very similar in both compounds.

CCDC 947282 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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