

What information may be obtained from Re-determination of Crystal Structures?

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Besides simple reproducibility, what information may be obtained from re-determination of crystal structures?

In this commentary, we would like to consider this query based on some examples of re-determination of aqua-*cis*-(*L*-valinato) copper (II) complex. As is known well, amino acids have -NH₂ and -COOH groups or their charge separated species. In order to coordinate to a Cu²⁺ ion, they should be synthesized employing a high pH aqueous solvent to bias the equilibrium toward the -COO⁻ side generally. In addition, when two bidentate chelate ligands are coordinated, *cis*- and *trans*-structural isomers may be produced potentially. Since the *cis*-form is kinetically advantageous in general, while the *trans*-form is a thermodynamically advantageous product. Thus a *cis*-form may yield in a short time of synthesis quickly. In a study in which both were isolated [1], the *cis*-form affords a penta-coordinated quadrangular pyramidal geometry having an apical water ligand. Additionally, even in some cases of re-determination, disorder was reported in the amino acid substituent moiety in space group C2 [2-4].

However, there was a new report of aqua-*cis*-(*L*-valinato) copper (II) analyzed again in space group P1 [5]. Indeed, crystal polymorphisms are usually suspected when the crystal system or space group is different, and a comprehensive survey of organic matter in CSD was also reported [6]. Indeed, the latest polymorphism papers from crystallographic journals are organized by cause and viewpoint: phase transition due to temperature and pressure, nucleation, crystal growth, synthesis on the surface, discovery of new (the third or more) polymorphism, and pseudo-polymorphisms containing crystalline solvents, etc. However, in the example of non-disordered analysis of space group P1, lattice reduction and space group determination are important factors, and typical non-merohedral twin are suggested [7]. In fact, the same data was analyzed at 150 K by the space group C2, and it was confirmed that the disorder structure was identical to the previous report.

Recently, we have also obtained *L*-valine with copper (II) acetate monohydrate in a methanol solution (weakly acidic) at 313 K containing phenolic compound (2-hydroxy-5-methoxybenzaldehyde) as a by-product of the Schiff base copper complex [8]. When a single crystal of aqua-*cis*-(*L*-valinato) copper (II) was structurally analyzed at 173K, similar and low quality results

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to previous report of space group $C2$ were obtained (**FIG. 1**). Manually selection process of reciprocal spots was carried out for separation of the crystal domains with the diffraction image processing software APEX3; rejected about 1550 points out of the total reflection points 3580 and used about 2030 points (**FIG. 2**). The process suggested different features of non-merohedral twins due to synthetic conditions [9], though unrejected F_o and F_c structural factors correlated linearly.

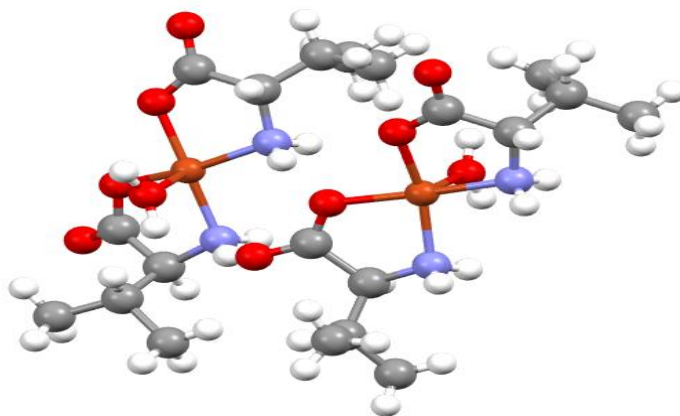


FIG. 1. Re-determination of crystal structure of aqua-*cis*-(*L*-valinato) copper(II) in space group $C2$.

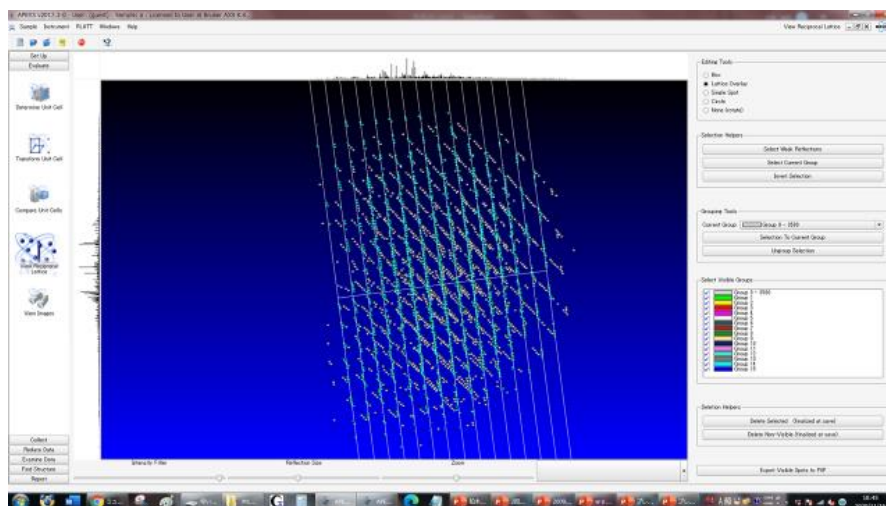


FIG. 2. Diffraction image processing using software APEX3 in which only blue diffractions were omitted as the small twin.

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