



## Do Thermally Mild Chemical Reactions (for Avoiding Fire Accidents) Give Rise to Unexpected Products?

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### Abstract

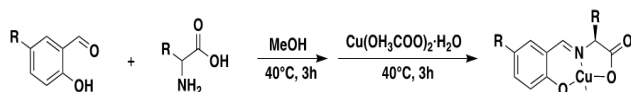
One of the most probable and frequent reasons for a chemical experiment fire accident may be dangerous heating as well as the reagent itself (e.g. volatility and ignition) during a chemical reaction. Some reaction methods without heating (such as long-time stirring at room temperature) and using advanced tools (such as a microfluidic device), which are associated with unusual intermediates kinetically and may result in yielding unexpected products thermodynamically. This paper focused on two complicated examples of crystal structure analysis of unexpected and/or normal products.

**Keywords:** Chemical reaction, Temperature, Schiff base metal complexes, Unexpected products, Crystal structure analysis.

### Introduction

Generally, heating during chemical reactions are common procedure to enhance reaction rate, though it may be common reason for fire accidents in chemical laboratory [1]. Not only for avoiding fire but also for obtaining products efficiently, alternative experimental conditions or methods can be selected at room temperature. One may be long-time reaction can help slow rate not to exceed activation energy to become usual intermediate kinetically. Another may be using sophisticated tools such as a microfluidic device, in which moving solvents, encounter of the reactant can be caused in a short time. Additionally, limited special environment may result in formation of unusual products thermodynamically [2].

In recent years, we have studied on preparation of (chiral) Schiff base metal complexes (**Scheme 1**) in hot alcohol solutions for several hours [3]. As for copper(II) complexes having chelate Schiff base ligands, typical reaction scheme can be described as Scheme 1.



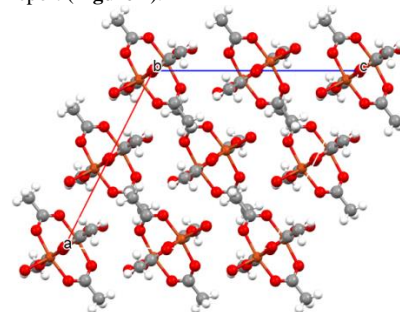
**Scheme 1:** Typical reaction scheme of metal complexes having (chiral) Schiff base ligands. Schiff base was prepared by condensation of aldehyde and primary amine to yield an imine (C=N) bond.

However, some unusual reactions yielded products of single crystals, of which structure analysis was complicated because there was also possibility of unexpected products. According to such working hypothesis, two strange examples after reactions of failed conditions found in our group are introduced below.

### Results and Discussion

#### Case 1: “Excess” hydrate of copper(II) acetate, $(\text{Cu}(\text{COOCH}_3)_2 \cdot \text{H}_2\text{O}) \cdot 0.5\text{H}_2\text{O}$

As recovery of the reactant (namely, no reaction occurred), copper(II) acetate hydrate as a metal source was found by X-ray crystallography. However, its cell constants and composition (containing 0.5 crystalline water) were different from the original and re-determination reports. Adsorption of crystalline solvents under different reaction conditions was expected firstly [4]. Due to too large thermal displacement parameters for 0.5  $\text{H}_2\text{O}$ , re-calculation after removing weak diffraction data in reciprocal space were carried out (We soon realized the mistake, so we didn't leave any wrong results.). Then it was solved as the following unit cell data:  $C2/c$ ,  $a=13.192(9)$ ,  $b=8.595(6)$ ,  $c=13.867(10)$  Å,  $\beta=116.913(11)^\circ$ ,  $V=1402.0(18)$  Å<sup>3</sup>, being identical to the original report (**Figure 1**).

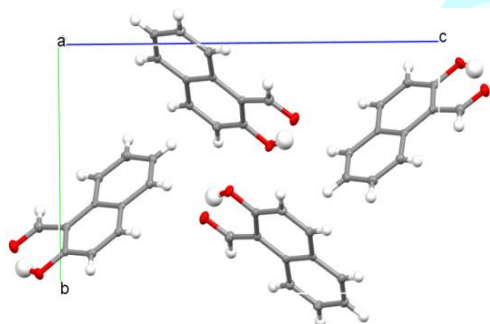


**Figure 1:** Re-determined crystal structure of  $\text{Cu}(\text{COOCH}_3)_2 \cdot \text{H}_2\text{O}$  as recovery of the reactant, which was identical to the original report.

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### Case 2: Not monoclinic but “triclinic” polymorphism of 2-hydroxy-1-naphthaldehyde ( $C_{11}H_8O_2$ )

As recovery of the reactant, a single crystal of 2-hydroxy-1-naphthaldehyde (instead of salicylaldehyde,  $o\text{-C}_6\text{H}_5(\text{OH})(\text{CHO})=C_{11}H_8O_2$ ) was obtained and its crystal structure was determined at low temperature (173K). An analysis program automatically judged to be *triclinic* P-1 with  $Z=4$  based on unit cell constants ( $a=5.626(2)$ ,  $b=9.360(4)$ ,  $c=15.522(7)\text{\AA}$ ,  $\alpha=90.027(5)^\circ$ ,  $\beta=80.695(6)^\circ$ ,  $\gamma=90.087(6)^\circ$ ,  $V=806.7(6)\text{\AA}^3$ . It cannot be negligible deviation of  $\alpha$  and  $\gamma$  from exact 90 degrees according to standard deviation reasonably. Two crystallographically independent molecules in asymmetric unit were perfectly identical, which suggest  $n$ -glide plane as a proof of *monoclinic*  $P2_1/n$  being similar to the original report measured at room temperature [5]. Therefore, we judged again systematic absence ( $0k0$ ) manually and confirmed crystallographic symmetry of unit cells, namely, Laue group  $2/m$  (of course, monoclinic crystal system) based on both  $2_1$  screw axis and  $n$ -glide plane. In this way, it was not polymorphism (same compounds taking different crystal structures) by phase transition but wrong determination of crystal system (Figure 2).



**Figure 2:** Re-determined crystal structure of 2-hydroxy-1-naphthaldehyde at 173K as recovery of the reactant, which was identical to the original report [5].

### Conclusion

In the two examples, humans corrected the crystallographic mistakes by the programs, but it can also be interpreted that the reaction conditions produced “subtle” products. In other word, this area is suspicious. Indeed, novel methods of chemical reaction or special condition of crystallization may result in thermodynamically unexpected products or unusual isolation of kinetically favored products, novel asymmetric synthesis of optical isomer (or racemization), unstable tautomer, chiral crystallization, new phase (polymorphism) of crystals, inclusion of guest molecules and so on, respectively. However, careful experiments must be also required to discuss such “delicate” chemistry.

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