Journal of the Indian Chemical Society 98 (2021) 100004

Contents lists available at ScienceDirect

Journal of the Indian Chemical Society

journal homepage: www.editorialmanager.com/JINCS/default.aspx

Synthesis of amino acid derivative Schiff base copper(II) complexes by microwave and wet mechanochemical methods

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ARTICLE INFO

Keywords:
Microwave synthesis
Mechanochemical synthesis
Amino acid
Schiff base
Copper complex

ABSTRACT

As resource- and time-saving and environmentally friendly synthetic methods than conventional one in a solution, microwave, and wet mechanochemical synthesis are tested for L-amino acid derivative Schiff base copper(II) complexes. Herein, we systematically compared efficiency (low-temperature, time, and yield (if possible to detect)) for both conventional solution method and microwave or mechanochemical methods. The wet mechanochemical synthesis promoted fast reaction (typically 20 min by mechanochemical vs 4 h by conventional) by a little amount of solvent for preparations of amino acid derivative Schiff base copper(II) complexes. New crystal structure of a five-coordinated square pyramidal copper(II) complex as one of the products of microwave method was also reported.

For effective preparation of materials, in the era of SDGs, environmentally friendly (*e.g.* tailor-made synthesis of amino acids [1,2] by mehanochemical method [3,4]) than microfluid including droplet method (needing large equipment) [5–7] have been required for synthesizing not only metal complexes besides conventional method (so-called liquid phase method in a solution) but also hybrid artificial metalloproteins which is easy to decompose by heating condition. As for the preparation of the L-amino acid derivative Schiff base copper(II) complexes, having potential application for photocatalysts [8,9], we have generally employed two-step reactions, namely (1) imine condensation of primary amine and aldehyde; (2) coordination of copper(II) ion from acetate source (Scheme 1). Herein, we compared with microwave [10] and wet mechanochemical syntheses [11–13] for the L-amino acid derivative Schiff base copper(II) complexes.

The merits of microwave synthesis are faster reaction speed by controlled heat transfer, safety, fewer reactants, improved reactivity, high yield, selectivity of heating, and reproducibility. Known L-amino acid chiral Schiff base complexes [14–20] were synthesized using the microwave synthesis apparatus (Biotage Initiator+). The green-colored products were characterized with IR and UV–vis spectra and so on (not shown). In the conventional liquid phase method (298 K), it took about (2 + 2 =) 4 h to complete the two-step reaction of Scheme 1 continuously, while about 10 min by microwave one-pot synthesis (358 K) as listed in Table 1. The products obtained in shorter time and higher yield were identified to be identical to that by conventional methods by comparing IR spectra. Microwave synthesis method may be effective in particular for **2**, **7**, **14**, and **15** (due to soluble leucine and electron-withdrawing 3,5-dichlorosalicylaldehyde). For all complexes, full characterization for new compounds has already reported in the original papers. Therefore, we confirmed that the same compounds could be prepared by different methods only using limited (mainly IR spectral) data. Unreported new crystal structure of **1** solved using programs of SHELXL [21] and so on is depicted in Fig. 1 and found to afford a five-coordinated square pyramidal geometry to form a chain structure. Dpending on bulkiness of ligands and conditions of preparation, coordination modes except for the tridentate Schiff base ligand can vary significantly.

Crystallographic data for **1** (CCDC 2045315): $C_{13}H_{15}CuNO_3$, Monoclinic, space group $P2_1$ (#4), $Z = 2$, $a = 9.7026(3)$, $b = 5.0944(2)$, $c = 13.6481(5)$ Å, $\beta = 109.5110(10)°$, $V = 635.87(4)$ Å^3, $\rho_{calc} = 1.550$ gcm^{-3}, $\mu = 1.716$ mm^{-1}, F(000) = 306, $S = 1.086$, $R_1[I > 2\sigma(I)] = 0.0490$, w$R2 = 0.1157$, Flack parameter = −0.002(16), $T = 293$ K.

On the other hand, the mechanochemical can be carried out under solvent-free or small amounts of solvent [11], mass transfer in mechanochemical reaction can proceed through a gas, a liquid, a solid phase, or any combination of [12] (microwave cannot be used for gas-emitting reactions due to a closed container). However, there are also some disadvantages of this method, for example, reactants and products stick to the mortar wall, low yield, difficult to adjust reaction temperature, and unreacted reactants need to be separated. Indeed, James and co-workers

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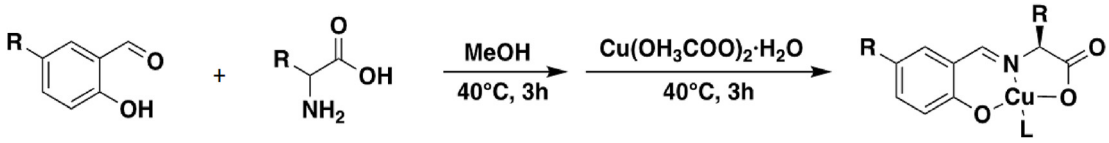
https://doi.org/10.1016/j.jics.2021.100004
Received 9 November 2020; Received in revised form 23 November 2020; Accepted 27 November 2020



Scheme 1. Typical reaction scheme in a solution for the L-amino acid derivative Schiff base copper(II) complexes. In the case of microwave synthesis, 40 °C, 3 h are 85 °C, 20 min.

Table 1
Summary of the results. *Up: conventional IR bands*, middle: microwave, down: mechanochemical. "AA" denotes amino acid. "Aldehyde" indicates substitution groups of salicylaldehyde (H denotes salicylaldehyde). "Time" indicates sum of reaction time of the first and the second steps. IR and UV (spectra) denote predominant bands of C═N and π -π*, respectively.

Entry [Ref.]	AA	aldehyde	Time/min	Yield/%	IR/cm^{-1}	UV–vis/nm	Temperature/°C
1 [15]	Leu	H	120 + 120	53.9	1617	400	45
			5 + 5	45.1	1646	378	85
			5 + 25	31.1	1611	378	25
2 [15]	Leu	3,5-Cl	120 + 120	50.7	1636	385	45
			5 + 5	31.2	1636	386	85
			10 + 10	53.9	1621	386	25
3 [15]	Ser	H	120 + 120	65.5	1634	364	45
			5 + 5	65.3	1645	386	85
			3 + 20	24.6	1609	386	25
4 [15]	Ser	3,5-Cl	120 + 120	64.0	1636	377	45
			5 + 5	49.2	1646	397	85
			10 + 10	27.4	1645	399	25
5 [16]	*Ala	H	120 + 120	19.2	1616	372	40
			5 + 5	67.0	1640	372	85
			5 + 25	13.0	1622	372	25
6 [16]	Ala	3,5-Cl	120 + 120	27.8	1613	388	40
			5 + 5	75.0	1644	388	85
			10 + 10	34.2	1608	388	25
7 [17]	*Thr	H	180 + 180	6.8	1631	390	40
			5 + 5	85.9	1633	377	85
			2 + 12	21.6	1611	377	25
8 [17]	*Thr	3,5-Cl	180 + 180	31.6	1628	400	40
			5 + 5	77.7	1636	401	85
			10 + 10	21.2	1606	401	25
9 [19]	*Val	H	180 + 120	50.5	1615	354	60
			5 + 5	85.9	1639	367	85
			5 + 35	21.6	1632	367	25
10 [19]	*Val	5-Cl	180 + 120	55.5	1623	354	60
			5 + 5	66.7	1636	418	85
			10 + 15	24.0	1627	383	25
11 [19]	*Val	5-Br	180 + 120	42.2	1630	354	60
			5 + 5	87.4	1637	377	85
			10 + 15	35.8	1620	377	25
12 [19]	*Val	5-MeO	180 + 120	44.8	1621	358	60
			5 + 5	80.2	1636	405	85
			5 + 10	28.5	1621	396	25
13 [18]	Arg	H	120 + 160	25.4	1644	370	60
			5 + 5	18.8	1633	369	85
			1 + 3	33.1	1633	369	25
14 [18]	Arg	5-Br	120 + 160	44.3	1635	370	60
			5 + 5	26.4	1636	380	85
			1 + 6	17.3	1633	380	25
15 [18]	Arg	5-MeO	120 + 160	10.0	1634	370	60
			5 + 5	31.2	1636	372	85
			2 + 10	44.2	1637	370	25
16 [14]	Lys	3,5-Cl	120	33.1	1635	380	45
			5 + 5	52.8	1626	380	85
			5 + 5	34.0	1636	380	25

reported a one pod two-step mechanochemical synthesis of Schiff base metal complexes at room temperature [13]. Synthesis by mechanochemical method and characterization of the same complexes are also listed (Table 1). Mechanochemical synthesis generally took only about 20 min at 298 K. Thus the formation of Schiff base copper(II) complex would depend on and may be supported by metal ion (Scheme 2). As for low yield, it could not be compared between previous and present data properly due to different conditions of concentration and temperature (solubility) of reaction solutions. Attempt to obtain good crystals suitable for X-ray analysis directly was unsuccessful from the product of mechanochemical synthesis, contrary to microwave method [22]. Thus, we could elucidate that mechanochemical synthesis may be effective for **12**, **14**, and **16**. Promoting by a little amount of solvent and local heat induced by mechanical pressure, which was also different from the microwave method, may attribute to these results.

For * marked complexes, single crystals of these complexes were isolated as imidazole coordinated ones for X-ray analysis in original papers. Therefore, IR C═N bands was mainly used for confirming the products and comparing the original reports.

We intend on prepare artificial metalloenzymes including these

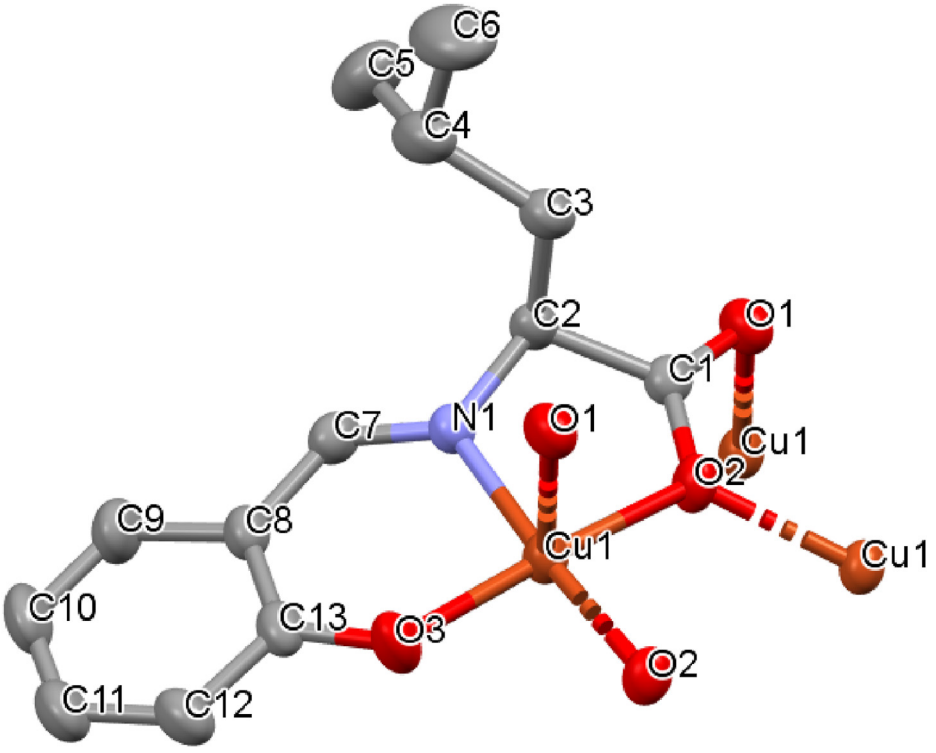
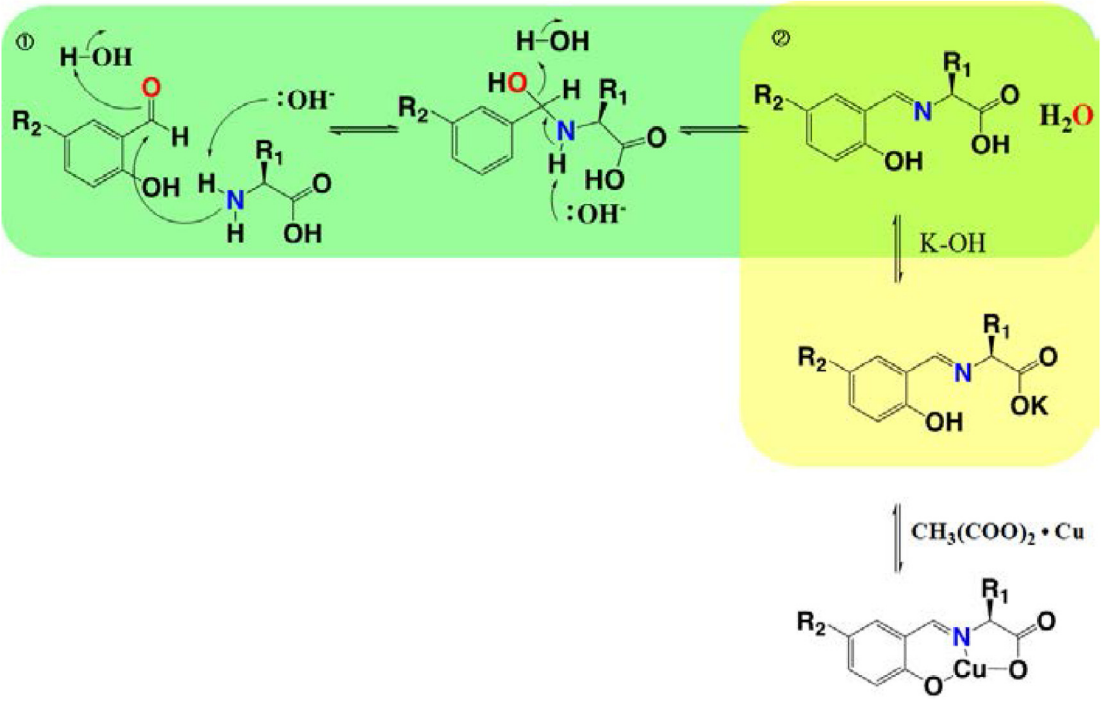


Fig. 1. Crystal structure of **1** as a product of microwave method. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Cu1–O3 = 1.880(4), Cu1–N1 = 1.923(5), dashed line Cu1–O2 (symmetry codes: 1-x, y-1/2, 2-z) = 1.982(4), Cu1–O2 = 2.012(4) (, and dashed line Cu1–O1 (symmetry codes: x, y-1, z) = 2.472(4)).



Scheme 2. Proposed mechanism of the L-amino acid derivative Schiff base copper(II) complexes for mehanochemical reaction.

copper(II) complexes having azo-groups in protein crystals [23], which could be also prepared preliminarly. From this viewpoint, we would have presented as a communication of improved preparation of the copper(II) complex at present.

Declaration of competing interest

There is no conflict of interest.

Acknowledgment

The authors thank Ms. Yuika Onami at Tokyo University of science for her help of X-ray crystallography. This work was partly supported by Grant-in-Aid for Scientific Research (A) KAKENHI (20H00336). This work was also performed under the Cooperative Research Program of "Network Joint Research Center for Materials and Devices".

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jics.2021.100004.

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