

Copper-based 2D-coordination polymer as catalyst for allylation of aldehydes

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Abstract

A copper-tartrate, $[\text{Cu}_2(\text{Tart})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, was synthesized at room temperature in aqueous media using copper chloride and D-tartaric acid. The compound crystallizes in the monoclinic system $P2_1$ space group and was characterized by infrared spectroscopy, thermogravimetry, X-ray powder diffraction and the results are in good agreement with the single crystal structure. Catalytic properties for allylation of aldehydes were investigated at different solvents, and the best conditions obtained were using a mixture of $\text{CH}_2\text{Cl}_2:\text{H}_2\text{O}$. The copper-tartrate obtained showed good performance as catalyst for different sub-strates and yields were between 62% and 95%.

Keywords: Coordination polymer Allylation Catalysis

1. Introduction

Since the 90's, coordination polymers (CPs) have emerged as a very versatile class of inorganic materials with applications in molecular separation [1], sensing [2], luminescence [3] and gas adsorption [4]. CPs has been also employed as efficient catalysts for several organic reactions, such as alcohol and sulphide oxidations [5], epoxidation of olefins [6], Knoevenagel condensation [7] and others [8–10]. Properties as crystallinity, intrinsic porosity and the possibility to incorporate organic/inorganic moieties can be adjusted during the method of synthesis which improves the versatility of these materials. In addition, the synthesis of chiral coordination polymers using organic linkers or chiral templates opens the possibility for the application of these materials in asymmetric synthesis [10].

The allylation of carbonyl compounds is an important reaction while in one step two functionalities can be incorporated in the product [11]. Furthermore, a new stereogenic center can be created in the reaction and several coordination compounds [12–14] and Lewis acids [15–17] have been widely used as catalyst for these reactions. Recently, a lanthanide-based 3D-coordination polymer

was used to promote allylation of aldehydes, resulting in the corresponding homoallylic alcohols with high yield, under mild reaction conditions [13,18]. Nonetheless, to our knowledge, the application of transition metals based coordination polymers as a catalyst in allylation of aldehydes reactions is not described in the literature. Within this context, this work describes a new strategy for synthesis of a copper coordination polymer using D-tartaric acid as ligand (Cu-Tart) and its application as a catalyst in the allylation of aldehydes. The compound was characterized by X-ray powder diffraction, elemental analysis, infrared spectroscopy and thermogravimetry. The copper-tartrate obtained shows catalytic properties for several substrates in allylation reaction using allyl-trifluoroborate as reagent.

2. Experimental

All reagents were analytical grade and used without previous purification.

2.1. Physical measurements

Elemental CHN analyses were performed on a CE Instruments model EA1110 elemental analyzer. The IR spectroscopy was carried out in a Bruker FT-IR model IFS66 spectrometer, in range of 4000–400 cm^{-1} . The TGA curve was obtained in a Shimadzu TGA

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60-H thermogravimetric analyzer under an N₂ atmosphere. ¹H NMR and ¹³C NMR data were recorded in CDCl₃ on a Varian Unity Plus 300 spectrometer. For the potassium allyltrifluoroborate, the NMR data (¹H, ¹³C, ¹⁹F, ¹¹B) were performed in DMSO-*d*₆. Coupling constants (*J*) for all spectra are reported in Hertz (Hz). The chemical shifts are reported as delta (δ) units in parts per million (ppm) relative to the solvent residual peak as the internal reference. Thin-layer chromatography plates (SIL G UV254, 0.20 nm, 20 × 20 cm) used were obtained from Macherey-Nagel.

2.2. Synthesis of Cu-Tart ([Cu₂(Tart)₂(H₂O)₂]₂·4H₂O)

2.2.1. Single crystal

In a flask containing a solution of *D*-tartaric acid (0.5 mmol, 75 mg) and iminodiacetic acid (0.5 mmol, 133 mg) in distilled water (10 mL) was added dropwise sodium hydroxide (0.1 mol/L solution) until pH = 7 followed by the addition of CuCl₂·2H₂O (1 mmol, 170 mg). The solution was kept at room temperature and after five days, the blue crystals obtained were filtered, washed with ethanol and water and air-dried to yield 14.6 mg (11%). Elemental analysis: Calc. for [Cu₂(C₄H₄O₆)₂(H₂O)₂]₂·4H₂O: C 17.9%; H 3.7%; Cu 78.4% Found: C 18.2%; H 4.3%; Cu 77.5%.

2.2.2. Powder

In a flask containing a solution of *D*-tartaric acid (0.5 mmol, 75 mg) in distilled water (10 mL) was added dropwise sodium hydroxide (0.1 mol/L solution) until pH = 7 followed by the addition of CuCl₂·2H₂O (1 mmol, 170 mg). The solution was kept at room temperature and after three days, the blue crystalline powder obtained was filtered, washed with ethanol and water and air-dried to yield 99.6 mg (75%).

2.3. Synthesis of the potassium allyltrifluoroborate

To a solution of B(OMe)₃ (8.15 mL, 7.59 g, 73.2 mmol) in THF (40 mL) was added dropwise allylmagnesium chloride (30 mL, 60 mmol, 2.0 M in THF) at -78 °C. The mixture was stirred for 30 min. The ice bath was removed. The yellow solution with a white precipitate was allowed to reach the room temperature over a 1 h period. Then, it was cooled to 0 °C and KHF₂ (23.4 g, 300 mmol) was added in one portion. This was followed by the dropwise addition of H₂O (30 mL). The ice bath was removed. The mixture was stirred for 30 min and then concentrated under high vacuum. The white solid was extracted with hot acetone (4 × 100 mL). The extracts were filtered through a Celite pad and the filtrate was concentrated

to afford a white solid. The solid was purified by dissolving in the minimum amount of hot acetone, followed by cooling to room temperature and precipitation with Et₂O. The solution was allowed to stand for 20 min to complete precipitation. The precipitate was collected and dried under high vacuum to yield 3.37 g (38%) of a powder white solid, which can be stored at room temperature without degradation. NMR data: ¹H NMR (300 MHz, DMSO-*d*₆) δ 5.84–5.73 (*m*, 1H, CH₂]CH), 4.54 (*d*, *J* = 12.6 Hz, 1H, CH₂]CH), 4.48 (*d*, *J* = 7.5 Hz, 1H, CH₂]CH), 0.91 (*sl*, 2H, CH₂BF₃K); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 142.85; 109.00; ¹¹B NMR (128 MHz, DMSO-*d*₆) δ 4.23 (*q*, *J*_{11B,19F} = 61.35 Hz, BF₃K); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -136.47 (*J*_{19F,11B} = 61.34 Hz, BF₃K).

2.4. General procedure for allylation of aldehydes

To a flask containing the appropriate aldehyde (0.1 mmol [1a: 15.1 mg, 1b: 14.1 mg, 1c: 10.6 mg, 1d: 13.6 mg, 1e: 12.4 mg, 1f: 16.4 mg, 1g: 15.6 mg, 1h: 10.0 mg, 1i: 13.2 mg, 1j: 9.8 mg]) in dichloromethane (3 mL) and distilled water (0.5 mL) was added potassium allyltrifluoroborate (1.1 mmol, 16.8 mg) followed by Cu-Tart (10 mol%, 5.3 mg). The biphasic mixture was stirred for 30 min and the reaction was monitored by thin-layer chromatography using UV light or vanillin as visualizing agents. The mixture was then diluted with CH₂Cl₂ (15 mL) and washed with water (3 × 15 mL). The organic phase was dried over anhydrous Na₂SO₄, filtered and the solvent was removed *in vacuo*. The products **3a-j** were purified using silica gel chromatographic column using a mixture of AcOEt/hexane (3:7).

3. Results and discussion

3.1. Structure and XRPD analysis

The copper-tartrate coordination polymer, [Cu₂(Tart)₂(H₂O)₂]₂·4H₂O, obtained was previously synthesized by Jian et al. using hydrothermal synthesis, however, with long reaction time and low yield [19]. More recently, the structure was also reported by Derikvand and co-workers [20]. In our case, the same compound was obtained starting from the metal salt and the ligand, using crystallization by slow evaporation of the solvent, resulting in crystalline powder (yield 75%) or single crystal (yield 11%, in the presence of iminodiacetic acid). The method used present cost and lower time reaction (for powder form) in comparison to literature [19,20]. The [Cu₂(Tart)₂(H₂O)₂]₂·4H₂O is a 2D-coordination polymer and crystallizes in the monoclinic crystal system and *P*2₁ space

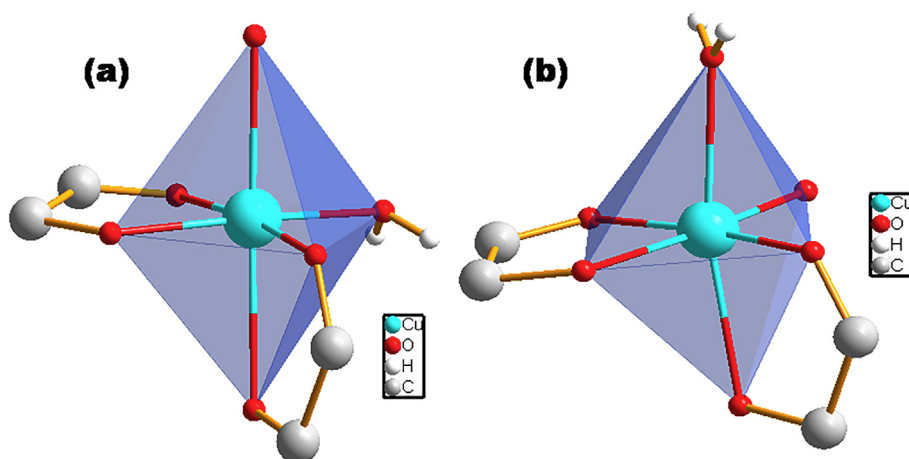


Fig. 1. Coordination polyhedra of (a) Cu1 and (b) Cu₂ in the [Cu₂(Tart)₂(H₂O)₂]₂·4H₂O network [19].

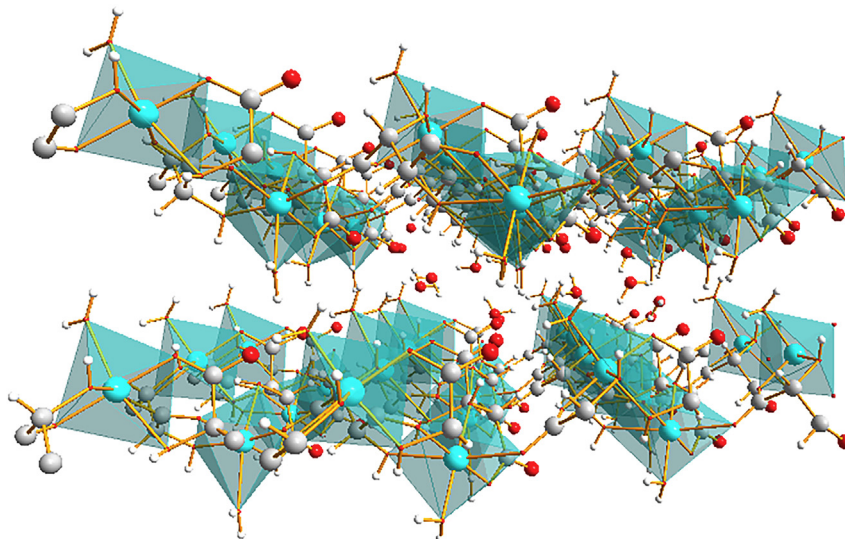


Fig. 2. 3D final packing of $[\text{Cu}_2(\text{Tart})_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$.

group [19]. Since a complete description of the structure were already reported [19,20], here we give only a brief description.

In the structure, there are two crystallographic independent Cu^{2+} cations, both (Cu1 and Cu2) in an octahedral environment with tetragonal distortion, and coordinated to five oxygen atoms from three ligand molecules and one oxygen atom from water (Fig. 1).

There are also two crystallographic independent tartrate anions linked to the cations via the carbonyl and hydroxyl groups, with *syn-anti-oxo*-bridging and chelating coordination modes. Each adjacent Cu1 are linked by the oxygen atoms of the Tart1 molecule, however, two crystallographic independent copper ions are connected by Tart2 anions. The two-dimensional networks are connected by the hydrogen bonds of the hydrated

water molecules and the final packing is shown in the Fig. 2 [19,20].

In the absence of iminodiacetic acid, the reaction led to a blue powder was obtained with higher yield. The experimental powder pattern (Fig. 3) confirms the same crystalline phase of the single crystal structure, with the most intense peaks near to 12° and 15° corresponding to (10-1) and (002) diffraction planes, respectively. The experimental diffractogram shows no additional signals in comparison to the calculated powder pattern, which indicates a high purity of the compound. The experimental observations may indicate an important role played by the iminodiacetate anions in the crystal growing of the compound. This result was similar to the literature, when *N*-donor auxiliary ligand was also used to produce single crystals at environmental conditions [20].

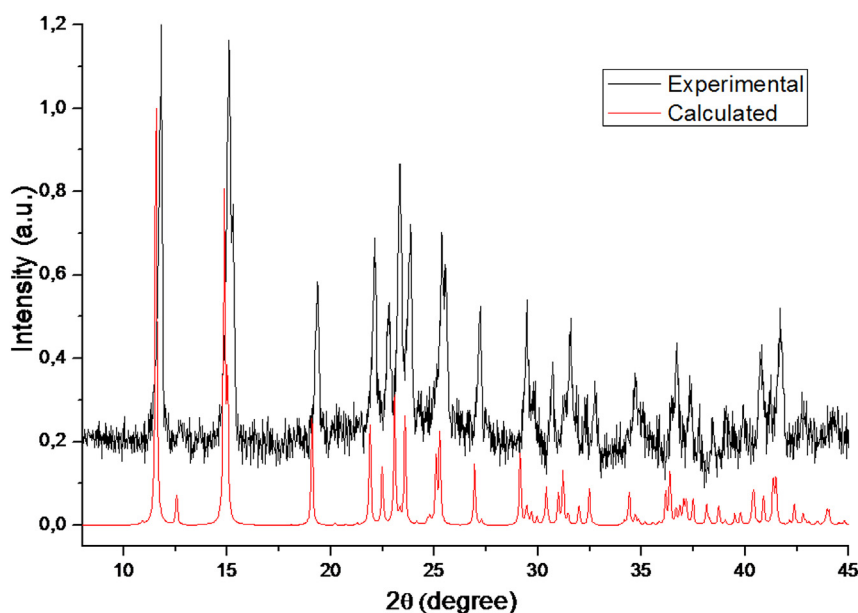
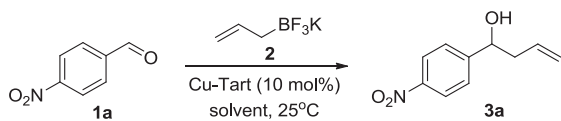


Fig. 3. Comparison between experimental and calculated (from the single crystal) powder patterns of the $[\text{Cu}_2(\text{Tart})_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$.

Table 1

Effect of solvent in the Cu-Tart catalyzed allylation of 4-nitrobenzaldehyde by potassium allyltrifluoroborate.



| Entry | Solvent | Time (h) | Yield (%) ^a |
|-------|---|----------|------------------------|
| 1 | CH ₂ Cl ₂ | 20 | 92 |
| 2 | CH ₂ Cl ₂ :H ₂ O (3:0.5) | 0.5 | 95 |
| 3 | H ₂ O | 13 | 48 |
| 4 | CH ₂ Cl ₂ :H ₂ O (3:0.5) | 24 | 9 ^b |

^a Isolated yield;

^b The reaction was performed without Cu-Tart.

3.2. Infrared spectroscopy and thermal analysis

The infrared spectrum of Cu-Tart (Fig. S1, Supplementary material) shows two signals at 3430 cm⁻¹ and 3262 cm⁻¹ corresponding to the asymmetric stretching of O–H from the water molecules and hydroxyl groups present in the ligand. The signals of methylene groups appear at 2991 cm⁻¹ (axial symmetric bending) and 2848 cm⁻¹ (axial asymmetric bending). Peaks at 1614 cm⁻¹ and 1601 cm⁻¹ are related to the carbonyl asymmetric stretching of the ligand. Signals at 1389 cm⁻¹ (C–O symmetric stretching), 1104 cm⁻¹ (C–H out-of-plane bending) and 993 cm⁻¹ (O–H...O, hydrogen bonds) were also observed [21].

The thermogravimetry was performed under N₂ atmosphere (Fig. S3, Supplementary material). The initial observed mass loss (17.3%) between 25 °C and 205 °C is attributed to the complete dehydration of the compound (calculated 17.2%). The ligand decomposition occurs between 205 °C and 360 °C with 51.8% of mass loss (calculated 52.3%). The remaining mass (30.9%) corresponds to formation of copper oxide (calculated 30.5%). All observations in the IR spectrum and TGA analysis are in good agreement with the literature [22,23].

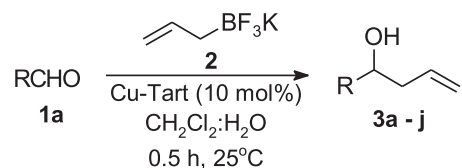
3.3. Catalytic properties

In order to evaluate the efficiency of Cu-Tart as catalyst for allylation of aldehydes, first the influence of solvent on the reaction of 4-nitrobenzaldehyde **1a** (1 equiv.) and potassium allyltrifluoroborate **2** (1.1 equiv.) was tested and the results are shown in Table 1. For the reaction using only dichloromethane a higher yield of **3a** was observed, but a longer reaction time was required to reaction completion (Table 1, entry 1). The addition of water (0.5 mL) as a co-solvent reduced the reaction time and **3a** was obtained in 95% yield (Table 1, entry 2). This result is attributed to the increase in the solubility of potassium allyltrifluoroborate in water. However, when only water was used as the reaction solvent longer reaction time and low yield was observed in comparison with the co-solvent (CH₂Cl₂:H₂O) experiment (Table 1, entry 3). It is interesting to note when the reaction was conducted in a mixture of dichloromethane:water without the Cu-Tart, a longer reaction time was required and a lower yield was observed, clearly indicating the catalytic effect of Cu-Tart (Table 1, entry 4).

The optimized conditions [CH₂Cl₂:H₂O (3:0.5) and Cu-Tart (10 mol%)] were applied to different aldehydes and the results are shown in Table 2. The method was reproducible for aldehydes containing different types of functional groups such as aliphatic, aromatic and α,β-unsaturated.

Table 2

Allylation of aldehydes with potassium allyltrifluoroborate catalyzed by Cu-Tart.

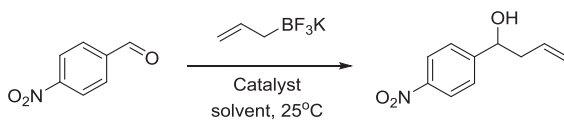


| RCHO | Product | Yield (%) ^a |
|------|---------|------------------------|
| | | 95 |
| | | 81 |
| | | 62 |
| | | 82 |
| | | 76 |
| | | 86 |
| | | 83 |
| | | 86 |
| | | 90 |
| | | 83 |

^a Isolated yield.

Table 3

Comparison of time and reaction yields for several catalysts in the allylation of 4-nitrobenzaldehyde by potassium allyltrifluoroborate.



| Solvent | Time (min) | Yield (%) | Catalyst | Ref. |
|---|------------|-----------|---|-------------------|
| CH ₂ Cl ₂ :H ₂ O (3:0.5) | 30 | 95 | [Cu ₂ (Tart) ₂ (H ₂ O) ₂]-4H ₂ O | This work |
| CH ₂ Cl ₂ :H ₂ O (1:0.1) | 15 | 93 | [Eu ₂ (fum) ₃ (H ₂ O) ₄]-3H ₂ O | [18] |
| CH ₂ Cl ₂ :H ₂ O (1:1) | 20 | 95 | Amberlyst A-15 | [24] |
| CH ₂ Cl ₂ :H ₂ O (1:1) | 15 | 94 | 8-Crown-6 | [25] |
| CH ₂ Cl ₂ :H ₂ O (1:1) | 45 | 89 | Oxalic acid | [26] |
| CH ₂ Cl ₂ :H ₂ O (1:1) | 120 | 90 | Citric acid | [26] |
| CH ₂ Cl ₂ :H ₂ O (1:1) | 40 | 93 | Benzoic acid | [26] |
| CH ₂ Cl ₂ :H ₂ O (1:1) | 60 | 92 | Ascorbic acid | [26] |
| CH ₂ Cl ₂ :H ₂ O (1:1) | 40 | 90 | Salicylic acid | [26] |
| MeOH | 60 | 93 | PhN(CH ₂ C ₆ H ₄) ₂ SbOSO ₂ CF ₃ | [15] ^a |

^a Reaction using tetraallyltin as reagent and room temperature.

No significant changes in the yield were observed when electron-withdrawing or electron-donating substituents were present in the starting material indicating that the reaction is not sensitive to electronic effects (Table 2, entries 1–2 and 4–6). A moderate yield was observed only when benzaldehyde was used as substrate (Table 2, entry 4). The Cu-Tart also exhibits high efficiency for aliphatic aldehydes (Table 2, entry 8) and when cinnamaldehyde was used as substrate, only the 1,2-addition product was observed, indicating the regioselectivity of the reaction (Table 2, entry 9). Starting from 4-nitrobenzaldehyde as substrate, an experiment was performed by increasing tenfold the initial concentration of the reactants and catalyst, to test the applicability of the method. In this case, the yield was also 96%, however, with longer time reaction (50 min). It is noteworthy that in all the experiments, the interaction of the catalyst with the reactants leads to its solubilization in the reaction medium.

Many compounds have been reported in the literature [14,24–26] as catalysts for allylation of aldehydes reactions using potassium allyltrifluoroborate. Some results of yield and reaction time are shown in Table 3 for the procedures starting with 4-nitrobenzaldehyde. Using the Cu-Tart coordination polymer, similar yields were obtained in comparison to other catalyst under equivalent reaction conditions, with lower reaction times compared to Bronsted acids [26], antimonium complexes [15] and organometallic compounds [27].

The catalyst used presents a chiral ligand in the structure, thus, the chiral induction was investigated for 4-nitrobenzaldehyde as substrate in different solvents (CH₂Cl₂, CH₂Cl₂/H₂O and acetonitrile). Isolated products were eluted in a chiral column chromatography (Figs. S27–S29 in Supplementary material) and no enantioinduction was observed, which can indicate that the catalytic activity was focused on the metal and not in the ligand. These results are also confirmed by Mosher's method.

Batey and co-workers proposed that the addition of tetra-coordinated boron to aldehydes promoted by Lewis acid may proceed through the interaction of tri-coordinated allyl-boron species [28–30]. This catalytic system involving Cu-Tart is complex, involving two liquid phases (water and dichloromethane) and one solid phase. Thus, Cu-Tar should act as a catalyst in two ways (a) activating the carbonyl group of the aldehydes on the substrates by coordination with Cu²⁺ ions; (b) and/or activating the allyltrifluoroborate and/or its hydrolyzed products through coordination with the metal ions [31]. In this way, the aldehyde molecules can react with activated allylic species on the surface of the catalyst

[18]. This behaviour could explain the reaction times and observed yields, which are practically independent of the aldehyde size. A detailed mechanism of [Cu₂(Tart)₂(H₂O)₂]-4H₂O catalysis is beyond the scope of the present contribution; however, controlled experiments and theoretical calculations are underway in our laboratories to clarify this mechanism.

4. Conclusions

In summary, we have demonstrated the high efficiency of the 2D-coordination network [Cu₂(Tart)₂(H₂O)₂]-4H₂O (Cu-Tart) as a catalyst for allylation of aldehydes. The Cu-Tart was obtained as powder or single crystals using two new simple synthetic routes and the characterization confirms the crystalline phase and purity of the compound. The method uses small amounts of catalyst and the products were obtained with high purity and yield at 25 °C with water as co-solvent.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.molstruc.2017.10.096>.

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