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Research Article

Synthesis and Structure of 2D Cobalt(II)-Tartrate Hydrate Coordination Polymers Crystallised from Aqueous Solution

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Abstract

Cobalt(II)-tartrate hydrate coordination polymer is successfully crystallisedfrom aqueous solution at room temperature. Unlike previous methods, diammonium tartrate was used and reacted directly with an aqueous solution of cobalt(II). Single crystal X-ray and ATR-IR analyses were performed toward the synthesized crystal. The crystal structure displaysa (6,3) 2D sheet which then grow into a 3D hydrogen-bonded network. Tetra- and hexa-dentate dianionic tartaric ligands are observed in the crystal structure, in which the hexadentate ligand connects four different cobalt centres. This method is considered feasible, affordable, and simple for the production of functional polymeric cobalt(II)-tartrate hydrate. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Diammonium tartrate; coordination polymers; aqueous solution; crystal structure; cobalt(II) tartrate

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1. Introduction

Coordination polymer (CPs), which is defined in IUPAC recommendation as "a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions" [1], have been widely explored in the last several decades due to their interesting properties such as porosity, magnetism, catalysis, chirality, *etc.* [2]. Due to this, CPs have been developed for gas storage, solvent guest exchange, catalyst, drug delivery systems study, *etc.* [3,4]. Harvesting good quality single crystal of CPs is crucial for structural analyses using XRD. The crystallization and structure can be affected by solvents [5], anions [6], temperature [7], moles ratio, metal ion, *etc.* A simple change in the synthesis condition might change the structure and properties of CPs [4].

Carboxylate based compounds and their derivatives are often used as building blocks to obtain CPs. The carboxylate group, sometimes along with other functional groups incorporated into the ligand, coordinate effectively with the metal ion. In fact, dicarboxylate can act as a bridging ligand in the making of CPs, for example, oxalate [8], malonate [9], succinate [10], tartrate [11], and benzenedicarboxylate [12]. Particularly tartrate, metal complexes of this anion have been explored since decades ago. Tartrate ion forms ionic bonding with the metal ion and their single crystal displays high optical non-

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linearity. It has also been developed for laser diodes in which different metal ion affects the material conductivity [13]. Tartrate inorganic salts are known for transducer [14] since ferroelectricity and piezoelectricity are commonly exhibited by their crystals [15-18].

Several methods to get tartrate complex were reported, namely solution, gel, and solvothermal. Melting method is considered unachievable, as tartrate will decompose before its melting point. Gel method gains the highest reputation to grow single crystal of tartrate metal complexes as most of these complexes are partly soluble in water [19]. However, this method deal with multi-steps and several factors such as pH, type of gel, concentration, *etc*., must be incorporated. Crystallization of tartrate metal complexes using solvothermal reaction is only reported by few papers [11], as this method using high temperature, which may cause decomposition of the tartrate hence lower the yield, and require specific high-cost advance instruments. Solution method comes as the least method to produce good quality of tartrate metal complex single crystals since many tartrate complexes are partly soluble in water and may form amorphous products. Anyhow, solution method was chosen in this work because it is simple and the possibility of getting good quality single crystals can be increased by adjusting the reaction condition.

This paper presents the synthesis of cobalt(II)-tartrate hydrate coordination polymer in an aqueous solution using diammonium tartrate. Diammonium tartrate is never been used previously for cobalt(II)-tartrate synthesis. Cobalt(II)-tartrate is a useful compound and being used in the production of Co_3O_4 nanoparticles, [20], as well as for semiconductors, transducers, and optics, *etc*., due to its optical, electric and magnetic properties [21-23]. Many cobalt(II)-tartrate crystallised in silica gel and in some of the papers, the physical properties of the product were deeply examined but not structurally characterised [21-23], for example is cobalt(II)-tartrate hydrate crystals reported by Ariponnammal and Srinivasan which has 1.33 eV energy gap and potential used for UV filters due to high absorption in UV-region (about 365.7 nm) [24]. Cobalt(II)-tartrate could forms a discrete complex, such as: $[Co(C_4H_5O_6)_2(H_2O)_2]\cdot 2H_2O$ [25] or coordination polymer, such as $\{[Co_2(C_4H_4O_6)2]\cdot 2H_2O\}_n$ [11], depends on the synthetic method.

To the best of our knowledge, synthesizing cobalt(II)-tartrate hydrate single crystal prepared in an aqueous solution specifically using diammonium tartrate has never been reported. Hence in this paper, we report the synthesis of and crystal structure of the cobalt(II)-tartrate hydrate coordination polymers. The crystal structure presented here is also different to previous works [11,25].

2. Materials and Method

2.1 Materials and measurements

Sigma–Aldrich chemicals ($Co(NO_3)_2\cdot 6H_2O$ and $(NH_4)_2(C_4H_4O_6)$) were used as received. Solid-state IR spectra were recorded by using an Agilent ATR spectroscope at 4000-650 cm^{-1} with sensitivity of 3. Low-temperature single-crystal X-ray diffraction experiments were performed using a Bruker Apex II KAPPA CCD with Mo-Ka radiation (l0.71073 Å) equipped with an Oxford Instruments nitrogen gas cryostream. Single crystals were mounted on nylon loops in viscous hydrocarbon oil. Crystals were quench-cooled to 123(2) K. Analysis of diffraction data collected with the Bruker Apex II KAPPA CCD was performed by using SAINT1 within the APEX2 [26] software package. Empirical absorption corrections were applied to all data by using SADABS [27]. The structures were solved using SHELXS [28] and refined using SHELXL-13 [28-30] within the graphical interface Olex2 [31].

2.2 Synthesis of the complex

Diammonium tartrate, $(NH_4)_2(C_4H_4O_6)$, (50 mg; 0.271 mmol) was dissolved in 10 mL water. The solution then added slowly to an aqueous solution of $Co(NO_3)_2\cdot 6H_2O$ (78.8 mg, 0.271 mmol, 5 mL) and stand at room temperature for 3 days resulting in a clear pink solution. Upon slow evaporation of the solution at room temperature, red block crystals start forming two weeks later. After a month, the crystals were isolated, washed with cold water and then air-dried for overnight (93 mg, 68%).

3. Result and Discussion

3.1 Synthesis of the complex

Formation of cobalt(II)-tartrate is based on a simple metathesis reaction between tartaric ions and Co(II) ions, as follows:

$$(NH_4)_2(C_4H_4O_6)_{(aq)} + Co(NO_3)_{2(aq)} \rightarrow 2\ NH_4NO_{3(aq)} + Co(C_4H_4O_6)_{(s)}$$

Diammonium tartrate was used instead of tartaric acid, as frequently used in other works [11,18,19,21,22], since diammonium tartrate gives different level of acidity in an aqueous solution. The acidity level of reaction condition influences the chemical equilibrium and the chemical species in the solution, thus affecting the crystallization process. Tartaric acid is a weak acid with pKa_1 = 2.98 and pKa_2 = 4.34 at 25°C for *L*-tartaric acid or pKa_1 = 3.17 and pKa_2 = 4.91 at 25 °C for meso-tartaric acid [32]. This indicates that the number of tartaric ions ($C_4H_4O_6^{2-}$) present in the solution are limited at certain pH value which eventually affects the stoichiometry and the crystal yield. On the other hand, if we use highly soluble tartaric salt (i.e. Na or K salt), the diffusion rate of tartaric ions ($C_4H_4O_6^{2-}$) in the solution is very high, therefore tartaric ions react much faster with cobalt(II) ions and amorphous products are likely precipitated.

The cobalt and the diammonium tartrate solutions were prepared in a dilute concentration and they were added slowly, instead of mixed and stirred directly, to avoid direct precipitation. After homogenous clear pink solution was obtained, the solution then slowly evaporated at room temperature by making few holes on the vial lid. Red tiny block crystals start forming after two weeks in which the solution was left for another month to get a bigger crystal and higher yield without leaving the solution to dryness. Hence, in this work, the yield reported here may not be the optimum yield.

In general, crystallization of cobalt(II)-tartrate hydrate coordination polymer in aqueous solution remains feasible, affordable because using less chemical and only requires one step reaction. Therefore, investigation on other transition metal tartrate (M(II) = Fe, Mn, Ni, Cu, Zn, Cd) complexes grown from an aqueous solution using diammonium tartrate is also conducted and their investigation is still ongoing.

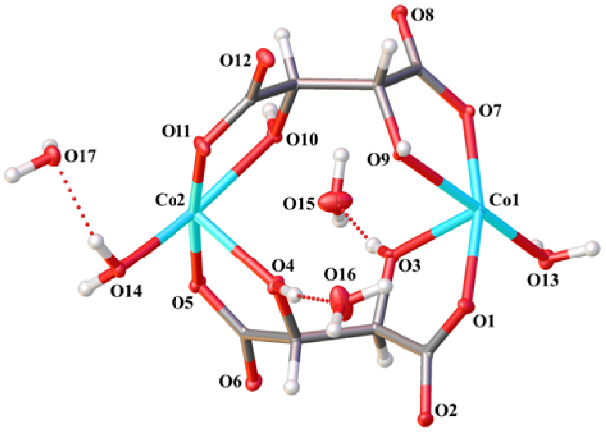

Figure 1. Asymmetric unit of $\{[Co_2(\mu\text{-}C_4H_4O_6)(\mu^4\text{-}C_4H_4O_6)(H_2O)_2]\cdot 3H_2O\}_n$ shown with thermal ellipsoids at 50% probability (except hydrogen atoms), hydrogen bonding are shown in red dots (light blue = cobalt, red = oxygen, gray = carbon, white = hydrogen)

3.2 Crystal structure

Crystal structure of $\{[Co_2(\mu\text{-}C_4H_4O_6)(\mu4\text{-}C_4H_4O_6)(H_2O)_2]\cdot 3H_2O\}_n$ was solved in orthorhombic space group $P2_12_12_1$ with cell parameters: *a* = 7.8484(2) Å, *b* = 11.1233(3) Å, *c* = 18.0812(5) Å, *a* = *b* = *g* = 90°, and volume = 1578.49(7) Å3. These parameters are different to other related paper published previously [11,21,25], but identical to those reported by Ariponnammal and Srinivasan [24]. However, Ariponnammal and Srinivasan's paper only mention a proposed chemical formula of the crystal which was $[Co(C_4H_4O_6)]\cdot 2H_2O$, generated from powder XRD analyses, thus the paper was not examining the structure of the complex [24].

The asymmetric unit of the complex consists of two cobalt centres bridged by one tetradentate and one hexadentate dianionic tartaric ion, two water molecules as ligand and three water molecules as lattice solvent (Figure 1). Both octahedral cobalt centre is surrounded by six oxygen atoms, which are from one water oxygen atom, one carboxylate and one hydroxyl oxygen atoms from the tetradentate tartaric ion, one carboxylate and one hydroxyl oxygen atoms from the hexadentate tartaric ion, and one carboxylate oxygen atom from another hexadentate tartaric ion. The chelating carboxylate and hydroxyl groups toward cobalt centre in both tetra- and hexadentate tartaric ions form five-membered chelate ring. Coordination modes of both tetra- and hexa-dentate tartaric ions are presented in Figure 2.

In both cobalt centres, the Co−O bond lengths ranges from 2.0348(18) to 2.1427(19) Å,

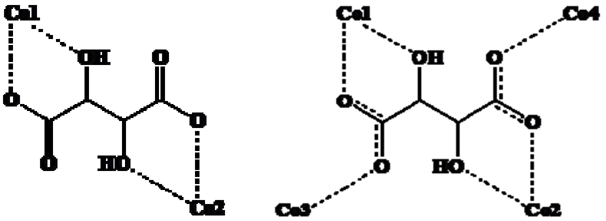

Figure 2. Coordination modes of tetra (left) and hexadentate (right) tartaric ions in the $\{[Co_2(\mu\text{-}C_4H_4O_6)(\mu^4\text{-}C_4H_4O_6)(H_2O)_2]\cdot 3H_2O\}_n$ (Co1···Co2 = 5.229 Å; Co2···Co4 = 5.447 Å; Co1···Co3 = 5.657 Å;Co3···Co4 = 8.545 Å)

whereas the angles ranges from 77.39(8) to 173.37(8)°, thus indicating that both cobalt centres have distorted octahedral geometry (Table 1). The Co1···Co2 distance bridged by both tetra- and hexadentate tartaric ions is 5.229 Å and forming a dinuclear cobalt(II) unit. This hexadentate ligand also bridges two other adjacent cobalt centres and each dinuclear cobalt(II) unit is connected to four neighbouring dinuclear cobalt(II) units, hence the crystal packing displays 2D polymeric structure (Figure 3). Assuming the tartrate ions as single linker (the chelate ring considered as a single point of connection to metal centre), the cobalt(II) centres exhibits 3-connected nodes, hence the 2D sheet could be referred to be having a (6,3) topology. Surprisingly, although the asymmetric unit, metal-ligand connectivity and the crystal colour are different, the (6,3) 2D coordination polymers resulted in this work has identical topology to coordination polymers reported by Gu and Yang [11].

The (6,3) sheets then grew into 3D hydrogen-bonded networks due to medium to strong hydrogen bonding interaction between the sheets involving lattice water molecules (O15, O16, O17), hydroxyl groups of the tartrate ligands (O3, O4, O9, O10) and water ligands

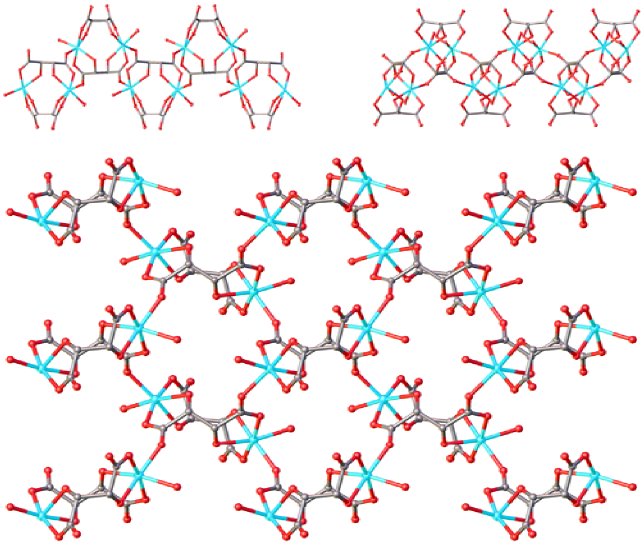

Figure 3. Crystal packing of $\{[Co_2(\mu\text{-}C_4H_4O_6)(\mu^4\text{-}C_4H_4O_6)(H_2O)_2]\cdot 3H_2O\}_n$ viewed from *a* (top left), *b* (top right), and *c* axis (bottom), CH hydrogen atoms and lattice water molecules are omitted for clarity

Table 2. Hydrogen bond D···A distances of the complex

D	H	A	D···A (Å)
O3	H3	O15	2.680(3)
O4	H4	O16	2.649(3)
O14	H14B	O17	2.805(3)
O15	H15A	O1#a	2.825(3)
O16	H16B	O5#b	2.805(3)
O17	H17A	O7#c	2.743(3)
O9	H9	O17#d	2.792(3)
O10	H10	O17#e	2.794(3)
O13	H13A	O6#f	2.807(3)
O13	H13B	O2#g	2.653(3)
O14	H14A	O2#h	2.686(3)

Symmetry:

#a = -1+x, +y, +z; #b =1+x, +y, +z;

#c = +x, 1+y, +z; #d = 1-x, -½+y, ½-z;

#e = -x, -½+y, ½-z; #f = ½+x, ½-y, 1+z;

#g = -½+x, ½-y, 1+z; #h = -½+x, $^3/_2$-y, 1+z.

Table 1. Selected bond lengths and angles around the cobalt centres

Bond Lengths (Å)		Angles (°)			
Co1-O7	2.0418(19)	O7-Co1-O3	91.48(8)	O4-Co2-O10	91.30(8)
Co1-O3	2.117(2)	O7-Co1-O13	97.86(8)	O14-Co2-O4	89.37(8)
Co1-O1	2.0363(19)	O7-Co1-O9	77.96(7)	O14-Co2-O8#2	81.11(7)
Co1-O13	2.0577(19)	O7-Co1-O12#1	97.10(8)	O14-Co2-O1	164.08(7)
Co1-O9	2.1427(19)	O3-Co1-O9	88.21(8)	O11-Co2-O4	94.94(8)
Co1-O12#1	2.0722(19)	O1-Co1-O7	167.30(8)	O11-Co2-O14	86.04(8)
Co2-O4	2.1147(19)	O1-Co1-O3	78.06(7)	O11-Co2-O5	172.23(8)
Co2-O14	2.0679(19)	O1-Co1-O13	88.80(8)	O11-Co2-O8#2	101.53(8)
Co2-O11	2.0348(19)	O1-Co1-O9	94.37(8)	O11-Co2-O10	78.05(7)
Co2-O5	2.0423(18)	O1-Co1-O12#1	94.60(8)	O5-Co2-O4	77.39(8)
Co2-O8#2	2.0756(19)	O13-Co1-O3	86.76(8)	O5-Co2-O14	95.02(8)
Co2-O10	2.1328(18)	O13-Co1-O9	173.37(8)	O5-Co2-O8#2	86.24(8)
Symmetry:		O13-Co1-O12#1	81.05(8)	O5-Co2-O10	100.65(8)
#1 = 1-x, -½+y, ½-z		O12#1-Co1-O3	165.93(8)	O8#2-Co2-O4	160.29(7)
#2 = -x, ½+y, ½-z		O12#1-Co1-O9	104.44(7)	O8#2-Co2-O1	102.58(7)

(O13, O14). The D···A hydrogen bond distancesare varying from 2.649(3) to 2.825(3) Å (Table 2). Crystallographic data of $\{[Co_2(\mu\text{-}C_4H_4O_6)(\mu^4\text{-}C_4H_4O_6)(H_2O)_2]\cdot 3H_2O\}n$ is given in Table 3.

3.3 ATR-IR Analysis

Table 3. Crystallographic data of $\{[Co_2(\mu\text{-}C_4H_4O_6)(\mu^4\text{-}C_4H_4O_6)(H_2O)_2]\cdot 3H_2O\}_n$

Chemical formula	$C_8H_{18}Co_2O_{17}$
Formula Mass	504.08
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	7.8484(2)
b/Å	11.1233(3)
c/Å	18.0812(5)
α/°	90
β/°	90
γ/°	90
Unit cell volume/Å^3	1578.49(7)
Temperature/K	123(2)
Z	4
Crystal size (mm)	0.10 x 0.15 x 0.25
m(mm^{-1})	2.198
Completeness	0.9957
Reflections measured	15942
Independent reflections	3955
Observed reflections ($I > 2\sigma(I)$)	3781
R_{int}	0.0273
Final R_1 values (obs. data)	0.0222
Final $wR(F^2)$ values (obs. data)	0.0507
Final R_1 values (all data)	0.0240
Final $wR(F^2)$ values (all data)	0.0517
Goodness of fit on F^2	1.057

In general, the ATR-IR spectrum of $\{[Co_2(\mu\text{-}C_4H_4O_6)(\mu^4\text{-}C_4H_4O_6)(H_2O)_2]\cdot 3H_2O\}_n$ is also identical to other cobalt(II)-tartrate hydrate reported previously [11,21,24], in which all the characteristic vibrational bands of tartaric ions (namely carboxylate, alkyl, hydroxyl groups) and water hydrate are present (Figure 4). The hydroxyl stretching peaks are observed at 3612 and 3444 cm^{-1} next to broad peaks around 3300-3100 which indicate the presence of water molecules. These peaks, along with O–H in-plane bending sharp peak at 1437 cm^{-1}, confirms the hydrous nature of the compound. Several medium peaks are observed around 2900-2700 cm^{-1} which correspond to the C–H alkyl stretch. At 1589 and 1560 cm^{-1}, very sharp peaks of symmetric and asymmetric stretch of the carboxylate groups are noticed. The sharp peaks at 1374, 1287, 1238, 1116, and 1045 cm^{-1} were also observed, which is belong to the C–O stretch of the tartrate in the compound. In addition, the characteristic C–H bending in tartrate are observed at 929 and 712 cm^{-1}.

4. Conclusions

Red block coordination polymer of $\{[Co_2(\mu\text{-}C_4H_4O_6)(\mu^4\text{-}C_4H_4O_6)(H_2O)_2]\cdot 3H_2O\}_n$ crystallizes from aqueous solution at room temperature using diammonium tartrate as the reactant The crystal structure, solved in orthorhombic space group $P2_12_12_1$, displays a dinu-

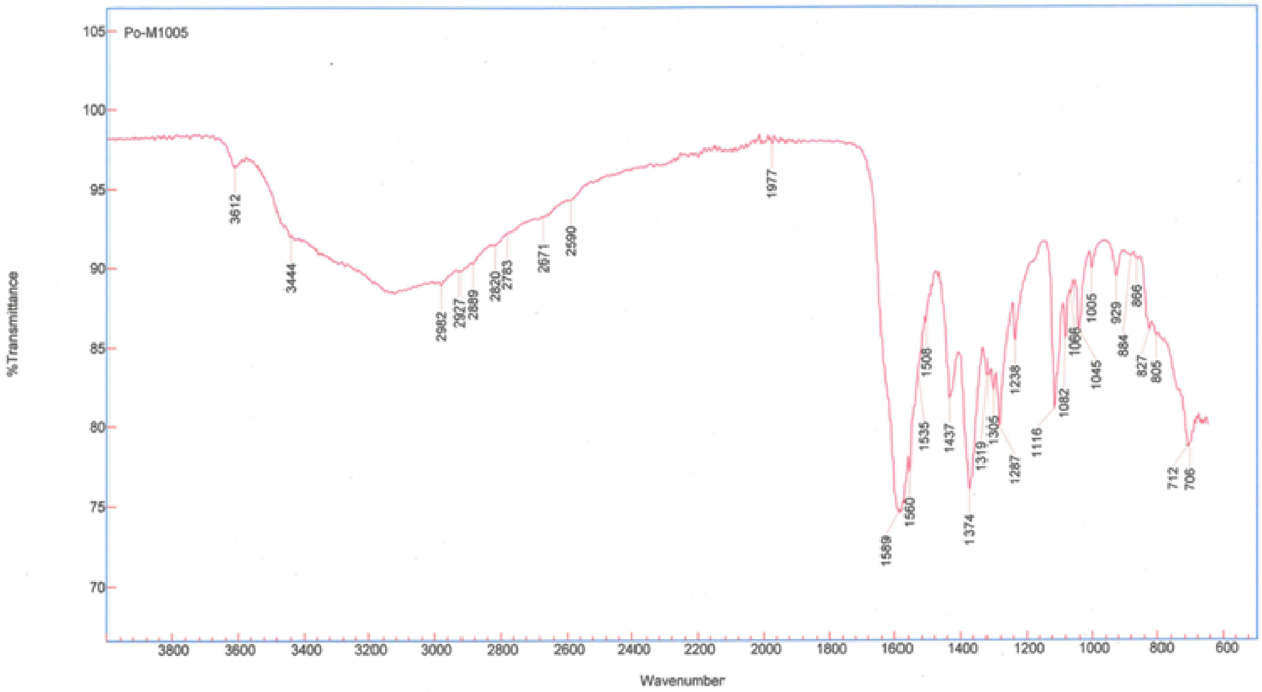

Figure 4. ATR-IR spectrum of the $\{[Co_2(\mu\text{-}C_4H_4O_6)(\mu^4\text{-}C_4H_4O_6)(H_2O)_2]\cdot 3H_2O\}_n$

clear cobalt(II) unit bridged bytetra- and hexadentate dianionic tartaric ions and forms a (6,3) 2D sheet which then grew into a 3D hydrogen-bonded network. Each hexadentate ligand connects four different cobalt centres. This aqueous technique is considered feasible, affordable and simple for the production of functional polymeric cobalt(II)-tartrate hydrate.

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