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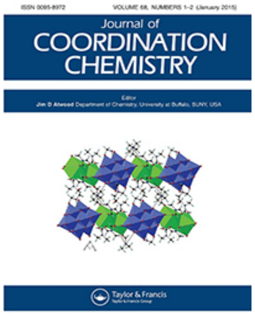

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# One-dimensional zinc(II) fumarate coordination polymers

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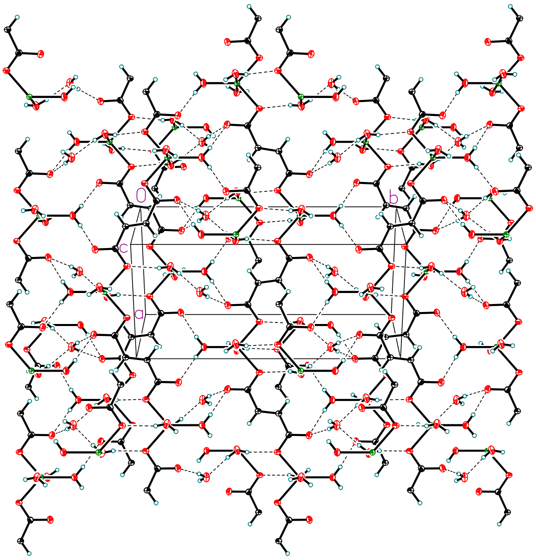

A new procedure developed for the synthesis and crystallization of various zinc(II) fumarate hydrate coordination polymers is described. In the first step, anhydrous Zn(II) fumarate, [Zn($C_4H_2O_4$)] (**1**), is synthesized from Zn(II) acetate and fumaric acid in methanol. Subsequently, this product is used as a starting material for growing small crystals of bis–aqua Zn(II) fumarate, [Zn($H_2O$)$_2$($C_4H_2O_4$)] (**2**), triaqua Zn(II) fumarate monohydrate, [Zn($H_2O$)$_3$($C_4H_2O_4$)]·$H_2O$ (**3**), tetraaqua Zn(II) fumarate, [Zn($H_2O$)$_4$($C_4H_2O_4$)] (**4**), and tetraaqua Zn(II) fumarate monohydrate, [Zn($H_2O$)$_4$($C_4H_2O_4$)]·$H_2O$ (**5**). All structures were determined or redetermined by X-ray structure analyses. The hitherto unknown compound **3** exhibits a zig-zag chain structure with five-coordinate Zn(II) ions.

*Keywords*: $Zn^{2+}$; Fumarate; Coordination polymer; Crystal structure; Trigonal bipyramidal

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## 1. Introduction

Metal–organic frameworks [1] and coordination polymers (CPs) [2], (as far as one can be distinguished from the other [3]), have attracted increasing interest during the past decades, due to various applications and properties [4]. The fumarate dianion, $^{-}$OOC–CH=CH=COO$^{-}$ is a useful linker, since its use as a ligand results in linear, rigid, metal–fumarate–metal bridges. Metal fumarates, such as Zn(II) fumarate hydrates, can in principle be synthesized from metal salts and fumaric acid, e.g. in water. However, the procedure has two drawbacks: (1) fumaric acid is poorly soluble in water at room temperature, hence organic solvents have to be used and (2) anions such as chloride, nitrate, or sulfate may be incorporated into the coordination network. Nevertheless, two Zn(II) fumarate phases could be crystallized in this way; namely, tetrahydrate (**4**) and pentahydrate (**5**) [5–7]. Syntheses using zinc oxide as starting material are hampered by the low solubility of ZnO in water. Friščić *et al.* used liquid-assisted grinding (LAG) of fumaric acid with ZnO and obtained the anhydrate (**1**), the dihydrate (**2**), the tetrahydrate (**4**), and the pentahydrate (**5**) as powders [8]. The interconversion between different hydrates is challenging; for example, heating the tetrahydrate does not result in the dihydrate, but directly in the anhydrate. Here, we report an alternative synthetic procedure. In the first step, zinc fumarate anhydrate is synthesized as a fine powder, from zinc(II) acetate and fumaric acid in methanol, followed by drying at 70 °C. Anhydrous zinc fumarate is water-soluble and hence, it is a very useful material for synthesizing various zinc fumarate hydrates. In the second step, zinc fumarate anhydrate is dissolved in water and crystallized by slow evaporation or by vapor diffusion using antisolvents such as acetonitrile or 2-propanol. The use of methanol in the first step was triggered by two observations: (1) fumaric acid and zinc acetate are both soluble in methanol, (2) previous studies in this field showed methanol to be a very good solvent for syntheses and crystallization from solution as well as for LAG experiments [9]. Using methanol as solvent, we previously crystallized a methanol-containing Co(II) fumarate, poly[$\mu_4$-fumarato-dimethanolcobalt(II)]. This 2-D CP loses its solvent molecules at room temperature and transforms to amorphous, we assume anhydrous, Co(II) fumarate. The product turned out to be a very good water-soluble precursor for further crystallization experiments, yielding new 2- and 3-D Co(II) fumarate CPs [10]. The observation, that amorphous, anhydrous metal(II) fumarates are quite soluble in water, prompts their use for the crystallization of metal(II) fumarate hydrates from aqueous solution.

To date, the crystal structures of four different Zn(II) fumarate CPs that contain no solvents except for water have been reported. The structures of anhydrous $Zn(C_4H_2O_4)$ (**1**) and the bis–aqua complex (**2**) have been determined using X-ray powder diffraction (XRPD) data [11]. The structures of the tetrahydrate (**4**) and pentahydrate (**5**) have also been determined from X-ray single-crystal data [7–9]. Whereas, **1** shows a 3-D structure with a tetrahedrally coordinated zinc(II), the other three complexes contain octahedrally coordinated zinc(II) cations, which are linked by fumarate anions into linear chains. In **2**, the Zn cations of neighboring chains are connected by $\mu_2$-water molecules into layers. In **4** and **5**, the chains are connected by hydrogen bonds only. Here, we report the synthesis, crystallization, and single-crystal structure analysis of the dihydrate $[Zn(H_2O)_2(C_4H_2O_4)]$ (**2**), which was previously only obtained as a powder, and of the hitherto unknown $[Zn(H_2O)_3(C_4H_2O_4)]\cdot H_2O$ coordination polymer (**3**). Furthermore, the other known Zn(II) fumarate CPs $[Zn(H_2O)_4(C_4H_2O_4)]$ (**4**) and $[Zn(H_2O)_4(C_4H_2O_4)]\cdot H_2O$ (**5**) could be crystallized, and their structures were redetermined by single-crystal analysis.

## 2. Experimental

### 2.1. *Reagents and techniques*

All solvents and reagents for synthesis and crystallization were of p.a. grade, purchased from Sigma Aldrich and used without further purification. XRPD was performed in transmission mode on a STOE Stadi-P diffractometer with a Ge (111) monochromator and a linear position-sensitive detector using Cu $K\alpha_1$ radiation ($\lambda$ = 1.5406 Å) at 25 °C from 2.0 to 79.99° in $2\theta$ with a scan speed of 150s per step and a PSD step size of 0.2° in $2\theta$. For data acquisition, the STOE software *WinX$^{POW}$* [12] was used. For the comparison of the measured diagrams with the single-crystal structures known from the CSD, calculated XRPD patterns were simulated. The elemental analyses (CH) were carried out on an Elementar (vario MICRO cube) elemental analyzer. About 1–4 mg of the samples were placed in a tin vessel and measured at 1423 K under a helium atmosphere with the addition of oxygen during the measurement. Thermogravimetric analyses (TGA) were performed on a TGA 92 (SETARAM) device. About 15–20 mg of the samples were placed in corundum crucibles and measured from 25 to 500 °C at a rate of 3 °C min$^{-1}$ under nitrogen. Differential scanning calorimetry (DSC) measurements were performed on a DSC 131 (SETARAM) device. About 25–30 mg of the samples was placed in an aluminum crucible and measured from 25 to 500 °C at a rate of 3 °C min$^{-1}$ under nitrogen.

### 2.2. *Syntheses*

**2.2.1. $Zn(C_4H_2O_4)$ (1).** The addition of 50 mL of a methanolic solution of $Zn(CH_3COO)_2\cdot 2H_2O$ (2.837 g, 12.9 mM) to 100 mL of a methanolic solution of fumaric acid (3 g, 25.8 mM) at room temperature yielded a colorless precipitate of **1**. The suspension was stirred for 60 min. The precipitate was isolated by filtration, washed with 50 mL of methanol, and dried for one day at 70 °C (yield: 97% based on zinc). The experimental XRPD pattern was in agreement with the calculated one from the known crystal structure of anhydrous zinc(II) fumarate determined from XRPD data [11]. Anal. Calcd for $C_4H_2ZnO_4$ (%): C, 26.77; H, 1.12. Found (%): C, 26.40; H, 1.25.

**2.2.2. $[Zn(H_2O)_2(C_4H_2O_4)]$ (2).** Colorless crystals of **2** could be obtained using the vapor diffusion technique. A vial containing 3 mL of an aqueous solution of **1** (0.020 g, 0.1 mM) was placed in a screw-top jar containing 8 mL of acetonitrile. The jar was closed. After two months at room temperature, single crystals of **2**, catena-(($\mu_2$-fumarato)-di-aqua-zinc(II)), had formed. Similarly, methanol, ethanol, or 1-propanol were used as antisolvents. Anal. Calcd for $C_4H_6ZnO_6$ (%): C, 22.29; H, 2.81. Found (%): C, 22.11; H, 2.69.

**2.2.3. $[Zn(H_2O)_3(C_4H_2O_4)]\cdot H_2O$ (3).** The same method as described above was used to obtain colorless crystals of **3** using 2-propanol instead of acetonitrile. After two weeks at room temperature, a mixture of single crystals of **3**, catena-(($\mu_2$-fumarato)-tri-aqua-zinc(II) monohydrate), and the known compound **4**, catena-(($\mu_2$-fumarato)-tetra-aqua-zinc(II)), had formed. Attempts for a selective crystallization of **3**, by varying the crystallization conditions, were not successful.

**2.2.4. $[Zn(H_2O)_4(C_4H_2O_4)]$ (4) and $[Zn(H_2O)_4(C_4H_2O_4)]\cdot H_2O$ (5).** Colorless crystals of **4** were obtained using evaporation crystallization. A vial containing 3 mL of an aqueous solution of **1** (0.020 g, 0.1 mM) was placed in a screw-top jar containing 8 mL of ethylene glycol. After two months at room temperature, single crystals were obtained. The compound was identified as the known compound **4**, catena-(($\mu_2$-fumarato)-tetra-aqua-zinc(II)), by X-ray single-crystal and powder diffraction. As an alternative, 3 g of $CaCl_2$ was used, instead of the ethylene glycol, to accelerate the crystallization.

Colorless crystals of **5** were obtained using vapor diffusion as described for the preparation of **2**, using acetone instead of acetonitrile. After three days at room temperature, single crystals were obtained. According to X-ray single-crystal and powder diffraction, the compound corresponds to the known phase **5**, catena-(($\mu_2$-fumarato)-tetra-aqua-zinc(II) monohydrate). Similarly, tetrahydrofuran can be used as antisolvent.

### 2.3. *X-ray crystallography*

Suitable single crystals of **2** and **3** were carefully selected under a polarizing microscope and mounted to the tip of a thin glass fiber, which was then placed and measured on a SIEMENS SMART 1 K area detector diffractometer, equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 166 K for **2** and 165 K for **3**. Repeatedly measured reflections remained stable for both compounds. An empirical absorption correction with SADABS [13] gave a correction factor between 0.539 and 0.621 for **2**. A numerical absorption correction based on six indexed crystal faces gave a transmission factor between 0.385 and 0.636 for **3**. Equivalent reflections were averaged. $R_{\text{int}}(I)$ is 0.037 for **2** and 0.053 for **3**. The structures were determined by direct methods using SHELXS-97 [14]. Hydrogens were taken from a difference synthesis and were refined. The H atom bonded to C was constrained for **2** using a riding model. The crystals of **2** were twinned. The twin relations are: $h' = h$, $k' = -k$ and $l' = -0.50\ h\ -l$. Thus, reflections of the two twin domains coincide for even values of $h$. The twin fraction refined to 0.469(2). The structures were refined by full-matrix least-squares refinement on $F^2$ values using SHELXL-97 [15]. The final difference density was between −0.75 and +1.58 e/Å$^3$ for **2** and between −0.30 and +0.45 e/Å$^3$ for **3**. A summary of the crystal data and structure refinement details is given in table 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Supplementary material. Selected interatomic distances and angles are given in tables 2 and 3.

## 3. Results and discussion

### 3.1. *Synthesis and crystallization*

The procedure, using Zn(II) acetate and fumaric acid in methanol, to synthesize the anhydrous Zn(II) fumarate (**1**) was successful. The anhydrate is comparably soluble in water as the above-mentioned Co(II) fumarate. Starting from **1**, it was possible to grow single crystals of the known tetra- (**4**) and pentahydrate (**5**) and, for the first time, of the known dihydrate (**2**) and a not previously described trihydrate (**3**). The vapor diffusion technique, in which a solid is dissolved in water, filled into a vial and placed into a screw-top jar containing the antisolvent, yielded, depending on the antisolvent, three different products. With acetonitrile, we obtained the dihydrate (**2**), with 2-propanol, a mixture of the new trihydrate (**3**) and the known tetrahydrate (**4**) and with acetone the pentahydrate (**5**). The inverse vapor

Table 1. Summary of crystal data, data collection, structure solution and refinement details for **2** and **3**.

| | **2** | **3** |
|---|---|---|
| Empirical formula | $C_4H_6ZnO_6$ | $C_4H_{10}ZnO_8$ |
| Formula weight | 215.46 | 251.49 |
| Description | Colorless block | Colorless rod |
| Crystal size (mm) | 0.12 × 0.14 × 0.16 | 0.18 × 0.18 × 0.40 |
| Temperature (K) | 166(2) | 165(2) |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ |
| Wavelength | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $C2/c$ |
| Unit cell dimensions | | |
| $a$ (Å) | 3.3784(7) | 7.7464(18) |
| $b$ (Å) | 10.335(2) | 15.932(2) |
| $c$ (Å) | 8.8369(19) | 7.0845(13) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 95.478(10) | 97.728(13) |
| $\gamma$ (°) | 90 | 90 |
| Volume (Å$^3$) | 307.14(11) | 866.4(3) |
| $Z$ | 2 | 4 |
| $\rho_{calc}$ (g cm$^{-1}$) | 2.330 | 1.928 |
| $F$ (0 0 0) | 216 | 512 |
| $\mu$ (mm$^{-1}$) | 3.975 | 2.850 |
| Absorption correction | Empirical | Numerical |
| Min. and max. transmission | 0.621, 0.539 | 0.636, 0.385 |
| $\theta$ Range for data collection (°) | 3.0–33.8 | 2.56–32.09 |
| Reflections collected | 4723 | 6929 |
| Independent reflections ($R_{int}$) | 1183 (0.037) | 1447 (0.053) |
| Data/restraints/parameters | 1183/0/61 | 1447/0/81 |
| Goodness of fit on $F^2$ | 1.15 | 1.081 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$][a] | 0.043, 0.111 | 0.020, 0.049 |
| $R_1$, $wR_2$ [all data][a] | 0.061, 0.119 | 0.022, 0.050 |
| Limiting indices | $-5 \le h \le 5$, $-15 \le k \le 13$, $-13 \le l \le 12$ | $-11 \le h \le 11$, $-23 \le k \le 23$, $-10 \le l \le 10$ |
| Completeness to $\theta$ max | 0.953 | 0.951 |
| $\delta\rho_{max}$, $\delta\rho_{min}$ (e/Å$^{-3}$) | 1.58, −0.75 | 0.45, −0.30 |

[a] $wR_2 = [\Sigma w(F^2_o - F^2_c)^2/\Sigma w(F^2_o)^2]^{1/2}$.

Table 2. Final interatomic distances (Å) and angles (°) for **2**.

| | | | | | |
|---|---|---|---|---|---|
| Zn(1)–O(1)#1 | 1.960(2) | Zn(1)–O(3) | 2.219(3) | C(1)–O(2) | 1.261(3) |
| Zn(1)–O(1) | 1.960(2) | O(3)–Zn(1)#4 | 2.201(3) | C(1)–C(2) | 1.486(4) |
| Zn(1)–O(3)#2 | 2.201(3) | O(3)–H(3A) | 0.86(4) | C(2)–C(2)#5 | 1.346(7) |
| Zn(1)–O(3)#3 | 2.201(3) | O(3)–H(3B) | 0.86(5) | C(2)–H(2A) | 0.95 |
| Zn(1)–O(3)#1 | 2.219(3) | O(1)–C(1) | 1.272(4) | | |
| | | | | | |
| O(1)#1–Zn(1)–O(1) | 180.0 | O(1)#1–Zn(1)–O(3) | 90.39(9) | H(3A)–O(3)–H(3B) | 107(4) |
| O(1)#1–Zn(1)–O(3)#2 | 91.17(9) | O(1)–Zn(1)–O(3) | 89.61(9) | C(1)–O(1)–Zn(1) | 129.37(19) |
| O(1)–Zn(1)–O(3)#2 | 88.83(9) | O(3)#2–Zn(1)–O(3) | 80.32(9) | O(2)–C(1)–O(1) | 125.2(3) |
| O(1)#1–Zn(1)–O(3)#3 | 88.83(9) | O(3)#3–Zn(1)–O(3) | 99.68(9) | O(2)–C(1)–C(2) | 118.7(3) |
| O(1)–Zn(1)–O(3)#3 | 91.17(9) | O(3)#1–Zn(1)–O(3) | 180.0 | O(1)–C(1)–C(2) | 116.1(3) |
| O(3)#2–Zn(1)–O(3)#3 | 180.0 | Zn(1)#4–O(3)–Zn(1) | 99.67(9) | C(2)#5–C(2)–C(1) | 122.2(4) |
| O(1)#1–Zn(1)–O(3)#1 | 89.61(9) | Zn(1)#4–O(3)–H(3A) | 100(3) | C(2)#5–C(2)–H(2A) | 119 |
| O(1)–Zn(1)–O(3)#1 | 90.39(9) | Zn(1)–O(3)–H(3A) | 115(3) | C(1)–C(2)–H(2A) | 119 |
| O(3)#2–Zn(1)–O(3)#1 | 99.68(9) | Zn(1)#4–O(3)–H(3B) | 118(3) | | |
| O(3)#3–Zn(1)–O(3)#1 | 80.32(9) | Zn(1)–O(3)–H(3B) | 116(3) | | |
| | | | | | |
| O(1)#1–Zn(1)–O(3)–Zn(1)#4 | −91.12(10) | O(3)#3–Zn(1)–O(1)–C(1) | −31.6(3) | | |
| O(1)–Zn(1)–O(3)–Zn(1)#4 | 88.88(10) | O(3)#1–Zn(1)–O(1)–C(1) | −111.9(3) | | |
| O(3)#2–Zn(1)–O(1)–C(1) | 148.4(3) | O(3)–Zn(1)–O(1)–C(1) | 68.1(3) | | |
| | | Zn(1)–O(1)–C(1)–O(2) | 13.3(5) | | |
| | | Zn(1)–O(1)–C(1)–C(2) | −168.0(2) | | |
| | | O(2)–C(1)–C(2)–C(2)#5 | 176.1(4) | | |
| | | O(1)–C(1)–C(2)–C(2)#5 | −2.7(6) | | |
| | | | | | |
| *Hydrogen-bonding contacts* | | | | | |
| D–H | *d*(D–H) | *d*(H···A) | ∠(D–H···A) | *d*(D–H···A) | A |
| O(3)–H(3A) | 0.86(4) | 1.88(4) | 155(4) | 2.678(3) | O(2)#4 |
| O(3)–H(3B) | 0.86(4) | 1.82(4) | 165(5) | 2.661(3) | O(2)#6 |

Note: Symmetry transformations used to generate equivalent atoms: #1 = −*x*, −*y* + 1, −*z* + 1; #2 = −*x* + 1, −*y* + 1, −*z* + 1; #3 = *x* − 1, *y*, *z*; #4 = *x* + 1, *y*, *z*; #5 = −*x*, −*y* + 1, −*z*; #6 = *x* + 1, −*y* + 1/2, *z* + 1/2.

diffusion technique in which the water diffuses out of the vial, accelerated by $CaCl_2$ or ethylene glycol, yielded the tetrahydrate (**4**). Although a huge number of crystallization experiments were performed, no clear correlation between the hydration state and the selection of solvent or antisolvent could be found. Furthermore, the outcome of the experiments also depended on the individual conditions applied. For example, crystallization with water as solvent and 2-propanol as antisolvent yielded crystals of **2**, **3**, or **4** or mixtures of them, depending on the crystallization conditions. The same was found for crystallization from water/2-butanone or water/1-propanol.

## 3.2. *Crystal structures of 2 and 3*

Single crystals of **2–5** could be obtained, and their crystal structures were determined by X-ray structure analysis.

### 3.2.1. Crystal structure of $[Zn(H_2O)_2(C_4H_2O_4)]$ (2).

The structure of the bis–aqua **2** has previously been determined from XRPD data collected at room temperature [9]. The resulting structure was of limited accuracy. Here, we report a more accurate structure from single-crystal X-ray data collected at low temperature.

Table 3. Final interatomic distances (Å) and angles (°) for **3**.

| | | | | | |
|---|---|---|---|---|---|
| Zn(1)–O(4) | 2.0407(11) | O(2)–C(2) | 1.2616(13) | C(1)–C(1)#2 | 1.3264(19) |
| Zn(1)–O(3) | 2.0658(9) | O(3)–H(3A) | 0.736(19) | C(1)–H(1A) | 0.932(14) |
| Zn(1)–O(3)#1 | 2.0658(9) | O(3)–H(3B) | 0.814(18) | O(4)–H(4A) | 0.823(16) |
| Zn(1)–O(1) | 2.0687(8) | C(2)–O(1) | 1.2705(13) | O(5)–H(5A) | 0.767(17) |
| Zn(1)–O(1)#1 | 2.0687(8) | C(2)–C(1) | 1.4911(14) | | |
| O(4)–Zn(1)–O(3) | 88.70(2) | O(3)–Zn(1)–O(1)#1 | 87.21(3) | O(2)–C(2)–C(1) | 117.74(9) |
| O(4)–Zn(1)–O(3)#1 | 88.70(2) | O(3)#1–Zn(1)–O(1)#1 | 94.50(4) | O(1)–C(2)–C(1) | 119.88(9) |
| O(3)–Zn(1)–O(3)#1 | 177.40(4) | O(1)–Zn(1)–O(1)#1 | 97.72(4) | C(2)–O(1)–Zn(1) | 104.84(6) |
| O(4)–Zn(1)–O(1) | 131.14(2) | Zn(1)–O(3)–H(3A) | 117.2(14) | C(1)#2–C(1)–C(2) | 123.52(12) |
| O(3)–Zn(1)–O(1) | 94.50(4) | Zn(1)–O(3)–H(3B) | 117.2(11) | C(1)#2–C(1)–H(1A) | 119.2(9) |
| O(3)#1–Zn(1)–O(1) | 87.21(3) | H(3A)–O(3)–H(3B) | 107(2) | C(2)–C(1)–H(1A) | 117.2(9) |
| O(4)–Zn(1)–O(1)#1 | 131.14(2) | O(2)–C(2)–O(1) | 122.35(9) | Zn(1)–O(4)–H(4A) | 126.4(11) |
| O(2)–C(2)–O(1)–Zn(1) | 9.09(11) | O(3)#1–Zn(1)–O(1)–C(2) | 87.22(7) | | |
| C(1)–C(2)–O(1)–Zn(1) | −168.96(7) | O(1)#1–Zn(1)–O(1)–C(2) | 178.61(7) | | |
| O(4)–Zn(1)–O(1)–C(2) | 1.39(7) | O(2)–C(2)–C(1)–C(1)#2 | −172.02(13) | | |
| O(3)–Zn(1)–O(1)–C(2) | −90.82(7) | O(1)–C(2)–C(1)–C(1)#2 | 6.12(18) | | |
| *Hydrogen-bonding contacts* | | | | | |
| D–H | *d*(D–H) | *d*(H···A) | ∠(D–H···A) | *d*(D–H···A) | A |
| O(3)–H(3A) | 0.74(2) | 2.058(19) | 169(2) | 2.7836(12) | O(1)#3 |
| O(3)–H(3B) | 0.813(17) | 1.920(17) | 173.4(16) | 2.7295(13) | O(5)#4 |
| O(4)–H(4A) | 0.823(15) | 1.990(15) | 172.5(15) | 2.8075(12) | O(2)#4 |
| O(5)–H(5A) | 0.769(18) | 2.089(18) | 173.6(19) | 2.8539(12) | O(2)#5 |

Note: Symmetry transformations used to generate equivalent atoms: #1 = $-x + 1, y, -z + 1/2$; #2 = $-x, -y, -z$; #3 = $-x + 1, -y, -z$; #4 = $-x + 1/2, -y + 1/2, -z$; #5 = $x, y, z$.

Compound **2** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains half a fumarate anion, one water molecule in the general position, and a Zn$^{2+}$ ion at a crystallographic inversion center. The Zn$^{2+}$ ion has octahedral coordination and is bonded to two symmetry-related fumarate groups and four water molecules. The Zn–O(fumarate) bond length is 1.960(2) and the Zn–O(hydrate) bond lengths are 2.202(3) and 2.219(3) Å, respectively (table 2). There is a crystallographic inversion center at the midpoint of the C=C double bond of the fumarate group. The fumarate group is approximately planar (mean deviation from plane: 0.013 Å). The Zn$^{2+}$ ions and fumarate anions form chains along the *c*-direction. These chains are connected in the *a*-direction by the bridging water molecules into layers parallel to the (0 1 0) plane as shown in figure 1. The layers are connected along the *b*-axis into a 3-D framework by O(water)–H···O(fumarate) hydrogen bonds (table 2). The second hydrogen of the water molecule is involved in an O(water)–H···O (fumarate) hydrogen bond within a layer as shown in figure 1.

### 3.2.2. Crystal structure of $[Zn(H_2O)_3(C_4H_2O_4)]\cdot H_2O$ (3).

Compound **3**, catena-(($\mu_2$-fumarato)-tri-aqua-zinc(II) monohydrate), has the same chemical composition as the known catena-(($\mu_2$-fumarato)-tetra-aqua-zinc(II)), $[Zn(H_2O)_4(C_4H_2O_4)]$ (**4**). However, the structures are clearly different.

Compound **3** crystallizes in the monoclinic space group $C2/c$. The asymmetric unit contains half of a fumarate group, a Zn$^{2+}$ on a twofold axis, one water molecule in the general position, and two water molecules both positioned on the twofold axes. The structure exhibits infinite zig-zag chains of triaquazinc fumarate units extended along the $2\mathbf{a} + \mathbf{c}$ vector as shown in figure 2. The Zn$^{2+}$ atom has a distorted trigonal bipyramidal

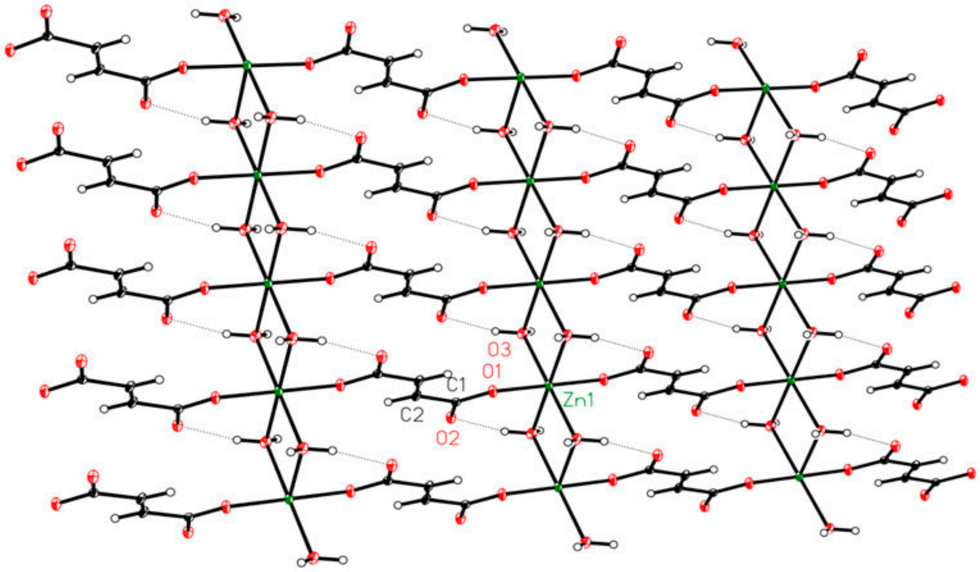

Figure 1. A view of the layer structure of $[Zn(H_2O)_2(C_4H_2O_4)]$ (**2**). Displacement ellipsoids of the non-H atoms are drawn at the 50% probability level. The intra-layer hydrogen bonds are shown as dotted lines. The direction of view corresponds approximately to [0 1 0].

conformation, with two water molecules in the axial positions, whereas the third water molecule and two fumarate ions occupy the three equatorial positions, thus the fumarate groups are located *cis* to each other. The Zn–O distances range from 2.041(1) to 2.069(1) Å (table 3).

There is an inversion center at the midpoint of the C=C double bond of the fumarate group. The fumarate group is almost planar; the dihedral angle between the plane of the C=C double bond (including adjacent atoms) and the plane of the carboxylate group is 7.1°. The fumarate groups act as a bridge between two $Zn^{2+}$ ions, leading to a 1-D coordination polymer.

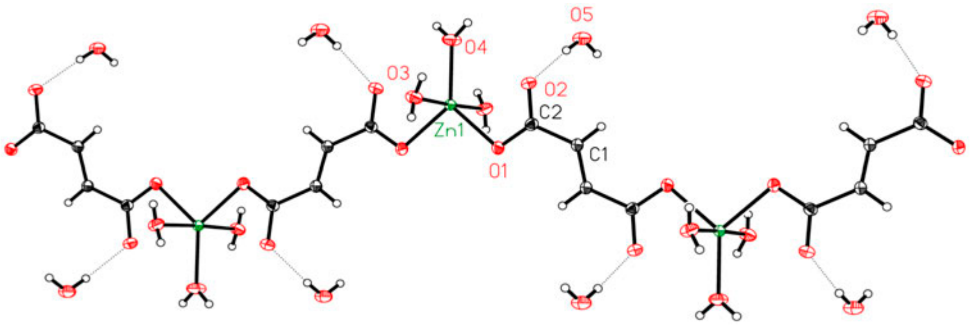

Figure 2. A view of the chain structure of $[Zn(H_2O)_3(C_4H_2O_4)]\cdot H_2O$ (**3**). Displacement ellipsoids of the non-H atoms are drawn at the 50% probability level. Dotted lines represent selected hydrogen bonds involving the non-coordinated water molecule.

The chains are connected by hydrogen bonding forming a 3-D network (table 3). The non-coordinated water molecule (O5) is located on a twofold axis and is an acceptor of two O(aqua)-H···O hydrogen bonds and a donor of two O–H···O(carboxylate) hydrogen bonds.

The structure of **3** differs considerably from the structure of its isomeric compound, [Zn$(H_2O)_4(C_4H_2O_4)$] (**4**). In **4**, the $Zn^{2+}$ ion is octahedrally coordinated to four water molecules and two fumarate ions [5, 6, 11].

### 3.2.3. Crystal structures of [Zn$(H_2O)_4(C_4H_2O_4)$] (4) and [Zn$(H_2O)_4(C_4H_2O_4)$]·$H_2O$ (5).

The single-crystal X-ray analyses of **4** and **5** confirmed the structures determined by Xu *et al.* [5, 6] and Friščić and Fábián [11].

### 3.2.4. Comparison of the structures of 1–5.

Including the structures presented here, five crystal structures of zinc(II) fumarates containing 0–5 water molecules as additional component are known. The structural motives depend on the amount of water in the structural formula. A 3-D network occurs in anhydrous zinc(II) fumarate [9]. The tetrahedral $Zn^{2+}$ is coordinated to O atoms with Zn–O distances between 1.93 and 1.94 Å. A 2-D layered structure is found in diaquazinc(II) fumarate (**2**). The octahedral $Zn^{2+}$ is coordinated to O atoms with Zn–O distances of 1.96 Å (carboxylate) and 2.20 Å (hydrate). Zig-zag chains occur in triaquazinc(II) fumarate monohydrate (**3**). The $Zn^{2+}$ has a distorted trigonal bipyramidal coordination with Zn–O distances between 2.04 and 2.07 Å. A linear chain is reported for tetraaquazinc(II) fumarate [6, 11] containing an octahedral $Zn^{2+}$ with Zn–O distances between 2.07 and 2.11 Å. Finally, tetraaquazinc(II) fumarate monohydrate [6] shows zig-zag chains. The $Zn^{2+}$ has an octahedral coordination with Zn–O distances between 2.07 and 2.09 Å. An overview of the hydration state, the coordination number, and the network of all presented zinc(II) fumarates is shown in table 4.

If the $Zn^{2+}$ ions in the structures of **3–5** could be replaced by a spin-bearing metal ion, e.g. $Co^{2+}$, without changing the coordination, these phases would be of great interest in the investigation of the dependence of spin exchange on the coordination geometry (trigonal bipyramidal, octahedral *trans*, and octahedral *cis*). Hitherto, only two octahedral *trans* phases [10, 16–18] and one octahedral *cis* [10] phase are known for $Co^{2+}$ fumarates.

Zinc(II) carboxylates exhibit a variety of structural motifs [19–22]. The most well-known coordination numbers for $Zn^{2+}$ ions are four and six, whereas five is less common. With bidentate ligands, a variety of coordination networks can be formed, including chains, layers, and 3-D networks. The zinc(II) fumarates exhibit $Zn^{2+}$ ions with coordination numbers of four, five, and six, and form chains, layers, and 3-D frameworks. Thus, they represent a considerable collection of examples of the variety of zinc(II) carboxylates.

Table 4. Overview of the hydration state, the coordination number, and the network of zinc(II) fumarates.

| Compound | Hydration state of $Zn^{2+}$ ions | Coordination | Position of fumarate ligands | Network |
|---|---|---|---|---|
| **1** | $(H_2O)_0$ | 4 (tetrahedral) | – | 3D |
| **2** | $(H_2O)_2$ | 6 (octahedral) | *trans* | 2D |
| **3** | $(H_2O)_3 \cdot H_2O$ | 5 (pentag. bipy.) | *cis* | 1D |
| **4** | $(H_2O)_4$ | 6 (octahedral) | *trans* | 1D |
| **5** | $(H_2O)_4 \cdot H_2O$ | 6 (octahedral) | *cis* | 1D |

In carboxylates, the carboxylate ligand itself can be a $\eta^2$-ligand. This is not observed for zinc(II) fumarates. Generally, the carboxylate bridges two $Zn^{2+}$ ions. Here, this is observed only for **1**.

In the zinc(II) fumarates, the two carboxylate groups always coordinate to different $Zn^{2+}$ ions, with the fumarate as linker between the $Zn^{2+}$ ions. Monomeric units, *i.e.* $Zn^{2+}$ ions without a connection to neighboring $Zn^{2+}$ ions, have not been found. However, such monomers are observed in zinc(II) complexes with maleic acid, the *cis* isomer of fumaric acid. In tetraaqua zinc(II) bis(hydrogenmaleate) [20], the $Zn^{2+}$ ion is coordinated to two non-bridging hydrogenmaleate anions. Both anions exhibit an intramolecular hydrogen bond between the COOH and the $COO^-$ groups, which could not be formed by (hydrogen) fumarates. Diaqua zinc(II) maleate [21] shows a 2-D layered structure with a coordination number of five for the $Zn^{2+}$ ion. The $Zn^{2+}$ ions are connected by maleate anions only. In contrast, diaqua zinc(II) fumarate (**2**) exhibits an octahedral coordination of $Zn^{2+}$, and the $Zn^{2+}$ ions are additionally linked by bridging water molecules.

The zinc(II) fumarates are also not isostructural to the zinc(II) succinates, which contain a $-CH_2-CH_2-$ unit instead of the $-CH=CH-$ unit. Two polymorphs of zinc(II) succinate anhydrate are known [22]; both structures differ from the zinc(II) fumarate (**1**).

### 3.3. *TGA and DSC results*

TGA and DSC measurements were performed for **1** and **2**. The TGA curve of $Zn(C_4H_2O_4)$ showed no mass loss from 25 to 347 °C. Thereafter, the compound decomposes between 393 and 478 °C, resulting in a residue with a weight fraction of 36.38% and corresponding to nanocrystalline hexagonal Zn(II) oxide also known as *zincite* [23] with a wurtzite structure as confirmed by XRPD. The DSC experiment shows no signals between 25 and 397 °C. Between 398 and 443 °C, a broad endothermic signal appears, again showing the decomposition of the compound, as observed in the TGA experiment. The structure of the resulting nanocrystalline hexagonal Zn(II) oxide was again confirmed by XRPD.

The DTA curve of the bis–aqua complex (**2**) shows two strong signals centered at 96 and 430 °C. The TGA shows no mass loss from 25 to 90 °C. Thus the 2-D CP is stable up to 90 °C. The TGA curve shows a dehydration of **2** with a weight loss of 15.35% upon heating from 91 to 108 °C. This agrees with the value of 16.62% calculated for the release of two water molecules per formula unit. This mass loss leads to anhydrous Zn(II) fumarate (**1**) known from the synthesis as determined by temperature-dependent XRPD at 150 °C. After cooling this sample to 25 °C, the anhydrate remains stable. Upon heating, the anhydrate (**1**) is stable up to 373 °C. Then a second mass loss occurs between 374 and 451 °C resulting in a residue with a weight fraction of 54.98% based on **2**. The final residue again corresponds to nanocrystalline hexagonal Zn(II) oxide as determined by XRPD.

The DSC curve for **2** shows no signal from 25 to 81 °C. Between 82 and 104 °C, a sharp endothermic signal occurs that is in agreement with the results of the TGA measurements and corresponds to the loss of two water molecules, leading again to the anhydrate as determined by XRPD. No further signals could be observed between 105 and 406 °C. Finally an exothermic signal between 406 and 447 °C occurs corresponding to the decomposition of the compound as observed in the TGA. The ensuing nanocrystalline hexagonal Zn(II) oxide again was confirmed by XRPD.

## 4. Conclusion

A solvent-based synthesis of the 3-D, anhydrous Zn(II) fumarate CP, previously only obtained by Friščić *et al.* using LAG experiments, is reported. This compound is more soluble in water than its hydrates. Thus, it is suitable for further crystallization experiments from aqueous solution. Vapor-diffusion crystallization experiments resulted in single crystals of the bis–aqua **2**, a compound that thus far had only been obtained as a powder. Additionally, single crystals of a new 1-D triaqua-Zn(II) fumarate monohydrate CP (**3**) could be crystallized. It is the first known metal(II) fumarate containing a trigonal bipyramidal coordinated metal(II) cation with no other ligands than water. In addition, all other known Zn(II) fumarate hydrates could be crystallized using the new strategy. The synthetic procedure developed here is suited to the synthesis of other metal fumarate hydrates.

## Supplementary material

Crystallographic data (excluding structure factors) for $[Zn(H_2O)_2(C_4H_2O_4)]$ (**2**) and $[Zn(H_2O)_3(C_4H_2O_4)]\cdot H_2O$ (**3**), reported in this paper, have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. 869977 for **1** and 869978 for **3**. Copies of available materials can be obtained, free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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## Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2014.978765].

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