

Two new cobalt(II) fumarates and a redetermination of tetraaquacobalt(II) fumarate monohydrate

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Received 24 June 2009

Accepted 31 July 2009

Online 19 August 2009

Poly[triaqua- μ_4 -fumarato-cobalt(II)], $[\text{Co}(\text{C}_4\text{H}_2\text{O}_4)(\text{H}_2\text{O})_3]_n$, (I), contains two symmetry-independent octahedrally coordinated Co^{2+} ions, both on inversion centers. One Co^{2+} ion is coordinated by two water molecules and four fumarate dianions, whereas the other Co^{2+} ion is surrounded by four water molecules and two fumarate dianions. Each fumarate dianion is bonded to three Co^{2+} ions, leading to a two-dimensional structure. The fumarate dianions are nonplanar; the angle between the planes of the two carboxylate groups is $54.9(2)^\circ$. The cobalt(II) fumarate layers are connected by hydrogen bonding into a three-dimensional network. Compound (I) is not isostructural with calcium(II) fumarate trihydrate [Gupta *et al.* (1972). *Acta Cryst.* **B28**, 135–139]. In poly[μ_4 -fumarato-dimethanolcobalt(II)], $[\text{Co}(\text{C}_4\text{H}_2\text{O}_4)(\text{CH}_3\text{O})_2]_n$, (II), the Co^{2+} ions are octahedrally coordinated by four fumarate dianions and two methanol molecules, leading to a three-dimensional structure. The fumarate group is planar. The Co^{2+} ions and the fumarate dianions both lie on inversion centers. Additionally, the one-dimensional structure of *catena*-poly[[[tetraaquacobalt(II)]- μ_2 -fumarato] monohydrate], $\{[\text{Co}(\text{C}_4\text{H}_2\text{O}_4)(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}\}_n$, (III), was redetermined at a higher resolution, and the space group $C2/c$ was confirmed.

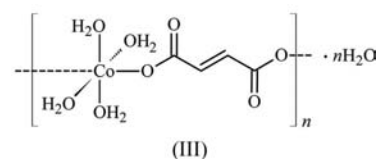
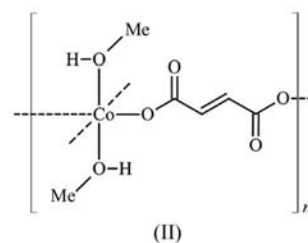
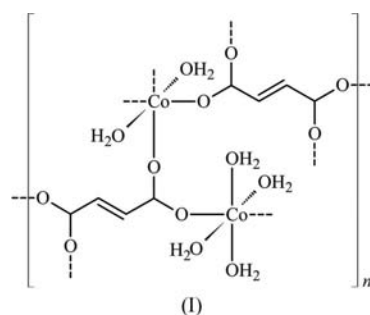
Comment

The octahedral coordination of Co^{2+} ions was first recognized by Werner (1893). To date, only two cobalt(II) fumarate complexes containing water molecules are known, namely cobalt(II) fumarate tetrahydrate [which is actually a tetraaquacobalt(II) fumarate (Konar *et al.*, 2003; Zheng & Xie, 2004; Padmanabhan *et al.*, 2008)] and cobalt(II) fumarate pentahydrate [which is actually a tetraaquacobalt(II) fumarate monohydrate (Gupta & Sinha, 1978; Konar *et al.*, 2003; Marsh & Spek, 2001; Porollo *et al.*, 1997)]. Compounds in which Co^{2+} ions [and other bivalent metal(II) ions] are bonded to satu-

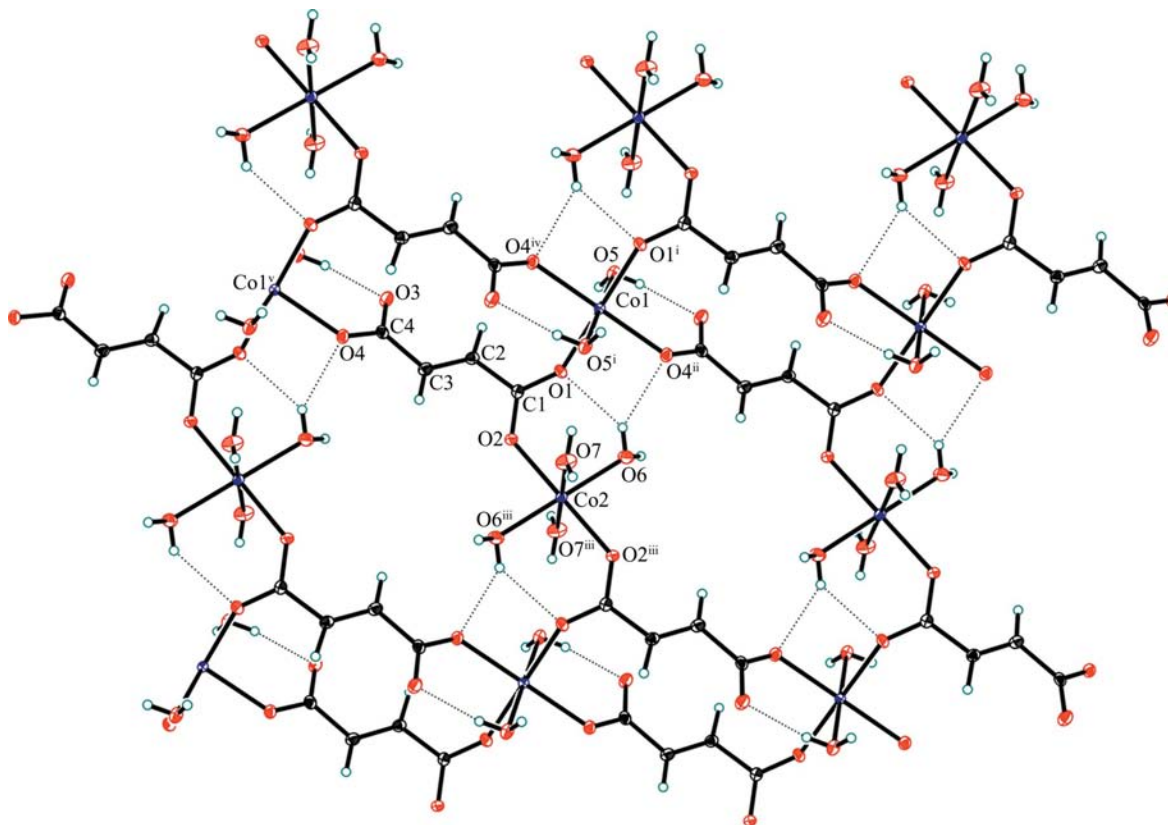
rated or unsaturated dicarboxylic acids, such as fumaric, maleic and succinic acid, have also been reported (*e.g.* Rao *et al.*, 2004; Yaghi *et al.*, 2003). In recent years, investigations of cobalt(II) fumarate phases containing additional organic ligands have been carried out (*e.g.* Chen *et al.*, 2007; Konar *et al.*, 2004; Liu *et al.*, 2003; Ma *et al.*, 2003; Manna *et al.*, 2007; Zhang *et al.*, 2004, 2005); ligands included benzimidazole, *o*-phenanthroline, pyrazine, and pyridine and its derivatives. These compounds form chain structures, layers or three-dimensional frameworks. Saturated dicarboxylic acids tend to form coordination polymers with open three-dimensional frameworks. In contrast, unsaturated dicarboxylic acids lead to metal(II) hydrate complexes with predominantly chain structures.

The cobalt(II) fumarate tetra- and pentahydrates built from the Co^{2+} ion and the fumarate dianion crystallize in one-dimensional polymeric chain structures (Gupta & Sinha, 1978; Konar *et al.*, 2003; Marsh & Spek, 2001; Padmanabhan *et al.*, 2008; Porollo *et al.*, 1997; Zheng & Xie, 2004). These chains are connected into a three-dimensional network by hydrogen bonds between water molecules and carboxylate groups.

We have prepared a novel cobalt(II) fumarate trihydrate and a cobalt(II) fumarate methanol disolvate and have also redetermined the structure of cobalt(II) fumarate pentahydrate.



The trihydrate, (I), forms two-dimensional layers parallel to the $(\bar{1}11)$ plane, as shown in Fig. 1. There are two symmetrically independent Co^{2+} ions, both on inversion centers. Atom Co1 is coordinated by two water molecules [Co1—O5 = 2.147(2) Å] and four fumarate dianions [Co1—O1 =

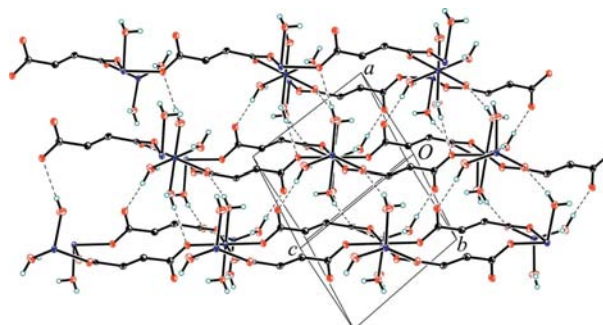

Figure 1

A layer of (I), parallel to the $(\bar{1}11)$ plane, showing the two symmetrically independent Co^{2+} ions and their coordination geometry. Hydrogen bonds are represented by dotted lines. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x - 1, y, z - 1$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $-x + 1, -y + 1, -z + 2$; (v) $x + 1, y, z + 1$.]

2.0686 (18) Å and $\text{Co1}-\text{O4} = 2.1133$ (18) Å], whereas atom Co2 is surrounded by four water molecules [$\text{Co2}-\text{O6} = 2.042$ (2) Å and $\text{Co2}-\text{O7} = 2.183$ (2) Å] and two fumarate dianions [$\text{Co2}-\text{O2} = 2.0755$ (18) Å]. Both Co^{2+} ions are coordinated in a distorted octahedral geometry. Hence, cobalt(II) fumarate trihydrate is actually a mixture of a tetraaquacobalt(II) fumarate and a diaquacobalt(II) fumarate. The fumarate group has a *trans* conformation, with a $\text{C1}-\text{C2}-\text{C3}-\text{C4}$ torsion angle of 175.6 (2)°. The carboxylate groups are rotated out of the plane; the angles between the plane of the central butene group and the planes of the two carboxylate groups are 32.0 (2) and 23.0 (1)°. The fumarate dianions act as bridging ligands, linking the two symmetrically independent Co^{2+} ions to form layers parallel to the $(\bar{1}11)$ plane. The layer is characterized by two different ring systems. There is a 14-membered ring, consisting of two Co1 atoms and two fumarate dianions, and a 22-membered ring, consisting of two Co1 atoms, two Co2 atoms and four fumarate dianions. The three independent water molecules act as donors for six different $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 1). Four of them connect the layers through an extensive hydrogen-bonding network to form a three-dimensional framework, as shown in Fig. 2. Within the layers the $\text{O6}-\text{H6B}$ group is involved in a rather weak bifurcated hydrogen bond, while the $\text{O5}-\text{H5B}$ group is involved in a rather strong hydrogen bond, as shown in Fig. 1. There is only one other report of a crystal structure of a metal(II) fumarate trihydrate, namely calcium(II) fumarate

trihydrate (Gupta *et al.*, 1972). Its coordination geometry, however, is not similar to that of (I), and comprises an eightfold-coordinated Ca^{2+} ion surrounded by two independent and two symmetry-related water molecules and three symmetry-related fumarate dianions.

Poly[μ_4 -fumarato-dimethanolicobalt(II)], (II), belongs to the group of cobalt(II) fumarates containing an additional organic ligand. The octahedrally coordinated Co^{2+} ion is located on a crystallographic inversion center. Each Co^{2+} ion is bonded to O atoms of four symmetry-related fumarate groups [$\text{Co1}-\text{O1} = 2.1060$ (10) Å and $\text{Co1}-\text{O2} = 2.1205$ (9) Å] and two O atoms of two symmetry-related


Figure 2

A packing diagram of (I), view direction $[1\bar{1}0]$, showing the layers connected *via* hydrogen bonds, leading to a three-dimensional structure. Hydrogen bonds are shown as dashed lines.

methanol molecules [$\text{Co1}-\text{O3} = 2.0657(10) \text{ \AA}$], as shown in Fig. 3. The methanol OH group donates an intramolecular hydrogen bond to carboxylate atom O2 (Table 2). The fumarate group is planar (the mean deviation from the plane is only 0.002 \AA) and has a crystallographic inversion center at

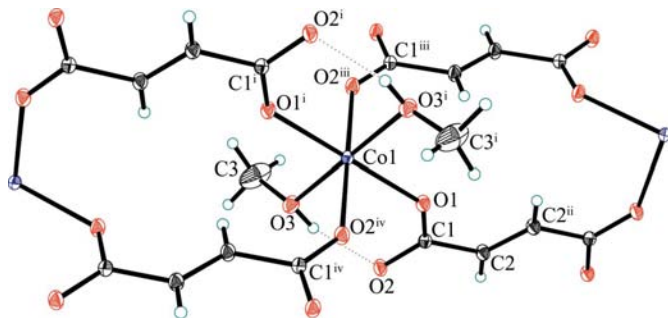


Figure 3
A section of (II), showing the coordination geometry of the Co^{2+} ion. [Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x + 1, -y, -z + 2$; (iii) $-y, z - \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.]

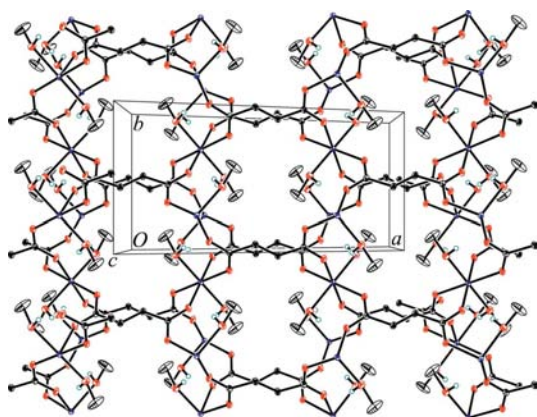


Figure 4
A packing diagram of (II), viewed along the c axis, showing the three-dimensional structure.

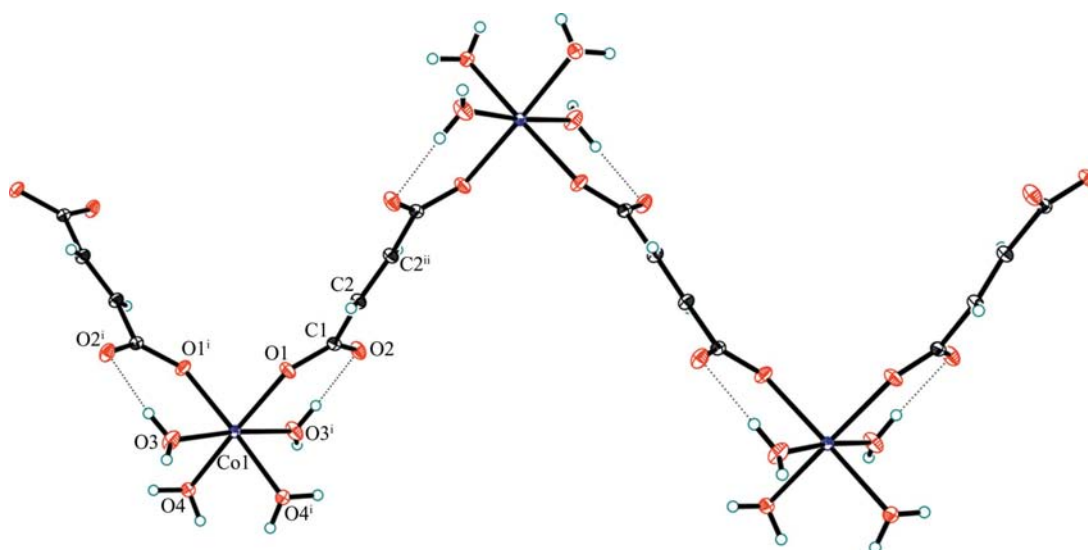


Figure 5
The chain structure of (III), showing the coordination geometry of the Co^{2+} ion. Hydrogen bonds are represented by dotted lines. [Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$.] The uncoordinated water molecule is not shown but lies between the chains.

the mid-point of the $\text{C}=\text{C}$ double bond. The Co^{2+} ions and fumarate dianions form a three-dimensional framework, as shown in Fig. 4. The structure is characterized by a system of 14-membered rings, consisting of two Co^{2+} ions and two fumarate dianions. Larger 22-membered rings consisting of four Co^{2+} ions and four fumarate dianions result in channels along the c -axis direction. The methanol ligands are located in these channels. The structure of (II) is clearly different from the structures of many two-dimensional coordination polymers that have been reported in the past few decades. Thus, the incorporation of a methanol ligand into cobalt(II) fumarate phases offers an interesting method for structural modification and the synthesis of further novel metal-organic framework structures.

There has been some confusion about the correct space group of the pentahydrate (III). The structure was originally determined by Gupta & Sinha (1978) in the space group $C2/c$. It was redetermined by Porollo *et al.* (1997) and refined in the noncentrosymmetric space group $C2$. Marsh & Spek (2001) showed that the coordinates of this structure could be transformed to $C2/c$. Two years later, the structure of (III) was redetermined by Konar *et al.* (2003) and refined in the noncentrosymmetric space group Cc . The present redetermination of the compound confirms the space group $C2/c$. The low R value (0.018) for the refinement in $C2/c$ shows that space groups $C2$ and Cc can be excluded. The Co^{2+} ion is located on a twofold axis and has an octahedral coordination. Two *cis* positions are occupied by two fumarate groups and the other positions are occupied by four water molecules. The Co^{2+} ions and fumarate dianions form one-dimensional zigzag chains along the c -axis direction, as shown in Fig. 5. These chains are connected by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 3) into a three-dimensional network, as shown in Fig. 6. There is a crystallographic inversion center at the mid-point of the $\text{C}=\text{C}$ double bond of the fumarate group. The angle between the plane of the central butene group and the planes of the two

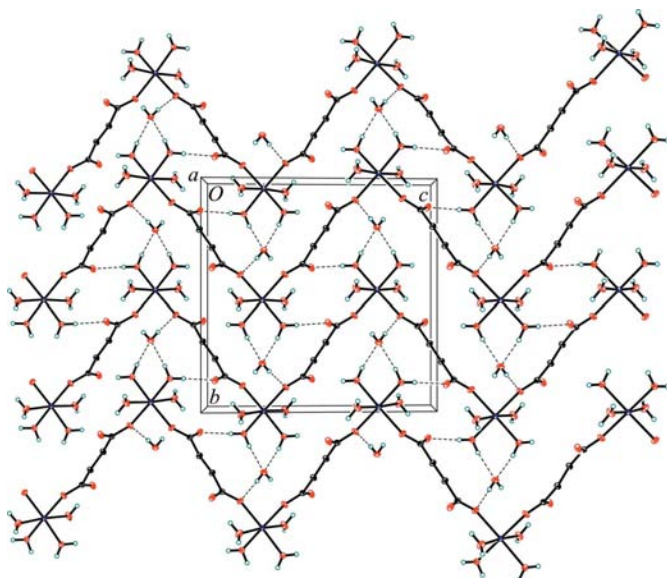


Figure 6
A packing diagram of (III), viewed along the *a* axis, showing the three-dimensional hydrogen-bonding system.

carboxylate groups is $25.9(1)^\circ$. A one-dimensional structure has also been observed in the crystal structure of cobalt(II) fumarate tetrahydrate (Konar *et al.*, 2003). There the fumarate groups are in *trans* positions with respect to the Co^{2+} ions, resulting in almost linear chains.

The site symmetries of the cobalt and fumarate ions for all four compounds are given in Table 4. The compounds reported demonstrate all three of the types of frameworks (one-, two- and three-dimensional) that are possible for these structures.

Experimental

A methanol solution (50 ml) containing fumaric acid (0.93 g, 8 mmol) was heated at 333 K for 1 h with stirring and then left to cool to room temperature. After the addition of a methanol solution (50 ml) containing $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (1 g, 4 mmol), a magenta-colored powder precipitated. The precipitate was filtered off, washed with methanol and dried for 3 h at 323 K. The powder pattern of the precipitate and the calculated powder pattern from the single-crystal structure of cobalt(II) fumarate methanol disolvate were compared and proved to be congruent. Red crystals of the title compounds were prepared by vapor diffusion, using water as solvent in all three cases: the antisolvents used for (I), (II) and (III) were acetone, methanol and ethanol, respectively. Crystals of (I) formed after four days, while crystals of compounds (II) and (III) formed after one week.

Compound (I)

Crystal data

$[\text{Co}(\text{C}_4\text{H}_2\text{O}_4)(\text{H}_2\text{O})_3]$ $\gamma = 92.82(3)^\circ$
 $M_r = 227.03$ $V = 379.8(2) \text{ \AA}^3$
 Triclinic, $P\bar{1}$ $Z = 2$
 $a = 6.8793(17) \text{ \AA}$ Mo $K\alpha$ radiation
 $b = 7.644(2) \text{ \AA}$ $\mu = 2.26 \text{ mm}^{-1}$
 $c = 8.026(3) \text{ \AA}$ $T = 167 \text{ K}$
 $\alpha = 101.51(2)^\circ$ $0.52 \times 0.20 \times 0.14 \text{ mm}$
 $\beta = 112.03(2)^\circ$

Data collection

Siemens SMART 1K CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\min} = 0.575$, $T_{\max} = 0.729$
 6668 measured reflections
 2411 independent reflections
 1660 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.091$
 $S = 1.00$
 2411 reflections
 145 parameters
 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 1.07 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.94 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H5A...O2 ^{vi}	0.79 (6)	1.97 (6)	2.755 (3)	170 (4)
O5—H5B...O3 ⁱⁱ	0.76 (4)	1.87 (4)	2.620 (3)	167 (4)
O6—H6A...O3 ^{vi}	0.87 (4)	1.83 (4)	2.694 (3)	175 (4)
O6—H6B...O1	0.79 (5)	2.20 (5)	2.833 (3)	138 (4)
O6—H6B...O4 ⁱⁱ	0.79 (5)	2.30 (5)	2.957 (3)	142 (4)
O7—H7A...O4 ^{vii}	0.76 (4)	2.18 (4)	2.936 (4)	175 (4)
O7—H7B...O5 ⁱ	0.80 (5)	2.17 (5)	2.971 (4)	176 (4)

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x - 1, y, z - 1$; (vi) $-x + 1, -y + 1, -z + 1$; (vii) $-x + 1, -y + 2, -z + 2$.

Compound (II)

Crystal data

$[\text{Co}(\text{C}_4\text{H}_2\text{O}_4)(\text{CH}_4\text{O})_2]$ $V = 808.9(4) \text{ \AA}^3$
 $M_r = 237.07$ $Z = 4$
 Monoclinic, $C2/c$ Mo $K\alpha$ radiation
 $a = 15.547(4) \text{ \AA}$ $\mu = 2.12 \text{ mm}^{-1}$
 $b = 7.020(2) \text{ \AA}$ $T = 165 \text{ K}$
 $c = 8.2270(13) \text{ \AA}$ $0.40 \times 0.26 \times 0.24 \text{ mm}$
 $\beta = 115.73(2)^\circ$

Data collection

Siemens SMART 1K CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\min} = 0.530$, $T_{\max} = 0.602$
 7132 measured reflections
 1611 independent reflections
 1402 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.061$
 $S = 1.01$
 1611 reflections
 70 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.64 \text{ e \AA}^{-3}$

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3A...O2	0.84 (2)	1.85 (2)	2.6485 (15)	159 (2)
C2—H2A...O1 ^v	0.91 (2)	2.57 (2)	3.1796 (18)	125.4 (17)

Symmetry code: (v) $x, -y, z + \frac{1}{2}$.

Compound (III)

Crystal data

[Co(C₄H₂O₄)(H₂O)₄]₂·H₂O
M_r = 263.07
 Monoclinic, *C*2/*c*
a = 5.2561 (11) Å
b = 13.145 (2) Å
c = 13.321 (3) Å
 β = 95.188 (16)°
V = 916.6 (3) Å³
Z = 4
 Mo *K*α radiation
 μ = 1.90 mm⁻¹
T = 166 K
 0.60 × 0.55 × 0.50 mm

Data collection

Siemens SMART 1K CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.301, *T_{max}* = 0.386
 8327 measured reflections
 1815 independent reflections
 1771 reflections with *I* > 2σ(*I*)
R_{int} = 0.025

Refinement

R[*F*² > 2σ(*F*²)] = 0.018
wR(*F*²) = 0.049
S = 1.04
 1815 reflections
 90 parameters
 All H-atom parameters refined
 Δρ_{max} = 0.56 e Å⁻³
 Δρ_{min} = -0.30 e Å⁻³

Table 3

Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3A...O4 ⁱⁱⁱ	0.809 (16)	2.121 (16)	2.9306 (11)	178.8 (17)
O3—H3B...O2 ⁱ	0.80 (2)	1.91 (2)	2.6481 (11)	153 (2)
O4—H4A...O5 ^{iv}	0.797 (18)	1.929 (18)	2.7062 (12)	164.8 (17)
O4—H4B...O2 ^v	0.844 (18)	1.879 (18)	2.7098 (11)	167.6 (16)
O5—H5A...O1	0.761 (16)	1.958 (16)	2.7122 (10)	171.4 (17)

Symmetry codes: (i) -*x* + 1, *y*, -*z* + ½; (iii) *x* + 1, *y*, *z*; (iv) *x* - ½, *y* + ½, *z*; (v) *x*, -*y* + 1, *z* - ½.

Table 4

Site symmetries for cobalt(II) fumarate trihydrate, (I), methanol disolvate, (II), pentahydrate, (III), and tetrahydrate (see *Comment*).

	Trihydrate	Methanol disolvate	Pentahydrate	Tetrahydrate
Space group	<i>P</i> 1̄	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	2	4	4	4
Co ²⁺	1̄, 1̄ ^a	1̄	2	1̄
Fumarate	1	1̄	1̄	1
Cobalt(II) fumarate topology	Two-dimensional	Three-dimensional	One-dimensional	One-dimensional

Note: (a) two symmetry-independent Co²⁺ ions.

The H atoms of the methyl group of (II) were constrained [C—H = 0.98 Å and *U_{iso}*(H) = 1.5*U_{eq}*(C)]. All other H atoms in (I), (II) and

(III) were located in difference Fourier syntheses and were freely refined [C—H = 0.93 (3) and 1.00 (3), 0.91 (2), and 0.928 (14) Å, respectively]. The crystal of (I) was twinned. The twin relations were *h*_{twin} = *h*, *k*_{twin} = -0.115*h* - *k* and *l*_{twin} = -0.870*h* - *l*. The twin fraction refined to 0.241 (4).

For all compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINTE* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

The authors thank Edith Alig and Lothar Fink (University of Frankfurt) for measurement of the powder patterns and scientific discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3108). Services for accessing these data are described at the back of the journal.

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