# A triclinic polymorph of *catena*-poly[[diaqua-cobalt(II)]-$\mu$-{$\mu$-mellitato-$\kappa^2 O^1$:$O^4$-bis[penta-aquacobalt(II)]]}-$\kappa^4 O^2$,$O^3$:$O^5$,$O^6$] hexahydrate]

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A second, triclinic, polymorph of the title compound, {[Co$_3$(C$_{12}$O$_{12}$)(H$_2$O)$_{12}$]·6H$_2$O}$_n$, is reported. This polymorph forms a three-dimensional framework through O—H···O hydrogen-bond interactions between the one-dimensional [Co$_3$\{C$_6$(COO)$_6$\}$_3$(H$_2$O)$_{12}$]$_n$ chains and the solvent water molecules. The mellitate ligand lies on an inversion center.

## Key indicators

Single-crystal X-ray study

$T$ = 291 K

Mean $\sigma$(C–C) = 0.003 Å

$R$ factor = 0.027

$wR$ factor = 0.080

Data-to-parameter ratio = 16.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

## Comment

The structure of an orthorhombic form (space group *Pbca*, $Z$ = 4) of the title compound, (I), has been reported (Robl & Hentschel, 1991), where the crystals were grown from an aqueous ethanol solution at ambient temperature. We now report the structure of a triclinic polymorph (space group $P\bar{1}$, $Z$ = 1, Fig. 1), for which the crystals were synthesized from an aqueous solution under hydrothermal conditions at 473 K. For convenience, we denote the previously reported orthorhombic polymorph as (I) and the triclinic polymorph reported here as (II).



(II)
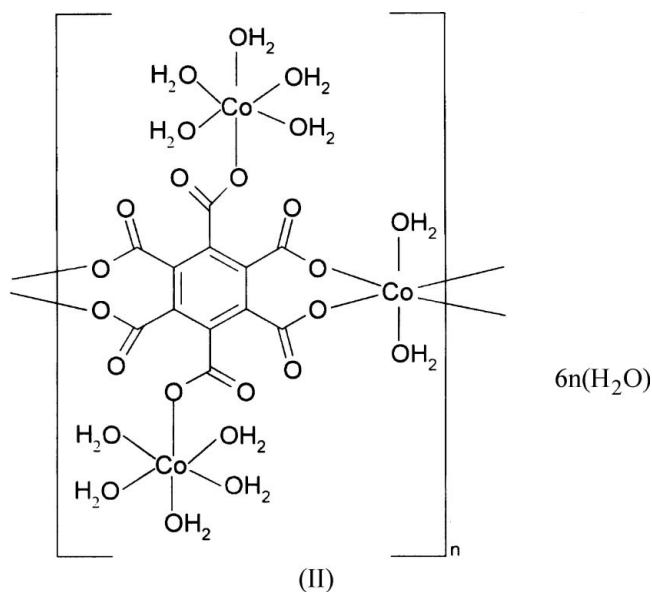
Triclinic (II) is built up from one-dimensional [Co$_3$\{C$_6$(COO)$_6$\}$_3$(H$_2$O)$_{12}$]$_n$ chains and solvent water molecules, as illustrated in Fig. 1. There are two crystallographically independent Co atoms, Co1 is located at an inversion center, and coordinated in an octahedral geometry by two crystallographically equivalent water molecules and four O atoms of two adjacent carboxylate groups from two different mellitate anions (but crystallograohically equivalent); Co2 is octahedrally coordinated by five water molecules
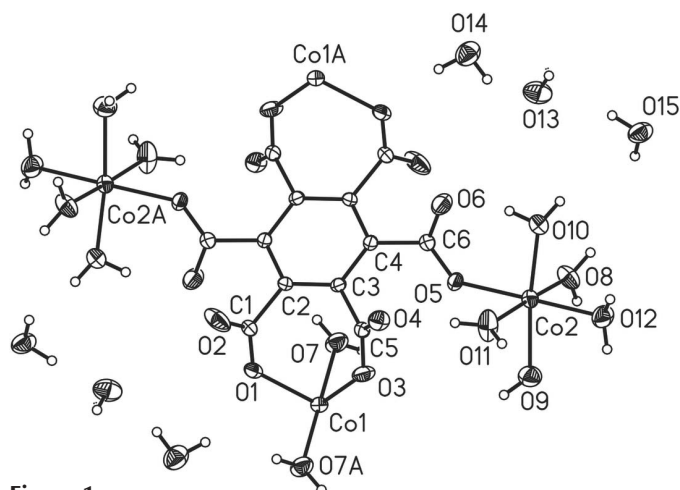
**Figure 1**
The asymmetric unit of (II), showing 35% displacement ellipsoids [symmetry code: (A) $1 - x, -y, 2 - z$].

and one O atom of a carboxylate group. The Co—O bond distances range from 2.059 to 2.132 Å (Table 1). Interatomic distances and angles of the mellitate anion are within the ranges for mellitic acid (Darlow, 1961). The centroid of the mellitate anion coincides with a crystallographic inversion center. The hexaanion $C_6(COO)_6^{6-}$ in this structure functions as a bridge to connect Co1 atoms into chains parallel to the [100] direction, while the C6-carboxylate group acts only as a monodentate ligand to bind the Co2 atom, which is also coordinated by five water molecules. All of the above features are similar to those in orthorhombic (I). However, there are some evident differences in the hydrogen-bonding inter-actions, as shown in Fig. 2. In orthorhombic (I), the coordinated water molecule O8 acts as donor in the hydrogen bonds to the uncoordinated carboxylate atom O6 and the coordinated carboxylate O3 atom of an adjacent chain, while in triclinic (II), atom O8 forms interchain hydrogen bonds to the coordinated carboxylate atoms O1 and O5 of a neighboring chain. The coordinated water molecule O10 is hydrogen-bonded to the uncoordinated carboxylate O4 atom in (I) and to atom O2 in (II), respectively. As a result, the one-dimensional neutral chains are linked into two-dimensional layers parallel to the (001) plane in (I) and to the (010) plane in (II). The plane of the aromatic rings in adjacent layers in (I) are parallel to $(02\bar{1})$ and (021), respectively, and the coordinated water molecule O10 forms a hydrogen bond to O11 of an adjacent layer, generating a three-dimensional network. The planes of the aromatic rings in (II) are strictly parallel, and no hydrogen-bonding interactions exist between adjacent layers, which are connected into a three-dimensional framework by the coordinated water molecules through O—H···O hydrogen-bonding interactions.

## Experimental

A mixture of CoCl₂·6H₂O (0.237 g, 1.0 mmol), mellitic acid (0.105 g, 0.5 mmol) and NaOH (0.03 g, 1.5 mmol) in an aqueous solution was sealed in a 20 ml Telfon-lined antoclave and heated to 473 K for

120 h, then cooled to 373 K at a rate of 5 K h⁻¹, and held for 10 h, followed by further cooling to room temperature. Red needle-shaped crystals were obtained in a yield of 75% based on the initial CoCl₂·6H₂O input.

*Crystal data*

| | |
|---|---|
| $[Co_3(C_{12}O_{12})(H_2O)_{12}]\cdot 6H_2O$ | $Z = 1$ |
| $M_r = 837.20$ | $D_x = 1.840$ Mg m⁻³ |
| Triclinic, $P\bar{1}$ | Mo $K\alpha$ radiation |
| $a = 8.4910\,(17)$ Å | Cell parameters from 989 |
| $b = 9.6550\,(19)$ Å | reflections |
| $c = 10.812\,(2)$ Å | $\theta = 3.3–26.7°$ |
| $\alpha = 70.66\,(3)°$ | $\mu = 1.74$ mm⁻¹ |
| $\beta = 67.36\,(3)°$ | $T = 291\,(2)$ K |
| $\gamma = 72.18\,(3)°$ | Block cut from needle, red |
| $V = 755.5\,(3)$ Å³ | $0.2 \times 0.2 \times 0.18$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 3435 independent reflections |
| | 3034 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.017$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $\theta_{max} = 27.5°$ |
| | $h = -10 \rightarrow 1$ |
| $T_{min} = 0.698$, $T_{max} = 0.723$ | $k = -12 \rightarrow 11$ |
| 4119 measured reflections | $l = -14 \rightarrow 13$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.049P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.027$ | $+ 0.4002P]$ |
| $wR(F^2) = 0.080$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 0.98$ | $(\Delta/\sigma)_{max} = 0.002$ |
| 3435 reflections | $\Delta\rho_{max} = 0.43$ e Å⁻³ |
| 206 parameters | $\Delta\rho_{min} = -0.41$ e Å⁻³ |
| H-atom parameters constrained | Extinction correction: *SHELXL97* |
| | Extinction coefficient: 0.0067 (16) |

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Co1—O1 | 2.0588 (16) | Co2—O8 | 2.0790 (15) |
| Co1—O3 | 2.0930 (16) | Co2—O12 | 2.1034 (17) |
| Co1—O7 | 2.1322 (15) | Co2—O9 | 2.1138 (15) |
| Co2—O11 | 2.0596 (16) | Co2—O5 | 2.1702 (15) |
| Co2—O10 | 2.0788 (15) | | |

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O7—H7A···O12ⁱ | 0.85 | 2.24 | 2.992 (2) | 147 |
| O7—H7B···O14ⁱⁱ | 0.85 | 2.03 | 2.839 (2) | 159 |
| O8—H8A···O1ⁱⁱⁱ | 0.85 | 1.85 | 2.694 (2) | 178 |
| O8—H8B···O5ⁱ | 0.85 | 1.99 | 2.799 (2) | 159 |
| O9—H9A···O5ⁱ | 0.85 | 2.47 | 3.144 (2) | 137 |
| O9—H9B···O15ⁱᵛ | 0.85 | 1.96 | 2.810 (2) | 177 |
| O10—H10A···O6ᵛ | 0.85 | 1.84 | 2.655 (2) | 160 |
| O10—H10B···O2ⁱⁱⁱ | 0.85 | 1.88 | 2.723 (2) | 176 |
| O11—H11A···O4 | 0.85 | 2.01 | 2.832 (2) | 162 |
| O11—H11B···O15ᵛ | 0.85 | 1.90 | 2.738 (2) | 168 |
| O12—H12A···O13ᵛ | 0.85 | 1.91 | 2.738 (2) | 165 |
| O12—H12B···O14ᵛⁱ | 0.85 | 1.87 | 2.713 (2) | 174 |
| O13—H13A···O2ᵛⁱⁱ | 0.85 | 2.00 | 2.835 (2) | 170 |
| O13—H13B···O4ⁱⁱⁱ | 0.85 | 1.95 | 2.799 (2) | 174 |
| O14—H14A···O4ⁱⁱⁱ | 0.85 | 2.11 | 2.916 (2) | 157 |
| O14—H14B···O13ᵛⁱ | 0.85 | 1.92 | 2.768 (2) | 173 |
| O15—H15A···O3ⁱⁱⁱ | 0.85 | 1.95 | 2.785 (2) | 166 |
| O15—H15B···O6ᵛⁱⁱⁱ | 0.85 | 1.93 | 2.734 (2) | 158 |

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

All water H atoms were found in a difference map, relocated in idealized positions (O—H = 0.85 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(O)$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.



**Figure 2**
The differences between the interchain hydrogen bonds (dashed lines) in (I) and (II).

## References

Bruker (1998). *SMART* (Version 5.16), *SAINT* (VERSION 6.01) and *SHELXTL* (VERSION 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.
Darlow, S. F. (1961). *Acta Cryst.* **14**, 159–166.
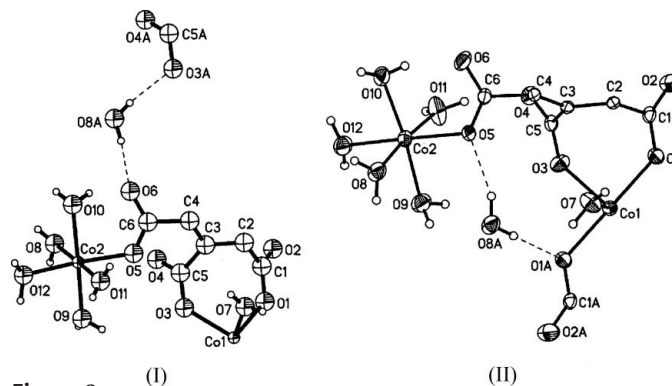Robl, C. & Hentschel, S. (1991). *Z. Naturforsch. Teil B*, **46**, 1188–1189.
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