

The two-dimensional coordination polymer tetraaquamesaconatobarium(II), $[\text{Ba}(\text{C}_5\text{H}_4\text{O}_4)(\text{OH}_2)_4]_n$

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Key indicators

Single-crystal X-ray study

$T = 293 \text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$

H-atom completeness 34%

R factor = 0.046

w R factor = 0.132

Data-to-parameter ratio = 19.0

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

The structure of $[\text{Ba}(\text{C}_5\text{H}_4\text{O}_4)(\text{OH}_2)_4]_n$ consists of two-dimensional rectangular grid layers, built up from the self-assembly of zigzag chains of edge-sharing $\{\text{BaO}_9\}$ polyhedra linked by bridging bidentate mesaconate anions ($\text{C}_5\text{H}_4\text{O}_4^{2-}$) through different coordination modes of the carboxylate groups. The polymer layers form a three-dimensional network *via* $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bond interactions between the coordinated water molecules and the O atoms of the carboxylate groups.

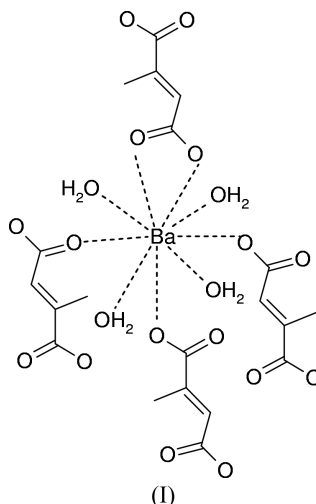
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Comment

Unsaturated carboxylic acids and their derivatives display interesting reactivity patterns when they are heated and/or irradiated in the solid state (Díaz de Delgado *et al.*, 1991; Case & Foxman, 1994; Vela *et al.*, 2000; Xiao *et al.*, 2000; Odani *et al.*, 2001). The nature of the reactions in the solid state is determined by the control that the crystalline lattice exerts. In general, the preorganization of molecules and the orientation of double bonds in the crystal determine the nature of the reaction products. For example, we have reported that, when barium hydrogen itaconate monohydrate is heated to about 473 K, an unusual isomerization to barium citraconate occurs in the solid state as a consequence of the arrangement of the molecules in the starting material (Briceño *et al.*, 1999).



In this work, we report the X-ray diffraction study of barium mesaconate tetrahydrate, (I), and its thermal behavior. This study is part of a systematic investigation of the structure–reactivity relationships in the solid state of metal complexes of α,β -unsaturated carboxylic acids. In spite of the simplicity of mesaconic acid (methylmaleic acid), and its similarity to maleic and fumaric acids (*cis*- and *trans*-butene-

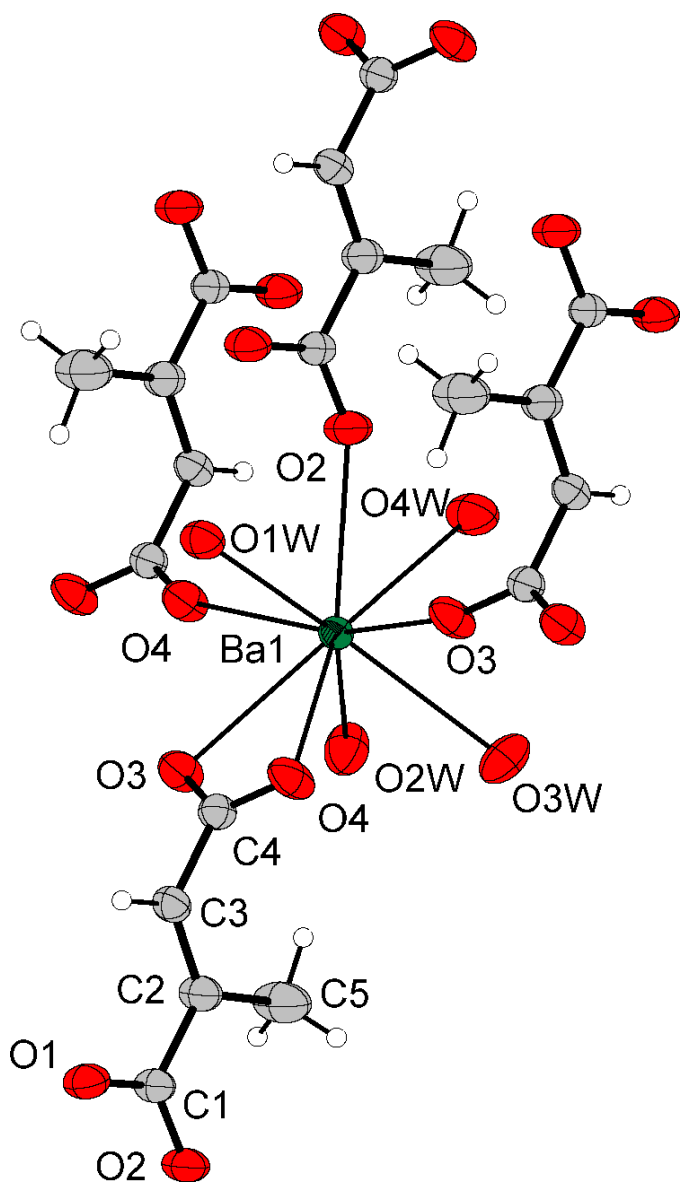


Figure 1
Coordination environment of the Ba atom in $[\text{Ba}(\text{C}_5\text{H}_4\text{O}_4)(\text{OH}_2)_4]_n$. Displacement ellipsoids are shown at the 50% probability level.

dioic acids, respectively), the structural chemistry of its salts and complexes is unknown. Only the structure of potassium mesaconate (Gupta & Yadav, 1975) has been reported, as indicated by a search in the Cambridge Structural Database (Version 5.23; Allen & Kennard, 1993).

In the structure of (I), the Ba atoms are coordinated by nine O atoms, as shown in Fig. 1. Five of these O atoms come from four different mesaconate anions and four O atoms come from water molecules. The Ba–O distances range from 2.683 (3) to 2.967 (4) Å. The disposition of the O atoms around the Ba atom can be described as a distorted monocapped rectangular antiprism. Edge-sharing polyhedra form unidimensional zigzag chains along the *b* axis, which are linked through bridging bidentate mesaconate anions (Fig. 2). The carboxylate groups display different coordination modes. The

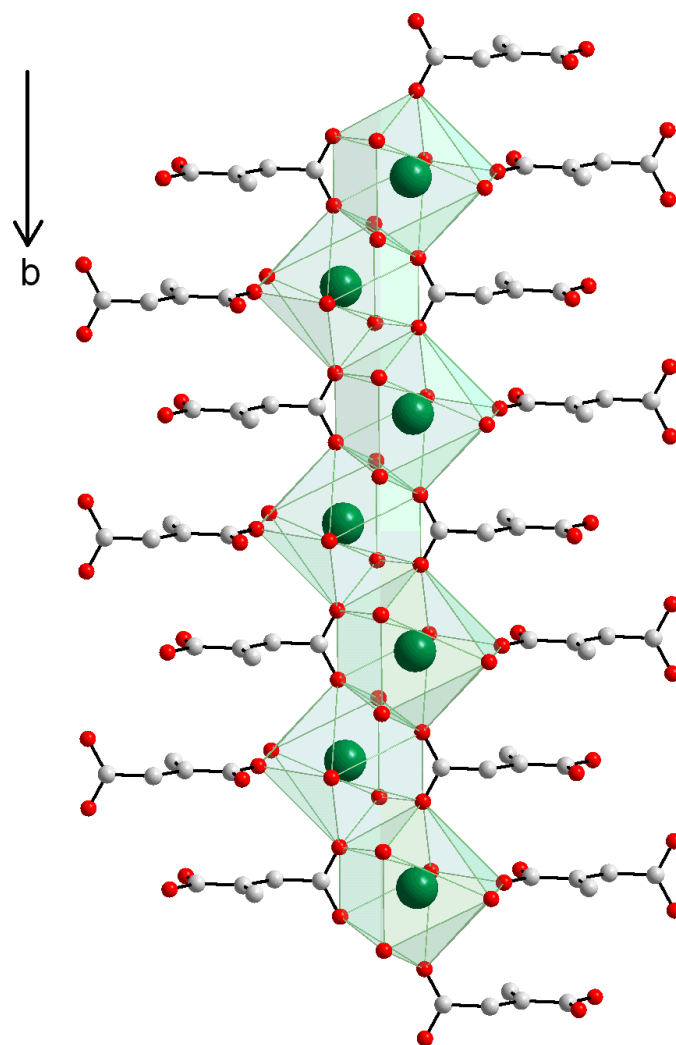


Figure 2
Zigzag chains of $[\text{BaO}_9]$ polyhedra in the structure of $[\text{Ba}(\text{C}_5\text{H}_4\text{O}_4)(\text{OH}_2)_4]_n$.

O1/C1/O2 carboxylate acts as monodentate group through the O2 atom, while O3/C4/O4 displays a combination of symmetrical chelating and monoatomic *anti-anti* bridging modes, allowing the coordination to three different Ba atoms. The dihedral angle between the planes containing the carboxylate groups is approximately $89.8 (1)^\circ$. These coordination modes induce self-assembly of the chains of barium polyhedra with the mesaconate anions, as well as their arrangement in a parallel and alternate head-to-tail fashion, and produce two-dimensional rectangular grid layers parallel to the *bc* plane (Fig. 3). The polymer layers interact through extensive hydrogen bonds between water molecules and carboxylate O atoms: $\text{O1W} \cdots \text{O3W}^{\text{i}}$ 2.836 (3), $\text{O1W} \cdots \text{O2W}^{\text{ii}}$ 2.833 (2) and $\text{O2W} \cdots \text{O1}^{\text{iii}}$ 2.807 (3) Å [symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-1 + x, y, z$], among others, along the *c* axis.

The disposition of the double bonds in neighboring molecules is parallel, and a series of infinite contacts along the *b* axis is observed. An analysis of the distances for such contacts indicates that there are contacts $\text{C2} \cdots \text{C2}^{\text{iv}}$ [symmetry code:

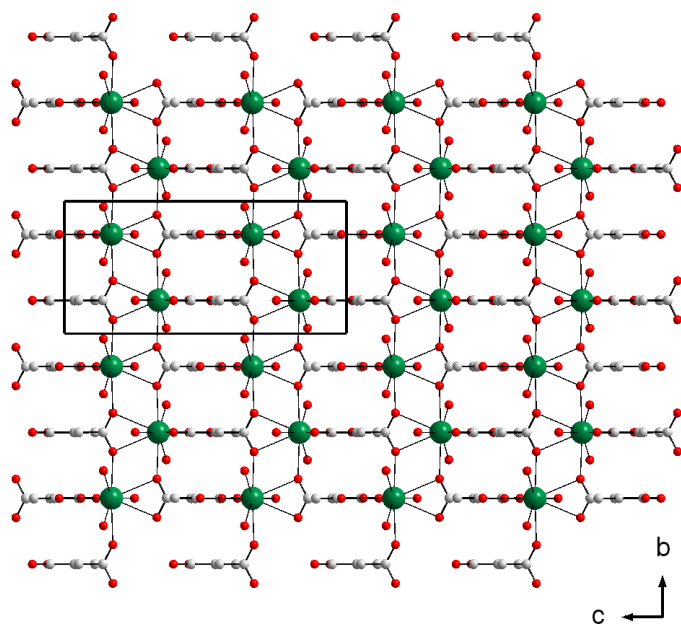


Figure 3
Projection of the structure of $[\text{Ba}(\text{C}_5\text{H}_4\text{O}_4)(\text{OH}_2)_4]_n$ on the bc plane.

(iv) $-x + 1, -y + 1, -z + 1$] along this direction at a distance of 4.168 (2) Å. In spite of these favorable structural characteristics for reactivity in the solid state, thermal analysis (TGA and DSC) and FT-IR spectra indicate that the material does not react upon heating. It is stable between 473 and 613 K, which corresponds to the temperature range between dehydration and decomposition of the organic ligand.

It is worth noting that the analysis of the results using *PLATON* (Spek, 1990) suggested the existence of a unit cell (2) with half of the volume of the experimentally determined cell, (1). They are related by the following transformation matrix: $[a, b, c]_2 = [\frac{1}{2}, 0, \frac{1}{2}, 0, 1, 0][a, b, c]_1$. The dimensions of the proposed smaller cell are: $a = 8.323$ (1), $b = 7.478$ (1), $c = 8.893$ (1) Å, $\beta = 105.92$ (1)°, space group $P2_1/m$. *PLATON* also indicated pseudo-*B* centering and the possibility of maintaining cell 1 but in space group $P2_1/m$. Solution and refinement of the structure in cell 1 using space groups $P2_1/m$ and $P2/m$ were not successful.

A careful examination of the data set collected showed that 1125 out of the 2446 unique reflections can only be accounted for using the larger cell. Even though the majority of the superstructure reflections are rather weak, 376 of those reflections have $F_o > 4\sigma(F_o)$. It may be noticed that the majority of the atoms have y coordinates equal or close to $\frac{1}{4}$ and that only a few of the O atoms are clearly removed from such a position. After the reduction of the unit cell proposed by *PLATON*, the atoms with y coordinates equal or close to $\frac{1}{4}$ are assigned to special positions with $y = \frac{1}{4}$. In the case of the Ba atom, the value obtained for its y -coordinate in the structure refinement carried out in the larger cell [$y = 0.24927$ (2)] is statistically different from $\frac{1}{4}$. Also, after the reduction, in order to accommodate the number of O atoms in the small unit cell in general positions, they should have half of the occupancy factors indicated by the multiplicity of their positions.

Because of the substructure–superstructure relationship that exists between cells 1 and 2, we believe that the experimentally determined unit cell (cell 1) should be used in order to properly describe the structure of the compound under study. Sub-superstructure relationships have been observed in other metal dicarboxylates, for example lithium hydrogen maleate dihydrate (Díaz de Delgado *et al.*, 1993).

Experimental

The title compound was prepared by reaction of mesaconic acid ($\text{C}_5\text{H}_6\text{O}_4$) and BaCO_3 in a 1:1 ratio in water. The mixture was maintained under continuous stirring for 24 h. The resulting solution was filtered and allowed to evaporate slowly at ambient temperature. After 2–3 weeks, colorless crystals suitable for X-ray analysis formed. The IR spectra were recorded from KBr discs, using a PE-1725X FT-IR spectrometer. IR (cm^{-1}): $\nu(\text{br}, \text{O}-\text{H})$ 3495, $\nu(\text{w}, \text{C}=\text{C})$ 1627, $\nu(\text{s}, \text{C}=\text{O}_{\text{asym}})$ 1501, $\nu(\text{s}, \text{C}=\text{O}_{\text{sym}})$ 1389–1335. In order to study the reactivity in the solid state, samples of approximately 80 mg of the material were placed in a reactor connected to a vacuum line and heated at 473, 543, 613 and 823 K. In each case, once the desired temperature was reached, the temperature was kept constant for 10 min. Thermogravimetric analyses (TG and DTG) and differential scanning calorimetry measurements (DSC) were performed in a Dupont 951 Thermal Analyzer and a Dupont 990 cell, under a dynamic dry nitrogen atmosphere at a flow rate of 50 ml s^{-1} and a heating rate of 20 K min^{-1} . The temperature range was 298–873 K. TGA and DSC data: weight loss to step 1: 21.29% (calculated 21.34%), 343–443 K, *endo*; step 2: 20.20% (calculated 20.16%), 673–783 K, *endo*.

Crystal data

$[\text{Ba}(\text{C}_5\text{H}_4\text{O}_4)(\text{H}_2\text{O})_4]$
 $M_r = 337.49$
Monoclinic, $P2_1/n$
 $a = 8.893$ (1) Å
 $b = 7.478$ (1) Å
 $c = 16.582$ (2) Å
 $\beta = 105.13$ (1)°
 $V = 1064.5$ (2) Å³
 $Z = 4$
 $D_x = 2.106$ Mg m^{-3}
 $D_m = 2.07$ (2) Mg m^{-3}

D_m measured by neutral buoyancy
in $\text{CHCl}_3/\text{CH}_2\text{I}_2$
Mo $K\alpha$ radiation
Cell parameters from 25
reflections
 $\theta = 20.0$ – 35.0°
 $\mu = 3.75$ mm^{-1}
 $T = 293$ (2) K
Prism, colorless
 $0.60 \times 0.35 \times 0.28$ mm

Data collection

Nicolet P3/F (Crystal Logic)
diffractometer
 θ – 2θ scans
Absorption correction: ψ scan
(North *et al.*, 1968)
 $T_{\text{min}} = 0.220$, $T_{\text{max}} = 0.350$
4858 measured reflections
2446 independent reflections
1478 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -11 \rightarrow 11$
 $k = -9 \rightarrow 9$
 $l = 0 \rightarrow 21$
3 standard reflections
every 97 reflections
intensity decay: <0.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.133$
 $S = 1.18$
2446 reflections
129 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0728P)^2 + 0.0708P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 2.06$ e Å⁻³
 $\Delta\rho_{\text{min}} = -2.88$ e Å⁻³
Extinction correction: *SHELXL97*
Extinction coefficient: 0.045 (2)

Table 1Selected geometric parameters (\AA , $^\circ$).

Ba1—O3 ⁱ	2.683 (3)	C1—O2	1.250 (6)
Ba1—O4 ⁱⁱ	2.685 (3)	C1—O1	1.278 (6)
Ba1—O2	2.796 (4)	C1—C2	1.495 (7)
Ba1—O1W	2.838 (4)	C2—C3	1.352 (6)
Ba1—O3 ⁱⁱⁱ	2.853 (3)	C2—C5	1.523 (6)
Ba1—O4 ⁱⁱⁱ	2.855 (3)	C3—C4	1.492 (5)
Ba1—O2W	2.861 (3)	C4—O4	1.248 (4)
Ba1—O3W	2.862 (3)	C4—O3	1.253 (4)
Ba1—O4W	2.967 (4)		
O2—C1—O1	122.8 (4)	C1—C2—C5	118.2 (5)
O2—C1—C2	117.1 (4)	C2—C3—C4	121.6 (4)
O1—C1—C2	120.1 (4)	O4—C4—O3	122.4 (4)
C3—C2—C1	121.1 (4)	O4—C4—C3	119.0 (3)
C3—C2—C5	120.6 (5)	O3—C4—C3	118.6 (3)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $1-x, 1-y, -z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$.

Two unassigned extremes of residual density, positive 2.06 e \AA^{-3} (0.17, 0.25, 0.20) and negative -2.88 e \AA^{-3} (0.13, 0.25, 0.12), were observed approximately 0.7 and 0.9 \AA from atom Ba1. The water H atoms were not located; all other H atoms were refined as riding.

Data collection: *COLLECT* in *UCLA Crystallographic Package* (Strouse, 1988); cell refinement: *LEAST* in *UCLA Crystallographic Package*; data reduction: *REDUCE* in *UCLA Crystallographic Package*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996–1998); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 1990).

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