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catena-Poly[[(acetato-κ^2O,O')triaquabarium(II)]-μ_3-acetato-κ^4O:O,O':O']

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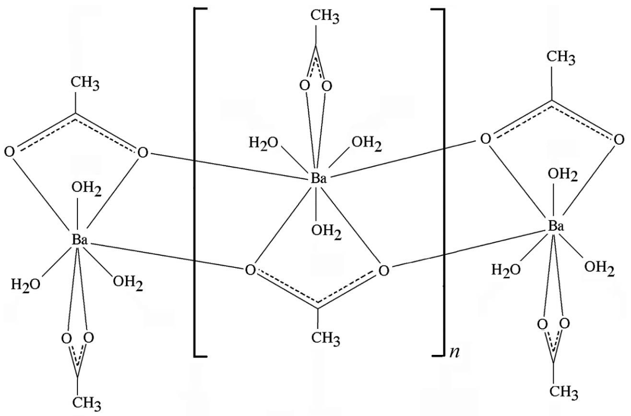
The present form of barium acetate, formulated as [Ba$(C_2H_3O_2)_2(H_2O)_3]_n$, is the largest reported hydrate of the salt and this leads to a distinct structural behaviour setting it apart from the rest of the family. The compound is a linear polymer with a nine-coordinate $Ba(O_{aqua})_3(O_{acetate})_6$ monomer unit. The non-H part of the structure is ordered according to $C2/m$ symmetry, while the disordered water H atoms only abide by this symmetry in a statistical sense. Each molecule is halved by a mirror plane bisecting the Ba centre, one water molecule and one acetate ligand, while containing the other acetate ligand. The chains are interconnected by a disordered water–water/acetate O—H⋯O hydrogen-bonding network involving all water H atoms. The structure and stability of this phase are compared with the other known acetates of barium which differ in the degree of hydration.

Comment

Barium acetate is known to present a variety of hydration states, the X-ray crystal structures having been reported (Cambridge Structural Database, Version 5.29 of November 2007; Allen 2002) for a monohydrate, $Ba(C_2H_3O_2)_2{\cdot}H_2O$, (II) (Groombridge *et al.*, 1985), an anhydrous form, $Ba(C_2H_3O_2)_2$, (III) (Gautier-Luneau & Mosset, 1988), and a partially hydrated form, $[Ba(C_2H_3O_2)_2]_6{\cdot}3.5H_2O$, (IV) (Leyva *et al.*, 2007). We report here the crystal structure of the title trihydrate, $Ba(C_2H_3O_2)_2{\cdot}3H_2O$, (I), which although characterized by a thorough vibrational study 20 years ago (Maneva & Nikolova, 1988) has not been studied so far from a crystallographic point of view.

Fig. 1 shows a schematic view of the (linear) polymeric structure of (I), built up by a Ba centre, three water molecules and two acetate ligands, one (acetate 2) acting in a simple chelating mode and the second (acetate 1) in a μ_3-κ^4O,O' chelating double-bridging mode. This leads to a Ba⋯Ba distance along the chain of 4.608 (1) Å, comparable with the separation in monohydrate (II) (4.586 Å), but longer than those in the less hydrated forms [4.330 Å in partial hydrate (IV) and 4.338 Å in anhydrate (III)].

Each $Ba(C_2H_3O_2)_2(H_2O)_3$ unit in (I) is halved by a mirror plane which passes through the Ba1 centre and one water molecule (O2*W*), while bisecting both perpendicular acetate ligands; acetate 2, through all four non-H atoms (C12, C22, O12 and O22, which thus lie on special positions in the mirror plane) and acetate 1 through atoms C11 and C21.



(I)

Due to chelation, the BaO_9 polyhedron is rather deformed, with a wide range of coordination angles [45.69 (11)–152.83 (14)°], which makes the resulting geometry difficult to describe in terms of a regular model. The water molecules are more loosely bound to Ba than are the carboxylate O atoms, as inferred from the coordination distances (Table 1). Total bond valence (Brown & Altermatt, 1985) on Ba1 amounts to 2.283, with a mean value of 0.277 for acetate O atoms and 0.206 for water O atoms.

As explained in the *Refinement* section, only the non-H part of the structure follows a strict $C2/m$ symmetry. The H atoms follow it only on average, and to accommodate them in a noncolliding way, the local symmetry must be lowered to $\overline{1}$, as shown in Fig. 2. The possible centrosymmetric H-atom arrays give rise to noncolliding H-atom distributions and sensible hydrogen-bonding schemes (Table 2), while providing an

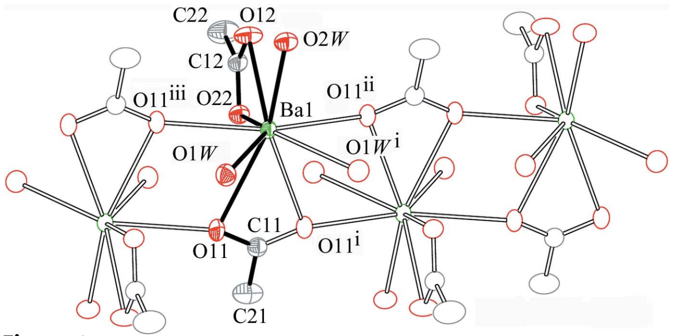


Figure 1
A molecular diagram of (I), showing the way in which chains are formed along the *b* axis. Independent atoms are drawn as octant-shaded displacement ellipsoids at the 40% probability level, connected by solid bonds, while symmetry-related atoms are shown as open ellipsoids connected by hollow bonds. H atoms have been omitted for clarity. [Symmetry codes: (i) $x, -y+1, z$; (ii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z$.]

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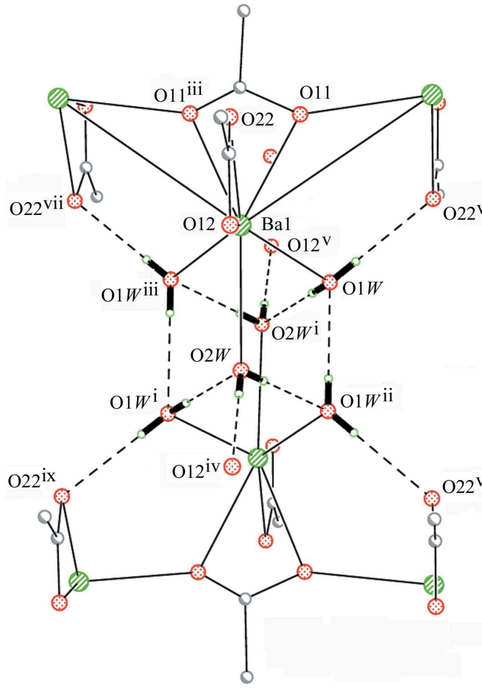

Figure 2
A schematic representation of one of the possible locally centrosymmetric water H-atom dispositions leading (on average) to a $C2/m$ distribution compatible with the heavy-atom space group. The figure is built up around the symmetry centre at ($\frac{1}{2}$, $\frac{1}{2}$, 0), giving rise to the symmetry operation (i). [Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 1, y, -z$; (iii) $x, -y + 1, z$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $x,y,1 + z$; (vi) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (vii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$; (viii) $x + \frac{1}{2}, -y + \frac{1}{2}, z$; (ix) $x + \frac{1}{2}, y + \frac{1}{2}, z$.]

'average' model compatible with the electron-density map. The polymeric structure consists of ribbons (Fig. 1) which run along b and are in turn interconnected by the disordered set of water–water/acetate O—H$\cdots$O hydrogen bonds, where all water H atoms take part. The first entry in Table 2 corresponds to an intrachain contact, while the remaining entries are the interchain interactions along the a- and c-axis directions (Fig. 3)

As expected, the four structurally characterized barium acetates present a predictable inverse relationship between water content and crystal density (Table 3). In addition, all but (I) present a stable three-dimensional structure at room temperature. It might be concluded that, in the particular case of the structure reported here, the large number of coordinated water molecules has the effect of reducing the covalent links between the Ba polyhedra, thus 'opening' the three-dimensional structure into the one-dimensional structure displayed by (I), a fact presumably associated with its intrinsic instability.

Experimental

Crystals of (I) were obtained through a two-step low-temperature recrystallization procedure. A concentrated aqueous solution of the as-purchased monohydrated salt was initially left at 255 K until chilled, and warmed to 268 K afterwards. After 10–15 d, and with the solution almost dry, very large colourless blocks of (I) appeared suddenly. Thermogravimetric analysis suggested a water content of three molecules per formula unit, a fact confirmed by the structural analysis. The specimens are unstable at room temperature: if dry, they decompose within a few hours, losing crystalline character; if left in a drop of mother liquor, they are digested and the stable monohydrate grows.

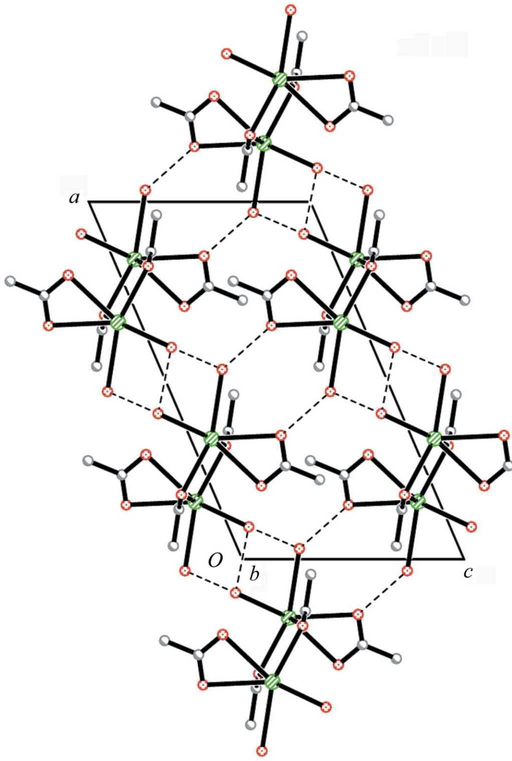

Figure 3
A schematic packing view of (I), projected down b, the chain direction. Disordered H atoms have been omitted for clarity. Short O$\cdots$O contacts resulting from the hydrogen bonding are shown as dashed lines.

Crystal data

$[Ba(C_2H_3O_2)_2(H_2O)_3]$
$M_r = 309.48$
Monoclinic, $C2/m$
$a = 16.020$ (3) Å
$b = 7.4892$ (15) Å
$c = 9.1211$ (18) Å
$\beta = 113.23$ (3)°
$V = 1005.6$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 3.95$ mm^{-1}
$T = 263$ (2) K
0.28 × 0.18 × 0.14 mm

Data collection

Rigaku AFC-6 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.39$, $T_{max} = 0.58$
2492 measured reflections
1069 independent reflections
1006 reflections with $I > 2\sigma(I)$
$R_{int} = 0.066$
3 standard reflections every 150 reflections intensity decay: <2%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.085$
$S = 1.12$
1069 reflections
85 parameters
15 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 2.00$ e Å^{-3}
$\Delta\rho_{min} = -1.75$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ba1—O11^{i}	2.722 (3)	Ba1—O12	2.845 (5)
Ba1—O22	2.810 (4)	Ba1—O2*W*	2.866 (5)
Ba1—O11	2.833 (3)	Ba1—O1*W*	2.918 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1*W*—H1*WB*···O22^{ii}	0.85 (2)	1.90 (2)	2.744 (4)	174 (5)
O1*W*—H1*WC*···O1*W*^{iii}	0.85 (2)	2.02 (3)	2.763 (6)	145 (5)
O1*W*—H1*WA*···O2*W*^{iv}	0.85 (2)	1.97 (2)	2.800 (5)	164 (5)
O2*W*—H2*WA*···O1*W*^{iii}	0.85 (2)	2.04 (2)	2.800 (5)	147.4 (19)
O2*W*—H2*WB*···O12^{v}	0.85 (2)	2.02 (2)	2.705 (7)	137 (3)

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

Table 3
Water content *versus* density for all known $Ba(C_2H_3O_2)_2(H_2O)_n$ compounds.

Structure	n	ρ (Mg m^{-3})	Structure type	Room-temperature stability
(III)	0	2.53	Three-dimensional	Stable
(IV)	0.583	2.328	Three-dimensional	Stable
(II)	1	2.26	Three-dimensional	Stable
(I)	3	2.044	One-dimensional	Unstable

Crystals of (I) are unstable at room temperature and decompose easily in the X-ray beam. After several unsuccessful attempts, a complete data set was finally collected on a single specimen under a soft N_2 cooling stream (*ca* 260 K). The non-H part of the structure could be easily solved and refined in centrosymmetric space group *C*2/*m*, with the molecule halved by a mirror plane, but H-atom assignment posed a problem because the positions from the Fourier synthesis were unacceptable due to collision/superposition, *e.g.* the electron-density maxima, and their symmetry-related images generated by the full space-group symmetry, generated around each O*W* atom an almost perfect CH_3-like umbrella which was sterically incompatible with their neighbours.

An analysis of the possible hydrogen-bonding interactions and the scheme which they suggested led to an acceptable centrosymmetric H-atom configuration, not abiding by the full space-group symmetry (see Fig. 2 for a typical example), but which could explain the lost '2' and '*m*' symmetries and the electron-density maps when overlapped. Thus, *C*2/*m* should be considered as the 'non-H' space group, but when H atoms are taken into account this is true only in an 'average' sense. The refinement was accordingly performed in *C*2/*m* with this disordered H-atom distribution. Acetate H atoms were included at calculated positions, with O—C—C—H torsion angles left free to refine, a procedure which also resulted in rotationally disordered CH_3 sets. O—H distances were restrained to 0.85 (2) Å. In all cases, U_{iso}(H) values were set at $1.5U_{eq}$(C,O).

Data collection: *MSC*/*AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC*/*AFC Diffractometer Control Software*; data reduction: *MSC*/*AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-NT* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3131). Services for accessing these data are described at the back of the journal.

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