

[Ba₆(C₂H₃O₂)₁₂(H₂O)_{3.5}], a new hydrate of barium acetate

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A new barium acetate phase, di- μ_5 -acetato-tri- μ_4 -acetato-tri- μ_3 -acetato-tri- μ_2 -acetato- μ_2 -acetato-triaquaahemiaqua-hexabarium(II), of analytical formula [Ba₆(C₂H₃O₂)₁₂(H₂O)_{3.5}], is

described. The asymmetric unit contains six independent Ba centres with coordination numbers varying from 7 to 10 arising from bonding to 12 crystallographically independent acetate ligands and four molecules of water, one of which is disordered over two sites both of occupancy 0.5. Bonding to the acetate ligands creates a completely connected three-dimensional structure. All H atoms of the water molecules participate in hydrogen bonding.

Comment

The title compound, (I), is the serendipitous product of unsuccessful attempts to replicate the reportedly simple and reproducible preparation of barium acetate trihydrate, Ba(C₂H₃O₂)₂·3H₂O (Maneva & Nikolova, 1988), which has been characterized by an IR vibrational study. The structure of (I) can be compared with those of the monohydrate, Ba(C₂H₃O₂)₂·H₂O, (II) (Groombridge *et al.* 1985), and the anhydrous barium acetate, Ba(C₂H₃O₂)₂, (III) (Gautier-Luneau & Mosset, 1988).

The complex asymmetric unit of (I) is shown in Fig. 1; the 12 independent acetate ligands are distinguished from one another by suffixes A–L. Table 1 displays relevant data concerning the

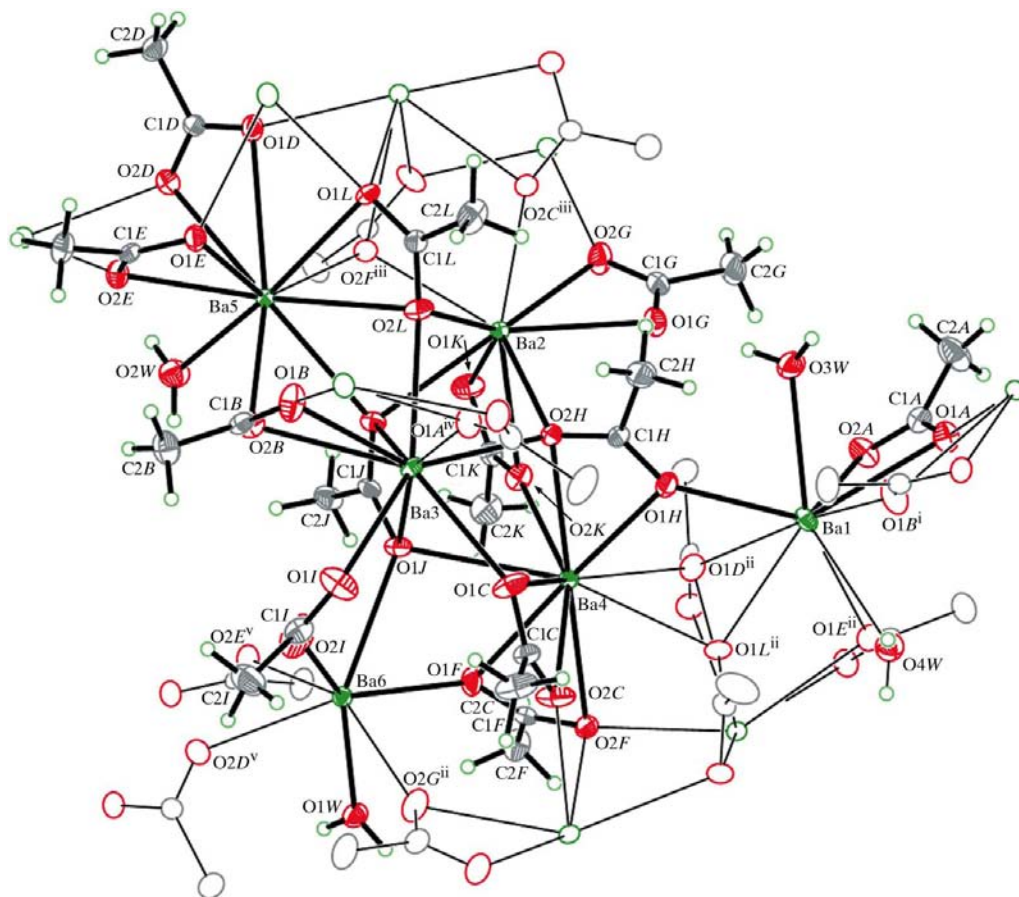


Figure 1

A molecular diagram of (I), showing the atom-numbering scheme and the complex interconnection network. Independent atoms are drawn as full displacement ellipsoids at the 25% probability level and symmetry-related atoms as open ellipsoids. H atoms are shown as small spheres of arbitrary radii. The 12 independent acetate ligands are indicated by the suffixes A–L. [Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + 1, -y, -z$.]

different Ba coordination polyhedra for crystallographically independent atoms Ba1–Ba6 in (I), along with similar data for (II) and (III). For a complete survey in the case of (I), see the supplementary material. The bond distances given in Table 1 show no significant differences (on average) between the three known structures. The structures differ, however, in the number of independent Ba atoms and, especially for (I), in the diversity of coordination numbers observed. In (I), the coordination number for Ba1 (8 or 9, average 8.5) arises because of

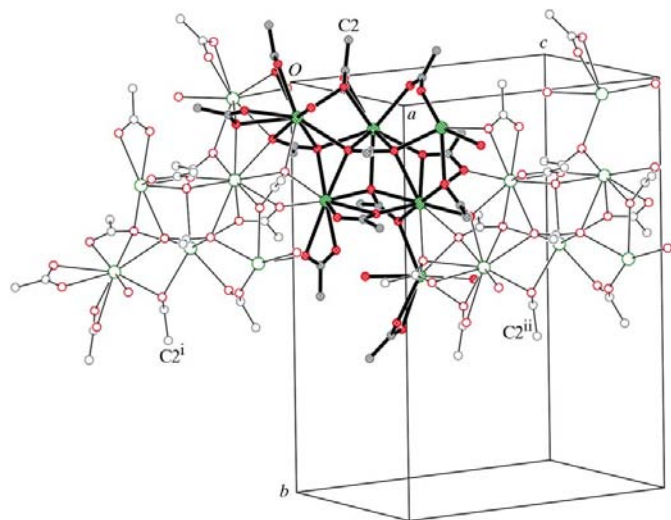


Figure 2
Ribbon propagation in (I) in the [101] direction. Heavy lines indicate the asymmetric unit and thin lines indicate symmetry-related units. All H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x + 1, y, z + 1$.]

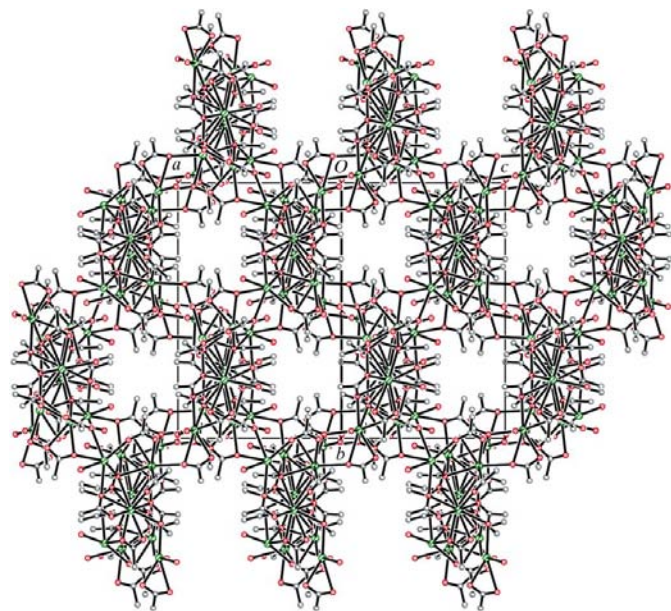


Figure 3
A view of the structure of (I) down the [101] direction, showing the channels formed by the packing of the ribbons of Fig. 2. All H atoms have been omitted for clarity.

the disorder of a coordinating water molecule (O4W) over two sites related by a crystallographic centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and therefore bonded to one or other (but not both simultaneously) of a pair of similarly symmetry-related Ba1 atoms.

In (I), the summation of the coordination numbers given in Table 1 shows the presence of 53.5 Ba–O bonds. Of these, three and a half involve coordinating water molecules and the remainder are bonds to acetate ligands. All of the acetate ligands, with the sole exception of ligand I, chelate Ba centres as bidentate ligands with bite angles in the range 43.06 (11)–46.14 (12)° [mean 44.8 (10)°] and at rather long Ba–O distances [mean 2.83 (10) Å]. The bite angles contribute, to some extent, to the somewhat irregular coordination of the Ba cations. This leaves 27 Ba–O_{acetate} bonds to create connectivity between different Ba centres. As a consequence, the connectivity of each acetate ligand ranges from a maximum of five different Ba cations (for acetate J) to a minimum of two (for acetates A, G and K). This results in complete three-dimensional connectivity between the Ba centres, which are then separated by Ba···Ba distances in the range 4.330 (2)–4.724 (2) Å. Fundamental to the three-dimensional connectivity are ribbons of BaO_n polyhedra propagating in the [101] direction and whose width is in the [010] direction (Fig. 2). As shown in Fig. 3, these ribbons are interconnected in the $[\bar{1}01]$ direction but, in terms of the number of Ba–O bonds, with weaker connectivity than is present in the ribbons themselves. Clearly seen in Fig. 3 are the channels containing hydrophobic methyl groups running through the structure created by the packing of the ribbons.

As shown in Table 2, all of the H atoms of the water molecules participate in hydrogen-bond formation. This also contributes to the three-dimensional connectivity of the structure of (I).

Experimental

Crystals of (I) were obtained by the low-temperature recrystallization from aqueous solution of the as-purchased monohydrated salt at 268 K. After leaving the saturated solution unattended in the refrigerator for about 6 months, very large colourless blocks were observed, which proved to correspond to a previously unknown hydrate of barium acetate. Thermogravimetric analysis suggested a degree of hydration of about 0.6 H₂O per Ba, a figure later confirmed by the structural analysis, which gave a more precise value of 0.583 H₂O per Ba.

Crystal data

[Ba ₆ (C ₂ H ₃ O ₂) ₁₂ (H ₂ O) _{3.5}]	$V = 4551.6 (19) \text{ \AA}^3$
$M_r = 1595.62$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 14.040 (3) \text{ \AA}$	$\mu = 5.19 \text{ mm}^{-1}$
$b = 19.903 (4) \text{ \AA}$	$T = 294 (2) \text{ K}$
$c = 17.721 (4) \text{ \AA}$	$0.36 \times 0.24 \times 0.20 \text{ mm}$
$\beta = 113.19 (3)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	38138 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	10282 independent reflections
$T_{\min} = 0.24, T_{\max} = 0.36$	8906 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.042$

Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.040$$

$$wR(F^2) = 0.087$$

$$S = 1.11$$

10282 reflections

559 parameters

13 restraints

H atoms treated by a mixture of independent and constrained refinement

$$\Delta\rho_{\max} = 1.21 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.79 \text{ e } \text{\AA}^{-3}$$

Table 1

Comparison of selected structural parameters for the Ba coordination environments in compounds (I), (II) and (III).

Bond valences were calculated according to the method of Brown & Altermatt (1985).

Compound	Cation (coordination number)	Bond valence	Average Ba—O (Å)	Range of Ba—O (Å)
(I) ^a	Ba1 (8 and 9)	1.98 and 2.16	2.81 (8) and 2.82 (8)	2.695 (4)–2.944 (4)
	Ba2 (9)	2.24	2.81 (7)	2.692 (4)–2.891 (4)
	Ba3 (9)	2.09	2.84 (10)	2.686 (4)–2.962 (4)
	Ba4 (10)	2.20	2.85 (11)	2.671 (4)–3.075 (4)
	Ba5 (10)	2.03	2.90 (10)	2.715 (4)–3.035 (4)
	Ba6 (7)	2.19	2.72 (5)	2.651 (4)–2.800 (4)
(II) ^b	Ba1 (8)	2.01	2.81 (7)	2.691–2.927
(III) ^c	Ba1 (8)	2.22	2.81 (7)	2.641–3.083
	Ba2 (9)	2.10	2.72 (5)	2.711–2.927

References: (a) this work; (b) Groombridge *et al.* (1985); (c) Gautier-Luneau & Mosset (1988).

Table 2

Hydrogen-bond geometry (Å, °).

<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>
O1W—H1WA...O2A ⁱ	0.85 (4)	1.88 (4)	2.728 (6)	173 (8)
O1W—H1WB...O1K ⁱⁱ	0.85 (4)	1.95 (4)	2.731 (6)	153 (7)
O2W—H2WA...O2B ⁱⁱⁱ	0.85 (4)	2.26 (4)	3.015 (6)	149 (6)
O2W—H2WB...O2J ⁱⁱⁱ	0.85 (4)	1.93 (4)	2.740 (7)	158 (8)
O3W—H3WA...O1G	0.85 (4)	1.91 (4)	2.746 (6)	170 (7)
O3W—H3WB...O1I ^{iv}	0.85 (4)	1.91 (4)	2.702 (7)	155 (6)
O4W—H4WA...O1E ^{iv}	0.85 (4)	2.05 (5)	2.885 (19)	166 (15)
O4W—H4WB...O1B ⁱⁱ	0.85 (4)	2.33 (7)	3.130 (17)	157 (18)

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + 1, -y, -z$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Methyl H atoms were placed in calculated positions, with C—H = 0.96 Å, and refined using a riding model, while the torsion angles of the methyl groups were also refined. Water H atoms were located in difference maps and their coordinates refined with restrained O—H distances of 0.85 (1) Å and H...H distances of 1.40 (2) Å. In all cases, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}, \text{O})$.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2001); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2001); 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: BM3038). Services for accessing these data are described at the back of the journal.

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