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Crystal Structure of Anhydrous Barium Acetate

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The crystal structure of the title compound has been determined by X-ray diffraction methods. It crystallizes in the tetragonal system, space group $I4_1/a$ with refined lattice parameters: $a = 9.901(3)$ Å, $b = 27.362(8)$ Å, and $Z = 16$. The structure consists of a tridimensional network of interconnected $Ba_4(CH_3COO)_8$ units. The four Ba atoms are linked by four μ_2–O and four μ_3–O. These formal associations Ba_4L_8 are associated in the three directions by double μ_2–O bridges. The barium surrounding is a very distorted monocapped square antiprism. The two independent acetate groups show different bonding schemes. © 1988 Academic Press, Inc.

Introduction

Barium titanate, $BaTiO_3$, is extensively used as a ferroelectric compound. It is generally prepared from a mixture of oxides BaO and TiO_2 or from a mixture of $BaCO_3$ and TiO_2. However, there is an alternative route in the preparation of such a compound: the sol–gel process based on the polycondensation of metal alkoxides or other metal compounds. This process is now widely used for the preparation of new glasses and ceramics (*1*). It allows preparations at lower temperatures and a better control of the microstructural characteristics.

The crystallization of barium titanate from gels occurs around 650°C. Below this temperature, the products are X-ray amorphous. The investigation of the local order was undertaken in these phases by the large angle X-ray scattering (LAXS) method (*2*). The so obtained distributions of interatomic distances in the gel or amorphous products are rather difficult to understand. A modelling of the local order is required and can only be done with the help of structural knowledge about the surroundings of titanium and barium atoms.

The $BaTiO_3$ gel is obtained from a mixture of barium acetate in glacial acetic acid, methanol, and tetraethoxytitanium (IV) (molar ratio Ba/Ti = 1/1). When the barium salt is removed from this starting solution, the evaporation leads to a rather peculiar hexanuclear complex of titanium, built up of two trinuclear oxo-centered units (*3*). This complex gives a picture of the possible surrounding of titanium atoms in the starting gel.

When the titanium complex is removed from the starting solution, a gel of barium acetate is obtained. LAXS measurements on this gel and a solution of $Ba(CH_3COO)_2$ in acetic acid show the same local order. Moreover, very good single crystals of anhydrous barium acetate can be grown from the gel. All these clues suggest that the bar-

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TABLE I

CRYSTALLOGRAPHIC EXPERIMENTAL DETAILS

I. Crystal data	
Formula, $Ba(CH_3COO)_2$	F_w, 255.43
Crystal system, Tetragonal	Space group, $I4_1/a$ 2nd setting
$a = 9.901(3)$ Å	$V = 2682.3$ Å^3
$c = 27.362(8)$ Å	$\rho_{exp} = 2.51(3)\ g \cdot cm^{-3}$
	$\rho_{calc} = 2.53\ g \cdot cm^{-3}$ $Z = 16$
Linear absorption factor (λMoKα)	$\mu = 58.654\ cm^{-1}$
Morphology, parallelepiped	
Crystal dimensions, 0.50 × 0.50 × 0.43 mm	
II. Intensity measurements	
Temperature, 293 K	Radiation, λMoKα
Monochromator: graphite (220)	$\lambda = 0.71069$ Å
Cryst. detector dist., 207 mm	"Take-off" angle, 3.5°
Detector aperture, horizontal, 2.5 mm	
vertical, 4 mm	Maximum 2θ, 80°
Scan type, θ–2θ	Scan width, $(0.9 + 0.35 \tan \theta)°$
III. Structure determination and refinement	
Determination:	Patterson methods
Hydrogen atoms:	Included as a fixed contribution to the structure factor
Anomalous dispersion:	All nonhydrogen atoms
Least-squares weights:	$4F_o^2/\sigma^2(F_o^2)$
Reflections included:	3335 with $I > 3\sigma(I)$
Refined parameters:	82
Unweighted agreement factor:	$R = \Sigma(k\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma(k\lvert F_o) = 0.042$
Weighted agreement factor:	$R_w = [\Sigma_w(k\lvert F_o\rvert - \lvert F_c\rvert)2/\Sigma(k\lvert F_o\rvert)2]1/2 = 0.056$

ium environment is the same in the gel and in the crystalline solid. Thus, the investigation of the crystal structure was of importance and is reported hereafter.

Experimental Part

1. Data Collection

A transparent colorless parallelepiped (0.5 × 0.5 × 0.43 mm) has been chosen in a commercial batch from Fluka. After optical alignment on an Enraf–Nonius CAD4 diffractometer, the angular coordinates of 25 *hkl* reflections within a 2θ range of 14–33° were centered automatically and least-squares refined to give the final lattice parameters (Table I).

Details for the data collection of the intensity of the reflections are indicated in Table I.

2. Structural Analysis and Refinement

The reflections were corrected for Lorentz and polarization factors. Absorption corrections were also applied but they gave further on negligible improvement, probably because of the almost isotropic shape of the crystal.

Scattering factors were taken from Cromer and Waber tables (*4*). Anomalous dispersion effects were included in F_c and their values were those of Cromer and Liberman (*5*).

The structure was solved using an automatic Patterson procedure with the SHELXS 86 program (*6*). The deconvolu-

TABLE II

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT TEMPERATURE FACTORS ($A^2 \times 100$) WITH e.s.d.'S IN PARENTHESES

Atom	x/a	y/b	z/c	U_{eq}/U_{iso}
Ba	0.54097(3)	0.48623(3)	0.08475(1)	1.59(1)
O1	0.3906(6)	0.5992(5)	0.0072(2)	3.5(2)
O2	0.3548(6)	0.7116(5)	0.0743(2)	3.2(2)
O3	0.2934(5)	0.4544(5)	0.1378(2)	3.3(2)
O4	0.3587(7)	0.2640(6)	0.1073(3)	5.1(3)
C1	0.3301(6)	0.6875(6)	0.0309(2)	2.1(2)
C2	0.2233(9)	0.7720(9)	0.0062(3)	4.5(4)
C3	0.2931(6)	0.3293(6)	0.1370(2)	2.4(2)
C4	0.213(1)	0.251(1)	0.1776(4)	5.7(6)

Hydrogen atomic positional and thermal parameters

Atom	x/a	y/b	z/c	$U(A^2 \times 100)$
H21	0.212	0.740	−0.031	5.0
H22	0.253	0.877	0.007	5.0
H23	0.128	0.759	0.025	5.0
H41	0.161	0.323	0.201	5.0
H42	0.282	0.192	0.199	5.0
H43	0.140	0.185	0.161	5.0

tion of the Patterson function leads to the localization of the barium atom and its surrounding. The remaining atoms were located from successive difference Fourier maps. The hydrogen atoms were added to the structure factor calculations but their positions were not refined.

A total of 3335 reflections having intensities $I \geq 3\sigma(I)$ were used in the refinements. The final cycle of refinement, including 82 variable parameters, converged with unweighted and weighted agreement factors $R_1 = 0.042$ and $R_2 = 0.056$. All calculations were performed on a Vax 11730 computer using the SHELX 76 program (7).

Results and Discussion

Final positional and thermal parameters of the atoms are given in Table II. Tables III and IV list selected interatomic distances and angles.

The crystal structure can be described as a tridimensional network of interconnected $Ba_4(CH_3COO)_8$ basic units.

This Ba_4L_8 formal association is generated by a $\bar{4}$ axis (Fig. 1). The four barium atoms are strongly linked by four μ_2–O (O_3, O_3^{ii}, O_3^{iii}, O_3^{v}) and four μ_3–O (O_2, O_2^{ii}, O_2^{iii}, O_2^{v}) atoms belonging to acetate groups; they shape a flattened tetrahedron with four short distances (4.338 Å) and two long distances (5.286 Å) (see Table III).

The $\bar{4}$ axis of the space group forces each Ba_4L_8 basic unit to be connected to four other ones. These connections are ensured

TABLE III

BOND DISTANCES IN ANGSTROMS

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ba	O1	2.824(6)	O1	C1	1.242(8)	Ba	Ba i	4.7162(4)
Ba	O2	2.909(5)	O2	C1	1.237(8)	Ba	Ba iv	4.7478(4)
Ba	O3	2.866(5)	O3	C3	1.239(7)	Ba	Ba iii	5.2859(4)
Ba	O4	2.912(7)	O4	C3	1.225(9)	Ba	Ba ii	4.3385(4)
Ba	O1 i	2.740(5)	C1	C2	1.51(2)	Ba	Ba v	4.3385(4)
Ba	O2 ii	2.752(5)	C3	C4	1.57(1)			
Ba	O2 iii	3.178(5)						
Ba	O3 ii	2.691(6)						
Ba	O4 iv	2.740(5)						

Note. Numbers in parentheses are estimated standard deviations in the least-significant digits. Equivalent positions: (i) $1 - X, 1 - Y, -Z$; (ii) $\frac{5}{4} - Y, \frac{1}{4} + X, \frac{1}{4} - Z$; (iii) $1 - X, \frac{3}{2} - Y, Z$; (iv) $1 - X, \frac{1}{2} - Y, Z$; (v) $-\frac{1}{4} + Y, \frac{5}{4} - X, \frac{1}{4} - Z$.

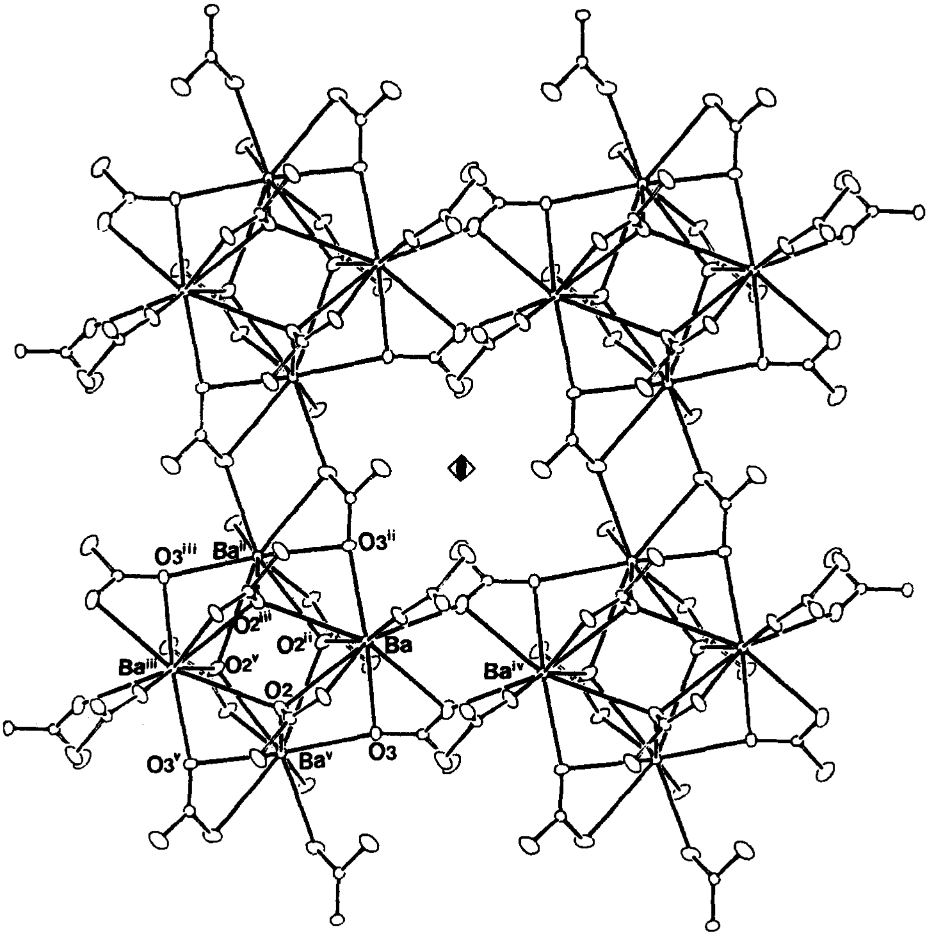

FIG. 1. ORTEP drawing of a layer of $Ba_4(CH_3COO)_8$ basic units generated by a 4 axis, parallel to the (001) plane.

by two μ_2–O bridges, leading to a barium–barium distance of 4.748 Å. This linkage results in a kind of layer (Fig. 1), expanding parallely to the (001) plane at a mean altitude $z = \frac{1}{8}$.

The stacking of these layers, along the [001] direction, is generated by the 4_1 axis of the space group (Fig. 2a). Each Ba_4 tetrahedron from one layer (e.g., at $z = \frac{1}{8}$) is connected to four other units, two at $z = \frac{3}{8}$ and two at $z = -\frac{1}{8}$ (Fig. 2b). These connections are insured by double μ_2–O bridges, leading to barium–barium distances of 4.716 Å.

The barium environment is achieved by nine oxygen atoms from seven acetate groups (Fig. 3). These nine neighbors form a very distorted monocapped square antiprism. The two square faces are defined by O1–O2–O3–O4 (plane 1) and $O1^{i}$–$O2^{ii}$–$O2^{iii}$–$O4^{iv}$ (plane 2) (see Table V for the least-squares planes). These two faces make a dihedral angle equal to 9.0(4)°. The capping atom is $O3^{ii}$. The barium atom is

TABLE IV

BOND ANGLES IN DEGREES

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	Ba	O2	44.7(1)	O3	Ba	O2 iii	115.3(1)
O1	Ba	O3	88.4(2)	O3	Ba	O3 ii	133.1(2)
O1	Ba	O4	97.5(2)	O3	Ba	O4 iv	95.6(2)
O1	Ba	O1 i	64.1(2)	O4	Ba	O1 i	96.5(2)
O1	Ba	O2 ii	120.4(1)	O4	Ba	O2 ii	97.2(2)
O1	Ba	O2 iii	74.4(1)	O4	Ba	O2 iii	158.8(2)
O1	Ba	O3 ii	128.4(2)	O4	Ba	O3 ii	132.9(2)
O1	Ba	O4 iv	135.9(2)	O4	Ba	O4 iv	59.6(2)
O2	Ba	O3	65.9(1)	O1 i	Ba	O2 ii	164.8(2)
O2	Ba	O4	102.0(2)	O1 i	Ba	O2 iii	97.4(1)
O2	Ba	O1 i	107.7(1)	O1 i	Ba	O3 ii	95.1(2)
O2	Ba	O2 ii	75.9(1)	O1 i	Ba	O4 iv	80.6(3)
O2	Ba	O2 iii	58.4(1)	O1 ii	Ba	O2 iii	71.5(1)
O2	Ba	O3 ii	117.4(1)	O1 ii	Ba	O3 ii	70.6(2)
O2	Ba	O4 iv	161.1(2)	O1 ii	Ba	O4 iv	100.7(2)
O3	Ba	O4	43.9(2)	O2 iii	Ba	O3 ii	61.6(1)
O3	Ba	O1 i	130.0(2)	O2 iii	Ba	O4 iv	138.9(2)
O3	Ba	O2 ii	65.2(1)	O3 ii	Ba	O4 iv	77.7(2)
Ba	O1	Ba i	115.9(2)	Ba iii	O2	Ba v	93.8(1)
Ba	O2	Ba iii	120.5(2)	Ba	O3	Ba v	102.7(2)
Ba	O2	Ba v	100.1(1)	Ba	O4	Ba iv	114.3(2)
C1	O1	Ba	98.1(4)	C1	O1	Ba i	144.6(4)
C1	O2	Ba	94.1(4)	C1	O2	Ba iii	109.4(4)
C1	O2	Ba v	141.6(4)	C3	O3	Ba	95.9(4)
C3	O3	Ba v	160.2(4)	C3	O4	Ba	94.0(5)
C3	O4	Ba iv	145.0(5)				
O1	C1	O2	122.8(6)	O3	C3	O4	122.6(6)
O1	C1	C2	119.7(6)	O3	C3	C4	118.8(7)
O2	C1	C2	117.5(6)	O4	C3	C4	118.6(6)

Note. Numbers in parentheses are estimated standard deviations in the least-significant digits. Equivalent positions: (i) $1 - X, 1 - Y, -Z$; (ii) $\frac{5}{4} - Y, \frac{1}{4} + X, \frac{1}{4} - Z$; (iii) $1 - X, \frac{3}{2} - Y, Z$; (iv) $1 - X, \frac{1}{2} - Y, Z$; (v) $-\frac{1}{4} + Y, \frac{5}{4} - X, \frac{1}{4} - Z$.

displaced toward this atom; it is at 0.676(1) Å from the plane 2 and 1.830(1) Å from the plane 1. The great distortion from the ideal antiprism can be explained by:

–a great dispersion in the Barium oxygen distances, from 2.691(6) Å for Ba-O_3^{ii} to 3.178(5) Å for Ba-O_2^{iii}.

–the bonding of two bidentate acetate groups, leading to very narrow O–Ba–O angles (44.7(1)° and 43.9(2)°) and, consequently, very short oxygen–oxygen distances (2.176(8) and 2.161(8) Å).

The same kind of deformations have already been observed in the structure of barium acetate monohydrate and strontium acetate hemihydrate (*8*).

The connections between the barium antiprisms are quite intricate and lead to a rather dense packing. Inside a Ba_4 tetrahedron, each antiprism shares two faces with two other ones: the Ba environment is thus linked to those of the Ba^{ii} and Ba^{v} (see Fig. 1). Moreover, the Ba and Ba^{iii} polyhedron share an edge. Inside the above described layer, the Ba polyhedron are edge shared

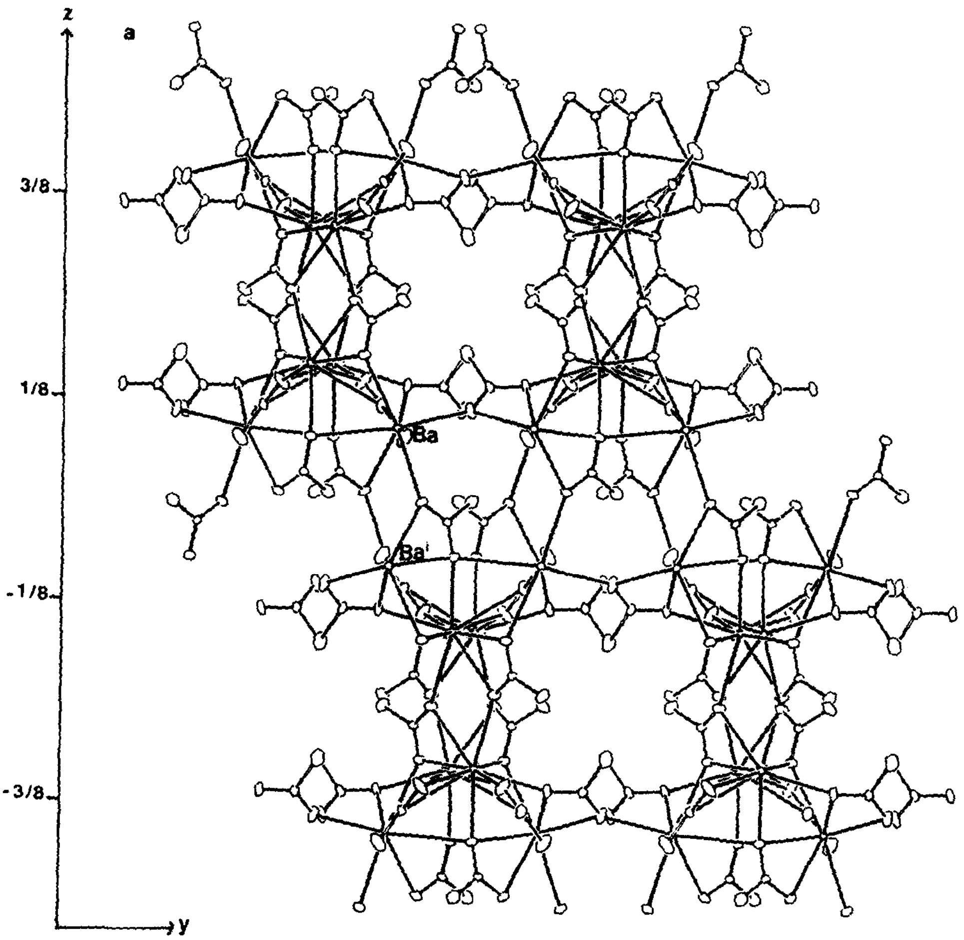

FIG. 2a. Projection of the structure onto the (100) plane.

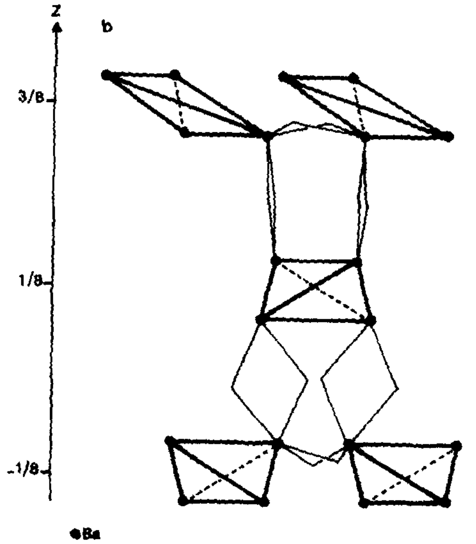

FIG. 2b. Connection of the Ba_4L_8 units along the [001] direction.

TABLE V

LEAST-SQUARES PLANES

	Atoms defining the plane	Distance to the least-squares plane (Å)	Other atoms	Distance to the least-squares plane (Å)
Plane 1	O_1	0.098(6)	Ba	−1.830
	O_2	−0.139(5)		
	O_3	0.151(5)		
	O_4	−0.111(7)		
Plane 2	O_1^i	0.338(6)	Ba	0.676(1)
	O_2^{ii}	0.367(5)	O_3^{iii}	−1.927(5)
	O_2^{iii}	−0.347(5)		
	O_4^{iv}	−0.358(7)		
Plane 3	O_1	0.002(5)	Ba	−0.285(1)
	O_2	0.002(5)	Ba^i	0.588(1)
	C_1	−0.005(6)	Ba^{iii}	2.637(1)
	C_2	0.001(9)	Ba^v	−1.504(1)
Plane 4	O_3	−0.007(5)	Ba	−1.100(1)
	O_4	−0.007(7)	Ba^{iv}	−0.410(1)
	C_3	0.019(6)	Ba^v	−0.027(1)
	C_4	−0.005(11)		

Note. Dihedral angles between planes: 1 and 2, 9.04(35)°; 3 and 4, 113.47(32)°.

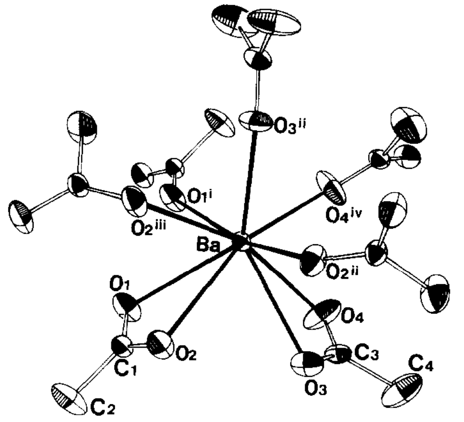

FIG. 3. ORTEP drawing of the barium environment.

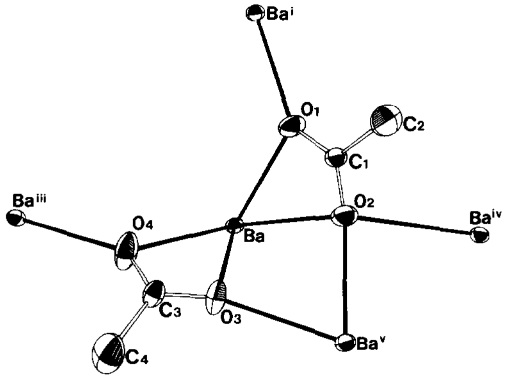

FIG. 4. Coordination scheme of the two independent acetate groups.

with those of the Ba^{iv} and also along the [001] axis to the Ba^{i} antiprisms.

The two crystallographically independent acetate groups show two different coordination schemes.

The first one (C1–C2–O1–O2) is coordinated to four barium atoms (Fig. 4), with a μ_2–O and a μ_3–O. This group is perfectly planar (see Table V). Two barium atoms, Ba and Ba^{i}, are almost located in this plane and two other lie on both sides.

The second acetate group (C3–C4–O3–O4) is coordinated to three barium atoms (Fig. 4) with two μ_2–O. This group shows a slight distortion from the planarity (0.019(6) Å for C3).

The localization of the barium atoms with regard to the mean plane of this group is rather unusual: the three Ba atoms are on the same side (see Table V) with Ba^{v} almost lying in the plane (−0.027(1) Å).

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