METAL-ORGANIC COMPOUNDS

Acta Cryst. (1994). C**50**, 1387–1390

Tetra-μ_4-oxo-tris(2-propanol)tetrakis[tetrakis(2-propanolato)titanium]tetrabarium

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(*Received* 10 *September* 1993; *accepted* 6 *April* 1994)

Abstract

The title compound, $[Ba_4\{\mu_3\text{-}OTi(C_3H_7O)_4\}_4(C_3H_7OH)_3]$, is a $BaTiO_3$ molecular precursor. The structure is based on a Ba_4 tetrahedral cluster with all faces capped by $OTi(O^iPr)_4$ groups. Two of the faces are symmetrically capped (three μ_2-O atoms) and two are unsymmetrically capped (two μ_2-O atoms and one μ_3-O atom).

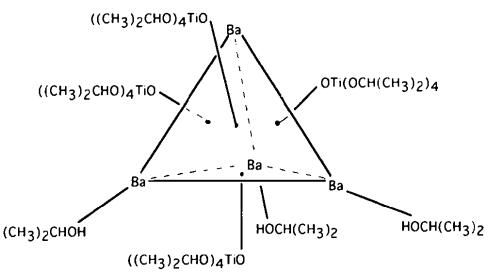
Comment

The thermal transformation of organometallic compounds is of interest in the sol–gel production of ceramics. Two areas of current interest are the formation of ferroelectric ceramics, *e.g.* $BaTiO_3$, and high-temperature superconductors, *e.g.* $YBa_2Cu_3O_7$. Sol–gel methods are also employed in the production of high purity, microcrystalline powders for fabrication of electronic components.

Traditionally, $BaTiO_3$ ceramics have been prepared by the high-temperature solid-state reaction of TiO_2 and $BaCO_3$. Two factors make organometallic syntheses preferable to solid-state reactions: firstly, transformations to ceramic states occur at lower temperatures, and secondly, organometallic purity levels are higher and of greater consistency. By studying the thermal transformation of heterometallic structures, information leading to better control of structural homogeneity at these lower transformation temperatures can be obtained.

Recently a crystalline compound was found to yield the ferroelectric ceramic barium titanate upon thermal decomposition (Kirby, 1988). This material forms in 1:1 anhydrous solutions of mixed barium and titanium isopropoxides. We have obtained similar results under controlled conditions using solutions prepared in an Ar glove box (H_2O < 5 p.p.m., CO_2 < 1 p.p.m.), acetone being used to initiate crystallization and inhibit effects of hydride-transfer reactions, such as occur in the Meerwein–Ponndorf–Verley oxidation of secondary alcohols to ketones.

The isolated material in the present study, (I), is an unsymmetrical tetramer built on a tetrahedral barium cluster exhibiting Ba—Ba interatomic distances which are close to those in the bulk metal. The four faces of the tetrahedron are capped by the titanyl O atoms of four $OTi(O^iPr)_4$ moieties (Fig. 1). The faces of the tetrahedron are bonded to the $OTi(O^iPr)_4$ groups in two different ways. The Ba_{123} face is capped by a trigonal bipyramidal $OTi(O^iPr)_4$ group, the μ_3-titanyl O atom being axial and the three equatorial alkoxides bridging (μ_2) Ti1 to the three Ba atoms. The coordination of the Ba_{134} face is similar. The coordination of the other two faces is less symmetrical (Fig. 2). The geometry at Ti is now better described as square pyramidal with the titanyl O atom axial. Two μ_2 bonds are formed to the triangular faces (Ba_{124} and Ba_{234}) by two O atoms of the basal plane of the pyramid (O8, O10 and O14, O16), a third basal O atom (O9 and O15) forming a μ_3-bridge to the same Ba atoms. The fourth alkoxide O atom does not bridge and there is no bridging involving the third Ba atom (Ba2 or Ba4) on these two faces.



(I)

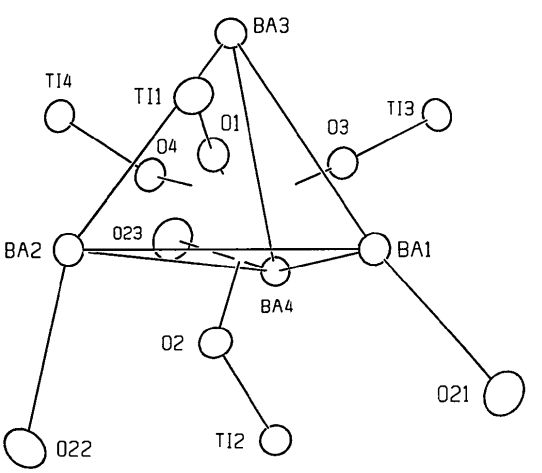


Fig. 1. *ORTEP*II plot showing the capped tetrahedral metal cluster.

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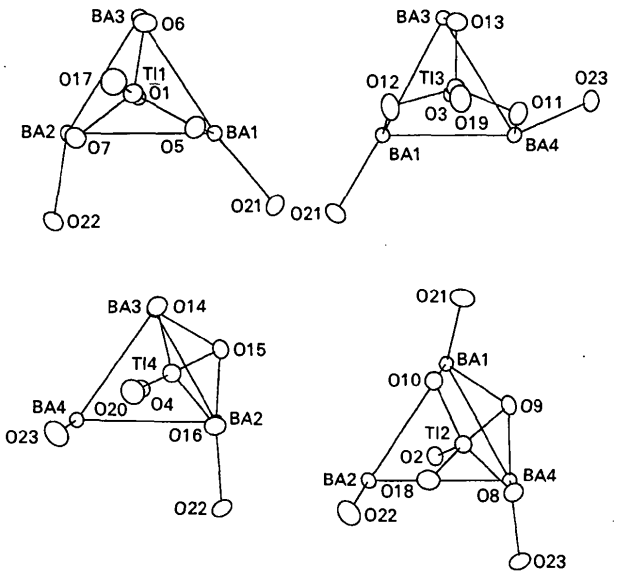

Fig. 2. *ORTEP*II plots showing details of the bonding to each of the four faces of the Ba tetrahedron. C and H atoms are omitted for clarity.

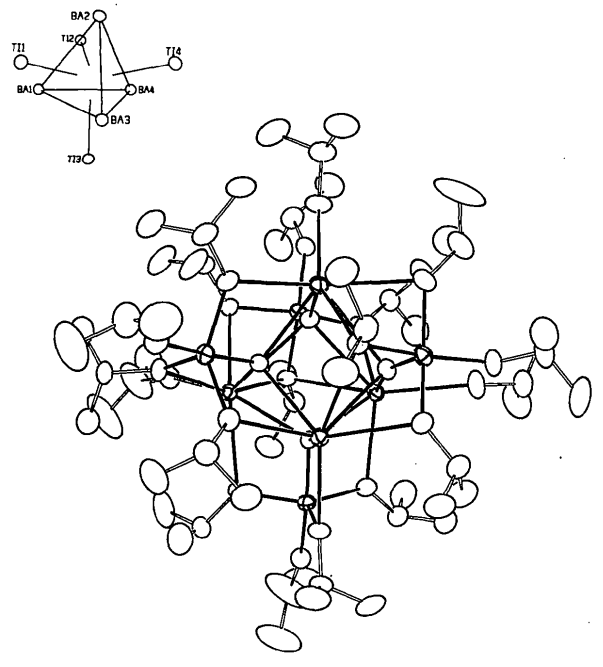

Fig. 3. Drawing of the molecule showing the non-H atoms. Ellipsoids correspond to 50% probability contours of atomic displacement. Principal axes are shown for Ba and Ti atoms with Ba—O and Ti—O bonds darkened.

As expected, the Ti—O bonds may be differentiated by their lengths, although the ranges for similar bonds are quite large. The titanyl bonds [1.714 (2)–1.795 (2) Å] are shorter than the non-bridging bonds [1.877 (3)–1.906 (3) Å] which tend to be shorter than the bridging bonds [1.886 (3)–1.999 (3) Å].

The coordination sphere of three of the Ba atoms (Ba1, Ba2 and Ba4) is completed by a 2-propanol molecule; Ba3, however, is not solvated. It is tempting to interpret the inter-O-atom distances between the OH groups of the alcohol and neighboring alkoxides [2.684 (4)–2.832 (4) Å] as evidence of hydrogen bonding; however, there are other O···O contacts between alkoxide groups that are even shorter. The three hydroxyl H-atom positions are included on the basis of predicted stereochemistry and assignment of standard oxidation states. They were not located experimentally and could not be unambiguously assigned.

Experimental

All reactions were carried out in dry solvents under a blanket of Ar. 1.00 g of barium diisopropoxide was dissolved in 2.56 g of 2-propanol. Addition of 2.80 g of toluene and 1.11 g of titanium tetraisopropoxide was followed by stirring and the further addition of 0.23 g of acetone. After approximately 5 min, an intense light green color appeared. Colorless crystals were visible after standing for 24 h.

Crystal data

$[Ba_4Ti_4O_4(C_3H_7O)_{16}\text{-}(C_3H_7OH)_3]$	Mo $K\alpha$ radiation
M_r = 1930.67	λ = 0.71073 Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/n$	θ = 11.5–12.4°
a = 13.7601 (7) Å	μ = 2.224 mm^{-1}
b = 26.229 (2) Å	T = 173 K
c = 24.106 (3) Å	Rod
β = 101.219 (7)°	0.35 × 0.25 × 0.22 mm
V = 8533 (2) Å^3	Colorless
Z = 4	
D_x = 1.50 Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	12 833 observed reflections [$I > 3.0\sigma(I)$]
θ/θ scans	R_{int} = 0.027
Absorption correction: empirical	θ_{max} = 25.97°
T_{min} = 0.904, T_{max} = 0.999	$h = 0 \rightarrow 16$
16 586 measured reflections	$k = 0 \rightarrow 32$
15 210 independent reflections	$l = -29 \rightarrow 29$
	3 standard reflections frequency: 50 min intensity variation: −8.31%

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.005
R = 0.027	$\Delta\rho_{max}$ = 0.797 e Å^{-3}
wR = 0.037	$\Delta\rho_{min}$ = −0.104 e Å^{-3}
S = 1.203	Extinction correction: none
12 833 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
793 parameters	
H atoms refined using a riding model	
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ba1	0.08926 (1)	0.411414 (8)	0.206435 (8)	0.01946 (5)
Ba2	0.18654 (1)	0.294878 (8)	0.336387 (8)	0.02115 (5)
Ba3	−0.05275 (1)	0.385932 (8)	0.340278 (8)	0.02052 (5)
Ba4	−0.08108 (1)	0.280562 (8)	0.201479 (8)	0.02052 (5)
Ti1	0.20061 (5)	0.43448 (2)	0.35536 (3)	0.0235 (2)
Ti2	0.13939 (5)	0.28833 (2)	0.15841 (2)	0.0206 (1)
Ti3	−0.18253 (4)	0.41000 (2)	0.19843 (3)	0.0221 (2)
Ti4	−0.02853 (5)	0.26168 (2)	0.37852 (3)	0.0236 (2)
O1	0.1231 (2)	0.38756 (9)	0.31422 (9)	0.0203 (6)
O2	0.1247 (2)	0.29823 (9)	0.22645 (9)	0.0234 (6)
O3	−0.0746 (2)	0.37509 (9)	0.23042 (9)	0.0205 (6)
O4	−0.0266 (2)	0.28284 (9)	0.3115 (1)	0.0242 (6)
O5	0.2173 (2)	0.47134 (9)	0.2903 (1)	0.0270 (6)
O6	0.0797 (2)	0.45658 (9)	0.3794 (1)	0.0299 (6)
O7	0.2939 (2)	0.3772 (1)	0.3755 (1)	0.0289 (7)
O8	0.0384 (2)	0.23661 (9)	0.1345 (1)	0.0288 (6)
O9	0.0319 (2)	0.33549 (9)	0.12600 (9)	0.0246 (6)
O10	0.2275 (2)	0.34584 (9)	0.1475 (1)	0.0271 (6)
O11	−0.2349 (2)	0.3427 (1)	0.1719 (1)	0.0316 (7)
O12	−0.0881 (2)	0.4616 (1)	0.1831 (1)	0.0365 (7)
O13	−0.2188 (2)	0.4279 (1)	0.2674 (1)	0.0278 (6)
O14	−0.1224 (2)	0.3083 (1)	0.4027 (1)	0.0301 (7)
O15	0.0667 (2)	0.31593 (9)	0.41254 (9)	0.0259 (6)
O16	0.0901 (2)	0.21968 (9)	0.3939 (1)	0.0313 (7)
O17	0.2773 (2)	0.4750 (1)	0.4116 (1)	0.0363 (7)
O18	0.2445 (2)	0.24017 (9)	0.1632 (1)	0.0282 (6)
O19	−0.2846 (2)	0.4417 (1)	0.1470 (1)	0.0356 (7)
O20	−0.1171 (2)	0.2051 (1)	0.3684 (1)	0.0341 (7)
O21	0.1703 (2)	0.4401 (1)	0.1120 (1)	0.0374 (7)
O22	0.3116 (2)	0.2317 (1)	0.2816 (1)	0.0390 (7)
O23	−0.1699 (2)	0.1991 (1)	0.2498 (1)	0.0413 (8)
C1	0.2704 (3)	0.5178 (1)	0.2870 (2)	0.0293 (9)
C2	0.2055 (4)	0.5561 (2)	0.2515 (2)	0.062 (2)
C3	0.3619 (4)	0.5086 (2)	0.2637 (2)	0.065 (2)
C4	0.0611 (3)	0.4978 (2)	0.4151 (2)	0.039 (1)
C5	−0.0417 (3)	0.4926 (2)	0.4269 (2)	0.049 (1)
C6	0.0731 (4)	0.5481 (2)	0.3877 (2)	0.071 (2)
C7	0.3910 (3)	0.3761 (2)	0.4095 (2)	0.034 (1)
C8	0.4266 (3)	0.3211 (2)	0.4145 (2)	0.047 (1)
C9	0.4619 (3)	0.4085 (2)	0.3832 (2)	0.047 (1)
C10	0.0435 (3)	0.1851 (1)	0.1187 (2)	0.033 (1)
C11	−0.0511 (4)	0.1709 (2)	0.0774 (2)	0.063 (2)
C12	0.0606 (4)	0.1512 (2)	0.1693 (2)	0.058 (2)
C13	−0.0307 (3)	0.3334 (2)	0.0717 (2)	0.034 (1)
C14	−0.0818 (4)	0.3841 (2)	0.0582 (2)	0.048 (1)
C15	0.0254 (4)	0.3172 (2)	0.0264 (2)	0.054 (1)
C16	0.3311 (3)	0.3462 (1)	0.1725 (2)	0.030 (1)
C17	0.3480 (3)	0.3674 (2)	0.2308 (2)	0.056 (1)
C18	0.3882 (3)	0.3755 (2)	0.1360 (2)	0.065 (2)
C19	−0.3304 (3)	0.3270 (2)	0.1432 (2)	0.036 (1)
C20	−0.3802 (3)	0.2963 (2)	0.1822 (2)	0.049 (1)
C21	−0.3199 (4)	0.2970 (2)	0.0911 (2)	0.055 (1)
C22	−0.1097 (3)	0.5134 (2)	0.1704 (3)	0.073 (2)
C23	−0.0901 (5)	0.5448 (2)	0.2237 (4)	0.119 (2)
C24	−0.0457 (5)	0.5301 (2)	0.1289 (3)	0.083 (2)
C25	−0.3039 (3)	0.4584 (1)	0.2703 (2)	0.033 (1)
C26	−0.3976 (3)	0.4271 (2)	0.2560 (2)	0.052 (1)
C27	−0.2929 (4)	0.4821 (2)	0.3284 (2)	0.055 (1)
C28	−0.2229 (3)	0.3056 (2)	0.4076 (2)	0.039 (1)
C29	−0.2889 (4)	0.3040 (2)	0.3495 (2)	0.059 (2)
C30	−0.2473 (3)	0.3504 (2)	0.4415 (2)	0.056 (1)
C31	0.0936 (3)	0.3161 (2)	0.4724 (1)	0.032 (1)
C32	0.0607 (4)	0.3654 (2)	0.4956 (2)	0.053 (1)
C33	0.2036 (3)	0.3075 (2)	0.4901 (2)	0.050 (1)
C34	0.1034 (3)	0.1670 (2)	0.3869 (2)	0.048 (1)
C35	0.1122 (4)	0.1547 (2)	0.3271 (2)	0.062 (2)
C36	0.1933 (5)	0.1495 (2)	0.4284 (2)	0.093 (2)
C37	0.3426 (4)	0.4936 (2)	0.4599 (2)	0.053 (1)
C38	0.3577 (6)	0.5492 (2)	0.4555 (3)	0.107 (2)
C39	0.3123 (4)	0.4772 (3)	0.5132 (2)	0.074 (2)
C40	0.3072 (3)	0.2241 (2)	0.1268 (2)	0.042 (1)
C41	0.2704 (4)	0.2413 (2)	0.0666 (2)	0.064 (1)
C42	0.3215 (4)	0.1672 (2)	0.1296 (2)	0.057 (1)
C43	−0.3408 (6)	0.4658 (2)	0.1009 (3)	0.118 (2)
C44	−0.4019 (5)	0.5064 (2)	0.1139 (3)	0.100 (2)
C45	−0.3617 (5)	0.4402 (3)	0.0497 (2)	0.089 (2)
C46	−0.1444 (3)	0.1668 (2)	0.4036 (2)	0.045 (1)
C47	−0.0979 (4)	0.1761 (2)	0.4649 (2)	0.055 (1)
C48	−0.2552 (4)	0.1612 (2)	0.3948 (2)	0.069 (2)
C49	0.1971 (5)	0.4668 (2)	0.0669 (2)	0.088 (2)
C50	0.1712 (7)	0.5180 (2)	0.0625 (3)	0.123 (3)
C51	0.2087 (5)	0.4359 (2)	0.0187 (2)	0.083 (2)
C52	0.3951 (3)	0.1977 (2)	0.2907 (2)	0.046 (1)
C53	0.4176 (4)	0.1822 (2)	0.3507 (2)	0.070 (2)
C54	0.4819 (4)	0.2239 (3)	0.2736 (3)	0.075 (2)
C55	−0.2264 (3)	0.1535 (2)	0.2377 (2)	0.044 (1)
C56	−0.2694 (5)	0.1516 (2)	0.1756 (3)	0.076 (2)
C57	−0.1623 (4)	0.1078 (2)	0.2568 (2)	0.061 (2)

Table 2. *Selected geometric parameters* (Å, °)

Ba1—Ba2	4.3950 (3)	Ba4—O2	2.817 (2)
Ba1—Ba3	4.1387 (3)	Ba4—O3	2.573 (2)
Ba1—Ba4	4.1446 (3)	Ba4—O4	2.612 (2)
Ba1—O1	2.625 (2)	Ba4—O8	2.770 (3)
Ba1—O2	3.032 (2)	Ba4—O9	2.984 (2)
Ba1—O3	2.614 (2)	Ba4—O11	2.657 (2)
Ba1—O5	2.876 (2)	Ba4—O23	2.824 (3)
Ba1—O9	2.784 (2)	Ti1—O1	1.795 (2)
Ba1—O10	3.106 (3)	Ti1—O5	1.895 (3)
Ba1—O12	2.733 (2)	Ti1—O6	1.954 (3)
Ba1—O21	2.825 (3)	Ti1—O7	1.974 (3)
Ba2—Ba3	4.0834 (3)	Ti1—O17	1.877 (3)
Ba2—Ba4	4.4291 (3)	Ti2—O2	1.711 (2)
Ba2—O1	2.603 (2)	Ti2—O8	1.947 (2)
Ba2—O2	2.622 (2)	Ti2—O9	1.969 (2)
Ba2—O4	2.894 (2)	Ti2—O10	1.985 (3)
Ba2—O7	2.683 (2)	Ti2—O18	1.907 (3)
Ba2—O15	2.752 (3)	Ti3—O3	1.787 (2)
Ba2—O16	2.879 (3)	Ti3—O11	1.966 (3)
Ba2—O22	2.888 (3)	Ti3—O12	1.960 (3)
Ba3—Ba4	4.2985 (3)	Ti3—O13	1.886 (3)
Ba3—O1	2.617 (2)	Ti3—O19	1.878 (3)
Ba3—O3	2.622 (2)	Ti4—O4	1.714 (2)
Ba3—O4	2.832 (2)	Ti4—O14	1.948 (3)
Ba3—O6	2.641 (2)	Ti4—O15	1.999 (2)
Ba3—O13	2.821 (2)	Ti4—O16	1.945 (3)
Ba3—O14	2.808 (3)	Ti4—O20	1.906 (3)
Ba3—O15	2.827 (2)		
Ba2—Ba1—Ba3	57.080 (5)	O1—Ba1—O9	119.38 (7)
Ba2—Ba1—Ba4	62.403 (5)	O1—Ba1—O10	108.32 (7)
Ba2—Ba1—O1	32.62 (5)	O1—Ba1—O12	107.32 (8)
Ba2—Ba1—O2	35.74 (4)	O1—Ba1—O21	147.07 (7)
Ba2—Ba1—O3	75.23 (5)	O2—Ba1—O3	74.16 (7)
Ba2—Ba1—O5	79.59 (5)	O2—Ba1—O5	111.44 (6)
Ba2—Ba1—O9	90.27 (5)	O2—Ba1—O9	54.94 (6)
Ba2—Ba1—O10	79.18 (4)	O2—Ba1—O10	55.71 (7)
Ba2—Ba1—O12	128.11 (6)	O2—Ba1—O12	127.87 (7)
Ba2—Ba1—O21	130.28 (6)	O2—Ba1—O21	108.21 (7)
Ba3—Ba1—Ba4	62.522 (5)	O3—Ba1—O5	118.71 (7)
Ba3—Ba1—O1	37.78 (5)	O3—Ba1—O9	75.74 (7)
Ba3—Ba1—O2	78.68 (5)	O3—Ba1—O10	122.06 (7)
Ba3—Ba1—O3	37.84 (5)	O3—Ba1—O12	56.41 (8)
Ba3—Ba1—O5	81.84 (5)	O3—Ba1—O21	140.18 (7)
Ba3—Ba1—O9	108.34 (5)	O5—Ba1—O9	158.75 (7)
Ba3—Ba1—O10	133.74 (5)	O5—Ba1—O10	106.15 (7)
Ba3—Ba1—O12	72.52 (6)	O5—Ba1—O12	106.35 (7)
Ba3—Ba1—O21	172.54 (6)	O5—Ba1—O21	97.86 (7)
Ba4—Ba1—O1	79.73 (5)	O9—Ba1—O10	53.21 (6)
Ba4—Ba1—O2	42.82 (4)	O9—Ba1—O12	94.63 (7)
Ba4—Ba1—O3	36.61 (5)	O9—Ba1—O21	74.47 (7)
Ba4—Ba1—O5	137.59 (5)	O10—Ba1—O12	140.76 (7)
Ba4—Ba1—O9	46.03 (5)	O10—Ba1—O21	53.56 (7)
Ba4—Ba1—O10	85.50 (5)	O12—Ba1—O21	100.54 (8)
Ba4—Ba1—O12	85.15 (5)	Ba1—Ba2—Ba3	58.298 (5)
Ba4—Ba1—O21	120.47 (5)	Ba1—Ba2—Ba4	56.027 (4)
O1—Ba1—O2	67.47 (7)	Ba1—Ba2—O1	32.93 (5)
O1—Ba1—O3	71.87 (7)	Ba1—Ba2—O2	42.48 (5)
O1—Ba1—O5	57.87 (7)	Ba1—Ba2—O4	76.83 (5)

Ba1—Ba2—O7	76.19 (5)	O4—Ba3—O15	56.26 (6)	O4—Ba3—O14	60.80 (7)	O11—Ti3—O13	111.6 (1)
Ba1—Ba2—O15	101.36 (5)	O6—Ba3—O13	111.56 (7)	O11—Ti3—O19	90.2 (1)	Ba1—O3—Ba4	106.10 (8)
Ba1—Ba2—O16	135.63 (5)	O6—Ba3—O14	126.92 (7)	O12—Ti3—O13	107.0 (1)	Ba1—O3—Ti3	113.5 (1)
Ba1—Ba2—O22	101.50 (6)	O6—Ba3—O15	87.56 (7)	O12—Ti3—O19	90.5 (1)	Ba3—O3—Ba4	111.68 (8)
Ba3—Ba2—Ba4	60.497 (5)	O13—Ba3—O14	107.30 (7)	O13—Ti3—O19	100.3 (1)	Ba3—O3—Ti3	107.6 (1)
Ba3—Ba2—O1	38.64 (5)	O13—Ba3—O15	160.16 (7)	O4—Ti4—O14	102.2 (1)	Ba4—O3—Ti3	113.2 (1)
Ba3—Ba2—O2	84.22 (5)	O14—Ba3—O15	54.35 (7)	O4—Ti4—O15	91.6 (1)	Ba2—O4—Ba3	90.98 (7)
Ba3—Ba2—O4	43.90 (5)	Ba1—Ba4—Ba2	61.570 (5)	O4—Ti4—O16	101.3 (1)	Ba2—O4—Ba4	107.01 (9)
Ba3—Ba2—O7	84.98 (5)	Ba1—Ba4—Ba3	58.671 (5)	O4—Ti4—O20	105.0 (1)	Ba2—O4—Ti4	92.34 (9)
Ba3—Ba2—O15	43.67 (5)	Ba1—Ba4—O2	47.01 (5)	O14—Ti4—O15	81.4 (1)	Ba3—O4—Ba4	104.22 (7)
Ba3—Ba2—O16	86.58 (5)	Ba1—Ba4—O3	37.29 (5)	O14—Ti4—O16	151.6 (1)	Ba3—O4—Ti4	93.0 (1)
Ba3—Ba2—O22	154.33 (5)	Ba1—Ba4—O4	84.42 (5)	O14—Ti4—O20	94.8 (1)	Ba4—O4—Ti4	153.6 (1)
Ba4—Ba2—O1	74.39 (5)	Ba1—Ba4—O8	87.99 (5)	O15—Ti4—O16	82.3 (1)	Ba1—O5—Ti1	98.45 (9)
Ba4—Ba2—O2	36.97 (5)	Ba1—Ba4—O9	42.18 (4)	O15—Ti4—O20	163.5 (1)	Ba3—O6—Ti1	104.7 (1)
Ba4—Ba2—O4	34.33 (5)	Ba1—Ba4—O11	85.19 (5)	O16—Ti4—O20	94.3 (1)	Ba2—O7—Ti1	103.80 (9)
Ba4—Ba2—O7	130.46 (5)	Ba1—Ba4—O23	154.50 (5)	Ba1—O1—Ba2	114.45 (8)	Ba4—O8—Ti2	90.45 (9)
Ba4—Ba2—O15	89.21 (4)	Ba2—Ba4—Ba3	55.767 (4)	Ba1—O1—Ba3	104.30 (7)	Ba1—O9—Ba4	91.80 (7)
Ba4—Ba2—O16	84.28 (5)	Ba2—Ba4—O2	34.05 (5)	Ba1—O1—Ti1	110.8 (1)	Ba1—O9—Ti2	94.81 (8)
Ba4—Ba2—O22	95.73 (5)	Ba2—Ba4—O3	74.87 (5)	Ba2—O1—Ba3	102.96 (8)	Ba4—O9—Ti2	83.97 (8)
O1—Ba2—O2	74.42 (7)	Ba2—Ba4—O4	38.67 (5)	Ba2—O1—Ti1	112.81 (9)	Ba1—O10—Ti2	85.16 (9)
O1—Ba2—O4	76.92 (7)	Ba2—Ba4—O8	87.72 (5)	Ba3—O1—Ti1	110.9 (1)	Ba4—O11—Ti3	103.95 (9)
O1—Ba2—O7	57.31 (7)	Ba2—Ba4—O9	87.09 (4)	Ba1—O2—Ba2	101.78 (7)	Ba1—O12—Ti3	103.2 (1)
O1—Ba2—O15	74.29 (7)	Ba2—Ba4—O11	130.56 (5)	Ba1—O2—Ba4	90.17 (6)	Ba3—O13—Ti3	97.5 (1)
O1—Ba2—O16	124.84 (8)	Ba2—Ba4—O23	97.23 (5)	Ba1—O2—Ti2	92.38 (9)	Ba3—O14—Ti4	88.9 (1)
O1—Ba2—O22	130.40 (8)	Ba3—Ba4—O2	78.04 (5)	Ba2—O2—Ba4	108.98 (9)	Ba2—O15—Ba3	94.08 (7)
O2—Ba2—O4	71.20 (7)	Ba3—Ba4—O3	34.53 (5)	Ba2—O2—Ti2	152.7 (1)	Ba2—O15—Ti4	90.77 (9)
O2—Ba2—O7	112.11 (7)	Ba3—Ba4—O4	39.69 (5)	Ba4—O2—Ti2	94.08 (9)	Ba3—O15—Ti4	87.34 (8)
O2—Ba2—O15	123.29 (7)	Ba3—Ba4—O8	138.34 (5)	Ba1—O3—Ba3	104.46 (7)	Ba2—O16—Ti4	88.19 (9)
O2—Ba2—O16	114.87 (7)	Ba3—Ba4—O9	100.67 (4)				
O2—Ba2—O22	70.25 (7)	Ba3—Ba4—O11	76.19 (6)				
O4—Ba2—O7	128.87 (7)	Ba3—Ba4—O23	98.42 (6)				
O4—Ba2—O15	56.34 (7)	O2—Ba4—O3	78.64 (7)				
O4—Ba2—O16	58.80 (7)	O2—Ba4—O4	72.61 (7)				
O4—Ba2—O22	120.83 (7)	O2—Ba4—O8	60.45 (7)				
O7—Ba2—O15	87.97 (8)	O2—Ba4—O9	55.20 (6)				
O7—Ba2—O16	131.01 (7)	O2—Ba4—O11	132.20 (7)				
O7—Ba2—O22	106.65 (8)	O2—Ba4—O23	122.29 (7)				
O15—Ba2—O16	54.83 (7)	O3—Ba4—O4	73.42 (7)				
O15—Ba2—O22	155.24 (8)	O3—Ba4—O8	124.47 (7)				
O16—Ba2—O22	101.44 (8)	O3—Ba4—O9	72.86 (7)				
Ba1—Ba3—Ba2	64.621 (5)	O3—Ba4—O11	57.68 (7)				
Ba1—Ba3—Ba4	58.807 (5)	O3—Ba4—O23	127.78 (8)				
Ba1—Ba3—O1	37.92 (5)	O4—Ba4—O8	121.03 (7)				
Ba1—Ba3—O3	37.70 (5)	O4—Ba4—O9	121.81 (7)				
Ba1—Ba3—O4	82.02 (5)	O4—Ba4—O11	108.36 (8)				
Ba1—Ba3—O6	76.58 (6)	O4—Ba4—O23	70.14 (7)				
Ba1—Ba3—O13	84.22 (5)	O8—Ba4—O9	53.61 (7)				
Ba1—Ba3—O14	142.82 (5)	O8—Ba4—O11	129.13 (8)				
Ba1—Ba3—O15	106.21 (5)	O8—Ba4—O23	106.21 (8)				
Ba2—Ba3—Ba4	63.736 (5)	O9—Ba4—O11	91.29 (7)				
Ba2—Ba3—O1	38.40 (5)	O9—Ba4—O23	159.34 (8)				
Ba2—Ba3—O3	81.24 (5)	O11—Ba4—O23	100.90 (8)				
Ba2—Ba3—O4	45.12 (5)	O1—Ti1—O5	92.7 (1)				
Ba2—Ba3—O6	85.14 (6)	O1—Ti1—O6	85.4 (1)				
Ba2—Ba3—O13	140.62 (5)	O1—Ti1—O7	84.4 (1)				
Ba2—Ba3—O14	87.08 (5)	O1—Ti1—O17	167.7 (1)				
Ba2—Ba3—O15	42.24 (5)	O5—Ti1—O6	110.0 (1)				
Ba4—Ba3—O1	76.80 (5)	O5—Ti1—O7	114.5 (1)				
Ba4—Ba3—O3	33.79 (5)	O5—Ti1—O17	99.6 (1)				
Ba4—Ba3—O4	36.09 (4)	O6—Ti1—O7	134.7 (1)				
Ba4—Ba3—O6	132.93 (6)	O6—Ti1—O17	90.5 (1)				
Ba4—Ba3—O13	80.00 (5)	O7—Ti1—O17	90.3 (1)				
Ba4—Ba3—O14	87.83 (5)	O2—Ti2—O8	100.3 (1)				
Ba4—Ba3—O15	90.91 (5)	O2—Ti2—O9	93.8 (1)				
O1—Ba3—O3	71.87 (7)	O2—Ti2—O10	101.6 (1)				
O1—Ba3—O4	77.82 (7)	O2—Ti2—O18	105.8 (1)				
O1—Ba3—O6	57.88 (8)	O8—Ti2—O9	83.3 (1)				
O1—Ba3—O13	121.26 (7)	O8—Ti2—O10	155.4 (1)				
O1—Ba3—O14	124.64 (7)	O8—Ti2—O18	92.6 (1)				
O1—Ba3—O15	72.82 (7)	O9—Ti2—O10	84.3 (1)				
O3—Ba3—O4	69.13 (7)	O9—Ti2—O18	160.5 (1)				
O3—Ba3—O6	111.87 (8)	O10—Ti2—O18	92.0 (1)				
O3—Ba3—O13	59.57 (7)	O3—Ti3—O11	84.4 (1)				
O3—Ba3—O14	118.59 (7)	O3—Ti3—O12	84.8 (1)				
O3—Ba3—O15	119.38 (7)	O3—Ti3—O13	95.0 (1)				
O4—Ba3—O6	130.22 (7)	O3—Ti3—O19	164.7 (1)				
O4—Ba3—O13	110.26 (7)	O11—Ti3—O12	140.6 (1)				

Data collection and cell refinement: *CAD-4 Software* (Enraf–Nonius, 1977). Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: direct methods *MULTAN* (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN CIF IN*.

We thank the National Science Foundation (grant No. DMR-9202565) for their direct support of this effort. We also thank the College of Arts and Sciences of the University of Toledo for generous financial support of the X-ray diffraction facility.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1009). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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