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Synthesis and crystal structure of the double barium–titanium methoxide $[Ba_2Ti_4O(OMe)_{18}(MeOH)_7]\cdot MeOH$

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Abstract—The X-ray diffraction study of crystals isolated from solutions obtained by reaction of $Ba(OMe)_2$ with $Ti(OMe)_4$ (molar ratio 1 : 2) in methyl alcohol was carried out; the crystals of the methanol solvate of the double barium-titanium methoxide, $[Ba_2Ti_4O(OMe)_{18}(MeOH)_7]\cdot MeOH$ (**1**), contain two Ba^{2+} cations with different environments and two kinds of anionic binuclear titanium complexes with and without oxo-ligand, and thus can be formulated as $[Ba(MeOH)_2]^{2+}[Ba(MeOH)_5]^{2+}[Ti_2O(OMe)_8]^{2-}[Ti_2(OMe)_{10}]^{2-}\cdot MeOH$. © 1997 Elsevier Science Ltd

Keywords: bimetallic alkoxide; oxoalkoxide; structure; precursor; sol-gel.

Since the first works concerning preparation of $BaTiO_3$ from metal alkoxides [1] much attention has been paid to this method. Afterwards, different oxide phases of the $BaO–TiO_2$ system were also synthesized by hydrolysis of metal alkoxides [2]. Recently, the work is concentrated on the search for the precursors for barium titanates with different Ba : Ti ratio and their structural characterization. Bimetallic barium-titanium alkoxides and oxoalkoxides were isolated with their structures being solved by X-ray diffraction [3–5]. We have been carrying out systematic study of reactions of titanium and alkaline-earth metal alkoxides. The structural characterization of the bimetallic alkoxides allows us to elucidate the true precursors for complex oxides in the alkoxide systems. Previously we reported the solubility diagrams for $M^{II}(OR)_2$–$Ti(OR)_4$–L, (M = Ca, Ba; R = Et, i-Pr, Bu, L = C_6H_6, ROH), as well as the synthesis and structural characteristics of the complexes $M^{II}[Ti_2(OEt)_9]_2$, M = Ca (**2**), Ba (**3**), $BaTi_2(OEt)_{10}\cdot 5EtOH$, $Ba_4Ti_2O(OEt)_{14}\cdot 8EtOH$, and $BaTiO(OPr\text{-}i)_4\cdot 7/8i\text{-}PrOH$ (**4**) [6–9]. The formation of complex oxoalkoxides in the studied systems is primarily due to reactions of uncontrolled oxidative decomposition of barium alkoxides by the traces of oxygen [10], and therefore occurs mostly in solutions with the Ba : Ti ratio higher than 1 : 1 [9]. This work concerns the preparation and structural characterization of a double barium-titanium methoxide, the study of the methoxide system being of particular interest as it has been demonstrated that barium methoxide practically does not undergo such oxidative decomposition [10].

EXPERIMENTAL

For synthesis of $[Ba_2Ti_4O(OMe)_{18}(MeOH)_7]\cdot MeOH$ (**1**) solution of $Ba(OMe)_2$ in MeOH (3.67 g, with the concentration of 4.65 mas.%, 3.07 mmol) was saturated with $Ti(OMe)_4$ (1.06 g, 6.14 mmol) at room temperature without agitation. In about 12 h all the introduced $Ti(OMe)_4$ dissolved to give transparent solution. In a day precipitation with

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formation of large prismatic crystals began, sometimes the crystals were a few cm long. Anal. Calcd for $C_{26}H_{86}Ba_2O_{27}Ti_4$: C, 24.07; H, 6.63; Ba, 21.9; Ti, 14.78. Found: C, 24.17; H, 9.04; Ba, 21.10; Ti, 14.86. The yield of crystals comprised 82%.

The X-ray diffraction pattern of the powder was indexed in the parameters determined for the single crystal. On drying *in vacuo* at 20°C loss of MeOH was observed and resulted in amorphization of the crystals.

X-ray diffraction study

Data were collected with a Siemens P3/PC diffractometer at 143°K; no absorption correction was applied. Crystal data and experimental details are given in Table 1. The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation. Eight hydroxyl H-atoms were located in the difference Fourier synthesis and included in the refinement with isotropic thermal parameters. All methyl H-atoms were placed in the geometrically calculated positions and included in the refinement using the riding model approximation with the $U_{iso}(H) = 1.5U_{eq}(C)$, where the $U_{eq}(C)$ is the equivalent isotropic temperature factor of the carbon atom bonded to the corresponding H atom. All calculations were carried out on IBM PC with the help of SHELXTL PLUS 5 (gamma version) program. Selected bond lengths and angles are summarized in Tables 2 and 3, respectively.

Table 1. Crystal data and experimental details for $[Ba_2Ti_4O(OMe)_{18}(MeOH)_7] \cdot MeOH$ (**1**)

Empirical formula	$C_{26}H_{86}Ba_2O_{27}Ti_4$
Mol. wt	1297.3
Crystal colour, habit	colorless prism
Crystal system	triclinic
Space group	$P\bar{1}$
Cell constants	
a (Å)	13.463(5)
b (Å)	14.095(6)
c (Å)	16.380(6)
α (°)	82.95(3)
β (°)	80.22(3)
γ (°)	63.99(3)
V (Å^3)	2749(2)
Z	2
D_{calcd} (g cm^{-3})	1.567
Temp (K)	143
Radiation	MoKα (λ = 0.71073)
Scan mode	θ–2θ
$2\theta_{max}$ (°)	56
Total unique refls.	13,045
Observed refls	7526 ($I > 2\sigma(I)$)
No. of parameters	876
R_1 (on F for obs. refls)[a]	0.0659
wR_2 (on F^2 for all refls)[b]	0.1754

[a] $R_1 = \Sigma | F_o - | F_c || / \Sigma(F_o)$ for observed reflections.

[b] $wR_2 = \sqrt{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]}$ for all reflections.

Table 2. Selected bond lengths (Å) for **1**

Ba(1)—O(1)	2.615(6)	Ti(1)—O(10)	1.915(6)
Ba(1)—O(2)	2.849(6)	Ti(1)—O(11)	1.837(6)
Ba(1)—O(4)	3.106(6)	Ti(1)—O(12)	1.886(6)
Ba(1)—O(5)	2.857(6)	Ti(2)—O(2)	1.980(6)
Ba(1)—O(22)	2.837(7)	Ti(2)—O(3)	2.114(6)
Ba(1)—O(23)	2.789(7)	Ti(2)—O(4)	2.092(6)
Ba(1)—O(24)	2.773(7)	Ti(2)—O(13)	1.801(6)
Ba(1)—O(25)	2.731(7)	Ti(2)—O(14)	1.891(6)
Ba(1)—O(26)	2.744(8)	Ti(2)—O(15)	1.912(6)
Ba(2)—O(1)	2.706(6)	Ti(3)—O(6)	2.059(6)
Ba(2)—O(2)	2.812(6)	Ti(3)—O(7)	2.091(6)
Ba(2)—O(3)	2.902(6)	Ti(3)—O(8)	2.017(6)
Ba(2)—O(5)	2.828(6)	Ti(3)—O(9)	1.916(6)
Ba(2)—O(6)	2.806(6)	Ti(3)—O(16)	1.873(6)
Ba(2)—O(7)	2.805(6)	Ti(3)—O(17)	1.795(7)
Ba(2)—O(9)	2.899(6)	Ti(4)—O(1)	1.695(6)
Ba(2)—O(20)	2.720(7)	Ti(4)—O(6)	2.130(6)
Ba(2)—O(21)	2.751(7)	Ti(4)—O(7)	2.112(6)
Ti(1)—O(3)	2.089(6)	Ti(4)—O(8)	2.287(6)
Ti(1)—O(4)	2.061(6)	Ti(4)—O(18)	1.908(7)
Ti(1)—O(5)	1.980(6)	Ti(4)—O(19)	1.887(6)

RESULTS AND DISCUSSION

An X-ray structural study of the complex shows that the crystal structure of **1** is made up of two anionic binuclear titanium complexes, $[Ti_2O(OMe)_8]^{2-}$ and $[Ti_2(OMe)_{10}]^{2-}$, two Ba^{2+} cations, $[Ba(MeOH)_2]^{2+}$ and $[Ba(MeOH)_5]^{2+}$, and one additional methanol molecule, which is not coordinated by any metal atoms (Fig. 1). Both anionic species, as far as we are concerned, have no literature precedents, although a very close analogue of $[Ti_2(OMe)_8]^{2-}$, namely binuclear monoanionic ethylate complex $[Ti_2(OEt)_9]^-$, has been reported in the structures of both barium and calcium derivatives **2** and **3** [8]. The peculiarity of the $[Ti_2O(OMe)_8]^{2-}$ anion lies in the presence of the oxo atom O(1) which occupies one of the 'terminal' positions at one of the Ti atoms. This oxo atom in fact acts as a μ_3-bridge and along with the Ti(4) atom is coordinated by both Ba^{2+} cations which is quite typical of the oxo-atoms in all structurally characterized barium-titanium alkoxide systems. The Ti—O_{oxo} bond [Ti(4)—O(1) 1.695(6) Å] is the shortest Ti—O distance in the structure of **1** and is even noticeably shorter than the 'titanyl' Ti═O bonds. 1.71–1.79 Å in $[TiO(OPr)_4]^-$ anionic moieties in the structure of **4** [9]. The presence of the Ti═O double bond is also corroborated by the IR spectra of the crystal of **1**, which contain a strong narrow band at 850 cm^{-1} typical of the titanyl groups.

The presence of the oxo-atom causes significant redistribution of bond lengths in the relevant binuclear titanium anion as compared to the bond lengths pat-

Table 3. Selected bond angles (°) for **1**

O(11)—Ti(1)—O(12)	92.2(3)	O(16)—Ti(3)—O(7)	166.1(3)
O(11)—Ti(1)—O(10)	91.9(3)	O(9)—Ti(3)—O(7)	85.5(3)
O(12)—Ti(1)—O(10)	100.8(3)	O(8)—Ti(3)—O(7)	79.2(2)
O(11)—Ti(1)—O(5)	179.6(3)	O(6)—Ti(3)—O(7)	71.7(2)
O(12)—Ti(1)—O(5)	88.2(3)	O(1)—Ti(4)—O(19)	98.1(3)
O(10)—Ti(1)—O(5)	87.9(3)	O(1)—Ti(4)—O(18)	98.6(3)
O(11)—Ti(1)—O(4)	94.0(3)	O(19)—Ti(4)—O(18)	100.7(3)
O(12)—Ti(1)—O(4)	93.3(3)	O(1)—Ti(4)—O(7)	92.1(3)
O(10)—Ti(1)—O(4)	164.5(3)	O(19)—Ti(4)—O(7)	161.9(3)
O(5)—Ti(1)—O(4)	86.0(2)	O(18)—Ti(4)—O(7)	92.6(3)
O(11)—Ti(1)—O(3)	93.7(3)	O(1)—Ti(4)—O(6)	90.3(3)
O(12)—Ti(1)—O(3)	167.7(3)	O(19)—Ti(4)—O(6)	94.9(3)
O(10)—Ti(1)—O(3)	89.9(3)	O(18)—Ti(4)—O(6)	160.7(3)
O(5)—Ti(1)—O(3)	85.9(2)	O(7)—Ti(4)—O(6)	69.9(2)
O(4)—Ti(1)—O(3)	75.4(2)	O(1)—Ti(4)—O(8)	157.7(3)
O(13)—Ti(2)—O(14)	94.0(3)	O(19)—Ti(4)—O(8)	92.7(3)
O(13)—Ti(2)—O(15)	93.0(3)	O(18)—Ti(4)—O(8)	98.6(3)
O(14)—Ti(2)—O(15)	100.6(3)	O(7)—Ti(4)—O(8)	73.0(2)
O(13)—Ti(2)—O(2)	177.3(3)	O(6)—Ti(4)—O(8)	69.2(2)
O(14)—Ti(2)—O(2)	88.0(3)	Ba(1)—O(1)—Ba(2)	102.6(2)
O(15)—Ti(2)—O(2)	88.4(3)	Ti(2)—O(2)—Ba(2)	110.4(2)
O(13)—Ti(2)—O(4)	93.2(3)	Ti(2)—O(2)—Ba(1)	115.1(2)
O(14)—Ti(2)—O(4)	91.9(3)	Ba(2)—O(2)—Ba(1)	94.4(2)
O(15)—Ti(2)—O(4)	165.6(3)	Ti(1)—O(3)—Ti(2)	103.7(3)
O(2)—Ti(2)—O(4)	84.9(2)	Ti(1)—O(3)—Ba(2)	103.9(2)
O(13)—Ti(2)—O(3)	92.5(3)	Ti(2)—O(3)—Ba(2)	103.3(2)
O(14)—Ti(2)—O(3)	165.1(3)	Ti(1)—O(4)—Ti(2)	105.5(3)
O(15)—Ti(2)—O(3)	92.5(3)	Ti(1)—O(4)—Ba(1)	102.6(2)
O(2)—Ti(2)—O(3)	85.1(2)	Ti(2)—O(4)—Ba(1)	102.5(2)
O(4)—Ti(2)—O(3)	74.3(2)	Ti(1)—O(5)—Ba(2)	109.8(2)
O(17)—Ti(3)—O(16)	98.8(3)	Ti(1)—O(5)—Ba(1)	114.1(2)
O(17)—Ti(3)—O(9)	98.3(3)	Ba(2)—O(5)—Ba(1)	93.9(2)
O(16)—Ti(3)—O(9)	95.2(3)	Ti(3)—O(6)—Ti(4)	94.2(3)
O(17)—Ti(3)—O(8)	96.4(3)	Ti(3)—O(6)—Ba(2)	98.7(2)
O(16)—Ti(3)—O(8)	96.5(3)	Ti(4)—O(6)—Ba(2)	89.5(2)
O(9)—Ti(3)—O(8)	159.6(3)	Ti(3)—O(7)—Ti(4)	93.8(2)
O(17)—Ti(3)—O(6)	165.5(3)	Ti(3)—O(7)—Ba(2)	97.9(2)
O(16)—Ti(3)—O(6)	94.4(3)	Ti(4)—O(7)—Ba(2)	89.9(2)
O(9)—Ti(3)—O(6)	86.4(3)	Ti(3)—O(8)—Ti(4)	90.8(2)
O(8)—Ti(3)—O(6)	76.1(2)	Ti(3)—O(9)—Ba(2)	99.2(2)
O(17)—Ti(3)—O(7)	94.9(3)		

tern observed in the structures of its analogues in **2** and **3**. The Ti(4)—O(1) bond is naturally considerably shorter than all other 'terminal' Ti—O bonds in the $[Ti_2O(OMe)_8]^{2-}$ species (1.795–1.916 Å). The *trans*-influence of the oxo-atom causes significant elongation of the Ti(4)—O(8) bond (2.287(6) Å) which occupies the transposition with respect to the Ti(4)—O(1) bond [the O(1)—Ti(4)—O(8) bond angle is equal to 157.7(3)°], as compared to other 'bridging' bonds in the $[Ti_2O(OMe)_8]^{2-}$ anion. Moreover, two other 'bridging' bonds involving the Ti(4) atom, bearing the oxo-substituent [Ti(4)—O(6) 2.130(6) and Ti(4)—O(7) 2.112(6) Å] seem to be somewhat longer than three remaining 'bridging' bonds in the dianion involving the Ti(3) atom, which is not bonded to the oxo-atom [Ti(3)—O(6) 2.059(6), Ti(3)—O(7) 2.091(6), Ti(3)—O(8) 2.017(6) Å]. It is also noteworthy that similar to what is observed for structures **2** and **3** the additional coordination of the 'bridging' O(6) and O(7) atoms by the Ba(2) atom does not cause any elongation of the Ti—O bonds involving these atoms, whereas the additional coordination of the 'terminal' O(9) atom by the Ba(2) obviously makes the Ti(3)—O(9) bond [1.916(6) Å] considerably longer than two other terminal bonds involving Ti(3) atom [Ti(3)—O(16) 1.873(7), Ti(3)—O(17) 1.795(7) Å].

The $[Ti_2O(OMe)_{10}]^{2-}$ anion features principally different structure which has two rather than three 'bridging' alkoxyl groups thus representing two titanium coordination octahedra sharing a common edge rather than a common face as in $[Ti_2O(OMe)_8]^{2-}$ species in the present structure and in the $[Ti_2(OEt)_9]^{-}$ anions in the structures of **2** and **3**. The

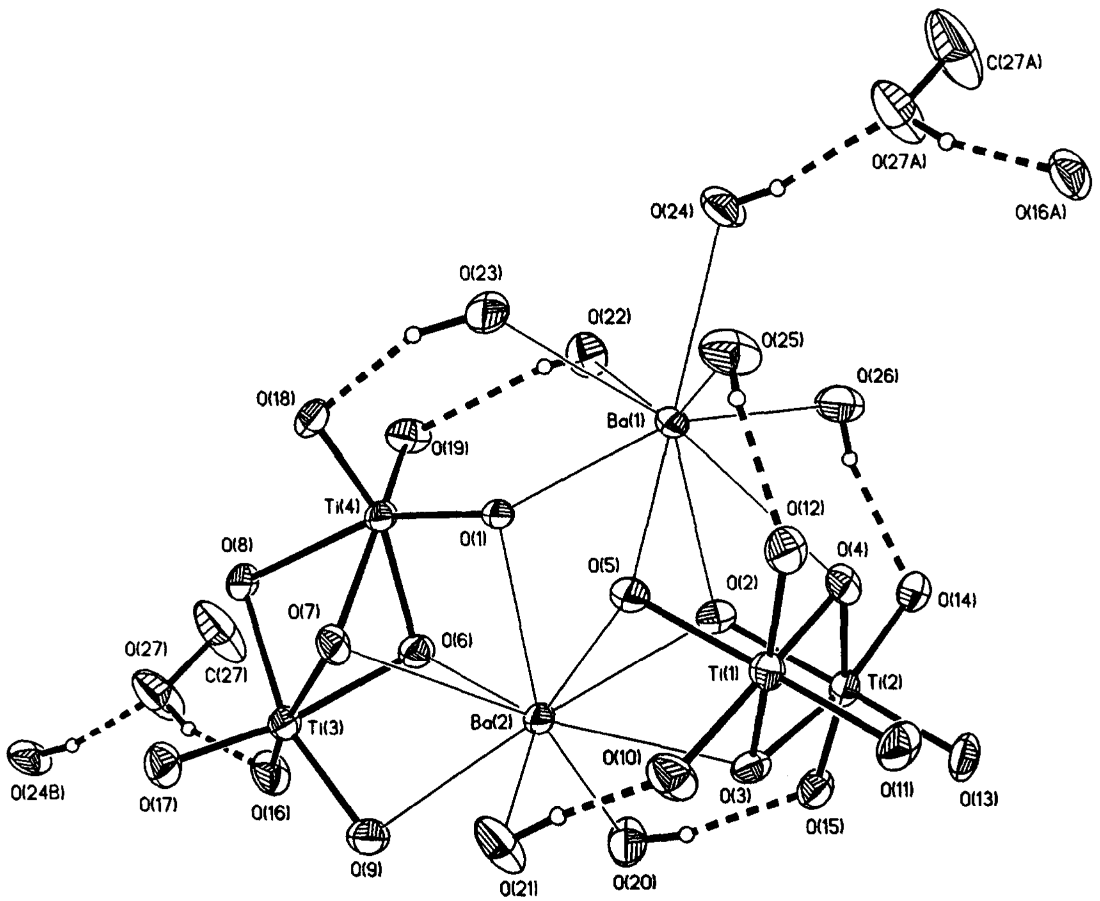

Fig. 1. The fragment of the crystal structure of $[Ba_2Ti_4O(OMe)_{18}(MeOH)_7] \cdot MeOH$ (**1**). Me groups in methoxyl ligands and in methanol molecules coordinated by the Ba atoms are omitted for clarity. All methanol oxygen atoms are shown together with the attached H atoms; the only oxo atom is labelled O(1).

$[Ti_2O(OMe)_{10}]^{2-}$ anion is approximately symmetrically coordinated by two Ba^{2+} cations. Each of the cations is coordinated by two 'terminal' and one 'bridging' OMe-groups of the $[Ti(OMe)_{10}]^{2-}$ anion. Quite similarly to what has been observed for the $[Ti_2O(OMe)_8]^{2-}$ anion in **1** and $[Ti_2(OEt)_9]^{-}$ anions in **2** and **3**, the additional coordination of the oxygen atoms of the 'terminal' OR-groups by the alkaline-earth metal atom causes considerable elongation of the relevant Ti—O bonds. This effect is even more pronounced for $[Ti_2(OMe)_{10}]^{2-}$ in (**1**), as each of the 'terminal' O(2) and O(5) atoms is coordinated simultaneously by two Ba^{2+} cations. Indeed, the Ti(1)—O(5) and Ti(2)—O(2) bonds [1.980(6) and 1.980(6) Å] are considerably longer than the analogous Ti(1)—O(11) and Ti(2)—O(13) bonds [1.837(6) and 1.801(6) Å] involving the O(11) and O(13) atoms which do not form any additional bonding to the Ba^{2+} cations.

Each Ba atom is coordinated by nine oxygen atoms, the Ba(1) atom being bonded to one oxo-, three methoxo- and five solvating methanol oxygen atoms, whereas the Ba(2) atom being bonded to one oxo-, six methoxo- and two solvating methanol oxygens. Such coordination number of the Ba^{2+} cations is higher than those observed in the earlier studied barium-titanium containing alkoxide systems, which is probably due to the presence in **1** of the most compact methoxy groups in contrast to **2**, **4**, the derivatives of higher aliphatic homologs. The coordination polyhedra of both Ba atoms represent the monocapped square antiprisms with the O(1) and O(24) atoms capping the O(2), O(5), O(6), O(7) and O(22), O(23), O(25), O(26) faces of the antiprisms of the Ba(2) and Ba(1) atoms, respectively. It is noteworthy that the shortest Ba—O bonds in the coordination environments of both Ba atoms involve the O(1) oxo-atom [Ba(1)—O(1) 2.615(6) and Ba(2)—O(1) 2.706(6) Å], whereas the longest Ba—O bonds are those of the 'bridging' methoxo-groups of the $[Ti_2(OMe)_{10}]^{2-}$ anions [Ba(1)—O(4) 3.106(6) and Ba(2)—O(3) 2.902(6) Å].There are eight independent H-bonds in the structure of (**1**), six of which [O(20)···O(15) 2.61(1), O(21)···O(10) 2.61(1), O(22)···O(19) 2.73(1), O(23)···O(18) 2.76(1), O(25)···O(12) 2.68(1), O(26)···O(14) 2.61(1) Å] are intramolecular with respect to the $Ba_2Ti_4O(OMe)_{18}(MeOH)_7$ aggregates. Two intermolecular H-bonds

[O(24)···O(27′) $(x, y+1, z)$ 2.70(1), O(27)···O(16) 2.67(1) Å] involve the $C(27)H_3O(27)H$ methanol molecules, which are not directly coordinated by any metal atom. These molecules serve as the bridges which link the $Ba_2Ti_4O(OMe)_{18}(MeOH)_7$ aggregates in the infinite chains along the *b*-axis.

Earlier we established, that polymeric alkoxides may participate in the complexation reaction only in the presence of oxo groups at least in the trace amounts. In case of the derivatives of $[M(OR)_n]_\infty$ and $M'(OR)_m$ (M = Ni, Co, Fe^{III}, Cr^{III}; M′ = Al, Nb, Zr, etc.) the oxo groups originated from the water molecules [11]. Along with the oxoalkoxide, bimetallic alkoxide complexes which do not contain any oxo groups may precipitate from the reaction mixtures. The composition of the crystals in particular case is obviously determined by the relative stability of the complexes of both types [12,13].

Although by now simple and bimetallic oxoalkoxides of the variety of metals were isolated and characterized the origin of oxo-atoms in the molecules remains obscure [14]. Trace quantities of H_2O (or O_2) may facilitate autocatalytic decomposition of metal alkoxides [15]. It is noteworthy that in contrast to the previously studied barium–titanium alkoxide systems, in this case the oxoalkoxide is formed in the excess of titanium rather than barium. The particular stability of complex **1** should be attributed to the tendency of the Ba atom to increase its coordination number in the environment of rather small methoxyl/methanol ligands. The involvement of the oxo atom provides the additional way of increasing the coordination number of the metal atom at the least possible sterical expenses.

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