

Na₆[Ti₅O₁₂(OH)₂]: A New Titanate Containing $\frac{1}{\infty}$ [Ti₅O₁₂(OH)₂]⁶⁻ Ribbonsby Michael Würle^{a)}, Volker Lorenzen^{a)}, and Reinhard Nesper^{*a)b)}^{a)} Laboratory of Inorganic Chemistry, ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich
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Wolfgang-Pauli-Strasse 10, CH-8093 ZürichDedicated to Professor *Jean-Claude Bünzli* on the occasion of his 65th birthday

Na₆[Ti₅O₁₂(OH)₂] is the first structurally characterized sodium oxohydroxotitanate. The compound can be prepared *via* hydrothermal treatment of TiO₂ (Anatas) in NaOH (10N) for 96 h at 250° in an autoclave. The crystal structure of Na₆[Ti₅O₁₂(OH)₂] consists of infinite ribbons $\frac{1}{\infty}$ [Ti₅O₁₂(OH)₂]⁶⁻. The orthorhombic arrangement has *Pbcn* (No. 60) symmetry with the lattice constants *a* = 18.668(4) Å, *b* = 6.5333(13) Å, and *c* = 9.829(2) Å.

Introduction. – Alkali titanates are known to exhibit good ion-exchange properties, due to their layered or open framework structures and their redox-activity [1]. Since control of particle size and morphology of the titanates is difficult when using conventional solid-state or flux methods, solvothermal methods constitute a promising alternative [1]. The reaction of NaOH solution with TiO₂ under solvothermal conditions in an autoclave can lead to a multitude of different compounds. It seems, that reaction temperature and duration play an important role, on which phase is formed in the course of the hydrothermal synthesis. Several different Na-titanates, Na₂Ti₆O₁₃, Na₂Ti₃O₇, and Na₁₆Ti₁₀O₂₈, were crystallized under hydrothermal conditions at 500° in the NaOH/TiO₂/H₂O system using rutile as starting material by *Hyushin* [2]. *Ma et al.* report the formation of titanate nanotubes by hydrothermal treatment of anatase in concentrated NaOH at 110–150° for 12–72 h [3]. The walls are most likely formed by lepidocrocite layers. The crystal structure of the titanates consists of Ti–O-octahedra as the main building unit. The octahedra can be connected in many different ways, giving rise to a stunning structural diversity. Whereas for potassium with K[TiO₂(OH)] an oxohydroxotitanate is known [1], Na₆[Ti₅O₁₂(OH)₂] is the first structurally characterized sodium oxohydroxotitanate.

Experimental. – *Synthesis.* Na₆[Ti₅O₁₂(OH)₂] was prepared by heating 5 g of TiO₂ (Anatase; *Acros*, Lot. A014127201) in 150 ml of 10N NaOH for 96 h at 250° in a *Teflon*-lined autoclave of 250 ml volume. The compound is obtained in form of very thin, colourless needles.

Results and Discussion. – *Structural Characterization.* A suitable crystal was selected under a microscope using polarized light and X-ray data collection being performed on a *Stoe IPDS* diffractometer. Structure determination and refinement

were achieved with the programs SHELXS-97 and SHELXL-97 [4], respectively, embedded in the program package WinGX [5]. The structure was solved by direct methods. In a full-matrix least-squares refinement based F^2 all atoms, except the ones belonging to a split position, were refined by anisotropic displacement parameters. As it was not possible to locate H-atoms, they were not included in the refinement process. Crystallographic details and atomic positions of the structure determination are given in *Tables 1* and *2*, respectively.

Table 1. *Crystal Data and Structure Refinement for Na₆[Ti₅O₁₂(OH)₂]*

Empirical formula	Na ₆ Ti ₅ O ₁₂ (OH) ₂
M_r	603.46
Crystal size [mm ³]	0.40 × 0.05 × 0.05
Temp. [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	orthorhombic
Space group	<i>Pbcn</i> (No. 60)
Unit cell dimensions [Å]	$a = 18.668(4)$, $b = 6.5333(13)$, $c = 9.829(2)$
Volume [Å ³]	1198.8(4)
Z	4
D_x (calc.) [Mg/m ³]	3.344
Absorption coefficient [mm ⁻¹]	3.488
$F(000)$	1160
θ range for data collection	3.30–30.22°
Index ranges	$-26 \leq h \leq 25$, $-9 \leq k \leq 9$, $-13 \leq l \leq 13$
Reflections collected	14394
Independent reflections	1727 [$R_{\text{int}}^{\text{a}}$] = 0.1080]
Completeness to $\theta = 30.22^\circ$	96.7%
Data/restraints/parameters	1727/0/118
Goodness-of-fit on F^2	1.057
Final R indices [$I > 2\sigma(I)$]	R_1^{b}] = 0.0370, wR_2^{c}] = 0.0943
R indices (all data)	$R_1 = 0.0493$, $wR_2 = 0.1015$
Largest diff. peak and hole	0.664 and $-0.773 \text{ e } \text{Å}^{-3}$

^a) $R_{\text{int}} = \sum |F_0^2 - F_c^2| / \sum F_0^2$. ^b) $R = \sum (w(|F_0 - F_c|)) / \sum F_0$. ^c) $wR = (\sum (w(|F_0^2 - F_c^2|)^2) / \sum w(F_0^2)^2)^{1/2}$; $w = 1/(F_0^2) + (gP)^2 + kP$; $P = \text{Max}(F_0^2, 0) + 2F_c^2/3$; $k, g = \text{weights}$.

In the crystal structure of Na₆[Ti₅O₁₂(OH)₂], all Ti-atoms are coordinated by six O-atoms in an octahedral manner. These Ti(O,OH)₆-octahedra are connected by common edges, forming ${}^1_{\infty}[\text{Ti}_5\text{O}_{12}(\text{OH})_2]^{6-}$ -ribbons (*Fig. 1*). This way of connecting edge sharing octahedra is also found in lepidocrocite (FeO(OH)), where it leads to infinite 2D-layers, however. The ribbons in Na₆[Ti₅O₁₂(OH)₂] can be described by sections of the layers found in lepidocrocite FeO(OH) [6]. They are built of rows of five octahedra each, which are shifted against each other by one octahedron position, leading to the formation of ‘zig-zag’ ribbons (*Fig. 2*). The ribbon direction is tilted against the normal of the octahedra-rows by about 58°. Ribbons with a similar type of connectivity of the octahedra are found in Tl₂Ti₄O₉ [7]. Here, however, the rows consist of only four octahedra and are not shifted against each other. Therefore, in this case the ribbon direction is perpendicular to the row direction. Tl₂Ti₄O₉ is a member of a series of isotopic M₂Ti₄O₉ tetratitanates (M = Li, Na, K, Rb, Cs, Tl, and Ag), where the ribbons

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters [\AA^2] for $\text{Na}_6[\text{Ti}_5\text{O}_{12}(\text{OH})_2]$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	$U(\text{eq})$	Occupancy (SOF)
Ti(1)	0.0745(1)	0.1274(1)	0.0161(1)	0.009(1)	1
Ti(2)	0	0.8839(1)	1/4	0.009(1)	1
Ti(3)	0.1519(1)	0.1184(1)	0.2800(1)	0.011(1)	1
Na(1)	0.2398(1)	0.3577(2)	0.0360(1)	0.021(1)	1
Na(2)	0	0.3953(3)	1/4	0.047(1)	1
Na(3)	0.1477(1)	0.6242(2)	0.2630(2)	0.024(1)	1
Na(4)	0.0768(1)	0.6136(3)	0.0103(2)	0.015(1)	0.527(5)
O(1)	0.0345(1)	0.3095(3)	0.8799(2)	0.010(1)	1
O(2)	0.1070(1)	0.3155(3)	0.1458(2)	0.010(1)	1
O(3)	0.1593(1)	0.0873(3)	0.9231(2)	0.011(1)	1
O(4)	0.9704(1)	0.0943(3)	0.1101(2)	0.012(1)	1
O(5)	0.0950(1)	0.9204(3)	0.1645(2)	0.011(1)	1
O(6)	0.2350(1)	0.0999(3)	0.2097(2)	0.017(1)	1
O(7a)	0.1793(2)	0.3507(6)	0.3992(5)	0.013(1)	SOF(Na4)
O(7b)	0.1618(3)	0.3436(7)	0.4240(5)	0.013(1)	1-SOF(Na4)

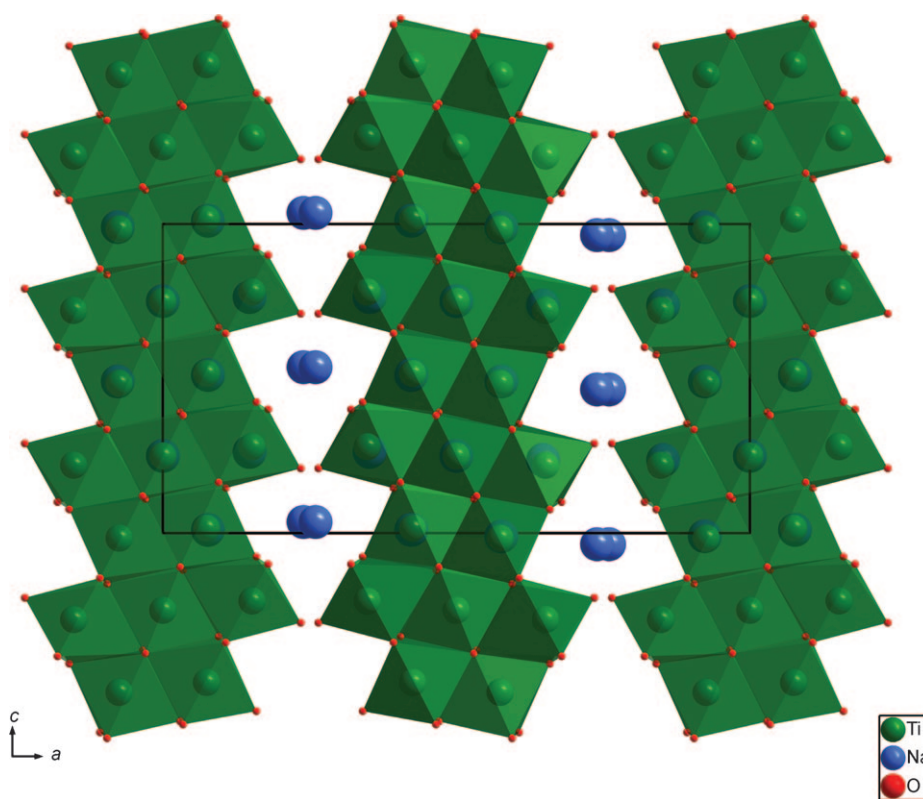


Fig. 1. A view of the crystal structure of $\text{Na}_6[\text{Ti}_5\text{O}_{12}(\text{OH})_2]$ along the crystallographic b -axis. The O-atom coordination around the Ti-atom positions is shown with green transparent polyhedra. The $[\text{Ti}_5\text{O}_{12}(\text{OH})_2]^{6-}$ -ribbons run along the c -axis, the angle between the normal on the 5-membered octahedra-rows and the c -axis is about 58° .

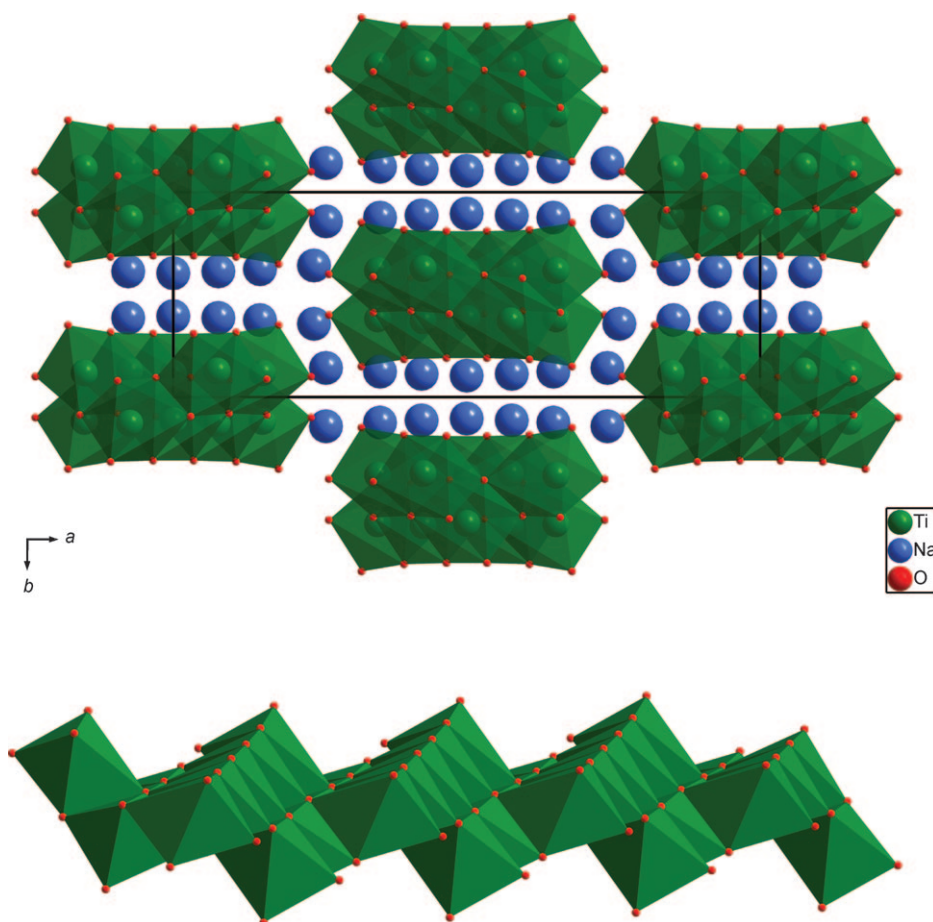


Fig. 2. A view of the crystal structure of $\text{Na}_6[\text{Ti}_5\text{O}_{12}(\text{OH})_2]$ along the crystallographic c -axis (upper part); in the lower part, a view of an isolated ribbon is given, in order to show the zig-zag arrangement formed by 5-membered octahedra-rows which are connected by common edges

are formed by rows of four octahedra ($n = 4$). Up to now there is only one compound claimed to consist of ribbons with $n = 5$, $\text{Cs}_2\text{Ti}_5\text{O}_{11}$ [8], where no shift of the octahedra-rows against each other is found.

The observed Ti–O interatomic distances are distributed unevenly in a broad range between 1.701(2) Å and 2.530(2) Å. The spread of the individual Ti–O distances in the Ti(1)–O and Ti(2)–O octahedra is very close to the mean value, while the variation of Ti–O distances in the Ti(3)–O octahedron is much larger (Table 3), however. The shortest distance is comparable with the Ti–O distance of 1.7086 Å reported for $\text{Na}_2\text{Ti}_3\text{O}_7$ [9], the longest Ti(3)–O(4) being close to the value of 2.5389 Å, found in the high temperature modification of BaTi_2O_5 [10]. The large distortion of the Ti(3)–O₆ coordination polyhedron makes it reasonable to better interpret the short Ti(3)–O(6) contact as a titanyl group. In that case the coordination polyhedron is better described

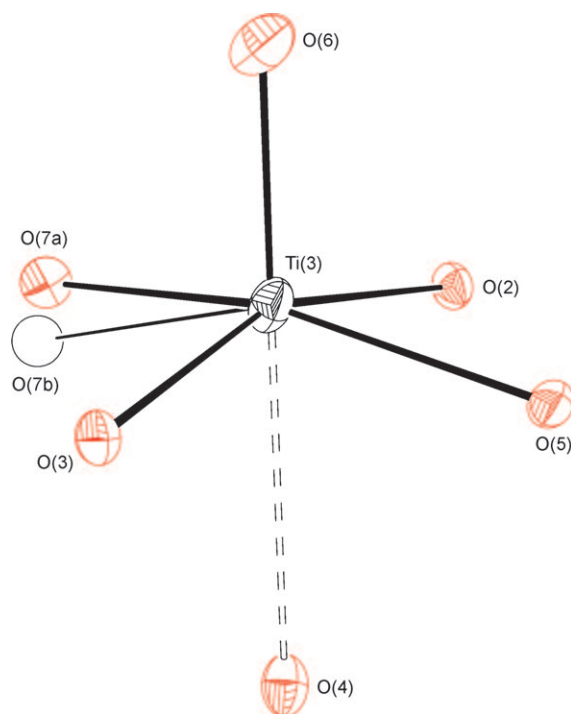


Fig. 3. Inner coordination of $Ti(3)$ by O -atoms. $O(7a)$ and $O(7b)$ are split positions of a single O -atom site. It should be noted that the short $Ti-O(6)$ contact has the long $Ti(3)-O(4)$ distance in *trans*-conformation implying $Ti(3)-O(6)$ to be a titanyl group.

Table 3. Selected Interatomic Distances for $Na_6[Ti_5O_{12}(OH)_2]$

Atom-Pair	Distance (s.u.) [\AA]	Mean distance [\AA]
$Ti(1)-O(3)$	1.8472(18)	1.9984
$Ti(1)-O(2)$	1.8715(19)	
$Ti(1)-O(1)$	1.9407(18)	
$Ti(1)-O(5)$	2.0254(19)	
$Ti(1)-O(4)$	2.0825(19)	
$Ti(1)-O(4)$	2.1632(19)	
$Ti(2)-O(1)$	1.9080(18)	1.9687
$Ti(2)-O(1)$	1.9081(18)	
$Ti(2)-O(5)$	1.9768(18)	
$Ti(2)-O(5)$	1.9768(18)	
$Ti(2)-O(4)$	2.0213(18)	
$Ti(2)-O(4)$	2.0213(18)	
$Ti(3)-O(6)$	1.701(2)	2.0413 ^{a)}
$Ti(3)-O(3)$	1.9504(19)	
$Ti(3)-O(7a)$	1.984(4)	
$Ti(3)-O(5)$	2.0233(18)	
$Ti(3)-O(2)$	2.0259(18)	
$Ti(3)-O(7b)$	2.050(5)	
$Ti(3)-O(4)$	2.530(2)	

^{a)} In the case of the disordered O -atom site, the mean value of the distances $Ti(3)-O(7a)$ and $Ti(3)-O(7b)$ was used for the calculation.

as a quadratic pyramid similar to those which typically occur in V^{5+} oxides. This view is supported by the fact that the short Ti(3)–O(6) contact is just *trans*-standing to the long Ti(3)–O(4), as displayed in *Fig. 3*. As O(4) has four normal Ti–O distances plus the far Ti(3) neighbour, it is somewhat overcoordinated by 4 + 1 titanium atoms.

Further details of the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the CSD number 420651.

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