

LITHIUM TRINIOBATE(V), LiNb_3O_8

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Preliminary information.

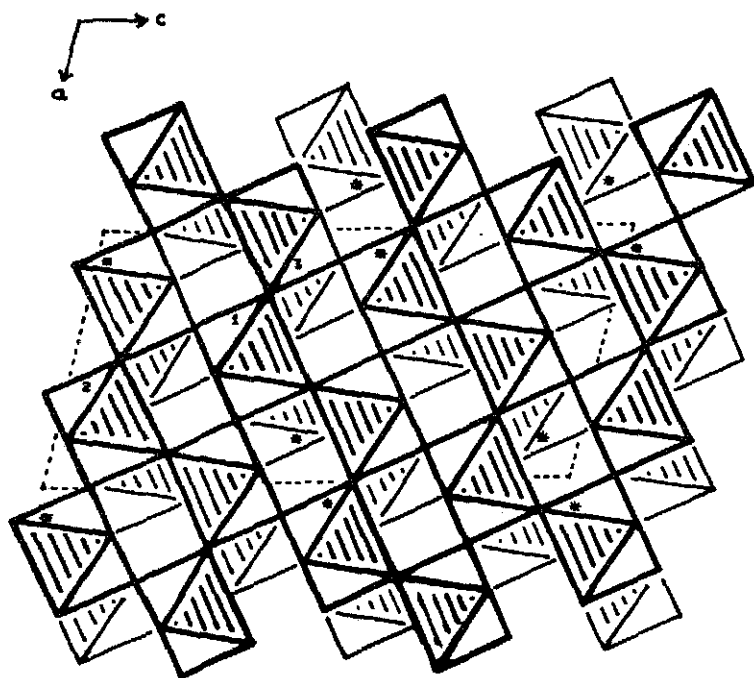
Although brief reference to the title compound has been made in the past by Lundberg and Andersson (1965), and Whiston and Smith (1965), no structure has been published. Recently, Andersson and Galy (1970) have, however, suggested an hypothetical MX_2 structure based on hexagonally close-packed anions and octahedrally coordinated cations, which AB_3O_8 compounds may adopt. We now report the crystal structure of LiNb_3O_8 and show the analogous tantalate, LiTa_3O_8 , to be isomorphous.

Crystal Data.

- (a) LiNb_3O_8 : $\underline{a} = 7.459(4)$, $\underline{b} = 5.034(4)$, $\underline{c} = 15.270(7)\text{\AA}$
 $\beta = 107.33(3)^\circ$, $\underline{Z} = 4$, space group $\text{P}2_1/\text{c}$
(from single crystal diffractometry, $\text{CuK}\alpha$)
- (b) LiTa_3O_8 : $\underline{a} = 7.41(5)$, $\underline{b} = 5.10(4)$, $\underline{c} = 15.12(10)\text{\AA}$,
 $\beta = 107.2(1)^\circ$, $\underline{Z} = 4$, space group $\text{P}2_1/\text{c}$
(from rotation and Weissenberg photographs).

Intensity data, structure determination and refinement.

From a spherical crystal boule, 1520 independent reflections were measured by a single crystal Picker diffractometer using MoK α radiation, but 664 of these were not used in the determination, their values being less than the background count. The structure was solved by three-dimensional Patterson and Fourier methods (heavy atom method) and refined by full-matrix least-squares. In the final refinement (conventional $R = 0.038$) the 232 strongest reflections, found to be suffering from secondary extinction, were omitted.



Atomic coordinates.

	$\underline{x/a}(\sigma)$	$\underline{y/b}(\sigma)$	$\underline{z/c}(\sigma)$	$\underline{B}(\sigma)$
Nb(1)	0.49156(10)	0.23019(19)	0.33157(5)	0.56(2)
Nb(2)	0.74905(11)	0.24547(20)	0.07491(6)	0.60(2)
Nb(3)	0.98323(11)	0.24198(19)	0.33549(5)	0.56(2)
O(1)	0.9997 (9)	0.0592 (13)	0.0979 (5)	0.27(11)
O(2)	0.4147 (10)	0.0680 (13)	0.2178 (5)	0.24(10)
O(3)	0.7634 (10)	0.0987 (14)	0.3444 (5)	0.30(11)
O(4)	0.5371 (11)	0.4202 (13)	0.1006 (5)	0.44(11)
O(5)	0.9120 (10)	0.4126 (13)	0.2148 (5)	0.26(10)
O(6)	0.6460 (9)	0.3958 (13)	0.4609 (4)	0.16(10)
O(7)	0.1467 (9)	0.0643 (13)	0.4513 (4)	0.18(11)
O(8)	0.2774 (10)	0.4149 (13)	0.3445 (5)	0.22(10)
Li	0.2381 (38)	0.2317 (71)	0.0765 (20)	2.95(89)

Distances.

Nb(1) - O(2)	1.849(7) Å	Nb(2) - O(6 ^v)	1.825(7) Å
- O(8)	1.908(7)	- O(7 ^{iv})	1.878(7)
- O(4 ⁱⁱⁱ)	1.919(7)	O(4)	1.949(8)
- O(2 ^{iv})	2.065(7)	O(1)	2.027(7)
- O(3)	2.086(7)	O(8 ⁱⁱⁱ)	2.114(7)
- O(6)	2.137(7)	O(5)	2.281(7)
Average 1.994 Å		Average 2.012 Å	
Nb(3) - O(3)	1.833(7) Å	Li - O(6 ⁱⁱⁱ)	2.056(29)
O(1 ^{vii})	1.877(7)	O(1 ⁱⁱ)	2.090(30)
O(5)	1.958(7)	O(7 ^v)	2.097(29)
O(7 ⁱ)	2.032(7)	O(3 ^{iv})	2.209(30)
O(5 ^{vi})	2.075(7)	O(2)	2.319(29)
O(8 ⁱ)	2.327(8)	O(4)	2.350(30)
Average 2.017 Å		Average 2.187 Å	
Nb(2) - Nb(3 ^{vii})	3.237(1) Å	Li - Nb(1 ^{iv})	3.263(28) Å
- Nb(3 ^{vi})	3.264(1)	- Nb(1 ⁱⁱⁱ)	3.275(28)
- Nb(1 ^{iv})	3.569(1)	- Nb(2 ^{viii})	3.355(27)
Nb(1) - Nb(1 ⁱⁱⁱ)	3.570(1)	- Nb(3 ⁱⁱⁱ)	3.454(28)

Asymmetric units:

i	$1+\underline{x}, \underline{y}, \underline{z}$	v	$\underline{x}, \frac{1}{2}-\underline{y}, -\frac{1}{2}+\underline{z}$
ii	$-1+\underline{x}, \underline{y}, \underline{z}$	vi	$2-\underline{x}, -\frac{1}{2}+\underline{y}, \frac{1}{2}-\underline{z}$
iii	$1-\underline{x}, -\frac{1}{2}+\underline{y}, \frac{1}{2}-\underline{z}$	vii	$2-\underline{x}, \frac{1}{2}+\underline{y}, \frac{1}{2}-\underline{z}$
iv	$1-\underline{x}, \frac{1}{2}+\underline{y}, \frac{1}{2}-\underline{z}$	viii	$1-\underline{x}, -\underline{y}, -\underline{z}$

Comments.

The oxygen atoms are hexagonally closed-packed in the direction $[\bar{1}01]$, with the metal atoms occupying half of the octahedral sites in an ordered manner. This results in metal-oxygen octahedra linked by edge-sharing into infinite chains, running in the \underline{b} -(prism) axis direction, which in turn are joined to neighbouring chains by common corners. The LiO_6 octahedron (asterisked in the figure) is slightly larger than the three independent NbO_6 octahedra (numbered corresponding to the central niobium atom) which do not differ markedly in size. The $[0\bar{1}0]$ view of the idealised structure shows it to be different from the hypothetical AB_3O_8 structure type given by Andersson and Galy (1970), but to contain certain features from the $\alpha\text{-PbO}_2$ structure.

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