Crystal Structures of Some Niobium and Tantalum Oxides, Part VI. The Structure of H–LiTa₃O₈

G. D. FALLON,* B. M. GATEHOUSE,* R. S. ROTH†
AND S. A. ROTH‡

* Chemistry Department, Monash University, Clayton, Victoria, Australia 3168, and † Inorganic Materials Division, National Bureau of Standards, Washington, D.C., 20234, U.S.A. ‡ Department of Chemistry, University of Illinois, 61801, U.S.A.

H–LiTa$_3$O$_8$ crystallizes in the orthorhombic system with unit-cell dimensions (from single crystal date) $a = 16.702(8)$, $b = 3.840(4)$, $c = 8.929(5)$ Å, and space group Pmma, $z = 4$. The structure was solved by analogy with the structure of LiNb$_6$O$_{15}$F and refined by Fourier and least-squares refinement techniques. Of the 983 unique reflections measured by counter techniques, 739 with $I \geq 3\sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.060 ($Rw = 0.067$). H–LiTa$_3$O$_8$ has the same basic structure as the compounds LiNb$_6$O$_{15}$F, β–Ta$_3$O$_7$F and Nb$_2$WO$_8$; its relationship to these and other structures is discussed.

Introduction

As part of a systematic study of alkali metal niobium and tantalum oxide systems the synthesis of the compound LiTa$_3$O$_8$ in three crystallographic modifications was reported (1). The form designated L-LiTa$_3$O$_8$ was shown to be iso-structural with LiNb$_3$O$_8$ (2); the structure of the form designated M-LiTa$_3$O$_8$ was recently determined and its relationship to the mineral Wodginite discussed (3). The structure of both the L- and M- forms of LiTa$_3$O$_8$ have been shown to be based upon slightly distorted hexagonal close-packed arrays of oxygen anions with Ta^{5+} ions occupying octahedral sites in an ordered fashion. The Li$^+$ ions in M-LiTa$_3$O$_8$ were not located by the X-ray diffraction experiment; however, subsequent powder neutron diffraction analysis (4) has confirmed very closely the Li$^+$ ion positions reported for L-LiTa$_3$O$_8$, and confirmed the Li$^+$ sites predicted (3) for M-LiTa$_3$O$_8$.

It was noted earlier (5) that the unit-cell dimensions of H-LiTa$_3$O$_8$ were very similar to those of LiNb$_6$O$_{15}$F (6, 7), β-Ta$_3$O$_7$F (8) and Nb$_2$WO$_8$ (9); attention has also been drawn to this relationship in several other publications (10, 11). The electrical properties of LiTa$_3$O$_8\beta$ (H-LiTa$_3$O$_8$) were reported recently (12) and it was shown that ionic conductivity was due to the movement of lithium ions in tunnels in the lattice.

The quantitative determination of the structure of H-LiTa$_3$O$_8$ is presented here. A preliminary report was made elsewhere (13).

Experimental

The single crystals of H-LiTa$_3$O$_8$ were prepared by heating a 1 : 1 mole ratio mixture

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of $LiTaO_3$ and Ta_2O_5 in a sealed platinum tube for 16 hr at $1573 \pm 10°C$ and then quenching in water. This form of $LiTa_3O_8$ is stable from 1135°C to the melting point of $1600 \pm 10°C$.

A small single crystal, approximately spherical in shape with a radius of 0.025 mm was selected for data collection and mounted on a quartz capillary using "Resiweld 5"; the following data were collected using a Philips PW 1100 computer controlled diffractometer. The unit-cell parameters were determined in a manner previously described (3).

Crystal data. $H-LiTa_3O_8$, $M = 677.8$, $a = 16.702(8)$, $b = 3.840(3)$, $c = 8.929(5)$ Å, orthorhombic, $U = 572.7$ Å^3, $d_c = 7.86$ g cm^{-3}, $z = 4$. Insufficient material was available to enable a density measurement to be made. $F(000) = 336$, $\mu = 602$ cm^{-1} for Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å). Systematic absences were observed for $hk0$, $h = 2n + 1$ suggesting space groups $Pmma$ (D_{2h}^5, No-51), $Pmc2_1$ or $Pma2$. Refinement indicates that the X-ray data is not inconsistent with $Pmma$.

Intensity measurements. Intensity measurements were made with the crystal described above using the diffractometer and Mo$K\alpha$ radiation monochromated with a flat graphite crystal ($2\theta = 12.16°$). A unique data set was collected using the θ-2θ scan technique with a scan width of 1.2° and scan speed of 0.0168° s^{-1}. 983 unique reflections were collected with $3° < \theta(\text{Mo-}K\alpha) < 30°$, of which 739 having $I \geq 3\sigma(I)$ were used in the subsequent refinement. Three non-coplanar reference reflections were measured every 2 hr and no systematic variation in these intensities was detected. The data were processed in the manner described earlier (3).[1]

The scattering factors for Ta° (corrected for anomalous dispersion) and O were taken from Cromer and Waber (15). All comput-

ing was performed on the Monash University CDC 3200 computer. The major programs were MONLS, a modified version of the full-matrix least-squares program of Busing, Martin and Levy (16), MONDLS, a block-diagonal least-squares program adapted from the "SF" series of Shiono (17) and the Fourier summation program MONFR (18).

Structure Solution and Refinement

The centrosymmetric space group $Pmma$ was chosen for solving the structure and the initial Ta positions were taken to correspond with those of Nb in $LiNb_6O_{15}F$ (7) as a result of the similarity of unit-cell dimensions and space group. This model gave $R = 0.126$

$$(R = \sum ||F_0| - |F_c|| / \sum |F_0|;$$

$$Rw = \sum \{w(|F_0| - |F_c|)^2 / \sum w|F_0|^2\}^{1/2}).$$

The oxygen atom coordinates were found from the subsequent Fourier difference synthesis. A number of full-matrix least-squares refinement cycles of the isotropic model, refining all variable parameters with observed data weighted by $1/\sigma^2(F)$, reduced R to 0.102 and Rw to 0.123. use of the block-diagonal least-squares technique, varying metal atom positional and anisotropic thermal parameters and oxygen positional and isotropic thermal parameters reduced R to 0.064 and Rw to 0.075.

At this stage a number of intense low angle reflections showed discrepancies between F_0 and F_c that could probably be attributed to extinction. The worst affected reflections were 010, 020, 030, 302 and 312; these were given zero weight in the final refinement cycles. Refinement was terminated when all parameter shifts were less than 0.1 σ; at this stage R was 0.060 and Rw 0.067. Lithium atom sites could not be located in the final Fourier difference synthesis. Final positional

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[1] No absorption correction was applied ($\mu R = 1.5$).

and thermal parameters are reported in Table I.[1]

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Discussion and Structure Description

The structure of H–LiTa$_3$O$_8$ is very similar to that of LiNb$_6$O$_{15}$F and consists of groups of five TaO$_6$ octahedra edge-shared to a pentagonal bipyramidal TaO$_7$ unit. These blocks of polyhedra are corner-shared with one another in the manner illustrated in Fig. 1. Ta–O bond lengths in the pentagonal bipyramid range from 1.92–2.15 Å (mean

[1] A table of observed and calculated structure factors has been deposited as Document No. NAPS–03316 with the ASIS National Auxiliary Publications Service, C/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number and remitting $5.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make check or money order payable to "Microfiche Publications".
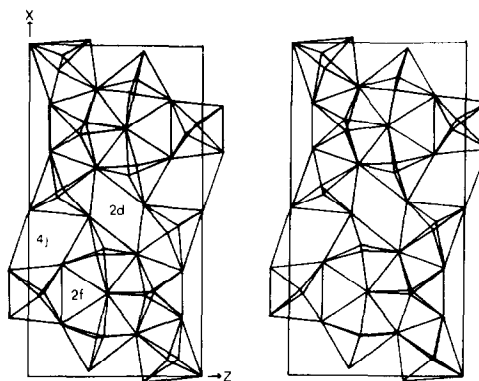

FIG. 1. A stereoscopic view of the structure of H–LiTa$_3$O$_8$ showing the possible lithium sites 2d, 2f and 4j.

2.05 Å) and in the slightly distorted octahedra range from 1.89–2.08 Å (mean 1.94 Å). Bond lengths are set out in detail in Table II.

There are three possible sites for lithium ions; there are the 2d sites of space group $Pmma$ at 0, $\frac{1}{2}$, $\frac{1}{2}$ and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, the 4j sites with parameters approximately 0.08, $\frac{1}{2}$, 0.09 and

TABLE I

FINAL ATOMIC PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Atoms with anisotropic temperature factors[a]

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ta(1)	0.25	0.0	0.6872(3)	0.0003(1)	0.0198(22)	0.0010(3)	0.0	0.0	0.0
Ta(2)	0.1323(1)	0.0	0.3927(2)	0.0004(1)	0.0205(15)	0.0010(2)	0.0	0.0001(1)	0.0
Ta(3)	0.0601(1)	0.0	0.8113(2)	0.0003(1)	0.0139(14)	0.0012(2)	0.0	0.0000(1)	0.0
Ta(4)	0.25	0.0	0.0540(4)	0.0004(1)	0.0528(32)	0.0012(3)	0.0	0.0	0.0

(b) atoms with isotropic temperature factors

Atom	x/a	y/b	z/c	B(Å^2)
O(1)	0.25	0.0	0.447(8)	2.4(14)
O(2)	0.131(2)	0.0	0.620(4)	0.9(6)
O(3)	0.178(3)	0.0	0.882(5)	1.8(8)
O(4)	0.25	0.5	0.692(8)	2.5(14)
O(5)	0.161(4)	0.0	0.186(7)	3.8(13)
O(6)	0.018(3)	0.0	0.343(6)	2.4(9)
O(7)	0.121(5)	0.5	0.407(8)	5.4(17)
O(8)	0.0	0.0	0.0	0.6(8)
O(9)	0.054(5)	0.5	0.827(8)	5.2(17)
O(10)	0.25	0.5	0.069(13)	6.0(28)

[a] The temperature factor is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE II[a]

Ta(1)-O(4)	1.920(2)	Ta(2)-O(5)	1.91(6)
Ta(1)-O(4)[II]	1.920(2)	Ta(2)-O(7)	1.934(9)
Ta(1)-O(2)	2.07(4)	Ta(2)-O(7)[II]	1.934(9)
Ta(1)-O(2)[I]	2.07(4)	Ta(2)-O(6)	1.96(6)
Ta(1)-O(3)	2.11(5)	Ta(2)-O(1)	2.02(2)
Ta(1)-O(3)[I]	2.11(5)	Ta(2)-O(2)	2.03(4)
Ta(1)-O(1)	2.15(7)		
Ta(3)-O(6)[III]	1.90(5)	Ta(4)-O(5)	1.89(6)
Ta(3)-O(9)	1.928(7)	Ta(4)-O(5)[I]	1.89(6)
Ta(3)-O(9)[II]	1.928(7)	Ta(4)-O(10)	1.925(8)
Ta(3)-O(8)[IV]	1.961(2)	Ta(4)-O(10)[II]	1.925(8)
Ta(3)-O(3)	2.07(5)	Ta(4)-O(3)[V]	1.95(5)
Ta(3)-0(2)	2.08(4)	Ta(4)-O(3)[VI]	1.95(5)

I	$\frac{1}{2}-x, y, z$	IV	$x, y, 1+z$
II	$x, y-1, z$	V	$x, y, z-1$
III	$-x, y, 1-z$	VI	$\frac{1}{2}-x, y, z-1$

[a] Some of the errors in this table are very low due to the small contribution to the bond length of the z parameter.

the nine-coordinate $2f$ sites at $\frac{1}{4}$, $\frac{1}{2}$, ~0.29, between the triangular groups of octahedra. The sites are marked in the stereoscopic view of the structure shown in Fig. 1. The four lithium ions could presumably occupy the $2d$ and $2f$ sites fully, or the $4j$ sites fully. It is suggested below that full occupancy of the $4j$ site is the more likely possibility. Based on the numbering system used for H–LiTa$_3$O$_8$ (Fig. 2) and LiNb$_6$O$_{15}$F (7) the dimensions of the two tunnels associated with the $2d$ and $4j$ sites may be considered together with the
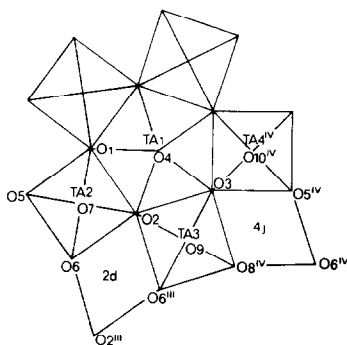

FIG. 2. Projection of the Ta(1) pentagonal bipyramid and the Ta(2) to Ta(4) octahedra edge-shared to it. The numbering scheme used is also given here.

dimensions of the same tunnels in the structure of Nb$_2$WO$_8$. The structure of Nb$_2$WO$_8$ (Nb$_4$W$_2$O$_{16}$) is very similar to that of the two compounds above except that the c-axis dimension is doubled in Nb$_2$WO$_8$ presumably as a result of the shift of the metal atoms off the plane that is a mirror plane in *Pmma*.

It is suggested here that full occupancy of the $4j$ site (above the midpoint of O(8^{IV})–O(5^{IV})) would be indicated by the decrease in the O(6^{III})–O(6) distance caused by the presence of lithium ions on both sides of the tunnel containing the $2d$ site (see Table III). The O(6^{III})–O(6) distance would be somewhat greater in LiNb$_6$O$_{15}$F as the site would only be half occupied and greater again in Nb$_2$WO$_8$ in which there is no lithium. A concomitant decrease would be expected in the O(6^{IV})–O(3) distance. These considerations, however, are only suggested by the trend in the figures given in Table III, and clearly the location of the lithium ions by neutron diffraction will resolve this question; experiments to this end are in progress (4).

Attention has been drawn above to the relationship between H–LiTa$_3$O$_8$ (Li$_2$Ta$_6$O$_{16}$), LiNb$_6$O$_{15}$F, β–Ta$_3$O$_7$F (Ta$_6$O$_{14}$F$_2$) and Nb$_2$WO$_8$ (Nb$_4$W$_2$O$_{16}$). A further formulation can be added to this series in the compound LiTa$_5$MoO$_{16}$(1) where, compared with H–LiTa$_3$O$_8$ or H–Li$_2$Ta$_6$O$_{16}$, replacement of Ta(V) by Mo(VI) has removed the necessity for the presence of two lithium ions to neutralize the electrical charge.

It appears that the structure described here and formed by a number of other compositions is a particularly stable "host"

TABLE III

	H–LiTa$_3$O$_8$	LiNb$_6$O$_{15}$F	Nb$_2$WO$_8$
O(2^{III})–O(2)	4.88(8)	4.81(4)	4.91(4)
O(6^{III})–O(6)	2.87(10)	2.95(5)	3.03(4)
O(6^{IV})–O(3)	4.91(7)	4.80(3)	4.73(3)
O(8^{IV})–O(5^{IV})	3.16(6)	3.23(2)	3.20(2)

lattice, in the same way as the hexagonal and tetragonal tungsten bronze structures may be regarded as stable "host" lattices and in which electrical neutrality is achieved by the occupancy of several sites by a variety of ions. The derivation of this structure from that of ReO_3 was recently described (10) in terms of antiphase boundaries with a cylindrical surface and of interpolated atoms requiring more space than is available in the original square tunnels of the perovskite type in ABO_3.

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