

Note on the Crystal Structures of a Niobium-rich Phase in the $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ System and of the Isostructural Compound $N\text{-Nb}_2\text{O}_5$

ROLF NORIN and BERTIL NOLANDER

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden

In their paper on phases in the $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ -system, Reisman and Holtzberg¹ reported a new oxide, stable at temperatures below 1268°C, for which they proposed the formula $\text{Li}_2\text{Nb}_{23}\text{O}_{71}$, based on density measurements. Whiston and Smith² determined the unit cell dimensions of this oxide and reformulated it as $\text{Li}_2\text{Nb}_{24}\text{O}_{61}$. They found the value of 3.8 Å for the shortest crystallographic axis which suggested that there might be crystal structure relationships with other niobium-rich mixed oxide phases, some of which had previously been studied at this department.^{3,4} The new phase (here denoted as phase *A*) has therefore been prepared and its crystal structure has been investigated.

Intimate mixtures of high purity Nb_2O_5 and Li_2CO_3 were tempered at temperatures of 1000–1300°C for 1–7 days. Some of the samples were melted prior to tempering. The samples were examined using Guinier and Weissenberg techniques and the results of the phase analysis are given in Table 1. Our observations are seen to agree with those made in the two investigations mentioned above. The unit cell dimensions were calculated on an IBM 360/65 computer using a program written by Lindqvist and Wengelin.⁵

Weissenberg photographs $h0l-h2l$ of phase *A* always revealed twinning of the crystals, which made the indexing of the powder pattern difficult. A careful examination of the two overlapping reciprocal lattices made it, however, possible to index all the reflexions (Table 2). The cell dimensions found (Table 2) do not, however agree with those found by Whiston and Smith. It seems likely that they did not observe the twinning, but based their cell on a combination of the two interpenetrating lattices.

The powder pattern of phase *A* is almost identical with that obtained from a sample

Table 1. Phases found in samples prepared by heating mixtures of Nb_2O_5 and Li_2CO_3 . Phase *B* has been given the formula $\text{Li}_2\text{O}\cdot 4\text{Nb}_2\text{O}_5$ by Reisman and Holtzberg¹ and LiNb_2O_8 by Whiston and Smith.²

Li/Nb molar ratio	Heat treatment	Phases found
1/23	melted and tempered at 1250°C for 2 d	<i>H-Nb₂O₅</i> + <i>A</i>
	tempered at 1250°C for 4 d	<i>H-Nb₂O₅</i> + <i>A</i>
1/12	melted and tempered at 1250°C for 4 d	<i>A</i>
	tempered at 1200°C for 3 d	<i>A</i>
1/9	melted and tempered at 1200°C for 3 d	<i>A</i> + <i>B</i>
	tempered at 1250°C for 3 d	<i>A</i> + <i>B</i>
1/3	tempered at 1100°C for 4 d	<i>B</i>

of $N\text{-Nb}_2\text{O}_5$ (Table 3) which was kindly placed at our disposal by Dr. Gruehn. This suggests that the two phases are isostructural. The crystal structure of $N\text{-Nb}_2\text{O}_5$ has been determined by Andersson,⁶ and can be described as being a member of the group B_2Cmn ⁷ of a series of homologous structures. For this compound both *m* and *n* are 4. The unit cell dimensions of $N\text{-Nb}_2\text{O}_5$ given by Andersson ($a=28.51$ Å, $b=3.830$ Å, $c=17.48$ Å and $\beta=120.80^\circ$) are not, however, in agreement with our data (Table 3). The oxide $\text{Nb}_{12}\text{O}_{29}$ (mon)⁸ is also a member of this group B_2Cmn but with $m=3$ and $n=4$. The crystal structure of $N\text{-Nb}_2\text{O}_5$ can be derived from that of $\text{Nb}_{12}\text{O}_{29}$ (mon) by extending all the blocks of NbO_6 -octahedra by one layer, *i.e.* from $3 \times 4 \times \infty$ to $4 \times 4 \times \infty$. The unit cell dimensions of a structure, derived in this way, would be $a=28.4$ Å, $b=3.83$, $c=17.6$ and $\beta=125^\circ$,

Table 2. Crystallographic data for phase A.

Unit cell dimensions: $a=28.52\pm 0.02$ Å, $b=3.828\pm 0.002$ Å, $c=17.55\pm 0.01$ Å and $\beta=124.98\pm 0.04^\circ$.

Systematically absent reflexions: hkl with $h+k=\text{odd}$, $h0l$ with $h=\text{odd}$.

Possible space groups: $C2$, Cm , and $C2/m$.

Powder pattern data. $\text{CuK}\alpha_1$ -radiation. $\lambda=1.54051$ Å.

I_{obs}	$\sin^2\theta_{\text{obs}} \times 10^5$	d_{obs}	hkl	$\sin^2\theta_{\text{calc}} \times 10^5$	d_{calc}
vw	287	14.38	0 0 1	287	14.38
vvw	318	13.66	2 0 $\bar{1}$	317	13.69
vw	1152	7.176	0 0 2	1148	7.190
vw	1217	6.982	4 0 $\bar{1}$	1215	6.987
vvw	1269	6.838	4 0 $\bar{2}$	1266	6.845
w	2585	4.791	0 0 3	2582	4.793
w	2629	4.750	6 0 $\bar{2}$	2629	4.750
m	4151	3.781	1 1 0	4157	3.778
vw	4237	3.742	1 1 $\bar{1}$	4241	3.740
w	4586	3.597	0 0 4	4591	3.595
w	4653	3.571	1 1 1	4646	3.573
w	4673	3.563	8 0 $\bar{3}$	4676	3.562
vw	4860	3.494	$\left\{ \begin{array}{l} 8 0 \bar{2} \\ 4 0 \bar{5} \end{array} \right.$	$\left\{ \begin{array}{l} 4861 \\ 4862 \end{array} \right.$	$\left\{ \begin{array}{l} 3.493 \\ 3.493 \end{array} \right.$
vvw	4908	3.477	1 1 $\bar{2}$	4900	3.480
vvw	5713	3.223	1 1 2	5709	3.224
w	5880	3.176	5 1 $\bar{2}$	5887	3.174
vvw	6956	2.920	6 0 $\bar{6}$	6952	2.921
vw	7174	2.876	0 0 5	7173	2.876
w	7343	2.842	1 1 3	7346	2.842
vvw	7555	2.802	8 0 $\bar{6}$	7564	2.801
s	7693	2.777	$\left\{ \begin{array}{l} 7 1 \bar{2} \\ 7 1 \bar{3} \end{array} \right.$	$\left\{ \begin{array}{l} 7685 \\ 7702 \end{array} \right.$	$\left\{ \begin{array}{l} 2.779 \\ 2.775 \end{array} \right.$
m	7928	2.736	1 1 $\bar{4}$	7937	2.743
vw	8247	2.682	7 1 $\bar{1}$	8241	2.682
vw	8283	2.676	7 1 $\bar{4}$	8293	2.675
vvw	9163	2.545	3 1 $\bar{5}$	9162	2.545

Table 3. Crystallographic data for $N\text{-Nb}_2\text{O}_5$. Unit cell dimensions: $a=28.53\pm 0.02$ Å, $b=3.827\pm 0.003$ Å, $c=17.58\pm 0.02$ Å and $\beta=125.10\pm 0.08^\circ$.

Systematically absent reflexions: hkl with $h+k=\text{odd}$, $h0l$ with $h=\text{odd}$.

Possible space groups: $C2$, Cm , $C2/m$. $Z=16$.

Powder pattern data. $\text{CuK}\alpha_1$ -radiation. $\lambda=1.54051$ Å.

I_{obs}	$\sin^2\theta_{\text{obs}} \times 10^5$	d_{obs}	hkl	$\sin^2\theta_{\text{calc}} \times 10^5$	d_{calc}
vw	287	14.38	0 0 1	287	14.38
vvw	315 ^a	13.71	2 0 $\bar{1}$	316	13.70
vw	1148	7.189	0 0 2	1148	7.189
vvw	1224	6.962	4 0 $\bar{1}$	1216	6.984
vw	2581	4.794	0 0 3	2583	4.792
w	2625	4.754	6 0 $\bar{2}$	2628	4.751
s	4166	3.774	1 1 0	4160	3.777
vvw	4240 ^a	3.741	1 1 $\bar{1}$	4244	3.739
m	4595	3.593	0 0 4	4593	3.594
w	4650	3.572	1 1 1	4650	3.572
m	4670	3.564	8 0 $\bar{3}$	4673	3.563
vw	4860 ^a	3.494	8 0 $\bar{2}$	4864	3.492
vvw	5725 ^a	3.225	1 1 2	5715	3.222
w	5883	3.176	5 1 $\bar{2}$	5888	3.174
vw	7177	2.875	0 0 5	7176	2.875
vw	7348	2.842	1 1 3	7353	2.840
s	7703	2.775	$\left\{ \begin{array}{l} 7 1 \bar{2} \\ 7 1 \bar{3} \end{array} \right.$	$\left\{ \begin{array}{l} 7688 \\ 7700 \end{array} \right.$	$\left\{ \begin{array}{l} 2.778 \\ 2.776 \end{array} \right.$
m	7938	2.734	1 1 $\bar{4}$	7939	2.734
vw	8263	2.680	7 1 $\bar{1}$	8251	2.682
vw	8273 ^a	2.678	7 1 $\bar{4}$	8286	2.676
w	8880	2.586	8 0 1	8883	2.584
w	9428	2.509	7 1 $\bar{5}$	9446	2.506

^aDiffuse reflexion. Approximative value, not included in the refinement.

which is in good agreement with our data for $N\text{-Nb}_2\text{O}_5$.

A comparison of preliminarily calculated structure factors with those observed for phase A indicates that this phase must exhibit the same arrangement of niobium and oxygen atoms as that of $N\text{-Nb}_2\text{O}_5$. The present phase analysis, as well as the earlier ones,^{1,2} indicate a content of lithium in phase A of 6–14 mol %. The calculated density for $N\text{-Nb}_2\text{O}_5$ is 4.50 g cm⁻³ based on the present cell dimensions. The observed density for phase A of 4.60 g cm⁻³ indicates a content of about 20 mol %

Li_2O . Samples with this composition, however, always contain a phase B (cf. Table 1) together with phase A. Thus the most likely composition is 10–12 mol % Li_2O , which is also consistent with the amounts of sample weighed in.

Further investigation of phase A is in progress to determine the details of its crystal structure and to obtain a more accurate value of its composition.

The authors wish to thank Professor G. Lundgren for valuable discussions, Dr. R. Gruehn for providing a sample $N\text{-Nb}_2\text{O}_5$ and Dr. S. Jagner for revising the text.

The investigation forms part of a research programme supported by the *Swedish Natural Science Research Council*.

1. Reisman, A. and Holtzberg, F. *J. Am. Chem. Soc.* **80** (1958) 6503.
2. Whiston, C. D. and Smith, A. J. *Acta Cryst.* **19** (1965) 169.
3. Norin, R. *Acta Chem. Scand.* **23** (1969) 1210.
4. Norin, R. and Dahlén, B. *Acta Chem. Scand.* **23** (1969) 1826.
5. Lindqvist, O. and Wengelin, F. *Arkiv Kemi* **28** (1967) 179.
6. Andersson, S. *Z. anorg. allgem. Chem.* **351** (1967) 106.
7. Andersson, S. *Bull. Soc. Chim. France* **1965** 1088.
8. Norin, R. *Acta Chem. Scand.* **20** (1966) 871.

Received January 4, 1971.

NMR Spectra of Trimethylsilylated Oligosaccharides and their Alditols

CARL GUSTAF HELLERQVIST,
OLLE LARM and BENGT LINDBERG

*Institutionen för Organisk Kemi, Stockholms
Universitet, S-113 27 Stockholm, Sweden*

NMR spectrometry of trimethylsilylated oligosaccharides has been used to establish the anomeric nature of the sugar residues.^{1,2} An advantage of the trimethylsilylation is that the signals from the anomeric protons become well separated from other protons in the sugar residues, which are shifted upfield. Reduction of the oligosaccharide to the corresponding alditol eliminates the anomeric proton of the reducing sugar residue and NMR of trimethylsilylated oligosaccharide alditols has recently been used in connection with structural studies on *Salmonella* lipopolysaccharides.³⁻⁶

In the present investigation, chemical shifts and coupling constants for the anomeric protons of some trimethylsilylated

Table 1. NMR parameters for the anomeric proton of the glycosidic linkage in some trimethylsilylated oligosaccharides and their alditols.

Oligosaccharide	Chemical shift ppm (τ values)	Coupling constant Hz
<i>O</i> - β -DG <i>p</i> (1 \rightarrow 2)DG ^a	5.49	6.5
<i>O</i> - β -DG <i>p</i> (1 \rightarrow 2)DG-ol	5.63	6.5
<i>O</i> - α -DG <i>p</i> (1 \rightarrow 4)DG	5.13	3.4
<i>O</i> - α -DG <i>p</i> (1 \rightarrow 4)DG-ol	4.74	3.0
<i>O</i> - β -DG <i>p</i> (1 \rightarrow 4)DG	5.57	6.5
<i>O</i> - β -DG <i>p</i> (1 \rightarrow 4)DG-ol	5.20	6.5
<i>O</i> - α -DG <i>p</i> (1 \rightarrow 6)DG	5.02	3.0
<i>O</i> - α -DG <i>p</i> (1 \rightarrow 6)DG-ol	5.40	3.0
<i>O</i> - β -DG <i>p</i> (1 \rightarrow 6)DG	5.78	7.0
<i>O</i> - β -DG <i>p</i> (1 \rightarrow 6)DG-ol	5.82	7.0
<i>O</i> - β -DGal <i>p</i> (1 \rightarrow 4)DG	5.65	6.5
<i>O</i> - β -DGal <i>p</i> (1 \rightarrow 4)DG-ol	5.38	6.5
<i>O</i> - α -DGal <i>p</i> (1 \rightarrow 6)DG	5.10	3.0
<i>O</i> - α -DGal <i>p</i> (1 \rightarrow 6)DG-ol	5.45	1.0
<i>O</i> - β -DGal <i>p</i> (1 \rightarrow 6)DGal	5.52	6.5
<i>O</i> - β -DGal <i>p</i> (1 \rightarrow 6)DGal-ol	5.81	6.5
MeO- α -DMan <i>p</i>	5.61	1.5
MeO- β -DMan <i>p</i>	5.80	1.5
<i>O</i> - β -DG <i>p</i> (1 \rightarrow 1)-DMan-ol	5.74	7.0
<i>O</i> - β -DG <i>p</i> (1 \rightarrow 3)-DMan-ol	5.40	6.5
<i>O</i> - β -DGal <i>p</i> (1 \rightarrow 2)-glycerol	5.18	1.5

^aDG = D-glucose, DG-ol = D-glucitol etc.

oligosaccharides and their alditols have been determined (Table 1). For all the substances listed in the table, except the gentiobiitol derivative, the signal from the anomeric proton was well separated from the other signals. As the disaccharides occurred as α/β -mixtures, the signals given by the different anomeric protons were readily identified.

As expected all the β -D-glucosides and the β -D-galactosides showed high coupling constant, 6.5–7.0 Hz, and the correspond-