

## On the Crystal Structures of Nb<sub>59</sub>O<sub>147</sub>F and Nb<sub>65</sub>O<sub>161</sub>F<sub>3</sub>

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In his study on the formation of oxide fluorides of niobium(V) Andersson<sup>1</sup> characterised the two compounds Nb<sub>31</sub>O<sub>77</sub>F and Nb<sub>17</sub>O<sub>42</sub>F as members of the homologous series of structures, Nb<sub>3n+1</sub>(O,F)<sub>8n-2</sub> (*n*=10 and 11), originally formulated by Gatehouse and Wadsley.<sup>2</sup> Gruehn<sup>3</sup> prepared two new niobium oxide fluorides

with the compositions 28Nb<sub>2</sub>O<sub>5</sub>·Nb<sub>2</sub>O<sub>7</sub>F and 28Nb<sub>2</sub>O<sub>5</sub>·3Nb<sub>2</sub>O<sub>7</sub>F. He assumed these compounds to be intergrowths of *H*-Nb<sub>2</sub>O<sub>5</sub> and Nb<sub>31</sub>O<sub>77</sub>F, and of Nb<sub>31</sub>O<sub>77</sub>F and Nb<sub>17</sub>O<sub>42</sub>F, with formulae Nb<sub>59</sub>O<sub>147</sub>F and Nb<sub>65</sub>O<sub>161</sub>F<sub>3</sub>, corresponding to the intergrowths Nb<sub>47</sub>O<sub>118</sub><sup>4</sup> and Nb<sub>55</sub>O<sub>132</sub>.<sup>5,6</sup>

In order to test the validity of Gruehn's assumptions, crystals from his samples have been examined with Guinier and Weissenberg methods at this Department. Using the Weissenberg photographs *h0l*–*h2l* of crystals from the single phase samples, the powder patterns of the two oxide fluorides could be indexed in detail. Powder pattern data were refined and cell dimensions calculated on a digital computer, using a program written by Lindqvist and Wengelin<sup>7</sup> (see Tables 1 and 2).

Table 1. Crystallographic data for Nb<sub>59</sub>O<sub>147</sub>F. Unit cell dimensions: *a*=(73.29±0.03) Å; *b*=(3.828±0.002) Å; *c*=(21.17±0.02) Å; β=(104.19±0.04)°. *Z*=2. Powder pattern data. CuKα<sub>1</sub> radiation. λ(CuKα<sub>1</sub>)=1.5405 Å.

<i>I</i> obs	sin <sup>2</sup> θ × 10 <sup>5</sup> obs	<i>d</i> obs	<i>h k l</i>	sin <sup>2</sup> θ × 10 <sup>5</sup> calc	<i>d</i> calc
vw	188	17.75	4 0 0	188	17.75
m	530	10.58	2 0 $\bar{2}$	531	10.57
vw	692	9.259	2 0 2	690	9.273
vw	1596	6.097	12 0 $\bar{1}$	1593	6.103
w	2128	5.280	4 0 $\bar{4}$	2123	5.286
vst	2257	5.127	0 0 $\bar{4}$	2254	5.130
st	2831	4.578	16 0 $\bar{1}$	2829	4.580
vw	4062	3.822	1 1 0	4065	3.820
vst	4229	3.746	1 1 1	4225	3.747
vw	4343	3.696	3 1 $\bar{1}$	4240	3.741
vst	4441	3.655	5 1 0	4346	3.695
w	4628	3.580	20 0 $\bar{1}$	4441	3.655
vvst	4884	3.485	7 1 0	4628	3.580
w	5001	3.444	2 0 $\bar{6}$	4880	3.487
vvw	5055	3.426	9 1 0	5004	3.443
vst	5266	3.357	10 0 $\bar{6}$	5050	3.428
vvw	5364	3.326	1 1 $\bar{3}$	5272	3.355
w	6034	3.136	2 0 6	5358	3.328
vw	6226	3.087	13 1 0	6038	3.135
vst	7382	2.835	20 0 $\bar{5}$	6227	3.087
st	7448	2.822	3 1 $\bar{5}$	7382	2.835
vst	7686	2.778	17 1 0	7448	2.822
st	8098	2.707	1 1 5	7686	2.778
vw	8204	2.689	19 1 $\bar{2}$	8099	2.707
vw	9037	2.562	18 0 $\bar{7}$	8198	2.690
st	9148	2.547	0 0 8	9016	2.565
st	9512	2.497	18 0 5	9122	2.550
			22 0 $\bar{7}$	9519	2.497

Table 2. Crystallographic data for  $\text{Nb}_{85}\text{O}_{161}\text{F}_3$ . Unit cell dimensions:  $a=(81.16\pm 0.03)$  Å;  $b=(3.829\pm 0.002)$  Å;  $c=(21.15\pm 0.02)$  Å;  $\beta=(103.97\pm 0.04)^\circ$ .  $Z=2$ . Powder pattern data.  $\text{CuK}\alpha_1$  radiation.  $\lambda(\text{CuK}\alpha_1)=1.5405$  Å.

$I$ obs	$\sin^2\theta \times 10^5$ obs	$d$ obs	$h k l$	$\sin^2\theta \times 10^5$ calc	$d$ calc
w	534	10.54	2 0 $\bar{2}$	531	10.57
vw	675	9.375	2 0 2	673	9.389
vw	1777	5.778	14 0 $\bar{1}$	1767	5.795
vw	2123	5.286	4 0 $\bar{4}$	2123	5.286
st	2258	5.126	0 0 4	2253	5.132
vw	2923	4.505	18 0 $\bar{1}$	2921	4.507
vvst	4224	3.748	3 1 $\bar{1}$	4220	3.750
vvst	4389	3.677	22 0 $\bar{1}$	4380	3.680
vw	4521	3.623	$\left\{ \begin{array}{l} 7 1 0 \\ 7 1 \bar{1} \end{array} \right.$	4515	3.625
vw	4779	3.523	6 0 $\bar{6}$	4776	3.524
vvst	4905	3.478	2 0 $\bar{6}$	4896	3.481
st	5274	3.354	1 1 $\bar{3}$	5271	3.355
vw	5333	3.335	18 0 3	5324	3.338
vw	6208	3.091	15 1 0	6199	3.094
st	7395	2.833	3 1 $\bar{5}$	7388	2.834
m	7504	2.812	19 1 0	7500	2.813
vvst	7666	2.782	1 1 $\bar{5}$	7666	2.782
st	8095	2.707	21 1 $\bar{2}$	8084	2.709
vw	8252	2.681	5 1 $\bar{5}$	8250	2.682
vw	8611	2.625	4 0 $\bar{8}$	8599	2.627
vw	9015	2.565	0 0 8	9014	2.565
m	9127	2.550	20 0 $\bar{5}$	9120	2.551

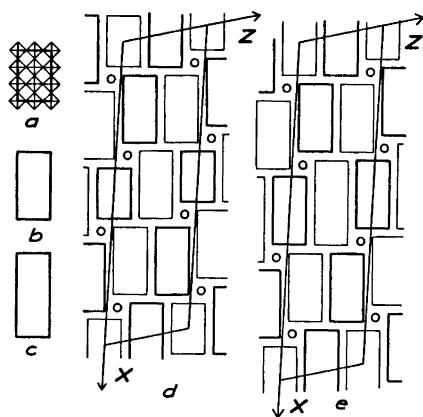


Fig. 1. Idealized projections on the  $xz$ -plane showing: *a.* a block with  $\text{ReO}_3$ -structure, having the dimensions  $3 \times 4 \times \infty \text{Nb}(\text{O},\text{F})_6$ -octahedra; *b.* a block with  $3 \times 5 \times \infty \text{Nb}(\text{O},\text{F})_6$ -octahedra; *c.* a block with  $3 \times 6 \times \infty \text{Nb}(\text{O},\text{F})_6$ -octahedra; *d.* the crystal structure of

$\text{Nb}_{59}\text{O}_{147}\text{F}$ ; and *e.* the crystal structure of  $\text{Nb}_{85}\text{O}_{161}\text{F}_3$ . The simplified representation of the block projections, introduced by Allpress *et al.*<sup>8</sup>, is used. Only the outlines of the blocks of niobium atoms are shown. In (*a*) the  $\text{Nb}(\text{O},\text{F})_6$ -octahedra have been drawn with fine lines. In (*d*) and (*e*), fine lines indicate blocks with Nb in  $y=0$ , and heavy lines blocks with Nb in  $y=\frac{1}{2}$ . The circles indicate the positions of niobium atoms in tetrahedral positions.

The observed unit cell parameters agree well with those calculated for the intergrowths  $\text{Nb}_{59}\text{O}_{147}\text{F}$  ( $a=73.4$  Å,  $b=3.83$  Å,  $c=21.2$  Å,  $\beta=104.4^\circ$ ), and  $\text{Nb}_{85}\text{O}_{161}\text{F}_3$  ( $a=81.0$  Å,  $b=3.83$  Å,  $c=21.2$  Å,  $\beta=104.1^\circ$ ). Idealized representations of the two intergrowth structures are given in Fig. 1.

Weissenberg photographs of all crystals investigated were found to show a characteristic type of disorder. The same type of disorder is observed in Weissenberg photographs of  $\text{Nb}_{47}\text{O}_{116}$  and  $\text{Nb}_{53}\text{O}_{132}$ .

Using electron diffraction, Allpress<sup>6</sup> has found that in  $Nb_{53}O_{132}$ , ordered regions, built up of sheets of  $Nb_{25}O_{63}$  alternating with sheets of  $H-Nb_2O_5$ , are interrupted by disordered regions. The disorder in the Weissenberg photographs might be due to this lack of order in the crystal structure. Because of this disorder, space groups could not be predicted from the reciprocal lattices. Allpress<sup>6</sup> found  $Nb_{53}O_{132}$  to be *C*-centered, and the same symmetry is assumed to be valid even for  $Nb_{47}O_{116}$ ,  $Nb_{59}O_{147}F$ , and  $Nb_{65}O_{161}F$ .

The general formula  $Nb_{3n+1}(O,F)_{8n-2}$  could be expressed as  $Nb_{3n+2}(O,F)_{8n-4}$ , with doubled *n* values for each member. This formula also includes the intergrowth phases, the members of this series hitherto characterised being:  $Nb_{11}O_{27}$  ( $Nb_{44}O_{108}$ , *n* = 14),  $Nb_{47}O_{116}$  (*n* = 15),  $Nb_{25}O_{62}$  ( $Nb_{50}O_{124}$ , *n* = 16),  $Nb_{53}O_{132}$  (*n* = 17),  $H-Nb_2O_5$  ( $Nb_{55}O_{140}$ , *n* = 18),  $Nb_{50}O_{147}F$  (*n* = 19),  $Nb_{31}O_{77}F$  ( $Nb_{62}O_{154}F_2$ , *n* = 20),  $Nb_{65}O_{161}F_3$  (*n* = 21) and  $Nb_{17}O_{42}F$  ( $Nb_{68}O_{168}F_4$ , *n* = 22).

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1. Andersson, S. *Acta Chem. Scand.* **19** (1965) 1401.
2. Gatehouse, B. M. and Wadsley, A. D. *Acta Cryst.* **17** (1964) 1545.
3. Gruehn, R. *Naturwiss.* **54** (1967) 645.
4. Gruehn, R. and Norin, R. *Z. anorg. allgem. Chem.* **367** (1969) 209.
5. Gruehn, R. and Norin, R. *Z. anorg. allgem. Chem.* **355** (1967) 176.
6. Allpress, J. G. *J. Solid State Chem.* **1** (1969) 66.
7. Lindqvist, O. and Wengelin, F. *Arkiv Kemi* **28** (1967) 179.
8. Allpress, J. G., Sanders, J. V. and Wadsley, A. D. *Acta Cryst.* **B 25** (1969) 1156.

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## Studies on Orchidaceae Alkaloids

### XXIV.\* A Pyrrolizidine Alkaloid from *Phalaenopsis cornu-cervi* Rehb. f.

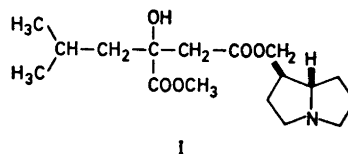
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A new alkaloid, cornucervine ( $C_{17}H_{29}NO_5$ , **I**) has been isolated from *Phalaenopsis cornu-cervi* Rehb. f. Acid methanolysis of **I** gave an amino alcohol identified as trachelanthamidine, (-)-*exo*-1-hydroxy-methylpyrrolizidine ( $C_8H_{16}NO$ ), and an optically active compound ( $C_{10}H_{18}O_5$ ) indistinguishable (GLC, MS, NMR) from a synthetic sample of racemic dimethyl 2-isobutylmalate.

The latter compound was synthesised by condensation of methyl isobutyl ketone with diethyl carbonate to ethyl 5-methyl-3-oxo-hexanoate, and thereafter preparation of the cyanohydrine followed by acid methanolysis.

The intense peak **M** - 59 ( $59 = COOCH_3$ ) and the absence of a peak **M** - 73<sup>2</sup> ( $73 = CH_2COOCH_3$ ) in the mass spectrum of **I** demonstrates the nature of the methyl ester grouping in cornucervine, which accordingly has structure **I**. The absolute configuration of the isobutylmalate residue has not yet been determined.



*Experimental.* IR, MS, and NMR spectrometry and preparative gas chromatography were performed as previously described.<sup>2</sup> Optical rotations were measured on a Perkin-Elmer 141 polarimeter, and analytical GLC was carried out on a 3% SE-52 on Chromosorb AW DMCS column (0.2 × 180 cm) using a Perkin-Elmer 900 chromatograph. The high resolution mass spectra were measured on an Atlas SM 1 instrument.

\* For No. XXIII in this series, see Ref. 1.