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The Crystal Structure of Nb_2WO_8

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The crystal structure of Nb_2WO_8 has been determined and refined from three-dimensional X-ray data. The orthorhombic cell dimensions are $a = 3.946$ Å, $b = 17.616$ Å, $c = 16.617$ Å. The space group is *Pbcm*. The atomic arrangement is related to that of the compound $LiNb_6O_{15}F$.

Several studies of the phase relationships in the system $Nb_2O_5 - WO_3$ have been performed. The compound Nb_2WO_8 was first reported by Fiegel *et al.*[1] and later confirmed by Roth and Wadsley.[2] The cell dimensions and probable space groups were determined from X-ray diffraction powder photographs taken by Roth and Waring.[3] The photographs showed a pattern very similar to that of $LiNb_6O_{15}F$ [4] and therefore an X-ray crystallographic investigation was started and the results will now be reported.

EXPERIMENTAL

For the synthesis of the compound Nb_2WO_8 stoichiometric amounts of H-Nb_2O_5 (Kawecki, 99.99 %) and WO_3 (Matheson, Coleman & Bell, reagent grade) were mixed and heated in a sealed platinum tube at 900°C for two days. The specimen thus obtained gave sharp powder reflexions. Even by prolonged heating at that temperature, however, it was not possible to grow crystals big enough for X-ray single crystal studies. It was observed that the presence of slight amounts of lithium fluoride to the sample increases the rate of crystal growth substantially. Thus, in order that crystals of Nb_2WO_8 would be produced, a very small amount of lithium fluoride was added to the mixture of the starting oxides which was then heated in a sealed platinum tube at 1000°C for four days. The sample contained colourless, plate-like crystals. The powder pattern of the material was identical with the one obtained from the compound prepared in the absence of lithium fluoride.

The unit cell dimensions were determined from a Guinier X-ray powder photograph taken with Cu$K\alpha_1$ radiation and with potassium chloride ($a = 6.2930$ Å at 25°C) [5] as an internal standard. Accurate cell parameters were obtained by least squares refinement. The powder pattern is listed in Table 1 and the unit cell dimensions are given in Table 2.

Intensity data from a rather plate-shaped single crystal measuring $0.03 \times 0.08 \times 0.08$ mm^3 were collected with an integrating Weissenberg camera using Ni-filtered CuK radiation. The $0kl$, $1kl$ and $2kl$ reflexions were recorded by multiple film technique and visually estimated by means of a standard scale.

Corrections were applied for Lorentz and polarization factors as well as for absorption. The atomic scattering factors, given by Cromer and Waber,[6] were used with the

Table 1. The Guinier powder pattern of Nb_2WO_8 ($CuK\alpha_1$ radiation).[a]

h k l	d_{obs}	$10^5 \times \sin^2 \theta_{obs}$	$10^5 \times \sin^2 \theta_{calc}$	*I*
0 2 0	8.819	762	764	vvw
0 0 2	8.317	857	858	s
0 2 3	4.699	2687	2695	w
0 4 0	4.414	3044	3056	vw
0 4 1	4.268	3257	3271	m
1 0 0	3.953	3797	3805	vs
0 4 2	3.892	3917	3915	s
0 2 4	3.761	4194	4198	vs
1 0 2	3.568	4660	4663	w
0 4 3	3.451	4980	4988	vs
1 3 0	3.282	5508	5524	m
1 3 1	3.223	5713	5739	w
1 1 3	3.168	5912	5928	m
0 2 5	3.113	6123	6129	s
1 3 2	3.050	6376	6383	m
1 4 1 0 6 1	2.895	7078	7076 7092	s
1 1 4	2.826	7426	7430	w
1 4 2 0 0 6 0 6 2	2.772	7723	7720 7726 7736	s
1 2 4	2.725	7991	8003	s
0 4 5	2.654	8425	8422	m
0 2 6	2.644	8484	8490	m
1 5 0	2.630	8575	8581	w
1 4 3 1 5 1	2.599	8785	8793 8796	s
1 3 4	2.572	8969	8958	w
1 1 5	2.517	9364	9362	vvw
1 5 2	2.511	9410	9439	w
1 2 5	2.446	9919	9935	s
0 6 4	2.399	10310	10311	vw
1 5 3	2.373	10538	10512	w
1 3 5 1 6 1	2.335	10878	10890 10897	s
0 2 7	2.293	11288	11280	vw
1 0 6 1 6 2	2.269	11525	11531 11541	m
1 1 6	2.249	11733	11722	w
0 8 0 1 4 5	2.204	12218	12227 12227	m
0 4 7	2.091	13574	13573	w
0 0 8	2.079	13724	13735	w
0 2 8	2.023	14496	14500	m
2 0 0	1.977	15177	15221	s
0 8 4	1.946	15663	15661	m

[a] 32 additional reflexions with smaller d_{obs} were also used in the least squares refinement of the unit cell dimensions.

real and imaginary part of the anomalous dispersion correction being applied to the scattering curves.

The calculations were performed on the computers IBM 360/75 and IBM 1800. The programs used are listed in Table 6.

STRUCTURE DETERMINATION

The Weissenberg photographs confirmed the orthorhombic symmetry and showed systematic absences $0kl$ for $k=2n+1$ and $h0l$ for $l=2n+1$. These conditions gave the space group *Pbcm* (No. 57). If the first condition were accidental the space group would be $Pmc2_1$.

The appearance of the Weissenberg photographs showed the structure to be related to $LiNb_6O_{15}F$ but with a doubled unit cell. It was also concluded that this was probably associated with a displacement of the metal atoms from the equatorial plane. The atomic parameters given for $LiNb_6O_{15}F$ were used as starting values in the full matrix least squares refinement. The shifts of the metal atoms were found by trial and error. The refinement was based on 593 independent reflexions. At the beginning of the refinement, the Nb and W atoms were assumed to be statistically distributed over the metal positions. However, the temperature factors and a difference synthesis after the refinement to an R-value of 0.10 indicated that the distribution was not strictly random. Refinement of the Nb/W ratio at each site led to an R-value

Table 2. Crystallographic data for Nb_2WO_8.

Space group: *Pbcm*

Unit cell dimensions:	Point positions	Numbering of the atoms
	x,y,z	(n 1)
	$\bar{x},\bar{y},\bar{z}$	(n 2)
$a=$ 3.949(1) Å	$\bar{x},\bar{y},\frac{1}{2}+z$	(n 3)
$b=17.622(3)$ Å	$x,y,\frac{1}{2}-z$	(n 4)
$c=16.626(3)$ Å	$x,\frac{1}{2}-y,\bar{z}$	(n 5)
Unit cell content :$8Nb_2WO_8$	$\bar{x},\frac{1}{2}+y,z$	(n 6)
Density: $d_{obs}=5.64$ g cm^{-3}	$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$	(n 7)
$d_{calc}=5.72$ g cm^{-3}	$x,\frac{1}{2}-y,\frac{1}{2}+z$	(n 8)

Atom (n)	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$	The atom fraction of W
$M(1)$	0.9448	(9)	0.19837	(10)	0.13164	(11)	1.00	(5)	0.37(6)
$M(2)$	0.9720	(9)	0.40697	(13)	0.05943	(15)	1.10	(5)	0.17(5)
$M(3)$	0.0694	(10)	0.02727	(13)	$\frac{1}{4}$		1.06	(5)	0.70(7)
$M(4)$	0.0585	(15)	0.34344	(17)	$\frac{1}{4}$		1.17	(7)	0.24(6)
O(1)	0.486	(11)	0.2023	(14)	0.1286	(15)	2.2	(9)	
O(2)	0.526	(10)	0.4062	(14)	0.0601	(16)	2.3	(8)	
O(3)	0.547	(14)	0.0245	(20)	$\frac{1}{4}$		1.9	(9)	
O(4)	0.535	(13)	0.3433	(15)	$\frac{1}{4}$		0.6	(6)	
O(5)	0.998	(7)	0.1667	(10)	0.0227	(12)	0.3	(3)	
O(6)	0.013	(7)	0.3099	(10)	0.1332	(11)	0.4	(3)	
O(7)	0.020	(8)	0.0937	(11)	0.1645	(14)	1.1	(4)	
O(8)	0.012	(8)	0.4399	(11)	0.1750	(12)	0.8	(4)	
O(9)	0.012	(10)	0.2248	(15)	$\frac{1}{4}$		0.4	(4)	
O(10)	0		0		0		1.8	(7)	

Table 3. Observed and calculated structure factors for Nb_2WO_8. The scale factor has been applied on the calculated F values.

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	2	11.22	11.91	0	-14	0	4.40	4.67	1	4	13	24.76	23.33	1	14	3	14.50	15.78
0	0	4	2.62	2.92	0	-14	1	9.38	9.82	1	4	17	3.78	3.51	1	14	4	4.00	4.26
0	0	6	18.19	19.32	0	-14	3	15.63	15.60	1	4	18	9.61	8.12	1	14	6	5.89	5.32
0	0	8	21.39	22.32	0	-14	4	5.22	4.84	1	4	19	11.35	9.51	1	14	9	5.98	5.51
0	0	10	31.74	35.29	0	-14	6	4.91	5.28	1	5	1	3.85	4.22	1	14	10	4.78	4.97
0	0	16	27.41	27.60	0	-14	9	5.72	5.80	1	5	3	9.65	10.16	1	14	11	3.22	3.14
0	0	18	8.82	8.79	0	-14	10	5.05	4.59	1	5	5	4.91	5.27	1	14	13	17.74	17.37
0	0	20	3.71	3.90	0	-14	11	2.44	3.02	1	5	13	9.60	8.24	1	14	15	5.15	5.20
0	-2	1	2.75	2.35	0	-14	13	15.36	15.96	1	6	0	4.90	5.32	1	15	8	4.53	4.51
0	-2	2	2.04	1.53	0	-14	15	5.23	5.20	1	6	1	20.60	21.42	1	15	9	3.84	4.48
0	-2	3	4.20	3.17	0	-16	0	15.41	15.08	1	6	2	15.50	15.57	1	15	13	3.24	2.94
0	-2	4	17.41	25.02	0	-16	1	8.45	9.30	1	6	4	6.90	7.04	1	15	14	2.37	2.39
0	-2	5	24.73	27.80	0	-16	2	3.09	3.70	1	6	5	8.85	7.93	1	16	4	16.94	17.41
0	-2	6	11.14	11.40	0	-16	4	15.98	16.95	1	6	7	16.33	16.53	1	16	5	6.08	6.96
0	-2	7	6.56	6.46	0	-16	5	6.67	6.40	1	6	8	31.77	31.27	1	16	6	16.85	17.28
0	-2	8	16.64	15.64	0	-16	6	17.53	17.13	1	6	9	22.17	20.30	1	16	7	6.34	6.86
0	-2	9	9.72	9.44	0	-16	7	7.00	7.08	1	6	11	8.51	8.03	1	16	8	3.58	3.86
0	-2	10	3.51	3.82	0	-16	8	3.77	2.62	1	6	12	4.83	4.09	1	16	9	8.47	8.34
0	-2	11	15.49	15.67	0	-16	9	9.00	8.62	1	6	13	7.02	6.13	1	16	10	13.65	13.89
0	-2	12	15.44	15.56	0	-16	10	13.94	13.88	1	6	14	7.67	7.80	1	16	12	9.96	10.40
0	-2	14	7.95	7.72	0	-16	12	10.44	10.20	1	6	15	10.39	10.11	1	16	13	4.61	5.10
0	-2	15	7.78	7.88	0	-16	13	4.52	4.71	1	6	17	15.52	14.57	1	16	14	7.15	6.70
0	-2	18	7.03	5.97	0	-16	14	6.73	6.67	1	6	18	16.77	15.98	1	-12	0	2.14	2.31
0	-2	20	8.43	7.89	0	-18	0	14.63	14.72	1	6	19	4.03	4.47	1	-14	0	4.91	5.43
0	-4	0	5.01	4.98	0	-18	1	1.98	2.76	1	7	0	3.80	4.57	1	-15	0	3.78	2.73
0	-4	1	6.36	4.98	0	-18	4	6.17	6.17	1	7	2	4.11	3.63	1	-15	1	4.85	5.67
0	-4	2	13.00	13.44	0	-18	5	15.03	15.34	1	7	4	9.97	9.97	1	-15	2	4.40	4.30
0	-4	3	28.47	36.85	0	-18	6	5.32	4.29	1	7	5	7.37	6.47	1	-16	0	13.98	14.23
0	-4	5	12.57	13.06	0	-18	8	7.21	7.26	1	7	6	7.84	8.10	1	-16	1	8.27	8.80
0	-4	6	3.38	3.66	0	-18	10	8.90	8.76	1	7	10	4.62	4.97	1	-16	2	3.02	2.99
0	-4	7	12.54	12.45	0	-18	11	8.94	8.68	1	7	12	5.83	6.21	1	-17	5	4.90	5.24
0	-4	8	20.05	18.54	0	-18	12	3.14	4.47	1	7	14	4.18	4.36	1	-17	8	3.70	3.81
0	-4	10	4.43	4.25	0	-20	0	11.12	10.76	1	8	0	16.99	17.47	1	-17	11	3.27	3.25
0	-4	11	7.47	7.79	0	-20	1	3.61	3.47	1	8	3	7.94	7.53	1	-18	0	16.25	15.39
0	-4	13	24.44	24.29	0	-20	2	4.80	4.70	1	8	4	17.88	17.93	1	-18	4	6.14	6.94
0	-4	18	8.31	7.52	0	-20	3	8.49	8.63	1	8	5	24.03	23.43	1	-18	5	16.26	15.27
0	-4	19	10.35	9.59	0	-20	4	9.35	10.52	1	8	6	7.36	6.97	1	-18	6	5.00	4.57
0	-6	0	4.88	6.15	0	-20	5	2.97	2.86	1	8	7	7.96	8.12	1	-18	8	6.87	7.64
0	-6	1	25.73	26.31	0	-20	6	2.45	2.24	1	8	8	9.08	8.91	1	-18	10	9.83	9.53
0	-6	2	19.83	20.44	0	-20	7	5.92	6.12	1	8	9	6.34	5.97	1	-18	11	8.35	8.37
0	-6	4	8.42	8.88	0	-20	9	3.83	4.23	1	8	10	5.12	4.68	1	-18	12	4.35	5.01
0	-6	5	8.85	7.99	0	-22	0	3.18	4.90	1	8	11	10.88	9.36	1	-19	0	3.85	4.40
0	-6	7	17.53	18.13	0	-22	2	8.92	10.49	1	8	12	12.16	10.84	1	-19	1	3.43	4.15
0	-6	8	34.07	32.85	0	-22	3	2.57	4.67	1	8	13	3.04	3.04	1	-19	3	2.91	3.86
0	-6	9	21.71	21.60	1	0	2	9.50	9.36	1	8	14	5.20	5.61	1	-19	4	3.29	3.59
0	-6	11	9.55	8.12	1	0	4	1.93	2.25	1	8	15	4.10	5.13	1	-19	5	2.77	3.33
0	-6	12	4.78	5.30	1	0	6	13.13	14.00	1	8	16	5.47	5.64	1	-19	7	3.26	3.79
0	-6	13	7.01	5.89	1	0	8	19.97	19.70	1	8	18	4.35	4.56	1	-19	9	2.95	3.66
0	-6	14	10.15	8.73	1	0	10	33.14	33.47	1	9	0	12.00	14.02	1	-19	10	1.42	1.74
0	-6	15	11.41	10.50	1	0	16	27.35	27.46	1	9	1	2.04	2.38	1	-20	0	11.05	11.15
0	-6	17	15.15	14.42	1	0	18	8.78	8.57	1	9	2	3.76	4.30	1	-20	1	3.35	3.70
0	-6	18	15.91	15.36	1	0	20	3.83	3.51	1	9	5	4.97	4.50	1	-20	2	3.92	4.29
0	-6	19	4.46	4.19	1	1	1	2.66	2.93	1	9	6	4.95	5.71	1	-20	3	8.34	8.81
0	-8	0	17.03	17.69	1	1	2	5.14	5.10	1	9	8	6.59	7.59	1	-20	4	10.45	11.23
0	-8	3	9.38	7.78	1	1	3	3.46	1.85	1	9	10	8.26	7.91	1	-20	5	2.70	3.86
0	-8	4	18.91	18.97	1	1	4	10.70	9.72	1	9	16	8.01	7.14	1	-20	6	1.80	2.68
0	-8	5	23.74	24.78	1	1	5	8.86	7.95	1	9	18	3.00	3.82	1	-20	7	5.84	6.40
0	-8	6	7.22	6.98	1	1	6	4.32	3.53	1	10	0	20.22	21.10	1	-20	9	4.69	4.29
0	-8	7	9.39	9.19	1	1	11	5.43	4.95	1	10	1	13.18	13.90	1	-21	1	1.74	2.28
0	-8	8	8.92	9.14	1	1	12	7.14	7.06	1	10	2	13.75	14.37	1	-21	4	2.22	2.74
0	-8	9	6.85	6.98	1	1	14	5.29	5.14	1	10	3	8.70	8.34	1	-22	0	3.71	3.97
0	-8	11	11.67	9.83	1	1	20	3.30	2.99	1	10	4	21.47	21.93	1	-22	2	9.69	10.43
0	-8	12	11.44	10.81	1	2	3	4.07	3.12	1	10	5	16.57	15.95	2	0	2	5.10	4.72
0	-8	13	4.37	2.86	1	2	4	19.84	20.35	1	10	6	3.13	4.04	2	0	6	13.68	14.70
0	-8	14	6.15	5.45	1	2	5	21.97	22.35	1	10	7	9.40	8.55	2	0	8	13.49	13.70
0	-8	15	5.22	4.52	1	2	6	9.14	9.57	1	10	9	7.89	6.71	2	0	10	24.77	24.42
0	-8	16	6.44	5.33	1	2	7	5.73	5.71	1	10	10	9.27	7.96	2	0	16	22.82	23.54
0	-8	18	4.12	4.00	1	2	8	15.24	14.58	1	10	11	14.78	13.97	2	0	18	6.02	5.65
0	-10	0	21.77	22.22	1	2	9	9.92	9.65	1	10	12	17.97	16.52	2	-2	0	2.86	2.06
0	-10	1	13.80	15.42	1	2	11	14.31	14.50	1	10	13	4.44	4.21	2	-3	0	8.54	8.31
0	-10	2	14.75	15.70	1	2	12	16.04	15.25	1	10	14	15.64	15.44	2	-4	0	5.87	6.30
0	-10	3	7.67	8.77	1	2	14	8.46	7.94	1	10	15	10.94	10.48	2	-7	0	6.89	7.24
0	-10	4	21.36	23.25	1	2	15	9.10	8.13	1	10	16	9.64	9.82	2	-8	0	13.63	14.16
0	-10	5	16.81	16.66	1	2	18	7.57	6.81	1	10	17	6.34	5.84	2	-10	0	18.55	19.73
0	-10	6	4.38	4.18	1	2	20	8.58	8.15	1	10	18	4.17	3.90	2	-11	0	6.27	6.85
0	-10	7	9.33	9.30	1	3	0	5.60	3.89	1	11	0	3.64	4.01	2	-12	0	2.98	3.40
0	-10	9	7.88	7.68	1	3	1	12.34	11.90	1	11	4	4.89	6.01	2	-13	0	7.28	6.53
0	-10	10	7.36	7.17	1	3	2	6.90	6.57	1	11	5	2.62	3.24	2	-14	0	3.57	3.75
0	-10	11	14.24	13.79	1	3	3	4.80	4.35	1	12	1	14.36	15.38	2	-15	0	5.98	5.09
0	-10	12	17.49	16.73	1	3	5	2.11	1.81	1	12	2	8.85	9.36	2	-16	0	12.38	12.99
0	-10	14	16.33	14.89	1	3	7	10.28	9.68	1	12	3	11.67	12.42	2	-17	0	4.93	4.94
0	-10	15	11.17	10.25	1	3	8	9.85	8.52	1	12	4	11.96	11.76	2	-18	0	10.64	11.92
0	-10	16	10.34	9.06	1	3	9	11.49	10.89	1	12	5	5.02	5.73	2	-19	0	7.26	7.32
0	-10	17	6.25	6.08	1	3	10	2.18	1.53	1	12	6	4.58	5.35	2	-20	0	9.38	10.47
0	-10	18	4.43	4.05	1	3	11	3.29	3.70	1	12	7	14.19	14.19	2	-1	1	4.20	4.43
0	-12	1	15.63	16.16	1	3	15	3.92	4.62	1	12	8	14.52	14.94	2	-1	2	7.54	8.24
0	-12	2	8.22	8.51	1	3	17	6.56	6.86	1	12	9	15.24	15.63	2	-1	3	5.56	4.44
0	-12	3	12.70	13.65	1	3	18	4.34	3.97	1	12	12	4.85	5.59	2	-1	4	15.21	16.97
0	-12	4	11.95	12.77	1	3	19	3.16	3.55	1	12	13	5.17	8.45	2	-1	5	12.01	12.15
0	-12	5	5.05	4.58	1	4	0	5.25	4.26	1	12	15	6.94	4.47	2	-1	6	6.79	6.82
0	-12	6	6.00	6.14	1	4	1	5.65	4.22	1	12	17	8.29	9.21	2	-1	11	8.82	7.78
0	-12	7	14.79	15.32	1	4	2	11.80	11.36	1	13	2	4.45	5.19	2	-1	12	12.43	12.15
0	-12	8	14.99	14.79	1	4	3	28.17	29.73	1	13	3	6.84	7.48	2	-1	13	4.28	3.44
0	-12	9	15.91	16.18	1	4	5	9.36	10.19	1	13	5	5.97	7.14	2	-1	14	9.71	8.79
0	-12	12	6.06	6.14	1	4	7	12.03	11.95	1	13	8	5.94	6.73	2	-1	15	3.51	4.34
0	-12	13	9.37	8.65	1	4	8	19.35	17.25	1	13	11	3.66	3.99	2	-2	1	2.36	2.76
0	-12	15	4.46	4.94	1	4	10	3.96	4.01	1	13	13	6.28	6.42	2	-2	3	4.40	4.11
0	-12	17	9.74	9.29	1	4	11	7.29	6.81	1	14	1	8.82	9.12	2	-2	4	17.07	17.21

Table 3. Continued.

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
2	-2	5*	20.87	23.13	2	-6	3	3.77	3.27	2	-15	6	4.40	4.20	2	-9	11	5.77	5.43
2	-2	6	8.24	8.21	2	-7	3	4.89	4.30	2	-16	6	13.88	14.45	2	-10	11	11.68	11.24
2	-2	7	5.61	5.78	2	-8	3	8.89	9.13	2	-18	6	3.35	3.41	2	-13	11	7.25	7.07
2	-2	8	14.06	14.31	2	-9	3	4.03	3.92	2	-4	7	10.40	9.60	2	-14	11	3.91	3.95
2	-2	9	7.95	7.74	2	-10	3	4.54	5.00	2	-6	7	13.51	12.78	2	-15	11	2.59	1.91
2	-2	11	13.88	14.31	2	-11	3	3.87	2.31	2	-7	7	3.52	3.37	2	-17	11	5.96	5.35
2	-2	12	12.56	11.75	2	-12	3	10.57	11.06	2	-8	7	9.64	9.41	2	-7	12	10.94	10.80
2	-2	14	5.04	5.25	2	-13	3	12.42	12.78	2	-10	7	6.76	6.23	2	-8	12	10.04	8.86
2	-2	15	8.64	7.81	2	-14	3	12.74	13.59	2	-11	7	4.68	4.92	2	-10	12	15.11	14.03
2	-2	18	5.93	6.58	2	-15	3	4.90	4.19	2	-12	7	10.77	11.69	2	-11	12	6.05	6.90
2	-3	1	19.74	21.05	2	-17	3	2.96	3.61	2	-13	7	4.57	3.99	2	-12	12	5.61	5.28
2	-3	2	9.84	9.91	2	-19	3	6.73	6.77	2	-14	7	2.11	1.92	2	-13	12	3.66	2.25
2	-3	3	7.67	8.04	2	-20	3	6.22	8.07	2	-15	7	4.73	4.17	2	-15	12	3.89	4.21
2	-3	5	4.25	4.18	2	-6	4	6.08	5.53	2	-16	7	6.50	5.72	2	-16	12	7.18	7.83
2	-3	7	17.00	16.75	2	-7	4	16.54	16.96	2	-19	7	6.59	6.76	2	-3	13	2.52	2.78
2	-3	8	15.01	13.59	2	-8	4	15.86	14.61	2	-6	8	15.45	15.16	2	-4	13	18.87	19.80
2	-3	9	17.05	18.71	2	-10	4	18.17	18.21	2	-6	8	26.91	27.26	2	-5	13	14.08	13.52
2	-3	10	4.51	3.22	2	-11	4	9.36	9.95	2	-8	8	8.65	7.52	2	-6	13	5.94	6.20
2	-3	11	7.11	6.76	2	-12	4	11.80	11.02	2	-9	8	13.23	13.55	2	-7	13	5.38	4.71
2	-3	15	8.30	8.27	2	-14	4	3.65	3.27	2	-11	8	5.57	4.40	2	-8	13	4.68	4.64
2	-3	16	4.15	3.07	2	-15	4	3.99	4.72	2	-12	8	13.01	12.97	2	-12	13	7.58	7.73
2	-3	17	11.51	12.09	2	-16	4	12.73	13.60	2	-13	8	11.63	11.26	2	-13	13	11.53	11.10
2	-3	18	6.43	6.61	2	-17	4	3.37	3.01	2	-15	8	7.95	7.75	2	-14	13	14.00	14.53
2	-3	19	6.69	6.26	2	-18	4	6.30	6.35	2	-16	8	4.07	4.33	2	-15	13	5.35	5.02
2	-4	1	6.40	5.50	2	-19	4	6.24	6.07	2	-17	8	6.40	6.43	2	-6	14	7.36	7.12
2	-5	1	6.51	6.14	2	-20	4	7.87	8.56	2	-18	8	5.64	4.98	2	-7	14	7.80	7.72
2	-6	1	18.86	18.94	2	-4	5	9.19	7.32	2	-19	8	1.89	1.93	2	-8	14	4.46	4.30
2	-7	1	3.98	3.79	2	-5	5	9.61	9.86	2	-5	9	4.77	4.35	2	-10	14	12.17	13.15
2	-9	1	5.43	4.14	2	-6	5	5.74	5.73	2	-6	9	16.43	16.03	2	-11	14	4.32	4.68
2	-10	1	11.03	11.33	2	-7	5	12.42	10.49	2	-7	9	6.55	5.46	2	-13	14	3.81	3.37
2	-11	1	2.98	2.55	2	-8	5	19.20	20.49	2	-8	9	7.42	6.81	2	-6	15	8.63	8.35
2	-12	1	11.61	11.38	2	-9	5*	20.68	23.14	2	-10	9	5.24	5.04	2	-8	15	4.16	3.71
2	-14	1	8.78	8.67	2	-9	5	8.52	7.69	2	-11	9	5.66	4.88	2	-9	15	4.65	3.35
2	-15	1	8.47	9.27	2	-10	5	13.63	12.73	2	-12	9	12.99	12.30	2	-10	15	9.45	8.55
2	-16	1	6.80	7.23	2	-11	5	6.02	4.96	2	-14	9	4.93	4.58	2	-12	15	2.63	3.01
2	-18	1	2.70	2.37	2	-12	5	5.24	6.01	2	-15	9	7.59	7.52	2	-13	15	3.69	3.62
2	-19	1	7.47	7.44	2	-13	5	12.05	12.37	2	-16	9	7.78	6.66	2	-7	16	4.50	4.90
2	-20	1	2.38	2.36	2	-16	5	5.79	5.95	2	-4	10	5.75	5.23	2	-8	16	4.84	4.71
2	-4	2	9.69	10.30	2	-17	5	8.87	8.60	2	-7	10	8.19	8.28	2	-9	16	11.28	12.17
2	-6	2	15.48	16.28	2	-18	5	13.00	14.15	2	-9	10	15.06	13.24	2	-10	16	8.21	9.01
2	-7	2	7.49	7.29	2	-19	5	6.15	5.94	2	-10	10	6.76	7.50	2	-11	16	2.73	2.98
2	-9	2	8.35	8.16	2	-20	5	2.86	3.61	2	-13	10	4.33	3.78	2	-4	17	3.08	3.12
2	-10	2	12.76	13.34	2	-4	6	4.59	4.63	2	-14	10	4.26	3.71	2	-5	17	3.69	3.76
2	-12	2	7.46	7.77	2	-7	6	13.30	13.39	2	-15	10	4.38	3.93	2	-6	17	11.28	11.52
2	-13	2	8.24	8.58	2	-8	6	5.26	5.44	2	-16	10	13.35	12.06	2	-7	17	3.40	3.68
2	-15	2	7.21	7.48	2	-9	6	8.95	9.53	2	-4	11	4.89	4.47	2	-10	17	4.67	4.63
2	-17	2	2.99	3.04	2	-11	6	4.47	3.57	2	-5	11	3.59	3.09	2	-4	18	5.95	6.66
2	-19	2	3.24	2.14	2	-12	6	5.91	5.88	2	-6	11	5.90	6.16	2	-6	18	16.11	13.89
2	-20	2	3.29	3.91	2	-13	6	3.93	2.38	2	-7	11	5.47	4.82	2	-4	19	8.57	8.39
2	-4	3	26.89	27.93	2	-14	6	3.69	3.97	2	-8	11	8.46	8.20	2	-5	19	2.86	3.63
2	-5	3	15.74	15.86															

Table 4. Weight analysis obtained in the final cycle of the least squares refinement of Nb_2WO_8. w = weighting factor. $\Delta = ||F_{obs}| - |F_{calc}||$.

Interval F_{obs}	$\overline{w\Delta^2}$	Number of independent reflexions	Interval sin θ	$\overline{w\Delta^2}$	Number of independent reflexions
0.0 – 3.5	0.941	65	0.0 – 0.4595	1.096	102
3.5 – 4.5	0.816	76	0.4595 – 0.5790	0.792	89
4.5 – 5.5	1.067	66	0.5790 – 0.6627	1.126	67
5.5 – 6.5	1.099	54	0.6627 – 0.7294	1.036	58
6.5 – 8.0	0.821	65	0.7294 – 0.7858	0.790	52
8.0 – 9.5	1.066	64	0.7858 – 0.8350	1.306	43
9.5 – 12.0	1.395	58	0.8350 – 0.8790	0.746	50
12.0 – 15.0	1.104	53	0.8790 – 0.9190	0.982	46
15.0 – 19.0	0.861	55	0.9190 – 0.9558	0.725	47
19.0 – 35.0	0.825	31	0.9558 – 0.9900	1.678	33

of 0.065. In the final least squares cycles 6 strong reflexions were excluded rather than being corrected for extinction.

The structure factors were weighted according to Hughes' scheme.

The final values of atomic parameters, the observed and calculated structure factors and the weighting schemes are presented in Tables 2, 3, and 4, respectively.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of Nb_2WO_8 is visualized in Fig. 1. The oxygen network may be described as constructed of building units, each consisting of

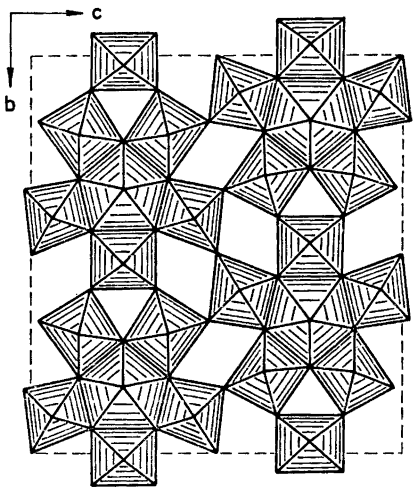

Fig. 1. The crystal structure of Nb_2WO_8 viewed along [100].

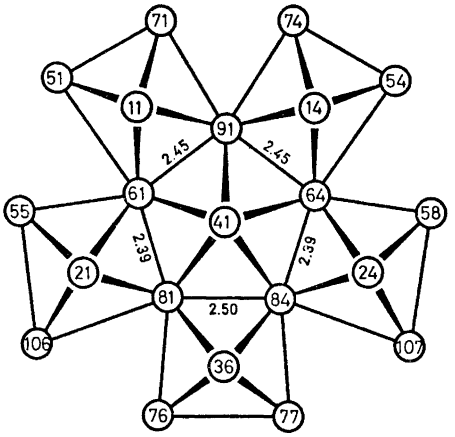

Fig. 2. The building unit of the pentagonal column. The circles represent oxygen atoms.

one pentagonal MO_7-bipyramid linked by equatorial edge-sharing to five MO_6-octahedra (see Fig. 2). Such units are further connected by corner-sharing in the same way as in the structure of $LiNb_6O_{15}F$. All the metal atoms in Nb_2WO_8 are displaced from $x = 0$ and this is associated with a small displacement of the oxygen atoms.

The interatomic distances with their standard deviations are given in Table 5 and the $M-O$ distances within the pentagonal bipyramid are shown in Fig. 3. The five $O-O$ distances, corresponding to edge-sharing between the pentagonal bipyramid and the octahedra, range from 2.39 Å to 2.50 Å and are quite similar to the corresponding distances in $LiNb_6O_{15}F$. The $O-O$ distances within the octahedra vary between 2.39 Å and 3.12 Å.

A different type of connection between the building block units described above is present in $NaNb_6O_{15}F$ ($NaNb_6O_{15}OH$) [7] but again the niobium atoms are situated in one plane.

When the building block units are stacked on top of each other, they form pentagonal columns running parallel to the shortest axis.

Table 5. Interatomic distances in Nb_2WO_8. Standard deviations are given within parentheses.

Metal – metal distances in Å		
$M(11)-M(41)$	3.257(3)	
$M(21)-M(41)$	3.378(3)	
$M(31)-M(41)$	3.279(4)	
Metal – oxygen distances in Å		Mean value
$M(11)-O(11)$	1.81(5)	
$-O(11)^a$	2.14(5)	
$-O(51)$	1.91(2)	1.97
$-O(61)^a$	1.98(2)	
$-O(71)$	1.95(2)	
$-O(91)$	2.04(1)	
$M(21)-O(21)$	1.77(4)	
$-O(21)^a$	2.18(4)	
$-O(55)^a$	1.89(2)	
$-O(61)^a$	2.11(2)	1.98
$-O(81)^a$	2.01(2)	
$-O(106)$	1.92(1)	
$M(36)-O(36)$	1.89(6)	
$-O(36)^a$	2.06(6)	
$-O(76)$	1.85(3)	
$-O(77)$	1.85(3)	1.95
$-O(81)$	2.01(2)	
$-O(84)$	2.01(2)	
$M(41)-O(41)$	1.88(6)	
$-O(41)^a$	2.07(6)	
$-O(61)$	2.04(2)	
$-O(64)$	2.04(2)	2.05
$-O(81)$	2.12(2)	
$-O(84)$	2.12(2)	
$-O(91)$	2.10(3)	

[a] Indicates that the atom belongs to the next unit cell.

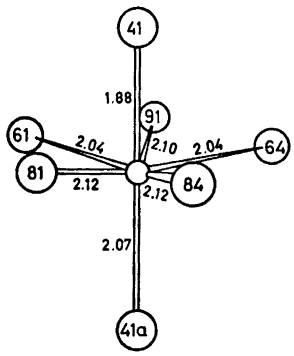

Fig. 3. The $M-O$ distances (Å) within the pentagonal MO_7 bipyramid.

Combinations of six- and seven-coordinated metal atoms have also been observed in structures of phases in the system $Nb_2O_5.WO_3 - WO_3$, for example in the structures of $Nb_{16}W_{18}O_{94}$ [8] and $Nb_{12}W_{11}O_{63}$,[9] which are composed of pentagonal columns linked to each other by means of additional strings of octahedra, running parallel to the columns.

A further discussions of possible combinations of the building block units and the presence of these in several crystal structures will soon be published elsewhere.

Table 6. Computer programs used for the crystallographic calculations. All programs are written in FORTRAN.

Program name and function. Computer.	Authors.
1. DATAP2. Lp- and absorption corrections. Preparative calculation for extinction correction according to Zachariasen's 1963-formula. IBM 360/75.	P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel. Modified by O. Olofsson and M. Elfström, Uppsala, Sweden. Inclusion of calculations for extinction correction by B. G. Brandt and S. Åsbrink, Stockholm, Sweden. Further modifications by B. G. Brandt and A. G. Nord, Stockholm, Sweden.
2. DRF. Fourier summations and structure factor calculations. IBM 360/75.	
3. LINUS. Full matrix least squares refinement of anisotropic extinction parameters, positional and thermal parameters, scale factors and partial occupancy factors. IBM 360/75.	A. Zalkin, Berkeley, USA. Modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden. Further modified by O. Lindgren, Göteborg and by A. G. Nord and B. G. Brandt Stockholm, Sweden.
4. DISTAN. Calculation of interatomic distances and bond angles with estimated standard deviations. IBM 360/75.	W. R. Busing, K. O. Martin and H. A. Levy, Oak Ridge, USA (program ORFLS). Modified by W. C. Hamilton and J. A. Ibers, New York, USA. Further modified by I. Carlbom, Stockholm, Sweden.
5. LAZY. Calculation of $\sin^2\theta$- and d-values from the measured reflexion sites of a Guinier powder photograph after internal standard correction. IBM 360/75, IBM 1800.	A. Zalkin, Berkeley, USA. Modified by A. G. Nord and B. G. Brandt, Stockholm, Sweden.
	A. G. Nord, Stockholm, Sweden.
6. PIRUM. Indexing of powder photographs and least squares refinement of unit cell parameters. IBM 1800.	P.-E. Werner, Stockholm, Sweden.

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