ACTA CHEMICA SCANDINAVICA 25 (1971) 2675–2687

A Refinement of the Crystal Structure of V_6O_{13}

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The crystal structure of V_6O_{13} has been refined on the basis of three-dimensional X-ray diffractometer data (Mo$K\alpha$ radiation). Least squares refinement has reached $R = 0.03$ for 436 measured independent reflections, for which $\sigma(F_o)/F_o \leq 0.20$. The structure proposed by Aebi [1] is confirmed. The V – O distances are in the range 1.642 – 2.276 Å ($\sigma \sim 0.003$ Å). The structure and the bond distances are compared with those reported in V_2O_5, $Li_{1-x}V_3O_8$, $Na_{2-x}V_6O_{15}$ and V_4O_9.

Until recently, the known oxides of vanadium, between the dioxide and divanadium pentoxide, only included V_6O_{13} and V_3O_7. The structure of V_6O_{13} was determined in 1948 by Aebi,[1] who described it as formed by VO_6 octahedra, linked together by edges and corners with V – O distances in the range 1.85 – 2.50 Å. A preliminary report [2] of the structure determination of V_3O_7 was published some time ago, and later on refined with a new data set taken with MoKα radiation.[3] The crystal structure of a new vanadium oxide, V_4O_9, has been reported by Wilhelmi and Waltersson.[4]

Since the positions of the oxygen atoms reported by Aebi [1] for V_6O_{13} were not determined with sufficient accuracy to allow a detailed comparison of the V – O bond lengths with those found in other vanadium oxides, we have undertaken a study, based on a new set of X-ray diffraction data, to determine the interatomic distances in V_6O_{13} more accurately.

PREPARATION

The starting materials were divanadium pentoxide (*p.a.*, LKB-Produkter, Stockholm, Sweden) and pure divanadium trioxide, kindly supplied by Dr. J. Galy (Service de Chimie Minérale de la Faculté des Sciences de Bordeaux, France). Single crystals of V_6O_{13} were prepared by treating a mixture of divanadium pentoxide and divanadium trioxide, with the gross composition $VO_{2.170}$, and water in a sealed platinum tube placed in an autoclave for 3 days at 600°C and 2 kb. The product contained several well shaped black prismatic crystals. The powder pattern from the crystals prepared in this way was identical with that of a polycrystalline specimen, prepared by heating the same oxide mixture at 650°C in a sealed platinum tube without water at normal pressure.

CELL DIMENSIONS, SINGLE CRYSTAL WORK AND DATA REDUCTION

Powder photographs were taken in a Guinier-Hägg focusing camera at 20°C with monochromatized Cu$K\alpha_1$ radiation and potassium chloride as internal standard ($a = 6.2930$ Å).[5] Refinement of the cell parameters was performed by the method of least squares, and the following cell dimensions and estimated standard deviations were obtained, in fair agreement with the values reported[1] earlier:

$a = 11.922(2)$ Å, $b = 3.680(1)$ Å, $c = 10.138(2)$ Å, $\beta = 100.87(2)°$, $V = 436.8$ Å^3.

The indexed powder pattern is listed in Table 1.

Table 1. Powder pattern of V_6O_{13}. Cu$K\alpha_1$ radiation. ($\lambda = 1.54050$ Å.)

h k l	d_{obs}	$10^5 \cdot \sin^2\theta_{obs}$	$10^5 \cdot \sin^2\theta_{calc}$	I_{obs}
0 0 1	9.92	603	598	v v w
2 0 0	5.850	1734	1731	w
2 0 $\bar{1}$	5.519	1948	1946	v v w
0 0 2	4.976	2396	2394	v w
1 1 0	3.511	4814	4814	v s
1 1 $\bar{1}$	3.370	5224	5221	v v w
0 0 3	3.320	5381	5387	s
1 1 1	3.252	5609	5605	v v w
4 0 $\bar{1}$	2.963	6757	6755	m
4 0 0	2.926	6931	6924	v v w
1 1 2	2.796	7590	7593	v v w
4 0 $\bar{2}$	2.757	7803	7783	v v w
3 1 $\bar{1}$	2.674	8297	8299	s
3 1 1	2.505	9454	9451	v v w
3 1 $\bar{2}$	2.496	9523	9519	v v w
1 1 $\bar{3}$	2.482	9630	9626	v w
0 0 5	1.9920	14952	14964	m
6 0 $\bar{1}$	1.9872	15024	15027	m
0 2 0	1.8401	17522	17526	s
2 2 0	1.7552	19258	19258	v v w
6 0 2	1.7102	20285	20278	v w
1 1 5	1.6911	20745	20739	v v w
0 0 6	1.6586	21568	21549	v v w
0 2 3	1.6094	22906	22914	m
4 2 $\bar{1}$	1.5629	24288	24282	w
7 1 $\bar{1}$	1.5454	24843	24843	s
3 1 5	1.5073	26114	26121	v w
7 1 1	1.4679	27534	27530	v v w
4 2 2	1.4457	28388	28381	v v w
6 0 4	1.4120	29757	29765	w
7 1 2	1.3911	30660	30670	v v w
6 2 $\bar{1}$	1.3503	32540	32553	s
6 2 2	1.2525	37821	37805	v v w
0 0 8	1.2444	38313	38309	v v w
0 2 6	1.2323	39069	39075	v v w
1 3 0	1.2198	39877	39867	v v w
7 1 4	1.2096	40552	40541	v v w

A well-shaped prismatic crystal with the dimensions: 0.168 (along the unique b axis) × 0.0128 × 0.0114 mm³ was selected and mounted along the b axis. Preliminary investigation by means of oscillation and Weissenberg photographs proved it to be suitable for data collection.

The intensity data were collected with a Siemens automatic diffractometer, using Nb-filtered Mo$K\alpha$ radiation and scintillation detector with pulse height discrimination.

Four standard reflections were measured ten times during the data collection period, and no significant variation in their intensities was found.

Each reflection was measured according to the 5-values technique. A constant scan range of $\Delta\theta = \pm 0.50°$ was used for all reflections.

An estimated standard deviation for the net intensity was obtained from the expression $\sigma(I) = (I_b + I_t)^{\frac{1}{2}}$, where I_t and I_b are the total and background counts. All $I(hkl)$ within two octants of the reciprocal lattice sphere out to $\theta = 30.0°$ were registered, giving a total number of 715 observations. The criterion that $\sigma(F_o)/F_o$ should be less than 0.20 was used to determine whether a reflection should be included in the refinement. The number of reflections with $\sigma(F_o)/F_o > 0.20$ was 258.

The intensities were corrected for Lorentz and polarization effects, as well as for absorption. The linear absorption coefficient $\mu = 65.9$ cm^{-1} was used in calculating absorption factor for each reflection. The factor (A) ranged from 0.914 to 0.935 in the formula $I = I_{obs}/A$. Mass absorption coefficients were taken from Ref. 6. Recent HFS atomic scattering factors [7] were used with the real and imaginary part of the anomalous dispersion correction being applied to the scattering curves. The calculations were performed on the computers IBM 1800 and IBM 360/75. The programs used are reviewed in Table 2.

REFINEMENT OF THE STRUCTURE

It was initially assumed that $C2/m$ (No. 12) was the correct space group.[1] The atomic positions given by Aebi were used as starting coordinates. The 28 positional parameters, the 10 isotropic temperature factors, and the scale factor were refined by full-matrix, least-squares calculations. The discrepancy index $R = ||\sum F_o| - |F_c||/\sum|F_o|$ for the measured data was initially 0.26. Convergence was rapid and led to $R = 0.06$. It became apparent that some strong low angle reflections were suffering from secondary extinction. The least squares procedure was now continued with the full matrix program LINUS, refining also a secondary extinction parameter. The final R value was 0.027. The weighted R_w value defined by the expression $R_w = (\sum w\Delta^2)^{\frac{1}{2}}/(\sum wF_o^2)^{\frac{1}{2}}$ was at this stage 0.024.

The structure factors were weighted according to the formula

$$w = (\sigma|F_o|^2 + a + b|F_o| + |c|F_o|^2 + d|F_o|^3 + e|F_o|^4)^{-1}$$

with $a = 2.0$, $b = -2.0 \times 10^{-2}$, $c = -1.5 \times 10^{-4}$, $d = 2.0 \times 10^{-6}$, and $e = 2.5 \times 10^{-8}$.

Attempts were also made to refine the structure of V_6O_{13} in the space groups Cm (No. 8) and $C2$ (No. 5). The coordinates thus obtained did not differ significantly from the values found for $C2/m$, which was therefore considered as the actual symmetry of the compound.

Table 2. Computer programs used for the crystallographic calculations. All programs written in FORTRAN IV.

No.	Program name and function. Computer.	Authors.
1	DRF. Fourier summations and structure factor calculations. IBM 360/75.	A. Zalkin, Berkeley, U.S.A. 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.
2	LALS. Full matrix least squares refinement of positional and thermal parameters and of scale factors. IBM 360/75.	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A. Modified by A. Zalkin, Berkeley, USA, and by J.-O. Lundgren, R. Liminga and C.-I. Brändén, Uppsala, Sweden. Further modified by O. Lindgren, Göteborg, and by B. G. Brandt and A. G. Nord, Stockholm, Sweden.
3	DISTAN. Calculation of interatomic distances and bond angles with estimated standard deviations. IBM 360/75.	A. Zalkin, Berkeley, U.S.A. Modified by A. G. Nord and B. G. Brandt, Stockholm, Sweden.
4	DATA. Reflexion data handling including storing on disk, correction of erroneous reflexions or inclusion of new ones in a data set stored on disk; index transformation. IBM 360/75.	B. G. Brandt, Stockholm, Sweden.
5	POWDER. Generation of $\sin^2\theta$ values. Indexing of powder lines from preliminary cell constants. Refinement of cell constants. IBM 360/75.	O. Lindqvist and F. Wengelin, Göteborg, Sweden. Modified by B. G. Brandt and A. G. Nord, Stockholm, Sweden.
6	DATAPH. Lp- and absorption corrections. Preparative calculations for anisotropic extinction corrections. IBM 360/75.	P. Coppens, L. Leiserowitz and D. Rabinowich, Rehovoth, Israel. Inclusion of calculations for anisotropic extinction correction by P. Coppens and W. C. Hamilton, New York, U.S.A. Modified by I. Carlbom, Stockholm, Sweden.
7	LINUS. Full matrix least squares refinement of anisotropic extinction parameters, positional and thermal parameters, scale factors and partial occupancy factors. IBM 360/75.	W. R. Busing, K. O. Martin and H. A. Levy, Oak Ridge, U.S.A. (program ORFLS). Modified by W. C. Hamilton and J. A. Ibers, New York, U.S.A. Further modified by I. Carlbom, Stockholm, Sweden.
8	SIP. Generation of steering paper tape for SIEMENS AED. IBM 360/75.	R. Norrestam, Stockholm, Sweden.
9	VIP. Angle settings for three-circle diffractometers. IBM 1800.	R. Norrestam, Stockholm, Sweden.
10	SIMSA. Interpretation of output on paper tape from SIEMENS AED and evaluation of intensities. IBM 1800.	R. Norrestam, Stockholm, Sweden.

The final positional and thermal parameters, together with their standard deviations, are shown in Table 3. A weighting scheme analysis from the final cycle of refinement is given in Table 4. Table 5 gives a list of the final observed and calculated structure factors for the 436 refined reflections. 94 reflections with F_c values ≥ 12, but excluded from the refinement because of the criterion $\sigma(F_o)/F_o$, are included in the table (marked with one asterisk (*)).

Reflections omitted due to: occasional disturbances in the data collection procedure or suffering from suspected multiple diffraction (**) and insufficient extinction correction (***) are also included.

Table 3. The crystal structure of V_6O_{13}.

Space-group: $C2/m$ (No. 12)

Unit cell dimensions: $a = 11.922$ (2) Å
$b = 3.680$ (1) Å
$c = 10.138$ (2) Å
$\beta = 100.87°$ (2)

Unit cell content: 2 V_6O_{13}

Point set		Numbering of the atoms
2(*b*)	$\frac{1}{2},0,0$	(*n*1)
	$0,\frac{1}{2},0$	(*n*2)
4(*i*)	$x,0,z$	(*n*1)
	$\bar{x},0,\bar{z}$	(*n*2)
	$\frac{1}{2}+x,\frac{1}{2},z$	(*n*3)
	$\frac{1}{2}-x,\frac{1}{2},\bar{z}$	(*n*4)

Atom (*n*)	Point set	$x+\sigma(x)$	y	$z+\sigma(z)$	$B+\sigma(B)$
V(1)	4(*i*)	0.35180 (12)	0	−0.00041 (14)	0.530 (18)
V(2)	4(*i*)	0.41262 (9)	0	0.36310 (11)	0.301 (19)
V(3)	4(*i*)	0.71322 (9)	0	0.36513 (11)	0.276 (19)
O(1)	4(*i*)	0.17883 (34)	0	0.00052 (41)	0.62 (7)
O(2)	4(*i*)	0.88194 (34)	0	0.38776 (41)	0.52 (7)
O(3)	4(*i*)	0.24898 (34)	0	0.40773 (41)	0.47 (7)
O(4)	2(*b*)	1/2	0	0	0.91 (11)
O(5)	4(*i*)	0.38604 (35)	0	0.19688 (44)	0.72 (8)
O(6)	4(*i*)	0.67817 (35)	0	0.20062 (42)	0.64 (8)
O(7)	4(*i*)	0.56262 (35)	0	0.40863 (44)	0.63 (7)

Table 4. Weight analysis obtained in the final cycle of the least squares refinement of V_6O_{13}. $\Delta = ||F_{obs}| - |F_{calc}||$, w = weighting factor. The $\overline{w\Delta^2}$ values have been normalized.

Interval F_{obs}	$\overline{w\Delta^2}$	Number of independent reflections	Interval $\sin\theta$	$\overline{w\Delta^2}$	Number of independent reflections
0.0 – 22.0	1.483	41	0.0 – 0.237	1.432	65
22.0 – 25.0	1.304	42	0.237 – 0.298	0.900	48
25.0 – 30.0	1.160	54	0.298 – 0.341	0.636	54
30.0 – 38.0	0.706	68	0.341 – 0.376	1.153	50
38.0 – 44.0	1.278	40	0.376 – 0.405	0.671	42
44.0 – 55.0	0.744	48	0.405 – 0.430	0.984	48
55.0 – 68.0	0.635	41	0.430 – 0.453	0.920	42
68.0 – 85.0	0.967	45	0.453 – 0.473	1.321	34
85.0 – 115.0	0.792	42	0.473 – 0.492	0.792	26
115.0 – 250.0	1.327	15	0.492 – 0.510	1.039	27

Table 5. Observed and calculated structure factors (see text).

H	K	L	F_o	F_c
0	0	1	40.1	37.9
0	0	2	90.1	85.7
0	0	3	219.6	221.0
0	0	4	70.8	70.3
0	0	6	96.5	97.7
0	0	7	34.4	34.6
0	0	8	129.2	127.8
0	0	9	27.3	25.4
0	0	10	35.9	37.2
0	0	11	102.7	101.4
0	0	13	25.4	20.9
0	0	14	71.7	71.0
2	0	-11	27.4	28.4
2	0	-9	29.0	30.2
2	0	-6	56.9	57.8
2	0	-3	60.6	60.0
2	0	-2	26.5	25.7
2	0	-1	45.0	43.6
2	0	1	39.9	38.5
2	0	2	53.3	53.1
2	0	3	23.8	23.1
2	0	5	82.9	82.0
2	0	8	42.4	41.6
2	0	10	29.1	30.6
2	0	11	19.9	19.2
2	0	13	23.0	21.8
4	0	-14	41.1	43.5
4	0	-13	37.4	36.0
4	0	-12	57.9	57.2
4	0	-11	48.7	47.7
4	0	-10	18.0	17.7
4	0	-9	94.2	94.5
4	0	-8	24.5	25.2
4	0	-6	155.7	154.5
4	0	-5	30.0	30.7
4	0	-4	67.9	68.6
4	0	-3	61.7	63.5
4	0	-2	57.4	55.9
4	0	0	84.6	81.3
4	0	1	41.0	39.7
4	0	2	99.3	100.1
4	0	4	27.4	28.0
4	0	5	138.0	135.6
4	0	6	36.3	35.8
4	0	7	23.9	21.4
4	0	8	73.1	74.3
4	0	9	29.7	29.7
4	0	10	76.6	76.1
4	0	11	21.3	20.7
4	0	12	34.5	31.0
6	0	-12	68.2	65.1
6	0	-11	25.6	25.2
6	0	-9	86.0	85.9
6	0	-7	59.0	60.2
6	0	-6	137.3	138.6
6	0	-5	45.3	44.7
6	0	-4	140.2	137.9
6	0	-3	48.9	48.9
6	0	-2	23.6	23.8
6	0	0	25.5	27.4
6	0	1	55.1	55.9
6	0	2	136.3	135.9
6	0	3	50.2	51.2
6	0	5	65.9	62.8
6	0	6	28.5	25.6
6	0	7	95.6	94.5
6	0	8	17.9	13.5
6	0	9	23.3	24.3
6	0	10	81.8	79.9
8	0	-12	26.4	23.8
8	0	-10	30.7	28.8
8	0	-7	41.6	42.2
8	0	-4	18.5	18.4
8	0	-2	27.2	26.9
8	0	-1	39.5	40.0
8	0	2	18.2	15.0
8	0	4	34.7	33.9
8	0	7	22.0	23.0
8	0	10	22.6	21.2
10	0	-12	30.4	30.4
10	0	-10	87.3	88.8
10	0	-9	35.1	33.4
10	0	-7	106.6	108.3
10	0	-6	36.3	35.8
10	0	-5	64.2	64.6
10	0	-4	37.0	39.2
10	0	-3	38.7	38.7
10	0	-2	114.9	115.6
10	0	-1	38.1	39.1
10	0	0	22.0	21.1
10	0	1	77.3	78.6
10	0	3	18.1	19.4
10	0	4	106.3	105.7
10	0	5	38.0	34.7
10	0	6	23.9	21.7
10	0	7	64.7	65.7
10	0	8	36.6	35.5
10	0	9	78.1	77.3
12	0	-10	22.2	24.3
12	0	-7	33.3	32.5
12	0	-5	34.3	35.1
12	0	-2	52.5	53.2
12	0	-1	18.1	12.6
12	0	0	20.4	16.5
12	0	1	34.5	37.6
12	0	3	38.3	36.0
12	0	6	32.3	31.8
14	0	-8	71.5	72.0
14	0	-5	49.9	49.8
14	0	-4	22.6	23.9
14	0	-3	37.7	41.8
14	0	-2	61.8	61.3
14	0	-1	24.5	22.1
14	0	0	41.3	42.2
14	0	3	72.7	74.3
1	1	-9	45.0	44.6
1	1	-8	37.2	35.3
1	1	-7	34.1	34.3
1	1	-6	87.4	88.8
1	1	-5	55.1	57.3
1	1	-2	19.7	15.5
1	1	-1	31.3	31.7
1	1	1	37.6	36.6
1	1	2	48.1	48.6
1	1	3	62.5	62.6
1	1	4	24.6	25.3
1	1	5	110.2	109.4
1	1	6	18.3	21.0
1	1	8	60.2	58.5
1	1	10	26.6	24.5
1	1	11	41.3	40.7
3	1	-14	65.9	66.0
3	1	-11	51.6	51.7
3	1	-10	40.8	44.0
3	1	-9	102.9	103.9
3	1	-8	35.0	38.8
3	1	-6	138.7	138.8
3	1	-5	39.2	39.9
3	1	-4	55.0	53.4
3	1	-3	29.0	35.4
3	1	-2	57.8	57.7
3	1	-1	111.3	109.6
3	1	0	95.1	95.0
3	1	1	53.9	52.0
3	1	2	39.0	44.6
3	1	3	36.5	36.3
3	1	4	27.3	28.4
3	1	5	141.3	142.3
3	1	6	18.3	20.0
3	1	8	97.0	97.7
3	1	10	61.8	60.6
3	1	11	48.1	46.2
3	1	12	58.5	57.7
3	1	13	69.6	67.3
5	1	-6	18.8	21.0
5	1	-1	28.0	27.1
5	1	1	18.2	18.6
7	1	-12	85.1	85.2
7	1	-10	57.1	57.9
7	1	-9	56.4	56.4
7	1	-8	39.7	41.0
7	1	-7	110.5	111.6
7	1	-6	72.9	74.4
7	1	-5	17.1	20.5
7	1	-4	130.1	131.0
7	1	-3	15.6	17.2
7	1	-2	35.5	35.6
7	1	0	50.5	51.6
7	1	1	78.9	78.1
7	1	2	80.6	81.2
7	1	3	40.4	38.9
7	1	4	154.5	155.2
7	1	5	22.3	22.6
7	1	7	92.2	91.9
7	1	9	47.2	45.5
7	1	10	66.4	65.3
7	1	11	22.1	21.2
9	1	-11	30.3	30.8
9	1	-10	53.0	53.3
9	1	-9	26.0	26.3
9	1	-7	51.9	51.9
9	1	-6	34.0	33.6
9	1	-5	27.5	27.4
9	1	-2	38.6	38.6
9	1	-1	20.1	20.2
9	1	1	27.7	26.4
9	1	4	56.4	57.2
9	1	7	43.1	43.8
9	1	8	31.1	31.3
9	1	9	30.7	31.9
9	1	10	23.7	18.5
11	1	-12	23.6	20.0
11	1	-10	54.8	55.7
11	1	-8	29.2	26.7
11	1	-7	72.6	73.9
11	1	-6	20.7	17.7
11	1	-5	50.7	54.1
11	1	-4	25.7	24.5
11	1	-2	98.4	98.1
11	1	1	61.2	62.3
11	1	3	50.2	52.1
11	1	4	51.6	51.1
11	1	5	19.6	19.6
11	1	6	42.8	42.9
13	1	-10	42.3	44.1
13	1	-9	24.9	27.3
13	1	-8	69.6	72.7
13	1	-7	42.6	43.7
13	1	-5	91.5	91.8
13	1	-2	115.4	116.4
13	1	0	58.1	59.9
13	1	1	50.9	52.5
13	1	2	33.3	33.9
13	1	3	109.5	108.6
13	1	6	73.4	74.4
0	2	1	26.7	25.6
0	2	2	55.2	55.5
0	2	4	52.8	53.9
0	2	6	77.4	77.9
0	2	7	30.2	30.5
0	2	8	107.0	107.1
0	2	9	22.8	21.2
0	2	10	29.3	29.7
0	2	11	92.1	90.8
2	2	-11	26.1	25.1
2	2	-9	28.5	25.4
2	2	-6	44.4	44.8
2	2	-3	44.5	44.7
2	2	-2	19.0	17.1
2	2	-1	27.7	27.7
2	2	0	58.1	56.5
2	2	1	26.9	26.0
2	2	2	37.6	38.6
2	2	3	18.0	18.1
2	2	5	60.9	62.4
2	2	8	38.0	35.6
2	2	10	27.5	26.3
4	2	-13	33.9	33.1
4	2	-12	54.4	52.4
4	2	-11	44.7	41.7
4	2	-9	82.6	82.0
4	2	-8	20.7	20.1
4	2	-6	120.0	122.3
4	2	-5	25.5	26.1
4	2	-4	54.6	54.5
4	2	-3	54.0	54.7
4	2	-2	43.1	42.5
4	2	1	26.5	28.6
4	2	2	84.9	83.9
4	2	4	18.9	21.4
4	2	5	109.8	108.5
4	2	6	28.7	30.0
4	2	7	24.9	20.4
4	2	8	64.3	63.7
4	2	9	26.7	26.7
4	2	10	69.8	68.1
6	2	-12	58.4	59.4
6	2	-11	22.3	21.0
6	2	-9	73.0	74.4
6	2	-7	50.6	50.6
6	2	-6	106.9	108.0
6	2	-5	36.6	36.9
6	2	-4	108.6	108.5
6	2	-3	35.3	35.3
6	2	-2	20.2	18.4
6	2	-1	182.0	184.7
6	2	0	18.6	22.2
6	2	1	42.0	41.9
6	2	2	106.5	106.4
6	2	3	42.7	42.1
6	2	4	114.7	116.5
6	2	5	52.2	52.1
6	2	6	20.9	23.1
6	2	7	82.3	81.9
6	2	9	24.6	20.2
6	2	10	71.4	72.7
8	2	-12	27.0	21.7
8	2	-10	27.2	25.8
8	2	-7	35.9	36.2
8	2	-2	22.5	21.6
8	2	-1	30.6	32.2
8	2	4	28.4	28.9
8	2	7	20.5	20.6
10	2	-10	82.6	81.2
10	2	-9	29.7	29.7
10	2	-7	94.6	94.9
10	2	-6	32.5	32.0
10	2	-5	54.8	55.9
10	2	-4	35.2	36.1
10	2	-3	34.7	34.0
10	2	-2	97.8	97.9
10	2	-1	30.4	32.3
10	2	0	18.2	18.3
10	2	1	69.7	70.4
10	2	4	91.1	92.7
10	2	5	32.4	31.4
10	2	7	60.3	59.7
10	2	8	35.6	32.9
12	2	-7	28.0	28.6
12	2	-5	27.4	30.7
12	2	-2	44.7	45.7
12	2	1	34.1	32.7
12	2	3	32.8	31.8
12	2	6	29.4	28.8
12	2	-5	42.2	46.1
14	2	-4	21.1	22.2
14	2	-3	35.3	37.7
14	2	-2	52.3	55.3
14	2	-1	22.9	20.7
14	2	0	38.0	39.9
14	2	3	67.2	67.7
1	3	-11	53.4	52.4
1	3	-9	32.9	33.5
1	3	-8	29.2	28.1
1	3	-7	24.3	25.3
1	3	-6	61.0	60.0
1	3	-5	33.4	34.3
1	3	-3	60.8	61.3
1	3	0	91.5	90.2
1	3	1	21.0	22.4
1	3	2	90.5	91.0
1	3	3	42.1	41.7
1	3	4	18.7	18.8
1	3	5	68.1	69.3
1	3	8	47.2	45.2
1	3	10	23.1	18.3
1	3	11	35.2	34.0
3	3	-11	44.5	42.3
3	3	-10	34.4	35.8
3	3	-9	80.1	80.3
3	3	-8	23.0	23.4
3	3	-6	96.8	97.5
3	3	-5	21.0	25.5
3	3	-4	33.0	32.8
3	3	-3	43.1	41.7
3	3	-2	34.8	37.7
3	3	-1	69.2	68.7
3	3	0	62.5	60.6
3	3	1	33.6	34.6
3	3	2	49.3	47.3
3	3	3	22.9	22.7
3	3	4	18.7	18.6
3	3	5	100.0	99.8
3	3	7	19.2	15.8
3	3	8	77.5	75.8
3	3	9	36.0	36.5
3	3	10	50.0	49.5
5	3	-10	45.4	46.5
5	3	-9	45.0	45.7
5	3	-8	33.0	33.1
5	3	-7	82.9	83.3
5	3	-6	50.2	50.3
5	3	-4	93.6	94.2
5	3	-2	25.3	22.2
5	3	-1	128.1	128.6
5	3	1	55.4	54.6
5	3	2	59.4	58.7
5	3	3	31.9	30.5
5	3	4	109.6	110.3
7	3	7	75.1	74.6
7	3	-10	34.7	34.0
7	3	-9	22.2	19.9
7	3	-7	41.2	41.7
7	3	-6	24.8	24.8
7	3	-5	21.7	19.8
7	3	-4	19.7	14.9
7	3	-3	22.2	22.1
7	3	-2	28.7	29.4
7	3	0	18.9	17.8
7	3	1	22.0	24.0
7	3	4	45.6	45.9
7	3	7	37.9	36.8
9	3	-7	58.1	58.7
9	3	-5	41.0	43.3
9	3	-2	76.3	74.9
9	3	1	52.7	50.0
9	3	3	37.2	40.9
9	3	4	38.8	41.2
9	3	-5	76.1	76.2
9	3	-2	91.6	93.7
9	3	-1	36.3	34.7
9	3	0	47.2	48.9
9	3	1	42.5	43.4
9	3	3	19.9	16.4
9	3	4	28.8	28.9
9	3	-4	92.2	92.7
9	3	-1	34.6	35.4
9	3	1	98.1	97.6
9	3	3	52.1	50.9
9	3	4	23.6	24.1
9	3	7	76.1	76.4
9	3	-3	22.4	18.2
9	3	-2	28.0	28.5
9	3	1	29.1	27.6
9	3	4	31.5	31.2
9	3	7	19.4	15.0
9	3	8	24.8	23.1
9	3	9	39.8	39.0
11	3	-4	25.4	26.2
11	3	-2	78.9	80.3
11	3	1	29.1	27.9
11	3	3	15.0	19.5
11	3	4	38.0	35.2
11	3	7	74.1	74.1
13	3	-2	25.9	27.5
13	3	1	76.1	74.1
13	3	3	58.1	57.6
2	4	2	72.4	72.3
2	4	4	13.8	8.4
2	4	7	71.6	69.1
2	4	8	24.2	26.6
2	4	10	71.3	70.5
4	4	-3	23.5	19.8
6	4	-1	109.9	109.2
6	4	0	22.3	15.9
6	4	1	23.6	24.9
6	4	2	69.3	68.6
6	4	3	27.5	30.2
6	4	4	77.5	75.0
6	4	5	36.8	36.2
6	4	-7	25.5	26.7
6	4	-1	21.5	21.2
6	4	4	25.4	20.9
8	4	-4	27.2	29.1
8	4	-3	27.0	26.8
8	4	-2	70.1	70.9
8	4	-1	22.0	22.1
8	4	1	55.0	55.2
8	4	-3	41.8	39.8
8	4	0	51.5	52.5
8	4	3	23.2	27.0
3	5	-1	42.9	42.9
3	5	0	36.5	38.2
3	5	1	25.5	23.9
3	5	2	37.8	36.8

H	K	L	F_c
2	0	11	25
2	0	13	8
2	0	15	10
2	0	16	10
2	0	17	10
2	0	18	10
2	0	19	10
4	0	16	10
4	0	17	10
4	0	18	12
4	0	19	12
6	0	18	12
6	0	18	12
6	0	18	12
6	0	18	12
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8	0	18	12
8	0	18	12
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14	0	18	12
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3	1	18	17
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5	1	18	17
7	1	18	17
7	1	18	17
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9	1	18	17
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13	1	18	17
13	1	18	17
2	2	18	17
2	2	18	17
4	2	18	17
4	2	18	17
6	2	18	17
6	2	18	17
8	2	18	17
8	2	18	17
10	2	16	10
1	5	1	15
1	5	2	19
3	5	2	26

H	K	L	F_c
2	0	0	86
4	0	1	175
1	1	11	64
1	1	3	92
9	1	0	167
3	1	13	60
3	1	12	52
3	1	7	28

H	K	L	F_c
0	0	5	236
6	0	4	149
0	2	0	294

H	K	L	F_c
2	2	1	17
2	2	2	13
2	2	11	16
2	2	8	14
2	2	6	21
2	2	10	22
2	2	6	14
2	2	4	14
2	2	0	14
2	2	2	17
2	2	4	12
2	2	2	18
2	2	4	13
2	2	6	15
2	2	8	16
2	2	10	14
2	2	12	16
2	2	14	20
2	2	16	13
2	2	18	14
2	2	20	13
2	2	22	17
4	2	1	14
4	2	3	14
4	2	5	17
4	2	7	15
4	2	9	19
4	2	11	19
4	2	13	22
4	2	15	15
4	2	17	20
4	2	19	13
4	2	21	14
4	2	23	14
6	2	0	22
6	2	2	14
6	2	4	16
6	2	6	19
6	2	8	14
6	2	10	14
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6	2	18	22
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8	2	11	14
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8	2	15	14
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8	2	21	14
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12	2	18	14
12	2	20	14
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3	3	14	14
3	3	16	14
3	3	18	14
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5	3	19	14
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7	3	13	14
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7	3	17	14
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9	3	10	14
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9	3	18	14
9	3	20	14
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11	3	5	14
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11	3	9	14
11	3	11	14
11	3	13	14
11	3	15	14
11	3	17	14
11	3	19	14
13	3	0	14
13	3	2	14
13	3	4	14
13	3	6	14
13	3	8	14
13	3	10	14
13	3	12	14
13	3	14	14
13	3	16	14
13	3	18	14
13	3	20	14
1	5	3	158
1	5	5	170
1	5	7	151

A three-dimensional difference Fourier synthesis was computed in sections 0.3 Å apart along the *b* axis. The function showed no unusual features and no signs of any significant anisotropy of the thermal vibration. The residual peaks showed a maximum height of ~ 14 % of the medium oxygen peak in the corresponding oxygen electron density maps ($F_{obs} - F_{metal}$-synthesis). Since the calculated isotropic temperature factors of all atoms are low, any anisotropy must be low in an absolute sense.

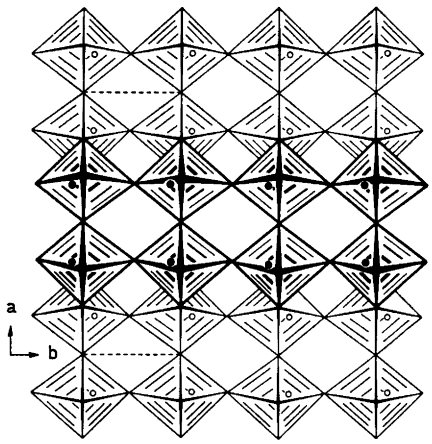

Fig. 1. The crystal structure of V_2O_5, projected on (001). It is regarded as built up of distorted VO_6 octahedra at two levels, joined by corners and edges. The extension of the unit cell is indicated by the broken lines.

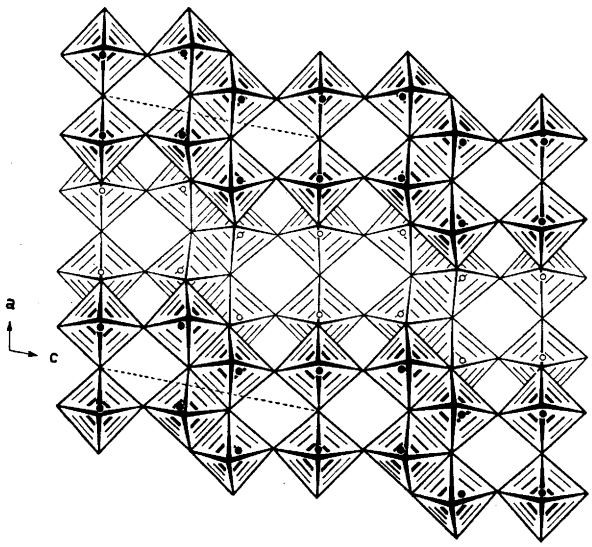

Fig. 2. The crystal structure of V_6O_{13}, projected on (010).

DISCUSSION

The structure of V_6O_{13} can be visualized as composed of distorted octahedra, connected by sharing corners and edges as illustrated in Figs. 2 and 3. For comparison, the structure of V_2O_5 is shown in Fig. 1. There are three crystallographically non-equivalent vanadium and seven non-equivalent oxygen atoms in the structure of V_6O_{13}. For principles of the numbering of the atoms, see Table 3. It is convenient, when discussing the details in the structure, to consider it as composed of two kinds of structural elements, as shown in Fig. 3.

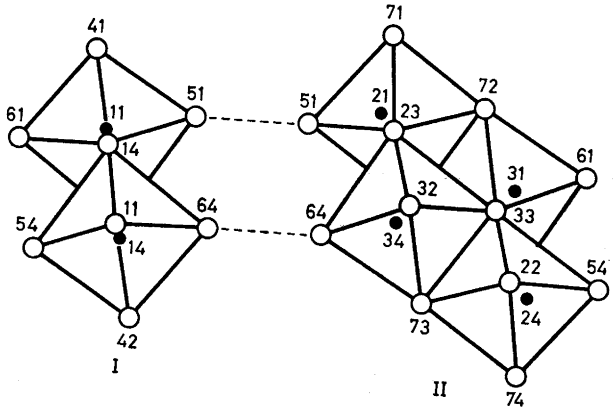

Fig. 3. The two types of structure elements that can be distinguished in V_6O_{13}. The elements form single zig-zag strings (I) and double zig-zag ribbons (II) with infinite extension normal to the plane of the paper. For numbering of the atoms, see Table 3.

The $V(1)O_6$ octahedra are joined by edge-sharing among themselves, forming single zig-zag strings running in the *b* direction (Fig. 3, I). By corner-sharing, the strings link together, forming single sheets parallel to the *ab* plane. The $V(2)O_6$ and $V(3)O_6$ octahedra also form zig-zag strings, running in the *b* direction by edge-sharing, but they are joined by edge-sharing in the *ac*-plane to double zig-zag strings or ribbons, extending along *b* (Fig. 3, II). By further edge-sharing (also in the *ac*-plane), these ribbons are joined together, forming double sheets parallel to the *ab*-plane. The single and double sheets are joined by additional common corners, forming a three-dimensional lattice (Fig. 2).

The structures of V_2O_5,[8,9] $Li_{1+x}V_3O_8$,[10] $Na_{2-x}V_6O_{15}$[10,11] and also V_4O_9[4] are related to that of V_6O_{13}. The structure of V_2O_5 (see Fig. 1) contains single strings (structure element I, Fig. 3) of vanadium-oxygen polyhedra, built up in the same manner as the $V(1)O_6$ octahedra in V_6O_{13}. By corner-sharing, identical strings are linked together, forming sheets. The actual structure shows, however, a considerable distortion from a regular octahedral coordination towards a bipyramidal arrangement (*vide infra*). However, in order to facilitate the comparison, the bipyramids are regarded as distorted VO_6 octahedra in Fig. 1.

Table 6. Interatomic distances (in Å) and bond angles in V_6O_{13}. Standard deviations in the last decimal place are given within parentheses. For principles of the numbering of the atoms, see Table 3.

(a) *Structure element I*, the single zig-zag string

Metal oxygen distances

V(11) – O(41)		1.766 (1)
– O(14)	(2×)	1.876 (1)
– O(51)		1.964 (5)
– O(61)		1.993 (4)
– O(11)		2.064 (4)

Bond angles			Bond angles at V(1)	Distances between the oxygen atoms
O(41) – V(11) – O(11)			179.6 (2)	3.830 (4)
O(41)	O(14)	(2×)	101.2 (2)	2.815 (3)
O(41)	O(51)		89.0 (2)	2.618 (4)
O(41)	O(61)		89.4 (2)	2.649 (4)
O(11)	O(14)	(2×)	78.8 (2)	2.504 (5)
O(11)	O(51)		90.7 (2)	2.865 (6)
O(11)	O(61)		91.0 (2)	2.894 (6)
O(14)	O(14)		157.6 (3)	3.680 (1)
O(14)	O(51)	(2×)	90.2 (2)	2.721 (4)
O(14)	O(61)	(2×)	90.1 (2)	2.740 (4)
O(51)	O(61)		178.4 (2)	3.958 (6)

Metal-metal separations (<3.50 Å)

V(11) – V(14)	3.047 (2)

(b) *Structure element II*, the double zig-zag ribbon

Metal-oxygen distances

V(21) – O(51)		1.655 (5)
– O(71)		1.761 (4)
– O(23)	(2×)	1.902 (1)
– O(32)		2.084 (4)
– O(72)		2.277 (5)
V(31) – O(61)		1.641 (4)
– O(33)	(2×)	1.919 (1)
– O(72)		1.928 (4)
– O(22)		1.981 (4)
– O(32)		2.261 (4)

Bond angles			Bond angles at V(21) and V(31)	Distances between the oxygen atoms
O(51) – V(21) – O(32)			102.3 (2)	2.925 (6)
O(51)	O(23)	(2×)	97.4 (2)	2.677 (4)
O(51)	O(71)		104.9 (3)	2.708 (6)
O(51)	O(72)		176.5 (2)	3.930 (6)
O(32)	O(23)	(2×)	76.1 (2)	2.462 (4)
O(32)	O(71)		152.8 (2)	3.738 (6)
O(32)	O(72)		74.1 (2)	2.633 (6)
O(23)	O(23)		150.7 (3)	3.680 (1)
O(23)	O(71)	(2×)	100.2 (2)	2.810 (4)
O(23)	O(72)	(2×)	81.8 (2)	2.751 (4)
O(71)	O(72)		78.6 (3)	2.589 (9)
O(61) – V(31) – O(32)			176.8 (2)	3.901 (6)
O(61)	O(33)	(2×)	103.4 (2)	2.800 (4)

Table 1. Continued.

O(61)	O(22)		100.1 (2)	2.786 (6)
O(61)	O(72)		99.4 (3)	2.728 (6)
O(32)	O(33)	(2×)	77.2 (2)	2.621 (6)
O(32)	O(22)		83.1 (2)	2.821 (6)
O(32)	O(72)		77.4 (2)	2.633 (6)
O(33)	O(33)		146.9 (3)	3.680 (1)
O(33)	O(22)	(2×)	78.3 (2)	2.462 (4)
O(33)	O(72)	(2×)	97.2 (2)	2.886 (4)
O(22)	O(72)		160.5 (2)	3.852 (6)

Metal-metal separations (< 3.50 Å)

V(21) – V(34)	(2×)	3.009 (1)
– V(22)		3.141 (2)
– V(31)		3.377 (2)
V(31) – V(24)	(2×)	3.009 (1)
– V(34)	(2×)	3.275 (2)
– V(21)		3.377 (2)

The structures of the vanadium bronzes $Li_{1+x}V_3O_8$ and $Na_{2-x}V_6O_{15}$, investigated several years ago by Wadsley,[10,11] contain double zig-zag ribbons of VO_6 octahedra (Fig. 3, II), as well as strings of VO_5 bipyramids (Fig. 3, II), arranged in different ways, to provide room for the alkali ions. A survey of the V – O distances is given in Table 7 (see also Table 8). The structure elements I and II will now be discussed in turn. A further discussion, also including V_3O_7 and V_4O_9, will be given elsewhere.[3]

Table 7. The observed V – O distances (in Å) in the single zig-zag strings (I) and the double zig-zag ribbons (II) in V_6O_{13}, compared with the corresponding values found in $Li_{1+x}V_3O_8$,[10] $Na_{2-x}V_6O_{15}$,[11] and V_4O_9.[4] Standard deviations within parentheses.

	V_6O_{13}	$Li_{1+x}V_3O_8$	$Na_{2-x}V_6O_{15}$	V_4O_9	
I	1.766 (1)	1.78 (3)	1.78 (5)	1.91 (1)	1.94 (2)
	1.876 (1)	1.88 (3)	1.91 (5)	1.88 (1)	1.92 (1)
	1.876 (1)	1.88 (3)	1.91 (5)	1.88 (1)	1.92 (1)
	1.964 (5)	1.60 (3)	1.56 (5)	1.64 (2)	1.66 (2)
	1.993 (4)	2.86 (3)	2.68 (5)	2.50 (2)	3.00 (2)
	2.064 (4)	2.06 (3)	2.00 (5)	1.94 (2)	1.96 (2)
	V_6O_{13}	$Li_{1+x}V_3O_8$	$Na_{2-x}V_6O_{15}$	V_4O_9	
II	1.761 (4)	1.59 (3)	1.58 (5)	1.63 (2)	
	1.902 (1)	1.88 (3)	1.89 (5)	1.89 (1)	
	1.902 (1)	1.88 (3)	1.89 (5)	1.89 (1)	
	1.655 (5)	1.99 (3)	1.80 (5)	1.99 (2)	
	2.277 (5)	1.96 (3)	2.16 (5)	1.98 (1)	
	2.084 (4)	2.26 (3)	2.34 (5)	2.23 (2)	
	1.928 (4)	1.72 (3)	1.95 (5)	1.87 (1)	
	1.919 (1)	1.88 (3)	1.89 (5)	1.90 (1)	
	1.919 (1)	1.88 (3)	1.89 (5)	1.90 (1)	
	1.641 (4)	1.64 (3)	1.56 (5)	1.60 (2)	
	2.261 (4)	2.36 (3)	2.32 (5)	2.40 (2)	
	1.981 (4)	2.10 (3)	2.01 (5)	2.02 (1)	

I. This structure element, a single zig-zag string of octahedra sharing edges and corners, is very common and occurs in many binary and ternary vanadium oxide structures. Each octahedron shares two edges and has three vertices in common with other octahedra. The distortion of the octahedral coordination for V_6O_{13} around the vanadium atoms, apparent from Fig. 3 I, is demonstrated by the differences in the metal-oxygen distances listed in Table 6a. The metal atoms are displaced from the octahedral centres in such a way that the V – V distances across the shared edges are increased. As a consequence of this displacement, the V – O bonds within the octahedra vary from 1.77 Å to 2.06 Å (mean value 1.92 Å) in length. It can be seen that the range of bond lengths is significantly smaller for the $V(1)O_6$ octahedron, as compared to corresponding distances found in structure element II (Table 6b). This reflects the different function of the $V(1)O_6$ octahedra in the structure. The V – O distances are in good agreement with the values observed [12] in VO_2 (1.76 – 2.06 Å, mean value 1.94 Å, see Table 8). The V(1) – V(1) distances across the shared edges are 3.05 Å. The O – O separation ranges from 2.50 Å to 2.89 Å. The O(11) – O(14) distance is as short as expected for an edge shared between two polyhedra.

II. The double zig-zag ribbon (Fig. 3, II), also a common structural element, is composed of two different octahedra. Each $V(2)O_6$ octahedron shares four edges and has one vertex in common. The corresponding numbers for the $V(3)O_6$ octahedra are five and one. It is seen from Table 6b that the tendency towards 5-coordination is pronounced. If the two long bonds V(21) – O(72) and V(31) – O(32) are disregarded, the double zig-zag ribbon of octahedra changes into two separate single chains of edge-sharing square pyramids, running in the *b*-direction. The short *A*-bonds (nomenclature according to Ref. 13) are in the range 1.64 – 1.65 Å, and the basal *B*-bonds are in the ranges 1.76 – 2.08 Å (mean value 1.91 Å) for $V(2)O_6$, and 1.92 – 1.98 Å (mean value 1.93 Å) for $V(3)O_6$. The sixth weak bonds (bond type *C*) are 2.28 and 2.26 Å, respectively. The square pyramid configuration is very common for tetravalent and pentavalent vanadium compounds, and the values found in this investigation for the V(2) and V(3) polyhedra are in close agreement with the mean values given by Evans and Block:[13] *A* bonds 1.60 Å, *B* bonds 1.91 Å.

The character of the vanadium-oxygen bonds in VO_2(mon), V_6O_{13}, V_3O_7, and V_2O_5 has been estimated by means of the empirical logarithmic relation between bond length d_n and bond number n, introduced by Pauling:[14]

$$d_n - d_1 = 2k \log n$$

This formula was used by Byström and Wilhelmi,[15] and by Evans,[16] on several vanadium oxygen compounds. Later on, Kihlborg [17] has demonstrated that the same relation is applicable to molybdenum oxides.

If it is assumed that $\sum n$ is 4 and 5 for the vanadium atoms in VO_2(mon)[12] and V_2O_5,[9] respectively, the values of the constants d_1 and k will have values close to 1.789 and 0.390 Å. The single bond distance, 1.789 Å, *viz.* the distance to an oxygen atom equally shared by two vanadium atoms, is quite reasonable and in fair agreement with the value used by Evans [16] ($d_1 = 1.81$ Å). The value of k is very close to that used by earlier authors. The result of a bond number calculation for V_6O_{13} is given in Table 8.

Too much attention should not be paid to the individual values of bond numbers obtained in this way. There is, however, a trend in the values which is in accordance with the assumption based on chemical arguments (*vide infra*), that the V^{4+} atoms are preferentially located in the V(3) and V(1) octahedra, whereas the V^{5+} atoms are mainly located inside the V(2) polyhedra. Thus the observed bond number sums in V_6O_{13} for the V(2) and V(3) atoms are 4.67 and

Table 8. Estimated bond distributions in V_6O_{13} and related vanadium oxygen compounds, calculated according to the expression $d_n = 1.789 - 0.78 \log n$.

Structure	d_n (Å)		n	$\sum n$ (observed)		$\sum n$ (expected)
VO_2 (mon)	1.762		1.08			
	1.865		0.80			
	1.892		0.74			
	2.015		0.51			
	2.026		0.50			
	2.063		0.45	4.08		4.00
V_6O_{13} V(1)	1.766		1.07			
	1.876	(2×)	0.77			
	1.964		0.60			
	1.993		0.55			
	2.064		0.44	4.20		
V(2)	1.655		1.48			
	1.761		1.09			
	1.902	(2×)	0.72			
	2.084		0.42			
	2.277		0.24	4.67		
V(3)	1.641		1.55			
	1.919	(2×)	0.68			
	1.928		0.66			
	1.981		0.55			
	2.261		0.25	4.37		
				4.41	(mean value)	4.33
V_2O_5	1.585		1.83			
	1.780		1.03			
	1.878	(2×)	0.77			
	2.021		0.50			
	2.785		0.05	4.95		5.00

4.37, respectively, significantly larger than for the V(1) atoms, *viz.* 4.20. It seems relevant to compare the result of this bond number calculation with investigations of Mo substituted crystals of $Na_{2-x}V_6O_{15}$, reported recently.[18,19] It was found there, that the three crystallographically distinguishable sites are not chemically equivalent. It was assumed that the Mo atoms enter the structure as Mo^{6+} ions, substituting for V^{5+} ions, and it was also found that the Mo atoms substitute exclusively into one of the two octahedra, forming the double zig-zag chain. This site corresponds to the V(2) octahedron in the structure of V_6O_{13} with the bond number 4.67.

The structure of V_6O_{13} can be visualized in terms of two different crystallographic shear mechanisms in a basic ReO_3-type arrangement of atoms. In V_2O_5, the shear planes separate narrow slabs of ReO_3-type extending over two octahedra only. This kind of shear has been characterized as of the V_2O_5-type.[20] The structure represents the end member ($n=2$) of a homologous series M_nX_{3n-1}.[21] If another set of shear planes, perpendicular to the first, are introduced in the V_2O_5 structure, the net result is the loss of more oxygen, and the structure of V_6O_{13} is formed. This phase appears to be the only known member ($n=3$) of a series $V_{2n}O_{5n-2}$. Electron microscope observations[22,23] and LEED studies[24] seem to give some experimental evidence for a dislocation mechanism for the production of shear planes in V_2O_5. However, recent electron microscope studies by Tilley and Hyde[25] have not given any support to the hypothesis of a direct transformation of V_2O_5 to V_6O_{13}. The existence of oxides intermediate in composition between V_2O_5 and V_6O_{13}, *e.g.* V_3O_7 and V_4O_9, also makes such a transformation less probable.

Acknowledgements. We wish to thank Professor Arne Magnéli for his stimulating interest in these studies. The investigation forms part of a research program, financially supported by the *Swedish Natural Science Research Council.*

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Received December 30, 1970.