

Vanadium Pentoxide — a Compound with Five-Coordinated Vanadium Atoms

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In the attempts to solve the structure of CrO_3 (Byström and Wilhelmi¹) it was found that the calculations of the atomic parameters in one direction could be considerably simplified if it was assumed that the distance O—O within the oxygen tetrahedron around the chromium atoms was not shorter than 2.4 Å. A survey of the distances in already known structures showed that in structures with tetrahedra or octahedra around the central atom the shortest O—O distances are generally 2.4 Å or longer. However, in V_2O_5 according to Ketelaar's determination² there are considerably shorter O—O distances (of only 2.14 Å), and therefore a recalculation of the atomic parameters in that compound was of interest.

The dimensions of the unit cell are according to Ketelaar $a = 11.48 \pm 0.01$ Å, $b = 4.36 \pm 0.005$ Å and $c = 3.55 \pm 0.005$ Å. The structure which he suggests is described in C_{2v}^7 - $Pmnn$ with the atoms in the following positions:

4 V in 4 (b): x, y, z	$x = 0.148$	$y = 0.097$	$z = 0$
4 O in 4 (b): x, y, z	$x = 0.148$	$y = 0.45$	$z = 0.92$
4 O in 4 (b): x, y, z	$x = 0.20$	$y = 0.03$	$z = 0.46$
2 O in 2 (a): $0, y, z$		$y = 0.03$	$z = 0.89$

This arrangement leads, according to Ketelaar, to a structure built up by a two-dimensional network of tetrahedra in the xz -plane. However, Machatschki³ has suggested that the structure is composed of double chains of the composition $(\text{V}_2\text{O}_5)_\infty$.

THE STRUCTURE DETERMINATION

From powder photographs taken in focussing cameras the following cell dimensions were calculated (Cr—K, $\lambda_a = 2.2909 \text{ \AA}$) $a = 11.519 \pm 0.006 \text{ \AA}$, $b = 4.373 \pm 0.002 \text{ \AA}$, $c = 3.564 \pm 0.002 \text{ \AA}$.

Weissenberg photographs of the $hk0$, $hk1$, $h0l$, and $h1l$ reflexions (Cu—K) showed that the space group must be D_{2h}^{13} or C_{2v}^7 , as was also found by Ketelaar.

The values of $|F_{\text{obs}}|$ were calculated according to the formula $|F_{\text{obs}}| = K \sqrt{\frac{I}{PL}}$. The value of K was adjusted so that for each layer line $\sum |F_{\text{obs}}| = \sum |F_{\text{calc}}|$. The scattering factors of V^{5+} and O^{2-} were used in the calculations of F_{calc} . No corrections for the decrement in $f_{v^{5+}}$, due to the wave length of the used radiation, were made. However, the bonds in V_2O_5 are probably to a large extent covalent and thus the scattering factor of $f_{v^{5+}}$ is too low. Hence the decrement in the f values is, to a certain extent, allowed for.

The xy -projection has in both these space groups a centre of symmetry. A recalculation of the F values of the $hk0$ reflexions with Ketelaar's parameters showed that the agreement with the observed values was so good that the signs of the structure factor of most of the reflexions could be established. Already in the second calculation of the projection of the electron density all reflexions were used and, as the confirmatory calculation of the F -values showed, with correct signs. The final adjustment of the parameters was made from a careful trial and error process.

The parameters in the xy -plane are:

$$\begin{array}{llll}
 4 \text{ V} : 2\pi x_1 = 53.5^\circ \pm 0.5^\circ & x_1 = 0.1486 \pm 0.0015 & 2\pi y_1 = 38^\circ \pm 1^\circ & y_1 = 0.105 \pm 0.003 \\
 4 \text{ O}_1 : 2\pi x_2 = 53.5^\circ \pm 1.5^\circ & x_2 = 0.149 \pm 0.004 & 2\pi y_2 = 165^\circ \pm 5^\circ & y_2 = 0.458 \pm 0.014 \\
 4 \text{ O}_2 : 2\pi x_3 = 115^\circ \pm 1.5^\circ & x_3 = 0.320 \pm 0.004 & 2\pi y_3 = 0^\circ \pm 5^\circ & y_3 = 0.000 \pm 0.014 \\
 2 \text{ O}_3 : & & 2\pi y_4 = 0^\circ \pm 2^\circ & y_4 = 0.000 \pm 0.006
 \end{array}$$

The errors in the parameters are partly deduced from the trial and error process (V and O_2) and partly from the electron density projection (O_1 and O_3). As will be seen from Table 1, the largest differences $|F_{\text{obs}}| - |F_{\text{calc}}|$ are found for two strong reflexions at low glancing angles (200 and 010). This is certainly due to the difficulty of estimating the intensities and not to parameter-errors, and therefore in the final Fourier synthesis, F_{calc} was used instead of F_{obs} for these reflexions.

As will be seen from Fig. 1 a, the maxima from V and O_2 partly overlap in the xy -projection and thus the O_2 positions are not clearly shown. Therefore a new Fourier synthesis was made using the values of $F_{\text{obs}} - F_V$ instead of F_{obs}

Table 1. V_2O_5 . Comparison between observed and calculated F -values (Cu-K radiation) for $hk0$ and hkl reflexions. Reflexions marked with an asterisk are observed only for Cu-K β radiation.

hkl	$ F_{\text{obs}} $	F_{calc}	hkl	$ F_{\text{obs}} $	F_{calc}
200	47	- 36	330	48	- 46
400	65	- 62	430	32	25
600	74	76	530	< 11	- 2
800	18	16	630	< 11	- 4
1000	43	- 41	730	35	40
1200	14	17	830	11	- 13
1400	33	31	930	18	- 20
1600 *	< 25	- 19	1030	29	26
010	50	70	1130	24	- 23
110	29	31	040	14	- 15
210	12	- 11	140	9	5
310	47	- 43	240	11	7
410	14	- 14	340	13	- 9
510	< 7	- 2	440	33	25
610	42	40	540	< 14	- 1
710	33	33	640	14	- 10
810	< 12	2	740	11	7
910	11	11	840	12	- 10
1010	12	- 12	940	< 11	- 4
1110	11	- 15	1040	32	30
1210	11	12	050	23	- 23
1310	16	21	150	< 13	0
1410	13	13	250	12	10
020	56	59	350	< 11	- 1
120	26	27	450	28	31
220	7	- 11	550	< 8	1
320	41	- 41	650	15	- 16
420	14	- 15	060 *	< 23	- 11
520	< 8	- 2	160 *	25	- 18
620	32	37	260 *	< 25	5
720	39	34	360 *	30	34
820	< 11	3	101	(~ 47) **	58
920	18	- 16	301	51	- 46
1020	< 11	- 9	501	11	- 8
1120	19	- 19	701	75	67
1220	11	11	901	14	- 14
1320	30	- 26	1101	36	- 33
030	13	- 9	1301	40	45
130	31	31	011	42	44
230	< 9	6	111	19	27

**) Not registered in this photograph.

<i>hkl</i>	$ F_{\text{obs}} $	F_{calc}	<i>hkl</i>	$ F_{\text{obs}} $	F_{calc}
211	16	- 12	131	20	- 15
311	7	4	231	16	- 14
411	45	- 32	331	45	41
511	7	- 6	431	38	- 37
611	28	26	531	< 9	- 2
711	33	30	631	24	31
811	11	11	731	17	- 15
911	< 11	0	831	14	14
1011	30	- 26	931	16	19
1111	21	- 16	1031	30	- 35
1211	< 9	5	1131	9	9
1311	22	29	041	9	11
021	52	43	141	20	- 17
121	17	17	241	< 9	- 3
221	15	- 12	341	38	38
321	< 7	- 2	441	9	- 8
421	40	- 33	541	< 9	- 2
521	7	- 5	641	7	7
621	31	28	741	17	- 20
721	24	25	841	< 9	3
821	13	12	941	16	20
921	< 9	2	051	< 8	2
1021	24	- 30	151	20	- 19
1121	9	- 13	251	< 9	0
1221	< 7	6	351	36	42
031	48	48			

(as in the former synthesis, F_{calc} was used for 200 and 010). Thus in this projection the V-atoms are eliminated, and the O₂ atoms showed up at the expected positions (Fig. 1 b).

The value of the quotient $R = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$ is very low, being only 0.10 for the *hk0* reflexions (the values for 200 and 010 are not incorporated in the value because of the estimation errors for the reflexions, see above) and 0.14 for the *hkl* reflexions.

Ketelaar stated that the intensities of the reflexions could not be accounted for, assuming the space group to be D_{2h}^{13} , and that therefore the space group must be C_{2v}^7 . However, we cannot confirm this statement. There are no discrepancies between observed and calculated intensities for the *hkl*, *h0l*, and *h1l* reflexions that indicate that the atoms must be moved from the positions in D_{2h}^{13} , which are parameter-free along the *z*-axis. It is true that

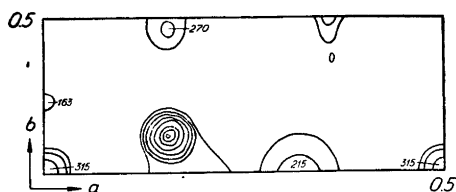


Fig. 1. a. V_2O_5 . Projection of the electron density on (001).

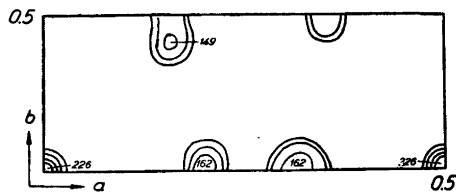


Fig. 1 b. V_2O_5 . Projection of the electron density on (001), with the V-atoms eliminated. The heights are on an arbitrary scale.

because of the habit of the crystals (the prisms have the c -axes parallel to the prism axes) it is more difficult to estimate the intensities of the $h0l$ and $h1l$ reflexions than the intensities of the $hk0$ reflexions. The reflexions $00l$ show up too weak compared with the $h00$ reflexions. As will be seen from Fig. 2, the quotient $\frac{F_{\text{obs}}}{F_{\text{calc}}}$ increases from about 0.5 for the $00l$ reflexions to about 2 for reflexions with high h -values.

An attempt to consider the influence of the habit of the crystals (and the temp. factor) has been made. In Fig. 2 the values of $\frac{F_{\text{obs}}}{F_{\text{calc}}}$ are plotted against h . A curve has been drawn, from which a correction factor K has been taken. The values of F_{obs} have been divided by this factor. As will be seen from Table 2, the agreement between $F_{\text{corr}} = \frac{1}{K} \cdot F_{\text{obs}}$ and F_{calc} is quite satisfactory and the value of R , using F_{corr} instead of F_{obs} in the formula is only 0.14. Thus the structure determination leads to the following centrosymmetrical arrangement of the atoms:

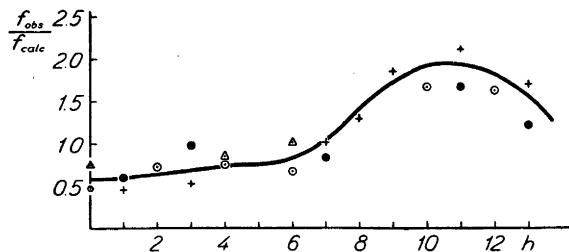


Fig. 2. $\frac{F_{\text{obs}}}{F_{\text{calc}}}$ plotted against h for reflexions $h0l$. Explanations in the text p. 1123.

Table 2. V_2O_5 . Comparison between observed and calculated intensities for $h0l$ and hll reflexions. *Cu-K* radiation.

hkl	$ F_{\text{obs}} $	F_{calc}	$ F_{\text{corr}} $	hkl	$ F_{\text{obs}} $	F_{calc}	$ F_{\text{corr}} $
101	27	58	47	1202	26	16	15
301	24	-46	38	103	18	31	28
501	< 18	-8	< 23	303	31	-32	42
701	70	67	70	503	< 18	-5	< 22
901	26	-14	15	703	38	46	38
1101	70	-33	37	903	20	-12	12
1301	77	45	51	1103	49	-29	26
002	44	92	71	1303*	49	42	33
202	15	-21	21	004	40	53	65
402	35	-46	46	204	< 18	-13	< 26
602	38	59	48	404	26	-31	34
802	18	14	14	604	40	39	47
1002	60	-36	33				

hkl	$ F_{\text{obs}} $	F_{calc}	hkl	$ F_{\text{obs}} $	F_{calc}
011	40	44	912	< 22	-13
111	17	27	1012	23	-12
211	13	-12	1112	20	-16
311	< 13	4	1212	15	11
411	29	-32	1312	17	20
511	< 18	-6	013	25	29
611	26	26	113	< 20	13
711	36	30	213	< 28	-7
811	21	11	313	< 22	-5
911	< 22	0	413	22	-21
1011	40	-26	513	< 21	-4
1111	26	-16	613	21	17
1211	< 23	5	713	23	24
1311	34	29	813	< 18	8
1411	20	18	913	< 16	0
012	40	48	1013	19	-21
112	17	20	014	23	30
212	< 17	-9	114	< 20	13
312	26	-31	214	< 20	-7
412	18	-15	314	20	-21
512	< 19	-1	414	< 18	-13
612	26	32	514	< 16	-1
712	21	26	614	20	24
812	< 22	3			

$$D_{2k}^{13} - Pmmn$$

$$4 \text{ V in } 4 (f) : x_1, y_1, 0; \bar{x}_1, y_1, 0; \frac{1}{2} + x_1, y_1, \frac{1}{2}; \frac{1}{2} - x_1, \bar{y}_1, \frac{1}{2}$$

$$4 \text{ O}_1 \text{ in } 4 (f) : x_2, y_2, 0$$

$$4 \text{ O}_2 \text{ in } 4 (f) : x_3, y_3, 0$$

$$2 \text{ O}_3 \text{ in } 2 (a) : 0, y_4, 0; \frac{1}{2}, \bar{y}_4, \frac{1}{2}$$

$$x_1 = 0.1486 \pm 0.0015 \qquad y_1 = 0.105 \pm 0.003$$

$$x_2 = 0.149 \pm 0.004 \qquad y_2 = 0.458 \pm 0.014$$

$$x_3 = 0.320 \pm 0.004 \qquad y_3 = 0.000 \pm 0.014$$

$$\qquad \qquad \qquad y_4 = 0.000 \pm 0.006$$

CRYSTAL HABIT AND ETCH FIGURES

Ketelaar's arguments for hemihedral symmetry are — besides the fact that he could not obtain agreement between observed and calculated intensities — that the habit of the crystals and the etch figures indicate a non-centrosymmetrical space group.

Crystals obtained from V_2O_5 -melts grow on the walls of small cavities, and are almost exclusively bounded by crystal faces in the prism-zone and at only one termination. This applies to crystals from two melts studied by us, as well as to that measured by Nordenskjöld⁴. Thus it is impossible to conclude from the habit of the crystals, whether the symmetry is holohedral or hemimorphous. However, as has been shown by Leydolt⁵, the symmetry of etch-figures corresponds to that of the face on which they are formed. This statement is not valid in some cases, *e. g.*

when the orientation of the etch-figures in relation to the symmetry elements of the crystal is influenced by the nature of the solvent^{6, 7},

when some chemical or mechanical strain exists in the structure⁶,

when the molecules of the solvent have only axial symmetry^{8, 9}

when there exist surface films or impurities¹⁰.

Wyckoff¹¹ and others have discussed various discrepancies between the symmetry derived from the crystal habit and that derived from the etch-figures, *e. g.* in Cu_2O , $CaWO_4$, and $PbWO_4$, and x-ray analyses of these compounds have shown that the etch figures and the atomic arrangement have the same symmetry¹²⁻¹⁴. Wyckoff has discussed the symmetry of the alkali-halides (KCl and NH_4Cl), derived from x-ray analysis and from etch-figures. His arguments as regards the discrepancies in symmetry that these two methods show are not valid. Later investigations show that etch-figures on pure KCl -crystals have the same symmetry as has the atomic arrangement, derived from x-ray data. The etch-figures on NH_4Cl , referred to by Wyckoff, were obtained by Tschermak on crystals, contaminated by iron¹⁵. This con-

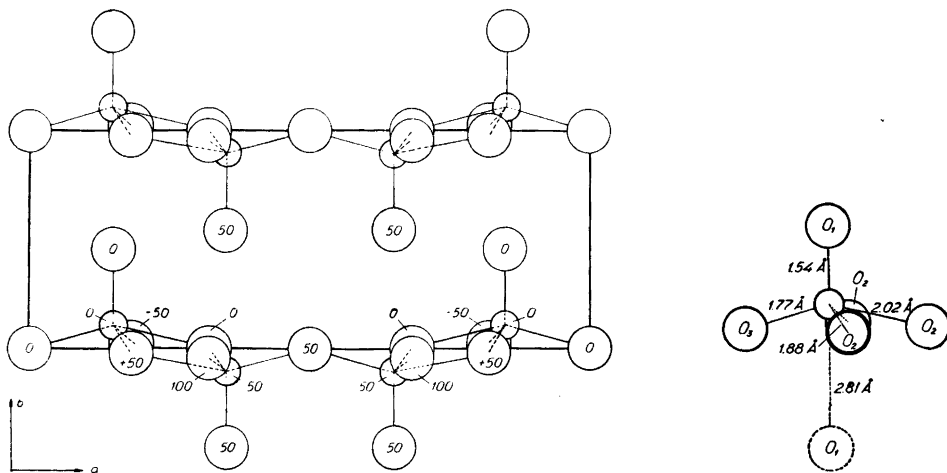


Fig. 3 a. V_2O_5 . Projection of the structure on (001). Small circles denote V-atoms, large circles O-atoms. The figures denote the height of the atoms in fraction of c . Superimposed oxygen atoms are symmetrically displaced.

Fig. 3 b. The coordination around one vanadium-atom. Full drawn lines correspond to the five strong V—O bonds and the dotted line shows the sixth, much weaker one. Bond lengths in Å. Explanations in the text, p. 1133.

tamination seems to be necessary for the formation of large crystals¹⁶ and has evidently some influence on the habit of the crystals.

To make certain that the solvent did not influence the symmetry of the etch-figures, three different etching agents were used, *viz.* 4 C NaOH, 0.1 C NaOH and 3 C H_2SO_4 . The etch pits obtained (all lying on 010 cleavage-planes) shown in Figs 4—6, clearly demonstrated the presence of a centre of symmetry in the structure of V_2O_5 . Thus the symmetry cannot be $C_{2v}-mm$ or D_2-222 and V_2O_5 must crystalize in the rhombic-holohedric (bipyramidal) class, *e. g.* $D_{2h}-Pmmn$. This is also shown by the determination of the atomic positions.

DISCUSSION OF THE STRUCTURE

The following interatomic distances are obtained:

$V - O_1 = 1.54 \pm 0.06 \text{ \AA}$	$O_1 - O_1 = 2.93 \text{ \AA}$
$V - 2O_2 = 1.88 \pm 0.04$	$O_1 - O_2 = 2.70 \text{ and } 2.80$
$V - O_2 = 2.02 \pm 0.08$	$O_1 - O_3 = 2.63$
$V - O_3 = 1.77 \pm 0.03$	$O_2 - O_2 = 2.39$
$(V - O_1 = 2.81 \text{ \AA})$	$O_2 - O_3 = 2.73$

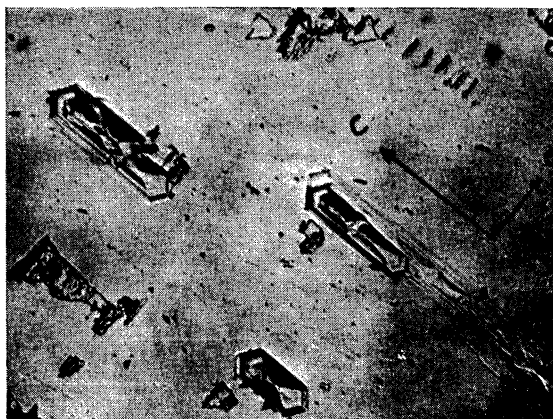


Fig. 4. Well developed, richly faceted etchpits. 3 C H₂SO₄, 8 min at 100° C. Orientation of axes indicated. Refl. light, one Nicol. magn. 360 x. (Phot. Brotzen.)

The structure is given in Fig. 3a. As will be seen, the vanadium atoms form five bonds, one with the O₁ atoms, three with the O₂ atoms and one with the O₃ atoms. These five oxygen atoms form distorted trigonal bipyramids around the vanadium atoms. The bipyramids are linked together by sharing corners in the *x* and *z* directions. In the *y*-direction, there can only be weak forces.

These forces between the layers may correspond to the longer V—O₁ distances of 2.81 Å. If this sixth oxygen atom is incorporated in the coordination figure, a very distorted octahedron is obtained. However, the pronounced cleavage of the substance along (010) shows that these bonds must be much weaker than the other five bonds and our description of the structure as built up by trigonal bipyramids is therefore more adequate.

In Fig. 3b the three kinds of oxygen atoms in the structure are shown. The O₁ atoms form only one strong bond (V—O = 1.54 Å). The O₃ atoms form two bonds (V—O = 1.77 Å) with the angle V—O₃—V = 125°. The O₂ atoms form three bonds (mean distance V—O = 1.93 Å) with the bond angles 104°, 104°, and 143°. The V—O₁ distance agrees closely with that found by Palmer¹⁷ in VOCl₃ (1.56 Å).

Nordenskjöld observed that the cleavage along (010) was perfect and could also be obtained along (100) and (001). Ketelaar confirmed the perfect cleavage along (010) and stated that he could obtain the cleavage along (100) but only with difficulty along (001). Obviously, the suggested structure requires a perfect cleavage along (010). Because of the short distances O₂—O₂,



Fig. 5. Different types of etch-pits. 3 C H₂SO₄, 8 min at 100° C. Refl. light, one Nicol, magn. 230 x. (Phot. Brotzen.)



Fig. 6 a. Diluted NaOH, 16 hours, 20° C. c-axis along the length-direction of the individuals. One welldeveloped pit to the left and to the right open fishbone-like etch figures. These are due to the tapering shape of the individuals and may not be interpreted as indications of hemihedral symmetry. Magn. 3 x. (Phot. Brotzen.)

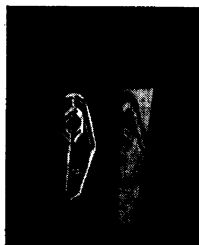


Fig. 6 b. Etch figures 0.10 N NaOH, 4 min 100° C. Schematic drawing illustrates the symmetry and the location of the small pit in the large one. c-axis in the length-direction. Cleavage plane somewhat inclined. Magn. 3 x. (Phot. Brotzen.)

which must imply very strong repulsing forces between the oxygen atoms, it can be expected that the V—O₂ bonds of 2.02 Å are those most easily broken of the V—O bonds (they correspond to the largest V—O distances) and thus the cleavage along (100) can be expected to be easier to obtain than that along (001), in agreement with Ketelaar's findings.

Ketelaar also investigated the colloid particles from a V_2O_5 hydrosol and found that the dimensions of the particles in the three lattice directions were $a \sim 20 \text{ \AA}$, $b \sim 10 \text{ \AA}$, and $c \sim 150 \text{ \AA}$. The structure, which we have suggested, obviously implies that the growth velocity in the b -direction must be very slow, as no primary metal-oxygen bonds operate in this direction. Further, it is probable that because of the short O—O distances (see above) the growth in the a -direction can be expected to be slower than in the c -direction, thus in agreement with the observed data.

SUMMARY

The crystal structure of V_2O_5 has been investigated. Contrary to Ketelaar², we found no evidence for hemihedral symmetry neither in the intensities of the x-ray reflexions nor in the etch-figures. According to our determinations the space group is D_{2h}^{13} — $Pm\bar{m}n$ and the atoms occupy the following positions:

4 V in 4 (f):	$x_1, y_1, 0; \bar{x}_1, y_1, 0; \frac{1}{2} + x_1, \bar{y}, \frac{1}{2}; \frac{1}{2} - x_1, \bar{y}_1, \frac{1}{2};$	$x_1 = 0.1486$	$y_1 = 0.105$
4 O_1 in 4 (f):	$x_2, y_2, 0;$	$x_2 = 0.149$	$y_2 = 0.458$
4 O_2 in 4 (f):	$x_3, y_3, 0;$	$x_3 = 0.320$	$y_3 = 0.000$
2 O_3 in 2 (a):	$0, y, 0; \frac{1}{2}, \bar{y}, \frac{1}{2}$		$y_4 = 0.000$

The vanadium atoms are surrounded by five oxygen atoms which form trigonal bipyramids around the V-atoms with V—O distances ranging from 1.54 \AA to 2.02 \AA . The weak cohesion of the crystals in the b -directions is probably due to a sixth much weaker V—O bond with a distance V—O of 2.81 \AA . The shortest O—O distance is 2.39 \AA .

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