

On the Crystal Structure of a New Vanadium Oxide, V_4O_9

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Recent work¹⁻⁴ in the system $VO_2-V_2O_5$ has revealed several new phases besides the well-established oxides V_6O_{13} ,^{5,6} and V_3O_7 .⁷⁻⁹ This article reports briefly on a new oxide with the formula V_4O_9 obtained within an investigation of the systems $VO_2-V_2O_5$ and $VO_2-V_2O_5-H_2O$ undertaken at this Institute.

Crystals of the new compound were prepared by decomposing V_2O_5 in supercritical water at 600°C and 2 kb in a sealed gold tube. (Reaction time 90 h, slow cooling.)

Weissenberg photographs of a prismatic single crystal were taken with Ni-filtered $CuK\alpha$ radiation with the prism axis chosen as rotation axis (identity period $b=3.70$ Å). The Laue symmetry was mmm . On the Weissenberg photographs $h0l-h2l$ and on the powder photograph (*v. infra*) the following reflections were absent: $0kl$ for $k+l=2n+1$; $hk0$ for $h=2n+1$. Thus, probable space groups are $Pnma$ or $Pn2_1a$.

The cell constants were derived from a Guinier-Hägg powder photograph.

$a=17.926 (\pm 4)$ Å, $b=3.631 (\pm 1)$ Å, $c=9.396 (\pm 2)$ Å, $V=612$ Å³.

The cell content was derived in the following way, only assuming that the oxygen-vanadium ratio was in the range VO_2 to $VO_{2.50}$. The density of the anion packing may be expressed in terms of the quotient V/n_O (V =unit cell volume in Å³ and n_O =number of oxygen atoms in the unit cell). This quantity has the value of 17.9, 17.5, 16.8, and 14.8 for V_2O_5 , V_3O_7 , V_6O_{13} , and VO_2 , respectively. It thus seemed likely that the number of oxygen atoms per unit cell in this case lies in the range $42 > n_O > 35$. This gives the alternatives 36 or 40 oxygen atoms, as in the space group $Pnma$ (or $Pn2_1a$) only fourfold and eightfold positions exist. The only possible number of the vanadium atoms is then 16, corresponding to a unit cell content of four formula units V_4O_9 . The value of V/n_O for V_4O_9 is 17.0. The powder pattern, listed in Table 1, is quite different

Table 1. Powder pattern of V_4O_9 , $CuK\alpha_1$ radiation.

hkl	$10^5 \times \sin^2\theta_{obs}$	$10^5 \times \sin^2\theta_{calc}$	I_{obs}
2 0 0	733	738	vw
1 0 1	852	857	vvw
2 0 1	1409	1410	vw
3 0 1	2337	2334	m
2 0 2	3436	3426	vw
4 0 1	3630	3626	w
3 0 2	4359	4350	vw
0 1 1	5170	5172	s
2 1 0	5237	5239	vw
5 0 1	5284	5287	w
1 1 1	5360	5357	m
1 0 3	6233	6232	w
6 0 0	6645	6646	vw
2 0 3	6789	6786	m
3 1 1	6830	6834	vw
1 1 2	7380	7373	m
4 1 0	7459	7454	vvw
4 1 1	8141	8126	vvw
3 1 2	8868	8850	vvw
4 0 3	9004	9002	vw
6 0 2	9336	9334	w
7 0 1	9719	9718	vvw
5 1 1	9808	9788	vvw

from that reported in Ref. 1 for a preparation, given the formula V_4O_9 , prepared in a different way.

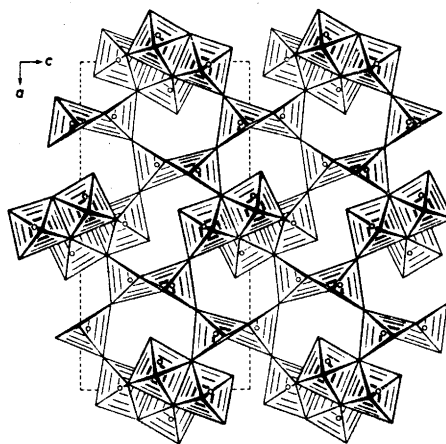


Fig. 1. The crystal structure of V_4O_9 projected on (010). Small open circles, vanadium atoms at $y=1/4$; black circles, vanadium atoms at $y=3/4$.

Table 2. The crystal structure of V_4O_{13} . Space group: $Pnma$. All atoms in positions 4(c).

	$x \pm \sigma(x)$	y	$z \pm \sigma(z)$	$B \pm \sigma(B)$
V(1)	-0.0059 (2)	1/4	0.2287 (3)	1.16 (13)
V(2)	0.0780 (2)	1/4	0.5385 (3)	1.26 (14)
V(3)	0.1675 (2)	1/4	0.2053 (3)	1.21 (13)
V(4)	0.3169 (2)	1/4	0.4566 (3)	1.13 (13)
O(1)	-0.0233 (6)	3/4	0.2740 (10)	3.06 (78)
O(2)	0.0480 (7)	3/4	0.5477 (11)	2.67 (64)
O(3)	0.1543 (6)	3/4	0.1579 (11)	2.06 (64)
O(4)	0.2969 (6)	3/4	0.5108 (11)	1.82 (43)
O(5)	0.0879 (6)	1/4	0.3401 (11)	0.65 (40)
O(6)	0.0435 (8)	1/4	0.0833 (12)	2.70 (65)
O(7)	0.3924 (6)	1/4	0.3551 (12)	1.92 (56)
O(8)	0.1639 (7)	1/4	0.5843 (11)	1.80 (53)
O(9)	0.2393 (6)	1/4	0.3124 (11)	2.02 (54)

Table 3. Interatomic distances (in Å) in V_4O_{13} . Standard deviations within parentheses.

Metal-oxygen distances (<3.3 Å)		Metal-metal distances (<3.6 Å)	
V(1)-O(6)	1.629 (12)	V(1)-V(3)	3.115 (4)
-O(1) (2 ×)	1.891 (3)	-V(2) (2 ×)	3.123 (3)
-O(5)	1.980 (10)	-V(2)	3.276 (4)
-O(7)	1.986 (11)		
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-O(2)	2.232 (11)		
V(2)-O(8)	1.599 (12)	V(2)-V(1) (2 ×)	3.123 (3)
-O(5)	1.872 (10)	-V(1)	3.276 (4)
-O(2) (2 ×)	1.895 (3)	-V(2) (2 ×)	3.411 (4)
-O(1)	2.016 (10)	-V(3)	3.517 (4)
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-O(2)	2.399 (12)		
V(3)-O(9)	1.635 (11)	V(3)-V(4) (2 ×)	2.972 (3)
-O(3) (2 ×)	1.884 (3)	-V(1)	3.115 (4)
-O(5)	1.908 (10)	-V(2)	3.517 (4)
-O(4)	1.936 (11)	-V(4)	3.572 (4)
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-O(6)	2.500 (13)		
V(4)-O(7)	1.655 (11)	V(4)-V(3) (2 ×)	2.972 (3)
-O(4) (2 ×)	1.919 (4)	-V(3)	3.572 (4)
-O(9)	1.942 (11)		
-O(3)	1.960 (11)		
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-O(8)	2.995 (12)		

It was noticed that the intensities of the $h0l$ and $h2l$ reflections in the Weissenberg photographs are nearly identical, and therefore all the atoms were assumed to be situated in planes normal to the short y axis and $b/2$ apart. The appearance of the Patterson projection $P(upw)$ suggested that the positions of the metal atoms are not parameter free.

The structure determination was started with the assumption that the space group $Pnma$ is the correct one, and that all the atoms are situated in 4(c): $\pm(x, \frac{1}{2}, z)$; $\pm(\frac{1}{2}+x, \frac{1}{2}, \frac{1}{2}-z)$. A plausible trial structure with all vanadium and oxygen atoms in 4(c) positions was thus derived with the vanadium atoms in five- as well as in six-coordination. The tentative structure (41

parameters) was then refined, using 316 $h0l$ and $h1l$ reflections with a full-matrix least-squares program. At the present stage of refinement the conventional R factor is 7%. The fractional atomic parameters obtained and the interatomic distances are given in Tables 2 and 3.

A schematic representation of the structure is given in Fig. 1. It is seen that highly distorted octahedra and square pyramids are the basic structural elements. The $V(1)O_6$ and $V(2)O_6$ octahedra form zig-zag strings running in the b direction by edge-sharing. They are also joined by edge-sharing in the ac plane to double zig-zag ribbons extending along b . The $V(3)O_4$ and $V(4)O_4$ square pyramids form single zig-zag strings in the b direction. These strings are joined by corner-sharing among themselves and to the double zig-zag ribbons to form a three-dimensional framework. The vanadium-oxygen distances in the ribbons (Table 3) are in the range 1.60–2.40 Å (sixfold coordination), and the distances in the single chains are in the range 1.64–1.96 Å (fivefold coordination).

The structure of V_4O_{13} can alternatively be described by regarding it as composed of vanadium atoms exclusively in square-pyramidal coordination with oxygen, with an additional sixth oxygen weakly coordinated (bond type C , nomenclature according to Ref. 10), through the base of the pyramid and opposite to a short apex bond (bond type A). The short A bonds are in the range 1.60–1.66 Å (mean value 1.63 Å), and the basal B bonds are in the range 1.87–2.02 Å (mean value 1.94 Å). The sixth weak bonds (bond type C) are 2.23 and 3.00 Å, respectively. The square pyramid configuration is very common for tetravalent and pentavalent vanadium compounds. Among the many crystal structures¹⁰ having shown its presence, the average A bond length is 1.60 Å, and B bond length 1.91 Å. The C bond varies from 2.18 to 2.97 Å, or is sometimes absent altogether.

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Spin Trapping of Some Phosphorus-centered Radical Species

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Intermediate free radicals with the radical center located on a phosphorus atom are considered to be formed in many reactions of organo-phosphorus compounds, for example in the addition of primary and secondary phosphines to olefins.¹ The radical species considered to be present in the latter reactions, *i.e.* phosphinyl radicals, $R^1R^2\dot{P}$, have not been demonstrated so far by the technique of ESR spectroscopy. On the other hand, the ESR spectra of phosphoranyl radicals such as $R^1R^2R^3\dot{P}OR$ and $R^1R^2\dot{P}(OR)_2$, formed by the addition of *t*-butoxy radicals to phosphines, have been recorded at about -80° .^{2,3}

This note describes the trapping as nitroxide radicals of some phosphorus-centered radical species. The trapping of short-lived free radicals as stable nitroxide