On the Crystal Structure of a New Vanadium Oxide, V_4O_9

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Recent work [1–4] 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_3O_7 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 Cu*K*α 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, $V=612$ Å.[3]

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 Å^3 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 from that reported in Ref. 1 for a preparation, given the formula V_4O_9, prepared in a different way.

Table 1. Powder pattern of V_4O_9. Cu$K\alpha_1$ radiation.

$h\,k\,l$	$10^5 \times \sin^2\theta_{obs}$	$10^5 \times \sin^2\theta_{calc}$	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

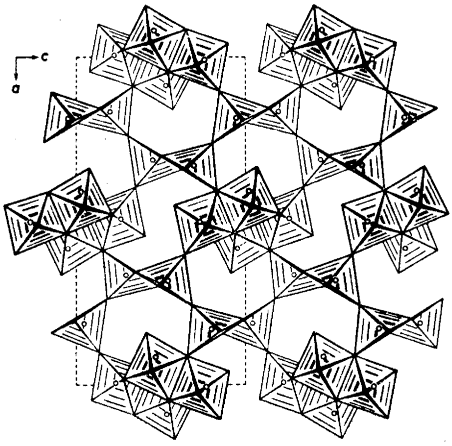

Fig. 1. The crystal structure of V_4O_9 projected on (010). Small open circles, vanadium atoms at $y=1/4$; black circles, vanadium atoms at $y=3/4$.

Table 2. The crystal structure of V_4O_9. 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_9. Standard deviations within parentheses.

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

Metal-metal distances (<3.6 Å)	
V(1)−V(3)	3.115 (4)
−V(2) (2×)	3.123 (3)
−V(2)	3.276 (4)
V(2)−V(1) (2×)	3.123 (3)
−V(1)	3.276 (4)
−V(2) (2×)	3.411 (4)
−V(3)	3.517 (4)
V(3)−V(4) (2×)	2.972 (3)
−V(1)	3.115 (4)
−V(2)	3.517 (4)
−V(4)	3.572 (4)
V(4)−V(3) (2×)	2.972 (3)
−V(3)	3.572 (4)

It was noticed that the intensities of the *h*0*l* and *h*2*l* 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*): $\pm(x,\frac{1}{4},z)$; $\pm(\frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z)$. 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 $V(3)O_5$ and $V(4)O_5$ 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_9 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 structures[10] 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 altogheter.

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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