

Le second complexe montre un comportement curieux mais explicable à la lumière de sa structure. Les différentes préparations semblent donner des compositions variables, du moins en ce qui concerne la teneur en eau. Elles font apparaître des paramètres réticulaires qui diffèrent de manière non négligeable d'un échantillon à l'autre. Nous avons également observé que ces paramètres sont susceptibles d'évoluer au cours du temps. Dans les échantillons qui ont servi à la détermination de la structure cristalline les paramètres de la maille monoclinique (groupe spatial $P2_1/a$) convergeaient vers les valeurs suivantes: $a = 15,25$, $b = 25,65$, $c = 24,00$ Å, $\beta = 104,7^\circ$. Cette maille contient quatre unités $[\text{Cu}_8(\text{tu})_{15}]$.

La structure, résolue par méthodes directes, fait apparaître très nettement l'organisation atomique du feuillet cationique (Fig. 1). Les distances Cu-S diffèrent significativement selon

le nombre de coordination du cuivre; pour Cu tricoordonné: Cu-S = 2,25 Å; pour Cu tétracoordonné: Cu-S = 2,34 Å. Griffith *et al.* (1976) observent des différences du même ordre dans $\text{Cu}_4(\text{tu})_6^{4+}$. Les positions des anions et des molécules d'eau sont beaucoup moins nettes; un important désordre semble régner à ce niveau. Nous attribuons les variations réticulaires observées au glissement des plans cationiques les uns sur les autres, probablement à la suite de changements de teneur en eau dans le cristal. Nous poursuivons l'affinement de la structure dont la description complète sera publiée ultérieurement.

Référence

GRIFFITH, E. H., HUNT, G. W. & AMMA, E. L. (1976). *J. Chem. Soc. Chem. Commun.* pp. 432-433.

Acta Cryst. (1978). **B34**, 1037-1039

Structural re-investigation of the low-temperature phase of V_6O_{13} . BY I. KAWADA, M. ISHII, M. SAEKI, N. KIMIZUKA, M. NAKANO-ONODA and K. KATO, *National Institute for Researches in Inorganic Materials, Kurakake, Sakura-mura, Niihari-gun, Ibaraki-ken 300-31, Japan*

(Received 28 June 1977; accepted 4 October 1977)

The crystal structure of the low-temperature (100 K) phase of V_6O_{13} was redetermined in the space group $P2_1/a$. The crystallographic data are $a = 11.96$ (1), $b = 3.713$ (3), $c = 10.07$ (2) Å, $\beta = 100.9$ (2)°, $Z = 2$, $D_x = 3.89$ g cm⁻³. The shifts of atomic positions from those of the room-temperature phase lie within 0.028 Å, except for the V(1) atom, which has moved 0.14 Å along the b axis, thus destroying the mirror planes found in the room-temperature phase.

Introduction

The structure of V_6O_{13} at room temperature was first determined by Aebi (1948) and refined later by Wilhelmi, Waltersson & Kihlborg (1971). Our refinement of this structure at room temperature with the samples synthesized in our laboratory (Saeki *et al.*, 1973) showed essentially the same results as those of Wilhelmi *et al.* (1971).

The metal-insulator transition of V_6O_{13} at about 150 K was investigated by Dernier (1974). He concluded that the space group of the low-temperature (120 K) phase was $C2$ and refined the structure in this space group. However, in our recent work (Kawada, Nakano, Saeki, Ishii, Kimizuka & Nakahira, 1973) it was confirmed that the space group was not $C2$ but $P2_1/a$. The present work has hence been undertaken to re-investigate with our single crystals the structure of V_6O_{13} at about 100 K in the latter space group.

Experimental

The crystals used in this experiment were synthesized from V_2O_3 and V_2O_5 by the chemical transport method (Saeki *et al.*, 1973). The chemical composition was $\text{V}_6\text{O}_{13.11}$ as determined by both oxidation to V_2O_5 and chelate analysis.

The lattice constants were determined with a powder specimen at 77 K. As V_6O_{13} tends to form twinned crystals, many samples were examined by precession photographs to obtain a single crystal suitable for the intensity measurement at low temperature. The size of the crystal thus obtained was $0.33 \times 0.22 \times 0.04$ mm.

Low temperature was attained by an apparatus (Rigaku) using a nitrogen gas stream whose temperature was maintained at 100 ± 2 K. During the cooling process, great care was taken to avoid the crystal breaking off owing to the volume change at the phase transition.

1345 reflections were measured on a Rigaku four-circle diffractometer using Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å); 117 of these were below the limit of observation. The intensities were corrected for absorption by the specimen ($\mu = 65.7$ cm⁻¹).

Structure refinement

The starting parameters of the low-temperature phase were taken from the results of our refinement of the room-temperature phase, with reference to those of Aebi (1948) and Wilhelmi *et al.* (1971). The positional and anisotropic thermal parameters were refined by the program *ORFLS* (Busing, Martin & Levy, 1962). The extinction correction of

Zachariassen (1968) was applied with the following simplified formula:

$$F_o = sF_c [1 + (\bar{g}/\sin 2\theta)(1 + \cos^4 2\theta)(1 + \cos^2 2\theta)^{-1} F_c^2]^{-1/4},$$

$$\bar{g} = 1.43 (4) \times 10^{-5}.$$

Scattering factors were taken from Hanson, Herman, Lea & Skillman (1964). The final value of R was 0.046 and the weighted R was 0.025 for 1166 observed reflections.*

Discussion

The structure consists of VO_6 octahedra which are connected by corner- and edge-sharing with each other

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33111 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates ($\times 10^5$ for V; $\times 10^4$ for O)

Numbers in parentheses in this and subsequent tables are estimated standard deviations of the last digits.

	<i>x</i>	<i>y</i>	<i>z</i>
V(1)	35201 (7)	3851 (23)	-144 (8)
V(2)	41302 (4)	155 (26)	36403 (6)
V(3)	71537 (4)	-113 (26)	36664 (6)
O(1)	1775 (2)	76 (10)	3 (3)
O(2)	8818 (2)	-18 (11)	3885 (2)
O(3)	2510 (2)	12 (11)	4092 (2)
O(4)	5000	0	0
O(5)	3845 (2)	32 (11)	1966 (2)
O(6)	6799 (2)	-35 (11)	1994 (2)
O(7)	5616 (2)	4 (12)	4071 (3)

(Fig. 1). This structure deviates slightly from that of the room-temperature phase. Except for the V(1) atom, which has moved 0.14 Å along the b axis (Fig. 2), the shift distances of the other atoms calculated from the parameter changes are 0.0008–0.028 Å parallel to the three axes. The atomic coordinates are given in Table 1.

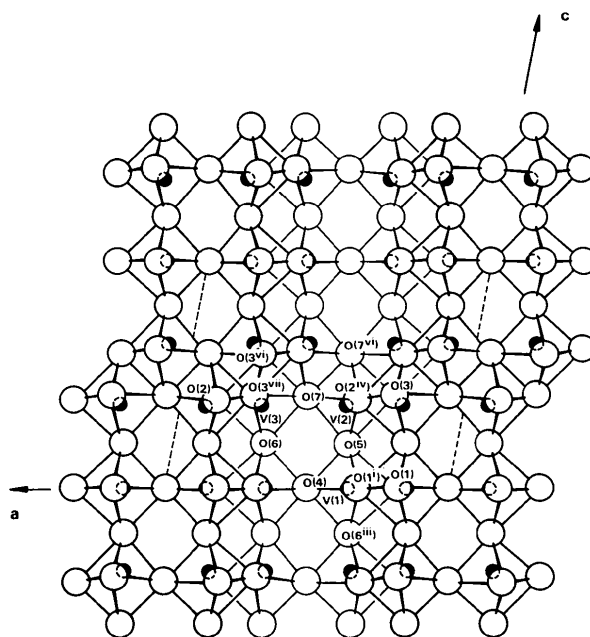


Fig. 1. The structure of the low-temperature phase of V_6O_{13} projected on (010).

Table 2. Interatomic distances (Å)

V(1) octahedron		V(2) octahedron		V(3) octahedron	
V(1)—O(1)	2.094 (3)	V(2)—O(2 ^{iv})	1.919 (4)	V(3)—O(2)	1.961 (3)
—O(1 ⁱ)	1.778 (4)	—O(2 ^v)	1.918 (4)	—O(3 ^{vii})	1.934 (5)
—O(1 ⁱⁱ)	2.003 (4)	—O(3)	2.073 (3)	—O(3 ^{viii})	1.935 (5)
—O(4)	1.773 (2)	—O(5)	1.655 (4)	—O(3 ^{vi})	2.217 (5)
—O(5)	1.963 (5)	—O(7)	1.748 (3)	—O(6)	1.657 (4)
—O(6 ⁱⁱⁱ)	1.962 (5)	—O(7 ^{vi})	2.267 (5)	—O(7)	1.957 (3)
O(1)—O(1 ⁱ)	2.542 (3)	O(2 ^{iv})—O(3)	2.464 (6)	O(2)—O(3 ^{vii})	2.464 (6)
—O(1 ⁱⁱ)	2.542 (3)	—O(5)	2.680 (6)	—O(3 ^{viii})	2.461 (5)
—O(5)	2.862 (7)	—O(7)	2.824 (6)	—O(3 ^{vi})	2.810 (6)
—O(6 ⁱⁱⁱ)	2.872 (6)	—O(7 ^{vi})	2.765 (5)	—O(6)	2.778 (7)
O(1 ⁱ)—O(4)	2.838 (4)	O(2 ^v)—O(3)	2.461 (5)	O(3 ^{vii})—O(3 ^{vi})	2.609 (4)
—O(5)	2.727 (6)	—O(5)	2.688 (6)	—O(6)	2.826 (6)
—O(6 ⁱⁱⁱ)	2.739 (5)	—O(7)	2.817 (6)	—O(7)	2.922 (6)
O(1 ⁱⁱ)—O(4)	2.801 (3)	—O(7 ^{vi})	2.754 (5)	O(3 ^{viii})—O(3 ^{vi})	2.609 (4)
—O(5)	2.704 (6)	O(3)—O(5)	2.903 (6)	—O(6)	2.815 (6)
—O(6 ⁱⁱⁱ)	2.718 (6)	—O(7 ^{vi})	2.622 (6)	—O(7)	2.929 (6)
O(4)—O(5)	2.620 (5)	O(5)—O(7)	2.698 (7)	O(3 ^{vi})—O(7)	2.622 (6)
—O(6 ⁱⁱⁱ)	2.651 (7)	O(7)—O(7 ^{vi})	2.591 (6)	O(6)—O(7)	2.738 (6)

Symmetry code

(i)	$\frac{1}{2} - x,$	$\frac{1}{2} + y,$	$-z$	(v)	$-\frac{1}{2} + x,$	$-\frac{1}{2} - y,$	z
(ii)	$\frac{1}{2} - x,$	$-\frac{1}{2} + y,$	$-z$	(vi)	$1 - x,$	$-y,$	$1 - z$
(iii)	$1 - x,$	$-y,$	$-z$	(vii)	$\frac{1}{2} + x,$	$\frac{1}{2} - y,$	z
(iv)	$-\frac{1}{2} + x,$	$\frac{1}{2} - y,$	z	(viii)	$\frac{1}{2} + x,$	$-\frac{1}{2} - y,$	z

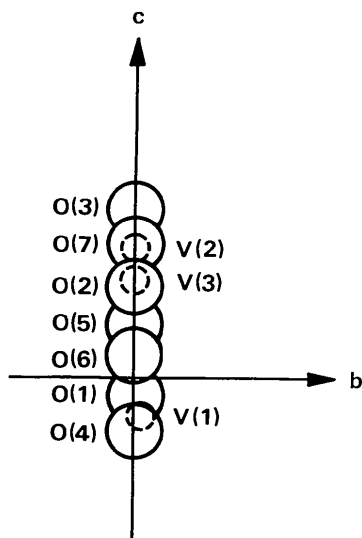


Fig. 2. Projection of the atoms of the asymmetric unit on (100).

Table 3. Bond angles around V atoms ($\angle\text{O}-\text{V}-\text{O}$) ($^{\circ}$)

For symmetry code see Table 2.

Around V(1) atom					
	O(1 ⁱ)	O(1 ⁱⁱ)	O(4)	O(5)	O(6 ⁱⁱⁱ)
O(1)	81.6 (1)	76.7 (1)	172.2 (1)	89.7 (2)	90.1 (2)
O(1 ⁱ)		158.3 (1)	106.1 (1)	93.4 (2)	94.1 (2)
O(1 ⁱⁱ)			95.6 (1)	86.0 (2)	86.6 (2)
O(4)				88.9 (2)	90.3 (2)
O(5)					172.4 (2)
Around V(2) atom					
	O(2 ^v)	O(3)	O(5)	O(7)	O(7 ^{vi})
O(2 ^{iv})	150.8 (1)	76.1 (1)	96.9 (2)	100.6 (2)	82.2 (1)
O(2 ^v)		76.0 (1)	97.3 (2)	100.3 (2)	81.9 (1)
O(3)			101.7 (2)	153.4 (1)	74.2 (2)
O(5)				104.9 (2)	175.9 (1)
O(7)					79.2 (2)
Around V(3) atom					
	O(3 ^{vii})	O(3 ^{viii})	O(3 ^{vi})	O(6)	O(7)
O(2)	78.5 (1)	78.3 (1)	84.3 (2)	100.0 (2)	161.9 (1)
O(3 ^{vii})		147.3 (1)	77.6 (1)	103.5 (2)	97.3 (1)
O(3 ^{viii})			77.5 (1)	102.9 (2)	97.6 (1)
O(3 ^{vi})				175.7 (2)	77.6 (2)
O(6)					98.2 (2)

The bond lengths and angles were calculated by the program *ORFFE* (Busing, Martin & Levy, 1964) and are listed in Tables 2 and 3.

An analysis of the valence balance was carried out for the V_6O_{13} low-temperature phase based on Pauling's empirical rule (Pauling, 1960; Marezio, McWhan, Dernier & Remeika, 1973; Dernier, 1974) applying the expression $d_n = 1.789 - 0.78 \log n$ given by Wilhelmi *et al.* (1971), where d_n is the bond length and n the bond number. This gave $\Sigma n = 4.22$, 4.64 and 4.27 for V(1), V(2) and V(3) respectively.

From the projection on to (100) of the atoms in the asymmetric unit (Fig. 2), it is obvious that the y parameter of V(1) deviates distinctly from the pseudo-mirror plane (which is a real mirror plane in the room-temperature phase), but the valence-balance analysis showed no distinct localization of V^{5+} at the V(1) site.

The authors wish to thank Professor M. Nakahira (Okayama College of Science) for suggesting this problem. They are also indebted to Professor Y. Iitaka (Faculty of Pharmaceutical Sciences, University of Tokyo), who kindly placed at their disposal a four-circle diffractometer for the intensity measurements of the room-temperature phase. Thanks are also due to Dr P. D. Dernier (Bell Laboratories), who kindly provided his unpublished data.

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