

discussions and Professor Arne Magnéli for his kind interest. Thanks are also due to Dr Sven Westman for revising the English text and to Mr Tomasz Niklewski for the density measurements.

This investigation has been supported by the Swedish Natural Science Research Council.

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A Refinement of the Crystal Structure of CsV₂O₅

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(Received 20 April 1976; accepted 20 August 1976)

The crystal structure of CsV₂O₅ has been refined on the basis of three-dimensional X-ray diffractometer data (Mo K α radiation). The structure proposed by Mumme & Watts [*J. Solid State Chem.* (1971), **3**, 319–322] is confirmed. The structure is monoclinic, $a = 7.021$ (1), $b = 9.898$ (2), $c = 7.783$ (1) Å, $\beta = 90.65$ (1)°, $Z = 4$, $V = 540.8$ Å³; space group $P2_1/c$ (No. 14). The final R_w is 0.027 for 1247 independent reflexions and 74 variables. The compound contains vanadium(V) atoms in tetrahedral coordination, $(V-O)_{av} = 1.718$ Å; and vanadium(IV) atoms in square-pyramidal coordination, $(V-O)_{av} = 1.882$ Å. No indications of a deviation from the CsV₂O₅ stoichiometry have been observed.

Introduction

During electrolysis of caesium vanadate melts, Reid & Watts (1970) found two new compounds. One was monoclinic with black, plate-like crystals and was

assigned the formula CsV₂O₅. A crystal structure analysis by Mumme & Watts (1971) confirmed this composition. The cell parameters of the monoclinic compound were reported to be $a = 7.008$ (5), $b = 9.977$ (5), $c = 7.729$ (5) Å and $\beta = 90.98$ (5)°.

This compound has also been studied by Fotief & Golofkin (1972) and Volkov, Curat & Fotief (1974), who give formulae of variable composition Cs_xV₂O₅.

Within a research programme being conducted at this Institute on mixed-valence (+IV and +V) compounds of vanadium, it was of interest to obtain more detailed information about the structure of CsV₂O₅. The *R* value reported by Mumme & Watts (1971) was rather high (14.4%), which suggests that the positions of the O atoms were not very accurate. In order to make possible a detailed comparison of the V—O bond lengths in this compound with those found in other mixed-valence V compounds (Wilhelmi, Waltersson & Kihlberg, 1971; Waltersson, Forslund, Wilhelmi, Andersson & Galy, 1974), a refinement of the CsV₂O₅ structure was thus deemed necessary. Another interesting aspect of the compound which also made a more detailed study desirable was the possibility of a nonstoichiometric composition.

Experimental

While the CsV₂O₅ crystals studied by Mumme & Watts were prepared by a melt-electrolysis method (Reid & Watts, 1970), the material used in the present investigation was obtained by heating a mixture of CsVO₃, V₂O₅ and V₂O₃ (mole ratios 5:1:1) in an evacuated silica tube at 500 °C for one month, in a way similar to that described by Volkov *et al.* (1974). The crystals are soluble in HCl but are unaffected by dilute ammonia, which makes it possible to separate them from a matrix consisting of caesium vanadates(V).

A powder photograph taken with a Guinier-Hägg camera (Cu Kα₁) was indexed from the information given by single-crystal intensities. The cell dimensions thus obtained differ significantly from those given by Mumme & Watts (1971). The deviations are explained by some mistakes in the indexing of their powder pattern. All their reflexion lines are observed in our powder

Table 1. Powder pattern of CsV₂O₅

Cu Kα₁ radiation (λ = 1.54050 Å). KCl internal standard (a = 6.2930 Å).

<i>hkl</i>	<i>d</i> _{obs}	10 ⁵ sin ² θ _{obs} (this work)	10 ⁵ sin ² θ _{obs} (Mumme & Watts, 1971)	10 ⁵ sin ² θ _{calc}	<i>I</i> _{obs}
1 1 1̄	4.631	2767	—	2764	<i>w</i>
0 2 1	4.173	3407	3397	3402	<i>s</i>
0 0 2	3.895	3911	3932	3918	<i>m</i>
1 2 1̄	3.600	4579	4576	4581	<i>s</i>
1 2 1	3.581	4627	4636	4630	<i>m</i>
2 0 0	3.506	4826	—	4815	<i>vw</i>
1 0 2	3.387	5173	5168	5171	<i>vs</i>
2 1 0	3.307	5426	5423	5421	<i>s</i>
1 1 2̄	3.233	5677	5670	5679	<i>vs</i>
1 1 2	3.205	5775	—	5777	<i>w</i>
0 2 2̄	3.058	6344	6349	6341	<i>s</i>
2 1 1̄				6351	
2 1 1	3.036	6437	6450	6449	<i>vs</i>
1 3 0	2.985	6657	6650	6654	<i>s</i>
1 2 2̄	2.813	7498	—	7496	<i>vw</i>
1 3 1	2.783	7659	7660	7658	<i>m</i>
0 3 2	2.516	9376	9343	9369	<i>m</i>
0 4 0	2.474	9693	—	9690	<i>m</i>
2 3 0	2.4041	10265	—	10266	<i>vw</i>
1 1 3̄	2.3715	10549	10535	10552	<i>m</i>
1 4 0	2.3339	10892	10891	10894	<i>m</i>
0 2 3	2.2984	11231	11247	11239	<i>s</i>
1 2 3	2.1771	12517	—	12516	<i>w</i>
0 4 2	2.0885	13602	—	13608	<i>m</i>
2 3 2̄	2.0524	14085	14062	14086	<i>m</i>
2 1 3̄				14090	
0 3 3̄				14267	
2 3 2̄	2.0385	14277	—	14283	<i>m</i>
3 0 2̄				14605	
1 4 2̄	2.0154	14607	—	14605	<i>vw</i>
1 4 2	2.0050	14759	14774	14763	<i>w</i>
1 4 2	1.9982	14859	—	14861	<i>vw</i>
3 1 2̄	1.9748	15213	—	15211	<i>w</i>
3 1 2	1.9561	15505	—	15505	<i>w</i>
0 0 4	1.9457	15671	15719	15674	<i>vw</i>
0 1 4	1.9086	16287	16256	16279	<i>w</i>

pattern, and the $\sin^2\theta_{\text{obs}}$ values (Cu $K\alpha_1$) are the same, within the experimental limits. The powder pattern is listed in Table 1, and the cell dimensions are given in Table 2.

No change of the $\sin^2\theta_{\text{obs}}$ values was observed in powder patterns of preparations of different starting compositions, which seems to rule out the possibility of a variable composition proposed by Volkov *et al.* (1974). The observed density of 3.87 g cm⁻³, determined by hydrostatic weighing (Niklewski, Kihlborg, Nygren & Sävborg, 1975), corresponds well with the theoretical value of 3.86 g cm⁻³ for four units of CsV₂O₅ in the elementary cell.

The single-crystal intensity data were collected on a Siemens automatic diffractometer with monochromatic Mo $K\alpha$ radiation, the θ - 2θ scan technique and the five-point measuring procedure. The crystal used had the dimensions 0.085 × 0.115 × 0.025 mm, and was mounted along the unique b axis. The scan range for the lattice points was $\Delta\theta = \pm 0.80^\circ$. The count was taken in 0.01° steps, with a step time of 1.2 s. Three standard reflexions were measured after every 47th lattice point. No significant change in their net intensities was observed.

1469 independent reflexions with $\theta \leq 30^\circ$ were measured. The intensity values for 1247 of these were

judged significant from the criterion $\sigma(I)/I \leq 0.40$, where $\sigma(I) = (I_i + I_b)^{1/2}$.

Lorentz-polarization, absorption and preparatory extinction corrections were applied to the data. The calculated linear absorption coefficient, $\mu(\text{Mo } K\alpha) = 103.0 \text{ cm}^{-1}$, was used in estimating a transmission factor for each reflexion (*International Tables for X-ray Crystallography*, 1962). This was done by the Gaussian integration method, with $4 \times 10 \times 10$ grid-points. The factor t in the formula $I = I_{\text{obs}}/t$ ranged from 0.398 to 0.862.

Refinement

The reflexions $h0l$: $l = 2n + 1$, and $0k0$: $k = 2n + 1$ were systematically absent, and confirm the space group $P2_1/c$ (No. 14) given by Mumme & Watts (1971). The positions of the metal atoms given by these authors explained all major peaks in a three-dimensional Patterson synthesis. The refinement of the structure was performed with a full-matrix least-squares program.

The scattering factors for neutral atoms were taken from McMaster, Kerr del Grande, Mallet & Hubbel (1969), and the anomalous scattering values from *International Tables for X-ray Crystallography* (1962).

The Cs occupancy factor was refined at a late stage of the refinement procedure giving a value of 1.012 (3). The result supports the assumption of full occupancy of the Cs positions. The final cycles of the refinement included anisotropic temperature factors and an isotropic extinction correction (altogether 74 variables). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. The final R and R_w values were 0.0320 and 0.0270 respectively. Statistical weights were applied to the structure factors.

The residual peaks in a final three-dimensional difference Fourier synthesis showed a maximum height of 7% of the smallest O peak in the corresponding F_o synthesis.

The final positional and thermal parameters, together with their e.s.d.'s and the r.m.s. thermal displacements,

Table 2. *The crystal structure of CsV₂O₅*

CsV₂O₅, $M_r = 314.79$. Space group $P2_1/c$ (No. 14). Cell dimensions: $a = 7.021$ (1), $b = 9.898$ (2), $c = 7.783$ (1) Å, $\beta = 90.65$ (1)°, $V = 540.84$ Å³. Density: 3.87 (observed), 3.86 g cm⁻³ (calculated). Cell content: 4 CsV₂O₅.

Atom (n)	Point set	x	y	z
Cs	4(e)	0.61681 (7)	0.12548 (5)	0.22076 (6)
V(1)	4(e)	0.88245 (17)	0.47744 (11)	0.16284 (13)
V(2)	4(e)	0.12122 (18)	0.29496 (11)	0.48682 (13)
O(1)	4(e)	0.11381 (76)	0.12791 (49)	0.18375 (50)
O(2)	4(e)	0.33237 (76)	0.32060 (51)	0.41300 (62)
O(3)	4(e)	0.67064 (73)	0.42575 (49)	0.11699 (60)
O(4)	4(e)	0.94991 (69)	0.36486 (50)	0.35861 (52)
O(5)	4(e)	0.06781 (62)	0.38510 (45)	0.02145 (50)

Table 3. *Final anisotropic temperature factors defined as*
 $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

β_{ij} values are given in Å² × 10⁵, e.s.d.'s are within parentheses. The r.m.s. components (R_i) of thermal displacements along the ellipsoid axes and the r.m.s. radial (R) thermal displacements are included.

Atom (n)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1 (Å)	R_2 (Å)	R_3 (Å)	R (Å)
Cs	870 (10)	362 (5)	841 (8)	-16 (7)	12 (6)	51 (6)	0.132	0.148	0.162	0.256
V(1)	537 (24)	119 (10)	312 (17)	14 (13)	-20 (16)	-9 (11)	0.076	0.097	0.117	0.170
V(2)	689 (25)	105 (10)	304 (17)	-26 (14)	62 (16)	-11 (11)	0.072	0.096	0.132	0.178
O(1)	1683 (131)	140 (43)	339 (74)	7 (78)	-124 (78)	106 (51)	0.064	0.114	0.206	0.244
O(2)	778 (123)	406 (58)	843 (93)	-162 (68)	129 (8)	-67 (57)	0.118	0.147	0.173	0.256
O(3)	664 (115)	361 (53)	632 (85)	-132 (64)	4 (76)	3 (53)	0.112	0.139	0.148	0.232
O(4)	1072 (113)	227 (48)	412 (71)	190 (69)	-166 (70)	6 (53)	0.089	0.112	0.174	0.225
O(5)	710 (98)	45 (41)	419 (68)	46 (59)	156 (64)	27 (47)	0.045	0.102	0.142	0.181

are given in Tables 2 and 3.* The most important distances and angles are given in Table 4. The V—O distances have been corrected for thermal motion (according to the riding-motion model).

Discussion

The structure of CsV₂O₅ given by Mumme & Watts (1971) is confirmed (see Fig. 1). The present investi-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32113 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Interatomic distances (Å) in CsV₂O₅*

Estimated standard deviations in the last decimal place are given in parentheses. The V—O distances are compared with those reported by Mumme & Watts (1971). The V—O distances, corrected for thermal motion according to the riding-motion model, are included.

(a) V(1)O₅ square pyramid

		Corrected	Mumme & Watts (1971)
V(1)—O(3)	1.609 (5)	1.616	1.52 (4)
—O(1)	1.909 (5)	1.918	1.89 (3)
—O(4)	1.942 (5)	1.947	1.91 (3)
—O(5)	1.942 (4)	1.944	1.92 (3)
—O(5)	2.010 (4)	2.012	2.03 (4)

Metal—metal separations

V(1)—V(1)	3.073 (2)	V(1)—V(2)	3.352 (2)
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Oxygen—oxygen distances

O(5)—O(5)	2.487 (9)	O(4)—O(5)	2.768 (6)
O(1)—O(5)	2.655 (6)	O(3)—O(5)	2.843 (7)
O(1)—O(4)	2.662 (7)	O(3)—O(5)	2.922 (7)
O(3)—O(4)	2.768 (7)	O(1)—O(3)	2.940 (7)

(b) V(2)O₄ tetrahedron

		Corrected	Mumme & Watts (1971)
V(2)—O(2)	1.616 (5)	1.626	1.56 (3)
—O(4)	1.701 (5)	1.708	1.77 (4)
—O(1)	1.714 (4)	1.722	1.73 (4)
—O(5)	1.842 (5)	1.843	1.91 (5)
—O(1)	2.881 (4)		

Oxygen—oxygen distances

O(1)—O(2)	2.670 (7)	O(1)—O(5)	2.858 (6)
O(2)—O(4)	2.749 (7)	O(2)—O(5)	2.889 (7)
O(1)—O(4)	2.769 (6)	O(4)—O(5)	2.896 (7)

(c) Cs coordination polyhedron

Cs—O(3)	3.104 (5)	Cs—O(4)	3.490 (5)
—O(3)	3.104 (5)	—O(1)	3.505 (5)
—O(3)	3.144 (5)	—O(1)	3.540 (5)
—O(2)	3.147 (5)	—O(4)	3.684 (5)
—O(2)	3.166 (5)	—O(5)	3.806 (4)
—O(2)	3.213 (5)		

gation has, however, indicated substantial shifts of the O atom positions, and changes in the interatomic distances exceeding those due to the deviations of the unit-cell dimensions (see above) (Table 4).

Mumme & Watts pictured the structure of CsV₂O₅ as formed by tetrahedra and distorted trigonal bipyramids. We prefer to describe the V(1)O₅ polyhedron observed in this structure as a square pyramid.

The layers formed by pairs of edge-sharing square pyramids and bridging tetrahedra (see Fig. 2) are held together by Cs atoms. Within a pair of square pyramids, the two apical O atoms are pointing in opposite directions. The remaining O atoms of the pyramids are shared with tetrahedra. The bridging V(1)—O distances are in the range 1.909–2.010 Å, and the apical V(1)—O(3) distance is 1.609 Å (see Fig. 3). The V(1)—V(1) separation of 3.073 Å is the V—V distance across the shared edge of the pair of square pyramids; it is the shortest observed in the structure,

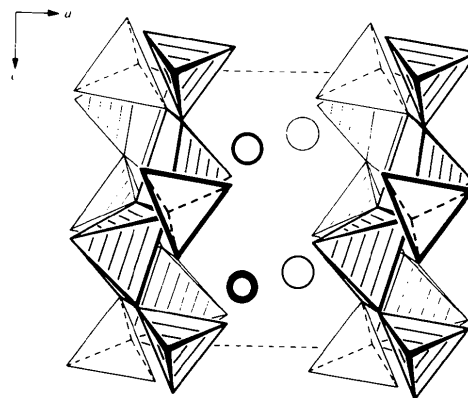


Fig. 1. The structure of CsV₂O₅ projected on (010), showing the layers formed by the V—O polyhedra and Cs atoms.

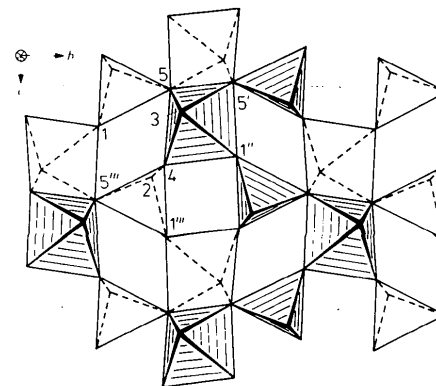


Fig. 2. One sheet of V—O polyhedra projected on (100), showing the linking between the pairs of square pyramids and the tetrahedra. The numbering of the O atoms is in accordance with that in Table 2. Symmetry code: (') $\bar{x}, \bar{y}, \bar{z}$; (') $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$; (') $x, \frac{1}{2} - y, \frac{1}{2} + z$ respectively.

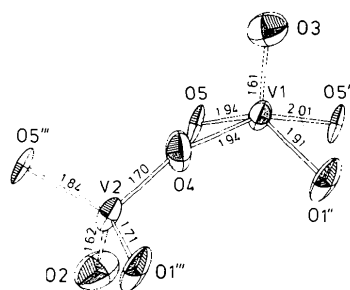


Fig. 3. The V(1) square pyramid and the V(2) tetrahedron in CsV_2O_5 . The thermal ellipsoids are drawn at 90% probability. The numbering of the atoms is in accordance with Fig. 2.

and is therefore accompanied by the closest O—O separation of 2.487 Å [i.e. the O(5)—O(5) distance over the shared edge]. The remaining O—O distances in the square pyramid are in the range 2.66–2.94 Å.

Three of the O atoms in the tetrahedron are bonded to square pyramids, while the fourth O is terminal. The bridging V(2)—O distances are in the range 1.701–1.842 Å, and the terminal V(2)—O(2) bond length (1.616 Å) is of the same magnitude as the apical V(1)—O(3) distance in the square pyramid. The V—V distance between the tetrahedron and the square pyramid is 3.352 Å. The O—O edges of the tetrahedron are in the range 2.67–2.90 Å.

Within the coordination sphere of the Cs atom, there are nine O atoms at 3.10–3.54 Å (mean 3.27 Å). There are two additional O atoms at 3.68 and 3.81 Å. The Cs coordination is shown in Fig. 4. The Cs—O distances are given in Table 4.

The O atoms have different functions in the structure (see Table 5). O(5) is bonded to three V atoms (O—V mean: 1.931 Å), and is not coordinated to Cs. The O(1) and O(4) atoms are shared between two V atoms (O—V mean: 1.817 Å) and are within the coordination sphere of two Cs atoms. The O(2) and O(3) atoms, each with just one V neighbour (O—V mean: 1.612 Å), are both coordinated to three Cs atoms.

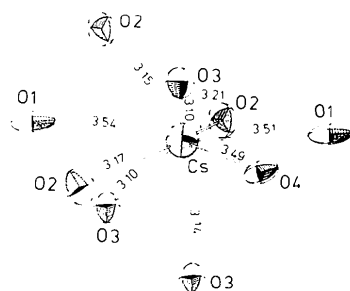


Fig. 4. The coordination of Cs atoms. The thermal ellipsoids are drawn at 90% probability.

Table 5. The environments of the oxygen atoms in CsV_2O_5

O—V distances (Å)		O—Cs distances (Å)	
	Mean		Mean
O(5)—V(2)	1.842	O(5)—Cs	3.806
—V(1)	1.942		
—V(1)'	2.010		
O(1)—V(2)	1.714	O(1)—Cs	3.505
—V(1)	1.909	—Cs'	3.540
O(4)—V(2)	1.701	O(4)—Cs	3.490
—V(1)	1.942	—Cs'	3.684
O(2)—V(2)	1.616	O(2)—Cs	3.147
		Cs'	3.166
		Cs''	3.213
O(3)—V(1)	1.609	O(3)—Cs	3.104
		—Cs'	3.104
		—Cs''	3.144

A comparison of the average V—O distance as a function of CN and oxidation number (see Waltersson, Forslund, Wilhelmi, Andersson & Galy, 1974) leads us to assume that the V^{5+} and V^{4+} atoms are segregated within the tetrahedron and the square pyramid respectively. The physical properties of CsV_2O_5 will be discussed in a forthcoming paper.

We wish to thank Dr Karl-Axel Wilhelmi for helpful discussions and Professor Arne Magnéli for his kind interest. Thanks are also due to Dr Sven Westman for revising the English text and to Mr Tomasz Niklewski for the density determination.

The investigation has been supported by the Swedish Natural Science Research Council.

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