Measurements on a single crystal of the electrical conductivity in the range 90–400 K showed the compound to be a semiconductor with an activation energy close to 0·07 eV.

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# The Crystal Structure of $Cs_2V_5O_{13}$

By KJELL WALTERSSON AND BERTIL FORSLUND

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, Fack, S-104 05 Stockholm, Sweden

The crystal structure of $Cs_2V_5O_{13}$ has been determined and refined to a final $R_w$ value of 0·019 from 267 independent reflexions and 35 variables. Three-dimensional X-ray diffractometer data (Mo $K\alpha$ radiation) were used. The space group is $I4mm$ (No. 107), and the unit-cell dimensions are $a = 7.762(1)$, $c = 11.746(2)$ Å, $V = 707.7$ Å, $Z = 2$. The new structure type can be visualized in different, complementary ways: it can be regarded as composed of $VO_4$ tetrahedra and $VO_5$ square pyramids in the ratio 4:1 (joined exclusively by corner-sharing) forming $_\infty^2(V_5O_{13}^{2-})$ layers, held together by $Cs^+$ ions; or composed of isolated isocyclic rings of $V_4O_{12}^{4-}$ tetramers and $VO^{2+}$ (vanadyl) and $Cs^+$ ions. The observed, averaged V–O distances for the four- and five-coordinated V atoms are 1·71 and 1·96 Å respectively; the V–O distance in the vanadyl ion is 1·587(16) Å. The $Cs^+$ ions have twelve nearest O neighbours in the range 3·24–3·54 Å. The structure is compared with those of $K_2V_3O_8$ and $K_3V_5O_{14}$.

## Introduction

During recent years, the formation conditions, crystal structures and physical properties (electrical and magnetic) of binary vanadium(IV,V) oxides and ternary, heavy alkali–metal vanadium(IV, V) oxides have been investigated at this Institute. The structures of the following compounds have been studied: $Cs_{0.35}V_3O_7$ (Waltersson & Forslund, 1977a), $Cs_{0.3}V_2O_5$ (Waltersson & Forslund, 1977b), and $CsV_2O_5$ (Waltersson & Forslund, 1977c).

Reid & Watts (1970) reported the synthesis of a new, reduced, ternary caesium vanadium oxide with tetragonal symmetry. Unit-cell dimensions were $a = 7.72$ and $c = 11.73$ Å. The compound was tentatively given the formula $Cs_{0.94}V_2O_{5.3}$. The preparative technique used was electrolysis at 540°C of a melt containing 37 mol% $Cs_2O$ and 63 mol% $V_2O_5$. Fotief & Golofkin (1972) also reported the preparation (by heating mixtures of $Cs_2CO_3$ and $V_2O_5$ at 500°C in vacuum) of a tetragonal phase with a suggested composition of $CsV_3O_{7.5}$. The powder pattern was consis-

tent with the cell given by Reid & Watts (see also Volkov, Curat & Fotief, 1974). The present paper reports the crystal-structure determination of the tetragonal phase.

## Experimental

Polycrystalline, pure (as judged from powder-pattern data) samples of the new tetragonal compound were obtained after reaction of $CsVO_3$, $V_2O_5$ and $V_2O_3$, in the mole ratio (8:5:1), in evacuated silica tubes at 450°C for one month.

Table 1. *Powder pattern of* $Cs_2V_5O_{13}$

Cu $K\alpha_1$ radiation ($\lambda = 1.54050$ Å). Internal standard KCl, $a = 6.2930$ Å.

| h k l | $d_{obs}$ | $10^5 \sin^2\theta_{obs}$ | $10^5 \sin^2\theta_{calc}$ | $I_{obs}$ |
|---|---|---|---|---|
| 0 0 2 | 5.858 | 1729 | 1720 | vvw |
| 1 1 0 | 5.470 | 1983 | 1969 | s |
| 1 1 2 | 4.002 | 3705 | 3689 | vs |
| 2 0 0 | 3.880 | 3942 | 3938 | vvw |
| 1 0 3 | 3.495 | 4858 | 4855 | m |
| 1 2 1 | 3.328 | 5357 | 5353 | m |
| 2 0 2 | 3.235 | 5669 | 5659 | vs |
| 0 0 4 | 2.936 | 6881 | 6880 | m |
| 2 2 0 | 2.743 | 7884 | 7877 | vs |
| 1 1 4 | 2.589 | 8854 | 8850 | s |
| 2 2 2 | 2.487 | 9595 | 9597 | w |
| 3 1 0 | 2.456 | 9840 | 9846 | m |
| 2 0 4 | 2.3427 | 10810 | 10819 | vw |
| 3 1 2 | 2.2649 | 11566 | 11566 | m |
| 1 0 5 | 2.2494 | 11726 | 11735 | vw |
| 3 0 3 | 2.1590 | 12728 | 12732 | vvw |
| 2 2 4 | 2.0056 | 14750 | 14757 | m |
| 4 0 0 | 1.9405 | 15756 | 15754 | s |
| 3 2 3 | 1.8866 | 16669 | 16670 | w |
| 3 1 4 | 1.8834 | 16725 | 16726 | m |
| 1 1 6 | 1.8444 | 17440 | 17450 | w |
| 0 2 6 | 1.7473 | 19432 | 19419 | s |
| 4 1 3 | 1.6967 | 20608 | 20609 | vvw |
| 4 2 2 | 1.6649 | 21405 | 21412 | vs |
| 4 0 4 | 1.6189 | 22636 | 22634 | m |
| 3 2 5 | 1.5871 | 23555 | 23551 | vw |
| 3 3 4 | 1.5530 | 24598 | 24603 | w |
| 5 0 1 | 1.5395 | 25034 | 25045 | vvw |
| 3 1 6 | 1.5305 | 25329 | 25327 | m |
| 5 1 0 | 1.5228 | 25586 | 25600 | vvw |
| 2 1 7 | 1.5112 | 25980 | 25994 | vvw |
| 5 1 2 | 1.4738 | 27314 | 27320 | m |
| 5 0 3 | 1.4430 | 28494 | 28485 | vw |
| 5 2 1 | 1.4310 | 28973 | 28984 | w |
| 1 1 8 | 1.4180 | 29505 | 29491 | vvw |
| 4 4 0 | 1.3720 | 31517 | 31507 | w |
| 5 1 4 | 1.3516 | 32478 | 32480 | m |
| 3 3 6 | 1.3368 | 33201 | 33204 | vw |
| 4 2 6 | 1.2987 | 35174 | 35173 | m |
| 6 0 2 | 1.2634 | 37167 | 37166 | w |
| 3 1 8 | 1.2602 | 37356 | 36368 | vw |
| 4 4 4 | 1.2430 | 38397 | 38388 | w |
| 5 2 5 | 1.2285 | 39310 | 39304 | vw |
| 6 2 0 | 1.2272 | 39393 | 39384 | w |
| 5 3 4 | 1.2123 | 40368 | 40357 | w |
| 4 0 8 | 1.1709 | 43272 | 43275 | w |

Crystals suitable for single-crystal X-ray work were grown from mixtures of $CsVO_3$, $V_2O_5$ and $V_2O_3$ (8:4:1) (corresponding to $Cs_{0.89}V_2O_{5.22}$ or $Cs_{1.33}V_3O_{7.83}$), which were heated in evacuated silica tubes at 550°C for one week.

The reddish-brown crystals are plate-like and opaque. They are not affected by dilute ammonia. The Cs/V ratio was determined by means of atomic absorption spectroscopy (for crystals selected from different samples) and found to be 0.39. The density, measured by hydrostatic weighing (Niklewski, Kihlborg, Nygren & Sävborg, 1975), was 3.39 g cm$^{-3}$.

The powder photographs were taken with a Guinier–Hägg camera at 20°C, Cu $K\alpha_1$ radiation, and KCl as an internal standard ($a = 6.2930$ Å; Hambling, 1953). Least-squares refinement of the cell parameters gave $a = 7.762(1)$ and $c = 11.746(2)$ Å. The powder pattern is listed in Table 1.

The selection of a suitable crystal for the intensity data collection and the determination of the systematic extinctions were performed by X-ray photographic methods (oscillation and Weissenberg techniques). The crystal used was $0.10 \times 0.10 \times 0.01$ ($c$) mm, and was mounted along the crystallographic $c$ axis.

The X-ray intensity data were collected on a Siemens AED automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation, and a scintillation counter with pulse-height discrimination.

The $\theta$–$2\theta$ scan technique was used. Each lattice point was measured with the five-values technique. The scan range for the individual reflexions was: $+\Delta\theta = 0.54 + 0.28$ tg $\theta$, and $-\Delta\theta = 0.51 + 0.28$ tg $\theta$. The intensity measurement was taken in steps of $0.01°$ in $\theta$, with a maximum step-time of 1.20 s. For strong reflexions the automatic attenuator mechanism was set to add attenuation filters. Three standard reflexions were measured after every 47th lattice point; these indicated no deterioration of the crystal.

All the possible reflexions (systematic extinctions excluded) within one octant of the reciprocal-lattice sphere with $\theta \leq 30°$ were registered, giving a total number of 616 observations.

The net intensity $I_n$ was calculated as $I_t - I_b$, and the estimated standard deviation was obtained as $\sigma(I_n) = (I_t + I_b)^{1/2}$. 477 reflexions were judged significant from the criterion $\sigma(I_n)/I_n \leq 0.40$.

Lorentz–polarization, absorption, and preparatory extinction corrections were applied to the data. The calculated linear-absorption coefficient, $\mu(Mo\ K\alpha) = 85.2$ cm$^{-1}$, was used in computing a transmission factor for each reflexion (*International Tables for X-ray Crystallography*, 1962). The absorption was estimated by the Gaussian integration method with $12 \times 12 \times 4$ grid-points. The factor $t$ in the formula $I = Lp \times I_n/t$ ranged from 0.423 to 0.934. The calculations were performed on IBM 1800 and IBM 360/75 computers.

## Structure determination and refinement

The reflexions systematically absent were $h + k + l$ odd, which indicates space groups $I4/mmm$ (No. 139), $I\bar{4}2m$ (No. 121), $I\bar{4}m2$ (No. 119), $I4mm$ (No. 107), $I422$ (No. 97), $I4/m$ (No. 87), $I\bar{4}$ (No. 82), and $I4$ (No. 79).

A careful investigation of the absorption-corrected structure amplitudes confirmed the Laue symmetry to be $4/mmm$, and this excluded space groups $I4/m$, $I\bar{4}$, and $I4$. The number of observations was now reduced to 267 independent reflexions, with $h \geq k$. As the chemical analysis was not thought to give conclusive evidence of the composition of the compound, the structure determination was undertaken without making any assumption about the number of atoms of the various atomic species. The investigation was started with the assumption that the space group $I4/mmm$ was correct. From a three-dimensional Patterson synthesis, tentative coordinates of Cs and V atoms were derived in point sets $4(d)$ and $8(h)$ respectively. In a following difference Fourier synthesis the peaks due to another set of V atoms were located in $4(e)$. This was found, however, to give unreasonably short V–V distances (2·3 Å), which excluded the symmetry $I4/mmm$. Therefore the structure determination was continued in the noncentrosymmetric space group $I4mm$ (No. 107). All the peaks in the Patterson map were now explained

### Table 2. The crystal structure of $Cs_2V_5O_{13}$

$Cs_2V_5O_{13}$, $M_r = 728.51$. Space group $I4mm$ (No. 107). Cell dimensions: $a = 7.762$ (1), $c = 11.746$ (2) Å, $V = 707.68$ Å$^3$. Cell content: 2 $Cs_2V_5O_{13}$. $D_{obs.} = 3.39$, $D_{calc.} = 3.40$ g cm$^{-3}$.

| Atom ($n$) | Point set | $x$ | $y$ | $z$ |
|---|---|---|---|---|
| Cs | 4($b$) | 0 | $\frac{1}{2}$ | $\frac{1}{4}$ |
| V(1) | 8($c$) | 0.22394 (12) | 0.22394 (12) | 0.00292 (47) |
| V(2) | 2($a$) | 0 | 0 | 0.64934 (36) |
| O(1) | 8($c$) | 0.31644 (72) | 0.31644 (72) | 0.11637 (79) |
| O(2) | 8($c$) | 0.30588 (92) | 0.30588 (92) | 0.89022 (83) |
| O(3) | 8($d$) | 0.27149 (105) | 0 | −0.01040 (118) |
| O(4) | 2($a$) | 0 | 0 | 0.78442 (139) |

with Cs atoms in point set 4($b$), and V atoms in 8($c$) and 2($a$). With least-squares methods, the metal positions were refined and the new coordinates were used for a further ($F_{obs.} - F_{metal}$) synthesis. The conventional $R$ value at this stage was 0·12.

In the following difference Fourier synthesis, O atoms were identified in point sets 8($c$), 8($d$) and 2($a$). With these O positions included, the $R$ value rapidly dropped to 0·05. The result of the structural analysis shows beyond reasonable doubt that the formula of the compound is $Cs_2V_5O_{13}$.

The structure was refined by means of a full-matrix least-squares program. In the final cycles of refinement, anisotropic temperature factors and isotropic extinction corrections, altogether 35 variables, were included. The scattering factors used were for neutral atoms (McMaster, Kerr del Grande, Mallet & Hubbel, 1969) and the $\Delta f'$ and $\Delta f''$ values for Mo $K\alpha$ radiation were taken from International Tables for X-ray Crystallography (1962). The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. The final $R$ and $R_w$ values were 0·0313 and 0·0194 respectively. Statistical weights were applied to the structure factors.*

The space group $I4mm$ is unambiguously determined by the positions of V(2) and O(4) in point set 2($a$). Therefore the space groups $I\bar{4}m2$, $I\bar{4}2m$ and $I422$ were also excluded.

The final positional and thermal parameters, together with their estimated standard deviations and numerical values of the r.m.s. displacements, are given in Tables 2 and 3. The most important distances and angles are given in Table 4. The V–O distances, corrected for thermal motion according to the riding-motion model, are included.

In a final three-dimensional ($F_o - F_c$) synthesis, the maximum residual peak showed a height of 16% of the smallest O peak in the corresponding $F_o$ synthesis.

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

$\beta_{ij}$ values are given in Å$^2$ $\times 10^5$, 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 ($n$) | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | $R_1$ | $R_2$ | $R_3$ | $R$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Cs | 868 (46) | 828 (44) | 359 (6) | 0 | 0 | 0 | 0.158 | 0.159 | 0.163 | 0.277 |
| V(1) | 354 (13) | 354 (13) | 429 (12) | 73 (25) | 165 (74) | 165 (74) | 0.088 | 0.093 | 0.188 | 0.277 |
| V(2) | 344 (33) | 344 (33) | 271 (30) | 0 | 0 | 0 | 0.102 | 0.138 | 0.138 | 0.200 |
| O(1) | 1017 (101) | 1017 (101) | 1160 (82) | 30 (256) | −608 (145) | −608 (145) | 0.099 | 0.174 | 0.321 | 0.378 |
| O(2) | 1758 (145) | 1758 (145) | 208 (81) | 1192 (367) | −12 (189) | −12 (189) | 0.120 | 0.131 | 0.300 | 0.349 |
| O(3) | 1035 (137) | 338 (90) | 808 (137) | 0 | 135 (232) | 0 | 0.101 | 0.174 | 0.241 | 0.313 |
| O(4) | 1406 (251) | 1406 (251) | 204 (130) | 0 | 0 | 0 | 0.119 | 0.207 | 0.207 | 0.316 |

## Description and discussion of the crystal structure

The crystal structure of $Cs_2V_5O_{13}$ is shown in Fig. 1. For the numbering of the atoms see Table 2 and Fig. 2. The unit cell contains ten V atoms in eight four-co-ordinated $V(1)O_4$ tetrahedra, and two five-coordinated $V(2)O_5$ square pyramids. The structure can be regarded as built up of $(V_5O_{17})$ units, composed of one central square pyramid and four tetrahedra linked together by corner-sharing. By further corner-sharing the $(V_5O_{17})$ units are linked together by eight shared oxygens to layers with the composition $^2_\infty(V_5O_{13})^{2-}$. The layers are situated at $z \sim 0$ and $z \sim \frac{1}{2}$.

Table 4. *Interatomic distances* (Å) *and bond angles* (°) *in* $Cs_2V_5O_{13}$

The e.s.d.'s in the last decimal place are given within parentheses.

(a) $V(1)O_4$ tetrahedron

Metal–oxygen distances

| | Uncorrected | Corrected |
|---|---|---|
| V(1)–O(2) | 1·600 (10) | 1·615 |
| –O(1) | 1·676 (9) | 1·706 |
| –O(3)  (2x) | 1·784 (3) | 1·797 |

Metal–metal separations

| | | |
|---|---|---|
| V(1)–V(1)  (2x)  3·477 (2) | V(1)–V(2) | 3·484 (4) |

| | Bond angles | Oxygen–oxygen distances |
|---|---|---|
| O(1)–V(1)–O(2) | 108·5 (5) | 2·659 (13) |
| –O(3)  (2x) | 113·5 (5) | 2·893 (10) |
| O(2)–V(1)–O(3)  (2x) | 103·5 (5) | 2·659 (10) |
| O(3)–V(1)–O(3) | 113·3 (5) | 2·980 (12) |
| V(1)–O(3)–V(1) | 154·0 (6) | |

(b) $V(2)O_5$ square pyramid

Metal–oxygen distances

| | Uncorrected | Corrected |
|---|---|---|
| V(2)–O(4) | 1·587 (16) | 1·607 |
| –O(1)  (4x) | 2·052 (8) | 2·075 |

Metal–metal separations

| | |
|---|---|
| V(2)–V(1)  (4x) | 3·484 (4) |

| | Bond angles | Oxygen–oxygen distances |
|---|---|---|
| O(1)–V(2)–O(1)  (4x) | 88·0 (1) | 2·850 (11) |
| –O(4)  (4x) | 100·9 (3) | 2·821 (14) |
| –O(1)  (2x) | 158·3 (12) | 4·030 (11) |

(c) Cs coordination sphere

| | | | |
|---|---|---|---|
| Cs–O(1)  (4x) | 3·244 (5) | Cs–O(3)  (2x) | 3·536 (13) |
| –O(2)  (4x) | 3·259 (5) | | |
| –O(3)  (2x) | 3·327 (13) | –O(4)  (2x) | 3·902 (2) |

The layers are held together by Cs ions. The terminal apical oxygens of the square pyramids and the unshared oxygens of the tetrahedra are pointing in opposite directions. The mean value of the V–O separations in the square pyramid is 1·96 Å, and the corresponding value for the tetrahedron is 1·71 Å.

The different functions of the O atoms can be summarized in the following way. The unshared oxygens, O(2) and O(4), belong to the tetrahedra and the square pyramids respectively. The distances V(1)–O(2) and V(2)–O(4) are 1·600 (10) and 1·587 (16) Å; the latter V–O separation is the shortest observed in the structure.

The O(1) and O(3) atoms belong to two V–O polyhedra: the O(1) atom to one tetrahedron and one square pyramid, the O(3) atom being the common corner of two tetrahedra. The V(1)–O(1) and O(1)–V(2) distances are 1·676 (9) Å and 2·052 (8) Å respectively. The bridging oxygen atom O(3) forms two equally long distances [V(1)–O(3)] of 1·784 (3) Å.

The Cs atom is coordinated to twelve oxygens in the range 3·24–3·54 Å, mean 3·31 Å, in good agreement with the 3·37 Å given in *International Tables for X-ray Crystallography* (1962). The Cs coordination polyhedron is shown in Fig. 3.
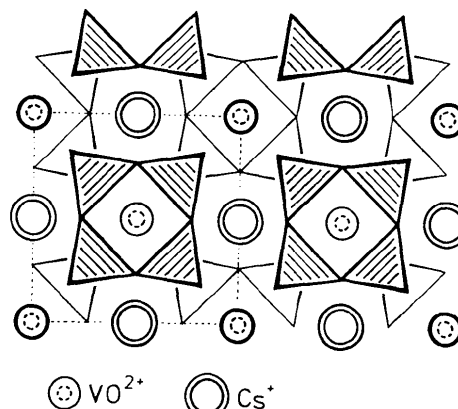


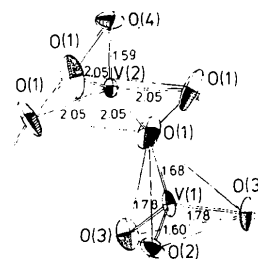Fig. 1. The structure of $Cs_2V_5O_{13}$ projected on (001).

$\bigodot VO^{2+}$   $\bigcirc Cs^+$



Fig. 2. The V(1) tetrahedron and the V(2) square pyramid in $Cs_2V_5O_{13}$. The thermal ellipsoids are drawn at 90% probability.

Considering only the primary cation and anion coordination numbers, the formula of $Cs_2V_5O_{13}$ can be written $^{[12]}Cs_2^{[5]}V^{[4]}O_8^{[1]}O_5$.

Interesting structural relations exist between $Cs_2V_5O_{13}$ and both $K_2V_3O_8$ (Galy & Carpy, 1975) and $K_3V_5O_{14}$ (Byström & Evans, 1959).

$K_2V_3O_8$ [or $K_2(VO)V_2O_7$] is isostructural with the mineral fresnoite, $Ba_2(TiO)Si_2O_7$ (Massé, Grenier & Durif, 1967; Moore & Louisnathan, 1967, 1969). In the latter the Ti atom is five-coordinated with tetragonal-pyramidal geometry. All the basal O atoms of the Ti—O square pyramid are shared by the adjacent $SiO_4$ tetrahedra, and the $SiO_4$ tetrahedra are joined in pairs forming $Si_2O_7$ groups. The TiO pyramid and the $Si_2O_7$ groups are linked into 'heterocyclic' five-membered rings, forming layers which are held together by Ba—O bonds.

In $K_2V_3O_8$ each tetrahedron is in contact with two square pyramids (and one tetrahedron), with V—O distances of $1.699(5)$ Å – to be compared with the somewhat shorter $V(1)$—$O(1)$ distance of $1.676(9)$ Å in $Cs_2V_5O_{13}$. The bridging V—O distances in the $V_2O_7$ groups are of the same magnitude in the two compounds, viz. $1.794$ (4) and $1.784$ (3) Å respectively. However, the angle $V(1)$—$O(3)$—$V(1)$ in the ion $V_4O_{12}^{4-}$ is considerably larger ($154.0°$) in the Cs than in the K compound. This difference is explained by the four-membered isocyclic ring $(V_4O_{12}^{4-})$ in $Cs_2V_5O_{13}$, contra the $V_2O_7^{4-}$ group in $K_2V_3O_8$. The short V—O distance in the pyramid in $K_2V_3O_8$ is $1.582$ (5) Å, i.e. exactly the same distance as observed in $Cs_2V_5O_{13}$ (see above).

A detailed analysis of the V—O distances in $K_3V_5O_{14}$ is hampered by the fact that the structure determination is of a preliminary character. Nevertheless, the architecture of $K_3V_5O_{14}$ is of interest in this context. The five pentavalent V atoms form almost regular five-membered rings of square pyramids and trigonal pyramids (distorted tetrahedra), joined by sharing neighbouring basal corners with the V atoms nearly in the same plane. All apices point in the same direction (along c), with short V—O distances of $1.5$–$1.6$ Å. The opposite V—O distances in all polyhedra are too long ($\sim 3.4$ Å) for bonding. The two-dimensional network, $_\infty^2V_5O_{14}^{3-}$, is held together by inserted K ions.

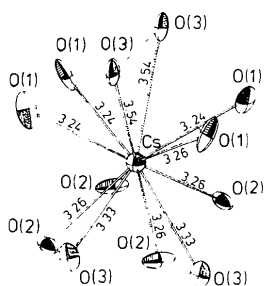The fact that the mean bond distance between a central atom (X) and its surrounding O atoms is relatively constant for the same coordination and oxidation numbers of the atom X has been emphasized by several authors, e.g. X = S (Baur, 1964); X = Cr (Wilhelmi, 1966; Löfgren, 1974); X = P (Baur & Khan, 1970); X = P, As, V (Shannon & Calvo, 1973); and X = V (Waltersson, Forslund, Wilhelmi, Andersson & Galy, 1974).

Of course it must be emphasized that such comparisons are only legitimate between structures which are refined to a considerable degree of accuracy, viz. those with estimated standard deviations in the X—O distances of $\sim 0.02$ Å. The number of structures fulfilling this requirement with regard to the vanadium(IV,V) compounds is limited. In $Cs_2V_5O_{13}$ (see above) the observed mean V—O distances (uncorrected for thermal motion) for the tetrahedra and the square pyramids are $1.71$ and $1.96$ Å respectively.

If it is assumed that the $V^{4+}$ are situated in the square pyramids and the $V^{5+}$ in the tetrahedra, excellent agreement is obtained for the mean value of the tetrahedra, viz. observed $1.71$, compared with the grand mean $1.72$ Å (Waltersson et al., 1974). For the square pyramids the situation seems to be quite different. The observed distances in other compounds containing five-coordinated $V^{4+}$ are in the range $1.88$–$1.90$ Å, compared with the mean distance of $1.96$ Å in $Cs_2V_5O_{13}$. If the structure of $Cs_2V_5O_{13}$ is described as built up of $V_4O_{12}^{4-}$ ions, formed by four tetrahedra, fused together by corner-sharing to isocyclic four-membered rings joined by vanadyl ($VO^{2+}$) and $Cs^+$ ions, no contradictory mean distances are observed. The V—O distance in the vanadyl group is quite normal, viz. $1.587(16)$ Å. Structure determinations of compounds containing such four-membered rings of $VO_4$ units appear not to have been reported before. However, results from cryoscopic investigations of aqueous solutions (Jahr & Schoepp, 1959) indicate the presence of tetrameric ion $V_4O_{12}^{4-}$. Accurate EMF measurements do not seem to exclude the presence of such a species (Ingri, 1976). The four-membered rings of tetrahedra are a common feature in several silicate structures, e.g. in axinite (Ito & Takéuchi, 1952), ekanite (Richard & Perrault, 1972), and baotite (Simonov, 1960). Vanadyl ions have also been found in cavansite and pentagonite structures, dimorphs of $Ca(VO)(Si_4O_{10}).4H_2O$ (Evans, 1973). In these structures, layers are formed by a network of Si tetrahedra joined by common corners. The $X_4O_{12}$ group (X = P) was first recognized by Pauling & Sherman (1937) in $Al(PO_3)_3$ [i.e. $Al_4(P_4O_{12})_3$], and later confirmed in $Cu_2P_4O_{12}$ (Laügt, Guitel, Tordjman & Bassi, 1972) and $Mg_2P_4O_{12}$ (for further references see Nord & Lindberg, 1975).



Fig. 3. The Cs coordination polyhedron in $Cs_2V_5O_{13}$. The thermal ellipsoids are drawn at 90% probability.

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# A Refinement of the Crystal Structure of CsV₂O₅

By Kjell Waltersson and Bertil Forslund

*Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, Fack, S-104 05 Stockholm, Sweden*

The crystal structure of $CsV_2O_5$ has been refined on the basis of three-dimensional X-ray diffractometer data (Mo $K\alpha$ 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 $CsV_2O_5$ 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 $CsV_2O_5$. 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)°.