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The Crystal Structure of Reduced Cesium Vanadate, CsV_2O_5

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Electrolysis of a 44 mole% Cs_2O, 56 mole% V_2O_5 melt at 585°C has resulted in the formation of CsV_2O_5 in single crystal form. This compound is monoclinic, space group $P2_{1/c}$, with $a = 7.008$ Å (5), $b = 9.977$ Å (5), and $c = 7.729$ Å (5), $\beta = 90.98°$ (5), and the structure analysis has shown it to contain vanadium V in tetrahedral and vanadium IV in distorted trigonal bipyramidal coordination. A sheet structure results from the formation of pairs of edge shared trigonal bipyramids crosslinked by the tetrahedra, with layers of Cs atoms separating the sheets.

Introduction

Vanadates of lighter alkali metals with the stoichiometry MV_2O_5 have been prepared by solid-state reaction previously. Galy and Hardy (*1*) prepared LiV_2O_5 by fusion of $LiVO_3$, V_2O_5, and VO_2 in sealed platinum tubes at 750°C. Similarly NaV_2O_5 (*2*) was formed by reaction of $NaVO_3$, V_2O_5, and VO_2 at 700°C. Both of these compounds were end members of the family of bronzes $MxV_{2-x}^{5+}V_x^{4+}O_5$ ($M = Li, Na$).

During electrolysis of cesium vanadate melts, Reid and Watts (*3*) found two new phases. Electrolysis of a melt containing 37 mole % Cs_2O, 63 mole % V_2O_5 gave dark colored columnar crystals which proved to have tetragonal symmetry. At 44 mole% Cs_2O, 56 mole% V_2O_5 electrolysis produced black plate-like crystals which were monoclinic. Only a small amount (<10 mg) of the second compound was separated from the melt and accurate chemical analysis was not possible. However, single crystal structural analysis of a crystal from this material has proved beyond reasonable doubt that this compound is CsV_2O_5.

Experimental

Unit cell data is listed in Table I and was obtained using a Guinier-type focussing camera. Potassium chloride was used as an internal standard, and final parameters were obtained by a least-squares treatment of the data given in Table II.

TABLE I

CRYSTALLOGRAPHIC DATA FOR CsV_2O_5

Symmetry	Monoclinic
Unit cell dimension	$a = 7.008 \pm .005$ $b = 9.977 \pm .005$ $c = 7.729 \pm .005$ $\beta = 90.98 \pm .05$
Systematically absent reflections	hol, $1 = 2n + 1$ $0k0$, $k = 2n + 1$
Possible space groups	$P2_{1/c}$
Z	4

The crystal examined was a thin plate. X-Ray data for the diffraction levels $k = 0, \ldots 5$ and the additional layer $0kl$ were obtained by the multiple-film technique from a crystal measuring .05 × .05 × .02 mm. The integrated equi-inclination method was used with Cu K_{α_1}, α_2 radiation. Intensities were measured visually against a standard scale, and the reduction to structure amplitude was made with an Elliott 803 computer. All subsequent computing was carried out on an IBM 360/44 computer at Canterbury University, Christchurch, N.Z., using the programming system devised by the Crystallography Unit at the Chemistry Department of that University.

Structure Determination

A total of 461 nonsymmetry related reflections were recorded around b and the observed data scaled

TABLE II

Powder Pattern of CsV_2O_5, Cu $K_{\alpha 1}$

$\sin^2 \theta_{obsd}$	$\sin^2 \theta_{calcd}$	$h\,k\,l$
.03397	.03383	0 2 1
.03932	.03981	0 0 2
.04576	.04578	0 1 2
.04636	.04631	1 2 1
.05168	.05116	1 0 $\bar{2}$
.05423	.05438	2 1 0
.05670	.05713	1 1 $\bar{2}$
.06349	.06358	2 1 $\bar{1}$
.06449	.06509	2 1 1
.06650	.06583	1 3 0
.07660	.07654	1 2 2
.09343	.09354	0 3 2
.10535	.10548	0 4 1
.10891	.10823	3 0 0
.11247	.11285	2 3 1
.14062	.14045	2 3 $\bar{2}$
.14774	.14819	1 4 2
.15719	.15696	3 1 2
.16256	.16266	3 3 0
.19436	.19397	2 3 3
.21368	.21328	3 4 $\bar{1}$

TABLE III

Atomic Positions and Thermal Parameters

	x	y	z	
Cs_1	.61681(49)	.12537(61)	.22049(55)	—
V_1	.1170(12)	−.0236(14)	.3370(12)	.72(22)
V_2	.1194(13)	.2063(14)	.9879(12)	.83(23)
O_1	.1150(55)	.1293(58)	.1808(50)	1.44(82)
O_2	.3363(51)	.1882(54)	.9188(99)	.58(75)
O_3	.6808(53)	.0686(55)	.6243(53)	.82(80)
O_4	.9479(52)	.1277(57)	.8547(49)	1.09(75)
O_5	.0718(46)	.1149(56)	.5184(−4)	.37(63)

Cs_1 Anisotropic thermal parameters

$B_{11} = .00324(64)$ $B_{12} = -.00014(67)$

$B_{22} = .0077(23)$ $B_{13} = -.0014(44)$

$B_{33} = .00931(72)$ $B_{23} = .00069(74)$

by comparison with the structure factors calculated for the final model, are available.[1] The systematically absent reflections defined the space group as $P_{2_{1/c}}$.

Initially a solution to this structure was sought using the Patterson Functions $P(u, o, w)$ and $P(o, v, w)$. However, as no result could be obtained using this method of attack, use finally was made at Canterbury of the local versions, SHNORM and SAP, of the Symbolic addition programs written by Ahmed et al. (*4*). Using the signs for 92 reflections obtained with these programs, a three-dimensional E-map was calculated and revealed the positions of the three metal atoms (Cs, V(1) and V(2)). Reiteration of electron density and structure factor calculations using all the three-dimensional data was used to locate directly and without assumption the positions of the five oxygen atoms.

By analogy with other oxide-bronze compounds prepared by electrolysis, for example, $K_{0.26}MoO_3$, $K_{0.28}MoO_3$ (*5*) and $Cs_{0.25}MoO_3$ (*6*), it was supposed that the composition of this compound would approximate to $Cs_{0.5}V_2O_5$ and structure factor calculations were initially carried out with an occupany factor of $\frac{1}{2}$ for cesium. However, it became increasingly obvious as the full details of the structure were forthcoming that the occupancy factor was much higher than one-half and when it was finally recognized that the compound was CsV_2O_5, R dropped to its lowest value of 14.4 for this stoichiometry. As a final check the Cs occupancy factor was refined. However, it did not reduce below .994 ± .038 in three cycles of refinement, the last two of which gave occupancy shifts of less than .0003. Atom positions and temperature factors are given in Table III.

Un-ionized scattering curves from the International Tables for X-ray Crystallography (*7*) were used for all atoms, and the cesium curve was corrected for anomalous dispersion. Full matrix least-squares refinement was carried out, and because of the reasonably high R value, a final difference Fourier was calculated and inspected closely to ensure that no additional atoms were present.

Extinction effects were not indicated from an examination of the final structure factors, and it is felt that absorption effects due to the irregular plate-like nature of the crystal must account for the rather high R factor.

As the structure had been satisfactorily defined at this stage, and absorption corrections based on the highly irregular shape of the crystal used would have been difficult to apply, they were not attempted.

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[1] A table of observed and calculated structure amplitudes from this analysis has been deposited as Document No. NAPS-01368 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Avenue, New York, N.Y. 10002. A copy may be secured by citing the document number and by remitting $5.00 for photocopies or $2.00 for microfiche. Advance payment is required. Make checks or money order payable to ASIS-NAPS.

Description and Discussion

Unlike NaV_2O_5 and LiV_2O_5, the vanadium atoms in CsV_2O_5 have two distinct coordinations, four (tetrahedral) and five (bipyramidal). Pairs of edge-shared trigonal bipyramids are bridged by tetrahedra to form sheets normal to (100). These sheets alternate with layers of cesium atoms (Fig. 1).

The trigonal bipyramids, although distorted, lie with their axes almost parallel to (100), and each one has an oxygen atom not taking part in the intra-layer bonding. The bond to this oxygen atom is directed nearly normal to this plane. The tetrahedral vanadium is in contact with three of the oxygen atoms of the trigonal bipyramids, one of which is already a shared atom. The tetrahedra, therefore, also have one oxygen atom not taking part in the bonding within the layer and again the bond to this atom is directed nearly normal to (100).

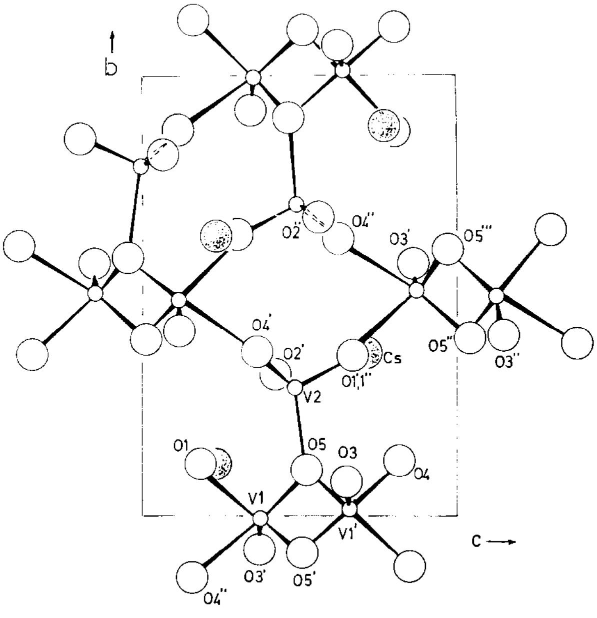

FIG. 1. The structure of CsV_2O_5 shown in (100) projection. Small open circles are vanadium atoms. Large open circles are oxygen atoms. Stippled circles are cesium atoms.

TABLE IV

BOND LENGTHS

Vanadium–Oxygen
V(1)–O(3) = 1.52(4)
O(1) = 1.89(3)
O(4) = 1.91(3)
O(5) = 1.92(3)
O(5)′ = 2.03(4)
V(2)–O(2) = 1.56(3)
O(1) = 1.73(4)
O(4) = 1.77(4)
O(5) = 1.91(5)

Cesium–Oxygen
Cs–O(2) = 3.11(4)
O(3) = 3.18(4)
O(2)′ = 3.11(4)
O(3)′ = 3.05(4)
O(3)″ = 3.20(4)
O(2)″ = 3.32(5)
O(1) = 3.53(5)
O(1)′ = 3.50(5)
O(4) = 3.54(5)
O(4)′ = 3.65(5)

Vanadium–Vanadium
V(1)–V(1)′ = 2.98(3)
V(1)–V(2) = 3.46(4)
V(2)′ = 3.50(4)
V(2)″ = 3.53(4)
V(2)‴ = 3.58(4)

A comparison of the average distances (Tables IV, V) for the vanadium–oxygen bonds in this structure shows the average tetrahedral distance to be much shorter than the average trigonal bipyramidal distance, even allowing for the effect of coordination number. It is concluded, therefore, that V^{5+} occupies the tetrahedral site and V^{4+} the trigonal bipyramidal. Reversal of the occupancies would result in a much less likely ratio of 5-coordinate V^{5+} to 4-coordinate V^{4+} average bond-length ratios (*8*), quite apart from the fact that 1.74 Å would be very short for an average 4-coordinate distance for V^{4+}. It agrees, for instance, quite closely with the average value of 1.75 found in $CrVO_4$ (*9*), where V^{5+} has tetrahedral coordination and has a similar environment in the structure, inasmuch as it occupies a bridging position between the Cr octahedra.

TABLE V

COMPARISON OF V^{4+}, V^{5+} SITE BOND LENGTHS IN $CrVO_4$, LiV_2O_5, NaV_2O_5 AND CsV_2O_5

	V^{4+}–oxygen bond distance	V^{5+}–oxygen bond distance	
Compound	Trigonal bipyramid	Trigonal bipyramid	Tetrahedral
LiV_2O_5	1.94	1.83	—
NaV_2O_5	1.88	1.82	—
CsV_2O_5	1.87	—	1.74
$CrVO_4$	—	—	1.75

Direct evidence for V^{4+} centers in the host lattice was obtained from the room-temperature ESR spectrum of the powdered material. This exhibited a single strong absorption line centered at $g = 1.96 \pm 0.1$ with a line width of only 96 G. This g value is characteristic for V^{4+} ions (*10*) and has also been obtained for the related vanadium bronze β-$Li_xV_2O_5$ (*11*). In this latter structure, the V^{4+} centers are located in octahedral site symmetry, with the V^{5+} ions in trigonal bipyramidal coordination (*12*).

The β-phase bronzes $M_xV_2O_5$, ($M = Na, Li, Cu$) show strong anisotropic conduction parallel to the tunnel or *b*-axis direction, which is attributed to cation–anion interactions between the V^{5+} bipyramidal sites and the V^{4+} octahedral ions via P_π orbitals of shared oxygen atoms rather than direct V^{4+}–V^{4+} hopping of electrons along the continuous octahedral-site chains which exist in these compounds (*12*).

CsV_2O_5 has isolated pairs of V^{4+} atoms in trigonal bipyramidal coordination at distances of 2.98 Å compared with the 3.36 Å V–V separation of the V^{4+} atoms in the β-phase bronzes. This comparatively short metal–metal distance in CsV_2O_5 may result in some direct cation–cation interaction in these V^{4+} sites as this distance is only .04 Å greater than the suggested theoretical distance Rc of 2.94 Å for direct orbital overlaps (*12*). Indeed the narrowness of the ESR line does support magnetic interaction between these two atoms (*13*). However, conductivity measurements show this compound to have a resistivity greater than 2.5×10^4 ohm-cm, so it is apparent that the O–V^{5+}–O linkages connecting the V^{4+} pairs together provide too discontinuous a path for conduction to take place in this compound.

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