

Acta Crystallographica Section C

**Crystal Structure  
Communications**

ISSN 0108-2701

---

## Caesium vanadium selenite, $\text{Cs}(\text{VO}_2)_3(\text{SeO}_3)_2$

**William T. A. Harrison**

---

### Electronic paper

This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

© 2000 International Union of Crystallography • Printed in Great Britain – all rights reserved

## Caesium vanadium selenite, $\text{Cs}(\text{VO}_2)_3(\text{SeO}_3)_2$

William T. A. Harrison

Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland  
Correspondence e-mail: w.harrison@abdn.ac.uk

Received 2 August 2000

Accepted 17 August 2000

Data validation number: IUC0000228

Caesium vanadium(V) selenite contains infinite sheets of distorted vertex-sharing  $\text{VO}_6$  octahedra, capped by selenite groups [ $d_{\text{av}}(\text{V}-\text{O}) = 1.927(4) \text{ \AA}$  and  $d_{\text{av}}(\text{Se}-\text{O}) = 1.709(3) \text{ \AA}$ ]. Interlayer caesium cations complete the structure [ $d_{\text{av}}(\text{Cs}-\text{O}) = 3.365(4) \text{ \AA}$ ].

### Comment

The title compound is another member of the family of layered phases (Harrison *et al.*, 1996) structurally related to hexagonal tungsten oxide, hex- $\text{WO}_3$  (Gérard *et al.*, 1979). It is built up from vertex sharing  $\text{VO}_6$  octahedra and  $\text{SeO}_3$  pyramids, fused together *via*  $\text{V}-\text{O}-\text{V}$  ( $\theta_{\text{av}} = 141.5^\circ$ ) and  $\text{V}-\text{O}-\text{Se}$  ( $\theta_{\text{av}} = 129.5^\circ$ ) bonds. Interlayer  $\text{Cs}^+$  cations complete the packing in  $\text{Cs}(\text{VO}_2)_3(\text{SeO}_3)_2$  which is isostructural with  $\text{NH}_4(\text{VO}_2)_3(\text{SeO}_3)_2$  (Vaughey *et al.*, 1994),  $\text{K}(\text{VO}_2)_3(\text{SeO}_3)_2$  (Harrison *et al.*, 1995) and  $\text{Cs}(\text{VO}_2)_3(\text{TeO}_3)_2$  (Harrison & Buttery, 2000).

The  $\text{VO}_6$  grouping shows a distinctive distortion mode with the V atom displaced by 0.36 Å from the geometric best centre (Balic Zunic & Makovicky, 1996) of its octahedron, essentially towards an octahedral edge (Harrison *et al.*, 1996). This situation results in two short ( $d < 1.67 \text{ \AA}$ ) V–O vertices, each of which is *trans* to a long ( $d > 2.16 \text{ \AA}$ ) V–O bond. The two remaining V–O bonds are of intermediate length. The short and long bonds are involved in V–O–V links and the intermediate length bonds participate in V–O–Se connections. A bond valence sum (BVS; Brown, 1996) of 5.05 results for vanadium (expected value = 5.00 for  $\text{V}^{\text{V}}$ ). The two Se atoms have threefold symmetry and their expected pyramidal geometry [BVS(Se1) = 3.95, BVS(Se2) = 3.96, expected = 4.00]. The 12-coordinate [ $d_{\text{av}} = 3.365(4) \text{ \AA}$ ] caesium cation, with site symmetry 3, serves to link adjacent anionic sheets by way of O–Cs–O bonds.

### Experimental

Initially, ‘ $\text{H}_2\text{SeO}_3$ ’ (dissolved  $\text{SeO}_2$ ; 8 ml 0.5 M), water (4 ml),  $\text{VO}_4\text{H}_2\text{O}$  (0.532 g) and  $\text{CsCl}$  (0.673 g) (starting ratio of Cs:V:Se = 1:1:1) were heated to 423 K in a 23-ml-capacity teflon-lined hydro-

thermal bomb for two days, resulting in a green plug, which was discarded, and a blue solution. The solution was evaporated to dryness to result in a blue–green glass (amorphous by X-rays) which was returned to the bomb with  $\text{H}_2\text{O}$  (5 ml) and heated to 423 K for a further four days. Product recovery by vacuum filtration and washing with water and acetone led to a mass of well faceted pleochroic (dark orange–brown along the hexagonal axis; yellow–green normal to the hexagonal axis) hexagonal prisms of the title compound. These prisms varied in shape from plate-like to rod-like.

### Crystal data

$\text{Cs}(\text{VO}_2)_3(\text{SeO}_3)_2$   
 $M_r = 635.65$   
Hexagonal,  $P6_3$   
 $a = 7.1613(5) \text{ \AA}$   
 $V = 516.01(6) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 4.091 \text{ Mg m}^{-3}$   
Mo  $K\alpha$  radiation

Cell parameters from 1888 reflections

$\theta = 3.29\text{--}29.35^\circ$   
 $\mu = 13.25 \text{ mm}^{-1}$   
 $T = 298(2) \text{ K}$   
Hexagonal column, yellow–green  
 $0.27 \times 0.08 \times 0.08 \text{ mm}$

### Data collection

Bruker SMART 1000 diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Bruker, 1999)  
 $T_{\text{min}} = 0.172$ ,  $T_{\text{max}} = 0.346$   
3428 measured reflections

966 independent reflections  
895 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.048$   
 $\theta_{\text{max}} = 30^\circ$   
 $h = -9 \rightarrow 7$   
 $k = -6 \rightarrow 9$   
 $l = -16 \rightarrow 16$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.063$   
 $S = 1.010$   
966 reflections  
57 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0336P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 2.23 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.80 \text{ e \AA}^{-3}$   
Extinction correction: SHELXL97  
Extinction coefficient: 0.0030(6)  
Absolute structure: Flack (1983)  
Flack parameter = 0.00(2)

The largest difference peak is 0.82 Å from Cs1. Friedel pairs were not merged to enable determination of the absolute structure. The structure has pseudosymmetry comparable with space group  $P6_3mc$ . However, the systematic absences are not consistent with  $P6_3mc$ , and the merging  $R$  factor of 0.131 for Laue group  $6/mmm$  is significantly larger than that for  $6/m$  (0.048). Structurally,  $P6_3mc$  appears to involve the V atom being placed at the centre of its octahedron, which is a very unlikely situation for a  $\text{V}^{\text{V}}$  system.

Data collection: SMART (Bruker, 1999); cell refinement: SMART; data reduction: SMART; program(s) used to solve structure: starting coordinates from isostructural material; program(s) used to refine structure: SHELXL97 (Sheldrick, 1997).

### References

- Balic Zunic, T. & Makovicky, E. (1996). *Acta Cryst.* **B52**, 78–81.  
Brown, I. D. (1996). *J. Appl. Cryst.* **29**, 479–480.  
Bruker (1999). SMART and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.  
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
Gérard, B., Nowogrocki, G., Guenot, J. & Figlarz, M. (1979). *J. Solid State Chem.* **29**, 429–434.  
Harrison, W. T. A. & Buttery, J. H. N. (2000). *Z. Anorg. Allg. Chem.* **626**, 867–870.  
Harrison, W. T. A., Dussack, L. L. & Jacobson, A. J. (1995). *Acta Cryst.* **C51**, 2473–2476.  
Harrison, W. T. A., Dussack, L. L., Vaughey, J. T., Vogt, T. & Jacobson, A. J. (1996). *J. Mater. Chem.* **6**, 81–87.  
Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.  
Vaughey, J. T., Harrison, W. T. A., Dussack, L. L. & Jacobson, A. J. (1994). *Inorg. Chem.* **33**, 4370–4375.