Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

$CsVP_2S_7$

Andreas Gutzmann, Christian Näther and Wolfgang Bensch*

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Olshausenstraße 40, D-24089 Kiel, Germany

Correspondence e-mail:
wbensch@ac.uni-kiel.de

Received 22 November 2004
Accepted 26 November 2004
Online 11 December 2004

The quaternary vanadium thiophosphate $CsVP_2S_7$ (caesium vanadium diphosphorus heptasulfide) was synthesized by reacting a mixture of Cs_2S_3, V, P_4S_3 and S. The crystal structure is composed of VS_6 octahedra, which are linked by bitetrahedral $[P_2S_7]$ groups to form two-dimensional anionic $[VP_2S_7]^-$ layers. The layers are stacked perpendicular to the crystallographic *c* axis and are separated by the Cs^+ ions. The VS_6 octahedra, the $[P_2S_7]$ groups and the Cs^+ ions are located in special positions. $CsVP_2S_7$ is isostructural to KVP_2S_7 and $RbVP_2S_7$.

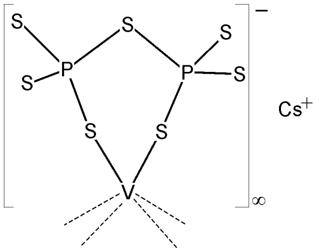
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(S–P) = 0.004 Å
R factor = 0.046
wR factor = 0.100
Data-to-parameter ratio = 23.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In the past few years, new quaternary thiophosphates have been synthesized applying alkali metal halides or the low-melting alkali metal thiophosphate fluxes. In general, $A_x[P_yS_z]$ (A = alkali metal) fluxes are formed by *in situ* fusion of A_2S_x, P_2S_5 and S. In our investigations of quaternary group IV and V thiophosphates, we have tried to develop alternative routes for the preparation of new compounds by a systematic variation of the reaction parameters, *e.g.* the use of binary transition metal sulfides or phosphides or P_4S_3 instead of P_2S_5 as educts. Applying this technique, several new quaternary thiophosphates with interesting structural features, such as $A_3M_2P_5S_{18}$ (A = Rb and Cs, and M = Zr and Hf; Gutzmann *et al.*, 2004*a*,*b*), $K_4VP_2S_9$ (Gutzmann *et al.*, 2004*c*), $Rb_2Nb_2P_2S_{11}$ (Gutzmann & Bensch, 2002), $Rb_4Ta_4P_4S_{24}$ (Gutzmann & Bensch, 2003), $K_{0.38}TaPS_6$ and $Rb_{0.46}TaPS_6$ (Gutzmann *et al.*, 2004*d*), have been obtained, demonstrating the high synthetic potential of the chemistry in alkali metal polythiophosphate fluxes. Analyzing the structures of the known ternary and quaternary vanadium thiophosphates, 1D-PV_2S_{10} (Brec, Ouvrard, Evain *et al.*, 1983), 2D-$P_{0.2}VS_2$ (Brec, Ouvrard, Freour *et al.*, 1983), 2D-$V_{0.78}PS_3$ (Ouvrard *et al.*, 1985), 2D-$V_2P_4S_{13}$ (Evain *et al.*, 1985), 0D-$K_4VP_2S_9$ (Gutzmann *et al.*, 2004*a*), 1D-$K_2VP_2S_7$ (Tremel *et al.*, 1995), 1D-$NaV_{0.84}P_2S_6$ (Coste *et al.*, 2003) and 2D-AVP_2S_7 (A = K and Rb; Kopnin *et al.*, 2000; Durand *et al.*, 1993), most of the compounds contain VS_6 octahedra as the general structural motif. Exceptions are



(I)

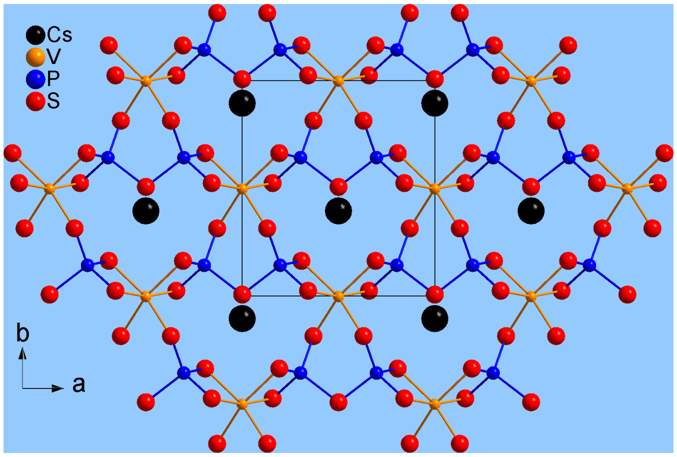


Figure 1
Crystal structure of CsVP$_2$S$_7$, viewed in the direction of the crystallographic *b* axis.

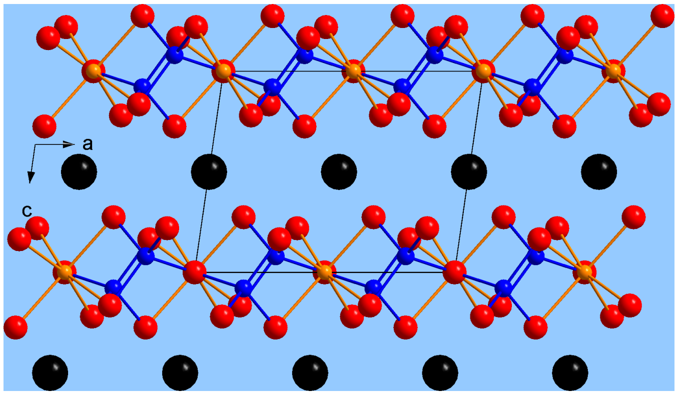


Figure 2
Crystal structure of CsVP$_2$S$_7$, viewed in the direction of the crystallographic *c* axis. Color code as in Fig. 1.

PV$_2$S$_{10}$ and K$_4$VP$_2$S$_9$ for which VS$_8$ and VS$_5$ polyhedra were observed. Applying the very successful method presented for quaternary alkali metal thiophosphates, we synthesized CsVP$_2$S$_7$, which is isostructural to AVP$_2$S$_7$ (A = K and Rb). We report here on the synthesis and structural characterization of this compound.

The crystal structure of CsVP$_2$S$_7$ is built up of [VP$_2$S$_7$]$^-$ layers and Cs$^+$ ions (Fig. 1). The [VP$_2$S$_7$]$^-$ anionic layers extending in the (010) plane are separated by about 4 Å and are stacked perpendicular to [001] (Fig. 2). The charge compensating Cs$^+$ ions are situated between the layers. The electronic situation of the title compound may be represented as [Cs$^+$][V^{3+}][P$_2$S$_7^{4-}$]. The main feature of this structure type is the presence of VS$_6$ octahedra, which are joined by [P$_2$S$_7$] groups to form the layered [VP$_2$S$_7$]$^-$ anion. The V—S distances of the strongly distorted octahedra range between 2.439 (3) and 2.457 (2) Å and are in good agreement with the data observed for AVP$_2$S$_7$ (A = K and Rb; Kopnin *et al.*, 2000; Durand *et al.*, 1993). Each VS$_6$ octahedron is surrounded by three symmetry-related pyrothiophosphate ligands sharing common edges with two [P$_2$S$_7$] units and sharing two common corners with the two [PS$_4$] tetrahedra of another bitetrahedral [P$_2$S$_7$]$^{4-}$ anion (Fig. 3). The P—S bond lengths range from 2.008 (4) to 2.138 (4) Å. The longest P—S bond is observed for the bridging S atom having bonds to two P atoms. The [PS$_4$] tetrahedra of the pyrothiophosphate ligands are strongly distorted, as is evidenced by the S—P—S angles. The connection scheme leads to the formation of cavities within the layers running along [001]. The Cs$^+$ cation is in a 12-fold coordination of each six S atoms from two adjacent [VP$_2$S$_7$]$^-$ layers. The mean Cs—S distance is 3.768 Å and is in good agreement with the sum of the ionic radii [1.84 Å for S^{2-} and 1.88 Å for Cs$^+$ (CN12); Shannon, 1976]. Interestingly, the anharmonic behavior of the alkali metal cation, as in the isostructural compounds AMP$_2$S$_7$ (A = K and Rb, and M = Cr, V and In; Kopnin *et al.*, 2000; Durand *et al.*, 1993), is not observed. In the electron density map of the title compound a regular distribution around the Cs$^+$ position is observed. In the isostructural K and Rb compounds, the alkali cations are coordinated by eight S atoms, whereas the Cs$^+$ ions in the title compound are surrounded by 12 S atoms. It is likely that this larger coordination number stabilizes the Cs$^+$ cation, leading to the harmonic behavior.

Experimental

CsVP$_2$S$_7$ was obtained by the reaction of Cs$_2$S$_3$ (0.24 mmol), V (0.72 mmol), P$_4$S$_3$ (0.24 mmol) and S (2.4 mmol). Cs$_2$S$_3$ was prepared from a stoichiometric ratio of the elements in liquid ammonia under an argon atmosphere. In an N$_2$-filled glove-box, the starting materials were thoroughly mixed and loaded into a glass ampoule. After evacuation (10^{-3} mbar) the ampoule was flame-sealed and placed in a computer-controlled furnace. The sample was heated to 823 K within 24 h. After four days the sample was cooled to room temperature at a rate of 3 K h^{-1}. To remove the excess Cs$_x$P$_y$S$_z$ flux, the resultant melt was washed with dry *N*,*N*-dimethylformamide and diethyl ether. The product was dried *in vacuo* and consisted of dark green needles which are stable in air and water. The yield based on vanadium was about 90%. The MIR spectra of CsVP$_2$S$_7$ displays strong absorptions at 598, 579, 526, 459 and 407 cm^{-1}. These absorptions are in good agreement with the vibrational frequencies reported for Na$_2$FeP$_2$S$_7$ (Menzel *et al.*, 1990) and may be assigned to P—S stretching modes.

Crystal data

CsVP$_2$S$_7$
M_r = 470.21
Monoclinic, $C2$
a = 8.6010 (17) Å
b = 9.5176 (19) Å
c = 6.7287 (13) Å
β = 98.17 (3)°
V = 545.23 (19) Å^3
Z = 2

D_x = 2.864 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 68 reflections
θ = 10–15°
μ = 5.77 mm^{-1}
T = 293 (2) K
Needle, green
0.15 × 0.05 × 0.05 mm

Data collection

Philips PW1100 four-circle diffractometer
ω/θ scans
Absorption correction: numerical (*X-SHAPE* and *X-RED*; Stoe & Cie, 1998)
$T_{\min}$ = 0.701, $T_{\max}$ = 0.738
1280 measured reflections
1205 independent reflections

979 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.044
$\theta_{\max}$ = 27.0°
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -8 \rightarrow 8$
3 standard reflections
every 120 min
intensity decay: none

Acta Cryst. (2005). E**61**, i6–i8 Gutzmann *et al.* • CsVP$_2$S$_7$ **i7**

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.100$
$S = 1.01$
1205 reflections
52 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.49$ e Å^{-3}
$\Delta\rho_{\min} = -0.63$ e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), 567 Friedel pairs
Flack parameter: −0.03 (4)

Table 1
Selected geometric parameters (Å, °).

P1—S3	2.008 (4)	Cs1—S3$^{\rm vii}$	3.548 (3)
P1—S1	2.013 (3)	Cs1—S3$^{\rm viii}$	3.548 (3)
P1—S2	2.027 (4)	Cs1—S1$^{\rm ix}$	3.705 (2)
P1—S4	2.138 (3)	Cs1—S2$^{\rm x}$	3.711 (3)
V1—S2$^{\rm ii}$	2.439 (3)	Cs1—S2$^{\rm v}$	3.711 (3)
V1—S3$^{\rm iii}$	2.453 (3)	Cs1—S1$^{\rm vii}$	4.004 (3)
V1—S3$^{\rm v}$	2.453 (3)	Cs1—S1$^{\rm viii}$	4.004 (3)
V1—S1$^{\rm ii}$	2.457 (2)	Cs1—S2$^{\rm x}$	4.108 (3)
Cs1—S4$^{\rm vi}$	3.5277 (13)	Cs1—S2$^{\rm vi}$	4.108 (3)
S3—P1—S1	110.13 (15)	S3$^{\rm iii}$—V1—S3$^{\rm v}$	89.17 (14)
S3—P1—S2	120.02 (16)	S2—V1—S1	82.00 (9)
S1—P1—S2	105.32 (14)	S2$^{\rm ii}$—V1—S1	90.23 (9)
S3—P1—S4	109.79 (15)	S3$^{\rm iii}$—V1—S1	82.78 (9)
S1—P1—S4	102.84 (15)	S3$^{\rm v}$—V1—S1	105.93 (10)
S2—P1—S4	107.33 (14)	S2—V1—S1$^{\rm ii}$	90.23 (9)
S2—V1—S2$^{\rm ii}$	99.35 (16)	S2$^{\rm ii}$—V1—S1$^{\rm ii}$	82.00 (9)
S2—V1—S3$^{\rm iii}$	163.10 (9)	S3$^{\rm iii}$—V1—S1$^{\rm ii}$	105.93 (10)
S2$^{\rm ii}$—V1—S3$^{\rm iii}$	87.99 (9)	S3$^{\rm v}$—V1—S1$^{\rm ii}$	82.78 (9)
S2—V1—S3$^{\rm v}$	87.99 (9)	S1—V1—S1$^{\rm ii}$	168.01 (17)
S2$^{\rm ii}$—V1—S3$^{\rm v}$	163.10 (9)		

Symmetry codes: (i) $-x+1, y, -z+1$; (ii) $-x, y, -z+1$; (iii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (v) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+1$; (vi) $x, y, z-1$; (vii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z$; (viii) $x+\frac{1}{2}, y-\frac{1}{2}, z$; (ix) $-x+1, y, -z$; (x) $x+\frac{1}{2}, y-\frac{1}{2}, z-1$.

The absolute structure was determined and is, according to the Flack (1983) *x* test, in agreement with the selected setting. The highest peak in the difference electron density map is located 0.97 Å from Cs1, and the deepest hole 1.27 Å from S4.

Data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *XCIF* in *SHELXTL* (Bruker, 1998).

Financial support by the state of Schleswig-Holstein and the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

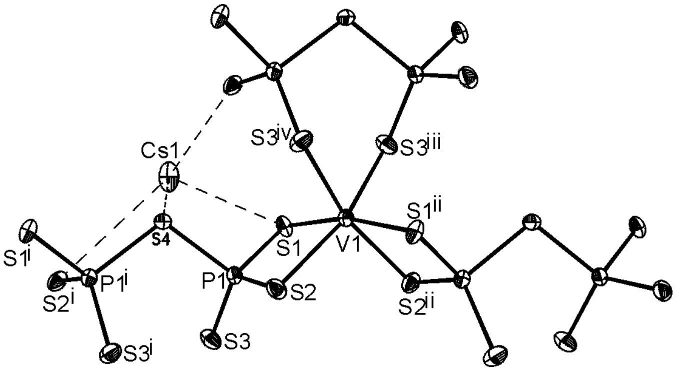


Figure 3
Crystal structure of $CsVP_2S_7$, with labeling and displacement parameters drawn at the 50% probability level, showing the interconnection of the VS_6 octahedra through $[P_2S_7]$ groups sharing common edges and corners. [Symmetry codes: (i) $1-x, y, 1-z$; (ii) $-x, y, -z+1$; (iii) $-\frac{1}{2}+x, -\frac{1}{2}+y, z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, -z+1$.]

References

Brandenburg, K. (1999). *DIAMOND*. Version 2.1c. Crystal Impact GbR, Bonn, Germany.
Brec, R., Ouvrard, G., Evain, M., Grenouilleau, P. & Rouxel, J. (1983). *J. Solid State Chem.* **47**, 174–184.
Brec, R., Ouvrard, G., Freour, R., Rouxel, J. & Soubeyroux, J. L. (1983). *Mater. Res. Bull.* **18**, 689–696.
Bruker (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Coste, S., Gautier, E., Evain, M., Bujoli-Doeuff, M., Brec, R., Jobic, S. & Kanatzidis, M. G. (2003). *Chem. Mater.* **15**, 2323–2327.
Durand, E., Evain, M. & Brec, R. (1993). *J. Solid State Chem.* **102**, 146–155.
Evain, M., Brec, R., Ouvrard, G. & Rouxel, J. (1985). *J. Solid State Chem.* **56**, 12–20.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gutzmann, A. & Bensch, W. (2002). *Solid State Sci.* **4**, 835–840.
Gutzmann, A. & Bensch, W. (2003). *Solid State Sci.* **5**, 1271–1276.
Gutzmann, A., Näther, C. & Bensch, W. (2004*a*). *Solid State Sci.* **6**, 205–211.
Gutzmann, A., Näther, C. & Bensch, W. (2004*b*). *Acta Cryst.* E**60**, i42–i44.
Gutzmann, A., Näther, C. & Bensch, W. (2004*c*). *Acta Cryst.* C**60**, i11–i13.
Gutzmann, A., Näther, C. & Bensch, W. (2004*d*). *Solid State Sci.* **6**, 1155–1162.
Kopnin, E., Coste, S., Jobic, S., Evain, M. & Brec, R. (2000). *Mater. Res. Bull.* **35**, 1401–1410.
Menzel, F., Ohse, L. & Brockner, W. (1990). *Heteroat. Chem.* **1**, 357–362.
Ouvrard, G., Freour, R., Brec, R. & Rouxel, J. (1985). *Mater. Res. Bull.* **20**, 1053–1062.
Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Stoe & Cie (1992). *DIF*4 (Version 7.09X/DOS) and *REDU*4 (Version 7.03). Stoe & Cie GmbH, Darmstadt, Germany.
Stoe & Cie (1998). *X-SHAPE* and *X-RED*. Version 1.03. Stoe & Cie GmbH, Darmstadt, Germany.
Tremel, W., Kleinke, H., Derstroff, V. & Reisner, C. (1995). *J. Alloys Compd.* **219**, 73–82.

i8 Gutzmann *et al.* • $CsVP_2S_7$ *Acta Cryst.* (2005). E**61**, i6–i8