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# $K_4VP_2S_9$

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The new quaternary group V thiophosphate $K_4VP_2S_9$ (tetrapotassium vanadium diphosphorus nonasulfide) was prepared by reacting a mixture of $K_2S_3$, VP, $P_4S_3$ and S. The crystal structure consists of discrete $[VS(PS_4)_2]^{4-}$ anions and $K^+$ cations. The $V^{4+}$ cation is in a fivefold coordination of S atoms which form a square-pyramidal environment. Each $VS_5$ group shares a common edge with two bidentate $[PS_4]$ tetrahedra, yielding the complete anion. The anions are stacked in the direction of the crystallographic *b* axis and are separated by the $K^+$ ions.

## Comment

Group V transition metal thiophosphates have been extensively investigated and are known for their low-dimensional crystal structures and interesting physical properties. In the structures of compounds in the *A*–*M*–P–S system (where *A* is an alkali metal and *M* is a group V metal), the dimensionality of the anionic parts varies from one-dimensional chains to three-dimensional interconnected networks. In our investigations of the *A*–*M*–P–S family, we have demonstrated that a systematic variation of the reaction parameters, *e.g.* temperature, reaction time, stoichiometry and type of starting materials, leads to the formation of new quaternary thiophosphates with interesting structural features. Very recently, we have prepared new quaternary thiophosphates with group V metals, such as $Rb_2Nb_2P_2S_{11}$ (Gutzmann & Bensch, 2002), $Rb_4Ta_4P_4S_{24}$ (Gutzmann & Bensch, 2003) and $Cs_2Ta_2P_2S_{12}$ (Gutzmann *et al.*, 2004), enhancing the rich structural chemistry. The structural features of the known two- and one-dimensional quaternary vanadium thiophosphates 2D-$AVP_2S_7$ (*A* is K or Rb; Kopnin *et al.*, 2000; Durand *et al.*, 1993), 1D-$K_2VP_2S_7$ (Tremel *et al.*, 1995) and 1D-$NaV_{0.84}P_2S_6$ (Coste *et al.*, 2003) are $VS_6$ octahedra connected by shared edges with either other $VS_6$ octahedra or with $[P_xS_y]^{n-}$ units. Using a molten alkali metal polythiophosphate flux, we have synthesized the first quaternary vanadium thiophosphate containing discrete $[VS(PS_4)_2]^{4-}$ anions, the title compound, $K_4VP_2S_9$. We report here the synthesis and structural characterization of this new compound.

The crystal structure of $K_4VP_2S_9$ is built up of discrete $[VS(PS_4)_2]^{4-}$ anions which are well separated by $K^+$ cations. The $V^{4+}$cation is in an unusual fivefold coordination of S atoms, forming a square-pyramidal environment. The V—S distances range from 2.1132 (9) to 2.3823 (19) Å. The mean V—S bond length of 2.324 Å is in good agreement with the sum of the ionic radii [1.84 Å for $S^{2-}$ and 0.53 Å for $V^{4+}$ (coordination number 5); Shannon, 1976]. The shortest V—S bond is observed to the non-coordinated terminal S1 atom at the top of the pyramid. The V atom is located 0.71 (1) Å above the square plane of the pyramid formed by atoms S2–S5.

Each $VS_5$ polyhedron shares common edges with two bidentate $[PS_4]^{3-}$ tetrahedra, forming the $[VS(PS_4)_2]^{4-}$ anion. In both $[PS_4]$ tetrahedra, two types of P—S bonds can be distinguished, depending on how the S atoms are bonded. They range from 1.9922 (17) to 2.100 (3) Å, with the shorter bond to the terminal S atoms. These differences in the P—S distances are a result of the partial double-bond character to the terminal S atoms. Very similar bond distances are found in, for example, $P_4S_{10}$ (Vos & Wiebenga, 1955), $K_4Pd(PS_4)_2$ (Chondroudis *et al.*, 1997) and $K_6[Cr_2(PS_4)_4]$ (Derstroff *et al.*, 1998). The S—P—S angles deviate from ideal tetrahedral geometry and range from 95.81 (10) to 114.76 (11)° for S—P1—S and from 96.46 (10) to 113.88 (11)° for S—P2—S. The smallest S—P—S angles are observed for the S atoms which are bound to the V atom.

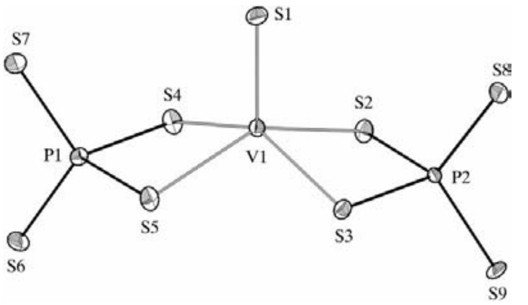

**Figure 1**
The crystal structure of the $[VS(PS_4)_2]^{4-}$ anion in $K_4VP_2S_9$, with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

The $[VS(PS_4)_2]^{4-}$ anions are stacked parallel to the crystallographic *b* axis and a similar arrangement is also found along the *a* axis, but the terminal S atoms of the $[VS_5]$ units show an up–down–up orientation in the latter direction. The four crystallographically independent $K^+$ cations are in an eightfold coordination. Cations K1 and K2 show an irregular sulfur environment, whereas cations K3 and K4 are in an approximately hexagonal–bipyramidal coordination. The residual negative charge on the terminal S atoms leads to shorter K—S distances, due to the greater electrostatic attraction. The mean K—S distances are 3.42 (9) Å for K1, 3.41 (9) Å for K2, 3.30 (11) Å for K3 and 3.31 (11) Å for K4. These values are in good agreement with the sum of the ionic radii [1.84 Å for $S^{2-}$ and 1.51 Å for $K^+$ (coordination number 8); Shannon, 1976].

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It should be mentioned that the configuration of $K_4VP_2S_9$ allows interesting speculation concerning the possibility of condensing several $[VS(PS_4)_2]$ fragments *via* the bidentate $[PS_4]$ tetrahedra or the terminal S1 atom to yield structures of higher complexity. This might be achieved if molecular precursor compounds such as the title compound were used in the synthesis. In that case, it would establish a new method for the synthesis of interesting solid-state thiophosphates.

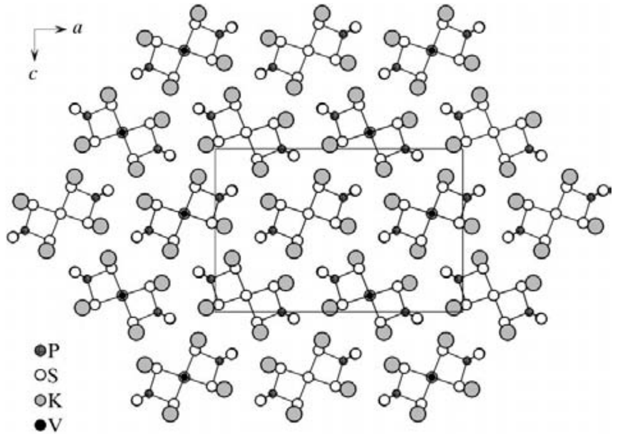

**Figure 2**
The crystal structure of $K_4VP_2S_9$, viewed in the direction of the crystallographic *b* axis.

## Experimental

The title compound, $K_4VP_2S_9$, was obtained by the reaction of $K_2S_3$ (0.8 mmol), VP (0.4 mmol), $P_4S_3$ (0.2 mmol) and S (2.4 mmol). $K_2S_3$ was prepared from a stoichiometric ratio of the elements in liquid ammonia under an argon atmosphere. VP was prepared by heating stoichiometric amounts of the elements at 1073 K in an evacuated silica tube. The starting materials were loaded into a glass ampoule, which was evacuated ($10^{-3}$ mbar; 1 mbar = 100 Pa) and flame-sealed. The ampoule was heated to 773 K at 25 K $h^{-1}$. After 4 d, the sample was cooled to 523 K at 2 K $h^{-1}$ and then to room temperature within 10 h. To remove unreacted $K_xP_yS_z$, the resultant melt was washed with dry *N*,*N*-dimethylformamide and diethyl ether. The product was dried *in vacuo* and consisted of red crystals which are air- and moisture-sensitive. The MIR spectra of $K_4VP_2S_9$ display strong absorptions at 499, 522, 577 and 619 $cm^{-1}$. Two additional weak absorptions are observed at 418 and 669 $cm^{-1}$. These values are comparable with those of $K_3Bi(PS_4)_2$ (McCarthy & Kanatzidis, 1996) and can be assigned to P—S stretching vibrations. In the transformed UV–Vis reflectance spectrum, the band gap was determined to be 2.03 eV, which is in agreement with the observed red colour of the single crystals.

### *Crystal data*

$K_4VP_2S_9$
$M_r = 557.82$
Orthorhombic, $Pna2_1$
$a = 19.3587$ (15) Å
$b = 6.7658$ (5) Å
$c = 12.7869$ (7) Å
$V = 1674.8$ (2) Å$^3$
$Z = 4$
$D_x = 2.212$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 8000 reflections
$\theta = 1.9$–28.2°
$\mu = 2.87$ mm$^{-1}$
$T = 180$ K
Polyhedron, red
0.25 × 0.20 × 0.10 mm

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| K1—S1$^{\rm i}$ | 3.288 (2) | K3—S3$^{\rm ii}$ | 3.4894 (12) |
| K1—S6$^{\rm ii}$ | 3.300 (2) | K4—S1 | 3.143 (3) |
| K1—S7$^{\rm i}$ | 3.334 (2) | K4—S5$^{\rm viii}$ | 3.220 (3) |
| K1—S4$^{\rm iii}$ | 3.451 (3) | K4—S8$^{\rm i}$ | 3.233 (2) |
| K1—S8$^{\rm iv}$ | 3.454 (2) | K4—S9$^{\rm i}$ | 3.274 (2) |
| K1—S9$^{\rm v}$ | 3.463 (2) | K4—S6$^{\rm vi}$ | 3.278 (2) |
| K1—S5$^{\rm i}$ | 3.5005 (13) | K4—S7 | 3.329 (2) |
| K1—S5$^{\rm ii}$ | 3.5346 (13) | K4—S4$^{\rm vi}$ | 3.4638 (13) |
| K2—S1 | 3.299 (2) | K4—S4 | 3.5007 (13) |
| K2—S9$^{\rm vi}$ | 3.308 (2) | V1—S1 | 2.1132 (9) |
| K2—S8 | 3.334 (2) | V1—S4 | 2.370 (3) |
| K2—S6$^{\rm iii}$ | 3.4202 (19) | V1—S3 | 2.377 (3) |
| K2—S7$^{\rm vii}$ | 3.4382 (19) | V1—S5 | 2.3774 (18) |
| K2—S3$^{\rm i}$ | 3.441 (3) | V1—S2 | 2.3823 (19) |
| K2—S2 | 3.4810 (13) | P1—S6 | 1.9922 (17) |
| K2—S2$^{\rm vi}$ | 3.5713 (13) | P1—S7 | 1.9963 (18) |
| K3—S1$^{\rm i}$ | 3.148 (3) | P1—S5 | 2.093 (3) |
| K3—S2 | 3.188 (3) | P1—S4 | 2.097 (3) |
| K3—S7$^{\rm iii}$ | 3.244 (2) | P2—S9 | 2.0042 (17) |
| K3—S9$^{\rm ii}$ | 3.2659 (19) | P2—S8 | 2.0073 (17) |
| K3—S6$^{\rm iii}$ | 3.274 (2) | P2—S3 | 2.083 (3) |
| K3—S8$^{\rm i}$ | 3.3166 (19) | P2—S2 | 2.100 (3) |
| K3—S3$^{\rm i}$ | 3.4811 (12) | | |
| S1—V1—S4 | 107.42 (9) | S6—P1—S5 | 112.47 (8) |
| S1—V1—S3 | 107.60 (8) | S7—P1—S5 | 112.70 (8) |
| S4—V1—S3 | 144.99 (3) | S6—P1—S4 | 109.58 (7) |
| S1—V1—S5 | 107.19 (4) | S7—P1—S4 | 109.86 (7) |
| S4—V1—S5 | 81.82 (7) | S5—P1—S4 | 95.81 (10) |
| S3—V1—S5 | 88.29 (9) | S9—P2—S8 | 113.88 (11) |
| S1—V1—S2 | 107.30 (4) | S9—P2—S3 | 109.17 (8) |
| S4—V1—S2 | 87.47 (9) | S8—P2—S3 | 109.31 (8) |
| S3—V1—S2 | 81.92 (7) | S9—P2—S2 | 113.08 (8) |
| S5—V1—S2 | 145.50 (3) | S8—P2—S2 | 113.45 (8) |
| S6—P1—S7 | 114.76 (11) | S3—P2—S2 | 96.46 (10) |

Symmetry codes: (i) $1-x, 1-y, z-\frac{1}{2}$; (ii) $1-x, 2-y, z-\frac{1}{2}$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, z$; (iv) $\frac{3}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (v) $\frac{3}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$; (vi) $x, y-1, z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (viii) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$.

### *Data collection*

Stoe IPDS diffractometer
$\varphi$ scans
Absorption correction: numerical [*X-SHAPE* (Stoe & Cie, 1998) and *X-RED* (Stoe & Cie, 1998)]
$T_{\rm min} = 0.510$, $T_{\rm max} = 0.753$
16 873 measured reflections
3999 independent reflections
3610 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\rm max} = 28.0°$
$h = -25 \rightarrow 25$
$k = -8 \rightarrow 8$
$l = -16 \rightarrow 16$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.127$
$S = 1.05$
3999 reflections
147 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1015P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 1.67$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -1.20$ e Å$^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0048 (8)
Absolute structure: Flack (1983), 1913 Friedel pairs
Flack parameter = 0.0 (4)

The crystal investigated was racemically twinned and, therefore, a twin refinement using *SHELXL*97 (Sheldrick, 1997) was performed, yielding a ratio of 0.42 (7):0.58 (7) for the two individuals. A refinement in the centrosymmetric space group *Pnma* was not successful. The largest peak in the difference map is located 1.42 Å from the V atom.

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND*

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(Brandenburg, 1999); software used to prepare material for publication: *CIFTAB* in *SHELXTL* (Bruker, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1159). Services for accessing these data are described at the back of the journal.

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