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# Tetrapotassium barium bis[tetrathiovanadate(V)], $K_4Ba[VS_4]_2$

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**Key indicators**

Single-crystal X-ray study
*T* = 153 K
Mean σ(V–S) = 0.001 Å
*R* factor = 0.024
*wR* factor = 0.065
Data-to-parameter ratio = 25.8

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



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The title compound, $K_4Ba[VS_4]_2$, has been synthesized by the reaction of V and S in a $K_2S$/BaS flux at 723 K. Its crystal structure is of the $K_4Eu[PS_4]_2$ structure type and comprises isolated tetrahedral $[VS_4]^{3-}$ anions separated by $K^+$ and $Ba^{2+}$ cations. The site symmetries of the atoms Ba, K1, K2, V, S1, S2, and S3 are 222, .2., ..*m*, ..*m*, ..*m*, 1, and ..*m*, respectively.

## Comment

The structures of a number of salts that contain the isolated $[VS_4]^{3-}$ anion are known (Table 2). Here we report the structure of the mixed-cation compound $K_4Ba[VS_4]_2$. This compound crystallizes in space group *Ibam* and is of the $K_4Eu[PS_4]_2$ structure type (Evenson & Dorhout, 2001).

Fig. 1 shows the asymmetric unit and Fig. 2 shows the unit-cell contents of $K_4Ba[VS_4]_2$. The crystal structure is composed of isolated tetrahedral $[VS_4]^{3-}$ anions and discrete $K^+$ and $Ba^{2+}$ cations. Each K and Ba cation is coordinated by eight S atoms in a distorted cube. The K—S and Ba—S distances (Table 1) are comparable to those of 3.130 (3)–3.771 (3) Å in $K_3[VS_4]$ (Dürichen & Bensch, 1996) and 3.144 (1)–3.403 (1) Å in $NaBa[VS_4]$ (Figueroa *et al.*, 2000), respectively. The geometries of the $[VS_4]^{3-}$ anion in the present and other known structures are compared in Table 2. In these relatively simple structures, the anion maintains its essentially tetrahedral geometry.

## Experimental

Crystals of $K_4Ba[VS_4]_2$ were obtained as black needles from a solid-state reaction of 1.0 mmol V (Alfa, 99.9%), 4.0 mmol S (Aldrich, 99.9%), 1.5 mmol $K_2S$ (Aldrich, 99%), and 0.5 mmol BaS (Aldrich, 99.9%). The mixture was loaded under Ar, sealed under $10^{-4}$ Torr (1 Torr = 133.322 Pa) in a fused-silica tube, heated in a furnace to

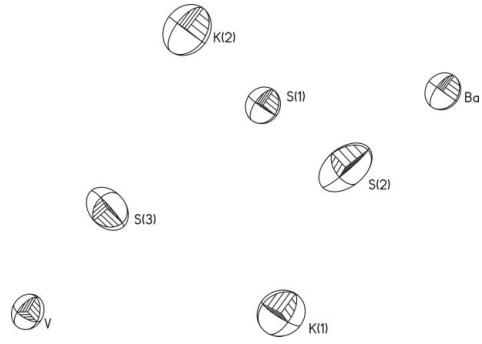


**Figure 1**
The asymmetric unit of $K_4Ba[VS_4]_2$, showing 99% probability displacement ellipsoids.

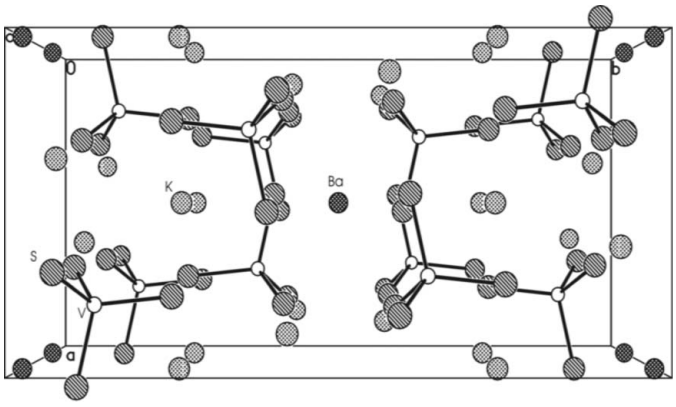


**Figure 2**
The unit-cell contents of $K_4Ba[VS_4]_2$.

723 K at 1 K min$^{-1}$, kept at 723 K for 3 d, cooled at 0.05 K min$^{-1}$ to 373 K, and then cooled to room temperature. The reaction mixture was washed with dimethylformamide, and then dried with acetone. It contained black needles and powder. The yield of these crystals was about 90%. Examination of selected needles with an EDX-equipped Hitachi S-3500 SEM led to results consistent with the stated composition.

*Crystal data*

$BaK_4S_8V_2$
$M_r$ = 652.10
Orthorhombic, *Ibam*
$a$ = 8.9553 (4) Å
$b$ = 18.3506 (9) Å
$c$ = 9.8947 (5) Å
$V$ = 1626.05 (14) Å$^3$
$Z$ = 4
$D_x$ = 2.664 Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu$ = 5.54 mm$^{-1}$
$T$ = 153 (2) K
Needle, black
0.306 × 0.042 × 0.038 mm

*Data collection*

Bruker SMART-1000 CCD diffractometer
$\omega$ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 2003)
$T_{min}$ = 0.307, $T_{max}$ = 0.820
9545 measured reflections
1083 independent reflections
1022 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.026
$\theta_{max}$ = 28.8°

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.065
$S$ = 1.66
1083 reflections
42 parameters
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 3.41 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.66 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Ba—S1 | 3.1713 (5) | K2—S2 | 3.2484 (6) |
| Ba—S2 | 3.2848 (6) | K2—S3 | 3.3177 (10) |
| K1—S3$^{i}$ | 3.2347 (5) | K2—S2$^{ii}$ | 3.3427 (8) |
| K1—S3 | 3.4423 (6) | K2—S2$^{iii}$ | 3.5507 (9) |
| K1—S2$^{i}$ | 3.5278 (9) | V—S3 | 2.1366 (9) |
| K1—S1 | 3.5849 (9) | V—S2$^{i}$ | 2.1477 (6) |
| K2—S1 | 3.1694 (10) | V—S1$^{iv}$ | 2.1622 (9) |
| S3—V—S2$^{i}$ | 110.49 (2) | S3—V—S1$^{iv}$ | 108.93 (4) |
| S2$^{v}$—V—S2$^{i}$ | 109.98 (4) | S2$^{i}$—V—S1$^{iv}$ | 108.45 (2) |

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

**Table 2**
Ranges of V—S distances (Å) and S—V—S angles (°) in inorganic structures containing the $[VS_4]^{3-}$ anion.

| Compound | V—S | S—V—S | V Sym[a] |
|---|---|---|---|
| $Cu_3[VS_4]$[b] | 2.219[c] | 109.47 | $\bar{4}3m$ |
| $K_4Ba[VS_4]_2$[d] | 2.137 (1)–2.162 (1) | 108.45 (2)–110.49 (2) | 222 |
| $Cs_2Ag[VS_4]$[e] | 2.176 (2) | 106.98 (7)–113.59 (6) | 222 |
| $K_2Ag[VS_4]$[f] | 2.178 (1) | 106.2 (1)–114.4 (1) | 222 |
| $Rb_2Ag[VS_4]$[f] | 2.177 (1) | 106.5 (1)–114.1 (1) | 222 |
| $K_2Cu[VS_4]$[g] | 2.177 (1) | 108.6 (1)–110.1 (1) | 222 |
| $Rb_2Cu[VS_4]$[h] | 2.1739 (7) | 109.03 (4)–109.78 (4) | 222 |
| $KCu_2[VS_4]$[i] | 2.146–2.233[c] | 109.19–109.93 | *m* |
| $KCu_2[VS_4]$[j] | 2.147–2.229[c] | 109.07–109.87 | *m* |
| $RbCu_2[VS_4]$[k] | 2.153 (7)–2.232 (5) | 109.05 (12)–109.9 (3) | *m* |
| $K_3[VS_4]$[g] | 2.147 (2)–2.163 (3) | 108.8 (1)–111.8 (1) | *m* |
| $Rb_3[VS_4]$[l] | 2.148 (2)–2.166 (2) | 108.69 (5)–111.76 (7) | *m* |
| $Cs_3[VS_4]$[l] | 2.141 (1)–2.170 (1) | 108.54 (4)–111.86 (6) | *m* |
| $NaBa[VS_4]$[m] | 2.127 (1)–2.166 (2) | 107.31 (6)–111.23 (6) | 1 |
| $Na_3[VS_4]$[n] | 2.134 (1)–2.163 (1) | 108.8 (0)–110.8 (1) | 1 |

Notes: (*a*) site symmetry of V; (*b*) Mujica *et al.*, 1998; (*c*) s.u. not given; (*d*) this work; (*e*) Tillinski *et al.*, 1998; (*f*) Bensch & Dürichen, 1996; (*g*) Dürichen & Bensch, 1996; (*h*) Rumpf *et al.*, 1997; (*i*) Peters *et al.*, 1996; (*j*) Bensch et al., 1996; (*k*) Tillinski *et al.*, 2001; (*l*) Emirdag-Eanes & Ibers, 2001; (*m*) Figueroa *et al.*, 2000; (*n*) Klepp & Gabl, 1997.

The structure was standardized by means of the program *STRUCTURE TIDY* (Gelato & Parthé, 1987). The highest residual electron density peak is at the Ba site.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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