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Na_3VOS_3

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The title compound, trisodium vanadium oxide trisulfide, has been synthesized by the reaction of the elements in an Li_2O/Na_2S flux at 723 K. The structure comprises isolated tetrahedral VOS_3^{3-} anions separated by Na^+ cations. The anion has symmetry *m*. Bond distances include V—O = 1.673 (2) Å, and V—S = 2.1746 (4) and 2.1971 (6) Å. Each Na^+ cation is coordinated in a distorted octahedron by one O and five S atoms.

Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(V–O) = 0.003 Å
R factor = 0.017
wR factor = 0.044
Data-to-parameter ratio = 19.8

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

Comment

Many compounds of the type A_3MQ_4 (A = alkali metal, M = group 5 or 15 element, and Q = S, Se) have been synthesized. The compounds K_3VS_4 (van den Berg & de Vries, 1964), K_3NbS_4 (Latroche & Ibers, 1990), K_3NbSe_4 (Latroche & Ibers, 1990), K_3TaS_4 (Latroche & Ibers, 1990), K_3TaSe_4 (Latroche & Ibers, 1990), Rb_3NbS_4 (Krause *et al.*, 1998), Cs_3NbSe_4 (Yun *et al.*, 1988), Cs_3TaSe_4 (Yun *et al.*, 1988), Rb_3AsSe_4 (Wachhold & Sheldrick, 1996), Rb_3SbS_4 (Bensch & Dürichen, 1996), Rb_3SbSe_4 (Wachhold & Sheldrick, 1996), Rb_3VS_4 (Emirdag-Eanes & Ibers, 2001), and Cs_3VS_4 (Emirdag-Eanes & Ibers, 2001) have the K_3VS_4 structure type. The compounds K_3SbS_4 (Bensch & Dürichen, 1997), K_3AsS_4 (Palazzi *et al.*, 1974), K_3SbSe_4 (Eisenmann & Zagler, 1989), $(NH_4)_3SbS_4$ (Wachhold & Sheldrick, 1996), Na_3VS_4 (Klepp & Gabl, 1997), and Na_3NbS_4 (Niewa *et al.*, 1998) have different structure types.

All these compounds are composed of isolated MQ_4^{3-} tetrahedral anions separated by the A^+ cations. There are no $Q—Q$ or $M—M$ bonds in these structures. Therefore, the oxidation states of A, M and Q are 1+, 5+, and 2−, respectively. These compounds crystallize in the orthorhombic,

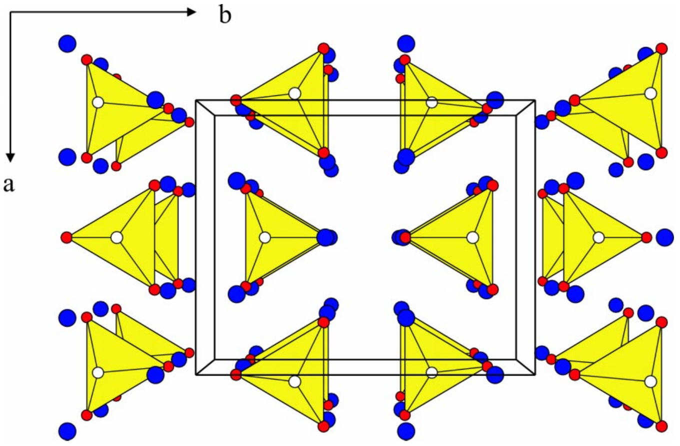

Figure 1
A perspective view of Na_3VOS_3 along [001]. The VOS_3 anion is plotted in the polyhedral representation (yellow), O atoms are shown as white spheres, S atoms as red spheres and Na atoms as blue spheres.

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tetragonal, or cubic systems. Their structures depend on the packing of the anions and cations, and hence on the sizes of the ions. For example, the space group of Na_3VS_4 is $P\overline{4}2_1c$ (Klepp & Gabl, 1997), that of K_3VS_4 is *Pnma* (in standard setting) (van den Berg & de Vries, 1964), and that of Na_3NbS_4 is *Fdd*2 (Niewa *et al.*, 1998). Thus, both the *A* and *M* cations affect the final structure.

The compound Na_3VOS_3 described here crystallizes in space group $Cmc2_1$ of the orthorhombic system with four formula units in the cell (Fig. 1). The structure contains discrete Na^+ cations and tetrahedral VOS_3^{3-} anions, instead of VS_4^{3-} anions as in Na_3VS_4. Bond distances include V—O = 1.673 (2) Å, and V—S = 2.1746 (4) and 2.1971 (6) Å. The VOS_3^{3-} anion is also found in $Ba_6V_4O_5S_{11}$ (Litteer *et al.*, 1997), where the corresponding bond distances are 1.682 (9), and 2.140 (4) and 2.169 (3) Å. The structure of Na_3VOS_3 is closely related to that of K_3SbS_4 (Bensch & Dürichen, 1997), which also crystallizes in space group $Cmc2_1$. However, in Na_3VOS_3 the two crystallographically independent Na^+ cations are each coordinated by one O and five S atoms in a distorted octahedron, whereas in K_3SbS_4 the two unique K^+ cations are coordinated by six and by seven S atoms.

Experimental

The compound Na_3VOS_3 was synthesized by the solid-state reaction of the elements in an Li_2O/Na_2S flux at 723 K. The mixture of 1.0 mmol V (Johnson Matthey Electronics, 99.5%), 5.0 mmol S (Alfa Aesar, 99.5%), 1.2 mmol Li_2O (Aldrich, 99+%), and 2.0 mmol Na_2S (Aldrich, 99%) was loaded into a fused-silica tube under an argon atmosphere in a glove-box. The tube was sealed under 10^{-4} Torr and then placed in a computer-controlled furnace. The sample was heated to 723 K at 5 K min^{-1}, kept at 723 K for 3 d, annealed at 0.05 K min^{-1} to 373 K, then cooled to room temperature. The reaction mixture was washed with dimethylformamide. In the reaction, the major component consisted of red flat needles of Na_3VOS_3. Analysis of these needles with an EDX-equipped Hitachi S-3500 SEM showed only the presence of Na, V, and S in the approximate ratio of 3:1:3. The compound is very sensitive to moisture and decomposes in water or acetone.

Crystal data

$Na_3(VOS_3)$
$M_r = 232.09$
Orthorhombic, $Cmc2_1$
$a = 9.6673$ (11) Å
$b = 11.9122$ (14) Å
$c = 5.8846$ (7) Å
$V = 677.66$ (14) Å^3
$Z = 4$
$D_x = 2.275$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3805 reflections
$\theta = 2.7$–28.8°
$\mu = 2.47$ mm^{-1}
$T = 153$ (2) K
Flat needle, red
0.58 × 0.16 × 0.04 mm

Data collection

Bruker SMART 1000 CCD diffractometer
0.3° ω scans
Absorption correction: by integration (*XPREP* in *SHELXTL*; Sheldrick, 2000)
$T_{min} = 0.337$, $T_{max} = 0.902$
3902 measured reflections
872 independent reflections
867 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 28.8°$
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.044$
$S = 1.15$
872 reflections
44 parameters
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0009 (5)
Absolute structure: Flack (1983)
Flack parameter = 0.21 (2)

Table 1
Selected geometric parameters (Å, °).

Na1—O	2.3228 (19)	Na2—S2^{iv}	2.8504 (9)
Na1—S1^{i}	2.8198 (10)	Na2—S2^{v}	2.9111 (7)
Na1—S1^{ii}	2.8403 (12)	Na2—S2^{vi}	3.0439 (9)
Na1—S2	3.0063 (5)	Na2—S2	3.2125 (7)
Na1—S2^{iii}	3.0063 (5)	V—O	1.6726 (18)
Na1—S1	3.0443 (12)	V—S2^{vi}	2.1746 (4)
Na2—O	2.3128 (10)	V—S1	2.1971 (6)
Na2—S1^{iv}	2.8361 (7)		
O—V—S2^{vi}	107.23 (3)	O—V—S1	106.91 (5)
S2^{vi}—V—S2^{vii}	115.15 (2)	S2^{vi}—V—S1	109.968 (17)

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

387 Friedel pairs were used for the refinement, which gave 0.79 (2)/0.21 (2) for the enantiomeric twin ratio.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXTL*.

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