inorganic compounds

Sodium trivanadium(III) bis(sulfate) hexahydroxide

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The title compound, $NaV_3(SO_4)_2(OH)_6$, was synthesized and found to crystallize in the trigonal space group $R\bar{3}m$ with the Na atom at a site with $\bar{3}m$ symmetry, the V atom at a site with $2/m$ symmetry, and the S and a terminal O atom at sites with $3m$ symmetry; the remaining two O atoms and the H atom are at sites with m symmetry. Octahedrally coordinated vanadium and tetrahedral sulfate ions share corners to form layers that are held together by hydrogen bonds and by sodium ions, which are located between the layers.

Comment

The structure of the title compound is built up of vanadium octahedra and sulfate tetrahedra (Fig. 1). Vanadium is coordinated by four equatorial hydroxyl groups and two apical O atoms from the sulfate ion. Hydroxyl groups are shared between two octahedra resulting in a two-dimensional $6^4 3^2$ net with large hexagonal cavities (Fig. 2). H atoms from the hydroxyl groups point into the cavities. The sulfate tetrahedra share corners with three vanadium octahedra and are located above and below the layer of vanadium octahedra. The fourth oxygen of the sulfate group points towards the holes of adjacent layers and makes hydrogen bonds with the hydroxyl groups from these layers (Table 2).

Sodium cations are located between the vanadium layers opposite to the sulfate ions, so that each Na atom is surrounded by six apical O atoms [Na—O1 2.760 (2) Å] of the vanadium octahedra (three from each layer).
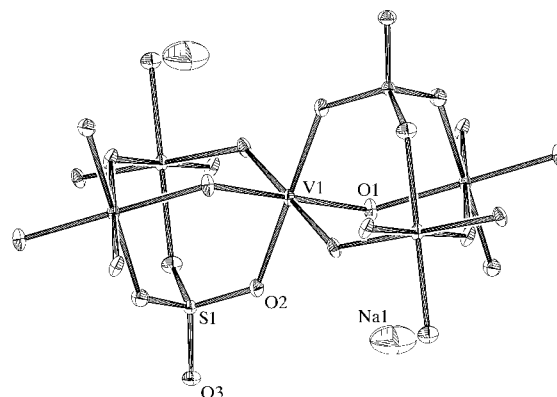

Figure 1
ORTEP-3 (Farrugia, 1997) drawing showing displacement ellipsoids in $NaV_3(SO_4)_2(OH)_6$ at 50% probability.

$NaV_3(SO_4)_2(OH)_6$ is isotypical to the following minerals: alunite [$KAl_3(SO_4)_2(OH)_6$] (Wang *et al.*, 1965), corkite [$PbFe_3(SO_4)(PO_4)(OH)_6$] (Giusepetti & Tadini, 1987), beaverite [$PbFe_3(SO_4)_2(OH)_6$] (Breidenstein *et al.*, 1992) and some other compounds. Tudo & La Place (1977) synthesized a vanadium compound with ammonium in the position of our sodium cation, *i.e.* $NH_4V_3(SO_4)_2(OH)_6$, however, the crystal structure was not determined.

Experimental

Oven-dried vanadyl sulfate hydrate (Aldrich), terephthalic acid disodium salt (Aldrich) and dimethyl sulfoxide (J. T. Baker) were
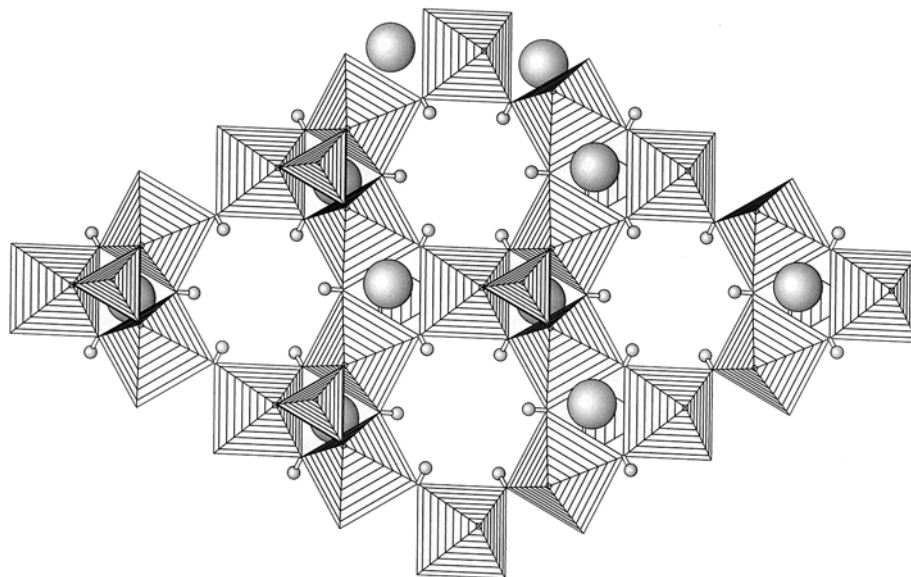

Figure 2
Diagram of a layer of the $[V_3(SO_4)_2(OH)_6]^-$ anion.

reacted solvothermally in a Parr autoclave in a 2:1:640 molar ratio at 473 K for 2 d. Two types of crystals were formed; red–brown trigonally deformed octahedra and long white crystals. The crystal structure of the red–brown crystals is reported here.

Crystal data

$NaV_3(SO_4)_2(OH)_6$	Mo $K\alpha$ radiation
$M_r = 470$	Cell parameters from 1353
Trigonal, $R\bar{3}m$	reflections
$a = 7.2821$ (6) Å	$\theta = 6.9$–$56.9°$
$c = 16.889$ (2) Å	$\mu = 3.19$ mm^{-1}
$V = 775.6$ (2) Å^3	$T = 293$ (2) K
$Z = 3$	Octahedral, brown
$D_x = 3.018$ Mg m^{-3}	$0.13 \times 0.12 \times 0.06$ mm

Data collection

CCD SMART Apex diffractometer	265 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.024$
Absorption correction: ψ scan	$\theta_{max} = 28.45°$
(*SADABS*; Sheldrick, 1996)	$h = -9 \rightarrow 9$
$T_{min} = 0.583$, $T_{max} = 0.790$	$k = -9 \rightarrow 8$
1643 measured reflections	$l = -22 \rightarrow 11$
272 independent reflections	Intensity decay: 0.001%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$+ 3.0070P]$
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.306$	$(\Delta/\sigma)_{max} < 0.001$
272 reflections	$\Delta\rho_{max} = 0.67$ e Å^{-3}
27 parameters	$\Delta\rho_{min} = -0.50$ e Å^{-3}
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å).

V1—O1	1.9835 (9)	S1—O2	1.478 (2)
V1—O2	2.051 (2)	S1—O3	1.457 (4)

Symmetry codes: (i) $1 - y, x - y - 1, z$; (ii) $\frac{2}{3} + y, \frac{4}{3} - x + y, \frac{1}{3} - z$; (iii) $\frac{5}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (iv) $1 - y, x - y, z$; (v) $1 - x + y, 1 - x, z$.

The unique H atom was located from a difference Fourier map and refined isotropically. The large U_{ii} values for the Na atom are

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O3^i	0.62 (4)	2.25 (4)	2.865 (3)	171 (6)

Symmetry code: (i) $1 + y, x, -z$.

probably due to thermal motion. An attempt to shift Na from the origin improved neither the R factors nor the displacement parameters.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL*97.

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