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Ethylenediammonium gallic vanadium hydrogen sulfate monohydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.036
wR factor = 0.098
Data-to-parameter ratio = 12.7

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

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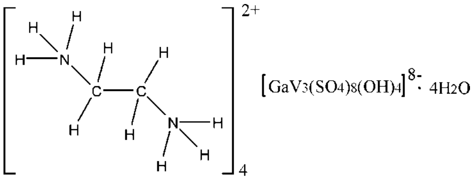
The title compound, tetrakis(ethylenediammonium) gallium trivanadium octakis(hydrogen sulfate) tetrahydroxide tetrahydrate, $(C_2H_{10}N_2)_4[GaV_3(SO_4)_8(OH)_4]\cdot4H_2O$, was obtained hydrothermally from an aqueous solution of $VOSO_4$, Ga_2O_3, ethylenediamine, glycol and sulfuric acid. The structure features a one-dimensional chain built from MO_6 octahedra (site symmetry $\overline{1}$, M = V or Ga) and bridging OH and SO_4 groups.

Comment

Over the past decade, the synthesis of new one-, two- and three-dimensional inorganic materials has received great attention, due to their functional applications in catalysis and in optical devices. As the building elements of inorganic frameworks, not only silicon and germanium (Plévert *et al.*, 2001; Xu, Fan, Chino *et al.*, 2004; Xu, Fan, Elangovan *et al.*, 2004; Xu, Cheng, Zhou *et al.*, 2006; Xu, Cheng & You, 2006), but also sulfates have been chosen to synthesize new frameworks (Doran *et al.*, 2002; Paul *et al.*, 2002). Layered mixed-valence iron sulfates exhibit interesting magnetic properties, while vanadosulfates have been found to possess unusual one-dimensional linear structures. In this work, we synthesized the title compound, (I).



(I)

As shown in Fig. 1, compound (I) features linear metal hydroxide sulfate chains, formed by MO_6 (M = V or Ga) octahedra and SO_4 tetrahedra, whose charge is balanced by an ethylenediaminium cation. Additionally, one molecule of water of crystallization is present (Fig. 1). The OH^- group links two metal ions as a bridging ligand coordinating to two metal sites. The SO_4^{2-} anions act as bidentate bridging ligands, yielding chains that run along the *a* axis (Fig. 2). A similar structure can be found in the pure vanadium compound $[H_3N(CH_2)_2NH_3][V^{III}(OH)(SO_4)_2]\cdot H_2O$ (Paul *et al.*, 2003), which is isostructural with (I).

Although the molar ratio of V:Ga is 1:1 in the starting mixture, the ratio in the reaction product is 3:1, and this was confirmed by elemental analysis and structure refinement. The occupancy factors for V and Ga on both metal positions were fixed at 0.75 and 0.25. The M—O bond lengths are between

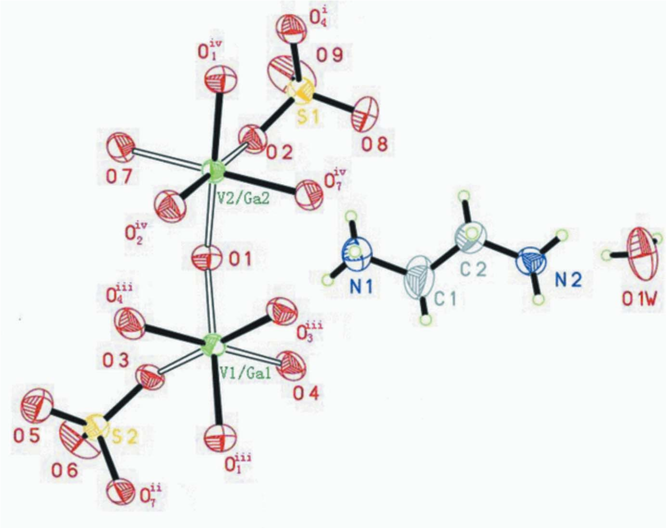


Figure 1
The structure of (I). Displacement ellipsoids are drawn at the 70% probability level. [Symmetry codes: (i) $x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, -y - 1, -z + 1$; (iii) $-x + 1, y + \frac{3}{2}, -z + \frac{1}{2}$; (iv) $x, y - 1, z$.]

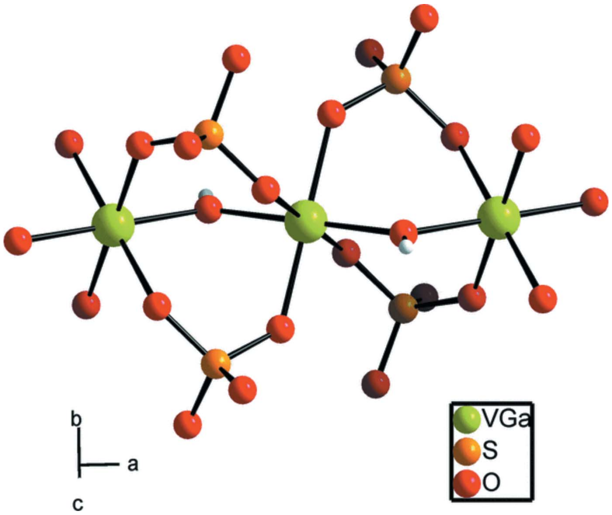


Figure 2
The metal hydroxide sulfate chain in (I).

1.938 (2) and 2.058 (2) Å, which are slightly shorter than the V—O distances in $[H_3N(CH_2)_2NH_3][V^{III}(OH)(SO_4)_2]\cdot H_2O$, most probably due to the partial subsitution of V by Ga.

The ethylenediammonium dications form a two-dimensional assembly by hydrogen-bonding interactions with the chains, as shown in Fig. 3. The water molecules are also involved in hydrogen bonding with the OH^- groups (Table 2).

A thermogravimetric (TG) analysis of the title compound reveals a weight loss of 5.6% between 323 and 513 K, which is attributed to the release of water of crystallization, followed by a weight loss of 66.2% from 513 to 1173 K, which is attributed to the release of ethylenediamine and SO_3. The calculated values for solvent water (5.2%), ethylenediamine (17.4%) and SO_3 (46.4%) are in good agreement with these results.

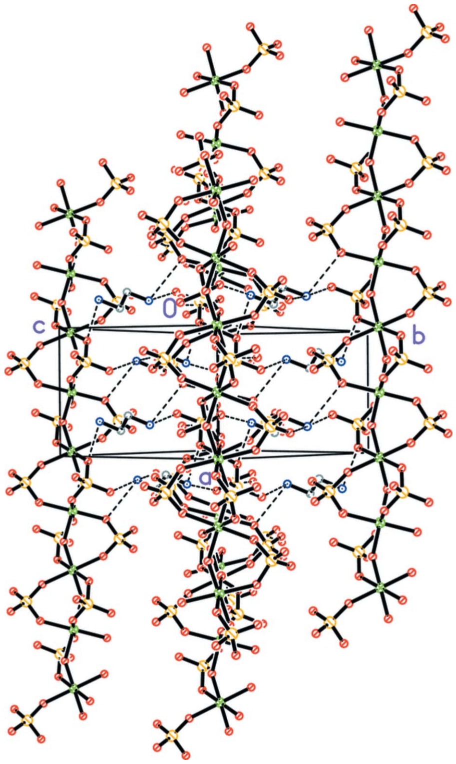


Figure 3
The crystal packing in the unit cell of (I), showing the hydrogen bonding (dashed lines).

Experimental

Brown rod-shaped crystals were synthesized hydrothermally from a mixture of $VOSO_4$ (98.4%, Shanghai Luyuan Reagent Company), Ga_2O_3 (99.9%, Shanghai Chemical Reagent Company), ethylenediamine (99.0%, Tianjing Kermel Chemical Reagents Development Centre), glycol (96.0%, Tianjing Kermel Chemical Reagents Development Centre), water and sulfuric acid (98%, Jinzhou Gucheng Chemical Reagent Company). In a typical synthesis, $VOSO_4$ (0.3204 g) and Ga_2O_3 (0.1893 g) were dissolved in a mixture of ethylenediamine (0.2404 g), glycol (5.4892 g) and water (5.0019 g), followed by the addition of H_2SO_4 (98%) (0.8703 g) with constant stirring. The mixture was kept in a 25 ml Teflon-lined steel autoclave at 443 K for 7 d. The autoclave was slowly cooled to room temperature, and then the product was filtered off, washed with distilled water and dried at room temperature. Brown rod-shaped crystals of (I) were obtained. Analysis, calculated for $(C_2N_2H_{10})[Ga_{0.25}V_{0.75}S_2O_8(OH)]\cdot H_2O$: C 6.89, H 3.81, N 8.02, V 11.01, Ga 5.10%; expected: C 6.96, H 3.77, N 8.12, V 11.09, Ga 5.05%.

Crystal data

$(C_2H_{10}N_2)_4[GaV_3(SO_4)_8(OH)_4]\cdot 4H_2O$
$M_r = 1379.68$
Monoclinic, $P2_1/c$
$a = 6.90440$ (10) Å
$b = 10.3038$ (2) Å
$c = 15.0875$ (3) Å
$\beta = 90.8470$ (10)°
$V = 1073.23$ (3) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 1.77$ mm^{-1}
$T = 293$ (2) K
0.20 × 0.11 × 0.10 mm

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Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.718$, $T_{\max} = 0.843$

11551 measured reflections
2118 independent reflections
1690 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.098$
$S = 1.05$
2118 reflections
167 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.61$ e Å^{-3}

Table 1
Selected bond lengths (Å).

*M*1—O1	1.940 (2)	*M*2—O1	1.942 (2)
*M*1—O4	2.007 (2)	*M*2—O7	2.010 (2)
*M*1—O3	2.051 (2)	*M*2—O2	2.038 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WB*···O8$^{\rm i}$	0.83 (4)	2.32 (4)	3.091 (4)	155 (4)
O1*W*—H1*WB*···O9$^{\rm i}$	0.83 (4)	2.51 (4)	3.193 (4)	141 (4)
N1—H1*D*···O8	0.89	2.31	2.975 (4)	131
N1—H1*E*···O5$^{\rm ii}$	0.89	2.12	2.919 (4)	149
O1*W*—H1*WA*···O6$^{\rm iii}$	0.84 (4)	2.11 (3)	2.925 (4)	165 (4)
O1—H1O···O1*W*$^{\rm iv}$	0.82 (2)	1.87 (2)	2.697 (4)	176 (3)
N2—H2*C*···O7$^{\rm v}$	0.89	2.05	2.894 (4)	159
N2—H2*D*···O9$^{\rm i}$	0.89	1.88	2.746 (4)	164
N2—H2*E*···O5$^{\rm v}$	0.89	2.10	2.958 (4)	162

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

The occupancy factors of V and Ga on each *M*1 and *M*2 site are 0.75 and 0.25, respectively. The Ga and V atoms at one metal position were refined with the same coordinates and anisotropic displacement parameters. H atoms of OH and water were located in a difference Fourier map and refined restrained; the O—H bond distances are 0.82 (2) and 0.84 (4) Å. H atoms of CH_2 and NH_3 groups were placed in calculated positions, with C—H = 0.97 Å and N—H = 0.89 Å, and treated as riding, with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$ or $1.5U_{\rm eq}(N)$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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