Tetrakis(tetramethylammonium) di-μ-sulfato-bis[oxosulfatovanadate(V)]

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The title compound, $(C_4H_{12}N)_4[V_2O_2(SO_4)_4]$, contains two independent tetramethylammonium cations, $[N(CH_3)_4]^+$, and a centrosymmetric dimeric anion, $[(VO)_2(SO_4)_4]^{4-}$. The V^{5+} cation has a square-pyramidal environment with the oxo group at the apex.

Comment

The continuing interest in vanadium intercalation compounds is due mostly to their potential applications as battery materials, electrochromic displays, catalysts *etc.* There has been much work performed on vanadium oxide frameworks using the tetramethylammonium ion (tma) as a template which also often functions as the counter-ion. In layered vanadium oxides, such as $tmaV_4O_{10}$ (Zavalij *et al.*, 1996), $tmaV_3O_7$ (Zavalij *et al.*, 1997), $tmaV_8O_{20}$ (Chirayil *et al.*, 1997) and others, the tma ion also plays the role of a separator, which keeps the layers from collapsing and thus stabilizes the structure. This work presents the crystal structure of the novel title compound, (I), of tma and vanadium oxide, with the additional presence of sulfate groups as part of the framework.

(I)
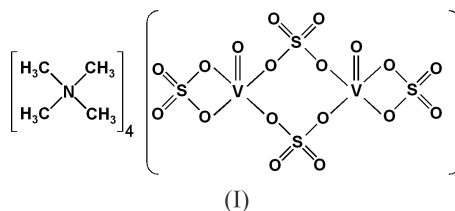
Large blue crystals of (I) were found to crystallize in the monoclinic system (Table 1) and to have the composition $[N(CH_3)_4]_2VO(SO_4)_2$. The structure is of an ionic type, with two independent tma cations and an anionic cluster complex of vanadyl sulfate, $[(VO)_2(SO_4)_4]^{4-}$, with the V atom in a square-pyramidal environment. This centrosymmetric cluster consists of a tetrameric ring (Fig. 1), formed by two square VO_5 pyramids alternating with two sulfate SO_4 tetrahedra by sharing corners. Unusually, the other two sulfate groups share edges with the base of each V square pyramid.

The coordination polyhedron of the V atom is square-pyramidal, with the doubly bonded (vanadyl) O atom at the apex and four O atoms from three sulfate groups forming the base. This typical V^{5+} polyhedron has a noticeably deformed base due to sharing one edge with the chelating sulfate group, yielding a much smaller O6—V—O8 angle compared with other angles between adjacent O atoms (Table 1). However, the O—V—O angles between opposite O atoms of the base are, as usual, close to $140°$.
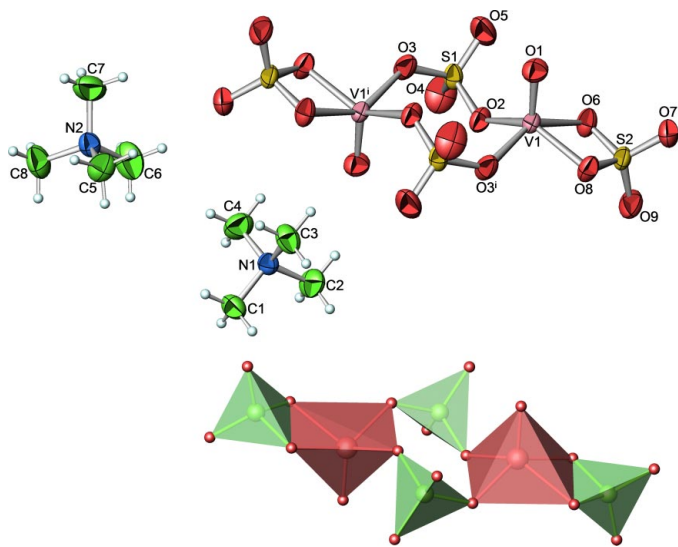
Figure 1
A view of the anionic $[(VO)_2(SO_4)_4]^{4-}$ dimer and two independent $[N(CH_3)_4]^+$ cations in (I). Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. At the bottom is a polyhedral representation of the vanadyl sulfate dimer. [Symmetry code (i) as in Table 1.]

The geometry of the tma ions in (I) does not deviate appreciably from ideal tetrahedral, whereas the tetrahedral sulfate ions are much less perfect, due to the presence of two terminal O atoms and two atoms bonded to V (Table 1). The vanadyl sulfate clusters and tma ions are packed *via* weak C—H···O hydrogen bonds (Fig. 2), with H···O distances in the range 2.4–2.5 Å and C···O distances in the range 3.3–3.5 Å.

Vanadyl sulfate and its salts with different ions (*e.g.* ammonium, potassium and others) are known to form a variety of frameworks and clusters. Thus, in monoclinic $K_3(VO)_2(SO_4)_4$ (Eriksen *et al.*, 1996) and orthorhombic $(NH_4)VO(SO_4)_2$ (Richter & Mattes, 1992), V square pyramids are linked into chains by sharing corners with a pair of SO_4
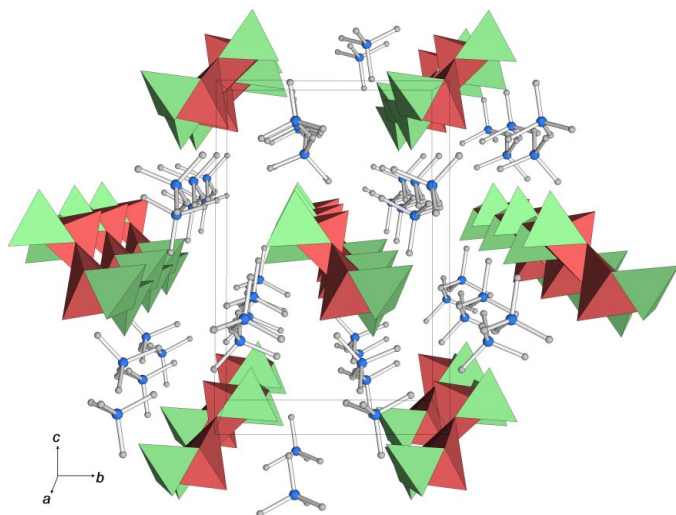
groups. However, in both these structures there is weak bond between the V atom of one chain and an O atom from another, which yields a layered structure and distorted octahedra – a typical V polyhedron. In the potassium vanadyl sulfate salt $K_4(VO)_3(SO_4)_5$ (Fehrmann *et al.*, 1989), and in vanadyl oxide sulfate, $V_2O_3(SO_4)_2$ (Richter & Mattes, 1992), the V atom also has distorted octahedral coordination and, by sharing corners with the sulfate group, forms a three-dimensional framework with zeolite-like tunnels, which are filled with K in the former but are empty in the latter compound. The dimeric vanadyl sulfate cluster was found only in $Cs_4V_2O_3(SO_4)_4$ (Nielsen *et al.*, 1993), where two V square pyramids share a corner with each other and, in addition, each of them shares a corner and an edge with sulfate groups.

Experimental

A cation-exchange resin was prepared in a column by stirring Amberlite IR-120 (plus) cation-exchange resin (about 80 g) in a beaker with deionized water (about 150 ml), packing the resulting resin mixture into a column and conditioning it by eluting with a dilute solution of HNO_3. Proton-exchanged $KMnO_4$ was then prepared using this cation-exchange resin by dissolving $KMnO_4$ (3.15 g) in deionized water (about 50 ml) and eluting this solution through the resin to form $HMnO_4$. The title compound was then prepared by the reaction of $VOSO_4$ (3.25 g) in a beaker with the $HMnO_4$ solution from the column and the addition of $[N(CH_3)_4]OH$ solution (about 1.5 ml, 25%) to the resulting mixture. A few drops of concentrated HNO_3 were added to bring the solution to a pH 3.3. After stirring the mixture for about 2 h, it was transferred to a 125 ml Teflon-lined autoclave, placed in an oven at 438 K and heated for 72 h. At the end of this heating, the pH of the mixture was 2.2. The product was filtered and rinsed with a small amount of water, and blue crystals of (I) were isolated.

Crystal data

$(C_4H_{12}N)_4[V_2O_2(SO_4)_4]$	$D_x = 1.574$ Mg m^{-3}
$M_r = 814.71$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2879
$a = 13.1346 (12)$ Å	reflections
$b = 9.2316 (9)$ Å	$\theta = 2.6$–$28.5°$
$c = 14.2385 (14)$ Å	$\mu = 0.86$ mm^{-1}
$\beta = 95.171 (2)°$	$T = 295 (2)$ K
$V = 1719.4 (3)$ Å^3	Prism, blue
$Z = 2$	$0.38 \times 0.36 \times 0.15$ mm

Data collection

Bruker SMART APEX three-circle diffractometer	3504 independent reflections
	3244 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan	$\theta_{max} = 26.4°$
(*XPREP* in *SHELXL*97;	$h = -16 \rightarrow 16$
Sheldrick, 1997)	$k = -11 \rightarrow 11$
$T_{min} = 0.758$, $T_{max} = 0.879$	$l = -17 \rightarrow 17$
18 354 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$+ 0.923P]$, where
$wR(F^2) = 0.078$	$P = [\max(F_o^2, 0) + 2F_c^2]/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
3504 reflections	$\Delta\rho_{max} = 0.45$ e Å^{-3}
231 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
Only H-atom U's refined	

Figure 2
A polyhedral view of the molecular packing for (I).

Table 1
Selected geometric parameters (Å, °).

V1—O1	1.5785 (14)	S2—O6	1.5151 (14)
V1—O2	1.9509 (13)	S2—O8	1.5216 (14)
V1—O3[i]	1.9702 (14)	N1—C4	1.487 (3)
V1—O8	1.9957 (13)	N1—C2	1.488 (2)
V1—O6	2.0043 (13)	N1—C3	1.488 (3)
S1—O5	1.4305 (17)	N1—C1	1.492 (3)
S1—O4	1.4382 (18)	N2—C5	1.480 (3)
S1—O3	1.4850 (14)	N2—C7	1.483 (3)
S1—O2	1.5052 (14)	N2—C8	1.484 (3)
S2—O7	1.4296 (15)	N2—C6	1.489 (3)
S2—O9	1.4314 (16)		
O1—V1—O2	111.03 (7)	O2—V1—O6	89.84 (6)
O1—V1—O3[i]	107.03 (8)	O3[i]—V1—O6	143.48 (6)
O2—V1—O3[i]	90.11 (7)	O8—V1—O6	69.98 (6)
O1—V1—O8	110.26 (7)	O5—S1—O4	114.49 (13)
O2—V1—O8	137.78 (6)	O3—S1—O2	106.48 (8)
O3[i]—V1—O8	86.11 (6)	O7—S2—O9	113.36 (10)
O1—V1—O6	107.00 (7)	O6—S2—O8	98.10 (7)

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

All H atoms were placed in calculated positions, with C—H distances of 0.96 Å, and their U_{iso}(H) values were refined individually.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2003).

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