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Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(S-O) = 0.002$ Å
 R factor = 0.013
 wR factor = 0.031
Data-to-parameter ratio = 12.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Potassium bis(μ -sulfato- $1\kappa O:2\kappa O'$)bis[*cis*-dioxido-*cis*-bis(sulfato- κO)tungstate(VI)]

The title compound, $K_8[\{W^{VI}O_2(SO_4)_2\}_2(\mu-SO_4)_2]$, precipitated from a melt of tungsten trioxide and potassium sulfate in potassium pyrosulfate. The W^{VI} coordination sphere in the independent $K_4[W^{VI}O_2(SO_4)_3]$ moiety is completed by inversion symmetry, resulting in a dimer with two bridging sulfate ligands and a unit cell with two dimeric units.

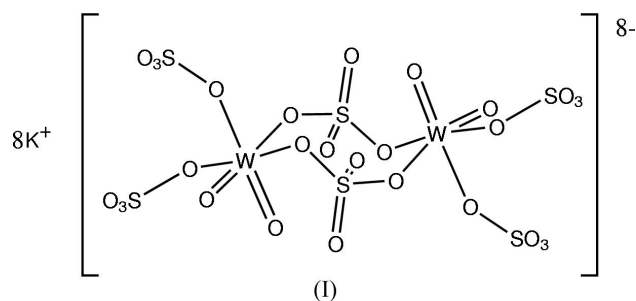
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Comment

Studies of the vanadium-based catalyst (Topsøe & Nielsen, 1947) used in industrial sulfuric acid production, where potassium pyrosulfate is the solvent, have led to the determination of the $K_2S_2O_7-V_2O_5$ phase diagram (Folkmann *et al.*, 1998), the characterization of both sodium and potassium pyrosulfate (Rasmussen *et al.*, 2001), and investigations of the ability of potassium pyrosulfate to dissolve transition metal oxides in general. A diverse range of novel sulfate compounds has precipitated from these melts (Borup *et al.*, 1990; Nørbygaard *et al.*, 1998; Berg & Thorup, 2005).



In contrast with many of the previously reported sulfate compounds precipitated from the melts, where the unit cells contain chains of anions, the unit cell of the title compound contains discrete $[\{W^{VI}O_2(SO_4)_2\}_2(\mu-SO_4)_2]^{8-}$ dimeric units

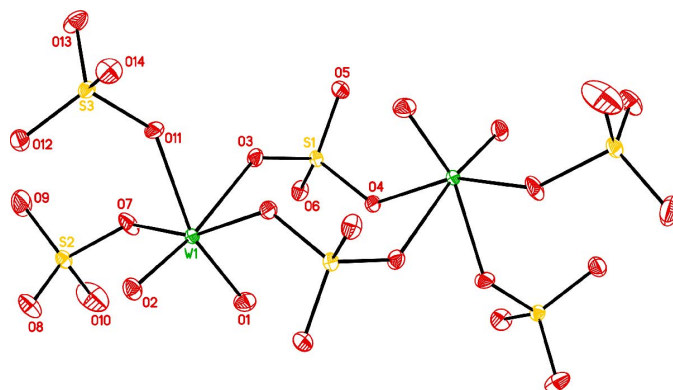


Figure 1

Plot of the anion, showing 50% probability ellipsoids. The K ions have been omitted for clarity.

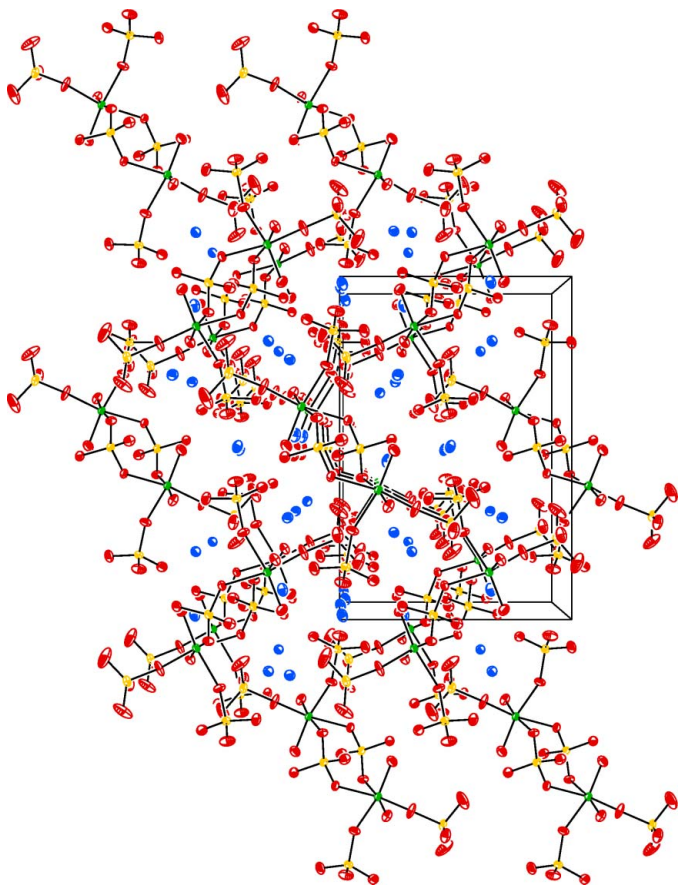


Figure 2
The crystal packing, viewed along the *c* axis.

(Fig. 1). Fig. 2 shows the packing of the dimers. Although dimeric anions are rare, the vanadium compound $\text{Cs}_4[\{\text{V}^{\text{V}}\text{O}(\text{SO}_4)_2\}_2(\mu\text{-O})]$, its K and Rb analogues (Nielsen *et al.*, 1993), and $\text{K}_8[\{\text{V}^{\text{V}}\text{O}(\text{SO}_4)_2\}_2(\mu\text{-O})(\mu\text{-SO}_4)_2]$ are notable examples (Rasmussen *et al.*, 2003).

The coordination sphere of the W atom contains two doubly bound O atoms, two terminally bound sulfate ligands and two bridging sulfate ligands; the dimeric unit thus contains two of the eight reported sulfate coordination modes (Tamasi & Cini, 2003). The tungsten coordination sphere is distorted from octahedral, with angles between any two *cis* O atoms deviating by as much as 18° from ideal (see Table 1). The bond length for W1—O2 is shorter than W1—O1, consistent with the fact that O2 is *trans* to the bridging sulfate, while O1 is *trans* to a terminally bound sulfate. The bond W1—O3 *trans* to O2 is significantly longer than the other W—O bonds. The W—O bond lengths are similar to those previously reported (Salles *et al.*, 1996).

The geometry of the sulfate ligands can be described as slightly distorted from tetrahedral, with angles ranging from $104.42(14)$ to $114.42(14)^\circ$. The S—O bond lengths of $1.441(2)$ – $1.464(2)$ Å for the S atoms bound to the terminal O atoms and the slightly longer S—O bond lengths of $1.4861(19)$ – $1.5700(19)$ Å for those bound to the coordinating O atoms compare reasonably with those previously reported

in complexes with similar coordination (Nielsen *et al.*, 1993; Rasmussen *et al.*, 2003; Berg & Thorup, 2005). The O8—K2 bond length of $3.401(2)$ Å is the longest of the O—K bond distances; the shortest O—K bond distances range from $2.610(2)$ to $2.692(2)$ Å. Three of the four independent potassium cations, *viz.* K1, K2, and K3, are eight-coordinate, while K4 is nine-coordinate.

Experimental

Crystals were grown from a melt of 20.3 mol% tungsten trioxide and 20.4 mol% potassium sulfate in potassium pyrosulfate, using the method described previously by Nørbygaard *et al.* (1998).

Crystal data

$\text{K}_8[(\text{WO}_2)_2(\text{SO}_4)_6]$
 $M_r = 1320.86$
 Monoclinic, $P2_1/n$
 $a = 9.4362(5)$ Å
 $b = 13.9625(7)$ Å
 $c = 10.1948(5)$ Å
 $\beta = 90.780(1)^\circ$
 $V = 1343.07(12)$ Å³
 $Z = 2$

$D_x = 3.266$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5682 reflections
 $\theta = 2.5$ – 28.0°
 $\mu = 10.38$ mm⁻¹
 $T = 120(2)$ K
 Tablet, colourless
 $0.18 \times 0.10 \times 0.05$ mm

Data collection

Bruker SMART/Platform CCD diffractometer
 ω scans
 Absorption correction: by integration (*XPREP*; Bruker, 2002)
 $T_{\min} = 0.245$, $T_{\max} = 0.619$
 13 095 measured reflections

2458 independent reflections
 2429 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 25.3^\circ$
 $h = -11 \rightarrow 11$
 $k = -16 \rightarrow 16$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.013$
 $wR(F^2) = 0.031$
 $S = 1.13$
 2458 reflections
 199 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0121P)^2 + 2.1788P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.58$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.44$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

W1—O1	1.7258 (19)	S2—O7	1.5700 (19)
W1—O2	1.7102 (19)	S3—O11	1.5296 (19)
W1—O3	2.2237 (19)	O2—K1	2.682 (2)
W1—O4 ⁱ	2.0302 (18)	O8—K1	2.681 (2)
W1—O7	1.9681 (19)	O6—K2 ⁱⁱ	2.610 (2)
W1—O11	2.0930 (18)	O5—K3 ⁱ	2.632 (2)
S1—O3	1.4861 (19)	O8—K4 ⁱⁱⁱ	2.692 (2)
S1—O4	1.5349 (19)	O8—K2	3.401 (2)
O2—W1—O1	101.20 (9)	O7—W1—O11	83.92 (8)
O2—W1—O7	97.61 (9)	O4 ⁱ —W1—O11	79.70 (8)
O1—W1—O7	97.03 (9)	O2—W1—O3	170.94 (8)
O2—W1—O4 ⁱ	96.59 (8)	O1—W1—O3	87.85 (8)
O1—W1—O4 ⁱ	94.34 (9)	O7—W1—O3	81.56 (8)
O7—W1—O4 ⁱ	159.71 (8)	O4 ⁱ —W1—O3	82.13 (7)
O2—W1—O11	98.49 (9)	O11—W1—O3	72.45 (7)
O1—W1—O11	159.97 (8)		

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

A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution. The highest peaks in the final difference Fourier map were 0.98 and

0.87 Å from atoms W1 and O1, respectively; the deepest hole was 0.74 Å from S3.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *CIFTAB* in *SHELX97-2* (Sheldrick, 2001).

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