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Potassium bis(μ-sulfato-1κO:2$\kappa O'$)bis[*cis*-dioxido-*cis*-bis(sulfato-κO)tungstate(VI)]

Susan J. Cline Schäffer* and Rolf W. Berg

The Technical University of Denmark, The
Department of Chemistry, Building 207,
DK-2800 Lyngby, Denmark

Correspondence e-mail: ss@kemi.dtu.dk

The title compound, $K_8[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]$, 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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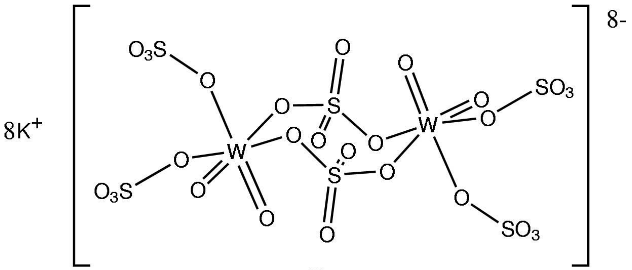
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(S–O) = 0.002 Å
R factor = 0.013
wR factor = 0.031
Data-to-parameter ratio = 12.4

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

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).



(I)

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 $[\{W^{VI}O_2(SO_4)_2\}_2(\mu\text{-}SO_4)_2]^{8-}$ dimeric units

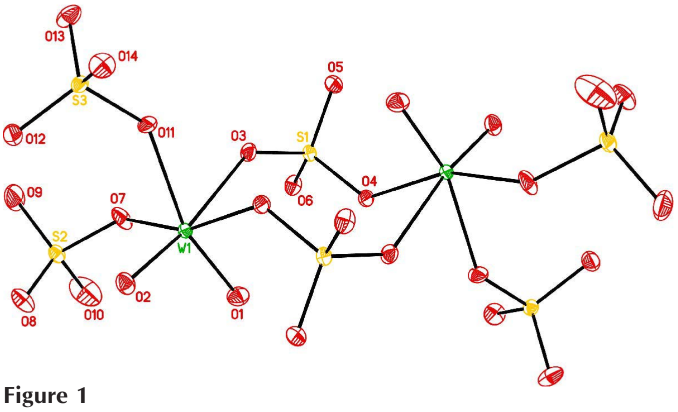


Figure 1
Plot of the anion, showing 50% probability ellipsoids. The K ions have been omitted for clarity.

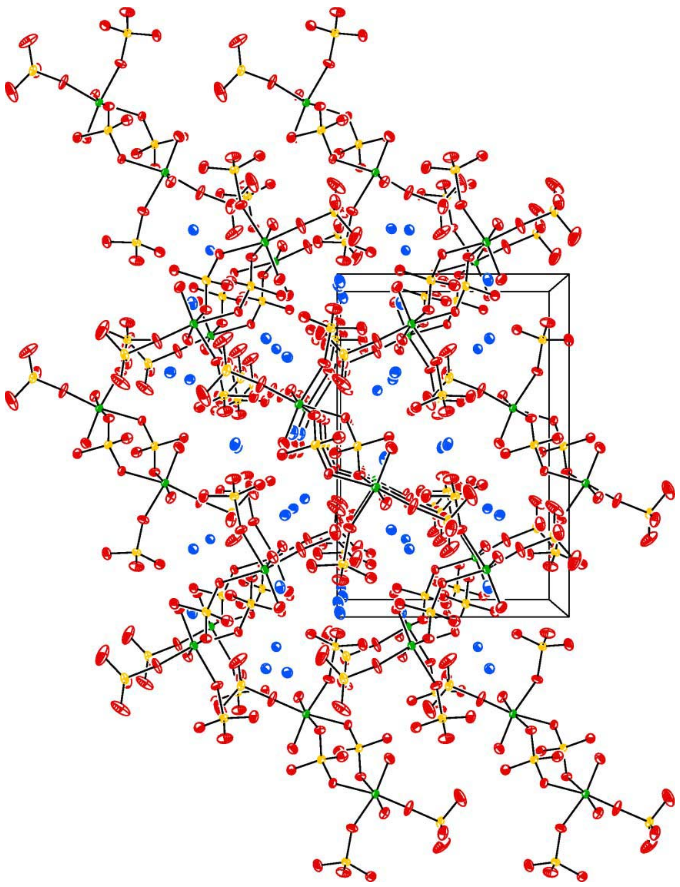


Figure 2
The crystal packing, viewed along the *c* axis.

(Fig. 1). Fig. 2 shows the packing of the dimers. Although dimeric anions are rare, the vanadium compound $Cs_4[\{V^{V}O(SO_4)_2\}_2(\mu\text{-}O)]$, its K and Rb analogues (Nielsen *et al.*, 1993), and $K_8[\{V^{V}O(SO_4)_2\}_2(\mu\text{-}O)(\mu\text{-}SO_4)_2]$ 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)°. 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

$K_8[(WO_2)_2(SO_4)_6]$
$M_r = 1320.86$
Monoclinic, $P2_1/n$
$a = 9.4362\ (5)$ Å
$b = 13.9625\ (7)$ Å
$c = 10.1948\ (5)$ Å
$\beta = 90.780\ (1)°$
$V = 1343.07\ (12)$ Å^3
$Z = 2$
$D_x = 3.266$ 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 × 0.10 × 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 $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 25.3°$
$h = -11 \rightarrow 11$
$k = -16 \rightarrow 16$
$l = -12 \rightarrow 12$

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 $P = (F_o^{\,2} + 2F_c^{\,2})/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.58$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ 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: *SAINT* (Bruker, 2002); data reduction: *SAINT*; 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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