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Bis(tetrabutylammonium) μ-oxalato-bis-[dibromidodioxidotungstate(VI)]

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Key indicators

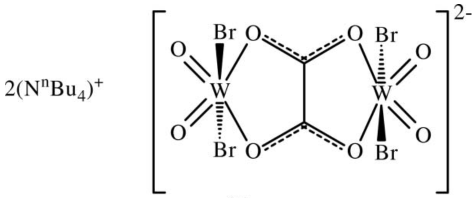
Single-crystal X-ray study
T = 160 K
Mean σ(C–C) = 0.006 Å
R factor = 0.026
wR factor = 0.063
Data-to-parameter ratio = 20.3

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

The title compound, $(C_{16}H_{36}N)_2[W_2Br_4(C_2O_4)O_4]$, has a centrosymmetric dinuclear anion in which two tungsten(VI) centres, with distorted octahedral coordination, are bridged by an oxalate dianion, forming two five-membered chelate rings. All atoms of the complex anion, except for the Br atoms, lie essentially in a plane.

Comment

The title compound, (I), was obtained as a by-product during research on the bromination of Keggin-type polyoxotungstate anions (Errington *et al.*, 2000), and the crystal structure was determined in order to identify the product.



(I)

Compound (I) is a bis(tetrabutylammonium) salt of an oxalate-bridged dinuclear tungsten anion (Fig. 1). The anion has crystallographic inversion symmetry, while the cations lie in general positions. The compound is isostructural with the analogous molybdenum(VI) complex having chlorido instead of bromido ligands (Liu *et al.*, 1988). The observed bridging mode of the oxalate dianion, with each of its O atoms coordinated to a metal centre, forming two chelate rings, is well known in transition metal structural chemistry; more than 600 examples are found in a search of the Cambridge Structural Database (Version 5.28 with one update, January 2007; Allen, 2002), four of which contain tungsten (two of them being polymorphs). The {W(oxalate)W} unit is planar; the oxido ligands lie *trans* to the oxalate O atoms, and the bromido ligands lie above and below this oxgen-coordinated equatorial plane, giving a somewhat distorted octahedral geometry for tungsten (Table 1); as expected, the bromido ligands are bent away from the oxido ligands and towards the oxalate bridge. The r.m.s. deviations (Å) for selected mean planes are 0.013 for W1 and the O atoms attached to it, 0.016 for each five-membered chelate ring, and 0.029 for all atoms except Br of the anion.

The *n*-butyl arms of the cations are fully extended, with all torsion angles around C—C bonds close to 180°. There are no unusual intermolecular interactions.

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Experimental

The title compound was prepared, as a side-product, from oxalyl bromide and $(^n\mathrm{Bu}_4\mathrm{N})_6[\mathrm{NaPW}_{11}\mathrm{O}_{39}]$, as described previously (Errington *et al.*, 2000). It was clearly distinguished from the yellow main product, being colourless.

Crystal data

$(C_{16}H_{36}N)_2[W_2Br_4(C_2O_4)O_4]$
$M_r = 1324.28$
Monoclinic, $P2_1/n$
$a = 9.8891$ (9) Å
$b = 18.0806$ (15) Å
$c = 13.2945$ (11) Å
$\beta = 90.905$ (2)°
$V = 2376.8$ (4) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 8.24$ mm^{-1}
$T = 160$ (2) K
0.32 × 0.32 × 0.16 mm

Data collection

Bruker SMART 1K CCD diffractometer
Absorption correction: multi-scan (*XPREP* in *SHELXTL*; Sheldrick, 2001)
$T_{\min} = 0.075$, $T_{\max} = 0.270$
12764 measured reflections
4689 independent reflections
4435 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.063$
$S = 1.17$
4689 reflections
231 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.21$ e Å^{-3}
$\Delta\rho_{\min} = -1.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

W1—Br1	2.5291 (4)	W1—O4$^{\mathrm{i}}$	2.249 (3)
W1—Br2	2.5103 (5)	C1—O3	1.247 (4)
W1—O1	1.712 (3)	C1—O4	1.247 (4)
W1—O2	1.710 (3)	C1—C1$^{\mathrm{i}}$	1.547 (7)
W1—O3	2.226 (2)		
Br1—W1—Br2	159.484 (16)	Br2—W1—O4$^{\mathrm{i}}$	82.40 (7)
Br1—W1—O1	94.96 (10)	O1—W1—O2	105.00 (14)
Br1—W1—O2	95.35 (10)	O1—W1—O3	161.90 (12)
Br1—W1—O3	80.87 (7)	O1—W1—O4$^{\mathrm{i}}$	89.35 (12)
Br1—W1—O4$^{\mathrm{i}}$	80.94 (7)	O2—W1—O3	92.96 (12)
Br2—W1—O1	96.74 (10)	O2—W1—O4$^{\mathrm{i}}$	165.48 (12)
Br2—W1—O2	97.81 (10)	O3—W1—O4$^{\mathrm{i}}$	72.62 (9)
Br2—W1—O3	82.80 (7)		

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

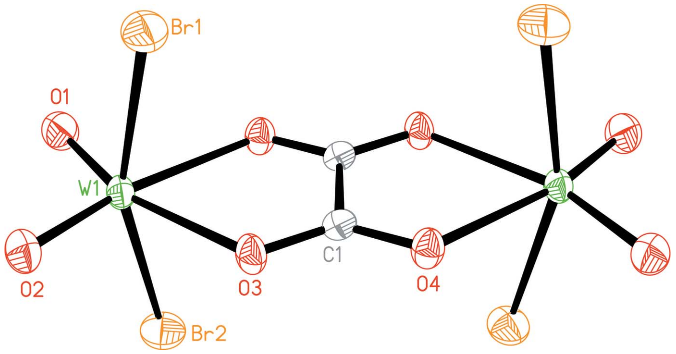

Figure 1
The structure of the anion with atom labels and 50% probability displacement ellipsoids. Unlabelled atoms are related to labelled atoms by the symmetry operation $(1 - x, -y, 1 - z)$.

H atoms were positioned geometrically and refined with a riding model (including free rotation about C—C bonds for the methyl groups), with C—H = 0.99 (CH_2) and 0.98 Å (CH_3), and with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ [$1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl groups]. The largest peak and deepest hole in the residual electron density map lie 1.00 and 0.89 Å, respectively, from the W atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: local programs; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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