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Cationic d^3–d^3 dinuclear compounds of tungsten: $[W_2(O_2CBu^t)_5]^+X^-$, where $X^- = BF_4^-$ and $CF_3SO_3^-$

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Abstract

Ditungsten hexapivalate, $W_2(O_2CBu^t)_6$, and triethyloxonium tetrafluoroborate, $Et_3O^+BF_4^-$, react in CH_2Cl_2 at room temperature to yield the 1:1 complex $[W_2(O_2CBu^t)_5][BF_4]$ (**1**), as a yellow crystalline solid. A similar reaction involving trimethylsilyltrifluoromethane-sulfonate, TMS-OTf, yields $[W_2(O_2CBu^t)_5][OTf]$ (**2**). Compounds **1** and **2** are 1:1 electrolytes in CH_3CN but show ion pairing in THF and CH_2Cl_2 solutions with the degree of ion pairing being greater for **2** than for **1**. Only **1** is soluble in toluene. ^1H NMR spectroscopy shows there are 3 types of O_2CBu^t ligands in the integral ratio 1:2:2 which is consistent with the structure found in the solid state for **1** which has a $(W{\equiv}W)^{6+}$ unit, W–W = 2.28(1) Å supported by three bridging pivalates and two chelating η^2-O_2CBu^t ligands. The local geometry about each tungsten is a distorted pentagonal pyramid, $W{\equiv}WO_5$, with relatively weak axial interactions (*trans* to the W≡W bond) to the BF_4^- counter anions, W–F = 2.50(1) Å (av.). This leads to an infinite polymeric structure in the solid state. Crystal data for $[W_2(O_2CBu^t)_5][BF_4]$ at −171 °C: $a = 29.44(1)$, $b = 36.05(1)$, $c = 20.80(1)$ Å, $\beta = 133.30(1)°$, $Z = 16$, $D_{calc} = 1.82$ g cm^{-3} and space group $C2/c$.

Introduction

Over the past decade we have developed an extensive chemistry of d^3–d^3 dimers of molybdenum and tungsten [1]. With a few exceptions the compounds have been neutral and when not neutral anionic, e.g. [2] $W_2Cl_7(THF)_2^-$ and $Mo_2(OCH_2Bu^t)_7^-$. Of course, perhaps the most famous of the anionic d^3–d^3 dimers are the homoleptic halide anions $M_2X_9^{3-}$ where X = Cl and Br that have the confacial bioctahedral geometry [3]. These have been known for several decades. Conspicuous by their absence are cationic complexes containing the central d^3–d^3 core with M–M triple bonds of configuration $\sigma^2\pi^4$. Previously our efforts to prepare cationic amido and alkoxide complexes from reactions such as that between $W_2Cl_2(NMe_2)_4$ and $AgPF_6$ resulted in intractable solids and rapid polymerization of tetrahydrofuran [4]. With the use of $Me_3SiOSO_2CF_3$(TMS-OTf), however, the mixed amido-triflate complex was prepared to eqn. (1) [4].

$$1,2\text{-}W_2Cl_2(NMe_2)_4 + 2TMS\text{-}OTf \xrightarrow[\text{toluene}]{22\ °C} 1,2\text{-}W_2(OTf)_2(NMe_2)_4 + 2TMS\text{-}Cl \quad (1)$$

The compound containing the mixed amido-triflate had very short W–N bonds, 1.92(1) Å (av.) and long W–O bond distances 2.07(1) Å. The latter may be compared with W–OR (alkoxide) distances of *c.* 1.90(2) Å that are typically found for $(W{\equiv}W)^{6+}$ containing compounds [5]. The addition of PMe_3 to 1,2-$W_2(OTf)_2(NMe_2)_4$ led to $W_2(NMe_2)_3(OTf)_3(PMe_3)_2$ and $W_2(NMe_2)_6$ by ligand redistribution reactions [4]. However, even in $W_2(NMe_2)_3(OTf)_3(PMe_3)_2$, which contained a central $PO_2NW{\equiv}WN_2OP$ core, the triflate ligands were definitely bonded with W–O = 2.20(1) Å at the tungsten atom having two NMe_2 ligands and the PMe_3 ligand [4].

During this work we also prepared the compound $W_2(OBu^t)_4(OTf)_2(PMe_3)_2$ according to eqn. (2) [4].

$$W_2(OBu^t)_6 + 2TMS\text{-}OTf \xrightarrow[\text{toluene}]{22\ °C} [W_2(OBu^t)_4(OTf)_2]_n + 2TMS\text{-}OBu^t \quad (2a)$$

$$[W_2(OBu^t)_4(OTf)_2]_n + 2nPMe_3 \xrightarrow[\text{toluene}]{22\ °C} n[W_2(OBu^t)_4(OTf)_2(PMe_3)_2] \quad (2b)$$

The solid state structure of this molecule, as determined by single-crystal X-ray diffraction, revealed a central core $PO_2O'W{\equiv}WO_2O'P$ where the W–O distances associated with the t-BuO ligands, 1.85(1) Å

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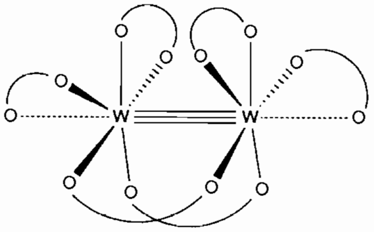
(av.) were notably much shorter than the long W–O distances to the triflate ligand, W–O = 2.18(2) Å. ^{1}H and ^{31}P NMR spectroscopy clearly revealed that the triflate ligands remained bound in solution [4].

We describe here our successful synthesis of what we believe to be the first cationic d^3–d^3 W≡W $\sigma^2\pi^4$ containing dinuclear compounds. Our synthetic strategy was based on the earlier observations that the $(W{\equiv}W)^{6+}$ moiety had the ability to increase its coordination number at each metal center from three to four without loss of the OTf ligand.

Results and discussion

The starting material of choice was the ditungsten hexapivalate $W_2(O_2CBu^t)_6$ which is known to adopt the structure **A** schematically shown below and is readily prepared from the reaction between $W_2(OBu^t)_6$ and pivalic acid (6 equiv.) [6].



A

Treatment of $W_2(O_2CBu^t)_6$ with $Et_3O^+BF_4^-$ in CH_2Cl_2 revealed a preference for the 1:1 stoichiometric reaction shown in eqn. (3). Attempts to prepare the dication, i.e. attempts to remove two O_2CBu^t ligands, were unsuccessful.

$$W_2(O_2CBu^t)_6 + Et_3O^+BF_4^- \xrightarrow[CH_2Cl_2]{22\ ^\circ C} [W_2(O_2CBu^t)_5][BF_4] + Et_2O + Bu^tCOOEt \quad (3)$$

The 1:1 salt, **1**, obtained in reaction (3) is a yellow crystalline solid. Purification of the product involved washing the residue (obtained upon removal of the solvent under vacuum) with diethyl ether and recrystallization from CH_2Cl_2/Et_2O. X-ray quality crystals were obtained by recrystallization from toluene.

A similar product involving the replacement of a pivalate ligand was obtained in the reaction shown in eqn. (4) that involves the use of TMS-OTf. Again use of an excess of TMS-OTf failed to remove more than one O_2CBu^t ligand

$$W_2(O_2CBu^t)_6 + TMF\text{-}OTf \xrightarrow[toluene]{22\ ^\circ C} [W_2(O_2CBu^t)_5][OTf] + Bu^tCOOTMS \quad (4)$$

The compound $[W_2(O_2CBu^t)_5][OTf]$ (**2**) was obtained as a yellow microcrystalline solid. It is completely insoluble in hexane and toluene but soluble in diethyl ether, dimethoxyethane, acetonitrile and tetrahydrofuran. Although insoluble in aromatic solvents, the triflate derivative **2** readily dissolves in toluene or benzene upon addition of small amounts of ether or THF. The ^{1}H NMR spectrum of $[W_2(O_2CBu^t)_5][OTf]$ was recorded in a 90:10 mixture of C_6D_6:THF-d_8.

^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy indicate that the complexes $[W_2(O_2CBu^t)_5]^+X^-$, where $X^- = BF_4^-$ and $OSO_2CF_3^-$, are essentially identical. They reveal the existence of pivalate ligands in the integral ratio 2:2:1 and support the presence of a non-fluxional cation.

Compounds **1** and **2** are air-sensitive, particularly in solution and should be handled under a dry and oxygen free atmosphere (N_2). The triflate derivative is far more robust, and may be handled for brief periods in air as a solid.

Conductivity measurements indicate that compounds **1** and **2** are 1:1 electrolytes in CH_3CN. The conductivity is less in THF than in CH_3CN and in CH_2Cl_2 there is evidently strong ion pairing. The data in Table 1 reveal the relative coordinating abilities of the anions $CF_3SO_3^- > BF_4^-$ and it is presumably the stronger $[W_2(\mu\text{-}CF_3SO_3)]_n$ linkages in the solid state that prevent the trifluoromethanesulfonate derivative from being soluble in solvents such as toluene.

Solid state and molecular structure of $[W_2(O_2CBu^t)_5][BF_4]$

In the space group *C*2/*c* there is an infinite polymer where two independent $[W_2(O_2CBu^t)_5][BF_4]$ units are linked by μ-η^1-η^1 BF_4^- anions. In addition there are 3 molecules of toluene per asymmetric unit. Thus in the unit cell there are 16 W_2 cations, which fall into two sets of eight equivalent $[W_2(O_2CBu^t)_5][BF_4]$ units. The repeat unit along the polymer is ABCDABCD, etc. and not ABCDDCBA.

In Fig. 1 we show the asymmetric unit containing the two W_2 units connected by a bridging BF_4^- anion. The B–F bond distances of those fluorine atoms that coordinate to tungsten are slightly longer than the other B–F bonds. To all intents and purposes the $W_2(O_2CBu^t)_5^+$ unit can be readily related to that of

TABLE 1. Molar conductance (Ω^{-1} mol^{-1} cm^3) of $[W_2(O_2CBu^t)_5][O_3SCF_3]$ and $[W_2(O_2CBu^t)_5][BF_4]$

Compound	Solvent		
	CH_3CN	THF	CH_2Cl_2
$[W_2(O_2CBu^t)_5][BF_4]$	121.4	23.0	8.9
$[W_2(O_2CBu^t)_5][O_3SCF_3]$	111.7	11.9	1.0

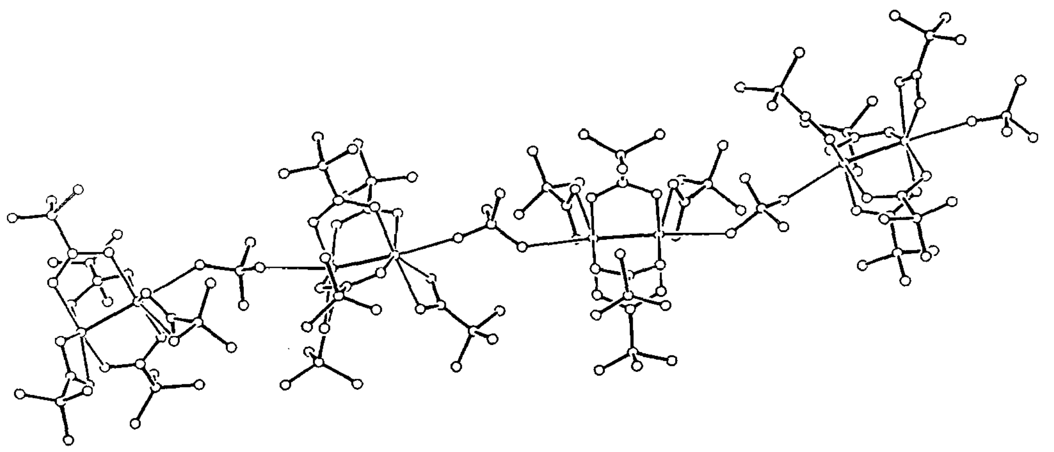
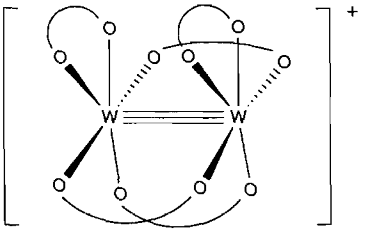


Fig. 1. Ball-and-stick drawing of the infinite polymer $[W_2(O_2CBu^t)_5][BF_4]$ showing only the asymmetric unit. Hydrogen atoms, solvents of crystallization, and alternative conformations for the two disordered pivalates (involving carbon atoms only) have been omitted for clarity.

the starting material by the removal of one O_2CBu^{t-} ligand with the maintenance of the strong (short) five W–O bonds at each W center. These lie in a pentagonal plane which is formed by three bridging (μ-)O_2CBu^t ligands and two η^2-chelating O_2CBu^t ligands (per W atom), as shown schematically in **B**. The drawing **B** emphasizes the close similarity to **A**.



B

TABLE 2. Selected bond distances (Å) for $[W_2(O_2CBu^t)_5][BF_4]$

Molecule A		Molecule B	
W(1)A–W(2)A	2.2762(14)	W(1)B–W(2)B	2.2824(13)
W(1)A–O(3)A	2.102(13)	W(1)B–O(3)B	2.132(12)
W(1)A–O(5)A	2.129(12)	W(1)B–O(5)B	2.161(11)
W(1)A–O(17)A	2.077(13)	W(1)B–1O(17)B	2.079(11)
W(1)A–O(24)A	2.089(12)	W(1)B–O(24)B	2.081(14)
W(1)A–O(31)A	2.086(12)	W(1)B–O(31)B	2.086(12)
W(1)A–F(41)B	2.506(11)	W(1)B–F(42)A	2.505(9)
W(2)A–O(10)A	2.129(13)	W(2)B–O(10)B	2.126(12)
W(2)A–O(12)A	2.134(12)	W(2)B–O(12)B	2.154(12)
W(2)A–O(19)A	2.120(12)	W(2)B–O(19)B	1.121(11)
W(2)A–O(26)A	2.077(12)	W(2)B–O(26)B	2.080(12)
W(2)A–O(33)A	2.059(12)	W(2)B–O(33)B	2.098(11)
W(2)A–F(38)A	2.503(11)	W(2)B–F(38)B	2.498(11)
F(38)A–B(39)A	1.455(24)	F(38)B–B(39)B	1.253(28)
F(40)A–B(39)A	1.34(3)	F(40)B–B(39)B	1.39(3)
F(41)A–B(39)A	1.336(23)	F(41)B–B(39)B	1.36(3)
F(42)A–B(39)A	1.409(25)	F(42)B–B(39)B	1.52(4)

Two views of the repeating subunit of the $[W_2(O_2CBu^t)_5][BF_4]$ polymer are given in Figs. 1 and 2. Selected bond distances and angles comparing the two independent units are given in Tables 2 and 3 respectively. A summary of crystal data is given in Table 4.

Conclusions

We have prepared the first cationic d^3–d^3 $(W{\equiv}W)^{6+}$ containing compounds and the $W_2(O_2CBu^t)_5{}^+$ cation seems quite electrophilic as judged by its ability to bind $BF_4{}^-$ and $CF_3SO_3{}^-$ anions. Further investigations of the chemistry of these cations are planned.

Experimental

General procedures

Standard Schlenk techniques and Vacuum Atmospheres Co. Dri-Lab systems were used for all syntheses and sample manipulations. All solvents were vigorously dried, deoxygenated and stored over 4 Å molecular sieves prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in dry and deoxygenated benzene-d_6 and/or tetrahydrofuran-d_8 on Varian XL-300 (299.86 MHz) and Bruker AM-500 (500.13 MHz) spectrometers and were referenced to residual protio impurities in the deuterated solvents. IR spectra were obtained from a Nicolet S10P FT-IR spectrometer. Conductivity measurements were made on ~2 mM solutions of the respective compounds with a YSI model 31A conductance bridge.

TABLE 3. Selected bond angles (°) for $[W_2(O_2CBu^t)_5][BF_4]$

W(2)A–W(1)A–O(3)A	105.9(4)
W(2)A–W(1)A–O(5)A	104.4(3)
W(2)A–W(1)A–O(17)A	89.9(3)
W(2)A–W(1)A–O(24)A	89.2(3)
W(2)A–W(1)A–O(31)A	89.7(3)
W(2)A–W(1)A–C(4)A	109.9(5)
W(2)A–W(1)A–F(41)B	168.96(27)
O(3)A–W(1)A–O(5)A	59.1(5)
O(3)A–W(1)A–O(17)A	145.4(5)
O(3)A–W(1)A–O(24)A	74.0(5)
O(3)A–W(1)A–O(31)A	133.4(5)
O(3)A–W(1)A–C(4)A	30.2(5)
O(3)A–W(1)A–F(41)B	84.6(5)
O(5)A–W(1)A–O(17)A	146.8(5)
O(5)A–W(1)A–O(24)A	133.0(5)
O(5)A–W(1)A–O(31)A	74.6(5)
O(5)A–W(1)A–F(41)B	83.7(4)
O(17)A–W(1)A–O(24)A	75.7(5)
O(17)A–W(1)A–O(31)A	75.7(5)
O(17)A–W(1)A–F(41)B	79.4(4)
O(24)A–W(1)A–O(31)A	151.4(5)
O(24)A–W(1)A–F(41)B	90.6(4)
O(31)A–W(1)A–F(41)B	85.2(4)
W(1)A–W(2)A–O(10)A	105.7(4)
W(1)A–W(2)A–O(12)A	106.3(3)
W(1)A–W(2)A–O(19)A	89.4(3)
W(1)A–W(2)A–O(26)A	89.2(4)
W(1)A–W(2)A–O(33)A	89.9(3)
W(1)A–W(2)A–F(38)A	174.21(27)
O(10)A–W(2)A–O(12)A	60.2(5)
O(10)A–W(2)A–O(19)A	144.3(4)
O(10)A–W(2)A–O(26)A	73.9(5)
O(10)A–W(2)A–O(33)A	134.5(5)
O(10)A–W(2)A–F(38)A	79.4(5)
O(12)A–W(2)A–O(19)A	146.5(5)
O(12)A–W(2)A–O(26)A	133.8(5)
O(12)A–W(2)A–O(33)A	74.5(5)
O(12)A–W(2)A–F(38)A	78.6(4)
O(19)A–W(2)A–O(26)A	74.2(5)
O(19)A–W(2)A–O(33)A	76.1(4)
O(19)A–W(2)A–F(38)A	84.8(4)
O(26)A–W(2)A–O(33)A	150.3(5)
O(26)A–W(2)A–F(38)A	89.5(4)
O(33)A–W(2)A–F(38)A	88.4(4)
W(2)B–W(1)B–O(3)B	108.9(3)
W(2)B–W(1)B–O(5)B	104.8(3)
W(2)B–W(1)B–O(17)B	89.2(3)
W(2)B–W(1)B–O(24)B	88.8(3)
W(2)B–W(1)B–O(31)B	88.0(3)
W(2)B–W(1)B–F(42)A	166.61(23)
O(3)B–W(1)B–O(5)B	146.2(4)
O(3)B–W(1)B–O(17)B	143.8(4)
O(3)B–W(1)B–O(24)B	75.3(5)
O(3)B–W(1)B–O(31)B	132.9(5)
O(3)B–W(1)B–F(42)A	84.3(4)
O(5)B–W(1)B–O(17)B	146.2(4)
O(5)B–W(1)B–O(24)B	135.5(5)
O(5)B–W(1)B–O(31)B	73.1(4)
O(5)B–W(1)B–F(42)A	83.8(4)
O(17)B–W(1)B–O(24)B	74.0(5)
O(17)B–W(1)B–O(31)B	76.9(4)
O(17)B–W(1)B–F(42)A	78.3(4)
O(24)B–W(1)B–O(31)B	150.8(5)
O(24)B–W(1)B–F(42)A	92.2(4)
O(31)B–W(1)B–C(4)B	103.3(5)
O(31)B–W(1)B–F(42)A	84.7(4)
W(1)B–W(2)B–O(10)B	105.0(4)
W(1)B–W(2)B–O(12)B	106.9(3)
W(1)B–W(2)B–O(19)B	88.8(3)
W(1)B–W(2)B–O(26)B	88.3(3)
W(1)B–W(2)B–O(33)B	89.8(3)
W(1)B–W(2)B–F(38)B	172.93(28)
O(10)B–W(2)B–O(12)B	59.3(5)
O(10)B–W(2)B–O(19)B	144.8(5)
O(10)B–W(2)B–O(26)B	74.0(5)
O(10)B–W(2)B–O(33)B	134.7(5)
O(10)B–W(2)B–F(38)B	77.9(5)
O(12)B–W(2)B–O(19)B	147.4(5)
O(12)B–W(2)B–O(26)B	133.0(5)
O(12)B–W(2)B–O(33)B	75.5(5)
O(12)B–W(2)B–F(38)B	80.2(4)
O(19)B–W(2)B–O(26)B	74.2(5)
O(19)B–W(2)B–O(33)B	76.2(5)
O(19)B–W(2)B–F(38)B	85.3(4)
O(26)B–W(2)B–O(33)B	150.4(5)
O(26)B–W(2)B–F(38)B	86.3(4)
O(33)B–W(2)B–F(38)B	92.6(4)
W(1)A–O(3)A–C(4)A	94.0(11)
W(1)A–O(5)A–C(4)A	94.0(12)
W(2)A–O(10)A–C(11)A	90.4(12)
W(2)A–O(12)A–C(11)A	90.3(11)
W(1)A–O(17)A–C(18)A	119.3(11)
W(2)A–O(19)A–C(18)A	118.9(12)
W(1)A–O(24)A–C(25)A	119.3(12)
W(2)A–O(26)A–C(25)A	119.7(12)
W(1)A–O(31)A–C(32)A	118.3(11)
W(2)A–O(33)A–C(32)A	118.5(11)
W(1)B–O(3)B–C(4)B	93.2(10)
W(1)B–O(5)B–C(4)B	90.6(9)
W(2)B–O(10)B–C(11)B	92.7(11)
W(2)B–O(12)B–C(11)B	91.1(12)
W(1)B–O(17)B–C(18)B	120.6(12)
W(2)B–O(19)B–C(18)B	118.8(11)
W(1)B–O(24)B–C(25)B	122.3(13)
W(2)B–O(26)B–C(25)B	121.5(11)
W(1)B–O(31)B–C(32)B	121.4(12)
W(2)B–O(33)B–C(32)B	118.8(11)
W(2)A–F(38)A–B(39)A	138.7(10)
W(1)B–F(42)A–B(39)A	131.0(12)
W(2)B–F(38)B–B(39)B	146.9(18)
W(1)A–F(41)B–B(39)B	136.6(14)
F(38)A–B(39)A–F(40)A	106.7(17)
F(38)A–B(39)A–F(41)A	108.4(16)
F(38)A–B(39)A–F(42)A	105.0(18)
F(38)A–B(39)A–F(41)A	114.5(21)
F(38)A–B(39)A–F(42)A	110.0(16)
F(38)A–B(39)A–F(42)A	111.6(18)
F(38)B–B(39)B–F(40)B	113.8(22)
F(38)B–B(39)B–F(41)B	121.2(26)
F(38)B–B(39)B–F(42)B	102.3(24)
F(40)B–B(39)B–F(41)B	111.0(22)
F(40)B–B(39)B–F(42)B	104.8(23)
F(41)B–B(39)B–F(42)B	101.0(19)

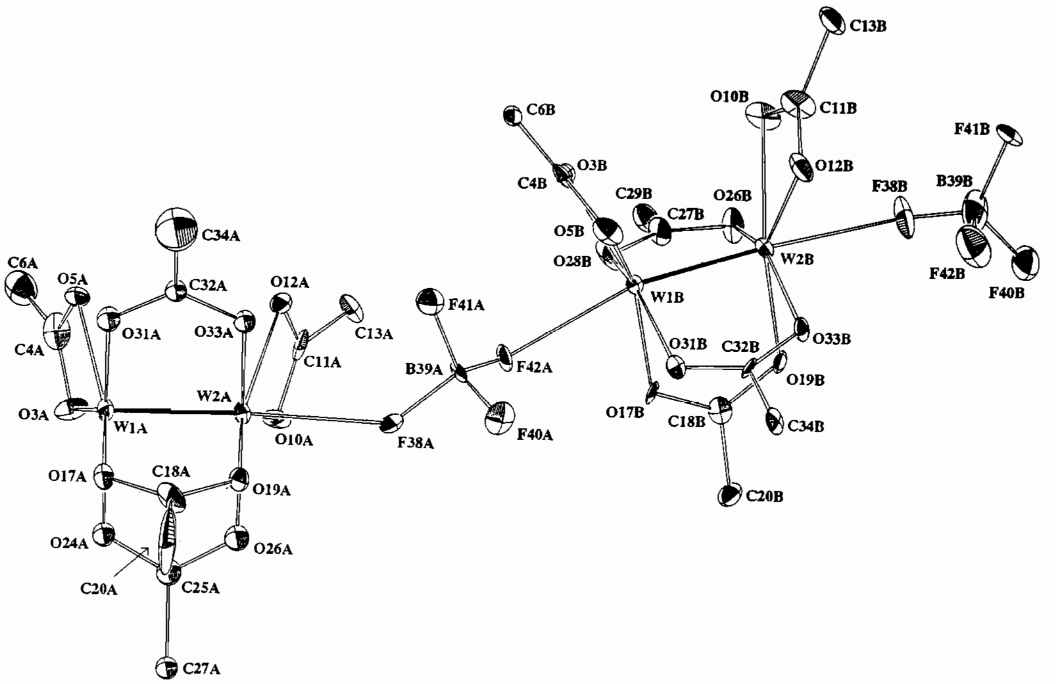


Fig. 2. ORTEP drawing of the core atoms for the asymmetric unit of $[W_2(O_2CBu^t)_5][BF_4]$ showing the atomic numbering scheme used in Table 1 and 2. The ellipsoids are drawn at the 30% probability level.

TABLE 4. Summary of crystal data for $[W_2(O_2CBu^t)_5][BF_4]$

Empirical formula	$W_2C_{25}H_{45}O_{10}BF_4 \cdot xC_7H_8$
Color of crystal	black
Crystal dimensions (mm)	0.12×0.10×0.13
Space group	*C*2/*c*
Cell dimensions	
Temperature (°C)	−173
a (Å)	29.442(11)
b (Å)	36.048(12)
c (Å)	20.799(7)
β (°)	133.30(1)
Z (molecules/cell)	16
Volume (Å^3)	16064.0(12)
Calculated density (gm/cm^3)	1.740
Wavelength (Å)	0.71069
Molecular weight	1052.27
Linear absorption coefficient (cm^{-1})	59.119
Detector to sample distance (cm)	22.5
Sample to source distance (cm)	23.5
Average *ω* scan width at half height	0.25
Scan speed (°/min)	8.0
Scan width (°+dispersion)	1.6
Individual background (s)	3
Aperture size (mm)	3.0×4.0
2*θ* Range (°)	$6<2\theta<45$
Total no. reflections collected	25330
No. unique intensities	10485
No. with *Fσ* 0.0	9585
No. with *Fσ* 2.33(*F*)	6295
R(*F*)	0.0498
$R_w(F)$	0.0479
Goodness of fit for the last cycle	0.920
Maximum *δ*/*σ* for last cycle	0.05

Chemicals

$W_2(O_2CBu^t)_6$ was prepared according to a previously described procedure [6]. Et_3OBF_4 and TMS-OTf were purchased commercially and used without further purification.

Syntheses

$[W_2(O_2CBu^t)_5][O_3SCF_3]$

Me_3Si-OTf (0.564 mmol, 0.109 ml) was added by μl syringe to a Schlenk flask containing a toluene (5 ml) solution of $W_2(O_2CBu^t)_6$ (0.513 mmol, 0.500 g). The reaction mixture was swirled once. Within seconds a yellow precipitate began to appear. After 10 min the product was collected by filtration over a medium porosity frit followed by two 3 ml toluene washings and two 3 ml hexane washings. The filtrate and washings were discarded. The product was dried under vacuum. Isolated yield 0.505 g, 95%.

^{1}H NMR (22 °C, C_6D_6/THF-d_8 (9/1)): 1.44 (s, 18H), 1.37 (s, 9H), 1.15 (s, 18H). $^{13}C\{^1H\}$ NMR (22 °C, C_6D_6/THF-d_8 (9/1)): 208.2, 206.2, 198.5 (s, 2:1:2 for $-O_2CC(CH_3)_3$); 41.0, 40.8, 40.3 (s, 1:2:2 for $-O_2CC(CH_3)_3$); 27.3, 27.2, 26.1 (s, 2:1:2 for $-O_2CC(CH_3)_3$; O_3SCF_3 unresolved.

IR (KBr pellet): 2970m, 2934m, 2874w, 1564w, 1534s, 1507s, 1489s, 1458s, 1429s, 1385m, 1368m, 1308m, 1227s, 1204s, 1177m, 1030s, 926m, 903w, 822w, 801w, 783w, 637s, 579w, 513w, 455m.

Anal. Calc. for $C_{26}H_{45}F_3O_{13}SW_2$: C, 30.54; H, 4.44. Found: C, 30.59; H, 4.03%.

$[W_2(O_2CBu^t)_5][BF_4]$

A solution of Et_3OBF_4 (500 μl, 1.0 M in CH_2Cl_2, 0.500 mmol) was added by syringe to a Schlenk flask containing a CH_2Cl_2 (5 ml) solution of $W_2(O_2CBu^t)_6$ (0.513 mmol, 0.500 g). The resulting yellow solution was stirred for 15 min at room temperature, the solvent evaporated *in vacuo* (0.01 Torr), and the residue dried (50 °C, 0.01 Torr, 1 h). Recrystallization was performed from diethyl ether (15 ml, $35 \rightarrow -34$ °C). Yield 325 mg (66%). Crystals suitable for X-ray diffraction were grown from toluene (60 °C → r.t.). ^1H NMR (22 °C, C_7D_8, 500 MHz): δ 1.45 (s, 18H), 1.37 (s, 9H), 1.19 (s, 18H).

$^{13}C\{^1H\}$ NMR (22 °C, C_7D_8): δ 208.0, 206.6, 199.5 (s, 2:1:2 for $-O_2\mathit{C}C(CH_3)_3$); 41.1, 40.8, 40.3 (s, 1:2:2 for $-O_2C\mathit{C}(CH_3)_3$); 27.4, 27.3, 26.3 (s, 2:1:2 for $-O_2CC(\mathit{C}H_3)_3$.

IR (KBr pellet): 2973m, 2875w, 2825w, 1638m, 1530s, 1502s, 1490s, 1427s, 1385m, 1367m, 1227s, 1130m, 1090br m, 1049m, 926m sh, 870m, 800m, 783m, 629s, 455m.

Anal. Calc. for $C_{25}H_{45}BF_4O_{10}W_2$: C, 31.27; H, 4.72. Found: C, 31.54; H, 4.61%.

Crystallographic studies

General operating procedures and listings of programs have been described previously [7]. A reviewer has pointed out that an alternate 'more reduced' unit cell could have been obtained with dimensions $a = 21.436$, $b = 36.048$, $c = 20.799$ Å and $\beta = 91.62°$. The space group for this choice of cell would be *I2/a*, but no change in metrical parameters for **1** would result.

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