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Key indicators

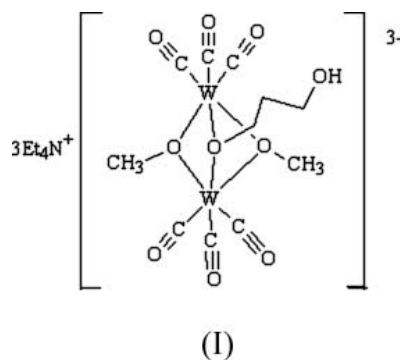
Single-crystal X-ray study
 $T = 110$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
Disorder in main residue
 R factor = 0.023
 wR factor = 0.061
Data-to-parameter ratio = 18.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tris(tetraethylammonium) μ -3-hydroxy-
propanolato-di- μ -methoxy-bis[tricarbonyl-
tungsten(0)]

In the crystal structure of the title compound, $(\text{C}_8\text{H}_{20}\text{N})_3[\text{W}_2(\text{CH}_3\text{O})_2(\text{C}_3\text{H}_7\text{O}_2)(\text{CO})_6]$, obtained from a ligand substitution reaction of $(\text{Et}_4\text{N})_3[\text{W}_2(\text{OMe})_3(\text{CO})_6]$, the trianion sits across a mirror plane such that one $\text{W}(\text{CO})_3$ group is unique and the two methoxy groups and all but the middle C atom of the 3-hydroxypropanolate ligand lie on the mirror plane. One and a half molecules of the tetraethylammonium cation are present to balance the charge in the asymmetric unit. The half molecule is situated with its N atom on a mirror plane and is disordered.

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Comment

Previously, we have presented the results of ligand exchange of the trianion of $(\text{Et}_4\text{N})_3[\text{W}_2(\text{OMe})_3(\text{CO})_6]$, (II), with aryl alcohols (Klausmeyer *et al.*, 2003). Subsequently, we reported the complete exchange reaction with an alcohol containing an sp^3 carbon (Klausmeyer & Adrian, 2004). In each of the previous examples, there was always complete exchange of all of the methoxy groups, regardless of how much of the new alcohol was added. In the present study, we were able to isolate the first known singly substituted derivative, $(\text{Et}_4\text{N})_3[\text{W}_2(\text{CO})_6(\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH})(\text{OCH}_3)_2]$, (I).



The trianion sits across a mirror plane such that one $\text{W}(\text{CO})_3$ group is unique and the two methoxy groups and all but the middle C atom (C7) of the 3-hydroxypropanolate ligand lie on the mirror plane. This forces the bridging ligands to be symmetric with respect to the $\text{W}(\text{CO})_3$ groups.

The environment around the W atom is distorted octahedral, comprised of three CO ligands and three O atoms from the bridging alkoxy ligands. The $\text{W}-\text{O}$ bond lengths are all slightly different from each other. For $\text{W}-\text{O}(\text{methoxy})$, the bond lengths average 2.198 (3) Å, and for $\text{W}-\text{O}(\text{diol})$, the bond length is slightly shorter at 2.1844 (18) Å.

The $\text{W}-\text{O}-\text{W}$ angles are nearly the same, averaging 96.2 (2)°. The bridging O atoms would all be expected to have

near tetrahedral geometry, but only the methoxy ligands approach this geometry, with the sum of their angles being 338.8° for O4 and 343.7° for O5. The angles around O6 of the 3-hydroxypropanolate ligand sum to 360.0°, which means it is planar. The planarity of this O atom is likely due to the pendant OH group of the 3-hydroxypropanolate ligand which bends back around toward the metal centers in order to engage in hydrogen bonding with the bridging O atoms, *viz.* O6 and O5 (Table 2). This would account for the deviation in geometry from the expected values.

Experimental

Complex (I) was obtained by the ligand-exchange reaction of (Et₄N)₃[W₂(OMe)₃(CO)₆] with 1 equivalent of 1,3-propanediol. In a typical experiment, (Et₄N)₃[W₂(OMe)₃(CO)₆] (0.100 g) was dissolved in CH₃CN (20 ml) and 1,3-propanediol (1 equivalent) in CH₃CN (15 ml) was added. This solution was stirred for 1 h at room temperature. The solvent was then removed at reduced pressure to a final volume of about 5 ml and the complex was precipitated from solution by addition of diethyl ether (60 ml), resulting in an oily precipitate. Diffraction quality crystals of (I) were obtained by slow diffusion of diethyl ether into a concentrated acetonitrile solution.

Crystal data

(C₈H₂₀N)₃[W₂(CH₃O)₂(C₃H₇O₂)(CO)₆]
M_r = 1063.66
 Orthorhombic, *Pnma*
a = 16.9476 (6) Å
b = 24.1286 (9) Å
c = 10.2457 (4) Å
V = 4189.7 (3) Å³
Z = 4
D_x = 1.686 Mg m⁻³
 Mo *Kα* radiation
 Cell parameters from 6700 reflections
 θ = 2.5–34.5°
 μ = 5.54 mm⁻¹
T = 110 (2) K
 Block, orange
 0.26 × 0.15 × 0.13 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.297, *T_{max}* = 0.485
 27355 measured reflections
 5181 independent reflections
 4411 reflections with *I* > 2σ(*I*)
R_{int} = 0.024
 θ_{max} = 28.3°
h = -22 → 22
k = -32 → 23
l = -13 → 11

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.023
wR(*F*²) = 0.060
S = 1.02
 5181 reflections
 274 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 7.8991P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.004
 $\Delta\rho_{max}$ = 2.55 e Å⁻³
 $\Delta\rho_{min}$ = -0.77 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

W1—O6	2.1844 (18)	O5—C5	1.411 (5)
W1—O4	2.1952 (19)	O5—W1 ⁱ	2.2010 (19)
W1—O5	2.2010 (19)	O6—C6	1.403 (4)
O4—C4	1.392 (5)	O6—W1 ⁱ	2.1844 (18)
O4—W1 ⁱ	2.1952 (19)		
C4—O4—W1 ⁱ	121.34 (15)	W1—O5—W1 ⁱ	95.77 (11)
W1 ⁱ —O4—W1	96.11 (11)	C6—O6—W1 ⁱ	131.62 (5)
C5—O5—W1	123.97 (13)	W1 ⁱ —O6—W1	96.74 (11)

Symmetry code: (i) *x*, -*y* + $\frac{3}{2}$, *z*.

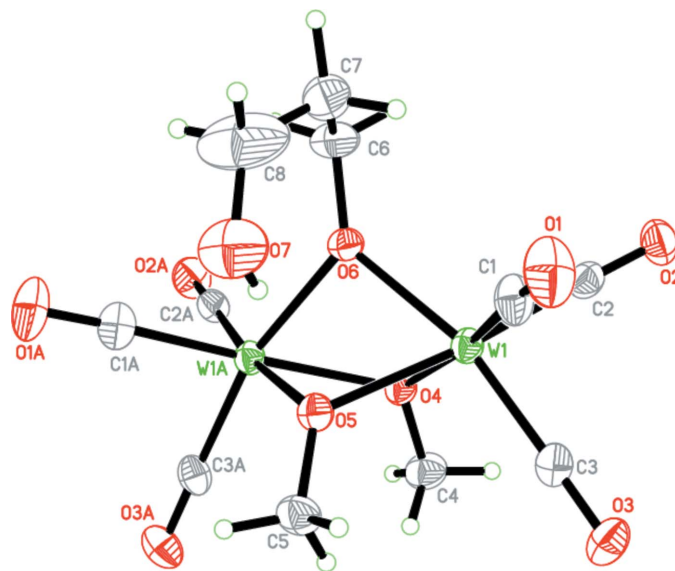


Figure 1

A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. Only one component of the disordered 3-hydroxypropanolate ligand is shown.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O7—H7...O5	0.84	2.02	2.838 (4)	163
O7—H7...O6	0.84	2.48	3.077 (4)	129

One and a half tetraethylammonium cations are present to balance the charge in the asymmetric unit. The half molecule is situated with N2 on a mirror plane and is disordered. Occupancies of the C atoms of the disordered cation were constrained to sum to unity, and one half of the molecule was modeled while the other is symmetry-generated. Refinement yielded a 0.51 (1)/0.49 (1) disorder of the C atoms. H atoms were included in calculated positions (C—H = 0.93 Å); isotropic displacement parameters were fixed [*U*_{iso}(H) = 1.2*U*_{eq}(C)]. The largest electron-density peak is 0.71 Å from atom W1. C7 is 50% occupied, the other 50% is generated by reflection across the mirror plane.

Data collection: *APEX-2* (Bruker, 2003); cell refinement: *APEX-2*; data reduction: *SAINT-Plus* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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References

Bruker (2003). *APEX-2* (Version 1.0-5) and *SAINT-Plus* (Version 6.25). Bruker AXS Inc., Madison, Wisconsin, USA.

Klausmeyer, K. K. & Adrian, R. A. (2004). *Acta Cryst.* **E60**, m1414–m1416.
Klausmeyer, K. K., Adrian, R. A., Khan, M. & Reibenspies, J. H. (2003).
Organometallics, **22**, 657–662.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.