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(3-Chloro-1,2-propanediolato-*O*,*O*′)-bis(2,3-dimethyl-2,3-butanediolato-*O*,*O*′)-tungsten(VI)

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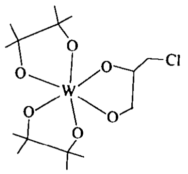
Abstract

The title compound, [W($C_3H_5ClO_2$)($C_6H_{12}O_2$)$_2$], is a mononuclear complex in which the central tungsten(VI) cation is surrounded by six oxygen donors of three chelating diolato ligands. The WO_6 unit adopts a distorted octahedral geometry.

Comment

As part of our study of tungsten(VI)–diolato complexes, the crystal structure of (3-chloro-1,2-propanediolato)-bis(2,3-dimethyl-2,3-butanediolato)tungsten(VI), (I), is reported.



(I)

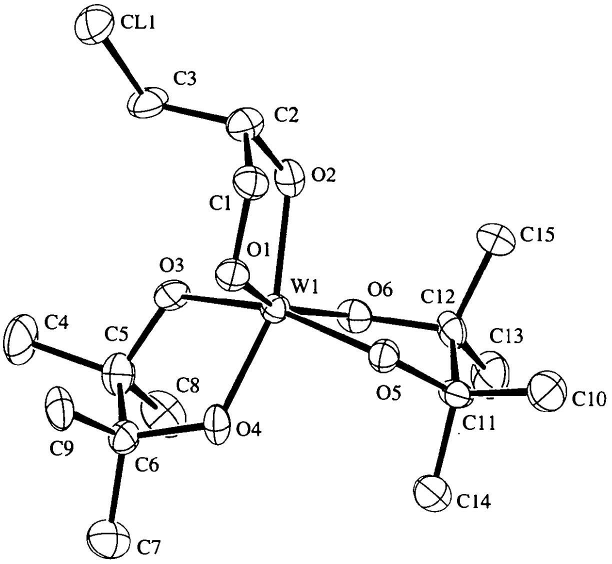


Fig. 1. Structure of the title compound showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

A drawing of the mononuclear complex is shown in Fig. 1. The W atom is surrounded by six O atoms of three chelating diolato ligands in a ($\lambda\lambda\lambda$)*lel*$_3$ conformation. The distorted octahedral WO_6 unit is similar to those found in other tris(diolato)tungsten(VI) complexes, such as [W(eg)$_3$], where H$_2$eg is 1,2-ethanediol (Scherle & Schröder, 1974), and [W(eg)(pin)$_2$] and [W(pin)$_3$], where H$_2$pin is 2,3-dimethyl-2,3-butanediol (Lehtonen & Sillanpää, 1994; Chisholm, Parkin, Streib & Eisenstein, 1994). In the title complex, the W—O distances range from 1.890 (8) to 1.905 (7) Å for the pin ligands, and are 1.930 (7) and 1.930 (8) Å for the 3-chloropropanediolato ligand. This lengthening of the W—O bonds may be due to the electronegative chloro substituent. A similar phenomenon is clearly seen in tungsten complexes with fluoro-substituted alcoholato ligands (Schrock, DePue, Feldman, Schaverien, Dewan & Liu, 1988).

Experimental

[W(eg)(pin)$_2$] (4.0 mmol, 1.91 g) and 3-chloro-1,2-propanediol (4.0 mmol, 0.33 ml) were dissolved in toluene in a distillation apparatus under an N_2 atmosphere. The solution was allowed to boil and H$_2$eg, which was liberated in the reaction, was distilled off as a toluene azeotrope. After evaporation of the solvent under vacuum, the white residue was crystallized from hot hexane (5.0 ml) in 85% yield. Crystals suitable for X-ray analysis were obtained by sublimation at 333 K and 0.5 Torr (1 Torr = 133.322 Pa).

Crystal data

[W($C_3H_5ClO_2$)($C_6H_{12}O_2$)$_2$]
$M_r = 524.68$
Triclinic
$P\bar{1}$
$a = 9.315$ (3) Å
$b = 12.995$ (5) Å
$c = 8.913$ (3) Å
$\alpha = 105.63$ (3)°
$\beta = 104.29$ (3)°
$\gamma = 69.98$ (3)°
$V = 961.9$ (6) Å^3
$Z = 2$
$D_x = 1.812$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 4.7$–$8.8°$
$\mu = 6.168$ mm^{-1}
$T = 293$ (2) K
Bright prism
0.14 × 0.10 × 0.10 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.83$, $T_{\max} = 1.00$
3614 measured reflections
3383 independent reflections
2628 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.038$
$\theta_{\max} = 25.01°$
$h = 0 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 150 reflections intensity decay: 2.8%

Refinement

Refinement on F^2
$R(F) = 0.0466$
$wR(F^2) = 0.1225$
$S = 1.056$
3383 reflections
208 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.117$ e Å^{-3}
$\Delta\rho_{\min} = -1.548$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
W1	0.08068 (5)	0.27828 (4)	0.12315 (6)	0.0332 (2)
Cl1	−0.4299 (4)	0.5992 (3)	0.1666 (5)	0.0744 (11)
O1	−0.0950 (8)	0.2970 (6)	0.2167 (9)	0.040 (2)
O2	0.0194 (8)	0.4375 (7)	0.2056 (9)	0.043 (2)
O3	−0.0015 (9)	0.3083 (6)	−0.0824 (9)	0.040 (2)
O4	0.0651 (8)	0.1372 (7)	0.0035 (8)	0.040 (2)
O5	0.2140 (8)	0.2111 (6)	0.2915 (8)	0.036 (2)
O6	0.2757 (8)	0.2879 (6)	0.1072 (9)	0.040 (2)
C1	−0.1522 (13)	0.4023 (9)	0.3185 (13)	0.042 (3)
C2	−0.1273 (13)	0.4875 (10)	0.2512 (14)	0.045 (3)
C3	−0.2459 (15)	0.5189 (11)	0.1094 (15)	0.053 (3)
C4	−0.1392 (16)	0.2649 (13)	−0.3443 (15)	0.066 (4)
C5	−0.0031 (14)	0.2200 (12)	−0.2192 (14)	0.050 (3)
C6	−0.0268 (12)	0.1275 (10)	−0.1516 (13)	0.039 (3)
C7	0.0334 (17)	0.0085 (11)	−0.2459 (15)	0.057 (3)
C8	0.1499 (16)	0.1863 (13)	−0.2731 (16)	0.063 (4)
C9	−0.1927 (13)	0.1484 (12)	−0.1354 (14)	0.051 (3)
C10	0.4576 (16)	0.1717 (12)	0.4707 (14)	0.058 (3)
C11	0.3803 (13)	0.1772 (9)	0.3013 (13)	0.040 (3)
C12	0.4044 (12)	0.2698 (10)	0.2351 (14)	0.043 (3)
C13	0.5530 (14)	0.2321 (13)	0.1689 (17)	0.064 (4)
C14	0.4257 (15)	0.0604 (11)	0.1991 (16)	0.058 (4)
C15	0.3942 (16)	0.3772 (11)	0.3536 (16)	0.060 (4)

Table 2. *Selected geometric parameters* (Å, °)

W1—O1	1.930 (7)	O1—C1	1.431 (13)
W1—O2	1.930 (8)	O2—C2	1.407 (13)
W1—O4	1.890 (8)	O3—C5	1.433 (15)
W1—O3	1.892 (7)	O4—C6	1.434 (12)
W1—O5	1.897 (7)	O5—C11	1.445 (13)
W1—O6	1.905 (7)	O6—C12	1.438 (13)
Cl1—C3	1.791 (12)		
O1—W1—O2	78.5 (3)	O3—W1—O6	90.0 (3)
O1—W1—O3	106.1 (3)	O4—W1—O5	90.7 (3)
O1—W1—O4	90.0 (3)	O4—W1—O6	106.9 (3)
O1—W1—O5	89.3 (3)	O5—W1—O6	78.3 (3)
O1—W1—O6	158.9 (3)	C1—O1—W1	117.1 (6)
O2—W1—O3	88.4 (3)	C2—O2—W1	118.1 (7)
O2—W1—O4	159.0 (3)	C5—O3—W1	121.6 (7)
O2—W1—O5	106.5 (3)	C6—O4—W1	120.6 (7)
O2—W1—O6	88.7 (3)	C11—O5—W1	120.4 (6)
O3—W1—O4	77.9 (3)	C12—O6—W1	120.2 (6)
O3—W1—O5	160.7 (3)		

Non-H atoms were refined anisotropically. H atoms were included in idealized positions with fixed displacement parameters (1.2 times the displacement parameter of the host atom). The tertiary C—H distances were fixed at 0.98 Å, the secondary C—H distances at 0.97 Å and the methyl group C—H distances at 0.96 Å. The largest maximum and minimum residual electron-density peaks were located about 1 Å from the W atom.

Data collection: *TEXSAN* (Molecular Structure Corporation, 1989). Cell refinement: *TEXSAN*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1247). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Chisholm, M. H., Parkin, I. P., Streib, W. E. & Eisenstein, O. (1994). *Inorg. Chem.* **33**, 812–815.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lehtonen, A. & Sillanpää, R. (1994). *Polyhedron*, **13**, 2519–2524.
Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Reseach Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Scherle, J. & Schröder, F. A. (1974). *Acta Cryst.* B**30**, 2772–2775.
Schrock, R. R., DePue, R. T., Feldman, J., Schaverien, C. J., Dewan, J. C. & Liu, A. H. (1988). *J. Am. Chem. Soc.* **110**, 1423–1435.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

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Diaqua(5,10,15,20-tetraphenylporphinato)iron(III) Perchlorate, $[Fe(C_{44}H_{28}N_4)(H_2O)_2]ClO_4$

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Abstract

The crystal structure of a new crystal form of $[Fe(TPP)(H_2O)_2]ClO_4$ has been determined. The asymmetric unit contains one molecule in a general position and a half molecule with required inversion symmetry. The two independent molecules have almost identical average values for the equatorial Fe—N$_p$ bond lengths [2.029 (4) and 2.028 (6) Å], and the axial Fe—O bond lengths are 2.140 (2) and 2.121 (3) Å for molecule 1 (in a general position) and 2.126 (2) Å for molecule 2 (in a

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