Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Tris(tetraethylammonium) tris(μ-4-pyridine-methanolato)bis[tricarbonyltungsten(0)] acetonitrile trisolvate

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Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.003 Å
R factor = 0.018
wR factor = 0.042
Data-to-parameter ratio = 26.3

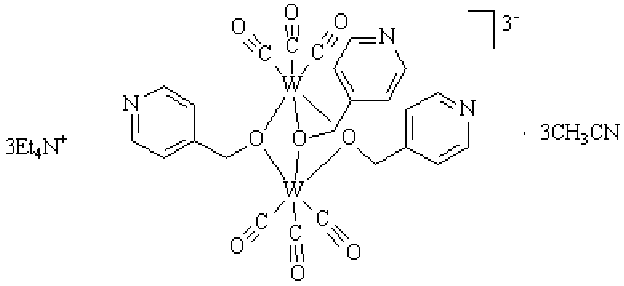
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 18 August 2004
Accepted 26 August 2004
Online 11 September 2004

The title compound, $(C_8H_{20}N)_3[W_2(C_6H_6NO)_3(CO)_6]\cdot 3C_2H_3N$, was obtained from a ligand-substitution reaction of $[Et_4N]_3[W_2(CO)_6(OMe)_3]$. The structure is an example of a triply bridged ditungsten(0) unit that contains an alkyl as well as an aryl portion. The aryl rings are seen to adopt a conformation considerably skew to the W···W axis, as opposed to the aryl alcohol derivatives previously characterized.

Comment

Previously, we have presented the results of ligand exchange of the trianion of compound $[Et_4N]_3[W_2(CO)_6(OMe)_3]$, (II), with aryl alcohols (Klausmeyer *et al.*, 2003). In this study, we present the results of exchange of a substituted carbinol ligand. When studying the aryl alcohol derivatives, it was noticed that each of them adopted a paddle-wheel-like arrangement of the rings about the W···W axis. To further explore the structural features of these complexes, we undertook the synthesis of a derivative containing both an aliphatic portion and an aryl ring to see the effect of having an sp^3 bridging O atom and an aryl ring. This paper reports the synthesis and X-ray analysis of the title compound, (I), which is a 4-pyridinemethanol derivative.



(I)

The environment around each of the W atoms is a distorted octahedron comprising three CO ligands and three O atoms from the bridging carbinol ligands (Fig. 1). The W—O bond lengths are all slightly different from each other (Table 1). The W—O—W bond angles show a dependence on the W—O bond lengths. For atom O7, the W—O—W bond angle is 93.62 (4)°, corresponding to the longest W—O bond length. As the O atom moves further from the W atoms the angle decreases accordingly.

The trend in bond lengths can be rationalized by looking at the sum of angles around the O atom; for atom O7 it is 333.3 (2)°, for O8 it is 354.2 (2)° and for O9 it is 347.8 (2)°. For both atoms O8 and O9, the angles suggest more of an sp^2

hybrid and for O7 the hybrid appears to be more sp^3. Since O8 and O9 appear to have at least some pure *p*-orbital character, this *p* orbital can interact with the W atoms, resulting in an increased bond order and shorter bond length. Atom O7, which is more of an sp^3 hybrid, lacks this *p*-orbital character and therefore cannot participate in further bonding with the W atoms.

The rings of aryl alcohol analogs of (I), such as that of tris-4-cyanophenol, are in a paddle-wheel-like arrangement, with the ring plane being roughly parallel to the W$\cdots$W axis (Klausmeyer *et al.*, 2003). The rings in (I) are considerably twisted with respect to the W$\cdots$W axis. The angles that the planes of the pyridine rings form with a plane defined by the O atom of the ligand and two W atoms are 66.92 (5)° for the N1-containing ring, 71.65 (4)° for the N2-containing ring, and 83.28 (4)° for the N3-containing ring.

Three tetraethylammonium cations are present to balance the charge of the trianion and three molecules of acetonitrile are present in the asymmetric unit. There are some long-range C—H$\cdots$O and C—H$\cdots$N interactions (Table 2). Atom O7 from the bridging ligand has a long-range interaction of 2.40 Å with atom H54*B* of a solvent molecule. Each of the pyridine rings also has long-range interactions with either a solvent molecule or a cation.

Experimental

The title compound, (I), was obtained by the ligand-exchange reaction of $[Et_4N]_3[W_2(CO)_6(OMe)_3]$, (II), with 3 equivalents of 4-pyridylcarbinol. In a typical experiment, (II) (0.100 g) was dissolved in CH_3CN (20 ml) and 3 equivalents of 4-pyridinemethanol in CH_3CN (15 ml) were added. This solution was stirred for 1 h at room temperature. The solvent was then removed at reduced pressure to 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 (yield 0.067 g, 55%). ^{1}H NMR: δ 8.40, 7.67 (*d*, 6H, $OCH_2C_5H_4N$), 5.34 (*s*, 6H, $OCH_2C_5H_4N$), 3.12 (*m*, 24H, Et_4N) 1.13 (*m*, 36H, Et_4N). ^{13}C NMR: δ 233.3 (CO), 159.3 ($OCH_2C_5H_4N$), 150.1, 122.6 76.8 ($OCH_2C_5H_4N$), 52.6 (Et_4N)), 7.5 (Et_4N). IR, ν(CO): 1842 (s), 1705 (*vs*).

Crystal data

$(C_8H_{20}N)_3[W_2(C_6H_6NO)_3(CO)_6]\cdot 3C_2H_3N$
$M_r = 1374.03$
Triclinic, $P\overline{1}$
$a = 12.6005$ (2) Å
$b = 14.0970$ (2) Å
$c = 18.3091$ (3) Å
$\alpha = 83.206$ (1)°
$\beta = 75.675$ (1)°
$\gamma = 70.433$ (1)°
$V = 2966.90$ (8) Å^3
$Z = 2$
$D_x = 1.538$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7145 reflections
$\theta = 2.6$–30.5°
$\mu = 3.93$ mm^{-1}
$T = 110$ (2) K
Prism, orange
0.19 × 0.13 × 0.11 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.506$, $T_{\max} = 0.646$
41376 measured reflections
17950 independent reflections
15425 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 30.6$°
$h = -18 \rightarrow 18$
$k = -20 \rightarrow 12$
$l = -25 \rightarrow 26$

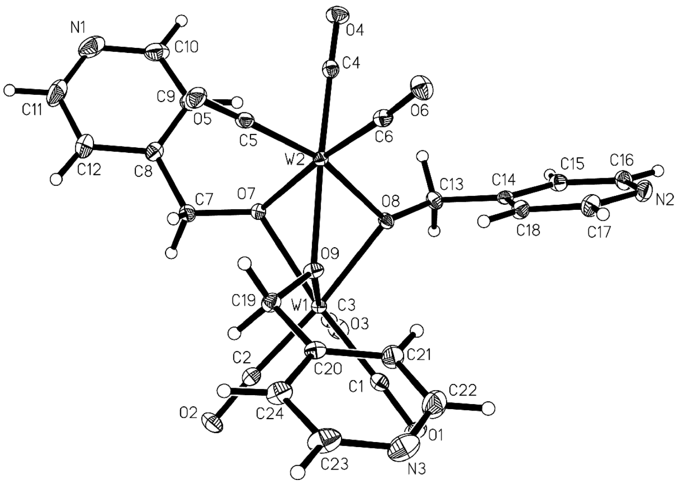


Figure 1
A view of the complex anion in (I), showing displacement ellipsoids at the 50% probability level.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.042$
$S = 1.03$
17950 reflections
682 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0198P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 1.01$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O7—W2	2.2311 (11)	O8—W2	2.1683 (10)
O7—W1	2.2352 (11)	O9—W1	2.1930 (11)
O8—W1	2.1660 (10)	O9—W2	2.1937 (11)
C7—O7—W2	118.79 (9)	W1—O8—W2	97.41 (4)
C7—O7—W1	120.87 (9)	C19—O9—W1	124.85 (10)
W2—O7—W1	93.62 (4)	C19—O9—W2	127.06 (9)
C13—O8—W1	127.33 (9)	W1—O9—W2	95.86 (4)
C13—O8—W2	129.49 (10)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C54—H54$B\cdots$O7$^{\rm i}$	0.98	2.40	3.378 (3)	174
C27—H27$B\cdots$N1$^{\rm ii}$	0.99	2.69	3.578 (3)	149
C27—H27$A\cdots$N3	0.99	2.60	3.464 (2)	146
C43—H43$B\cdots$N1$^{\rm ii}$	0.99	2.54	3.521 (2)	173
C50—H50$A\cdots$N2	0.98	2.62	3.423 (2)	139
C52—H52$A\cdots$N2$^{\rm iii}$	0.98	2.62	3.483 (3)	148
C25—H25$A\cdots$N3	0.99	2.64	3.470 (2)	141

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x - 1, 1 + y, z$; (iii) $1 - x, 1 - y, 1 - z$.

H atoms were included in calculated positions and treated as riding, with C—H distances of 0.95–0.99 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The highest peak is 0.80 Å from W1.

Data collection: *APEX*2 (Bruker, 2003); cell refinement: *APEX*2; data reduction: *SAINT-Plus* (Bruker, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:

SHELXTL (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

The Bruker X8 APEX diffractometer was purchased with funds received from the National Science Foundation Major Research Instrumentation Program (grant CHE-0321214). KKK thanks the Robert A. Welch Foundation for support (AA-1508).

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