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The Final Member of an Isologous Series of Arenetricarbonyl Complexes: $[W(\eta^6\text{-}C_6H_6)(CO)_3]$

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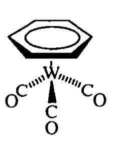
Abstract

Development of a reproducible synthesis of (η^6-benzene)tricarbonyltungsten by photolysis of $[W(CO)_6]$ has allowed the preparation of crystalline samples suitable for diffraction analysis. The material is isomorphous with both $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ and $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$, with the benzene ligand staggered with respect to the $W(CO)_3$ group. The benzene ligand exhibits bond-length alternation similar to that observed for the Cr and Mo complexes [average C—C short bond 1.397 (10) Å and average C—C long bond 1.424 (10) Å], and bond lengths to W are similar to bond lengths to Mo in $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ [W—C_{Ar} bonds range from 2.353 (5) to 2.375 (5) Å].

Comment

Since $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ was first reported (Fischer *et al.*, 1958) it has been seen as the archetypal transition metal monoarene complex, and as such it has been subject to exceptionally intensive structural studies. Early X-ray diffraction determinations of its molecular structure (Allegra & Natta, 1961; Bailey & Dahl, 1965) were followed by low-temperature X-ray and neutron diffraction studies (Rees & Coppens, 1973); these established a previously unobserved bond-length alternation within the coordinated benzene and provided a pioneering *X–N* electron-deformation map for the molecule. Discrepancies between this experimental map and theoretical predictions (Kok & Hall, 1985) were finally resolved by an *X–X* map obtained from a high resolution study at 100 K (Wang *et al.*, 1987).

Given the potential complementarity of the structural characterizations of $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ and $[W(\eta^6\text{-}C_6H_6)(CO)_3]$, (I), and the report in the original paper that both the Mo and W complexes could be prepared in a manner similar to that used for Cr by reaction of the appropriate hexacarbonyl with benzene (Fischer *et al.*, 1958), it is perhaps remarkable that only the Mo complex has been structurally characterized (Bürgi *et al.*, 1992). On closer inspection, however, the absence of diffraction data on the tungsten complex probably reflects the low 2% yield for the direct synthesis of $[W(\eta^6\text{-}C_6H_6)(CO)_3]$ and the weakness of other approaches; the reported yield from the reaction of benzene with $[W(NCCH_3)_3(CO)_3]$ is only 14% (King & Fronzaglia, 1966) and we have not found the promising approach *via* $[W(PMTA)(CO)_3]$ (Zanotti *et al.*, 1991) to be reliable (PMTA is *N,N,N′,N′,N″*-pentamethyldiethylenetriamine).



(I)

Our interest in the reduction chemistry of these systems (Leong & Cooper, 1987) recently led us to develop a photochemical approach to $[W(\eta^6\text{-}C_6H_6)(CO)_3]$ involving photolysis of $[W(CO)_6]$ in benzene in a manner similar to that reported for $[Cr(CO)_6]$ (Deckelmann & Werner, 1970; Kostermans *et al.*, 1989). This allows the synthesis of the material on a 2 g scale in *ca* 40% yield and affords crystalline samples of $[W(\eta^6\text{-}C_6H_6)(CO)_3]$. We now report the crystallographic characterization of the complex in the solid state.

Crystals of $[W(\eta^6\text{-}C_6H_6)(CO)_3]$ are isomorphous with those of the Cr and Mo analogs (Rees & Coppens, 1973; Wang *et al.*, 1987; Bürgi *et al.*, 1992), and belong to space group $P2_1/m$, with the molecule on a crystallographic mirror plane which contains the W atom and one carbonyl group. The benzene ligand is staggered with respect to the $W(CO)_3$ fragment, as is the case for the Cr and Mo complexes. This is to be expected given the isomorphic relationship between the crystals, but the conformation may not reflect any strong electronic preference since theory indicates a small energy difference (1.3 kJ mol^{-1}) between the staggered and eclipsed conformations of $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ (Albright *et al.*,

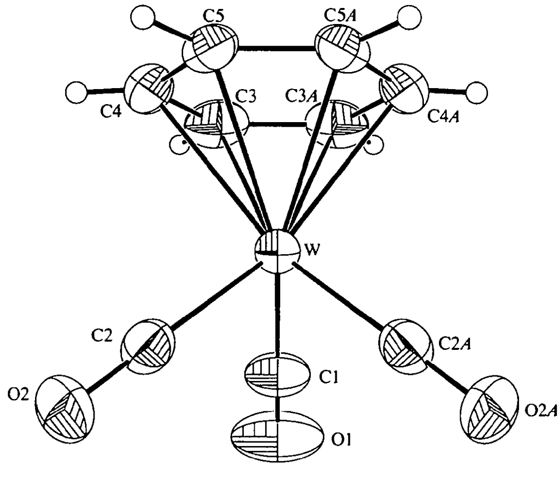


Fig. 1. The molecular structure of $[W(\eta^6\text{-}C_6H_6)(CO)_3]$ with displacement ellipsoids shown at the 50% probability level.

1977): eclipsed conformations have been established in the solid state for related molecules such as $[Cr(\eta^6\text{-}C_6H_5Me)(CO)_3]$ (van Meurs & van Koningsveld, 1977), $[Mo(\eta^6\text{-}C_6H_3Me_3)(CO)_3]$ (Koshland *et al.*, 1977) and $[M(\eta^6\text{-}C_6Et_6)(CO)_3]$ (M = Cr, Mo; Iverson *et al.*, 1981).

The benzene ligand in $[W(\eta^6\text{-}C_6H_6)(CO)_3]$ exhibits bond-length alternation similar to that observed for the Cr and Mo complexes, with an average C—C short bond of 1.397 (10) Å and an average C—C long bond of 1.424 (10) Å. The 0.027 (10) Å difference between these values is statistically marginally significant but is remarkably close to the more accurately determined values of 0.020 (2) and 0.017 (2) Å reported for low-temperature studies of the Cr and Mo complexes, respectively.

The similarity in radii of Mo and W as a consequence of the lanthanide contraction would lead us to expect similar metal–C bond lengths in $[W(\eta^6\text{-}C_6H_6)(CO)_3]$ and the Mo complex, and the average W—CO and W—C(benzene) bond lengths of 1.951 (6) and 2.365 (5) Å are indeed similar to (and may actually be slightly shorter than) the corresponding average bond lengths in $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$ [1.960 (1) and 2.375 (1) Å].

Experimental

Reactions and manipulations were carried out under a nitrogen atmosphere by means of standard Schlenk and cannula techniques. Samples of $[W(\eta^6\text{-}C_6H_6)(CO)_3]$ were prepared by photolysis of *ca* 2 g of $[W(CO)_6]$ in 500 ml of benzene with a 450 W Hg medium-pressure arc lamp. Crystals suitable for crystallographic analysis were obtained by diffusion of pentane into a saturated solution of $[W(\eta^6\text{-}C_6H_6)(CO)_3]$ in toluene at 277 K.

Crystal data

$[W(C_6H_6)(CO)_3]$
M_r = 345.99
Monoclinic
$P2_1/m$
a = 6.1119 (12) Å
b = 11.047 (2) Å
c = 6.7488 (13) Å
β = 101.23 (3)°
V = 446.9 (2) Å^3
Z = 2
D_x = 2.571 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 12.890 mm^{-1}
T = 208 (2) K
Plate
0.39 × 0.34 × 0.14 mm
Yellow

Data collection

Siemens $P3$ diffractometer
ω scans
Absorption correction: analytical
$T_{\min}$ = 0.096, $T_{\max}$ = 0.559
1479 measured reflections
1368 independent reflections
1292 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.037
$\theta_{\max}$ = 30°
$h = 0 \rightarrow 8$
$k = -1 \rightarrow 15$
$l = -9 \rightarrow 9$
3 standard reflections every 197 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.074
S = 1.259
1367 reflections
77 parameters
All H atoms refined, with C—H 0.82 (9)–1.07 (4) Å
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = −0.099

$\Delta\rho_{\max}$ = 1.995 e Å^{-3} (0.73 Å from W)
$\Delta\rho_{\min}$ = −1.665 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0018 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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	$U_{\rm eq}$
W	0.33299 (3)	1/4	0.03069 (3)	0.02402 (11)
O1	0.7062 (12)	1/4	0.4146 (11)	0.072 (3)
O2	0.0733 (10)	0.0592 (4)	0.2339 (8)	0.0543 (12)
C1	0.5642 (12)	1/4	0.2760 (11)	0.040 (2)
C2	0.1713 (9)	0.1302 (5)	0.1579 (8)	0.0352 (10)
C3	0.5933 (9)	0.1860 (6)	−0.1624 (8)	0.0411 (13)
C4	0.3950 (11)	0.1220 (5)	−0.2340 (8)	0.0379 (11)
C5	0.1939 (8)	0.1875 (5)	−0.3071 (7)	0.0329 (10)

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

W—C2	1.948 (5)	O2—C2	1.165 (7)
W—C1	1.956 (7)	C3—C4	1.405 (9)
W—C3	2.353 (5)	C3—C3$^{\rm i}$	1.414 (14)
W—C4	2.366 (5)	C4—C5	1.429 (8)
W—C5	2.375 (5)	C5—C5$^{\rm i}$	1.380 (11)
O1—C1	1.146 (9)		
C2—W—C2$^{\rm i}$	85.6 (3)	C1—W—Bz(centroid)	123.7 (2)
C2—W—C1	88.4 (2)	C2—W—Bz(centroid)	128.7 (2)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Data collection: *P3/PC* (Siemens, 1993). Cell refinement: *P3/PC*. Data reduction: *P3/PC*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1065). Services for accessing these data are described at the back of the journal.

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Polyol–Metal Complexes. 26.† A Three-Dimensional Triply-Connected Alkoxo–Metal Net in a Carbohydrate–Bismuth(III) Complex

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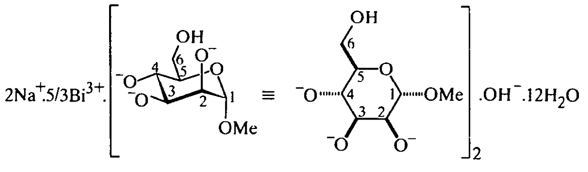
Abstract

A sodium (methyl-α-D-mannopyranosidato)bismuthate(III) hydroxide hydrate of formula $Na_2[Bi_{5/3}$(Me-α-D-Man*p*2,3,4H$_{-3}$)$_2$](OH).12H$_2$O, (I) (where Me-α-D-Man*p*2,3,4H$_{-3}$ is $C_7H_{11}O_6$), forms cubic crystals from alkaline aqueous solution. The carbohydrate-supported alkoxo–bismuth network of (I) resembles the silicon network in $SrSi_2$ [Pringle (1972). *Acta Cryst.* B**28**, 2326–2328], which is a 3,10-net according to Wells [*Structural Inorganic Chemistry* (1984), 5th ed., pp. 110–111, Oxford: Clarendon Press]. The mannoside residues act as trianionic triolate ligands with the O2, O3 and O4 atoms deprotonated.

Comment

Anionic carbohydrate ligands provide multidentate alkoxide patterns and may thus be used as convenient tools for the construction of alkoxo–metal clusters or networks. In this work, we report on the synthesis and structure of an alkoxo–bismuth(III) network, (I), which is supported by trianions derived from methyl-α-D-mannopyranoside by deprotonation of the hydroxyls at the C2, C3 and C4 positions. The trianionic ligands are depicted in the scheme below.



(I)

Crystals of (I) are grown from aqueous solutions of bismuth nitrate, the mannopyranoside and sodium hydroxide in a molar ratio of about 1:3:6. The structure determination revealed the cubic crystal class 23. Accordingly, neither the crystals nor small fragments were birefracting under crossed polarizers.

The carbohydrate-supported alkoxo–metal framework of (I) (Fig. 1) may be classified topologically by taking into account only the Bi atoms at the branching points of the network. As a result, the three-dimensional triply-connected net shown in Fig. 2, which is Wells's (1984) cubic 10,3-net, is obtained. The net resembles the one found in the silicon partial structure of $SrSi_2$ (Pringle, 1972). Accordingly, the space group of (I) is a maximal subgroup of the $SrSi_2$ space group $P4_332$, which itself is a maximal subgroup of the space group of the idealized net $I4_132$ (Wells, 1984).

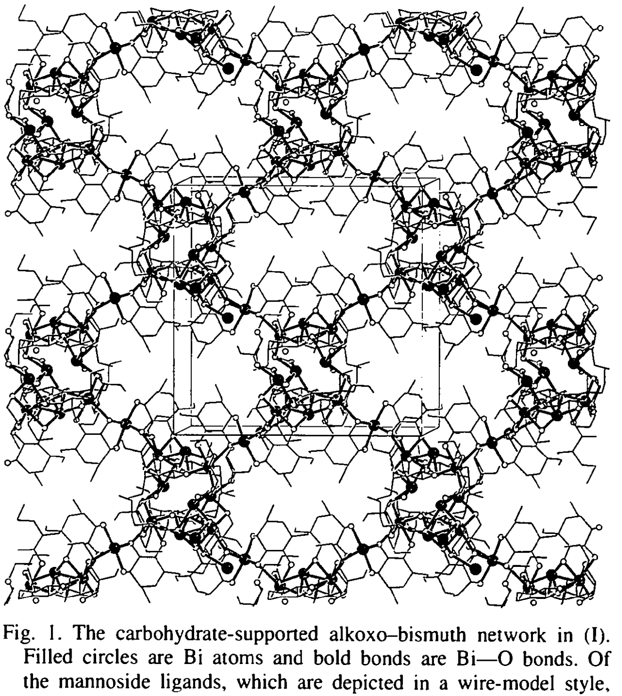


Fig. 1. The carbohydrate-supported alkoxo–bismuth network in (I). Filled circles are Bi atoms and bold bonds are Bi—O bonds. Of the mannoside ligands, which are depicted in a wire-model style, only the three deprotonated and bismuth-bonded hydroxy functions are drawn as open circles. The projection direction is the same as in Fig. 2.

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† Part 25: Burger & Klüfers (1997).