

Acta Cryst. (1999). C55, 881–882

Decacarbonyl(μ -hydrido)(μ -2-hydroxyethoxy)triosmium†

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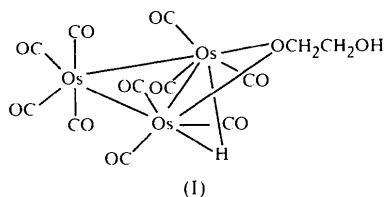
(Received 5 November 1998; accepted 9 February 1999)

Abstract

The title compound, $[\text{Os}_3(\mu\text{-H})(\mu\text{-OCH}_2\text{CH}_2\text{OH})(\text{CO})_{10}]$, is the first triosmium cluster derived from a glycol to be structurally characterized. The triosmium framework shows little structural effect on the glycol moiety.

Comment

The title compound, $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-OCH}_2\text{CH}_2\text{OH})$, (I), was originally obtained *via* a three-step synthesis starting from $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$, in an overall yield of 45% (Banford *et al.*, 1985). We have found that the reaction of the cluster $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-OH})$, obtainable from $\text{Os}_3(\text{CO})_{12}$ (Roberto *et al.*, 1997), with ethylene glycol gives (I) directly in an overall yield of 60% from $\text{Os}_3(\text{CO})_{12}$.



Compound (I) crystallizes in the triclinic system, with two crystallographically distinct molecules in the asymmetric unit (Fig. 1). The two molecules have very similar bond parameters, the most significant difference being the Os—Os bond lengths of the alkoxy-bridged edge, with a difference of 20σ . Although the Os—C and C—O bond parameters may appear to vary over a fairly wide range, as has been argued elsewhere (Leong *et al.* 1996), this may be largely the result of a lack of precision in defining the light-atom positions in a heavy-atom structure. This observation is demonstrated here in that variations in the sums of Os—C and C—O distances for the two molecules are small (3.03–3.09 and 3.01–3.08 Å, respectively; a range of $<3\sigma$ from their mean values).

† Systematic name: decacarbonyl-1 κ^3 C₂ κ^3 C₃ κ^4 C- μ -hydrido-1:2 κ^2 H- μ -(2-hydroxyethanolato)-1:2 κ^2 O'-triangulo-triosmium(3 Os—Os).

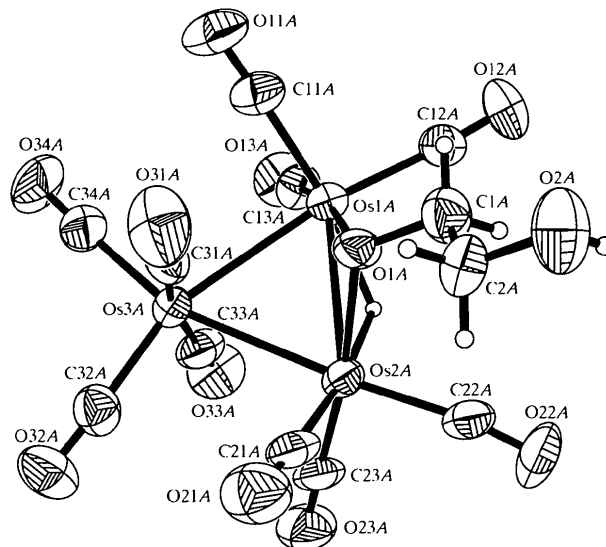


Fig. 1. ORTEP (Johnson, 1976) diagram (50% probability displacement ellipsoids), showing the atomic numbering scheme for molecule A of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-OCH}_2\text{CH}_2\text{OH})$.

Of greater interest is the negligible difference in the C—O bonds for the glycol moieties, which suggests that the triosmium framework has little structural effect on the organic fragment. The chemistry of this cluster is currently being investigated.

Experimental

A toluene solution of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-OH})$ was refluxed for 5 h under a nitrogen atmosphere with ethylene glycol. Rotary evaporation of the solution, followed by column chromatographic separation of the residue on silica, gave (I) as a bright yellow solid.

Crystal data

$[\text{Os}_3\text{H}(\text{C}_2\text{H}_5\text{O}_2)(\text{CO})_{10}]$
 $M_r = 912.77$
 Triclinic
 $P\bar{1}$
 $a = 9.0204(1) \text{ \AA}$
 $b = 13.9921(2) \text{ \AA}$
 $c = 15.8980(1) \text{ \AA}$
 $\alpha = 106.022(1)^\circ$
 $\beta = 90.673(1)^\circ$
 $\gamma = 98.479(1)^\circ$
 $V = 1904.63(4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 3.183 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 7915 reflections
 $\theta = 1.73\text{--}29.43^\circ$
 $\mu = 20.021 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block
 $0.227 \times 0.163 \times 0.138 \text{ mm}$
 Yellow

Data collection

Siemens SMART/CCD diffractometer

14 599 measured reflections
 9112 independent reflections

ω scans
Absorption correction:
empirical via ψ scan
(SADABS; Sheldrick,
1996)
 $T_{\min} = 0.012$, $T_{\max} = 0.047$

6628 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 29.43^\circ$
 $h = -12 \rightarrow 9$
 $k = -18 \rightarrow 18$
 $l = -16 \rightarrow 21$

Refinement

Refinement on F^2
 $R(F) = 0.051$
 $wR(F^2) = 0.141$
 $S = 1.006$
9112 reflections
495 parameters
H atoms treated by a
mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.010$
 $\Delta\rho_{\max} = 3.63 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -2.73 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å , $^\circ$)

Os1A—O1A	2.100 (9)	Os2B—O1B	2.112 (9)
Os1A—Os2A	2.7897 (7)	Os2B—Os3B	2.8104 (7)
Os1A—Os3A	2.8195 (7)	O1A—C1A	1.462 (17)
Os2A—O1A	2.109 (9)	O2A—C2A	1.418 (18)
Os2A—Os3A	2.8098 (7)	O1B—C1B	1.413 (16)
Os1B—O1B	2.108 (9)	O2B—C2B	1.41 (2)
Os1B—Os2B	2.8040 (7)	C1A—C2A	1.51 (2)
Os1B—Os3B	2.8282 (7)	C1B—C2B	1.50 (2)
Os2A—Os1A—Os3A	60.120 (18)	Os2B—Os1B—Os3B	59.866 (18)
Os1A—Os2A—Os3A	60.466 (18)	Os1B—Os2B—Os3B	60.495 (18)
Os2A—Os3A—Os1A	59.415 (18)	Os2B—Os3B—Os1B	59.640 (18)

The H atoms on the glycol fragment were placed in calculated idealized positions and allowed to ride on their attached C or O atoms. Of the two metal hydrides, one was located by a low angle ($2\theta < 30^\circ$) difference map and allowed to refine with restraints on the Os—H bond lengths to be equal, while the other was placed in a calculated position using the XHYDEX program (Orpen, 1997) and refined with the Os—H distance fixed at 1.84 (1) Å. The largest residual peak in the final difference map was $3.63 \text{ e } \text{Å}^{-3}$, at a distance of 0.95 Å from Os1A.

Data collection: SMART (Bruker, 1997). Cell refinement: SAINT (Bruker, 1997). Data reduction: SHELXTL (Bruker, 1997). Program(s) used to solve structure: SHELXTL. Program(s) used to refine structure: SHELXTL. Molecular graphics: ORTEPII (Johnson, 1976) in SHELXTL. Software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1235). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C55, 882–886

A monomeric and a dimeric copper(II) trigonelline adduct with chloride, and a dimeric copper(II) 1-methyl-2-pyrrole-carboxylate adduct with 3-methylpyridine

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(Received 1 October 1998; accepted 29 January 1999)

Abstract

In the crystal structure of *trans*-dichlorobis(trigonelline-*O,O'*)copper(II) (trigonelline is *N*-methylpyridinium-3-carboxylate), [CuCl₂(C₇H₇NO₂)₂], (I), the monomeric Cu^{II} complex has a distorted octahedral coordination. In the crystal structure of tetrakis(μ -trigonelline-*O:O'*)-bis[chlorocopper(II)] dichloride octahydrate, [Cu₂Cl₂(C₇H₇NO₂)₄]Cl₂·8H₂O, (II), the dinuclear Cu^{II} complex has a slightly elongated cage structure, with a Cu···Cu distance of 2.770 (1) Å. In the crystal structure of tetrakis[μ -(1-methylpyrrole-2-carboxylato)-*O:O'*]-bis[(3-methylpyridine-*N*)copper(II)], [Cu₂(C₆H₆NO₂)₄(C₆H₇N)₂], (III), the dinuclear Cu^{II} complex has a cage structure, with a Cu···Cu distance of 2.671 (1) Å. The magnetic $-2J$ value for (III) is 343 cm^{-1} ($H = -2J S_1 \cdot S_2$).

Comment

The title complexes, *trans*-dichlorobis(trigonelline)copper(II), (I), tetrakis(μ -trigonelline)bis[chlorocopper(II)] dichloride octahydrate, (II), and tetrakis[μ -(1-methylpyrrole-2-carboxylato)]bis[(3-methylpyridine)copper(II)], (III), all have a center of symmetry. The rotation angles (φ_{rot}) of the *N*-methylpyridyl ring relative to the COO⁻ moiety in the trigonelline ligands are 7.0 (3)^o in (I), and 14.2 (3) and 20.0 (3)^o in (II). The corresponding φ_{rot} values in other reported dimeric copper(II) benzoates range from 5.3 (4) to 19.5 (8)^o (Kawata *et al.*, 1992). The corresponding φ_{rot} angles of the *N*-methylpyrrole moieties of (III) are 1.7 (3) and 6.0 (3)^o.