# Structural Studies of Polynuclear Osmium Carbonyl Hydrides. 5.[1-4] Crystal Structure and Molecular Geometry of Di-$\mu$-hydrido-decacarbonyltriosmium, $(\mu\text{-H})_2Os_3(CO)_{10}$

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The complex $(\mu\text{-H})_2Os_3(CO)_{10}$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 8.603$ (2) Å, $b = 9.128$ (1) Å, $c = 11.893$ (2) Å, $\alpha = 91.46$ (1)°, $\beta = 98.96$ (1)°, $\gamma = 117.35$ (1)°, $V = 814.4$ (2) Å³, and $\rho(\text{calcd}) = 3.48$ g cm⁻³ for mol wt = 852.7 and $Z = 2$. A full sphere of diffraction data ($3° \leq 2\theta \leq 45°$; Mo K$\alpha$) was collected with a Syntex $P2_1$ automated four-circle diffractometer, using graphite-monochromatized radiation. The structure was solved via a combination of Patterson, Fourier, and least-squares refinement techniques, the final discrepancy indices being $R_F = 3.5\%$ and $R_{wF} = 3.6\%$ for the 2049 symmetry-independent reflections with $I > \sigma(I)$. The molecule has approximate $C_{2v}$ symmetry and consists of an isosceles triangular arrangement of osmium atoms in which Os(1) is linked to four terminal carbonyl ligands, while Os(2) and Os(3) are each linked to three such groups. The Os(2)–Os(3) vector is bridged by two $\mu$-bridging hydride ligands (which were not accurately located by the x-ray diffraction study). The nonbridged osmium–osmium bonds, Os(1)–Os(2) and Os(1)–Os(3), have bond lengths of 2.817 (1) and 2.812 (1) Å, respectively. The bis($\mu$-hydrido)-bridged osmium–osmium distance, Os(2)–Os(3), is reduced to a value of 2.681 (1) Å.

## Introduction

We are currently interested in the structural characterization of molecules with hydrido-bridged osmium–osmium bonds (and related species), and we have already completed x-ray diffraction studies of $Os_3(CO)_{12}$, $(\mu\text{-H})(H)Os_3(CO)_{11}$,[1] $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH}_2PMe_2Ph)$,[2] $(\mu\text{-H})(H)Os_3(CO)_{10}\text{-}(PPh_3)$,[3] $(H)Os_3Re(CO)_{15}$,[4] $(\mu\text{-H})Os_3(CO)_8[C(O-)C\text{-}(CHMe-)CHCHC(Et)]$,[5] and $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$.[6] There is, now, a good body of data concerning dimensions within both direct Os–Os bonds and monohydrido-bridged osmium–osmium bonds, i.e., the Os($\mu$-H)Os system. However, there is little information on dihydrido-bridged osmium–osmium bonds, i.e., the Os($\mu$-H)$_2$Os system. There have been brief allusions in the literature to the molecular geometry of $(\mu\text{-H})_2Os_3\text{-}(CO)_{10}$,[7,8] but no details have appeared. We now report the results of an accurate three-dimensional x-ray structural analysis of $(\mu\text{-H})_2Os_3(CO)_{10}$.

## Experimental Section

**(A) Collection of Diffraction Data.** A crystalline sample of $(\mu\text{-H})_2Os_3(CO)_{10}$ was kindly donated by Professor J. R. Shapley of the University of Illinois. The crystal selected for the structural analysis was a parallelepiped of approximate dimensions $0.10 \times 0.10 \times 0.10$ mm. It was mounted on the tip of a thin glass fiber and was fixed, with bees wax, into a eucentric goniometer.

A preliminary set of precession and cone-axis photographs revealed no symmetry save for the Friedel condition. The crystal was therefore assumed to be triclinic.

The crystal was transferred to a Syntex $P2_1$ four-circle diffractometer and was accurately centered. Determination of preliminary unit cell parameters, orientation matrix, and crystal quality (via a series of $\theta$–$2\theta$ and $\omega$ scans of reflections on principal axes) were carried out as described previously.[9]

All data in the shell defined by $25 < 2\theta < 30°$ were next collected at the maximum scan rate (29.3°/min). From these data, 12 strong Friedel pairs of reflections, well dispersed in reciprocal space, were selected for determination of accurate cell parameters via a least-squares procedure. Collection of intensity data was then carried out as described previously;[9] details are given in Table I.

Data were reduced to net intensities ($I$) and their esd's ($\sigma(I)$) as shown in eq 1 and 2; here CT is the count associated with the $\theta$–$2\theta$

$$I = \text{CT} - 2(B1 + B2) \tag{1}$$

$$\sigma(I) = [\text{CT} + 4(B1 + B2)]^{1/2} \tag{2}$$

scan, while $B1$ and $B2$ are the initial and final backgrounds. Following application of an isotropic linear decay correction, data were corrected for absorption by an empirical method. Several close-to-axial reflections, ($\chi_0 = 75$–90°) distributed over the $2\theta$ range used in data collection and each of fairly strong intensity (but not sufficiently strong to be affected by extinction), were measured at 36 positions around

**Table I.** Details of Data Collection for $(\mu_2\text{-H})_2Os_3(CO)_{10}$

| (A) Crystal Parameters at 23 °C | |
| --- | --- |
| Crystal system: triclinic | $\gamma = 117.350$ (8)° |
| Space group: $P\bar{1}[C_i^1$; No. 2] | $V = 814.4$ (2) Å³ |
| $a = 8.6025$ (17) Å | $Z = 2$ |
| $b = 9.1281$ (9) Å | |
| $c = 11.8934$ (15) Å | Mol wt = 852.7 |
| $\alpha = 91.456$ (9)° | $\rho(\text{calcd}) = 3.48$ g cm⁻³ |
| $\beta = 98.964$ (8)° | $\mu(\text{calcd}) = 247.8$ cm⁻¹ for Mo K$\alpha$ |

**(B) Measurement of Intensity Data**

Radiation: Mo K$\alpha$ ($\bar{\lambda} = 0.71073$ Å)
Monochromator: highly oriented graphite
Reflections measd: complete sphere from $2\theta = 3°$ to $2\theta = 45°$
Scan type: coupled $\theta$(crystal)–$2\theta$(counter)
Scan speed: 2.0°/min in $2\theta$
Scan range: symmetrical, over $[1.5 + \Delta(\alpha_1 - \alpha_2)]°$
Background measurement: stationary crystal, stationary counter; measured at beginning ($B1$) and end ($B2$) of the scan, each for one-quarter the time taken for the scan
Reflections collected: 4288 total, reduced to a unique set of 2144
Std reflections: the $22\bar{6}$, 140, and 411 reflections were measured after every 100 reflections. Their intensities decreased steadily by 5.2% (av) over the course of data collection

the diffraction vector (from $\psi = 0°$ to $\psi = 350°$, at intervals of 10°). Each reflection was used to define a normalized absorption curve vs. $\phi$, corrected for $\omega$ and $\chi$. The two curves bracketing the $2\theta$ value of the reflection under consideration were interpolated both in $2\theta$ and in $\phi$ to derive the absorption correction. Reflections used for the absorption curves were as follows: $11\bar{2}$ ($2\theta = 10.35°$, (maximum intensity)/(minimum intensity) = 1.57); $21\bar{2}$ (14.40°, 1.41); $32\bar{4}$ (24.62°, 1.40); $42\bar{4}$ (29.03°, 1.39); $52\bar{5}$ (34.85°, 1.35); $63\bar{5}$ (43.17°, 1.41). All curves were mutually consistent, with similar profiles and with maxima and minima observed at common values. The total of 4288 data was next averaged according to $\bar{1}$ symmetry, yielding 2144 unique reflections.

The agreement factor for averaging, $R(I)$, defined in eq 3, was 2.5%.

$$R(I) = [(\Sigma ||I| - |I_{av}||)/\Sigma |I|] \times 100 \; (\%) \tag{3}$$

The esd for an averaged intensity was taken as the larger of (i) that calculated from counting statistics and (ii) that calculated from the scatter from the mean.

Intensities were finally reduced to (unscaled) observed structure factor amplitudes by taking the square root of the intensity after correction for Lorentz and polarization factors. Esd's of $|F_o|$ values were calculated by finite differences, as shown in eq 4. If $F^2$ was

$$\sigma(|F_o|) = [|F^2| + \sigma(|F^2|)]^{1/2} - [|F^2|]^{1/2} \tag{4}$$

less than zero, $F$ was set equal to zero following calculation of $\sigma(|F_o|)$.

**(B) Solution and Refinement of the Structure.** All calculations were performed using an in-house Syntex XTL structure determination

system, consisting of the following: a Data General NOVA 1200 computer (24K of 16-bit word memory), a Diablo disk unit (1.2 million 16-bit words), and a locally modified version of the Syntex XTL conversational crystallographic program package.[10]

The analytical scattering factors compiled by Cromer and Waber[11a] were used throughout the analysis; both the real and imaginary components of anomalous dispersion[11b] were included for all nonhydrogen atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the final weights used are those shown in eq 5.

$$w = [\sigma^2(|F_o|) + (0.015|F_o|)^2]^{-1} \tag{5}$$

Discrepancy indices used below are defined in eq 6 and 7. The

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|}\right] \times 100 \ (\%) \tag{6}$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100 \ (\%) \tag{7}$$

"goodness-of-fit" (GOF) is defined in eq 8, where NO is the number

$$\text{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{(\text{NO} - \text{NV})}\right]^{1/2} \tag{8}$$

of observations and NV is the number of parameters varied.

The positions of the heavy atoms were determined from a three-dimensional Patterson synthesis, which also suggested that the true space group was the centrosymmetric $P\bar{1}$, rather than the noncentrosymmetric space group $P1$. Least-squares refinement of the positional and isotropic thermal parameters of the three osmium atoms converged with $R_F = 11.8\%$. A difference-Fourier synthesis now revealed the positions of all ten carbonyl ligands. Continued refinement of positional and isotropic thermal parameters for all 23 nonhydrogen atoms (93 parameters in all) converged with $R_F = 6.3\%$. A further three cycles of full-matrix least-squares refinement of positional and *anisotropic* thermal parameters for all nonhydrogen atoms (208 parameters, including the scale factor) led to convergence with $R_F = 3.7\%$, $R_{wF} = 3.8\%$, and GOF = 1.54. A careful survey of all data now suggested that (i) the 001 reflection was unreliable (its low-angle background was anomalously low, suggesting "clipping" by the back stop), and (ii) the data were affected by secondary extinction ($|F_o| < |F_c|$ for intense, low-angle data). The 001 reflection was removed from the data file and all data were corrected for secondary extinction by applying an empirical correction of the form shown in eq 9, where $g$ was found, graphically, to have a value of

$$|F_o|_{cor} = |F_o|_{uncor}(1.0 + gI_o) \tag{9}$$

$3.6 \times 10^{-7}$.

We now calculated a series of difference-Fourier maps (a) using all data, (b) using data with $(\sin\theta)/\lambda < 0.35$, and (c) using data with $(\sin\theta)/\lambda < 0.30$; the intention was to determine the positions of the two hydride ligands.[12-14] The largest peak on all maps was at ca. (0.49, 0.37, 0.24) and was approximately 1.4 Å from Os(2) and 1.7 Å from Os(3), in the position expected for a $\mu_2$-bridging hydride ligand; this feature had a peak height of 1.95 e Å$^{-3}$ on map $a$ and 1.23 e Å$^{-3}$ on map $c$. The second largest feature on all maps was at ca. (0.35, 0.38, 0.29) and had a peak height of 1.78 e Å$^{-3}$ on map $a$, and 0.93 e Å$^{-3}$ on map $c$. This feature is approximately 1.9 Å from Os(1), 1.5 Å from Os(2), and 1.6 Å from Os(3). It is *not* in the region where we would expect to observe the second $\mu$-hydride ligand. No other peaks were observed in positions attributable to hydride ligands. Attempts to include these observed features in the model as hydride ligands were not successful—the positions oscillated upon refinement and positional esd's were about 0.15 Å. We conclude, therefore, that we were unable to locate unambiguously the hydride ligands.

Refinement of all positional and anisotropic thermal parameters was now continued. Convergence $[(\Delta/\sigma)_{max} < 0.005]$ was reached after three cycles of full-matrix least-squares refinement; final discrepancy indices were $R_F = 3.5\%$, $R_{wF} = 3.6\%$, and GOF = 1.44 for those 2049 data for which $I > \sigma(I)$; for all 2143 independent reflections, $R_F = 3.7\%$ and $R_{wF} = 3.6\%$. The "overdetermination ratio" (i.e., number of observations included in the refinement:number of variables refined) was 9.85:1 (NO = 2049; NV = 208). The function

**Table II.** Final Positional Parameters, with Esd's[a] for $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$

| Atom | x | y | z |
|---|---|---|---|
| Os(1) | 0.11062 (6) | 0.31403 (6) | 0.21172 (4) |
| Os(2) | 0.38438 (6) | 0.23544 (6) | 0.29713 (4) |
| Os(3) | 0.47422 (6) | 0.54722 (6) | 0.25102 (4) |
| C(11) | 0.0146 (20) | 0.4555 (17) | 0.1547 (12) |
| C(12) | −0.1079 (19) | 0.1177 (18) | 0.2051 (11) |
| C(13) | 0.1289 (16) | 0.3810 (16) | 0.3722 (12) |
| C(14) | 0.1473 (15) | 0.2516 (16) | 0.0632 (12) |
| C(21) | 0.6012 (20) | 0.2300 (17) | 0.3572 (12) |
| C(22) | 0.2559 (16) | 0.1112 (17) | 0.4094 (12) |
| C(23) | 0.2899 (21) | 0.0371 (19) | 0.1964 (13) |
| C(31) | 0.7317 (20) | 0.6694 (18) | 0.2849 (12) |
| C(32) | 0.4403 (17) | 0.7154 (17) | 0.3213 (12) |
| C(33) | 0.4467 (18) | 0.6334 (18) | 0.1077 (13) |
| O(11) | −0.0428 (16) | 0.5405 (15) | 0.1208 (10) |
| O(12) | −0.2447 (15) | 0.0037 (13) | 0.1998 (11) |
| O(13) | 0.1431 (13) | 0.4167 (14) | 0.4654 (09) |
| O(14) | 0.1688 (14) | 0.2146 (15) | −0.0211 (09) |
| O(21) | 0.7299 (14) | 0.2250 (15) | 0.3955 (10) |
| O(22) | 0.1829 (15) | 0.0427 (15) | 0.4770 (10) |
| O(23) | 0.2439 (18) | −0.0751 (16) | 0.1305 (11) |
| O(31) | 0.8815 (13) | 0.7433 (14) | 0.3025 (09) |
| O(32) | 0.4146 (15) | 0.8106 (14) | 0.3656 (09) |
| O(33) | 0.4308 (15) | 0.6816 (15) | 0.0240 (09) |
| H(1)[b] | 0.499 | 0.371 | 0.196 |
| H(2)[b] | 0.485 | 0.443 | 0.384 |

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. They were calculated from the inverse of the final least-squares matrix. [b] Hydrogens are in calculated positions (see text).

**Table III.** Anisotropic Thermal Parameters[a] for $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Os(1) | 2.48 (2) | 2.35 (2) | 2.59 (2) | 0.92 (2) | 0.18 (2) | −0.07 (2) |
| Os(2) | 2.74 (2) | 2.48 (2) | 3.08 (3) | 1.12 (2) | 0.11 (2) | −0.05 (2) |
| Os(3) | 2.67 (2) | 2.31 (2) | 2.67 (2) | 0.61 (2) | 0.39 (2) | −0.03 (2) |
| C(11) | 5.1 (8) | 2.6 (6) | 4.4 (7) | 1.6 (6) | 0.3 (6) | −0.4 (5) |
| C(12) | 3.7 (7) | 3.4 (7) | 3.4 (7) | 1.3 (6) | 1.0 (5) | −0.6 (5) |
| C(13) | 3.0 (6) | 3.6 (7) | 3.0 (7) | 1.4 (5) | 0.6 (5) | −0.5 (5) |
| C(14) | 2.5 (5) | 3.3 (6) | 3.1 (7) | 1.2 (5) | −0.4 (5) | −0.4 (5) |
| C(21) | 4.5 (7) | 3.1 (7) | 3.8 (7) | 1.4 (6) | 0.4 (6) | −0.5 (5) |
| C(22) | 2.3 (5) | 3.6 (7) | 4.1 (7) | 1.1 (5) | 0.4 (5) | 0.8 (5) |
| C(23) | 5.9 (8) | 3.2 (7) | 3.7 (7) | 1.4 (6) | −0.2 (6) | −0.5 (6) |
| C(31) | 3.4 (7) | 3.5 (7) | 3.3 (7) | 0.1 (6) | 0.7 (5) | 0.6 (5) |
| C(32) | 3.3 (6) | 2.3 (6) | 4.4 (7) | 1.2 (5) | 0.2 (5) | 0.4 (5) |
| C(33) | 3.3 (6) | 3.9 (7) | 4.1 (8) | 1.1 (6) | 1.0 (5) | −0.1 (6) |
| O(11) | 7.3 (7) | 5.5 (6) | 6.8 (7) | 4.6 (6) | −0.3 (5) | 0.2 (5) |
| O(12) | 5.6 (6) | 2.9 (5) | 9.2 (8) | −0.2 (5) | 2.9 (6) | −0.3 (5) |
| O(13) | 4.8 (5) | 6.6 (6) | 3.2 (5) | 2.3 (5) | 1.1 (4) | −0.8 (4) |
| O(14) | 6.2 (6) | 7.3 (7) | 2.8 (5) | 3.8 (6) | 0.5 (4) | −0.7 (4) |
| O(21) | 4.0 (5) | 7.5 (7) | 6.9 (7) | 3.6 (5) | −0.1 (5) | −0.1 (5) |
| O(22) | 5.1 (5) | 6.0 (7) | 5.9 (6) | 1.7 (5) | 1.8 (5) | 2.2 (5) |
| O(23) | 9.2 (8) | 4.6 (6) | 7.1 (7) | 3.3 (6) | −1.2 (6) | −2.3 (6) |
| O(31) | 3.2 (5) | 5.4 (6) | 4.9 (6) | 0.3 (4) | 0.5 (4) | −0.7 (4) |
| O(32) | 7.3 (6) | 4.5 (6) | 5.6 (6) | 4.0 (5) | 0.7 (5) | −0.6 (4) |
| O(33) | 6.5 (6) | 6.6 (7) | 3.3 (5) | 1.6 (5) | 1.0 (4) | 1.9 (5) |

[a] These anisotropic thermal parameters are analogous to the usual form of the thermal parameter and have units of A². They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

$\sum w(|F_o| - |F_c|)^2$ showed no significant systematic variations as a function of $|F_o|$, $(\sin\theta)/\lambda$, identity or parity of Miller indices, or sequence number. The weighting scheme was thus deemed to be satisfactory.

Final positional and thermal parameters are collected in Tables II and III. Note that calculated values are given for the positions of H(1) and H(2). These values were determined in the following manner. Firstly, we determined the points of intersection of the pairs of vectors (a) C(22) → Os(2) and C(32) → Os(3) and (b) C(23) → Os(2) and C(33) → Os(3). (This led to individual osmium⋯ "hydrogen" distances of approximately 2.05 Å, which we believed
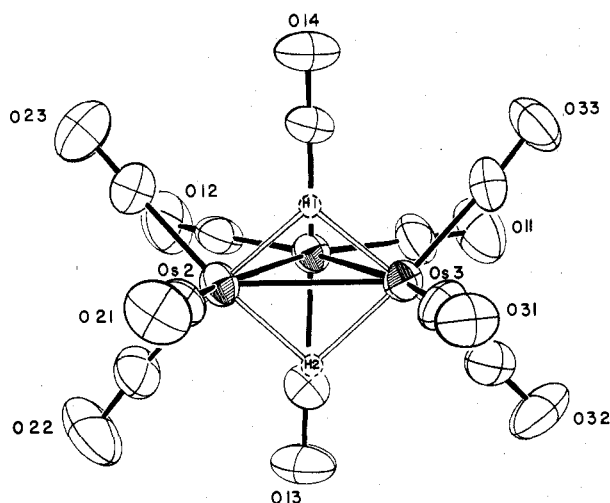
**Figure 1.** Geometry and labeling of atoms for the $(\mu\text{-H})_2Os_3(CO)_{10}$ molecule (ORTEP-II diagram; 50% probability ellipsoids for all nonhydrogen atoms). Note that the hydride ligands are in calculated positions (based upon Os–H = 1.85 Å and approximate octahedral distribution of ligands around Os(2) and Os(3)). The position for H(1) is consistent with data from difference-Fourier syntheses. That for H(2) is not (see text).

**Table IV.** Interatomic Distances (Å) with Esd's for $(\mu\text{-H})_2Os_3(CO)_{10}$

(A) Metal–Metal Distances

| | | | |
|---|---|---|---|
| Os(1)–Os(2) | 2.817 (1) | Os(2)–Os(3) | 2.681 (1) |
| Os(1)–Os(3) | 2.812 (1) | | |

(B) Metal–Carbon and Carbon–Oxygen Distances

| | | | |
|---|---|---|---|
| Os(1)–C(11) | 1.913 (16) | C(11)–O(11) | 1.146 (21) |
| Os(1)–C(12) | 1.898 (16) | C(12)–O(12) | 1.149 (20) |
| Os(1)–C(13) | 1.950 (14) | C(13)–O(13) | 1.118 (17) |
| Os(1)–C(14) | 1.957 (14) | C(14)–O(14) | 1.119 (18) |
| Os(2)–C(21) | 1.914 (18) | C(21)–O(21) | 1.151 (23) |
| Os(2)–C(22) | 1.917 (14) | C(22)–O(22) | 1.120 (19) |
| Os(2)–C(23) | 1.900 (15) | C(23)–O(23) | 1.144 (20) |
| Os(3)–C(31) | 1.934 (18) | C(31)–O(31) | 1.127 (22) |
| Os(3)–C(32) | 1.887 (15) | C(32)–O(32) | 1.127 (19) |
| Os(3)–C(33) | 1.922 (15) | C(33)–O(33) | 1.113 (19) |

to be too great, since the average Os–H distance in $(\mu_2\text{-H})(H)\text{-}Os_3(CO)_{10}(PPh_3)$[3] is 1.87 Å.) Secondly, we moved the "hydrogen atoms" along vectors from their previously calculated positions toward the center of the Os(2)–Os(3) bond until the Os–"H" distances were uniformly 1.85 Å. These positions were used only for preparation of the figures. The position determined for H(1) is very close to the largest peak on the difference Fourier maps (vide supra). That for H(2) is not close to the second largest feature on the difference Fourier maps!

A listing of final observed and calculated structure factor amplitudes is available (supplementary material).

## Results and Discussion

The crystal consists of discrete molecular units of $(\mu\text{-H})_2Os_3(CO)_{10}$ which are mutually separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. The geometry of the $(\mu\text{-H})_2Os_3(CO)_{10}$ molecule and the system used for labeling atoms are illustrated in Figure 1. Interatomic distances and their estimated standard deviations (esd's) are collected in Table IV; bond angles, with esd's, are listed in Table V.

The $(\mu\text{-H})_2Os_3(CO)_{10}$ molecule has approximate (but not exact) $C_{2v}$ symmetry in the crystalline state. One osmium atom [Os(1)] is linked to four terminal carbonyl ligands whereas the other two osmium atoms [Os(2) and Os(3)] are each linked to three such groups. Deviations of all atoms from the triosmium plane are arranged in Table VI.

The three osmium atoms define an isosceles triangle in which the nonbridged osmium–osmium distances are

**Table V.** Interatomic Angles (deg) (with Esd's) for $(\mu\text{-H})_2Os_3(CO)_{10}$

(A) Angles between Metal Atoms

| | | | |
|---|---|---|---|
| Os(2)–Os(1)–Os(3) | 56.88 (2) | Os(1)–Os(3)–Os(2) | 61.65 (2) |
| Os(1)–Os(2)–Os(3) | 61.47 (2) | | |

(B) Osmium–Osmium–Carbon Angles

| | | | |
|---|---|---|---|
| Os(2)–Os(1)–C(11) | 155.3 (5) | Os(1)–Os(2)–C(22) | 91.8 (4) |
| Os(3)–Os(1)–C(11) | 98.4 (5) | Os(3)–Os(2)–C(22) | 130.4 (4) |
| Os(2)–Os(1)–C(12) | 106.6 (5) | Os(1)–Os(2)–C(23) | 94.8 (5) |
| Os(3)–Os(1)–C(12) | 163.5 (5) | Os(3)–Os(2)–C(23) | 130.1 (5) |
| Os(2)–Os(1)–C(13) | 84.2 (4) | Os(1)–Os(3)–C(31) | 168.4 (5) |
| Os(3)–Os(1)–C(13) | 83.7 (4) | Os(2)–Os(3)–C(31) | 106.8 (5) |
| Os(2)–Os(1)–C(14) | 83.1 (4) | Os(1)–Os(3)–C(32) | 94.1 (5) |
| Os(3)–Os(1)–C(14) | 85.9 (4) | Os(2)–Os(3)–C(32) | 131.6 (5) |
| Os(1)–Os(2)–C(21) | 168.3 (5) | Os(1)–Os(3)–C(33) | 91.8 (5) |
| Os(3)–Os(2)–C(21) | 106.9 (5) | Os(2)–Os(3)–C(33) | 130.5 (5) |

(C) Carbon–Osmium–Carbon Angles

| | | | |
|---|---|---|---|
| C(11)–Os(1)–C(12) | 98.1 (7) | C(12)–Os(1)–C(13) | 93.7 (6) |
| C(11)–Os(1)–C(13) | 94.4 (6) | C(12)–Os(1)–C(14) | 94.0 (6) |
| C(11)–Os(1)–C(14) | 95.3 (6) | C(13)–Os(1)–C(14) | 166.7 (6) |
| C(21)–Os(2)–C(22) | 95.4 (6) | C(31)–Os(3)–C(32) | 95.0 (7) |
| C(21)–Os(2)–C(23) | 94.4 (7) | C(31)–Os(3)–C(33) | 95.7 (7) |
| C(22)–Os(2)–C(23) | 90.0 (7) | C(32)–Os(3)–C(33) | 88.0 (7) |

(D) Osmium–Carbon–Oxygen Angles

| | | | |
|---|---|---|---|
| Os(1)–C(11)–O(11) | 179.8 (14) | Os(2)–C(22)–O(22) | 178.0 (14) |
| Os(1)–C(12)–O(12) | 176.4 (14) | Os(2)–C(23)–O(23) | 174.2 (15) |
| Os(1)–C(13)–O(13) | 177.4 (13) | Os(3)–C(31)–O(31) | 178.2 (14) |
| Os(1)–C(14)–O(14) | 179.2 (13) | Os(3)–C(32)–O(32) | 176.9 (14) |
| Os(2)–C(21)–O(21) | 178.4 (14) | Os(3)–C(33)–O(33) | 179.1 (14) |

**Table VI.** Deviations (in Å) of Atoms for the Triosmium Plane in $(\mu\text{-H})_2Os_3(CO)_{10}$, Equation of Plane:[a] $0.3282X - 0.1375Y - 0.9346Z = -2.871$

| Atom | Dev | Atom | Dev |
|---|---|---|---|
| C(11) | 0.024 (15) | C(12) | -0.052 (14) |
| O(11) | 0.035 (12) | O(12) | -0.095 (13) |
| C(31) | 0.039 (14) | C(21) | -0.056 (15) |
| O(31) | 0.078 (10) | O(21) | -0.114 (12) |
| C(14) | 1.943 (14) | C(13) | -1.936 (14) |
| O(14) | 3.053 (11) | O(13) | -3.041 (11) |
| C(23) | 1.370 (15) | C(22) | -1.327 (14) |
| O(23) | 2.267 (13) | O(22) | -2.129 (12) |
| C(33) | 1.333 (16) | C(32) | -1.311 (14) |
| O(33) | 2.118 (11) | O(32) | -2.124 (11) |

[a] Cartesian coordinates.

Os(1)–Os(2) = 2.817 (1) Å and Os(1)–Os(3) = 2.812 (1) Å, (average = 2.815 ± 0.004 Å), whereas the di(μ-hydrido)-bridged osmium–osmium bond length is only 2.681 (1) Å—i.e., is reduced by ca. 0.134 Å relative to the nonbridged osmium–osmium linkage. The molecule is best formally represented by structure I in which the di(μ-hydrido)-bridged system



**I**
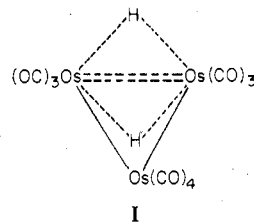
is illustrated (crudely) as a doubly protonated double bond.[15]

Figure 2 shows the $(\mu\text{-H})_2Os_3(CO)_{10}$ molecule projected onto the triosmium plane. The equatorial angles bordering the di(μ-hydrido)-bridged Os(2)–Os(3) bond are Os(3)–Os(2)–C(21) = 106.9 (5)° and Os(2)–Os(3)–C(31) = 106.8 (5)°. However, unlike the case of mono(μ-hydrido)-girdled osmium–osmium vectors, as in $(\mu\text{-H})(H)Os_3(CO)_{11}$[1] and $(\mu\text{-H})(H)Os_3(CO)_{10}(PPh_3)$,[3] there is no characteristic expansion of the adjacent equatorial Os–Os–CO angles. Thus, the diequatorial angle on Os(1) is C(11)–Os(1)–C(12) = 98.1
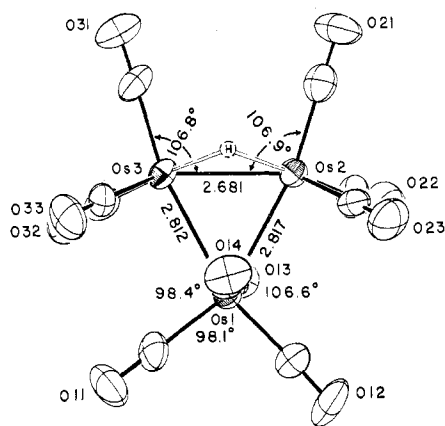
**Figure 2.** The $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ molecule projected onto its $\text{Os}_3$ plane (ORTEP-II diagram; 50% probability ellipsoids).

$(7)°$ while the adjacent angles, Os(2)–Os(1)–C(12) and Os(3)–Os(1)–C(11), have values of 106.6 (5) and 98.4 (5)°, respectively. This result is not too surprising since the $\mu$-bridging hydride ligands are, of course, each appreciably displaced from the equatorial plane (cf. Figure 1) and will be involved in little repulsive interaction with the adjacent equatorial carbonyl ligands.

The molecule has approximate $C_{2v}$ symmetry and there are, therefore, four chemically distinct locations for the carbonyl ligands. The mutually trans axial carbonyl ligands on Os(1) have the longest osmium–carbon distances [Os(1)–C(13) = 1.950 (14) Å and Os(1)–C(14) = 1.957 (14) Å], while the mutually cis equatorial ligands are associated with shorter osmium–carbon bond lengths [Os(1)–C(11) = 1.913 (16) Å and Os(1)–C(12) = 1.898 (16) Å]. This pattern is expected, since competition for back-donated $\pi$-electron density is severe for mutually trans $\pi$-acceptor ligands and minimal for carbonyl ligands trans to single metal–metal bonds. Similar patterns have been determined for $\text{Os}_3(\text{CO})_{12}$ [Os–CO(axial) = 1.946 (6) Å and Os–CO(equatorial) = 1.912 (7) Å][1] and for $\text{Ru}_3(\text{CO})_{12}$ [Ru–CO(axial) = 1.942 (4) Å and Ru–CO-(equatorial) = 1.921 (5) Å].[16]

The remaining group-theoretically distinct sets of carbonyl groups consist of (1) the equatorial ligands adjacent to the

$\text{Os}(\mu\text{-H})_2\text{Os}$ system, which are characterized by the bond lengths Os(2)–C(21) = 1.914 (18) Å and Os(3)–C(31) = 1.934 (18) Å, and (2) the set of four semiaxial ligands which are trans to the bridging hydride ligands, in which Os(2)–C(22) = 1.917 (14) Å, Os(2)–C(23) = 1.900 (15) Å, Os(3)–C(32) = 1.887 (15) Å, and Os(3)–C(33) = 1.922 (15) Å.

The Os–C–O systems are all, as expected, close to linear, with individual values ranging from Os(2)–C(23)–O(23) = 174.2 (15)° to Os(1)–C(11)–O(11) = 179.8 (14)°. The carbon–oxygen distances range from 1.113 (19) to 1.151 (23) Å.

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# The Crystal Structure of Tetrakis(ethylenethiourea)tellurium(II) Chloride Dihydrate: A Novel (+−+−) Square-Planar Conformer

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The structure of $[\text{Te}(\text{ethylenethiourea})_4]\text{Cl}_2\cdot2\text{H}_2\text{O}$ has been determined using single-crystal x-ray diffraction. The crystal is of the monoclinic class, $a = 18.70$ (3), $b = 7.82$ (1), $c = 18.34$ (3) Å, $\beta = 109.3$ (1)°. The space group has been reassigned as $P2/n$. The 2654 reflections were used to refine the structure by least squares to $R_1 = 0.039$ and $R_2 = 0.058$. The structure contains two independent $[\text{Te}(\text{etu})_4]^{2+}$ cations with nearly square-planar coordination of tellurium by sulfur. A new type of conformational isomer has been observed in which adjacent etu ligands are alternately oriented up and down with respect to the $\text{TeS}_4$ plane. The notation (+−+−) is proposed to designate such an isomer. Comparisons are made to 15 previously determined $\text{TeS}_4$, $\text{TeS}_2\text{Se}_2$, and $\text{TeSe}_4$ complexes all of which have the ++−− conformation.

## Introduction

Cheyne and Jones[1–3] have recently published a series of papers on the Mössbauer spectra of complexes of tellurium with thiourea (tu) and related derivatives. From single-crystal

spectra they were able to assign a negative nuclear quadrupole moment to the $^3/_2$ excited state in $^{125}\text{Te}$. From the work of Foss[4] and his school, Te(II)S$_4$ systems are known to form quite regular square-planar complexes and both the structural and Mössbauer results may be interpreted in terms of a stereochemically inert $5s^2$ electron pair and pure $5p$ bonding. Due to the early date at which many of the structural analyses were

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