# Synthesis and Characterization of $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$. The Eclipsed Rotamer of the Triply-Bonded $Os_2Br_8^{2-}$ Anion

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Treatment of $H_2OsBr_6$ with 1.5 equiv of $C_5Me_5H$ in a mixture of 48% HBr and methanol or ethanol at reflux for 3 h gives a brown precipitate which has the empirical formula "$(C_5Me_5)_2Os_2Br_4H$"; actually, this product is the unusual salt $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ where the cation is the conjugate acid of decamethylosmocene and the anion contains an Os−Os triple bond. This is the first $[Os_2X_8^{2-}]$ salt that has been prepared directly from a mononuclear precursor. Parent peaks due to both the cation and the anion have been observed by electrospray mass spectrometry and negative-ion fast atom bombardment mass spectrometry, respectively. The presence of a hydride ligand in the cation is shown by the singlet in the $^1H$ NMR spectrum at $\delta$ −15.65; the NMR spectrum is essentially identical with that of $[(C_5Me_5)_2OsH][PF_6]$. The brown color of $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ suggests that the anion adopts an eclipsed conformation ($D_{4h}$ symmetry) unlike other known salts of $[Os_2Br_8^{2-}]$, and this conclusion has been confirmed by a single-crystal X-ray diffraction experiment. The two crystallographically independent $[Os_2Br_8^{2-}]$ anions lie on sites of 3 and $\bar{3}$ symmetry; the Os−Os vectors are correspondingly disordered along each of three mutually perpendicular directions within the ordered cubes of bromine atoms. The Os−Os distances are 2.219(2) and 2.222(2) Å in the two independent anions; the average Os−Br distance is 2.46 Å. The cation adopts a bent metallocene structure with a dihedral angle between the two ring planes of 11°. A byproduct of the reaction of $H_2OsBr_6$ with $C_5Me_5H$ in ethanol is the osmium(II) carbonyl complex $(C_5Me_5)_2Os_2Br_2(\mu\text{-CO})$, where the bridging carbon monoxide ligand ($\nu_{CO}$ = 1740 cm$^{-1}$) is evidently generated from decarbonylation of the solvent. Crystal data for $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$: trigonal, space group $P\bar{3}$, with $a = b = 20.732(4)$ Å, $c = 9.780(2)$ Å, $\gamma = 120°$, $V = 3640.4(13)$ Å$^3$, $Z = 3$, $R_F$ [$I > 2\sigma(I)$] = 0.0325, and $R_{wF^2}$ [all data] = 0.0925 for 264 parameters refined without constraints against the 2633 observed data or all 3659 unique data, respectively.

## Introduction

Compounds that contain multiple bonds between two transition elements have been the subject of detailed experimental and theoretical studies over the last 30 years.[1] The archetypal examples of such species are salts of the octahalodimetalate anions, $[M_2X_8^{n-}]$, which are currently known for the elements Mo, W, Tc, Re, and Os.[1] The most recently discovered of these compounds are the octahalodiosmate(III) salts; unlike the other octahalodimetalate anions, which have bond orders of 3.5 or 4, the $[Os_2X_8^{2-}]$ anions have bond orders of 3.[2-7] This difference is reflected in the structures of these anions: whereas the dinuclear Mo, W, Tc, and Re anions invariably adopt eclipsed geometries of $D_{4h}$ symmetry, the $[Os_2X_8^{2-}]$ anions generally adopt staggered structures of $D_{4d}$ symmetry. This behavior arises from the lack of a $\delta$ component in the Os−Os bond, which can be described in terms of a $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration.

Interestingly, a few salts of $[Os_2Cl_8^{2-}]$ are known in which the two square-planar ligand sets about each osmium center are eclipsed.[3,5] In such a conformation, the nonbonded Cl···Cl contacts between the chloride ligands on the adjacent metal centers are shorter (and the steric repulsions somewhat larger) than those in the staggered conformation. Since crystal packing forces evidently can overcome the energetic cost of adopting the eclipsed structure, the potential energy surface for rotation of the two $OsCl_4$ units about the Os−Os bond must be relatively flat. To date, however, all known salts of the bromo and iodo anions $[Os_2Br_8^{2-}]$ and $[Os_2I_8^{2-}]$ possess staggered conformations.[4-6] Is it possible that these anions could also adopt eclipsed structures, given the proper cation? At least for the octabromodiosmate dianion, the answer is yes: we now describe the synthesis and X-ray crystal structure of the first salt to contain the eclipsed conformation of the $[Os_2Br_8^{2-}]$ anion.

## Results and Discussion

**Synthesis and Characterization of $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$.** All previously reported preparations of octahalodiosmate(III) salts[2-7] employ diosmium starting materials; most commonly used are the acetate or butyrate complexes of stoichiometry $Os_2(O_2CR)_4Cl_2$.[8] We have recently been investigating the use of hexabromoosmic acid, which can be prepared in one step from $OsO_4$,[9,10] as a convenient and readily available starting material for the preparation of new osmium complexes. Surprisingly, we have found that the $[Os_2Br_8^{2-}]$ anion can be prepared directly from this mononuclear precursor.

Treatment of $H_2OsBr_6$ with 1.5 equiv of $C_5Me_5H$ in a mixture of 48% HBr and methanol or ethanol at reflux for 3 h affords

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a brown precipitate of stoichiometry "$(C_5Me_5)_2Os_2Br_4H$". Although the product has a stoichiometry very similar to that of $(C_5Me_5)_2Os_2Br_4$,[11] it has a completely different structure and is more properly formulated as the unusual salt $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$.

$$4H_2OsBr_6 + 4C_5Me_5H + 3C_2H_5OH \rightarrow [(C_5Me_5)_2OsH]_2[Os_2Br_8] + 16HBr + 3CH_3CHO$$

The nonionic osmium complex $(C_5Me_5)_2Os_2Br_4$, which is the osmium analogue of the useful dinuclear ruthenium starting material $(C_5Me_5)_2Ru_2Cl_4$,[12,13] can also be synthesized from $H_2OsBr_6$ and $C_5Me_5H$ under slightly different conditions: the nonionic complex is obtained when the $H_2OsBr_6$ solution is freed as much as possible from excess HBr and when the ethanol solutions are refluxed for ca 40 min;[11] the salt is obtained when some excess HBr is present and when the ethanol solutions are refluxed for 3 h.

The cation in $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ is the conjugate acid of decamethylosmocene.[14] The positive-ion electrospray mass spectrum contains an envelope of peaks near *m/e* 463 that corresponds to the $[(C_5Me_5)_2OsH^+]$ cation. The $^1H$ NMR spectrum of the compound contains two singlets of relative intensity 30:1 at $\delta$ 1.98 ($C_5Me_5$) and −15.65 (Os−H), respectively. The $PF_6^-$, $O_2CCF_3^-$, and $O_3SCF_3^-$ salts of the $[(C_5Me_5)_2OsH^+]$ cation exhibit $^1H$ NMR resonances at essentially the same positions.[14-16] The IR spectrum of $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ contains no band assignable to the Os−H stretch; an Os−H bending vibration, however, is seen at 896 $cm^{-1}$. The Os−H stretch for $[(C_5Me_5)_2OsH][PF_6]$ has been reported to give a very weak broad band at 2164 $cm^{-1}$.[15] The $\nu_{MH}$ mode in monohydrido complexes is occasionally very weak despite being symmetry allowed,[17,18] and in such cases the M−H bond is thought to be of low polarity.[19]

The identity of the cation having been established, the microanalysis shows that the anion contains both osmium and bromine in a 1:4 ratio. The identity of the anion was established from the negative-ion fast atom bombardment (FAB) mass spectrum, which contains an envelope of peaks near *m/e* 1021 that correspond to the $[Os_2Br_8^-]$ ion. In addition, peaks with half-integral masses can be seen near *m/e* 510 that are due to the $[Os_2Br_8^{2-}]$ dianion.

Because the $[(C_5Me_5)_2OsH^+]$ cation is colorless, the brown color of $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ must arise from the anion. The other two known salts of the triply-bonded $[Os_2Br_8^{2-}]$ anion are green and the anions adopt staggered geometries of $D_{4d}$ symmetry.[2-4] Corresponding salts of the octachlorodiosmate dianion are either green or brown/pink depending on the cation; the brown and pink salts contain the eclipsed ($D_{4h}$) rotamer of the $[Os_2Cl_8^{2-}]$ anion. On the basis of these observations, we concluded that $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ must be a salt of the hitherto unknown eclipsed $[Os_2Br_8^{2-}]$ dianion. Interestingly, solutions of $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ in $CH_2Cl_2$ are brown but exhibit a greenish tint.

**Table 1.** Crystal Data for $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ at −75 °C

| | |
|---|---|
| space group: $P\bar{3}$ | $Z = 3$ |
| $a = b = 20.732(4)$ Å | mol wt = 1942.98 |
| $c = 9.780(2)$ Å | $\varrho_{calcd} = 2.659$ g $cm^{-3}$ |
| $\gamma = 120°$ | $\mu_{calcd} = 170.50$ $cm^{-1}$ |
| $V = 3640.4(13)$ Å$^3$ | size = 0.4 × 0.4 × 0.07 mm |

diffractometer: Enraf-Nonius CAD4
radiation: MoK$\bar{\alpha}$, $\bar{\lambda} = 0.710\,73$ Å
monochromator: graphite cryst, $2\theta = 12°$
scan range, type: $4.0 < 2\theta < 48.0°$, $\omega/\theta$
scan speed, width: 3−16° $min^{-1}$, $\Delta\omega = 1.50\,[1.00 + 0.35 \tan\theta]°$
rflctns: 12 035 total, 3659 unique, 2633 with $I > 2\sigma(I)$
internal consistency: $R_i = 0.069$

| | |
|---|---|
| $R_F\,[I > 2\sigma(I)] = 0.0325^a$ | variables = 264 |
| $R_{wF^2}$ [all data] $= 0.0925^b$ | constraints = 0 |

$^a R_F = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^b R_{wF^2} = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

**Isolation of $(C_5Me_5)_2Os_2Br_2(\mu\text{-CO})$ from the Reaction Solutions.** After the precipitate of $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ was collected as described above, the ethanol filtrate was cooled to −20 °C in hopes of obtaining additional product. Instead, after several days a different compound was obtained in low yield (4%) in the form of dark brown prisms. Analytical and spectroscopic data suggest that this product is the neutral dinuclear complex $(C_5Me_5)_2Os_2Br_2(\mu\text{-CO})$. Particularly diagnostic are the parent peaks near *m/e* = 840 in the electron impact (EI) mass spectrum, the IR stretch at 1740 $cm^{-1}$, and the $^{13}C$ NMR resonance at $\delta$ 225.2. The bridging carbonyl group undoubtedly arises from the decarbonylation of the alcohol solvent, a process that is readily promoted by late transition metals.[18,20,21]

**X-ray Crystal Structure of $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$.** A single crystal X-ray diffraction study of $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ was carried out to verify its structure. When crystallized by layering a $CH_2Cl_2$ solution with pentane, the compound is obtained as orange hexagonal plates that reflect the crystallographic symmetry. The structure was solved in the trigonal space group $P\bar{3}$ with six cations and three anions per unit cell. Crystal data are presented in Table 1, atomic coordinates are listed in Table 2, and selected bond distances and angles are given in Table 3.

ORTEP views of the cation and two crystallographically independent anions are shown in Figures 1 and 2, respectively, and a view down the *c*-axis of the unit cell is shown in Figure 3. The equivalent $[(C_5Me_5)_2OsH^+]$ cations occupy one set of 6-fold general positions. Although the metal-bound hydride ligand was not located in the Fourier difference maps, its presence is revealed by the "bent metallocene" structure of the cation. The dihedral angle between the two $C_5Me_5$ rings is 11.0(6)°, while the Cn(1)−Os(1)−Cn(2) angle involving the centroids of the $C_5Me_5$ rings is 168.5(4)°. The sum of these two angles (179.5°) is equal within experimental error to 180°, as expected for a metallocene structure in which the M−C distances are almost exactly equal. In the $[(C_5Me_5)_2OsH^+]$ cation, the Os−C distances all lie between 2.19(1) and 2.22(1) Å.

There are two crystallographically independent anions in the unit cell, and both clearly adopt eclipsed geometries unlike those

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**Table 2.** Atomic Coordinates ($\times 10^4$) for $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$

| | x | y | z |
|---|---|---|---|
| Os(1) | 3587(1) | 2936(1) | 3282(1) |
| Os(2) | 10(1) | −435(1) | 647(1) |
| Os(3) | 6669(1) | 2878(1) | 9664(1) |
| Os(4) | 6687(1) | 3761(1) | 8350(1) |
| Br(21) | 0 | 0 | 2988(2) |
| Br(23) | 21(1) | −1318(1) | −982(2) |
| Br(31) | 6667 | 3333 | 11991(2) |
| Br(33) | 6628(1) | 1981(1) | 7996(2) |
| Br(41) | 6667 | 3333 | 6011(2) |
| Br(43) | 6712(1) | 4686(1) | 10037(1) |
| C(1) | 4444(5) | 2602(6) | 3063(11) |
| C(2) | 4781(5) | 3384(6) | 2823(12) |
| C(3) | 4441(5) | 3493(5) | 1664(11) |
| C(4) | 3882(5) | 2771(6) | 1177(11) |
| C(5) | 3881(5) | 2231(5) | 2050(10) |
| C(6) | 4685(7) | 2242(6) | 4106(14) |
| C(7) | 5435(6) | 3976(6) | 3608(13) |
| C(8) | 4670(7) | 4211(6) | 968(14) |
| C(9) | 3432(7) | 2622(8) | −91(12) |
| C(10) | 3437(6) | 1404(6) | 1882(13) |
| C(11) | 2690(6) | 3206(6) | 3129(11) |
| C(12) | 2423(5) | 2539(6) | 3907(12) |
| C(13) | 2872(6) | 2712(6) | 5097(11) |
| C(14) | 3420(6) | 3487(5) | 5043(11) |
| C(15) | 3291(5) | 3788(5) | 3870(10) |
| C(16) | 2341(7) | 3281(8) | 1829(14) |
| C(17) | 1761(7) | 1782(6) | 3573(16) |
| C(18) | 2761(9) | 2197(7) | 6254(14) |
| C(19) | 3960(8) | 3925(7) | 6151(14) |
| C(20) | 3685(6) | 4589(5) | 3417(13) |

**Table 3.** Selected Bond Distances and Angles for $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$[a,b]

| | | | |
|---|---|---|---|
| | | Distances (Å) | |
| | | Cation | |
| Os(1)−C(1) | 2.216(9) | Os(1)−C(11) | 2.198(9) |
| Os(1)−C(2) | 2.212(10) | Os(1)−C(12) | 2.210(10) |
| Os(1)−C(3) | 2.219(9) | Os(1)−C(13) | 2.208(10) |
| Os(1)−C(4) | 2.222(11) | Os(1)−C(14) | 2.187(10) |
| Os(1)−C(5) | 2.203(9) | Os(1)−C(15) | 2.215(9) |
| | | Anion | |
| Os(2)−Os(2)$^{i}$ | 2.219(2) | Os(3)−Br(33) | 2.436(2) |
| Os(3)−Os(4) | 2.222(2) | Os(3)−Br(43)$^{iv}$ | 2.422(2) |
| Os(2)−Br(21) | 2.464(3) | Os(3)−Br(43)$^{v}$ | 2.468(2) |
| Os(2)−Br(23) | 2.436(2) | Os(4)−Br(33)$^{iv}$ | 2.487(2) |
| Os(2)−Br(23)$^{ii}$ | 2.446(2) | Os(4)−Br(33)$^{v}$ | 2.460(2) |
| Os(2)−Br(23)$^{iii}$ | 2.458(2) | Os(4)−Br(41) | 2.446(2) |
| Os(3)−Br(31) | 2.465(2) | Os(4)−Br(43) | 2.510(2) |
| | | Angles (deg) | |
| | | Cation | |
| Cn(1)−Os(1)−Cn(2) | 168.5(4) | | |
| | | Anion | |
| Os(2)$^{i}$−Os(2)−Br(23) | 104.35(9) | Br(23)−Os(2)−Br(21) | 152.57(7) |
| Os(2)$^{i}$−Os(2)−Br(23)$^{ii}$ | 103.77(8) | Br(23)$^{ii}$−Os(2)−Br(21) | 87.03(6) |
| Os(2)$^{i}$−Os(2)−Br(23)$^{iii}$ | 103.09(8) | Br(23)$^{iii}$−Os(2)−Br(21) | 86.78(5) |
| Os(2)$^{i}$−Os(2)−Br(21) | 103.08(7) | Br(43)$^{iv}$−Os(3)−Br(33) | 88.64(6) |
| Os(4)−Os(3)−Br(43)$^{iv}$ | 104.03(6) | Br(43)$^{iv}$−Os(3)−Br(31) | 86.70(5) |
| Os(4)−Os(3)−Br(33) | 102.76(7) | Br(33)−Os(3)−Br(31) | 154.46(6) |
| Os(4)−Os(3)−Br(31) | 102.73(6) | Br(43)$^{iv}$−Os(3)−Br(43)$^{v}$ | 153.36(7) |
| Os(4)−Os(3)−Br(43)$^{v}$ | 102.51(6) | Br(33)−Os(3)−Br(43)$^{v}$ | 87.72(6) |
| Os(3)−Os(4)−Br(41) | 104.61(6) | Br(31)−Os(3)−Br(43)$^{v}$ | 85.31(5) |
| Os(3)−Os(4)−Br(33)$^{v}$ | 104.25(6) | Br(41)−Os(4)−Br(33)$^{v}$ | 87.05(5) |
| Os(3)−Os(4)−Br(33)$^{iv}$ | 104.85(6) | Br(41)−Os(4)−Br(33)$^{iv}$ | 86.44(5) |
| Os(3)−Os(4)−Br(43) | 103.58(7) | Br(33)$^{v}$−Os(4)−Br(33)$^{iv}$ | 150.89(6) |
| Br(23)−Os(2)−Br(23)$^{ii}$ | 86.91(5) | Br(41)−Os(4)−Br(43) | 151.81(6) |
| Br(23)−Os(2)−Br(23)$^{iii}$ | 86.65(5) | Br(33)$^{v}$−Os(4)−Br(43) | 86.27(6) |
| Br(23)$^{ii}$−Os(2)−Br(23)$^{iii}$ | 153.14(7) | Br(33)$^{iv}$−Os(4)−Br(43) | 86.21(6) |

[a] Ring centroids are designated by Cn. [b] Symmetry equivalent coordinates are as follows: i, $(-x, -y, -z)$; ii, $(x - y, x, -z)$; iii, $(y, -x + y, -z)$; iv, $(-x + y + 1, -x + 1, z)$; v, $(-y + 1, x - y, z)$.

in all other known $[Os_2Br_8^{2-}]$ salts, which are staggered.[4] The anions lie on special positions of 3-fold and 3-fold rotoinversion

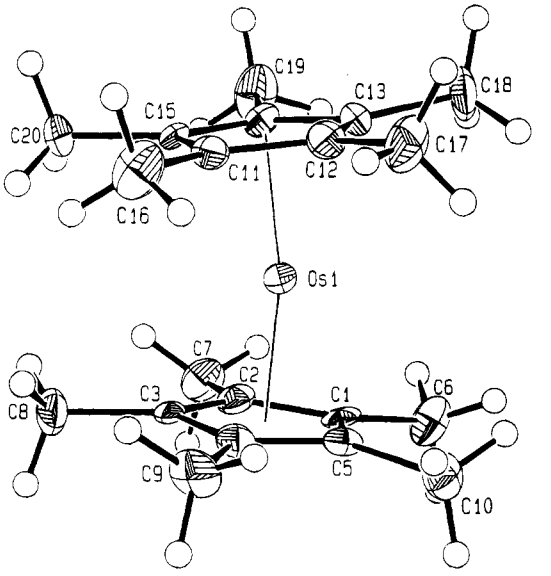


**Figure 1.** ORTEP diagram of the $[(C_5Me_5)_2OsH^+]$ cation; the hydride atom was not located. The 35% probability density surfaces are shown.

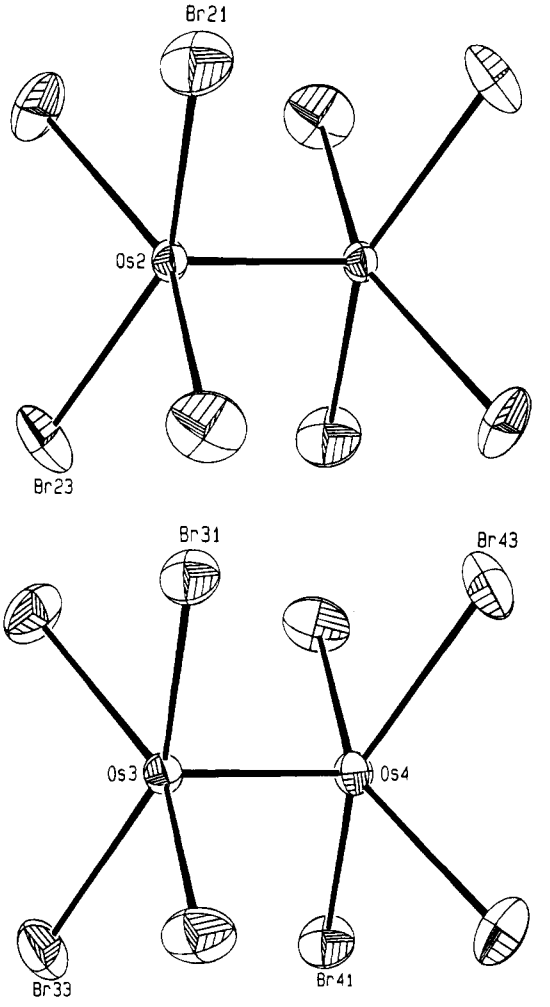


**Figure 2.** ORTEP diagram of the two crystallographically independent $[Os_2Br_8^{2-}]$ anions. The 35% probability density surfaces are shown.

symmetry, respectively. As a result, the osmium atoms of the $[Os_2Br_8^{2-}]$ anions are disordered with one-third occupancies over positions related by the 3 or $\bar{3}$ axes. In each anion, the bromine atoms show no evidence of disorder and are disposed in a quasi-cubic arrangement; the three Os−Os vectors are almost exactly orthogonal to each other and each points toward

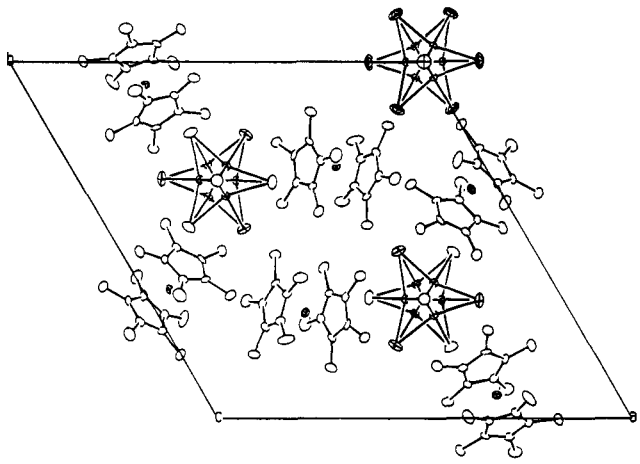

**Figure 3.** View of the unit cell contents down the *c*-axis, showing the packing of the cations and anions.

a different pair of opposite square faces of the $Br_8$ cubes. This situation resembles that of other eclipsed $[M_2X_8^{n-}]$ salts, in which the M−M units are almost invariably disordered in two or three orientations within the quasi-cubic array of eight halide atoms.[1,22]

The Os−Os bond distances in the two independent anions of 2.219(2) and 2.222(2) Å are nearly equal but both are slightly longer than the 2.196(1) Å distance observed for $[Os_2Br_8^{2-}]$ anions that adopt staggered conformations.[4] The somewhat longer Os−Os distance in the present compound presumably reflects the slightly greater steric repulsions between the bromide ligands in the eclipsed conformation; a similar lengthening is seen in the eclipsed vs staggered forms of the $[Os_2Cl_8^{2-}]$ anion.[3] The average Os−Br distance in $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ is 2.46 Å, and the average Os−Os−Br angle is 103.5°. There are two types of Br−Os−Br angles: the average trans angle is 152.7° while the average cis angle is 86.8°. The average Br−Os−Os−Br torsion angle is 0° by symmetry.

**Steric Analysis of the Eclipsed vs Staggered $Os_2X_8^{2-}$ Conformers.** The synthesis of a salt of the eclipsed conformer of the $[Os_2Br_8^{2-}]$ anion raises the question whether corresponding salts of the eclipsed iodo anion $[Os_2I_8^{2-}]$ should also exist. Most relevant to this question is an analysis of the steric repulsions present in these anions. The degree of steric repulsion can most easily be assessed by comparing the nonbonded X···X distance between halide atoms on opposite osmium atoms with twice the van der Waals radius for X. For the eclipsed $[Os_2Cl_8^{2-}]$ salts,[3,5] the nonbonded Cl···Cl distance is ca. 3.30 Å while twice the van der Waals radius of Cl is 3.60 Å; the van der Waals spheres therefore interpenetrate by only 0.30 Å. Evidently, the steric repulsions associated with the interpenetration of the van der Waals spheres in the octachlorodiosmate dianion are sufficiently small to be overcome by crystal packing (or electronic bonding) effects. For the eclipsed $[Os_2Br_8^{2-}]$ anion, however, the corresponding Br···Br distance is 3.37 Å and the van der Waals spheres interpenetrate by 0.53 Å.[23] The repulsions between the bromide ligands on opposite osmium atoms in $[Os_2Br_8^{2-}]$ are probably greater than the corresponding repulsions in $[Os_2Cl_8^{2-}]$, although the greater interpenetration of the van der Waals spheres in the octabromodiosmate dianion will be mitigated to some extent by the greater polarizability of Br vs Cl.

For a hypothetical eclipsed $[Os_2I_8^{2-}]$ dianion, the interpenetration of the van der Waals spheres is even more pronounced. On the basis of the known structure of the staggered conformer of $[Os_2I_8^{2-}]$[5,6] and the known structural differences between the eclipsed and staggered structures of $[Os_2Cl_8^{2-}]$ and $[Os_2Br_8^{2-}]$, we can estimate that the eclipsed $[Os_2I_8^{2-}]$ dianion should have an Os−Os distance of 2.25 Å, an Os−Os−I angle of 105°, and an Os−I distance of 2.65 Å. Given these parameters, the calculated I···I distance between iodide atoms on opposite osmium atoms is 3.62 Å, while twice the van der Waals radius for iodine is 4.30 Å; the van der Waals spheres would interpenetrate by 0.68 Å. By adopting the staggered conformation, the nonbonded I···I distance between iodide ligands on opposite osmium atoms increases to 4.12 Å, a distance that results in little interpenetration of the van der Waals surfaces. The analysis certainly suggests that the staggered conformer should be strongly favored, but we do not believe that the nonbonded repulsions in an eclipsed $[Os_2I_8^{2-}]$ anion are so large as to be prohibitive.[24]

## Experimental Section

All operations were carried out under argon or vacuum unless otherwise specified. Solvents were distilled under nitrogen from magnesium (ethanol and methanol), calcium hydride (dichloromethane), or sodium benzophenone (pentane). Pentamethylcyclopentadiene (Quantum Design), hydrobromic acid (Mallinckrodt), and osmium tetraoxide (Alfa) were used without further purification.

Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. The negative ion FAB mass spectra were obtained on a VG ZAB-SE mass spectrometer by dispersing the sample in a matrix of 3-nitrobenzyl alcohol, and the positive ion electrospray mass spectra were obtained on a VG Quattro mass spectrometer from $CH_2Cl_2$ solutions. Electron impact mass spectra were obtained on a Finnigan-MAT CH5 mass spectrometer with 70 eV electron energies. All peak envelopes matched the calculated isotope distribution patterns for the respective ions. The IR spectra were recorded on a Perkin-Elmer 1700 FT-IR instrument as Nujol mulls between KBr plates. The $^1H$ NMR data were recorded on a General Electric QE-300 spectrometer at 300 MHz, and the $^{13}C$ NMR data were recorded on a General Electric GN-500 spectrometer at 125 MHz. Chemical shifts are reported in $\delta$ units (positive shifts to high frequency) relative to $SiMe_4$. Melting points were measured on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon.

**Hydridobis(pentamethylcyclopentadienyl)osmium(IV) Octabromodiosmate(III), $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$.** A 100 mL round-bottomed flask fitted with a reflux condenser was charged with $OsO_4$ (1.0 g, 3.93 mmol) and 48% HBr (38 mL), and the mixture was refluxed for 2 h in air. The resulting red solution was concentrated to ca. 5 mL by rotary evaporation at 50 °C (note: allowing the bath temperature to exceed 50 °C or reducing the solution volume to less than ca. 5 mL considerably reduces the yield.) The residue (which consists of hexabromoosmic acid and excess HBr) was dissolved in ethanol (40 mL), and to this solution was added a solution of pentamethylcyclopentadiene (0.92 mL, 5.90 mmol) in ethanol (10 mL). The red solution was refluxed for 3 h and then cooled to room temperature; the brown microcrystalline precipitate was collected by filtration and dried under vacuum. Often (but not always), more product can be obtained in the form of microcrystals by cooling the supernatant to −20 °C. Yield: 0.60 g (32%). Mp: >280 °C. Anal. Calcd for $C_{40}H_{62}Br_8Os_4$: C, 24.7; H, 3.22; Br, 32.9. Found: C, 24.8; H, 3.30; Br, 32.7. MS (positive ion electrospray): *m/e* 463 $[(C_5Me_5)_2OsH^+]$. MS (negative ion FAB): *m/e* 1021 $[Os_2Br_8^-]$, 510.5 $[Os_2Br_8^{2-}]$. $^1H$ NMR ($CD_2Cl_2$, 25 °C): $\delta$ 1.98 (s, 60 H, $C_5Me_5$), −15.65 (s, 2H, Os−H). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 25 °C): $\delta$ 10.1 (s, $C_5Me_5$), 91.1 (s, $C_5Me_5$). IR ($cm^{-1}$): 1079 (m), 1036 (s), 896 (m).

(22) Cotton, F. A.; Eglin, J. L. *Inorg. Chim. Acta* **1992**, *198*−200, 13−22.
(23) For comparison, the Br−Br bond length in $Br_2$ is 2.284 Å. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 317.
(24) To date, however, it appears that $[(C_5Me_5)_2OsH]_2[Os_2I_8]$ cannot be prepared by treating $OsO_4$ with HI, followed by addition of $C_5Me_5H$ in ethanol.

The reaction of $H_2OsBr_6$ with $C_5Me_5H$ may also be carried out in methanol to give $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ in lower yield (21%).

**Dibromobis(pentamethylcyclopentadienyl)($\mu$-carbonyl)diosmium(II), $Cp^*_2Os_2Br_2(\mu$-CO).** The ethanol supernatant from the last step of the procedure above was cooled to −20 °C for 2 weeks, and the resulting dark brown prisms were isolated by filtration and dried under vacuum. Yield: 0.06 g (4%). Anal. Calcd for $C_{21}H_{30}Br_2OOs_2$: C, 30.1; H, 3.61. Found: C, 30.2; H, 3.64. MS (EI): *m/e* 840 [$Cp^*_2Os_2Br_2(CO)^+$], 812 [$Cp^*_2Os_2Br_2^+$]. $^1H$ NMR ($CD_2Cl_2$, 25 °C): $\delta$ 1.82 (s, $C_5Me_5$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 25 °C): $\delta$ 10.4 (s, $C_5Me_5$), 87.7 (s, $C_5Me_5$), 225.2 (s, CO). IR ($cm^{-1}$): 1740 (vs), 1702 (w), 1076 (w), 1025 (s), 957 (w), 798 (w), 566 (s), 550 (w), 537 (w), 527 (m).

**Crystallographic Study.**[25] Single crystals of $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$, grown from 1:1 dichloromethane/pentane, were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to −75 °C in a cold nitrogen gas stream on the diffractometer. Standard peak search and indexing procedures gave rough cell dimensions, and the diffraction symmetry was confirmed by inspection of the axial photographs. Least squares refinement using 25 reflections yielded the cell dimensions given in Table 1.

Data were collected in two quadrants of reciprocal space ($-h$, $\pm k$, $\pm l$) by using the measurement parameters listed in Table 1. Systematic conditions were consistent with a primitive trigonal or hexagonal space group; subsequent refinement confirmed the presence of an inversion center and established the space group to be $P\bar{3}$. The measured intensities were reduced by profile analysis and corrected for Lorentz−polarization effects. While corrections for crystal decay were unnecessary, an absorption correction was applied, the maximum and minimum transmission factors being 0.3048 and 0.0161. Thirty-three questionable reflections were deleted: 22 with imbalanced background counts, 5 with poorly-centered peak maxima, and 6 with dead-time counting errors. Symmetry-equivalent reflections were averaged to yield the set of unique data. All data were used in the least-squares refinement.

The structure was solved using direct methods (SHELXS-86) using Patterson and weighted difference Fourier methods. The correct position for the Os(1) atom was deduced from an *E*-map. One cycle of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed disordered positions for the osmium atoms of two independent anions arranged about 3-fold and 3-fold rotoinversion sites in the unit cell. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the bromine and carbon atoms. Methyl hydrogen atoms were optimized by rotation about the C−C bonds with idealized C−H distances of 0.98 Å and idealized C−C−H and H−C−H angles of 109.5°. The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0187P)^2 + 33.0642P\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. In the final cycle of least squares, the non-hydrogen atoms were refined with anisotropic thermal coefficients; for the methyl hydrogen atoms, isotropic thermal parameters were set equal to 1.2 times the $U_{eq}$ for the attached carbon atom. The hydridic hydrogen atom on Os(1) never surfaced in the difference maps. An isotropic extinction parameter was refined to a final value of $3.7(6) \times 10^{-4}$. Successful convergence was indicated by the maximum shift/error for the last cycle. Final refinement parameters are given in Table 1. The largest peak in the final difference Fourier difference map (3.28 e $Å^{-3}$) was located on the origin. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

The bond lengths and angles for the anions were somewhat less symmetric that expected, but an attempt to refine four independent Br atom positions for each osmium atom in the anions required unreasonable constraints to stabilize the least-squares matrix; this model was therefore rejected.

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**Supplementary Material Available:** Tables of hydrogen atom coordinates, anisotropic thermal parameters, and complete bond distances and angles for $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ (7 pages). Ordering information can be found on any current masthead page.

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(25) For details of the crystallographic data collection and refinement procedure, see: Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4977−4982.