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Structure of the High-Temperature Form of Osmium(IV) Chloride

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Received January 13, 1977

AIC70020Z

The high-temperature polymorph of OsCl₄ has been prepared in crystalline form by direct reaction of the elements; its structure has been determined by x-ray diffraction techniques. The space group is *Cmmm*. Unit cell dimensions are as follows: $a = 7.929$ (2), $b = 8.326$ (2), $c = 3.560$ (1) Å; $V = 235.0$ (1) Å³; $Z = 2$; $d = 4.69$ g cm⁻³. The structure, which consists of infinite chains of OsCl₆ octahedra sharing opposite edges with uniform Os–Os separations along the chains, appears to be the first AB₄ structure of its type. The Os–Os separation along the chain is 3.560 (1) Å, the Os–Cl(br) distance is 2.378 (2) Å, and the Os–Cl(nonbr) distance is 2.261 (4) Å. The structural and metal–metal bonding trends in nonmolecular transition metal tetrachlorides are discussed.

Introduction

The highest known chloride of osmium is the tetrachloride, first prepared early in this century.¹ Two polymorphs have been reported: an orthorhombic high-temperature form, made by reaction of osmium metal with chlorine,^{1–3} SO₂Cl₂,⁴ or CCl₄,⁵ at 400–600 °C, and a cubic low-temperature form, made by reacting OsO₄ with SOCl₂ at reflux⁵ or at room temperature.⁶ In both cases only powder diffraction data were recorded. Magnetic susceptibilities^{5–7} have also been reported for both forms of OsCl₄, but no detailed structural information has been available, making this the only existing transition metal tetrachloride of unknown structure.

In the tetrachlorides of Zr, Hf, Nb, Ta, Mo, W, Tc, Re, and Pt the metal ions are octahedrally coordinated by chloride ions, so that each metal ion shares four chloride ions with neighboring metal ions. The structures of these compounds differ primarily in the manner in which these chloride bridges are formed, and this is in turn apparently influenced by the degree of metal–metal interaction present. Chlorides of Zr,⁸ Hf,⁸ Tc,⁹ and Pt¹⁰ contain zigzag chains of MCl₆ octahedra sharing two edges such that the unshared chloride ions are cis; the metal–metal distances and magnetic moments for these compounds are consistent with the absence of metal–metal bonding. In NbCl₄,^{11,12} TaCl₄,¹³ α-MoCl₄,^{14,15} and WCl₄,¹⁶ the MCl₆ octahedra share opposite edges, and the metal–metal separations along the chains are alternately short and long, indicating a moderate degree of bonding between the paired metal ions. (β-MoCl₄, the high-temperature polymorph, has the FeCl₃ structure and lacks metal–metal interactions.¹⁷) In ReCl₄¹⁸ there are confacial bioctahedra which are then linked by shared chloride atoms, and within each bioctahedron the very short Re–Re distance, 2.728 (2) Å, indicates a bonding interaction.

It is easy to rationalize both the lack of bonding interactions between the d⁰ metal ions in ZrCl₄ and HfCl₄ and the moderate metal–metal bonding present in d¹ NbCl₄ and TaCl₄ and d² α-MoCl₄ and WCl₄. However, it is less clear why the metal–metal interactions in d³ TcCl₄ and ReCl₄ should be so dissimilar. In order to better understand the trends in structure and metal–metal bonding in the transition metal tetrachlorides, we have determined the structure of the high-temperature form of OsCl₄ by single-crystal x-ray diffraction techniques.

An additional consideration underlying our interest in this compound was the fact that Os(IV) is a d⁴ ion, isoelectronic with Cr(II), Mo(II), W(II), and Re(III), all of which form

compounds containing M–M quadruple bonds.¹⁹ Thus, the question of whether the high charge in this case would overwhelm the tendency of a d⁴ ion to engage in quadruple bond formation was clearly posed.

Experimental Section

Synthesis of OsCl₄. OsCl₄ was prepared by direct reaction of the elements using the method of Kolbin et al.³ The procedure involves use of an L-shaped Pyrex reaction tube, where one leg of the tube contains Os powder and is heated to 525 °C while the other leg contains liquid chlorine at room temperature. The high pressure (6–8 atm) generated is necessary to prevent dissociation of the product to OsCl₃ and Cl₂. The reaction was allowed to proceed for 5 days, by which time black crystals of OsCl₄ had formed in the hottest part of the tube. The crystals were not particularly air or water sensitive but were rather fragile, tending to crush into fine fibers when handled. A well-formed crystal of dimensions 0.139 × 0.083 × 0.300 mm was lightly coated with epoxy cement (to retard any slow reaction with the atmosphere) and was mounted for x-ray data collection.

X-Ray Data Collection. All data were collected at 21 ± 2 °C on a Syntex PI automated diffractometer using Mo Kα radiation monochromatized with a graphite crystal in the incident beam. The automatic centering and autoindexing procedures followed have been described elsewhere.²⁰ Preliminary photographs revealed orthorhombic symmetry. No systematic absences were evident other than those due to *C* centering (hkl , $h + k \neq 2n$), indicating *Cmmm*, *Cmm2*, and *C222* as possible space groups. The principal crystallographic data are as follows: $a = 7.929$ (2), $b = 8.326$ (2), $c = 3.560$ (1) Å; $V = 235.0$ (2) Å³, $d_{\text{calcd}} = 4.69$ for $Z = 2$ and a formula weight of 332.01.

A total of 221 unique reflections with $0 < 2\theta \leq 50^\circ$ were collected using the θ – 2θ scan technique, variable scan rates from 4.0 to 24.0°/min, and a scan range from $2\theta(\text{Mo K}\alpha_1) - 1.0^\circ$ to $2\theta(\text{Mo K}\alpha_2) + 1.0^\circ$. Intensities of three standard reflections measured after every 60 reflections showed no significant variation during data collection. Lorentz and polarization corrections and a numerical absorption correction²¹ (linear absorption coefficient 308.83 cm⁻¹) were applied. Transmission coefficients ranged from 0.0520 to 0.1512.

Solution and Refinement of the Structure. The structure was solved in the space group *Cmmm* (No. 65) and refined using all 221 unique reflections, all of which had $F_o^2 > 3\sigma(F_o^2)$. The positions of all atoms (Os, Cl(1), and Cl(2)) were determined using a three-dimensional Patterson function. The atomic coordinates and isotropic temperature factors were refined by three cycles of least-squares refinement to give the discrepancy indices (before application of the absorption correction)

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.248$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.370$$

Table I. Positional and Thermal Parameters^a and Their Estimated Standard Deviations

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Os	0.0 ^b	0.0	0.0	0.00507 (9)	0.00447 (8)	0.0201 (5)	0.0	0.0	0.0
Cl(1)	0.2852 (5)	0.0	0.0	0.0061 (5)	0.0103 (5)	0.038 (3)	0.0	0.0	0.0
Cl(2)	0.0	0.1894 (5)	0.5	0.0099 (5)	0.0048 (4)	0.028 (2)	0.0	0.0	0.0

^a The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^b Entries with no esd's are fixed by the symmetry of the space group.

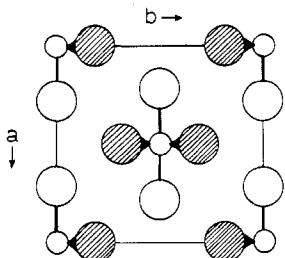


Figure 1. A projection of the unit cell on the *a*-*b* plane: small open circles, Os at *Z* = 0; large open circles, Cl(1) at *Z* = 0; large hatched circles, Cl(2) at *Z* = 1/2.

The function minimized during all least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor, *w*, equals $4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for *p* in the calculation of σ_{21} .

After correction for absorption, isotropic refinement to convergence gave $R_1 = 0.056$ and $R_2 = 0.072$. Refinement of all atoms anisotropically gave the final residuals $R_1 = 0.039$, $R_2 = 0.051$. The error in an observation of unit weight was 1.378. Observed and calculated structure factors are available.²²

In order to justify the assignment of the space group as *Cmmm* rather than *Cmm2* (*C222*, with the Os atom in position *a* and the two Cl atoms in positions *f* and *h*, is equivalent to *Cmmm*), the customary statistical tests were applied to the data. The zero-moment test of Howells, Phillips, and Rogers²³ was inconclusive. However, the distribution of *E* values was very close to that theoretically predicted for a noncentrosymmetric space group.²⁴ Therefore the structure was also refined in *Cmm2*, space group No. 35, which amounted to adding four parameters to the *Cmmm* refinement (*z* and β_{13} for Cl(1); *z* and β_{23} for Cl(2)). The final residuals obtained from this refinement were exactly the same as before: $R_1 = 0.039$, $R_2 = 0.050$. Refinements of both *x*, *y*, *z*, and \bar{x} , \bar{y} , \bar{z} orientations of the noncentrosymmetric space group resulted in identical residuals and F_{calcd} values. The change in the structure caused by changing the space group from *Cmmm* to *Cmm2* was scarcely significant: no bond distances changed by more than three estimated standard deviations, though some bond angles changed by as much as 5σ .

Since there is no chemically significant difference between the centric and acentric structures and because the residuals are identical even though the acentric refinement involves four more variables than the other, we have decided to report the OsCl₄ structure in the centrosymmetric space group *Cmmm*. It is possible that the statistical tests gave misleading results, since they are valid only when the electron distribution in the unit cell is approximately uniform, an assumption which is hardly justifiable in this case. Piezoelectric and second harmonic generation measurements, performed in another laboratory,²⁹ gave negative results; of course, it is possible that the signals were present but too small to detect.

Results and Discussion

The positional and thermal parameters are listed in Table I. A projection of the unit cell on the *a*-*b* plane is shown in Figure 1. The structure can be described as an approximate hexagonally closest packed array of chloride ions (the closest packed planes are parallel to the (110) plane) with Os⁴⁺ ions occupying half of the octahedral holes of every other layer, arranged to form infinite chains along the *c* axis of OsCl₆ octahedra sharing opposite edges. A portion of the OsCl₂Cl_{4/2} chain is illustrated in Figure 2. The local symmetry at the Os ion is *D*_{2h}.²⁵ Bond distances and angles for the symmetric structure are listed in Table II. The repeat distance along the chain direction (as confirmed by a long-exposure rotation photograph about [001]) is equal to one Os-Os separation,

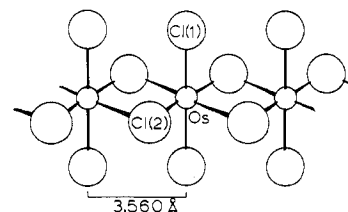


Figure 2. A portion of the OsCl₂Cl_{4/2} chain.

Table II. Interatomic Distances (Å) and Angles (deg)

Os-Os	3.560 (1)	Cl(1)-Os-Cl(1)	180.0 (0)
Os-Cl(1)	2.261 (4)	Cl(1)-Os-Cl(2)	90.0 (0)
Os-Cl(2)	2.378 (2)	Cl(2)-Os-Cl(2)	83.07 (13)
Cl(1)-Cl(2)	3.281 (3)	Os-Cl(2)-Os'	96.93 (13)

3.560 (1) Å. This distance is shorter than the metal-metal distances found in the non metal-metal bonded compounds ZrCl₄⁸ (Zr-Zr = 3.962 Å), TcCl₄⁹ (Tc-Tc = 3.62 Å), and α-PtI₄²⁶ (Pt-Pt = 3.95 Å) yet longer than the short metal-metal contacts reported for α-NbI₄²⁷ or NbCl₄^{11,12b} (Nb-Nb = 3.31 and 3.029 Å, respectively). Thus the Os-Os distance alone does not provide conclusive evidence for or against the presence of metal-metal bonding in OsCl₄. However, the absence of Os-Os pairing along the OsCl₂Cl_{4/2} chain and the fact that the OsCl₆ octahedra are distorted in such a way as to imply repulsion between the adjacent Os ions argue against such bonding, as does the paramagnetic moment^{5,7} (1.6 μ_B), which is no smaller than that found in K₂OsX₆,²⁸ X = F, Cl, Br, I (1.3-1.5 μ_B).

The high-temperature form of OsCl₄ is the first AB₄ compound yet reported with the structure described herein. However, this structure is closely related to the one shared by NbCl₄, TaCl₄, α-MoCl₄, and WCl₄. Both structures contain infinite chains of MCl₆ octahedra sharing opposite edges; the principal difference between them is the repeating unit for the chain, which is comprised of one metal-metal separation for OsCl₄ and two for the others. Single-crystal x-ray studies of NbCl₄^{11,12b} report that its structure (and presumably also that of TaCl₄, α-MoCl₄, and WCl₄) is monoclinic rather than orthorhombic like OsCl₄, but the x-ray powder patterns^{5,12-14,16} of all five compounds show reasonable agreement in their line positions and intensities, so the atomic positions in the two structures must be similar.

The metal-metal bonding trends observed in the nonmolecular transition metal tetrachlorides are understandable in terms of the previously observed bonding trends for these elements. For example, in the third transition period one finds no metal-metal bonding in HfCl₄ as expected for a d⁰ metal ion; bonding gets progressively stronger as more d electrons are available in TaCl₄, WCl₄, and ReCl₄. Apparently at this point the decreasing size of the M⁴⁺ ion establishes a reverse trend: with Os⁴⁺ and Pt⁴⁺, the d orbitals have contracted enough that orbital overlap is poor, and metal-metal bonding no longer occurs. The same trend also occurs in the second-row transition metals: no M-M bonding in ZrCl₄, moderate bonding in NbCl₄ and α-MoCl₄, and again no bonding in TcCl₄.

Acknowledgment. This work was supported, in part, by the National Science Foundation.

Registry No. OsCl₄, 10026-01-4.

Supplementary Material Available: Listing of structure factor amplitudes (1 page). Ordering information is given on any current masthead page.

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Cesium Octachlorodirhenate(III) Hydrate. The Correct Structure and Its Significance with Respect to the Nature of Metal-Metal Multiple Bonding

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Received January 24, 1977

AIC700648

The crystal structure of Cs₃Re₂Cl₈·H₂O has been redetermined. The unit cell contains four Re₂Cl₈²⁻ anions, two of which are anhydrous and have a Re-Re distance of 2.237 (2) Å and the other two of which are coordinated in both axial positions by water molecules, with Re-O = 2.66 (3) Å, and have an Re-Re distance of 2.252 (2) Å. This result is in harmony with generally accepted views about the nature of the quadruple bond and corrects the erroneous claim made earlier by others that the hydrated ion had the shorter Re-Re distance. The compound crystallizes in space group P2₁/c with the following unit cell parameters: *a* = 9.323 (3) Å, *b* = 13.377 (2) Å, *c* = 11.979 (2) Å, β = 95.13 (2) Å, *V* = 1488.1 (6) Å³. For *Z* = 4 and a formula weight of 939.85 the calculated density is 4.19 g cm⁻³.

Introduction

For several years, work has been conducted in this laboratory to establish a fundamental and important feature of strong M-M multiple bonds, namely, that the strength of such a bond (as evidenced, inversely, by the M-M distance) is reciprocally related to the strength of metal-ligand interactions along the extensions of the M-M axis. Ligands in these positions are called axial ligands, L_{ax}, and we have proposed, on the basis of structural evidence, and rationalized, in terms of the orbital overlaps involved, the rule that, other factors being held constant

$$dr_{MM}/dr_{ML_{ax}} < 0$$

Empirical evidence for this rule was first discussed by Cotton and Norman¹ who dealt with Mo₂(O₂CR)₄L₂ systems, employing both crystallographic and Raman data. It was demonstrated that when there is a very strong M-M quadruple bond, the binding of axial ligands is very weak. Nevertheless, even within this regime of strong M-M bonding and weak M-L_{ax} bonding it was shown that attachment of L_{ax} lengthens the M-M bond. Thus *r*_{MoMo} in Mo₂(O₂CCF₃)₄ is 2.090 Å and *ν*_{MoMo} is 397 cm⁻¹ whereas in Mo₂(O₂CCF₃)₄(py)₂, *r*_{MoMo} = 2.129 Å and *ν*_{MoMo} is 367 cm⁻¹.

Raman spectroscopy was also shown¹ to be a powerful tool for following this behavior, since the *ν*_{Mo-Mo} frequencies for Mo₂(O₂CCF₃)₄ were shown to decrease as the donor capacity (Lewis basicity) of the solvent in which the spectrum was run was increased. Similar results were published a little later by Ketteringham and Oldham.²

More recently, this relationship has been discussed further.^{3,4} It has been specifically observed that since the binding of axial ligands probably depends primarily on the use of the metal d_{z²} orbitals, which are also primarily responsible for the σ component of the M-M bond, increasing strength of the M-L_{ax} bonds must be correlated with decreasing strength of the M-M bond and thus with increasing M-M bond length.

In view of this line of thinking, we were surprised, and incredulous, to read⁵ that in Cs₃Re₂Cl₈·H₂O, there are two crystallographically independent Re₂Cl₈²⁻ ions, one having axially coordinated H₂O ligands and *r*_{ReRe} = 2.210 Å and the other lacking the axial ligands and having *r*_{ReRe} = 2.226 Å. It seemed evident from the discussion that this result was intended to be taken seriously. The structure was said to have been refined by least squares but the final discrepancy index was only 14.6%, the data used were measured photographically, and no absorption corrections were applied even though a large crystal (0.35 × 0.20 × 0.25 mm) of a substance with