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Gas-Phase Electron Diffraction Study of Tetrachlorooxoosmium(VI)

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Received February 20, 1986

The molecular structure of $OsOCl_4$ has been studied by gas-phase electron diffraction at an average nozzle temperature of 40 °C. The experimental data are fitted by a square-pyramidal model of C_{4v} symmetry in which the osmium atom is 0.709 (16) Å above the plane of the four chlorine atoms. The distances and angles are r_a(Os=O) = 1.663 (9) Å, r_a(Os—Cl) = 2.258 (5) Å, $\angle$O=Os—Cl = 108.3 (4)°, and $\angle$Cl—Os—Cl = 84.4 (3)°. The estimated uncertainities are 2σ plus estimates of errors arising from wavelength measurement, etc. The results are compared with those for $ReOCl_4$ and $WOCl_4$; thus the effect of having successively two, one, and no electrons in the d_{xy} orbitals of these C_{4v} species is observed. The best fit between the theoretical and experimental curves was obtained when the phase shift factors of osmium were replaced by those of lead.

Introduction

The shapes of main-group species in the gas-phase are readily understood by the application of simple rules that have been evolved by a number of workers.[2-4] For example, the observation that $XeOF_4$ has a C_{4v} structure[5] while SOF_4 has a C_{2v} structure[6] based upon a trigonal bipyramid (the oxygen atom being in the trigonal plane) is rationalized by assuming that the lone pair in $XeOF_4$ executes a stereochemical effect; the electron pairs around the xenon atom form an approximate octahedron. In the two compounds SOF_4 and $WOCl_4$ the central atoms have the same number of valence electrons, but whereas SOF_4 has, as stated above, a C_{2v} structure, molecular $WOCl_4$ has C_{4v} symmetry.[7] The formation of molecules with C_{4v} symmetry in the latter case is attributable to the participation of some of the tungsten d orbitals in the bonding. However the influence of d electrons on gas-phase molecular structures is not so well understood as comparatively few gas-phase structural studies on transition-metal compounds have been made and even fewer on groups of compounds with the same stoichiometry but differing numbers of d electrons. Accordingly we have commenced a study with the aim of determining the influence of an increasing number of d electrons (and the nuclear charge (Z)) on $MOCl_4$ species were M is a transition element. It is to be expected that the observed effects would be largely masked in the solid state; therefore, we have concentrated upon gas-phase electron diffraction structural determinations. We now report the structure of $OsOCl_4$, and so by considering the results with those already published for $ReOCl_4$[8] and $WOCl_4$[7] we are able to compare the data for d^2, d^1 and d^0 species of the same stoichiometry and for elements drawn from the same period of the periodic table.

Experimental Data and Structural Analysis

Tetrachlorooxoosmium(VI) was prepared by the published route[9] in which OsO_4 was allowed to react with BCl_3. We found that a higher yield and purer product was obtained if the reaction time was reduced from the recommended 24 h to 10 h.

Electron-diffraction photographs were obtained by using the Balzers' Edigraph KDG-2 apparatus of the University of Oslo.[10,11] Data were obtained at nozzle-to-plate distances of 49.789 and 24.791 cm and at a nozzle temperature of 40 °C. The electron wavelength (0.05865 Å) was calibrated against benzene.[12] Five plates from the short and six from the long camera distances were selected for analysis. The data were processed as previously described,[8,13-16] and an average curve was produced, which is shown in Figure 1.

Table I. Structural Results for $OsOCl_4$ and Related Molecules[a]

	$OsOCl_4$[b]	$ReOCl_4$[c]	$WOCl_4$[d]	$MoOCl_4$[e]
r_a(M=O)	1.663 (9)	1.663 (9)	1.685 (15)	1.658 (5)
r_a(M—Cl)	2.258 (5)	2.270 (5)	2.280 (3)	2.279 (3)
r_a(O···Cl)	3.196 (9)	3.148 (22)	3.177 (35)	3.108 (13)
r_a(Cl···Cl)(cis)	3.031 (8)	3.090 (17)	3.146 (15)	3.142 (8)
r_a(Cl···Cl)(trans)	4.287 (11)	4.367 (23)	4.449 (21)	4.440 (11)
		Amplitudes		
l(M=O)	0.047 (9)	0.031 (13)	0.045 (11)	0.043 (12)
l(M—Cl)	0.057 (3)	0.045 (3)	0.052 (4)	0.043 (12)
l(O···Cl)	0.098 (15)	0.110 (30)	0.095 (38)	0.099[f]
l(Cl···Cl)(cis)	0.091 (6)	0.095 (6)	0.122 (28)	0.125 (9)
l(Cl···Cl)(trans)	0.137 (20)	0.116 (18)	0.118 (20)	0.123 (8)
		Angles		
$\angle$O=M—Cl	108.3 (4)	105.5 (15)	102.4 (13)	102.8 (7)
$\angle$Cl—M—Cl	84.4 (3)	85.6 (11)	87.3 (5)	87.2 (3)
	Distance of Metal Atom from the Plane of Four Chlorine Atoms			
	0.709 (16)	0.607 (75)	0.490 (52)	0.505 (27)

[a] Distances [r_a for $OsOCl_4$, $ReOCl_4$, and $WOCl_4$ and r_g for $MoOCl_4$] and vibrational amplitudes are in Å, and angles are in deg. The error limits may have different meanings in the different investigations. [b] Data from present study. [c] Reference 8. [d] Reference 7. [e] Reference 19. [f] Constrained.

Data from the long and short camera distances were obtained over the s ranges of 2.00–14.75 $Å^{-1}$ and 4.00–29.00 $Å^{-1}$, respectively, at intervals of s = 0.25 $Å^{-1}$ (where $s = 4\pi\lambda^{-1}$ (sin θ) where 2θ is the scattering angle and λ is the electron wavelength). The reduced intensity data and the background curves are available as a supplementary publication.

A model with C_{4v} symmetry was found to be consistent with the experimental data. In such a model there are five different interatomic distances [r(Os=O), r(Os—Cl), r(O···Cl), r(Cl···Cl(trans)), and r(Cl···Cl(cis))]. These distances can all be defined by three parameters: r(Os—O), r(Os—Cl), and the $\angle$O=Os—Cl angle.

The scattering factors and phase shift factors were taken from the sets given in ref 17 and 18. The final results are given in Table I, and the correlation matrix for the refined parameters is shown in Table II.

The radial distribution curve was calculated in the usual manner after multiplication of the $s(I_m(s))$ values by $[Z_{Os}Z_{Cl}/f_{Os}f_{Cl}]\ \exp(-0.0025s^2)$. In Figure 2 are depicted the experimental and theoretical RD curves, the latter being generated by using the phase shift factors of osmium. RD curves were also calculated with the theoretical curves obtained with a variety of phase shift factors in place of those of osmium. In Figure 2

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Table II. Correlation Matrix (×100) for $OsOCl_4$ from the Refinement in Which the Phase Shift Factors for Lead Were Used

	σ(least squares)	r_1	r_2	∠	l_1	l_2	l_3	l_4	l_5
r(Os=O)	0.0023	100	15	−10	1	−2	1	−7	1
r(Os—Cl)	0.0008		100	26	1	−3	−7	−15	1
∠(O=Os—Cl)	0.50			100	−7	−6	−65	−56	3
l(Os=O)	0.0023				100	54	15	20	4
l(Os—Cl)	0.0009					100	17	25	6
l(O···Cl)	0.0076						100	77	2
l(Cl···Cl)(cis)	0.0029							100	3
l(Cl···Cl)(trans)	0.0101								100

Table III. Results of Six Refinements for $OsOCl_4$ in Which the Phase Shift Factors of Osmium, Platinum, Mercury, Lead, Polonium, and Radon Were Used Successively for the Osmium Atom[a]

phase shift factor	Os	Pt	Hg	Pb	Po	Rn
r_a(Os=O)	1.663 (12)	1.663 (11)	1.663 (10)	1.663 (9)	1.663 (12)	1.664 (17)
r_a(Os—Cl)	2.258 (6)	2.258 (6)	2.258 (5)	2.258 (5)	2.258 (5)	2.258 (6)
r_a(O···Cl)	3.194 (11)	3.195 (10)	3.195 (9)	3.196 (9)	3.196 (12)	3.194 (17)
r_a(Cl···Cl)(cis)	3.033 (9)	3.032 (8)	3.032 (8)	3.031 (8)	3.032 (10)	3.033 (14)
r_a(Cl···Cl)(trans)	4.288 (12)	4.288 (12)	4.287 (11)	4.287 (11)	4.287 (14)	4.289 (20)
			Amplitudes			
l(Os=O)	0.032 (19)	0.035 (16)	0.039 (12)	0.047 (9)	0.054 (11)	0.059 (14)
l(Os—Cl)	0.047 (5)	0.049 (5)	0.052 (3)	0.057 (3)	0.062 (3)	0.066 (4)
l(O···Cl)	0.087 (20)	0.089 (18)	0.091 (16)	0.098 (15)	0.106 (21)	0.115 (33)
l(Cl···Cl)(cis)	0.081 (8)	0.083 (7)	0.086 (6)	0.091 (6)	0.098 (8)	0.105 (11)
l(Cl···Cl)(trans)	0.125 (29)	0.127 (26)	0.131 (22)	0.137 (20)	0.144 (25)	0.149 (33)
			Angles			
∠O=Os—Cl	108.2 (5)	108.2 (5)	108.3 (4)	108.3 (4)	108.3 (7)	108.2 (11)
∠Cl—Os—Cl	84.4 (3)	84.4 (3)	84.4 (3)	84.4 (3)	84.4 (4)	84.4 (7)
			Distance of Os Atom above the Plane of Four Chlorine Atoms			
	0.705 (20)	0.706 (19)	0.707 (16)	0.709 (16)	0.708 (25)	0.705 (42)
R^b	0.168	0.149	0.125	0.111	0.136	0.176

[a] Errors are 2σ plus estimates of uncertainties in wavelength, etc. [b] $R = [\sum w_i\Delta_i^2/\sum w_i(I_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = [I_i(\text{obsd}) - I_i(\text{calcd})]$.

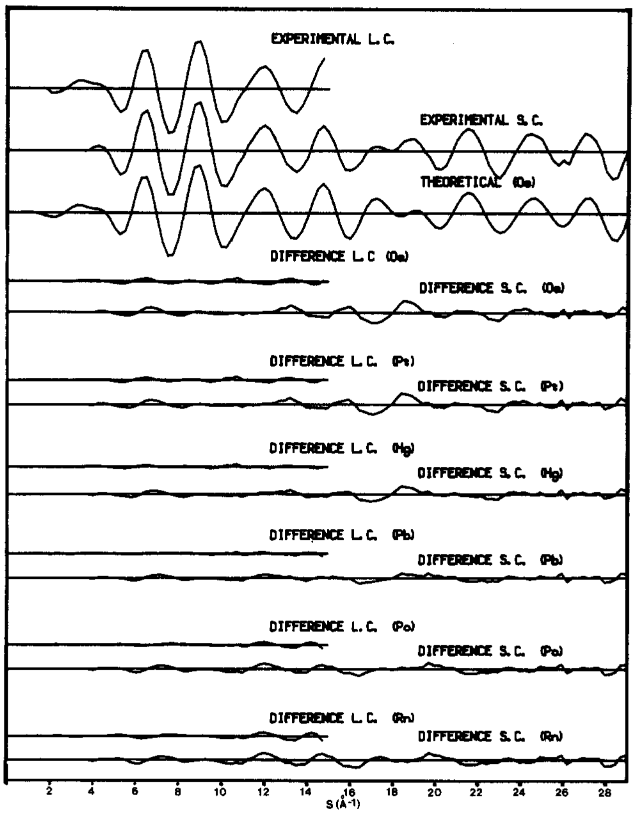

Figure 1. Intensity curves $sI_m(s)$ for $OsOCl_4$. The two experimental curves are averages for the plates at a given distance. The theoretical curves were calculated with the parameters given in Table III. Theoretical curves were also calculated in which the phase shift factors of Pt, Hg, Pb, Po, and Rn were used. The resulting difference curves are shown.

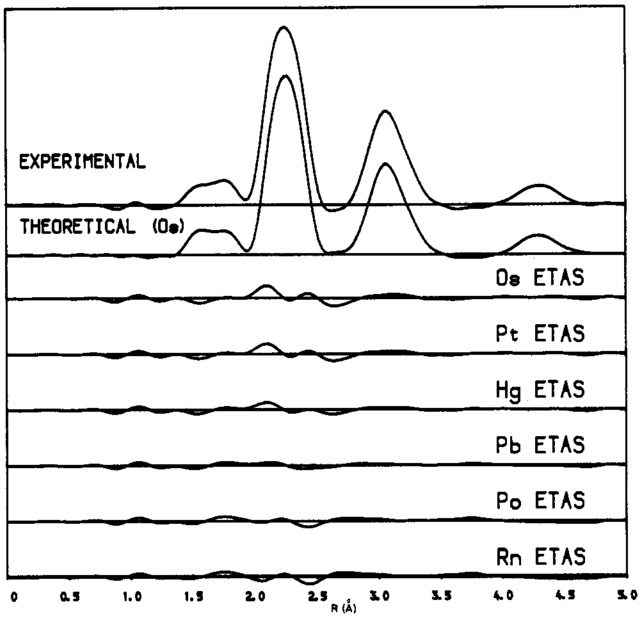

Figure 2. Radial distribution curves of $OsOCl_4$. The curves were calculated from the curves in Figure 1 after multiplication by $[Z_{Os}Z_{Cl}/f_{Os}f_{Cl}]\exp(-0.0025s^2)$ for theoretical data for the unobserved area $s < 2.0$ Å^{-1}. Difference curves are also shown for calculations in which the phase shift factors (η) of Pt, Hg, Pb, Po, and Rn were used instead of η(Os).

the resulting difference curves are shown.

From an examination of Figure 1 it is apparent that there are small differences between the theoretical [calculated with phase shift factors (η) of osmium] and experimental intensity curves $[s(I_m(s))]$ around s = 18 Å^{-1}. It is also apparent that $\eta_{Os} - \eta_{Cl} = \pi/2$ at a lower value of s in the experimental curve than in the theoretical curve. Therefore we decided to study the effect on the calculated theoretical curve of substituting the phase shift factors of osmium with those of neighboring elements in the periodic table. None of the refinements using data for elements of lesser atomic number than osmium were satisfactory. In Table III and Figures 1 and 2 are given the results for refinements using phase shift data for osmium, platinum, mercury, lead, polonium, and radon. Examination of the *R* factors, [the radial distribution and molecular intensity difference curves (Figures 1 and 2)], and the errors quoted in Table III reveal that the refinement in which phase shift factors for lead were used gave the lowest *R* factors and the smallest errors.

Changing the phase shift factors has no significant effect upon the distances and angles (see Table III) but does modify the amplitudes of vibration, there being a gradual increase in the amplitudes with increase in *Z*. Unfortunately complete vibrational spectroscopic data for $OsOCl_4$ are not available so we were unable to calculate reliable theoretical values for the vibrational amplitudes.

We can offer no good explanation for the results, but it would appear worthwhile to examine the effect of varying the phase shift factors when studying the structures of molecules containing atoms with a large nuclear charge.

Results and Discussion

The results obtained in our investigation of $OsOCl_4$ are consistent with the molecule having C_{4v} symmetry in the gas phase. There may be very small deviations from ideal C_{4v} symmetry but C_{3v} and C_{2v} models did not give a satisfactory fit to the data. The results for $OsOCl_4$ with those for $ReOCl_4$[8] $WOCl_4$,[7] and $MoOCl_4$[19] are included in Table I. The gas-phase structure of $OsOF_4$ has been determined by electron diffraction,[20] and a value of 1.624 (25) Å was assigned to r_a(Os=O). Thus the value for the fluoride appears to be shorter than that for the chloride [Δr_a(Os=O) = 0.037 (28) Å], which is in accord with r_a(W=O) being shorter in WOF_4[21] than in $WOBr_4$[22] [Δr_a(W=O) = 0.017 (9) Å]. These differences between the fluorides and chlorides have been attributed to electronegativity effects.

For the species $MOCl_4$ the variation in r_a(M=O) (M = Os, Re, W) with change in *Z* is small [r_a(W=O) − r_a(Os=O) = 0.024 (19) Å] and in view of the errors is probably not significant (see Table I). However, there are significant changes in r_a(M–Cl) (M = W, Re, Os) with the values being in the order r_a(W–Cl) > r_a(Re–Cl) > r_a(Os–Cl) [r_a(W–Cl) − r_a(Os–Cl) = 0.022 (7) Å] while r_a(W–Cl) is equivalent to r_a(Mo–Cl). The results show that the effect of increases in *Z* across a period is to cause decreases in r_a(M–Cl). In contrast the r_a(M–Cl) values for the 4d and 5d members of a given group appear to be constant, the latter observation being attributable to the "lanthanide contraction" reducing bond lengths for 5d species.

That the O=W—Cl angle in $WOCl_4$ is above 90° is a consequence of the influence of the electrons in the π component of the W=O bond. Indeed in $XeOF_4$[5] the O=Xe—F angle is greater than 90°, thus showing that interaction between the multiple bond and the cis fluorine atoms is greater than that of the fluorine atoms with the lone pair which is trans to Xe=O. The O=M—Cl angle is larger in the osmium compound than in the related tungsten species [∠O=Os—Cl − ∠O=W—Cl = 5.8 (1.4)°] with an accompanying decrease in the cis and trans Cl···Cl distances of 0.113 (17) and 0.159 (24) Å, respectively. The increase in ∠O=M—Cl along the series tungsten, rhenium, and osmium we do not believe is caused by an increase in steric requirements of the M=O double bond but is attributable to the steric influence of the presence of one electron in $ReOCl_4$, and two electrons in $OsOCl_4$, in the nonbonding d_{xy} orbital.

Acknowledgment. We thank NATO for a travel award to K.H. and D.A.R. (Grant No. 117/82) and the SERC for the support of C.J.H. We are grateful to Snefrid Gundersen of the University of Oslo for technical help.

Registry No. $OsOCl_4$, 36509-15-6.

Supplementary Material Available: Tables of total scattered intensities $s^4I_t(s)$ from each plate and calculated backgrounds for each plate (6 pages). Ordering information is given on any current masthead page.

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Transition-Metal Complexes of a Binucleating Clathrochelate Ligand: A Reinvestigation of the Crystal Structure

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Received February 27, 1986

The crystal structure of the complex $(LFeCo)BF_4$, where L is the ligand resulting from the condensation of 3 mol of 2-hydroxy-5-methylisophthalaldehyde and 2 mol of tris(aminoethyl)amine, has been rerefined in the rhombohedral space group $R\bar{3}c$: *a* = 11.833 Å, *c* = 49.603 Å, *Z* = 6. The two metal sites in the complex are structurally equivalent; the original refinement in space group *Cc* did not reveal this equivalence.

Recently, Timken, Marritt, Hendrickson, Gagnê, and Sinn (ref 1; hereinafter, TMHGS) reported the synthesis and magnetic properties of a number of binuclear metal complexes $(LM_1M_2)BF_4$, where M_1 and M_2 are transition metals Cu, Fe, Co, or Mn and L is the chelating ligand resulting from the Schiff-base condensation of 3 mol of 2-hydroxy-5-methylisophthalaldehyde and 2 mol of tris(aminoethyl)amine; both homobinuclear (M_1 = M_2) and heterobinuclear compounds were made. The structure of these compounds was characterized by a single-crystal X-ray diffraction analysis of the heterobinuclear Fe–Co compound; X-ray powder diffraction photographs indicated that all the compounds prepared, with the exception of a hydrated Cu–Cu species, are isostructural. The crystal structure of the prototypical Fe–Co compound was described as monoclinic, space group *Cc*, with the metal atoms occupying ordered, crystallographically distinct sites. On the other hand, Mössbauer measurements suggested that there is only "one type of coordination site" in the Fe–Mn complex.

We have reexamined the crystallographic data of THMGS and find that the structure of the Fe–Co compound is properly described in the rhombohedral space group $R\bar{3}c$ (No. 167) and that the two metal sites are equivalent.

Experimental Section

The monoclinic unit cell chosen by TMHGS has the dimensions *a* = 20.501 (10) Å, *b* = 11.833 (3) Å, *c* = 17.889 (9) Å, β = 112.44 (4)° and

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