CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE MATERIALS RESEARCH CENTER,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

A Mass Spectrometric Study of Transition Metal Oxo- and Thiohalides[1]

BY DONALD L. SINGLETON AND FRED E. STAFFORD*

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A molecular beam mass spectrometric study of $MoOCl_4$, $WOCl_4$, $WSCl_4$, $ReOCl_4$, and $OsOCl_4$ shows the vapors to be comprised primarily of the corresponding monomers. Because of the synthesis used, the vapor above a sample of $WOBr_4$ gave rise to the ions $W_2Br_n^+$ ($3 \leq n \leq 6$) (from W_2Br_6) and contained the molecules WBr_6 or WBr_5. All the oxo- and thiotetrahalides reacted with surfaces of the mass spectrometer to give volatile products and are likely to do so in microwave, electron diffraction, or matrix-isolation apparatuses. Other new species observed as impurities and/or reaction products are MoO_2BrCl, $W_2Br_xCl_y^+$ ($x + y \leq 6$, from the corresponding neutrals), $WOSCl_2$, WS_2Cl_2, $ReO_2Cl_2^+$, OsO_3Cl^+(?), $OsO_2Cl_2^+$, and OsO_2Cl^+. (The neutral progenitors of the species listed only as ions were not identified.) The fragmentation patterns of $MoOCl_4$, $WOCl_4$, $WOBr_4$, and $WSCl_4$ are similar with very weak (<1%) parent ions. Previous assignments of WOX_3^+ ($X = Cl, I$) to gaseous WOX_3 are therefore questioned. The parent ion abundance increases markedly in the series $WOCl_4$ (0.36%), $ReOCl_4$ (18%), $OsOCl_4$ (26%), as it does in the series $TaCl_5$, WCl_5. The fragmentation patterns measured for CrO_2Cl_2, MoO_2Cl_2, and MoO_2Br_2 are approximately identical. Except for the only reported dioxodifluoride, all the known group VIb dioxodihalide fragmentation patterns are similar, with the parent ion most intense. The fragmentation pattern of ReO_3Cl also was measured. Systematics in the fragmentation patterns of all the halide–oxohalide–oxide sequences are sought and discussed. For the group VIb oxo- and thiotetrahalides AP(parent − halogen) ≈ IP(parent), consistent with the extensive fragmentation observed. The electron-impact ionization potentials of the group VIb dioxodihalides are insensitive to changes of the central metal but are strongly dependent on the halogen. Evidence indicates that the ionized electron comes primarily from the oxygen in the fluoride but from the halogen in the others. Ionization potentials of four coordinated halides and oxohalides are correlated and predictions are made for $NbOCl_3$, H_2SO_4, ReO_3F, etc.

Introduction

The transition elements are versatile in forming a variety of volatile halides, oxohalides, and oxides about which much is known. The properties of the halides[2] and the oxohalides[3] have been reviewed. Recently, the thiohalide $WSCl_4$,[4,5] as well as other thiohalides,[4,6,7] has been reported. Relatively little is known, however, about their gas-phase structures, in part because their modes of vaporization are poorly known.

The diversity of the molecules of interest permits one to examine several series in which various of the structural properties are expected to vary systematically. Such series are $HfCl_4$, $TaOCl_3$, WO_2Cl_2, ReO_3Cl, OsO_4 or $MoCl_6$, $MoOCl_4$, MoO_2Cl_2, MoO_3. There are series where the halogen is changed, where oxygen is replaced by sulfur, and where the central atom is changed: $WOCl_4$ (d^0), $ReOCl_4$ (d^1), and $OsOCl_4$ (d^2).

By studying all of the members of one of these series, rather than, say, only the group VI dioxodihalides, one should be able to obtain many more experimental measurements than the independently variable parameters in a theoretical treatment.

The present study is concerned primarily with the group VI–VIII oxotetrahalides and with tungsten thiotetrachloride. For various reasons, however, certain dioxodihalides and other molecules also were studied. A motivation for undertaking the study was the report of infrared studies of various gaseous oxotetrahalides.[8-11] Since many of these molecules are six-coordinate polymers in the condensed phase and since the compounds in question decompose or react readily, it was thought appropriate to identify which molecules are present in the vapor phase. Such identification is obviously prerequisite to matrix isolation, electron diffraction, etc., studies.

Mass spectrometric analysis requires knowledge of fragmentation patterns and, particularly, of whether a molecule is likely to give a parent ion. This knowledge is especially important in the case of the transition elements and/or high-temperature systems, where versatility of oxidation state is common. While correlation of fragmentation patterns for organic molecules is relatively advanced[12] and beginnings have been made[13-15] for inorganic systems, this is still considered[16] to be the limiting factor in certain areas of high-temperature mass spectrometry. While the most reliable correlation seems to be with the spacing between the ionization potential and the appearance potential of the first fragment ion, this approach requires rather detailed knowledge. A more empirical approach, such as using trends in the periodic table, is desired.

The purposes of the present study are (1) to determine the modes of vaporization of $MoOCl_4$, $WOCl_4$, $WOBr_4$, $WSCl_4$, $ReOCl_4$, and $OSOCl_4$, (2) to determine the mass spectra, (3) to determine the electron-impact

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Table I

Synthetic Methods and Analyses for Oxo- and Thiotetrahalides[a]

			MYX_4 anal,[b] %					
			M		Y		X	
Compound	Method	Ref	Calcd	Found	Calcd	Found	Calcd	Found
$MoOCl_4$	$SOCl_2 + MoO_3$	22, 23	37.8	37.6	6.3	6.6	55.9	55.6
$WOCl_4$	$SOCl_2 + WO_3$	24	53.8	53.4	4.7	4.5	41.5	41.2
$WOBr_4$	$CBr_4 + WO_3$	25	35.4	33.9	3.1	3.2	61.5	59.7
$WSCl_4$	$S + WCl_6$	5	51.4	51.3	9.0	11.9	39.6	35.4
$ReOCl_4$	$O_2 + ReCl_5$	26	54.1	54.6			41.2	40.9
$OsOCl_4$	$Cl_2 + O_2 + Os$	27	c					

[a] Details are given also by Singleton.[20] [b] Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. [c] There was insufficient sample for chemical analysis.

appearance potentials for these and related molecules, and (4) to examine correlations of these last two properties. Because of a discrepancy between two published mass spectra[17,18] of MoO_2Cl_2, its fragmentation pattern and ionization potential were measured, as well as those of CrO_2Cl_2, MoO_2Br_2, and ReO_3Cl.[19,20] As a result, a correlation—the fifth purpose of our study—has been made for the IP's of various four-coordinate molecules. This correlation seems to be as accurate as the high-temperature electron-impact measurements.

Experimental Section

Preparation of Compounds.—Syntheses and manipulations were performed using vacuum and inert-atmosphere techniques[21] to avoid hydrolysis of the products. Salient features are given here and the details are reported elsewhere.[20]

CrO_2Cl_2.—An excess of lithium chloride was heated to 200° under vacuum with CrO_3, the red CrO_2Cl_2 product condensing in a trap immersed in liquid nitrogen. The product was purified by trap to trap distillation.

MoO_2Br_2.—A 20:1 mole ratio mixture of lithium bromide and molybdic anhydride was evacuated overnight in a Pyrex tube at 200°. The temperature was raised gradually to 450° over 48 hr while pumping on the mixture was continued. Brown crystals condensed on the cooler portions of the tube. These were used for the mass spectrometric study. This synthetic method is similar to one previously reported.[8]

The methods[22-27] used to prepare the oxo- and thiotetrahalides are summarized in Table I. The products were purified by vacuum sublimation. Exposure of all the compounds to light was minimized.

Mass Spectrometry.—Mass spectra were obtained with a molecular beam mass spectrometer (Nuclide Corp. Model 12-60 HT). The mass spectra reported here were obtained with nominally 70-eV ionizing electrons. The emission current was regulated at 1.2 mA, corresponding to a trap current of about 10^{-5} A. The ion repeller voltage was always zero with respect to the ionization chamber. The total pressure in the ion source chamber, as indicated by an ionization gauge, was about 1×10^{-7} Torr.

Positive ions were accelerated through 4000 V and momentum was analyzed by a 60° sector magnet with a 12-in. radius of curvature. By changing the magnetic field strength, different ion peaks were focused on a 50% transmission grid and the first dynode of a 20-stage Be–Cu electron multiplier with 3.3 kV applied across the dynode string.

A movable beam defining slit, called the shutter, was used to differentiate ions due to background molecules from those due to the molecular beam originating in the crucible.

Samples were introduced into the mass spectrometer by means of either an external inlet or a Knudsen cell. In both cases, an ionization gauge indicated a pressure of about 5×10^{-7} Torr in the crucible region of the mass spectrometer.

The external-inlet system was identical with that reported previously.[28] Sample vapor distilling from a Pyrex tube, maintained below room temperature, was regulated with a packless Hoke valve before entering a nickel Knudsen cell from which it effused through a 5×10^{-3} cm^2 orifice. The vapor also came in contact with stainless steel, Monel, aluminum, copper, and brass. Break-seal tubes eliminated exposure of the samples to the atmosphere.

Less volatile samples were introduced into the mass spectrometer by placing them directly in a nickel Knudsen cell which was heated to give sufficient vapor pressure. This Knudsen cell orifice was about 8×10^{-3} cm^2. The entire inlet port of the mass spectrometer was enclosed in a polyethylene glove bag. When the spectrometer was opened to change samples, the vacuum system, Knudsen cell, and sample were thus protected at all times by an atmosphere of liquid nitrogen boil-off. The Knudsen cell was heated to about 400° under vacuum in the mass spectrometer prior to placing the sample in it.

Data were collected with the aid of an on-line computer as described elsewhere.[29]

Appearance potentials were determined by the vanishing-current technique[30] using argon (IP = 15.76 eV)[31,32] or a mercury isotope (IP = 10.44 eV)[31-33] to calibrate the ionizing electron energy scale.

The mass to charge ratios of ion peaks were determined by counting background ion peaks or by appropriately measuring the magnetic field of the mass analyzer.

Data and Results

Ions were identified by mass number, isotopic distribution, shutter effect, dependence on inlet valve setting, sample temperature, and, for lower mass ions, the mass defect. In all cases, there was good agreement between the measured isotopic distribution of an ion and the distribution calculated from isotopic abundances of the atoms.[33] If the isotopes of two or more ions occurred at many of the same mass peaks, such as in the case of WS^+ (214–220) and WCl^+ (217–223), the percentage of each present was usually calculated by a linear least-squares treatment.[20]

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TABLE II

FRAGMENTATION PATTERNS (70 eV) OF CrO_2F_2, CrO_2Cl_2, MoO_2Cl_2, AND MoO_2Br_2

	CrO_2F_2	CrO_2Cl_2				MoO_2Cl_2			MoO_2Br_2	
Ion	Ref 52	This work	Ref 53	Ref 52	Ref 17	This work	Ref 17	Ref 18	This work	Ref 54
$MO_2X_2^+$	58	100	100	100	100	100	100	10	100	100
MO_2X^+	22	28	51	52	54.8	34	61.4	100	26	42.5
MO_2^+	3	5.2	12	14	16.0	3.6	12.8	13.1	3.4	7
MOX_2^+	42	2.2	4	2	3.1	2.2	3.8		1.8	2.4
MOX^+	17	10	25	19	27.8	7.5	19.0		6.9	12
MO^+	3	4.7	14	12	21.9	4.2	19.0	3.9	4.8	4.7
MX_2^+	100	2.0	4	2	4.0	1.1			1.1	1.7
MX^+	11	4.2	12	7	15.5	2.6	10.8		2.8	4.9
M^+	17	7.5	33	21	46.2	4.8	25.6	11.0	3.8	9.5

TABLE III

FRAGMENTATION PATTERNS (70 eV) OF MOX_4 AND $WSCl_4$ MOLECULES[a]

	VI					VII	VIII
Ion	$MoOCl_4$	$WOCl_4$	$WOBr_4$[d]		$WSCl_4$[c]	$ReOCl_4$	$OsOCl_4$
MYX_4^+	0.35	0.55	0.97	1.0	0.62	36.7	71.8
MYX_3^+	100	100	100	100	100	100	100
MYX_2^+		15.1	26.4	31.2	14.8	25.2	48.5
MYX^+		7.2	8.8	11.6	6.5	6.2	6.7
MY^+			3.6	5.4	2.4	1.9	3.1
MX_4^+	0.07	0.20	*b*	0.28	5.0	0.19	0.64
MX_3^+	3.8	4.2	*b*	6.3	7.6	4.9	8.8
MX_2^+		8.0	*b*	13.4	7.8	8.4	15.2
MX^+		5.2	*b*	9.4	5.0	6.4	10.2
M^+		3.7	*b*	5.4	3.6	5.2	12.0
X_2^+		<0.2	33.4	6.6	0.03	0.04	0.43
MYX_4^{2+}						0.17	
MYX_3^{2+}		1.7	1.2		2.4	5.0	1.1
MYX_2^{2+}		1.6	0.17		0.89	0.56	
MYX^{2+}		0.16	0.02		0.29	0.01	
MY^{2+}						0.01	
MX_4^{2+}			*b*			0.03	
MX_3^{2+}		1.3	*b*		0.53	1.6	1.3
MX_2^{2+}		1.8	*b*		0.65	0.75	0.12
MX^{2+}		0.62	*b*		0.35	0.30	
M^{2+}		0.09	*b*		0.07	0.17	0.15

[a] The numbers given are relative to MOX_3^+ or $WSCl_3^+$ taken as 100. [b] Ions from WBr_6 or WBr_5 interfere; see Singleton.[20] [c] The $WOCl_4$ impurity is subtracted out. [d] Gupta[40] values in the right column, where intensities are corrected for isotopes.

The reported intensities were not corrected for variation of secondary electron multiplier gain with mass nor for molecular complexity. The gains measured for $^{35}HCl^+$, $^{202}Hg^+$, and $^{282}MoO_2Br_2^+$ were 2 × 10^5, 1 × 10^5, and 1 × 10^5, respectively.

Individual compounds will be discussed with reference to the ions observed and the neutral molecules in the vapor. The tables of mass spectra give molecular *beam* intensities, unless the title specifically notes *total* (beam + background) intensity. The fragmentation patterns of the dioxodihalides are given in Table II, and those of the oxo- and thiotetrahalides are given in Table III.

Chromyl Chloride.—With the sample at −78° and using the external inlet, the only chromium-containing ions detected were due to CrO_2Cl_2.

Molybdenyl Chloride.—When the molybdenum oxotetrachloride sample was at 0° in the external inlet, only ions attributed to the impurity MoO_2Cl_2 were detected. The upper limit on the $MoOCl_3^+$ intensity, which is the most abundant ion in the $MoOCl_4$ fragmentation pattern, was 0.2% of the $MoO_2Cl_2^+$ intensity.

Molybdenyl Bromide.—The fragmentation pattern of MoO_2Br_2 was obtained using the Knudsen cell at 59°. The ions MoO_2BrCl^+, $MoO_2Cl_2^+$, and $MoOCl_3^+$ gave beam intensities 2.2, 3.0, and 0.01%, respectively, of the $MoO_2Br_2^+$ beam intensity. The first two ions are assigned to MoO_2BrCl and MoO_2Cl_2, which are probably formed by exchange reactions of MoO_2Br_2 with chloride residues. As will be evident later, $MoOCl_3^+$ is likely due to a $MoOCl_4$ impurity. No other molybdenum-containing ions were observed. The upper limit on the intensities of ions higher in mass than MoO_2Br_2 and originating from the crucible was 0.01% of the $MoO_2Br_2^+$ intensity.

Molybdenum Oxotetrachloride.—A large amount of MoO_2Cl_2 prevented obtaining a complete fragmentation pattern of $MoOCl_4$ using either the external inlet at about 25° or the Knudsen call at 36°. The MoO_2Cl_2 seemed to arise by reaction of $MoOCl_4$ on the spectrometer surfaces, as there was a considerable delay between opening the inlet valve of the external inlet and observing ions due to $MoOCl_4$. Ions attributed to MoO_2Cl_2 were detected during this interval, and their beam intensity decreased when the sample temperature was raised from 0° to about 25°, although their total intensity increased.

The appearance potentials of $MoOCl_4^+$ and $MoOCl_3^+$ were 10.6 ± 1 and 10.9 ± 0.5 eV, respectively. The vapor pressure at 36° of $MoOCl_3$ is about 8 × 10^{-7} Torr,[34] which is too low to account for the $MoOCl_3^+$ intensity. In contrast, $MoOCl_4$ sublimes easily under vacuum at 50°.

The partial fragmentation pattern of $MoOCl_4$ in Table III was obtained with the external inlet at about 25°. A threefold higher intensity and a low appearance

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potential of 10.1 ± 1 eV for $MoCl_4^+$ using the Knudsen cell at 36° indicated a binary chloride impurity. The upper limit on $I(MoCl_5^+)$ was 2% of the $MoOCl_3^+$ intensity.

The upper limit on higher mass ions formed from beam species, up to m/e 500 (mol wt of $MoOCl_4$ ~256), was 0.01% of the $MoOCl_3^+$ intensity. Under these conditions, the vapor above solid $MoOCl_4$ is monomeric, confirming results obtained with the Victor–Meyer method.[35]

Tungsten Oxotetrachloride.—No ions were attributed to impurities effusing from the crucible using the Knudsen cell at 25°, although there were residual background ions due to WO_2Cl_2.

The appearance potentials of $WOCl_4^+$ and $WOCl_3^+$ were 10.8 ± 0.5 and 10.0 ± 0.5 eV, respectively. It is unlikely that $WOCl_3$ contributes significantly to the $WOCl_3^+$ intensity since it is reported as an involatile solid.[36,37] The vapor pressure of $WOCl_4$ is 10^{-3} Torr at 25°,[38] which is sufficient to account for the observed intensity.

There was no evidence of a binary chloride impurity. The appearance potential of WCl_4^+ was 16.0 ± 1 eV, consistent with its being a fragment ion of $WOCl_4$.

The upper limit on the beam intensity of ions with mass higher than that of $WOCl_4^+$ (mol wt ~344), up to m/e 660, was 0.01% of the $WOCl_3^+$ intensity. These results show $WOCl_4$ vapor is monomeric, consistent with early vapor density measurements.[39]

Tungsten Oxotetrabromide.—The major ions resulting from the molecular beam are listed in Table III. The $WOBr_4$ sample was introduced with the Knudsen cell at 112°. The appearance potentials of $WOBr_4^+$ and $WOBr_3^+$ were 11.5 ± 0.5 and 10.5 ± 0.5 eV, respectively. Gupta,[40] in his recent mass spectrometric study of $WOBr_4$, obtained values of 10.3 ± 0.3 eV for $WOBr_4^+$ and 10.3 ± 0.2 eV for $WOBr_3^+$. Despite the suggestion by the appearance potentials, $WOBr_3$ is unlikely to contribute to the $WOBr_3^+$ intensity because solid $WOBr_3$ is isostructural[36] with the reportedly involatile $WOCl_3$. The total vapor pressure above $WOBr_4$ at 112° is about 2×10^{-3} Torr[41] and can account for the observed intensities.

The intense WBr_5^+ ion and the appearance potentials of WBr_5^+ (9.4 ± 0.5 eV) and of WBr_4^+ (9.8 ± 0.5 eV) indicate a binary bromide impurity. The upper limit on WBr_6^+ was 0.01% of the $WOBr_3^+$ intensity. Using the same starting materials but conditions different from those used in this study to prepare $WOBr_4$, Pouraud and Chaigneau[42] have isolated WBr_6. Gupta,[40] who used a different synthesis for $WOBr_4$, did not report a binary bromide impurity.

The appearance potential for Br_2^+ was close to values reported for the ionization potentials of Br_2 (10.5–10.7 eV).[31]

Small intensities, less than about 1% of the $WOBr_3^+$ intensity, of the ions WO_2BrCl^+, $WOBrCl^+$, $WO_2Cl_2^+$, $WOCl_3^+$, $WOCl_2^+$, and WCl_n^+, $4 \leq n \leq 1$, were likely due to WO_2BrCl, WO_2Cl_2, $WOCl_4$, and a binary tungsten chloride. There were also small amounts of $C_6Br_6^+$ and $C_6Br_5^+$, probably due to C_6Br_6, a possible impurity in the synthetic materials.

At 128°, ions containing two tungsten atoms were observed, which were not detected at 112°. The total intensities of these ions, of general formula $W_2Br_xCl_y$, $x + y \leq 6$, are listed in Table IV.

TABLE IV
RELATIVE TOTAL INTENSITIES OF DIMERS OBSERVED ABOVE THE $WOBr_4$ SAMPLE[a]

	Rel intens			Rel intens	
Ion	b	c	Ion	b	c
$WOBr_3^+$	100		$W_2Br_3Cl^+$	0.06	12
WBr_5^+	14.0		$W_2Br_4Cl_2^+$	0.20	41
$W_2Br_6^+$	0.20	41	$W_2Br_3Cl_2^+$	0.33	69
$W_2Br_5^+$	0.29	60	$W_2Br_2Cl_2^+$	0.03	6
$W_2Br_4^+$	0.04	9	$W_2Br_3Cl_3^+$	0.08	17
$W_2Br_3^+$	0.06	13	$W_2Br_2Cl_3^+$	0.14	28
$W_2Br_5Cl^+$	0.29	60	$W_2Br_2Cl_4^+$	0.01	2
$W_2Br_4Cl^+$	0.48	100	$W_2BrCl_4^+$	0.12	25

[a] The $WOBr_4$ sample temperature was 128°; nominal 70-eV ionizing electrons. In this table, all intensities are total intensities obtained by scanning over the ion peaks. [b] Intensities are normalized to $WOBr_3^+$, the most abundant ion containing tungsten. [c] Intensities are normalized to $I(W_2Br_4Cl^+)$.

The pressure in the ion source, 10^{-7} Torr, was too low for ion–neutral reactions to be significant. The ions $W_2Cl_n^+$, $n \leq 6$, have been detected previously[43,44] and assigned[44] to W_2Cl_6. In the present study, no dimer ions containing more than six halogens were observed, and by analogy with W_2Cl_6, the neutral progenitors would be $W_2Br_xCl_y$, $x + y = 6$. Upper limits on the intensities of $W_2BrCl_5^+$ and $W_3Cl_6^+$ are 1 and 7%, respectively, of the $WOBr_4^+$ intensity. About 50% of the total intensity of these ions was due to molecular beam species.

Very small ion currents around m/e 940 could not be identified but may have been due to $W_3Br_5^+$. Ions due to W_3Cl_9 have been reported[44] above solid WCl_4. Gupta[40] did not report detecting ions with more than one tungsten atom.

Tungsten Thiotetrachloride.—The mass spectrum of $WSCl_4$ was obtained with the sample at 68° in the Knudsen cell. The most intense ion was $WSCl_3^+$. The appearance potentials of $WSCl_4^+$ and $WSCl_3^+$ were 10.4 ± 1 and 9.5 ± 0.5 eV. Since $WSCl_3$ is reported to be an involatile solid,[4] it should not contribute to the beam intensity of $WSCl_3^+$. On the other hand, $WSCl_4$ sublimes readily[4,5] and hence can account for the $WSCl_4^+$ and $WSCl_3^+$ ions.

The intensities of WCl_5^+ and WCl_4^+ were 0.03 and 5.0% of the $WSCl_3^+$ intensity. The WCl_4^+ relative intensity is larger than that of WCl_4^+ in the oxotetrahalide fragmentation patterns. Fragmentation of WCl_5 cannot account for all the WCl_4^+ intensity, since it fragments to give the WCl_5^+:WCl_4^+ intensity ratio as 13:100.[43,44] Solid WCl_4 is not very volatile, but the possibility of WCl_6 contributing to the WCl_4^+ intensity cannot be eliminated.

There was a small amount of $WOCl_4$ which decreased with time, as evidenced by the behavior of the $WOCl_3^+$ intensity.

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The inability of the mass spectrometer to distinguish between $WO_2Cl_2^+$ and $WSCl_2^+$ prevented determination of the presence of WO_2Cl_2, if any.

The ions identified by their isotopic distribution and shutter effect as $WS_2Cl_2^+$, WS_2Cl^+, and WS_2^+ gave intensities 1.0, 0.30, and 0.05% of the $WSCl_3^+$ intensity. The appearance potentials of $WS_2Cl_2^+$ and WS_2Cl^+ were 10.5 ± 0.5 and 12.6 ± 0.5 eV. These ions are assigned to WS_2Cl_2.

Isotopic distributions identified the ions $WOSCl_2^+$, $WOSCl^+$, and WOS^+ which gave intensities 4.2, 1.2, and 0.18% of the $WSCl_3^+$ intensity. The appearance potentials of $WOSCl_2^+$ and $WOSCl^+$ were 10.6 ± 0.5 and 13.8 ± 0.5 eV The neutral progenitor of these ions is likely $WOSCl_2$.

The ions S_n^+, $1 \leq n \leq 8$, were detected. The most intense of these was S_8^+, a feature of the mass spectra of freely evaporating sulfur flowers and of rhombic and equilibrated sulfur in a Knudsen cell.[45] Sulfur flowers used to synthesize $WSCl_4$ were apparently included in the sample.

The upper limit on ions of mass higher than WCl_5^+, originating from the molecular beam, was 0.01% of the $WSCl_3^+$ intensity.

Rhenium Oxotetrachloride.—With the sample of $ReOCl_4$ at 0° in the external inlet, only ions due to ReO_3Cl were detected initially. Ion intensities attributed to $ReOCl_4$ grew in after about 2 hr. The mass spectrum of ReO_3Cl obtained during this time is given in Table V and compared with one obtained in a different run and one reported elsewhere.[46] Because the ions of $ReOCl_4$ were growing in, the intensities of the lower mass fragments of ReO_3Cl should be taken as upper limits. The fragment intensities reported by Büchler, *et al.*,[46] may include contributions from $ReOCl_4$ and $ReO_2Cl_2^+$ fragments. The appearance potentials of ReO_2Cl^+ and ReO_3^+ were 12.3 ± 0.5 and 15.6 ± 0.5 eV.

TABLE V
MASS SPECTRUM (70 eV) OF ReO_3Cl

	Rel intens				Rel intens		
Ion	*a*	*b*	*c*	Ion	*a*	*b*	*c*
ReO_3Cl^+	100	100	100	ReO^+	7	<10	(3)
ReO_3^+	28	26	41	$ReCl^+$	2	<20	
ReO_2Cl^+	4	<10	(11)[e]	Re^+	10	4	
ReO_2^+	7	10	(13)	HCl^+	84		
$ReOCl^+$	*d*	10	(15)	Cl^+	42		

[a] Observed as an impurity from the $ReOCl_4$ sample which was at ice bath temperature. The $ReOCl_4$ ion intensities increased during the run; the intensities for the ions of lower mass are therefore upper limits. [b] Observed as a minor impurity in $OsOCl_4$. The $OsOCl_4$ sample was at ice bath temperature. [c] See Büchler, Blackburn, and Stauffer.[46] [d] Not measured. [e] The ion $ReO_2Cl_2^+$ and ions due to $ReOCl_4$ also were observed and could have contributed to the ion intensities in parentheses.

The fragmentation pattern of $ReOCl_4$ is given in Table III. The appearance potentials of $ReOCl_4^+$, $ReOCl_3^+$, and $ReCl_4^+$ were 10.7, 12.3, and 16.5 eV, respectively, with uncertainties of ±0.5 eV. These are consistent with their assignment to the neutral progenitor $ReOCl_4$. The appearance potential data do not support the possibility of the recently isolated[47] $ReOCl_3$ contributing to the $ReOCl_3^+$ intensity.

The previously reported[46] $ReO_2Cl_2^+$ gave an intensity 0.34% of the $ReOCl_3^+$ intensity. Our upper limit on the intensity of $ReO_2Cl_3^+$ was 0.006% of the $ReOCl_3^+$ intensity. The appearance potential of $ReO_2Cl_2^+$ was 10.6 ± 0.5 eV. The possible neutral progenitors, ReO_2Cl_3 and ReO_2Cl_2, have never been isolated but ReO_2F_3 has.[48,49] Furthermore, the five-coordinate d^0 molecule likely will give only a very weak parent ion.

In the present study, the $ReOCl_4^+$:$ReOCl_3^+$:$ReOCl_2^+$ intensity ratio was 36.7:100:25.2, whereas Büchler, *et al.*,[46] obtained 27:100:90. The discrepancy in the $ReOCl_2^+$ value may be due to differing amounts of $ReO_2Cl_2^+$, which also fragments to give $ReOCl_2^+$.

The upper limit on ions of mass higher than that of $ReOCl_4^+$, originating from the molecular beam, was 0.01% of the $ReOCl_3^+$ intensity.

Osmium Oxotetrachloride.—The mass spectrum of $OsOCl_4$ was obtained with the $OsOCl_4$ sample at 0° in the external inlet. Initially, after opening the sample inlet valve, only ions due to OsO_4 were detected; ions due to $OsOCl_4$ appeared in about 15 min.

The appearance potentials of $OsOCl_4^+$ and $OsOCl_3^+$ were 11.3 ± 0.5 and 12.4 ± 0.5 eV; the ions are assigned to $OsOCl_4$. Osmium oxotrichloride has never been reported.

The intensity of OsO_4^+ was 13.5% of the $OsOCl_3^+$ intensity, and the OsO_4^+:OsO_3^+:OsO_2^+ relative intensities were 100:18:23. A previously reported[50] mass spectrum of OsO_4 gave 100:29.6:48.

Small intensities of other oxochloride ions were detected. The intensities of ions identified as $OsO_2Cl_2^+$ and OsO_2Cl^+ were 0.65 and 0.71% of the $OsOCl_3^+$ intensity. Other ion peaks may have been due to OsO_3Cl^+; the upper limit on this ion was 0.3% of the $OsOCl_3^+$ intensity.

A small amount of ReO_3Cl was present in the vapor.

The upper limit on shutterable ion intensities at masses higher than that of $OsOCl_4^+$ was 0.2% of the $OsOCl_3^+$ intensity.

Discussion

Identification of Molecules Present.—Two of the initial goals of this study were to validate the previous infrared spectral studies and to prepare for far-ir and other studies by (i) showing that the species assumed to be present were indeed present, (ii) identifying hitherto unknown molecules, and (iii) determining the identity of vapor-phase decomposition products or impurities, if any. These experiments either confirm or show the existence of $MoOCl_4$, $WOCl_4$, $WOBr_4$, $ReOCl_4$, $OsOCl_4$, and $WSCl_4$ as discrete monomeric molecules. WS_2Cl_2, which had been synthesized previously,[6] also was identified as a vapor. The mixed molecules MoO_2BrCl, WO_2BrCl, and $WOSCl_2$ were shown to exist. The comparable solids of the MOX_4 sequence—$WOCl_2Br_2$ and $WOCl_3Br$—are known.[3] Ions that could not be assigned to these or any other known compound were observed and suggest possibly fruitful synthetic endeavors. These ions and suggestions about their possible neutral progenitors are $ReOCl_2^+$ (ReO_2Cl_3 (*cf.* ReO_2F_3[48,49]) or ReO_2Cl_2; OsO_3Cl^+(?), $OsO_2Cl_2^+$,

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and OsO_2Cl^+ (*cf.* OsO_3F_2[27]); and $W_2Br_xCl_y^+$ ($x + y \leq 6$) (*cf.* W_2Cl_6[43,44]).

Because of its exceptional perceptivity, the mass spectrometer requires an exceptionally clean vacuum system. Furthermore, careful inert-gas techniques were used to prepare and transfer all samples. Consequently, we judge that the present conditions were as clean as or cleaner than what would be *generally* encountered in microwave, matrix-isolation, or electron diffraction apparatuses. In spite of this, $MoOCl_4$, $WSCl_4$, and $ReOCl_4$ showed extensive reaction with deposits and surfaces in the spectrometer, and ReO_3Cl formed a persistent background. The sample temperatures and pressures needed for microwave and matrix-isolation work are about the same as or higher than those used here, and the same problems are likely to arise.

Mass Spectra and Correlations.—It is important to be able to predict whether and to what extent a given molecule will give a parent ion. Some efforts have been directed to this end.[13-15] In contrast to the main-group elements, we see here that the transition element compound fragmentation patterns are less sensitive to changes of the central atom or the ligand. Consider the three-dimensional array of four-coordinate molecules formed by varying M and X in the series $TiCl_4$, $VOCl_3$, · · ·, OsO_4. For all the known heavier halides but not the fluorides which generally fragment more (titanium tetrafluoride and ZrF_4 give minuscule parent ion intensities[51]), the parent ion is of moderate to strong intensity. This is shown in Figure 1 and in Tables V and VI. All of the data of Table VI are from the present study and hence are internally consistent. It is seen that change of neither chalconide, halogen, nor central metal atom has much effect on the fragmentation pattern. Table II shows, however, that the mass spectrum measured[17,52,53,54] does depend on the spectrometer used. The present sector instrument gives much less fragment ion intensity than the sector and time-of-flight instruments used in the other studies. We believe that this is due to discrimination against fragment ions caused by the molecular beam configuration and focusing conditions of the present source.

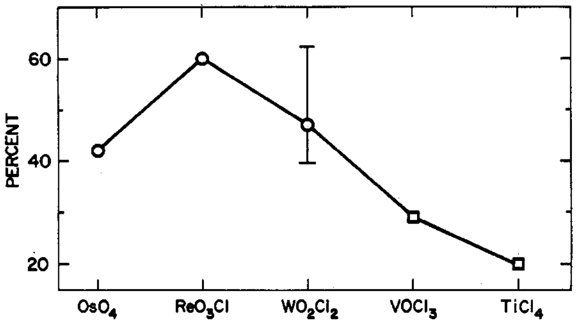

Figure 1.—Percentage contribution of the parent ion to the total singly charged ionization for the series OsO_4, ReO_3Cl, WO_2Cl_2, $VOCl_3$, $TiCl_4$. The vertical axis has the value 15% at the origin. The maximum for ReO_3Cl probably is not significant, because it may be instrumental. The data for ReO_3Cl were obtained with the molecular beam mass spectrometer used in the present work, which gave smaller relative fragment ion intensities than those obtained with other mass spectrometers. The error bar connects the points for MoO_2Cl_2 determined in the present work and by Dillard.[17]

TABLE VI

PARTIAL FRAGMENTATION PATTERNS (70 eV) OF WS_2Cl_2, $WOSCl_2$, CrO_2Cl_2, MoO_2Cl_2, AND MoO_2Br_2

	Rel intens[a]				
Ion	WS_2Cl_2	$WOSCl_2$	CrO_2Cl_2	MoO_2-Cl_2	MoO_2-Br_2
Parent$^+$	100	100	100	100	100
(Parent − Cl)$^+$	29	28	28	34	26
(Parent − 2Cl)$^+$	5	4	5	4	3

[a] All data are from the present study.

Since CrO_2F_2 fragments so extensively, we wonder what the case will be for the Mo and W compounds. In a following section, it will be argued that the ionized electron comes from a halogen-centered orbital in the case of the dioxodibromides and chlorides but from an oxygen orbital in the case of all the oxofluorides. However, chromium is more commonly found in lower valence states than molybdenum and tungsten. For this reason it will be interesting to observe whether fragmentation of the heavier element dioxodifluorides will be less severe or different in nature.

Table IV shows that none of the d^0 five-coordinate oxo or thiohalide molecules gives a parent ion with relative intensity greater than 1%. The same is true for the transition group V pentahalides.[3] For the pentahalides and these oxohalides, the appearance potentials of the parent ion and the (parent − halogen) ion are approximately equal to each other. This is consistent with the observation that the relative intensity of the parent ion depends, to a first approximation, on the width of the channel (AP(fragment) − IP(parent)) which permits formation of the parent but not the fragment.[14,15] If this channel is narrow, then the relative intensity of the parent is small and approaches zero as (AP − IP) approaches zero.

In view of the weak parent of the oxotetrahalides, the assignment[44,55] of $WOCl_3^+$ and WOI_3^+ to the oxotrihalides needs further examination.

With regard to six- and seven-coordinate d^0 molecules, such as are known give minuscule parent ion intensities.

The effect of going to d^1 and d^2 configurations is shown by Table IV and Figure 2. Intensities relative to the major peak are shown in the table while percentages of total ionization are shown in the figure. From less than 1% for the parent ions of the d^0 molecules, the percentage of total ion intensity rises to 18% for $ReOCl_4$ and to 26% for the d^2 $OsOCl_4$. At the same time, the intensity of the $MOCl_3^+$ drops. This appears to be general among the transition metal halides and oxohalides. In another five-coordinate series, the parent ion relative intensities are as follows: $TaCl_5$, not detectable;[56] WCl_5, 9%[44]; $ReCl_5$, "detectable."[57] In the two series

MoF_6		RuF_6	(RhF_6)	
WF_6	ReF_6	OsF_6	IrF_6	PtF_6

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(51) N. D. Potter, M. H. Boyer, F. Ju, D. L. Hildenbrand, L. Theard, and W. F. Hall, "Thermodynamic Properties of Propellant Combustion," AFOSR Report 70-2311TR, AD 715567 (1970); available from National Technical Information Service, Springfield, Va. 22151.

(52) G. D. Flesch, R. M. White, and H. J. Svec, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 339 (1969).

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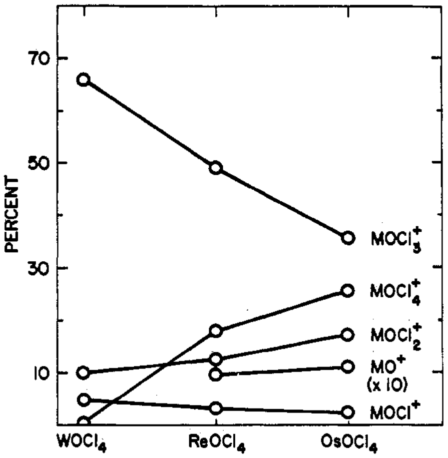

Figure 2.—Relative intensities of MOX_n^+ ions formed by impact of 70-eV electrons on $MOCl_4$ (M = W, Re, Os). The intensities are percentages of the total ionization. Note the decrease of $MOCl_3^+$ and the increase of the parent $MOCl_4^+$.

MoF_6 and WF_6 give little or no parent ion, whereas those of all the others except RhF_6 are "easily obtained."[58] Similarly, the parent intensity for ScF_3 is very low, whereas for TiF_3 it is the major intensity.[14,51]

Ionization Potentials.—The IP's and AP's of the first fragments of the oxotetrahalides are given in the text. Only low ion intensities were available for measurement and the uncertainties are high, especially for the IP's of the group VI molecules. For these, the IP and AP of MOX_3^+ are approximately equal, while for $ReOCl_4$ and $OsOCl_4$ the latter are about 1 eV higher. This is consistent with the idea[14,15] that the relative intensity of the parent ion goes to zero as the difference (AP − IP) goes to zero.

For the dioxodihalides, Table VII[17,41,52,53,55,59,60] shows that the ionization potential is sensibly independent of the central atom. Thus, the latest value[52] for CrO_2F_2 (12.91 eV) is about the same as those[59] for MoO_2F_2 (13.0) and WO_2F_2 (13.0). Likewise, the ionization potentials (Table VII) from various laboratories for CrO_2Cl_2 and MoO_2Cl_2 cluster just above 12 eV, while those for the dioxodibromides cluster at 11 eV.

TABLE VII

APPEARANCE POTENTIALS OF IONS FORMED FROM GROUP VIb DIOXODIHALIDES AND FROM TUNGSTEN OXOTHIODICHLORIDE AND DITHIODICHLORIDE

Molecule	$AP(MY_2X_2^+)$,[a] eV
CrO_2F_2	12.91[b]
	14.0[c]
CrO_2FCl	14.0[c]
CrO_2Cl_2	11.99[b]
	12.6[c]
	12.2[d]
MoO_2F_2	13.0[e]
MoO_2Cl_2	12.2
	12.3[d]
MoO_2BrCl	11.1
MoO_2Br_2	10.9
WO_2F_2	13.0[e]
WO_2Br_2	11.4[f]
WO_2I_2	10.4[g]
	13.4[h]
$WOSCl_2$	10.6
WS_2Cl_2	10.5

[a] Unless otherwise noted, the values are from the present study. The results of several determinations for each ion were within about 0.5 eV or better. [b] Flesch, White, and Svec.[52] [c] Flesch and Svec.[53] [d] Dillard.[17] [e] Zmbov, Uy, and Margrave.[59] [f] Gupta.[40] [g] Gupta.[55] [h] Schäfer, Geigling, and Rinke.[60]

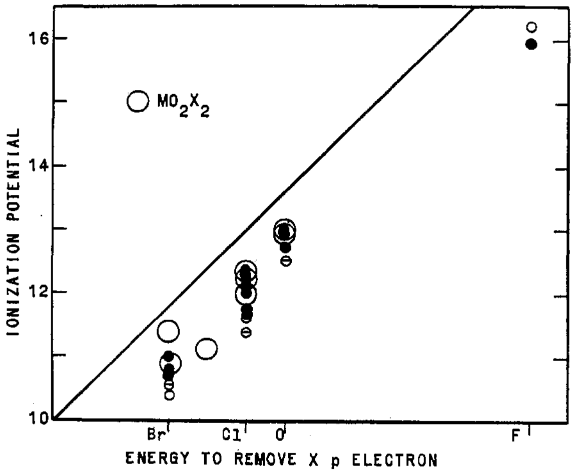

Figure 3.—Comparison of the ionization potentials (eV) of various molecules *vs.* the energy required to remove an electron from the highest filled p orbital of X. The large circles are for MO_2X_2 (see Table IX). The small circles are for BX_3,[62,65] MX_4 (M = C (open circles), Si, Ge, Sn, Ti),[61] POX_3 (barred circles), MOF_3 (V, Nb, Ta),[3] $VOCl_3$,[3] ReO_3Cl, and OsO_4.[31] Not shown are the values for S, Se, and TeF_6 which fall[62] at ≥15.7 eV and UF_6 (14.1 eV) nor a seemingly low value for TiF_4.[51] All the values for the oxygen-containing molecules are from electron-impact studies and are uncertain by 0.5–1 eV. The ionization potentials of the dioxodihalides are sensibly independent of the central metal but depend on the halogen, as tends to be the case for all the compounds shown. The IP's of the transition metal MOF_3, MO_2F_2, and OsO_4 fall at 12.7–13 eV indicating that the ionized electron comes from an O rather than an F orbital.

Photoelectron data are available for $TiCl_4$ and $TiBr_4$[61] and for the main group IV MX_4 (X = F, Cl, Br) molecules.[61,62] While there are important differences between the main and transition group compounds, in all cases the highest occupied molecular orbital is t_1 and predominantly of halogen p_π character. For the present purposes, formation of these molecular orbitals may be visualized as an upward shift (to smaller IP's) of the center of gravity of the appropriate atomic halogen p orbitals and then a splitting of these orbitals. The shift should become larger as the halogen becomes more like X^-; the available IP's of highly ionic species give an estimate of the limiting shift (eV): Cl, 12.97;[32] LiCl, 10.1;[31] $BeCl_2$, 12.6;[63] $CaCl_2$, 10.3;[64] $BaCl_2$, 9.2.[64] The shift in IP is only 4 eV in the most extreme of these cases. In addition, the combination of the AO's from the halogens is split. While many factors influence the exact position of the highest filled orbital, both the shift and the splitting are small, resulting in only very small changes in IP as the central atom is changed. By way of example, photon-impact ioniza-

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[62] A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, *ibid.*, **268**, 59 (1970).

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[64] D. L. Hildenbrand, *Int. J. Mass Spectrom. Ion Phys.*, **4**, 75 (1970).

tion potentials[32,61,62] for some chlorides are as follows (eV): Cl, 12.97; BCl_3, 11.7; CCl_4, 11.7; $SiCl_4$, 12.0; $GeCl_4$, 12.1; $SnCl_4$, 12.1.

To pursue the matter further, we plot as small circles in Figure 3 all these photoelectron data plus those for BX_3 (X = F, Cl, Br).[62,65] To these data are added the inherently less accurate electron-impact ionization potentials for POX_3,[3] MOF_3[3] (M = P, V, Nb, Ta), ReO_3Cl, and OsO_4.[31] Sulfuryl fluoride, SO_2F_2[3], is not shown but lies at 13.3 eV. The small open cricles are for CX_4, and the barred circles are for POX_3,[3] which seem to lie systematically lower than the other points. The dioxodihalide data (Table VII) are shown as the large circles. The positions along the horizontal axis are the energies to remove the outermost p electron from the free halogen atoms or from O; to anticipate our conclusions, the oxofluorides and OsO_4 are at the O position. The 45° line represents the IP's of the free atoms. Figure 3 shows, for this group of tetrahedral molecules (plus BX_3) with a relatively electronegative central atom (the lowest electronegativity is that of Ti at 1.5 eV), that the spread of IP's is less than 1 V for the bromides, chlorides, and oxides and that the shift from the free halogen (or O) IP is less than 1.5 eV. For the fluorides, this spread should be larger. The IP's of TiF_4 and ZrF_4 are reported as 13.0 ± 1 and 14.5 eV (taken equal to $AP(ZrF_3^+)$); that for TiF_4 seems low. To the extent that the electron-impact data are correct, we can predict IP's. Those of SO_2Cl_2, $NbOCl_3$, $TaOCl_3$, and WO_2Cl_2, for instance, ought to be ~12.0 eV; and those of H_2SO_4, H_2WO_4, etc., and of ReO_3F should be about 13.0 eV. The expected uncertainty in each of these, relative to our base data, is ±0.5 eV.

The interpretation of these observations is that for the oxobromides and oxochlorides the electron is removed from a nonbonding MO of predominantly halogen p_π character. For the oxofluorides and for OsO_4 (obviously) the electron is removed from an MO of predominantly O character. For MoO_2BrCl it should then come from a Br atom, consistent with an IP (11.1 ± 0.5 eV) that lies closer to the 10.9 ± 0.5 eV value for MoO_2Br_2 than to the 12.2 ± 0.5 eV value for MoO_2Cl_2. Furthermore, there are implications about the photoelectron spectra of the three-dimensional arrays of molecules $TiX_4 \cdots MoO_2X_2 \cdots OsO_4$ or $SiX_4 \cdots SO_2X_2$. The centers of gravity of the nonbonding orbitals formed from the p AO's should remain fairly constant irrespective of the central atom and should move in a predictable manner with changes of the other ligand groups. Thus in the sequences of MO_2X_2, there should be a set of bands due to the oxygens at 13+ eV while the halogen bands move from about 14–16 eV (F) to 12+ to 11+ eV for the chlorides and bromides.

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CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL,
CANOGA PARK, CALIFORNIA 91304

On Alkali Metal Fluoride–Iodine Pentafluoride Adducts

BY KARL O. CHRISTE

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The syntheses and properties of novel 1:3 adducts between alkali metal fluorides and IF_5 are described. Infrared and Raman spectra are reported for $CsF \cdot 3IF_5$, $CsIF_6$, $RbIF_6$, KIF_6, and a mixture of $RbIF_6$ with $RbF \cdot 3IF_5$. The previously reported discrepancies in the vibrational spectra of IF_6^- salts can be rationalized by assuming mixtures of 1:1 and 1:3 adducts. Powder diffraction X-ray data are given for KIF_6, $RbIF_6$, and $CsIF_6$. Partial pyrolysis, vibrational spectroscopy, and differential thermal analyses show no evidence for the existence of distinct 1:2 adducts as intermediate products from the decomposition of the 1:3 adducts. The previous conclusions are confirmed that IF_6^- is not octahedral and does not have a symmetry higher than C_{2v}. The FNO–IF_5 and FNO–BrF_5 systems were briefly studied. Whereas BrF_5 does not form an FNO adduct, IF_5 combines with FNO to form a white, crystalline 1:1 adduct having a dissociation pressure of about 30 mm at 21°.

Introduction

The vibrational spectra of the alkali metal fluoride–iodine pentafluoride adducts were previously studied by at least four different research groups.[1–4] All four groups reached the same conclusion that the IF_6^- anion is not octahedral. This conclusion was also supported by the results of a recent Mössbauer study.[5] However, the vibrational spectra reported by the four groups for IF_6^- differed strongly and no plausible explanation could be offered for these discrepancies. Recently, Klamm and Meinert reported[6] the formation of IF_4Cl by treating CsCl with IF_5. Their failure to isolate and characterize this novel, yellow, volatile compound was attributed[6] to rapid reaction with the glass container. Our attempts to duplicate Klamm and Meinert's observations[6] in an inert metal–Teflon reaction system were unsuccessful. The most volatile yellow reaction product was, as expected, Cl_2. However, from the material balance, it became obvious that the solid residue was not the expected $Cs^+IF_6^-$ but the novel $CsF \cdot 3IF_5$ adduct. Furthermore, the vibrational spectra of $CsF \cdot 3IF_5$ showed bands previously attributed[1,2] to

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