HALOGEN-EXCHANGE REACTIONS OF THE HEXAFLUORIDES OF OSMIUM, IRIDIUM AND RUTHENIUM – PREPARATION AND CHARACTERIZATION OF $Ir_2F_3Cl_6$, $Os_2Br_4F_5$ AND $Ir_2Br_4F_5$

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SUMMARY

Halogen-exchange reactions of the hexafluorides of osmium, iridium and ruthenium with a selected number of halogen-exchange reagents (BCl_3, BBr_3, BI_3 and CCl_4) have been studied. In every case mixed halides of these elements were formed. Stoichiometric mixed valence compounds of empirical formulae $Ir_2F_3Cl_6$, $Os_2Br_4F_5$ and $Ir_2Br_4F_5$ have been isolated and characterized by infrared and UV-visible spectroscopy, X-ray methods, magnetic measurements and other physical procedures. All three have been shown to be polymeric in nature. The compound of related stoichiometry, $Mo_2Cl_3F_6$, which is formulated as $(Mo_3Cl_9^{3+})(MoF_6^-)_3$, has been further studied by the above techniques and is contrasted with the mixed halides of osmium and iridium. Stoichiometric mixed halides could not be isolated from the ruthenium hexafluoride reactions.

INTRODUCTION

There are many general procedures used to prepare binary halides of the second and third row transition metals, most of which involve direct halogenation of the metal or metal oxide at 200 - 700°C with free halogen or a halogenating agent [1]. However, these conditions are unsatisfactory for the preparation of higher halides that are thermally unstable at or about room temperature unless sophisticated quenching procedures are used, such as in the preparation of the hexafluorides of ruthenium, rhodium and platinum [1,2].

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Recently, we reported the preparation of osmium pentachloride using
a halogen-exchange procedure which involved reaction of a high oxidation
state fluoride, in that case OsF_6, with an appropriate halogenating agent,
BCl_3, at low temperatures [3]. Previous investigations into the osmium-
chlorine system using direct halogenation of the metal had given the
tetrachloride as the highest binary chloride, together with other lower
chlorides depending on the reaction conditions [4-8]. Prior studies using
the halogen-exchange procedure have provided improved synthetic routes to
both $ReCl_6$ and UCl_6 [9,10], but the preparation of $OsCl_5$ was the first in
which a new higher binary halide had been obtained. We therefore decided
to investigate other halogen-exchange reactions of the hexafluorides of
osmium, iridium and ruthenium in an attempt to prepare new binary chlorides,
bromides and iodides of these elements. In passing, it should be noted that
halogen-exchange procedures have been used to prepare both binary and oxide
bromides and iodides of many non-transition elements from their respective
chlorides and oxide chlorides [11,12].

For the attempted preparation of higher binary halides (other than
fluorides) of the above metals, the halogen-exchange reagents chosen were
the trichloride, tribromide and triiodide of boron, and the tetrachloride of
carbon. Both boron and carbon are in fixed oxidation states, so that any
reduction in oxidation state of the metal product is due to the intrinsic
instability of a high oxidation state in a non-fluorine environment (or
mixed environment if a mixed halide) and not from any oxidation-reduction
reactions between the reactants and products of reaction. All of these
reactions can be conducted at very low temperatures, thus providing favor-
able conditions for the formation of any thermally unstable high valence
state products. Furthermore, with the exception of any metal-containing
products, all of the reactants and products are volatile, thus allowing for
easy separation and isolation of the desired products.

The products of reaction were all mixed halides of osmium, iridium and
ruthenium. Frequently, particularly when the halogen-exchange reagent was
CCl_4, the products were non-stoichiometric. However, with the boron halides,
stoichiometric compounds of empirical formulae $Ir_2F_3Cl_6$, $Os_2Br_4F_5$ and
$Ir_2Br_4F_5$ were isolated and characterized and shown to be polymeric.
Although mixed halides were formed in all reactions studied involving RuF_6,
stoichiometric compounds of ruthenium could not be isolated, even under the
stringent conditions used to prepare the three compounds listed above.

EXPERIMENTAL

Apparatus and Materials

All work was performed in Monel and Kel-F apparatus, essentially
similar to that described by Canterford and O'Donnell [13]. Reactions were
carried out in commercially available Kel-F tubes, or in small machined
Kel-F reaction tubes, as described previously in earlier reported redox
reactions of RuF_6 [14].

Osmium and iridium hexafluorides were prepared by heating their
respective metals (Os – Johnson, Matthey and Co., spectroscopic grade;
Ir – BDH, 99.95%) with an excess of fluorine in a monel reactor for 3 hours
at 350-400°C. Ruthenium hexafluoride was prepared by reaction of ruthenium
metal (Koch-Light, 99.99%) and fluorine at elevated temperatures with
isolation of the cooled product using the procedure described by Burns and
O'Donnell [14]. Molybdenum hexafluoride was prepared by reaction of the
metal, which had been previously hydrogenated at 1000°C to remove the oxide
coating, with fluorine at 300°C in a flow system.

The perfluoroalkanes, n-C_6F_{14} and n-C_7F_{16} (PCR), were stored over
P_4O_{10} and were distilled directly before use. Boron trichloride, tribromide
and triiodide, carbon tetrachloride and all other materials were of reagent
grade purity and, if volatile, were distilled or sublimed under vacuum prior
to use.

Reaction Procedures

Volatile reagents were transferred by vacuum distillation, while solid
reagents were handled in an argon-filled glove box. Preliminary work showed
that all of the halogen-exchange reactions were extremely exothermic,
invariably resulting in the formation of some free metal as a result of
thermal decomposition or further reaction of the products of reaction.
Similar observations had previously been made during the study of the
oxidation-reduction reactions of these hexafluorides [15]. Consequently,
most reactions were performed at low temperatures in the presence of an
n-perfluoroalkane solvent, either n-C_6F_{14} or n-C_7F_{16}, which could act as a
'thermal sink' and dissipate the thermal energy. Reactions were carried out

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by condensing a large excess of the halogen-exchange reagents onto a sample
of the particular hexafluoride, which had been previously dissolved in a
small quantity of n-perfluoroalkane and cooled to -196°C. The tube and
contents were then placed in an acetone-solid CO_2 cold bath (ca. -78°C) and
allowed to warm slowly to room temperature over about 12 hours. During
this period two layers formed as the n-perfluoroalkane and halogenating
agent melted and reaction took place as the latter slowly diffused into the
n-perfluoroalkane. The products and excess reactants were then allowed to
stand at room temperature for a further hour and, after removal of the
volatile products, excess reactant and n-perfluoroalkane, the solid product
was washed with a further sample of halogen-exchange reagent. This was done
to ensure that reaction was complete and, particularly for the reactions of
BBr_3 which produced free bromine, to ensure that no bromine remained
occluded or adsorbed on the sample. Some relevant analytical results are
reported in Table 1.

TABLE 1

Analytical results

Product	Metal %		F %		Cl or Br %	
	Theor.	Found	Theor.	Found	Theor.	Found
$Ir_2F_3Cl_6$	58.7	57.6	8.7	8.5	32.6	32.4
$Os_2Br_4F_5$	47.85	47.6	11.95	11.8	40.2	39.9
$Ir_2Br_4F_5$	48.1	47.3	11.9	11.7	40.0	39.1

Identification and Characterization of Products

Upon completion of a reaction the volatile products were removed and,
after fractionation if necessary, were identified by their infrared or mass
spectra. Solid products were transferred to a dry-box for subsequent
handling and were identified by chemical analysis and other procedures.
Osmium, iridium and ruthenium solid samples were decomposed in an
alkaline oxidative flux of $NaOH-Na_2CO_3-NaNO_3$ and the solid melts extracted
with water. Osmium was determined by the spectrophotometric method of Ayres
and Wells [16], while iridium was determined gravimetrically as the metal by
hydrogen reduction of the dioxide after separation from the extract by

filtration. Ruthenium in the extract was oxidized to a mixture of
ruthenate and perruthenate with $K_2S_2O_8$ and determined by the ruthenate-
perruthenate isosbestic point at 415 nm [17]. Fluoride was determined as
previously [15], while chloride, bromide and iodide were determined by
potentiometric titration with silver nitrate, after prior reduction of the
metal, when present, with hydrazine sulfate. This also served to reduce
any bromate and iodate, formed in the oxidative fusions, to bromide and
iodide.

Infrared, electronic diffuse reflectance and mass spectra were
obtained as described previously, as were X-ray powder and magnetic
measurements [3,15].

RESULTS AND DISCUSSION

The solid products of the halogen-exchange reactions of OsF_6, IrF_6
and RuF_6 studied in this work were invariably found to be mixed halides,
not binary halides as originally expected. Only the reaction of OsF_6 with
BCl_3 has led to the formation of a binary halide [3]. All of the reactions
were highly exothermic, requiring low temperature reaction conditions and
the use of an inert n-perfluoroalkane solvent to dissipate the heat of
reaction. In order to show that it was not solely the presence of the
n-perfluoroalkanes that caused the formation of the mixed halides, other
reactions were performed in which no n-perfluoroalkane was present.
These gave essentially the same products, which however were contaminated
with the free metal (and probably minor quantities of other unidentified
decomposition products as well). For example, reaction of OsF_6 and BBr_3
in the presence of n-perfluoroalkane gave a mixed halide of formulation
$Os_2Br_4F_5$ (see below). The same product together with some osmium metal
was obtained in the absence of n-perfluoroalkane and it was also obtained
in minor quantities when liquid bromine was used as the reaction medium
in place of the n-perfluoroalkane.

All of the mixed halide products had a formal oxidation state of
greater than IV, and many were non-stoichiometric with a variable compos-
ition, particularly those resulting from the CCl_4 reactions. This
suggests that a mixture of products may have formed in these reactions and
is not surprising in the latter as CCl_4 is known to be less effective than
BCl_3 in halogen-exchange reactions [3]. For example, reaction of OsF_6 with
CCl_4 has been shown to give a non-stoichiometric mixed halide product of

variable composition even on prolonged reaction at high temperatures (80 –
90°C), whereas reaction of OsF_6 and BCl_3 under essentially the same
conditions gave $OsCl_5$. Greatest success in this study was obtained for the
reactions of OsF_6 with BBr_3 and IrF_6 with both BCl_3 and BBr_3. These
reactions gave the stoichiometric, mixed valence, mixed halide products of
empirical formulae $Os_2Br_4F_5$, $Ir_2F_3Cl_6$ and $Ir_2Br_4F_5$. The properties and
characterization of these species are discussed below. While the above
reactions led to the controlled formation of stoichiometric products,
reaction of OsF_6 with BI_3 even in n–perfluoroalkane was still extremely
violent and gave a product contaminated with free metal. Therefore, in view
of the greater oxidant strength of IrF_6 and RuF_6 compared with that of OsF_6
[14,15], no reactions of BI_3 were attempted with these two hexafluorides.

The reactions of RuF_6 with BCl_3 and BBr_3 gave non–stoichiometric
mixed halides, despite great care in trying to keep the reaction conditions
as mild as possible. This is consistent with the previously reported
oxidant strengths RuF_6 > IrF_6 > OsF_6 [14,15]. The reactions of RuF_6 would
be expected to be more exothermic than those of IrF_6 and OsF_6 and this may
represent the limit of control of reaction conditions which can yield
stoichiometric products by these procedures.

The volatile products of the reactions of BCl_3, BBr_3 and BI_3 with the
hexafluorides were BF_3 and the respective mixed halide fluorides of boron,
together with chlorine, bromine or iodine, where appropriate. For CCl_4,
reactions gave the mixed chloride fluorides of carbon, and chlorine. Carbon
tetrafluoride was also observed as a product in the more violent reactions.

Characterization of $Ir_2F_3Cl_6$, $Os_2Br_4F_5$ and $Ir_2Br_4F_5$

As indicated above, the reactions of OsF_6 and IrF_6 with BCl_3 and BBr_3
produced a number of mixed halides of definite stoichiometry. Reaction of
IrF_6 with BCl_3 gave dark green $Ir_2F_3Cl_6$, while the reactions of OsF_6 and
IrF_6 with BBr_3 gave black $Os_2Br_4F_5$ and dark brown $Ir_2Br_4F_5$, respectively.
All three are mixed valence compounds of general formula M_2X_9, where M = Os
or Ir and X = F and either Cl or Br. Very few compounds of the transition
metals or actinides are known to have this stoichiometry. The best
characterized of the transition metal compounds is $Mo_2Cl_3F_6$, for which there
is good evidence that it has the ionic formulation $(Mo_3Cl_9^{3+})(MoF_6^-)_3$, with

a trimeric cluster cation similar to the rhenium(III) clusters [18]. Others are Mo_2F_9, speculated as having the ionic formulation $(MoF_3^+)(MoF_6^-)$ based on its physical properties [19,20], and a product of reported stoichiometry $Ir_2I_3F_6$ (prepared by reaction of IrF_6 with excess iodine) [21]. Structural determination shows the actinide species U_2F_9, to have a totally fluorine-bridged structure [22,23]. A sample of $Mo_2Cl_3F_6$ was prepared by the method of O'Donnell and Stewart [18] and investigated along with the mixed halides of osmium and iridium.

The three mixed halides of osmium and iridium were highly sensitive to moisture and each hydrolyzed instantly on addition to either water or base with the formation of the respective hydrated metal dioxide. Each was found to be insoluble in the halogen-exchange reagent used for its preparation, that is BCl_3 or BBr_3, and was insoluble in the n-perfluoroalkanes, CCl_4, CH_2Cl_2 and $CHCl_3$. Furthermore, $Os_2Br_4F_5$ and $Ir_2Br_4F_5$ were insoluble in bromine. In solvents of greater polarity and co-ordinating ability, such as acetonitrile, nitromethane and dimethylformamide, the mixed halides were insoluble or obviously reacted with dissolution. This insolubility in a wide range of solvents is indicative of a polymeric nature. In comparison, $Mo_2Cl_3F_6$ has been reported to react with water and nitrobenzene and to be insoluble in CCl_4, perfluoroheptane and trifluoroacetic acid, but is readily soluble in acetonitrile [18].

All three mixed halides were thermally stable and involatile up to $ca.$ 250°C, but above this temperature they decomposed with the formation of the respective free metals. This again suggests that the three compounds are polymeric, particularly when contrasted with the compound $Mo_2Cl_3F_6$, which has similar stoichiometry but which is largely ionic in nature. $Mo_2Cl_3F_6$ sublimes unchanged at 80°C and on further heating decomposes into $MoCl_3$ and MoF_6 [18].

X-ray powder examination of $Ir_2F_3Cl_6$ and $Ir_2Br_4F_5$ indicated that both were amorphous to X-rays. X-ray data were obtained for $Os_2Br_4F_5$; but the pattern, although simple could not be indexed on the basis of a cell of symmetry higher than orthorhombic, which is not surprising considering the empirical composition and hence probable low symmetry of the compound. X-ray powder photographs of $Mo_2Cl_3F_6$ were considerably more complicated than that of $Os_2Br_4F_5$ and could not be indexed on the basis of any simple cell, again suggesting low symmetry.

Spectroscopic Properties

Considerable evidence on the structural nature of the mixed halides was obtained from an infrared study. The infrared data for the solid mixed halides, including $Mo_2Cl_3F_6$, are listed in Table 2, together with an assignment of the bands.

The spectra of the three mixed halides of osmium and iridium exhibit bands in both the transition metal-terminal fluorine (760 - 600 cm^{-1}) and transition metal-bridging fluorine (570 - 510 cm^{-1}) stretching ranges [24,25]. Each of the pentafluorides and tetrafluorides of these elements also shows bands in the same two regions [26]. Importantly, these compounds are also known to have both terminal and bridging fluorine atoms from structural studies [27-29]. Hence the numerous peaks found in either region for the mixed halides presumably result from differences in oxidation state, that is IV or V, assuming little delocalization of valence (see below), and to differences in the symmetry of the environment around each atom. The appearance of the bridging stretches in the spectra indicates that all three compounds are indeed polymeric, in agreement with the solubility, volatility and thermal properties discussed above. Also, the terminal fluorine stretches indicate that these compounds do not have the U_2F_9 structure, as in this compound every fluorine atom bridges two uranium atoms.

The bands in the metal-chlorine and metal-bromine stretching regions are not as easy to assign to terminal or bridging halogens. Bands of this type appear to be very sensitive to oxidation state and co-ordination [24,25], and there are also little data for comparison. In view of the polymeric nature of the mixed halides and the complexity and range over which the bands appear, both bridging and terminal chlorine and bromine atoms are probably present.

The infrared data for $Mo_2Cl_3F_6$ also shed some light on the solid-state structure of this compound. The peak at 490 cm^{-1} seems to appear at too high a frequency to be a Mo-Cl stretch, and is accordingly assigned as a weak molybdenum-bridging fluorine stretch. This implies that there must be some covalent contribution to the interionic bonding, as is also evidenced by the high volatility of the compound. This could easily occur through co-ordination of fluorine atoms in the MoF_6^- anions to the vacant peripheral sites in the plane of the molybdenum atoms in $Mo_3Cl_9^{3+}$, much as occurs in the rhenium trihalides and related compounds [1]. This in turn would have the effect of lowering the symmetry of MoF_6^- anions, causing splitting of the degenerate modes and allowing formally Raman-active only

bands to appear in the infrared spectrum (and *vice versa*). Furthermore, co-ordination in this manner would also cause the remaining terminal-fluorine stretches to move to higher frequencies. Indeed, the above arguments seem consistent with the appearance of three terminal-fluorine stretches in the infrared spectrum, all at higher frequencies than found for the $\nu_1 (A_{1g})$ and $\nu_3 (T_{1u})$ modes of MoF_6^-, which have been reported at 667 and 623 cm^{-1}, respectively [1,30].

TABLE 2

Infrared data (cm^{-1}) for $Ir_2F_3Cl_6$, $Os_2Br_4F_5$, $Ir_2Br_4F_5$ and $Mo_2Cl_3F_6$ [a]

$Ir_2F_3Cl_6$	$Os_2Br_4F_5$	$Ir_2Br_4F_5$	$Mo_2Cl_3F_6$	Assignment
708 s [b]	695 m, sh	666 s	748 s, sp	
677 s	658 s	637 s	722 s	$\nu (M-F)_{terminal}$
644 s			684 s, sp	
526 s, br	530 m, br	560 m, sh	490 m	$\nu (M-F)_{bridging}$
		538 m, br		
380 m, sh			417 s	
357 m			396 sh	$\nu (M-Cl)$
321 m				
	262 w	265 w		
	241 m	232 m		$\nu (M-Br)$
	212 w, sh			

(a) Spectra recorded as Nujol mulls or as powders.

(b) Key: s = strong, m = medium, w = weak, sh = shoulder,
     br = broad, sp = sharp

Raman spectra could not be obtained for any of the four solid mixed halides because of decomposition of the compounds in the laser beam, despite the use of various exciting lines.

As the mixed halides of osmium and iridium were insoluble in or reacted with all solvents examined, electronic spectra were recorded by diffuse reflectance methods. All three mixed halides are very darkly coloured and, as expected, each exhibited a very strong absorbance over the entire range recorded (7,000 - 40,000 cm^{-1}). Spectra were also

recorded after dilution with well-dried magnesium oxide, with similar
results, but with slightly better definition. The band maxima are listed
in Table 3, together with data for $Mo_2Cl_3F_6$. Unlike the above compounds,
the spectrum of orange-brown $Mo_2Cl_3F_6$ exhibited a strong absorbance only
above $ca.$ 18,000 cm^{-1}.

TABLE 3

Electronic diffuse reflectance band maxima (cm^{-1}) for $Ir_2F_3Cl_6$, $Os_2Br_4F_5$,
$Ir_2Br_4F_5$ and $Mo_2Cl_3F_6$

$Ir_2F_3Cl_6$	$Os_2Br_4F_5$	$Ir_2Br_4F_5$	$Mo_2Cl_3F_6$
14,100 br [a]	13,300 br	20,800 sh	8,000 w
16,800	33,900	23,600	23,400 s
22,700			31,900 s

(a) Key: s = strong, w = weak, br = broad, sh = shoulder

The spectra of the three mixed halides are dominated by intense
halogen-to-metal charge transfer bands, which mask the weaker d-d
transitions. This is not surprising since strong charge transfer bands
also dominate the spectra of hexahalometallate complexes of all $4d$ and $5d$
transition elements when the halogen is chlorine, bromine and iodine [31].
In the case of fluorine, the bands occur well into the UV region. In view
of the lack of detail in the spectra and knowledge of the exact structures
of these compounds no attempt was made to interpret the charge transfer
bands, and hence it was not possible to establish the existence of one or
more mixed valence transitions, which are likely to appear in the visible
region [32].

Previously, absorption data have been recorded on $Mo_2Cl_3F_6$ in aceto-
nitrile solution [18]. Band maxima were observed at 14,100 (ε_{max} = 160) and
21,500 cm^{-1} (ε_{max} = 1,550 dm^3 cm^{-1} mol^{-1}). The appearance of these two
bands has been shown to be consistent with the proposed structure of a
trimeric cation (the MoF_6^- anion does not absorb appreciably in the visible
region). Comparison of the solid-state and solution spectra reveals some
apparent discrepancies. While the bands at 23,400 and 21,500 cm^{-1} corres-
pond to one another, no band comparable to that at 14,100 cm^{-1} in acetonit-

rile was observed in the solid state. This band, however is fairly weak in solution and may not be resolvable in the solid. Also, no band was reported in solution which would correspond to that at 8,000 cm^{-1} in the solid state. In this case it should be noted that in the solution spectra of Re_3Cl_9 and related species, in addition to bands at about 13,000 and 20,000 cm^{-1} corresponding to those for $Mo_2Cl_3F_6$ [18], a weak band is usually observed at $ca.$ 9,000 cm^{-1} ($\varepsilon_{max} \sim 50$) [33]. Thus this band may be quite weak for $Mo_2Cl_3F_6$ in solution, but relatively stronger in the spectrum of the solid. Because of absorption by the solvent, the band at 31,900 cm^{-1} could not have been observed in acetonitrile solution. The solution and solid-state spectra are therefore not inconsistent with one another, and the slight differences in the positions of the band maxima and relative intensitities of the bands may in fact be associated with probable distortions in the solid caused by fluorine bridging, as discussed above.

Magnetic Properties

All three mixed halides of osmium and iridium were found to be paramagnetic, with effective magnetic moments (μ_{eff}) per metal atom for $Os_2Br_4F_5$ $Ir_2F_3Cl_6$ and $Ir_2Br_4F_5$ of 2.12, 1.05 and 1.26 BM, respectively, at 294K.

Generally, binary and complex halides of osmium and iridium in oxidation states IV and V exhibit octahedral co-ordination [1,31]. Assuming that the mixed halides contain equal amounts of metal (IV) and metal (V) in octahedral or near-octahedral environments (from different halogens), then the expected magnetic moments of the compounds at room temperature may be calculated approximately, assuming no or little delocalization of valence. For $Os_2Br_4F_5$, μ_{eff} is calculated to be $ca.$ 2.5 BM per osmium atom, while for both $Ir_2F_3Cl_6$ and $Ir_2Br_4F_5$ μ_{eff} is $ca.$ 1.4 BM per iridium atom. The experimental values are slightly lower than the above values, but are not inconsistent with the metal atoms being hexaco-ordinated. The differences between the calculated values, which are only approximate, and the experimental values may arise from anti-ferromagnetic exchange interactions. Interactions of this type are characteristic of Class II mixed valence compounds, according to the classification of Robin and Day [32].

In the case of $Mo_2Cl_3F_6$ the magnetic data, both in acetonitrile solution and in the solid state, have been shown to be consistent with the proposed structure for this compound [18].

From all of the available evidence, as discussed above, it may be concluded that the three mixed halides of osmium and iridium are best formulated as polymeric compounds, and are not (essentially) ionic as is $Mo_2Cl_3F_6$. The compounds are certainly fluorine-bridged, and the possibility of bridging through chlorine or bromine cannot be discounted. Magnetic results are also consistent with hexaco-ordination of the metal atoms, which is the usual co-ordination exhibited by these elements in oxidation states IV and V, especially in the halides. That the mixed halides are highly polymeric and stable is also evidenced by the fact that they are inert to further halogen exchange at $100^{O}C$ in the boron trihalide used for their respective preparation, although infrared evidence shows that each contains metal-terminal fluorine bonds. Furthermore, the mixed halides show no tendency to exchange halogens (Cl or Br) on treatment with anhydrous hydrogen fluoride, even though this procedure has been found to be an effective method for replacing other halogens by fluorine in many binary halides of the transition metals and actinides [1,34]. It is apparent that the mixed oxidation state combination with empirical stoichiometry of M_2X_9 offers considerable stability as shown by the number of compounds that may be formed in a wide variety of reactions. However, without detailed X-ray or neutron studies on crystalline samples of these materials, little can be concluded regarding their actual structures and the arrangement of halogen atoms.

One final point of interest concerns the sequence of compounds $Ir_2F_3Cl_6$, $Ir_2Br_4F_5$ and $Ir_2I_3F_6$, the latter species having been reported by Robinson and Westland [21]. Assuming that $Ir_2I_3F_6$ has a related structure to the others, as is likely from its reported properties, then we see a novel example of the progressively decreasing tendency of the halogens to stabilize high oxidation states from fluorine to iodine. In this series of compounds of related stoichiometry and (polymeric) structure, $Ir_2I_3F_6$ requires a higher fluorine content than does $Ir_2Br_4F_5$ for stability, as does $Ir_2Br_4F_5$ relative to $Ir_2F_3Cl_6$.

Some Attempted Reactions of the Mixed Halides

The primary aim of this study was directed towards the preparation of new binary halides of osmium, iridium and ruthenium. As described above, halogen-exchange reactions of the respective hexafluorides led to the preparation of mixed halides. Some reactions of these species were subsequently examined as a method of obtaining binary halides.

The three stoichiometric mixed halides showed no reaction with PCl_3 or PBr_3, where appropriate, at $100^{0}C$, even though PF_3, an expected halogen-exchange product, has been shown to reduce both OsF_6 and IrF_6 to Os(IV) and Ir(IV), respectively [15]. However, $Ir_2F_3Cl_6$ was found to react with excess PCl_5 at $160^{0}C$ (a temperature at which it is partially dissociated into PCl_3 and chlorine) to give a rust coloured solid. Chemical analysis did not suggest that the product was of relatively simple or constant stoichiometry. It was shown to be a chloride fluoride of Ir(IV) containing bridging fluorine atoms as indicated by infrared examin-ation. Also, $Os_2Br_4F_5$ reacted with bromine at $250^{0}C$ to give a different mixed bromide fluoride of osmium, again with bridging fluorine atoms. In view of the polymeric nature of the starting materials, it is doubtful whether any reactions like those described above will lead to new binary halides.

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