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Preparation and Characterization of Osmium Pentachloride, a New Binary Chloride of Osmium

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Osmium pentachloride, a new binary chloride of osmium, has been prepared by the reaction of osmium hexafluoride with excess boron trichloride below room temperature. The pentachloride is isomorphous with rhenium pentachloride and has been characterized by X-ray methods, by infrared and UV-visible spectroscopy, and by magnetic and other physical procedures. Some reactions of the pentachloride are also reported in this paper. Reaction of osmium hexafluoride with carbon tetrachloride, known to be less effective than boron trichloride in halogen-exchange reactions, produces a nonstoichiometric product which probably contains several mixed halides of osmium.

Introduction

Several general procedures have been used to prepare binary halides of the second- and third-row transition metals, involving halogenation at temperatures in the range 200–700 °C of the respective metal or, in the case of chlorides, bromides, and iodides, the metal oxide, using either free halogen or a particular halogenating agent.[1] These conditions are unsatisfactory for the preparation of higher halides that are thermally unstable at or about room temperature, unless sophisticated quenching procedures are employed, as in the preparation of the thermally unstable hexafluorides of ruthenium, rhodium, and platinum.[1,2]

Many chlorides, bromides, and iodides of metals in high oxidation states that are difficult to prepare by direct halogenation have been prepared by halogen exchange of the highest oxidation state fluoride with an appropriate reagent at room temperature or below, e.g., uranium hexachloride[3] and rhenium hexachloride.[4] Similarly, halogen-exchange procedures have been used to prepare binary and oxide bromides and iodides of many non-transition elements from their respective chlorides and oxide chlorides.[5,6]

Many of the binary chlorides, bromides, and iodides of the second- and third-row transition metals in groups 4–7 have been fairly well characterized, the maximum group valence being exhibited in many cases. However, the maximum group valence becomes more difficult to attain in progressing across a row,[7,8] and the highest chlorides, bromides, and iodides of the platinum metals so far isolated are either trihalides or tetrahalides. To date, low-temperature preparative procedures involving halogen exchange have not been attempted in any of these systems.

For attempted preparation of the higher chlorides of these metals, we have selected as the halogen-exchange reagents the chlorides of boron and carbon. These were chosen because both boron and carbon are in their highest oxidation states, so that any reduction in oxidation state in the metal-containing product stems from 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. Furthermore, all of these reactions can be conducted well below room temperature, thereby providing favorable conditions for the formation of thermally unstable high valence state products. With the exception of the metal-containing products, all of the reactants and products are very volatile, allowing easy separation and isolation of the desired products of reaction.

This paper deals with the reactions of boron trichloride and carbon tetrachloride with osmium hexafluoride and the formation of higher chlorides of osmium.

There have been several investigations of the osmium–chlorine system, but the only compounds that have been firmly established are osmium trichloride and osmium tetrachloride.[9,10] More recently, evidence has been obtained for a compound of stoichiometry Os_2Cl_7.[11] However, all of these compounds have been produced as a result of reaction of osmium metal with chlorine,[9,10] carbon tetrachloride,[12,13] or sulfuryl chloride[14] at 400–700 °C, using a variety of pressure conditions. As pointed out above, this type of reaction may not necessarily lead to the preparation of the highest possible halide unless special techniques are employed.

When prepared by any of the above procedures, osmium tetrachloride exists in the high-temperature orthorhombic form, the structure of which has recently been established by a single-crystal X-ray study.[15] A second low-temperature cubic form of osmium tetrachloride has also been produced by the reaction of osmium tetraoxide and thionyl chloride at room temperature for 1 week[16] or under reflux (~79 °C) for a number of hours.[12,13] X-ray powder data have been reported for this form of osmium tetrachloride, as well as for osmium trichloride[10,11] and Os_2Cl_7,[11] but no detailed structural data are available for any of these species.

Interestingly, in their studies on the chlorination of osmium metal, Kolbin et al.[10] observed the formation of a small amount of sublimate that exhibited a higher chlorine content than that consistent with osmium tetrachloride. The formula of this sublimate was found to range from $OsCl_{4.08}$ to $OsCl_{4.31}$ and the material proved to be somewhat hygroscopic, unlike either polymorph of the tetrachloride. On the basis of these observations, these workers suggested that a binary chloride higher than the tetrachloride might well exist. Our investigations of the halogen-exchange reactions of osmium hexafluoride have led to the preparation and characterization of osmium pentachloride, a new binary chloride of osmium.

Experimental Section

Apparatus and Materials. All work was performed on a Monel and Kel-F vacuum line, similar to that described by Canterford and O'Donnell.[17] Reactions were carried out in Kel-F tubes and reagents were transferred from tube to tube by vacuum distillation through Kel-F "tee" and "cross" pieces.

Osmium metal (spectroscopic grade) and osmium tetraoxide were obtained from Johnson, Matthey and Co., Ltd., London. Boron trichloride, carbon tetrachloride, and all other materials were reagent grade and, if volatile, were purified by vacuum distillation before use.

Osmium hexafluoride was prepared by direct fluorination of the metal at 350–400 °C for 3 h in a Monel reactor, in the presence of excess fluorine. After this time had elapsed, the reactor was cooled to −78 °C in an acetone–dry ice cold bath and the excess fluorine was removed. When the reactor had warmed to room temperature, the hexafluoride was transferred to a stainless steel storage bottle which contained a little dry sodium fluoride to remove any hydrogen fluoride that might have been present in the sample.

Reactions of OsF_6 with BCl_3 and CCl_4. In a typical reaction, a very large excess of the appropriate chloride (2–3 g) was condensed onto a sample of osmium hexafluoride (0.1–0.2 g) at −196 °C. The Kel-F tube and contents were then allowed to warm up to room temperature. Reaction was seen to commence as the halogen-exchange reagent began to melt. Bubbles of volatile reaction products were observed and the yellow color of the hexafluoride darkened upon reaction with the chloride. After reaching room temperature, the products and excess reactant were allowed to stand for about 1 h to ensure that the reaction was complete, and then the volatile products and unused reactants were removed under vacuum. These were set aside for infrared and mass spectrometric examination, and the solid residue in the Kel-F tube was transferred to an argon-filled glovebox for subsequent investigation.

With boron trichloride, complete halogen exchange always occurred with the formation of osmium pentachloride. Anal. Calcd for $OsCl_5$: Os, 51.7; Cl, 48.3. Found: Os, 51.4; Cl, 47.9; Cl:Os = 5.00. The volatile products were boron trifluoride, the mixed chloride fluorides of boron, and also chlorine. Reaction of osmium hexafluoride with carbon tetrachloride always gave a black, nonstoichiometric involatile solid. The composition of this residue is discussed below. The volatile products were chlorine and the mixed chloride fluorides of carbon, but not carbon tetrafluoride.

Analysis and Characterization. Solid samples ($\sim$0.1 g) were decomposed with an alkaline oxidative flux of $NaOH-Na_2CO_3-NaNO_3$. The solidified melts were extracted with water, and osmium was determined by the spectrophotometric method of Ayres and Wells.[18] Reliable variations of this method have been described by Dwyer and Gibson[19] (for organic-containing materials) and Colton and Farthing.[16] Chloride was determined by potentiometric titration with silver nitrate, after prior reduction of the osmium with hydrazine sulfate.

Far-infrared spectra of solids were recorded on a Perkin-Elmer grating infrared spectrophotometer, Model 180, at Monash University. Samples were prepared as Nujol Mulls in small polyethylene packets, which were heat-sealed after the compounds had been introduced. Infrared spectra of volatile samples were obtained on a Perkin-Elmer grating infrared spectrophotometer, Model 457. Samples were contained in a 5-cm Monel gas cell fitted with Teflon gaskets and silver chloride windows.

Electronic diffuse reflectance spectra were recorded against barium sulfate on a Beckman DK-2A ratio recording spectrophotometer fitted with a reflectance attachment. Solids were mounted in an airtight cell similar to that described by Reid, Scaife, and Wailes.[20]

Mass spectra were recorded on an AEI MS9 instrument.

Conductances were measured in a cell consisting of a Kel-F tube fitted with a Kel-F taper plug and valve. The bright platinum electrodes were mounted in a Kel-F cartridge and the platinum wires, which passed through the plug, were covered with heat-shrinkable Teflon spaghetti tubing for their entire length within the tube, thereby providing a constant surface area for the electrodes. Conductances were measured with a Wayne-Kerr universal bridge, Type B221.

Samples for X-ray analysis were loaded inside the glovebox into Lindemann tubes (0.3- and 0.5-mm o.d.). These were temporarily sealed inside the box with Kel-F grease and brought outside where they were finally sealed with a flame. X-ray powder photographs were taken with a Philips Debye-Scherrer camera of diameter 11.46 cm on a Philips Industries, Ltd., X-ray generator, Model PW 1010/80, employing nickel-filtered Cu Kα radiation (λ (Kα) 1.5418 Å). Exposures ranged from 2 to 6 h. The positions of the arcs on the photographs were measured on a light box equipped with a vernier scale, with an accuracy of $\pm$0.005 cm. All line intensities were measured visually.

Magnetic susceptibility measurements were made with a PAR vibrating-sample magnetometer, Model 155, together with a PAR variable-temperature cryostat, Model 153. Magnetic measurements were made at a field strength of 11 000 G. Samples were handled in the glovebox and loaded into a small, sealable Kel-F capsule, which protected the material from hydrolysis. Susceptibilities were corrected for the diamagnetic susceptibility of the ligands by using Pascal's constants.[21]

Electron spin resonance spectra were obtained with a Varian V4502-15 system.

Integrated Intensity Refinement of the X-ray Powder Data. Preliminary examination of the X-ray powder photographs of osmium pentachloride showed that it was isomorphous and almost isodimensional with rhenium pentachloride, the structure of which has been reported by Mucker, Smith, and Johnson.[22]

The intensities of the powder lines were estimated visually by comparison with a standard line. Those reflections which were unobservably small were given an intensity of $^1/_2\, I_{\min}$, where $I_{\min}$ was the minimum observable intensity. A least-squares refinement of the powder data, using a Nelson–Riley drift term,[23] gave the lattice parameters given in Table I. The parameters for rhenium pentachloride are also given in this table for comparative purposes.

Table I. Crystal Data for Osmium Pentachloride and Rhenium Pentachloride

	$OsCl_5$	$ReCl_5$ [a]
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	9.17 (1)	9.24 (3)
b, Å	11.50 (1)	11.54 (3)
c, Å	11.97 (1)	12.03 (4)
β, deg	109.0 (1)	109.1 (3)
V, Å^3	1194	1212
formula wt	367.5	363.5
Z	8	8
d_{calcd}, g cm^{-3}	4.09	3.98

[a] Reference 22.

Table II. Positional Parameters for the Metal Atoms in Osmium Pentachloride from the Integrated Intensity Refinement[a]

atom[b]	x	y	z
Os(1)	0.308 (5)	0.120 (6)	0.290 (5)
Os(2)	−0.110 (7)	0.132 (6)	0.188 (4)

[a] Esd's are given in parentheses. $\bar{B}$ = 3.7 (4) Å^2. [b] The numbering system of the atoms is identical with that used by Mucker, Smith, and Johnson[22] for rhenium pentachloride.

The X-ray powder intensities were converted to $\sum_j JF_o^2$ values by using the expression

$$\sum_j JF_o^2 \propto I_0 \sin^2\theta \cos\theta (1 + \cos^2 2\theta)^{-1} A^*$$

where each line consists of j Bragg reflections with multiplicities J. The cylindrical absorption factor A^* was based on $\mu R = 15$, where μ is the linear absorption coefficient and R is the capillary radius, while the absorption corrections were obtained from tables of A^* vs. "θ".[46a]

All of the data out to an angle of 45° were used in the refinement of the osmium positional parameters, assuming chlorine positional parameters were those given for rhenium pentachloride, by minimizing the function

$$\sum_i w_i \Big(\sum_j JF_o^2 - \sum_j JF_c^2\Big)^2$$

where i is the the ith line of the pattern. The X-ray scattering curves for neutral osmium and chlorine were used,[46b] uncorrected for anomalous dispersion. An overall isotropic Debye–Waller temperature factor was assumed, and the computer program employed was a modification of ORFLS.[24] The final value of the residual

$$\sum_i \Big(\sum_j JF_o^2 - \sum_j JF_c^2\Big) \Big/ \sum_i \sum_j JF_o^2$$

at convergence in the refinement was 0.29 (but see ref 25). As expected, the positions of the osmium atoms (Table II), even at this level of refinement, were fairly close to the positions reported for the rhenium atoms in rhenium pentachloride, being within the errors in the coordinates ($<2\sigma$).

Results and Discussion

Preparation and Chemical Properties of $OsCl_5$. Osmium hexafluoride was found to undergo halogen exchange with boron trichloride and carbon tetrachloride; however, the pentachloride could only be prepared with the former reagent with reaction occurring well below room temperature according to eq 1, although, under the experimental conditions using

$$\mathrm{OsF_6 + 2BCl_3 \rightarrow OsCl_5 + 2BF_3 + {}^1/_2Cl_2} \tag{1}$$

excess boron trichloride, the mixed chloride fluorides of boron are always formed as well as boron trifluoride.

Osmium pentachloride is a black solid, is extremely moisture sensitive, and gives an odor of the tetraoxide when exposed to moist air. It is hydrolyzed immediately in basic solution with the formation of a transient green-yellow solution, from

Table III. Metal-Bridging and Terminal Chlorine Distances, Metal-Metal Distance, and Volume per Chlorine Atom for the Pentachlorides of the Second- and Third-Row Transition Metals

pentachloride	$(M-Cl)_{term}$, Å	$(M-Cl)_{bridg}$,[b] Å	$(M\cdots M)_{dimer}$, Å	V_{Cl}, Å^3	ref
$NbCl_5$	2.25, 2.30	2.56	3.95	32.3	28
$MoCl_5$	2.24, 2.25	2.53	3.84	31.1	29
$TaCl_5$[a]	2.28[b]	2.56	3.95	32.3	28
WCl_5	2.25[b]	2.53	3.84	30.7	30
$ReCl_5$	2.24[b]	2.47	3.74	30.3	22
$OsCl_5$	2.24[b]	2.42	3.63	29.8	this work

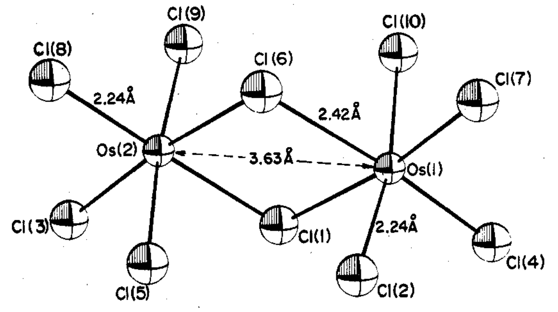
[a] Assumed to be identical with $NbCl_5$ on the basis of the X-ray powder data. [b] Average value.

which the hydrated dioxide slowly precipitates. In dilute or concentrated nitric acid, yellow solutions containing osmium(VIII) are formed immediately. The pentachloride is insoluble in nonpolar solvents like BCl_3, CCl_4, cyclohexane, and the *n*-perfluoroalkanes but is slightly soluble in more polar solvents such as dichloromethane and chloroform. It reacts with solvents of even higher polarity, or greater basicity; however, no attempt was made to isolate a solid product in any of these reactions.

As $OsCl_5$ was found to react with both nitromethane and acetonitrile and was insoluble in carbon tetrachloride, no conductance or ebullioscopic measurements could be undertaken in these solvents. This therefore precluded any direct comparisons with the extensive investigations of Kepert and Nyholm[26] on niobium pentachloride and tantalum pentachloride in nitromethane, acetonitrile, carbon tetrachloride, and carbon disulfide. However, as $OsCl_5$ was found to be slightly soluble in dichloromethane ($\epsilon = 9.1$ at 20 °C) without reaction, some simple conductance measurements were made in this solvent. The molar conductance at a concentration of 0.97×10^{-3} M was 1.4 Ω^{-1} cm^2 mol^{-1} at 20 °C. This value increased slightly upon dilution. Although dichloromethane is a poor solvent for this type of measurement, the value obtained suggests that $OsCl_5$ is essentially a nonelectrolyte since the limited amount of data that are available indicates that 1:1 electrolytes, at similar concentrations, have molar conductances of about 20–22 Ω^{-1} cm^2 mol^{-1} in this solvent at 25 °C.[27] The slight conductance is probably the result of reaction of the pentachloride with a small amount of water impurity in the solvent, similar to the conclusions drawn by Kepert and Nyholm[26] from their investigations of the pentachlorides of niobium and tantalum in nitromethane and acetonitrile.

Osmium pentachloride is quite stable at room temperature, either in a vacuum or in an inert atmosphere. However, decomposition does occur on heating. A vessel equipped with a water-cooled cold finger was used to heat a sample of the pentachloride in a static vacuum. Thermal decomposition was observed at about 160–170 °C to give free chlorine and a black residue, together with the appearance of some black sublimate on the cold finger. X-ray powder examination of the sublimed material and the residue indicated that both were the cubic low-temperature form of osmium tetrachloride.[13] This indicates that the inability to prepare $OsCl_5$ prior to this work may be attributed to the high temperatures required to chlorinate osmium metal, so that only the tetrachloride is produced in high yield.

Structural Determination. When prepared by low-temperature halogen exchange, $OsCl_5$ is fairly crystalline, especially if the reaction is carried out slowly. However, single crystals large enough for diffraction studies cannot be prepared by sublimation because of thermal instability or by recrystallization from a solvent because of low solubility and extreme susceptibility to hydrolysis. The structure of $OsCl_5$ was therefore investigated by an integrated intensity refinement of the X-ray powder data. This procedure has been described above (see Experimental Section). The pentachloride was found to be isomorphous with rhenium pentachloride, and the crystal data for both of these compounds are given in Table I, while the final positional parameters for the metal atoms in $OsCl_5$ are given in Table II. These are, as expected, little different from those of the metal atoms in $ReCl_5$.



Average bond angles :–
Cl(1) – Os(1) – Cl(6) = 83°
Cl(4) – Os(1) – Cl(7) = 95°

Figure 1. Some average bond lengths and angles in the $OsCl_5$ dimer. The numbering system of the atoms is identical with that used for rhenium pentachloride.[22]

The structural type exhibited by these two pentachlorides has been discussed in detail by Mucker, Smith, and Johnson[22] and is based upon a double-hexagonal close packing of chlorine atoms (an ABAC... sequence along the *b* axis), with the metal atoms occupying one-fifth of the octahedral holes. Two adjacent octahedra share an edge to form a dimeric unit, as shown in Figure 1. The other pentachlorides of the transition metals also contain similar dimeric units, but their structures are based upon hexagonal close packing of chlorine atoms. Therefore $ReCl_5$ and $OsCl_5$ are not isomorphous with the other transition-metal pentachlorides. Nevertheless, in both pentachloride structural types the metal atoms in their respective dimers are displaced away from each other from the centers of the chlorine octahedra. For $OsCl_5$, this leads to an Os$\cdots$Os distance of 3.63 (7) Å in the dimer. The bridging and terminal chlorine distances, the metal$\cdots$metal distance, and volume per chlorine atom (V_{Cl}) for each of the pentachlorides of the second- and third-row transition metals are listed in Table III. As can be seen, the metal–chlorine (bridging and terminal) distances and the metal$\cdots$metal distance in the dimer decrease across each transition-metal row, as does the volume per chlorine atom. The similarity of the data for the third-row compounds to those of their second-row congeners stems from the lanthanide contraction, while the steady decreases observed in the other parameters are consistent with the increase in polarizing ability of the central metal atom across each row. Thus, the nonbonding d electrons which enter the t_{2g} orbitals do not effectively screen the chlorine atoms from the steadily increasing nuclear charge, so that the bonding electrons and the nonbonding electrons on the chlorine atoms experience an increasing polarization across each of the two series.

Spectroscopic Properties. The far-infrared spectrum of $OsCl_5$ from 450 to 50 cm^{-1} is shown in Figure 2 and the data are listed in Table IV. Raman spectra could not be obtained because of decomposition of the sample in the laser beam, despite the use of various exciting lines. As the structural data

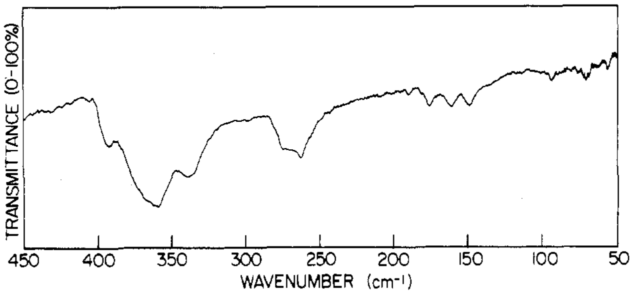


Figure 2. Far-infrared spectrum of $OsCl_5$ (Nujol mull) from 450 to 50 cm^{-1}.

Table IV. Infrared Data (cm^{-1}) and Assignments for the Pentachlorides of Niobium, Tantalum, Rhenium, and Osmium

$NbCl_5$[a]	$TaCl_5$[a]	$ReCl_5$[b]	$OsCl_5$	assignt
412 sh	409 s	402 sh	393 m	b_{3u}
400s	393 s	383 s	368 s	b_{1u}
	379 s		360 s	b_{2u}
359 s	359 s	357 s	339 m	b_{3u}
254 m, br	255 m	257 m	273 m	b_{3u}
226 m	231 mw	235 m	262 m	b_{2u}
200 w	203 vw	190 w	188 vw	b_{3u}
172 m	166 m	168 m	176 m	b_{1u}
157 m	150 m	154 w	161 m	b_{1u}
143 m	140 m	144 m	149 m	b_{2u}
118 m	121 m	110 w	94 w	b_{3u}
70 w, br[c]	73 w[c]	72 m[c]	70 w[c]	b_{2u}
		54 w	55 w	lattice mode?

[a] Reference 31. [b] Reference 32. [c] Polyethylene absorbs in this region.

indicate the presence of dimeric units in the solid state, an assignment of the far-infrared spectrum can be made based upon the normal-coordinate calculations and assignments of the far-infrared and Raman spectra of $NbCl_5$ and $TaCl_5$[31] and the subsequent assignment of the far-infrared spectrum of $ReCl_5$.[32]

For an isolated osmium pentachloride dimer of symmetry D_{2h}, there are 30 fundamental modes. Thirteen are infrared active and these thirteen fundamental vibrations can be broken down into four Os–Cl terminal stretches (b_{1u} + b_{2u} + 2 b_{3u}), two Os–Cl bridging stretches (b_{2u} + b_{3u}), one Os–Cl–Os deformation (b_{1u}) and six Cl–Os–Cl deformations (2 b_{1u} + 2 b_{2u} + 2 b_{3u}) based upon the schematics of symmetry coordinates for the species M_2Cl_{10}, as given by Beattie et al.[31] All of these modes will be found below about 400 cm^{-1}. A tentative assignment for $OsCl_5$ based on those of the other pentachlorides is given in Table IV, together with the assignments for these pentachlorides. As indicated above, the assignments were obtained by Beattie et al.[31] from calculated values of the fundamental modes, using normal-coordinate methods. However, as pointed out by these authors, with about 30 Raman and infrared-active fundamental modes spread over 300 cm^{-1} there will be, on the average, one band every 10 cm^{-1}, so that agreement between calculated and observed frequencies would be likely. Hence, these assignments cannot be taken too literally. As expected, the far-infrared spectra of molybdenum pentachloride[30] and tungsten pentachloride[30,33] are similar to those of the other pentachlorides and may be assigned in a similar way.

No reliable UV–visible solution spectra of $OsCl_5$ could be obtained because of the lack of a convenient solvent and the sensitivity of the compound to traces of moisture. However, the diffuse reflectance spectrum was recorded from 4000 to 40 000 cm^{-1}, both on the solid pentachloride and after dilution with well-dried magnesium oxide. The latter was used to avoid metallic reflectance effects. Both samples gave identical spectra, but slightly better definition was observed in the diluted sample. The spectrum is shown in Figure 3 (~8500–40 000 cm^{-1}) and shows two strong, broad bands centered at 15 400 and 23 300 cm^{-1}. At higher energies, another band appears at 37 600 cm^{-1}, while at lower energies, a well-defined shoulder appears at 9750 cm^{-1}. In the near-infrared region, peaks were observed at 4750 (m), 5450 (m), 6600 (m), and 6850 (m) cm^{-1}.

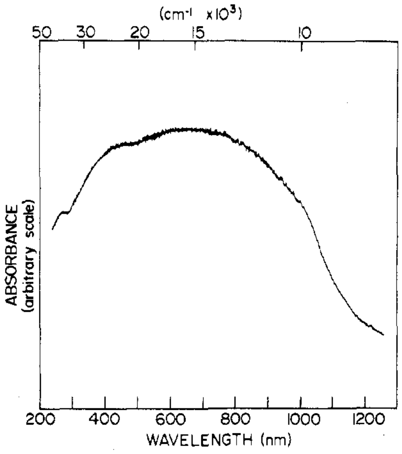


Figure 3. Reflectance spectrum of $OsCl_5$ from ~8500 to 40 000 cm^{-1}.

With the exception of the fluorides, the UV–visible spectra of hexahalometalate complexes of all 4d and 5d transition metals are dominated by intense halogen-to-metal electron-transfer bands. These bands mask the weaker d–d transitions. For the fluorides, the electron-transfer bands occur well into the UV region and are generally not observed. If the arguments presented by Jørgenson[34] are used, it is possible to assign the electron-transfer transitions of $OsCl_5$, assuming that the osmium atoms are situated in an octahedral environment of chlorine atoms. Structural evidence above indicates that, although there is some distortion of the chlorine environment around each atom, the departure from octahedral symmetry is not great. A similar procedure has been used by Edwards and Ward[32] to assign the spectrum of $ReCl_5$.

For the $TaCl_6^-$ and WCl_6^- anions[35] and $ReCl_5$,[32] the bands at 36 400, 29 000, and 21 000 cm^{-1}, respectively, have been assigned as the first Laporte-allowed transition, $2\gamma_{4u} \rightarrow 2\gamma_{5g}$ ($Cl(\pi) \rightarrow M_{t_{2g}}$) whereas the lower energy bands at 30 800, 25 400, and 16 200 cm^{-1}, respectively, have been assigned to the parity-forbidden $1\gamma_{4g} \rightarrow 2\gamma_{5g}$ transition. For $ReCl_5$, the bands at 38 500 and 43 000 cm^{-1} have also been assigned to the higher energy $1\gamma_{5u} \rightarrow 2\gamma_{5g}$ and $2\gamma_{4u} \rightarrow 2\gamma_{3g}$ transitions. These assignments are based upon the expected ordering of energies of the halogen π orbitals,[36] which is $1\gamma_{5g} < 1\gamma_{5u} < 2\gamma_{4u} < 1\gamma_{4g}$. In each of the hexahalometalate series the energy of the π electrons is considered to be constant,[37] while the energy of γ_{5g} varies linearly with q, the number of d electrons. For $q = 3$ (osmium(V), $5d^3$) the energy of the first Laporte-allowed transition is given by

$$V_1 - 3(E - A) + 2D$$

where D is the spin-pairing energy and $E - A$ represents the difference between the increased core attraction (E), on increasing the atomic number by one unit, and the average interelectronic repulsion energy (A).[38] The parameters $D \sim$ 3000 cm^{-1} and $E - A \sim 6000$ cm^{-1}, which have been found to account for the shift in the electron-transfer bands of the 5d transition series,[37] may be used to estimate the position of the first Laporte-allowed transition of $OsCl_5$ at about 24 000 cm^{-1}. The parity-forbidden first electron-transfer band will therefore appear at an even lower energy. Examination of the reflectance spectrum of $OsCl_5$ suggests that the strong band at 23 300 cm^{-1} may be assigned as the Laporte-allowed $2\gamma_{4u} \rightarrow 2\gamma_{5g}$ transition and that the other strong band at 15 400

Table V. Variation of the Magnetic Susceptibility with Temperature for Osmium Pentachloride

T, K	$10^6\chi_M'$, cgsu	T, K	$10^6\chi_M'$, cgsu
293	2741	175	3521
279	2817	162	3663
265	2857	151	3774
249	2994	137	3922
236	3086	123	4049
223	3155	111	4202
212	3226	102	4329
202	3322	93	4425
189	3425	80	4630

cm^{-1} is the parity-forbidden $1\gamma_{4g} \rightarrow 2\gamma_{5g}$ transition. The high energy band at 37 600 cm^{-1} may therefore be assigned as one of the $1\gamma_{5u} \rightarrow 2\gamma_{5g}$ or $2\gamma_{4u} \rightarrow 2\gamma_{3g}$ transitions, with the unobserved transition probably occurring somewhere above 40 000 cm^{-1}, out of the range over which the spectrum could be recorded. The value for the first Laporte-allowed transition corrected for the spin-pairing energy (σ_{cor}) may be used to calculate the optical electronegativity for osmium(V) from the expression

$$\sigma_{\text{cor}} = (\chi_{\text{opt}}[\text{X}] - \chi_{\text{opt}}[\text{M}]) \times 30000\ \text{cm}^{-1}$$

where $\chi_{\text{opt}}[\text{X}] = \chi_{\text{opt}}[\text{Cl}] = 3.0$ and $\chi_{\text{opt}}[\text{M}] = \chi_{\text{opt}}[\text{Os(V)}]$. This gives a value of ~2.4, which is consistent with both the trend for oxidation state (V) across the 5d transition series[32,34] [Ta(V) 1.8, W(V) 1.95, Re(V) 2.2, *Os(V) 2.4*, Ir(V)..., Pt(V) 3.0] and the trend with increasing state of oxidation of osmium[34] [Os(III) 1.95, Os(IV) 2.2, *Os(V) 2.4*, Os(VI) 2.6].

The ESR spectrum of the solid pentachloride consisted of a very broad signal, several hundred gauss wide, centered on a g value of ~2.0. No fine structure could be observed.

Magnetic Properties. The magnetic susceptibility data for OsCl_5 from 293 to 80 K are given in Table V. The pentachloride obeys the Curie–Weiss law over this range, giving a Weiss constant $\Theta_W = 230$ K and a value for μ_{eff}' of 3.39 μ_B ($\mu_{\text{eff}} = 2.54\ \mu_B$). The high Weiss constant is probably indicative of the presence of an antiferromagnetic interaction. Magnetic moments of octahedral t_{2g}^3 osmium(V) compounds are generally about 3.1–3.4 μ_B at room temperature, considerably less than the spin-only value of 3.87 μ_B as a consequence of the high spin–orbit coupling constant for osmium(V).[39] They are also expected to be independent of temperature. The effect of an asymmetrical ligand field on a t_{2g}^3 configuration is to cause some variation in the magnetic moment with temperature, but this is usually observed at low temperatures.[39]

Structural studies have shown that the osmium···osmium distance in the dimer is 3.63 Å, which is considerably longer than the sum of the metallic radii (2.70 Å). Furthermore, in the dimer, both osmium atoms are shifted from the centers of their respective octahedra of chlorine atoms away from each other. This would indicate that a direct metal–metal interaction is highly unlikely and suggests that the antiferromagnetic coupling is caused by superexchange interactions through the bridging chlorine atoms, i.e., a superexchange pathway, although the possibility of intermolecular exchange through the chlorine ligands (Os–Cl–Cl–Os) cannot be discounted.[39]

Hydrolytic Oxidation of Osmium Pentachloride. Osmium pentachloride showed no reaction with dry oxygen at 100 °C after 3 h, unlike the pentachlorides of molybdenum, tungsten, and rhenium which are reported to react quite readily with oxygen at room temperature.[1] However, the pentachloride did react with a small amount of water under the above conditions to give osmium oxide tetrachloride as one product. Furthermore, osmium pentachloride reacted with water, or perhaps oxygen, in a number of organic solvents to produce osmium oxide tetrachloride as shown by comparison of the UV–visible spectra of the resulting solutions with the spectra of this compound in the same solvents. A sample of osmium oxide tetrachloride, prepared by the method of Hepworth and Robinson,[40] exhibited an absorption band at 25 100 cm^{-1} and a slightly stronger band at 28 600 cm^{-1} over the range 12 000–36 400 cm^{-1} in carbon tetrachloride.

The formation of osmium(VI) in the above solutions can be rationalized in two ways. In the presence of oxygen, osmium pentachloride could simply be oxidized to osmium oxide tetrachloride in solution just as molybdenum pentachloride is oxidized to molybdenum oxide tetrachloride in organic solvents under the same conditions.[41] However, if water is the reactant, then the formation of osmium oxide tetrachloride could result from a disproportionation reaction such as

$$2\text{OsCl}_5 + \text{H}_2\text{O} \rightarrow \text{OsOCl}_4 + \text{OsCl}_4 + 2\text{HCl} \qquad (2)$$

Osmium pentachloride was also found to dissolve in acetonitrile with the formation of a brown solution, indicating reaction with the solvent. A UV–visible spectrum of the resultant solution was identical with the spectrum of a solution of osmium tetrachloride in acetonitrile, showing that reduction to osmium(IV) had occurred. This is not unexpected as the pentachlorides of molybdenum, tungsten, and rhenium are also reduced to the tetravalent state by acetonitrile.[42,43]

Osmium Hexafluoride–Carbon Tetrachloride Reaction. Reaction of osmium hexafluoride with carbon tetrachloride always gave a black, nonstoichiometric product containing both chlorine and fluorine and which exhibited a formal oxidation state between V and VI for osmium. The stoichiometry of the product also varied with the reaction conditions; however, complete exchange could not be obtained even when the product was heated with carbon tetrachloride at 80–90 °C for several hours. Presumably, variable amounts of a number of mixed chloride fluorides of osmium(V) and -(VI) were always formed in this reaction, thereby leading to the nonstoichiometry of the product.

Further evidence for the existence of these mixed halides was obtained in a number of reactions which were carried out well below room temperature, with only a slight excess of the tetrachloride. These reactions always gave a red-to-mauve volatile intermediate species. The formation of a red-to-brown volatile intermediate has also been observed in the reactions of rhenium hexafluoride with titanium tetrachloride and carbon tetrachloride, although the ultimate product in each case was rhenium hexachloride.[44] It was suggested that this intermediate was a mixed chloride fluoride of rhenium(VI), perhaps ReF_5Cl. This volatile red compound has actually been isolated from the reaction between rhenium pentachloride and elemental fluorine at 30 °C.[45] It is thermally unstable above −30 °C, giving rhenium hexafluoride and rhenium chlorides. The red-to-mauve material observed in this work was probably a mixed halide of osmium(VI), but no attempt was made to isolate the product.

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Registry No. OsCl_5, 71328-74-0; OsF_6, 13768-38-2; BCl_3, 10294-34-5; CCl_4, 56-23-5.

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Preparation, Spectroscopic Properties, and Crystal Structures of $Te_6(AsF_6)_4{\cdot}2AsF_3$ and $Te_6(AsF_6)_4{\cdot}2SO_2$: A New Trigonal-Prismatic Cluster Cation, Te_6^{4+}

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The compounds $Te_6(AsF_6)_4{\cdot}2AsF_3$ and $Te_6(AsF_6)_4{\cdot}2SO_2$ have been prepared by the reaction of elemental tellurium with AsF_5 in AsF_3 or SO_2 as solvent. Crystal structures of both compounds have been determined by three-dimensional X-ray counter measurements. Crystals of $Te_6(AsF_6)_4{\cdot}2AsF_3$ are monoclinic with $a = 14.832$ (9) Å, $b = 12.242$ (8) Å, $c = 15.301$ (9) Å, and $\beta = 96.59$ (7)°. The structure has been refined in the space group $C2/c$ to final agreement indices $R_1 = 0.082$ ($R_2 = 0.099$) for 1720 observed ($I > 3\sigma(I)$) data and $R_1 = 0.096$ ($R_2 = 0.109$) for all 2114 independent reflections. Crystals of $Te_6(AsF_6)_4{\cdot}2SO_2$ are triclinic with $a = 9.962$ (3) Å, $b = 10.681$ (4) Å, $c = 16.599$ (4) Å, $\alpha = 107.69$ (7)°, $\beta = 92.40$ (7)°, and $\gamma = 120.10$ (7)°. The structure of this compound has been refined in the space group $P\bar{1}$ to a final agreement index R_1 of 0.093 for 1829 reflections with $I > 3\sigma(I)$ and a weighted index R_2 of 0.087 for 2708 independent reflections. Both compounds contain the novel trigonal-prismatic Te_6^{4+} species and consist of Te_6^{4+} and AsF_6^- ions and either AsF_3 or SO_2. The cation in the SO_2 adduct is quite regular, within experimental error, but in the AsF_3 adduct it is slightly distorted. The Te–Te bond distances in the triangular faces range from 2.662 to 2.694 Å, while those between the faces are considerably longer, ranging from 3.062 to 3.148 Å. Electronic spectroscopic studies are also reported on the Te_6^{4+} cation and these have shown that the species, which was previously identified as "Te_n^{n+}" in highly acidic media, is actually the Te_6^{4+} cation.

Introduction

It has been known for a very long time that tellurium forms a deep red solution when dissolved in concentrated sulfuric acid.[1] Similarly, deep red solutions are also obtained when tellurium is dissolved in weak oleums or HSO_3F at room temperature.[2,3] Absorption spectra and conductometric and cryoscopic measurements on the solutions in HSO_3F led to the identification of the Te_4^{2+} cation in these media.[2,3] At the same time studies on the purple-red melts formed by the reaction of tellurium with $TeCl_4$ in molten $NaAlCl_4$ led Bjerrum and co-workers[4,5] to propose the presence of the species Te_{2n}^{n+}, which they believed to be Te_4^{2+}.

If the acid solutions described above are warmed or if the oleum is sufficiently strong (>~45% SO_3), then the colors of the solutions change from red to orange-yellow.[3,6] The same change may also be produced by addition of an oxidizing agent such as peroxydisulfate to the sulfuric acid solutions or $S_2O_6F_2$ to the HSO_3F solutions. Absorption spectra and conductometric, cryoscopic, and magnetic measurements on the solutions in HSO_3F suggested that the yellow species was tellurium in a 1+ oxidation state, and it was formulated as "Te_n^{n+}", where *n* is even as the cation was found to be diamagnetic. Furthermore, these studies also established that "Te_n^{n+}" could not be Te_2^{2+}, and was probably Te_4^{4+}, although higher molecular weight species such as Te_6^{6+} and Te_8^{8+} could not be ruled out.[3,6] In contrast, Paul and co-workers[7] concluded from similar studies in $H_2S_2O_7$ that the yellow species was Te_2^{2+}. Bjerrum[8] also concluded, from spectrophotometric measurements on solutions formed by the reduction of $TeCl_4$ with tellurium metal in $KAlCl_4$ melts buffered with KCl–$ZnCl_2$, that the species was Te_2^{2+}.

Solid compounds containing Te_4^{2+} and "Te_n^{n+}" are also well-known. It has been shown that oxidation of tellurium by $S_2O_6F_2$, AsF_5, and SbF_5 in SO_2 as solvent gives the compounds $Te_4(SO_3F)_2$, $Te_4(AsF_6)_2$, and $Te_4(Sb_2F_{11})_2$, respectively,[3] while the compounds $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$ have been

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