P)$(NH_3)_4Ru$], 88288-73-7; [(1,2-benzoquinone)$(NH_3)_4Ru^{II}]^{2+}$, 88288-74-8; [(DHB)$(NH_3)_4Ru^{III}]^+$, 88288-77-1; [(DHB$^-$)$(NH_3)_4$-Ru^{III}], 88288-75-9; $[(NH_3)_6Ru]^{3+}$, 18943-33-4; $[Cl(NH_3)_5Ru]^{2+}$, 21560-19-0; *cis*-$[Cl_2(NH_3)_4Ru]^+$, 25604-36-8; (2-(3,4-dihydroxyphenyl)ethanoato)tetraammineruthenium(III), 88288-76-0.

Supplementary Material Available: Listings of elemental analyses and representative UV–vis spectral data (1 page). Ordering information is given on any current masthead page.

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Osmium(V): Synthesis, Characterization, and Spectral Examination of Hexahalogeno Complexes

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Two new complex ions of osmium(V), $OsCl_6^-$ and $OsBr_6^-$, have been generated by oxidation in acidic acetonitrile with PbO_2 of the corresponding hexahalogenoosmate(IV) complex ions. The very stable $(Ph_4P)OsCl_6$ salt has been isolated and fully characterized. The $OsCl_6^-$ ion was found to be substitution inert and behaved as a potent one-electron oxidant. Its solution d–d spectral properties indicate a very low nephelauxetic ratio, β_{55}, and a correspondingly high covalency must be attributed to the complex. Examination of its ligand to metal charge-transfer spectrum has led to the reinstatement of Jørgensen's selection rule based on *j–j* coupling in modified form for $5d^3$ ions. The major features of the charge-transfer spectrum were predicted by using a single energy variable, representing the lowest energy Laporte-allowed transition, by mapping onto the d–d spectrum of the $5d^4$ $OsCl_6^{2-}$ ion. The optical electronegativity of Os(V) was found to be 2.45. The charge-transfer spectrum of the less stable $OsBr_6^-$ confirmed the selection rule and optical electronegativity for Os(V). This complex decomposed by a redox process in acetonitrile to afford the $[OsBr_5(NCCH_3)]^-$ ion.

Introduction

The chemistry of osmium in the V oxidation state has not been extensively studied, and only a handful of well-characterized compounds have been reported.[1] Information about such important properties as substitution rates, redox behavior, precise bond lengths, and electronic structure is very limited. The literature preparative routes to Os(V) are challenging at best. Reaction of $F_2(g)$ with osmium metal affords OsF_6, which may be used as a synthetic intermediate. Reduction of the hexafluoride with Si formed OsF_5, and the recently reported osmium pentachloride dimer, Os_2Cl_{10}, has been obtained from reaction of OsF_6 with BCl_3.[2–4] Alternatively, $OsCl_4$ may be oxidized to the OsF_6^- ion by treatment with BrF_3.[5] Most of the Os(V) complexes are prone to hydrolysis and decompose either by disproportionation or oxidation of water, so that handling of the compounds has also hindered the development of the chemistry of Os(V). This has led to the generally accepted belief that this oxidation state is inherently unstable.[6]

Although the spectral properties of hexahalogeno transition-metal complexes have been well studied, there still remain unresolved issues. In particular, the ligand to metal charge-transfer selection rules for metals with strong spin–orbit coupling are unclear. Jørgensen has suggested that the similarity of charge-transfer spectra of $5d^4$ and $5d^5$ ions may be the result of *j–j* coupling in the charge-transfer state.[7] On the other hand, it has been pointed out that a pure electrostatic limit also yields only one term for the excited state.[8] For $5d^3$ ions it was necessary to introduce both electrostatic and spin–orbit influences to rationalize the spectral properties of the Re^{4+} ion in cubic chloride and bromide host crystals. However, the transitions for Re^{4+} that could give insight to the selection rule dilemma are expected to occur in inaccessible or cluttered high-energy regions.[8–10]

Herein is reported the facile, bench-top synthesis of the stable $OsCl_6^-$ complex ion and its less stable bromo analogue. The chloro complex is particularly suited for study of the $5d^3$ charge-transfer bands because of their low energy and the availability of extensive information about the electronic structure of the one-electron-reduced $OsCl_6^{2-}$ ion. A previous claim[11] has been made for the pulse radiolytic generation of the $OsCl_6^-$ ion with Cl_2^-; however, the reported spectrum differs substantially from the findings here. A single-crystal X-ray structural determination has been carried out on $(Ph_4P)OsCl_6$ and will be reported subsequently.[12]

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Experimental Section

Materials. $(NH_4)_2OsCl_6$ and $(NH_4)_2OsBr_6$ were synthesized according to the procedures of Dwyer and Hogarth.[13] The tetraphenylphosphonium (Ph_4P^+) and tetraethylammonium (Et_4N^+) salts of the hexachloroosmate(IV) ion were prepared by precipitation from saturated solutions of $(NH_4)_2OsCl_6$ in 0.5 M aqueous HCl with Ph_4PBr and Et_4NCl, respectively. $(Et_4N)_2OsBr_6$ and $(Ph_4P)_2OsBr_6$ were prepared similarly by precipitation from cold solutions of $(NH_4)_2OsBr_6$ in 1 M aqueous HBr. $(Et_4N)_2IrCl_6$ was also obtained by metathesis from K_2IrCl_6, a kind gift of Professor R. M. Milburn. Anhydrous acetonitrile (AN), carefully distilled from phosphorus pentoxide, was employed throughout. The purity is crucial, as the Os(V) complexes react rapidly with traces of organic impurities in commercial grade AN. Tetraethylammonium perchlorate (TEAP) was dried under vacuum for 2 h at 50 °C before use.

Preparation of Tetraphenylphosphonium Hexachloroosmate(V), $(Ph_4P)OsCl_6$. Solid PbO_2 (0.120 g) was slurried in a solution of 0.60 g of $(Ph_4P)_2OsCl_6$ in anhydrous AN at 65 °C. The oxidation was initiated by addition of 7.0 mL of 1 M trifluoroacetic acid (HTFA) in AN with stirring. The virtually black reaction mixture was stirred at 65 °C for 7 min and then filtered while hot through a sintered glass funnel. The filtrate was allowed to cool at room temperature for 0.5 h and then at −5 °C for 1.5 h. The black crystalline product was collected by filtration, washed with a small volume of cold AN, and dried with a stream of air. The yield was 45–55%. Anal. Calcd for $(C_6H_5)_4POsCl_6$: C, 38.8; H, 2.72; Cl, 28.7. Found: C, 38.9; H, 2.75; Cl, 28.4. The isolated solid may be stored for months with no apparent decomposition without special precautions.

Oxidation of the $OsBr_6^{2-}$ Ion. Although facile decomposition precluded isolation of the hexabromoosmate(V) ion, solutions were prepared at low temperatures for spectral examination. A nearly saturated solution of $(Et_4N)_2OsBr_6$ in 1 M HTFA in AN in a centrifuge tube was cooled to about −40 °C. A tenfold molar excess of solid PbO_2 was added and the mixture allowed to warm to −10–0 °C with swirling for about 1 min. It was cooled again to −40 °C and centrifuged. An aliquot of the cold supernatant was diluted with cold AN and its visible spectrum recorded at 0 °C. If the $OsBr_6^{2-}$ ion were still present, the warming/cooling/centrifuging procedure was repeated until the starting material had been consumed. The cold solution at this stage contained the $OsBr_6^-$ ion, but warming to room temperature caused a second set of spectral changes to occur over a few minutes.

The decomposition product was isolated as follows. Solid PbO_2 (77 mg, 0.32 mmol) was added to a solution of 0.30 g of $(Et_4N)_2OsBr_6$ (0.32 mmol) in 15 mL of 0.25 M HTFA in AN. The slurry was stirred vigorously for 15 min, during which the odor of Br_2 could be detected. The reaction mixtures was centrifuged and the supernatant was rotary evaporated to dryness. The resultant solid was slurried with 5 mL of tetrahydrofuran and washed onto a glass frit. After being washed four times with 1.5 mL of tetrahydrofuran (until the filtrate was light purple), the very dark purple solid was dried with a stream of air for 10 min and then in a vacuum desiccator for 2 h (yield = 0.20 g). The visible spectrum of the solid dissolved in AN was essentially identical with spectra obtained from room temperature decomposition of dilute solutions of the $OSBr_6^-$ ion. The compound is formulated as $(C_2H_5)_4N[OsBr_5(NCCH_3)]$. Anal. Calcd: C, 15.8; H, 3.02; N, 3.68; Br, 52.6. Found: C, 15.9; H, 2.99; N, 3.69; Br, 52.5.

Spectral Measurements. A Cary 210 spectrophotometer was employed for UV and visible measurements. Near-infrared (NIR) spectra of solutions of $(Ph_4P)OsCl_6$ in AN were recorded against an AN reference on a Cary 14 spectrophotometer (courtesy of Professor H. Kalkar). Infrared measurements were obtained on a Perkin-Elmer 180 grating instrument.

Cyclic Voltammetry. Scanning voltammetric studies were carried out on conventional three-electrode cyclic voltammetry equipment, with output onto a Houston Omigraphics Model 2000 XY recorder. Unless otherwise noted, measurements were performed on anhydrous, deoxygenated AN solutions with 0.10 M TEAP as supporting electrolyte at a Pt working electrode against SCE at a scan rate of 50 mV s^{-1}.

Conductivity Measurements. An Industrial Instruments Model RC 16B2 conductivity bridge in the low-frequency mode was used in conjunction with a platinum black electrode conductivity cell with a cell constant of 1.0. Five AN solutions of Ph_4PBr and $(Ph_4P)_2OsCl_6$ in the concentration range 0.6–6 mM served as 1:1 and 2:1 reference electrolytes. They were found to have molar conductivities of 114 and 199 $cm^2\ \Omega^{-1}\ mol^{-1}$ at 23 °C, respectively. Under the same conditions $(Ph_4P)OsCl_6$ was found to have a molar conductivity of 107.

Magnetic Susceptibility. A Cahn Instruments Faraday balance (courtesy of Professor M. Clarke of Boston College) was used for magnetic measurements on $(Ph_4P)OsCl_6$ at 22 °C. After diamagnetic corrections, the susceptibility per mole was found to be 4400×10^{-6} cgs units, corresponding to $3.22 \pm 0.1\ \mu_B$ at 295 K. The diamagnetic contribution from the Ph_4P^+ ion was determined to be -167×10^{-6} cs/mol from measurements on Ph_4PBr. Diamagnetic corrections of Cl^- and Br^- ions were taken from Earnshaw.[14]

Results and Discussion

Characterization of the Hexachloroosmate(V) Ion. The $OsCl_6^-$ ion has been generated by oxidation of the $OsCl_6^{2-}$ ion with PbO_2 in acidic acetonitrile, and the Ph_4P^+ salt has been isolated as a black, crystalline solid. In addition to satisfactory elemental analyses for $(Ph_4P)OsCl_6$ (I), a single-crystal X-ray structural determination has shown the coordination shell around the Os(V) to be intact after oxidation, with shorter Os–Cl bond lengths than the $OsCl_6^{2-}$ ion.[12] Several other lines of evidence also support the assignment of a formal Os(V) oxidation state. A spectrophotometric titration of an acetonitrile of I with a solution of hydroquinone showed a linear decrease in absorbance at 500 nm with a sharp break after 0.95 equiv of hydroquinone (as a two-electron reductant) had been added. The spectrum at this point was essentially identical with that of the well-known hexachloroosmate(IV) ion.

The infrared spectrum of I in Nujol exhibited a strong asymmetric absorbance at 338, 330 sh cm^{-1} which can be attributed to an Os(V)–Cl stretching frequency. As would be expected, this band occurs at somewhat higher energy than the corresponding Os(IV)–Cl stretching mode, reported at 317 cm^{-1} for K_2OsCl_6.[1] In addition, a weak absorption for I was noted at 308 cm^{-1}.

The magnetic moment of I after diamagnetic corrections was found to be $3.22 \pm 0.1\ \mu_B$ at 295 K, in accord with the value of 3.23 μ_B reported for $CsOsF_6$.[15] The electronic ground state may be assigned analogously as a Γ_8 state (in Bethe octahedral double-group notation), which correlates the $^4A_2$ term of the $(t_{2g})^3$ configuration under Russell–Saunders coupling with the $(t_{3/2})^3$ configuration of the *j–j* coupling scheme.[16,17]

Conductivity and spectral measurements show the $OsCl_6^-$ ion to be inert toward solvolysis in AN, as might be anticipated for an octahedral d^3 ion. The molar conductivity of I in AN was consistent with a 1:1 electrolyte, and no indication of further dissociation was observed. Moreover, the visible spectrum of I in AN solution (see below) changed by less than 5% in absorbance in 20 h at 25 °C, and substantial changes should have been observable in these charge-transfer bands if the octahedral symmetry were broken by solvolysis. One cannot exclude the possibility that chloride loss in AN is thermodynamically unfavorable; however, even reaction of the $OsCl_6^-$ ion with water is quite slow, despite the great affinity of higher valent osmium for oxygen-containing ligands. Decomposition of a 1.3×10^{-4} M solution of I in 0.8 M HTFA in a 4:1 AN/H_2O mixture (∼11 M H_2O), monitored at 500

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[17] The $OsCl_6^-$ ion will be considered here within the framework of octahedral symmetry. Although the solid-state symmetry is reduced to C_{4v} around the osmium, the distortion is fairly small, and it is not known at this time if the distortion is present in solution.

Table I. Electrochemical Potentials from Cyclic Voltammetry

couple	$(E_a + E_c)/2$,[a] V	$E_a - E_c$, mV
$OsCl_6^-/OsCl_6^{2-}$	1.24	60
$OsCl_6^{2-}/OsCl_6^{3-}$	−0.68	85
$OsBr_6^-/OsBr_6^{2-}$	1.20	65
$OsBr_6^{2-}/OsBr_6^{3-}$	−0.55[b]	
$[OsBr_5(AN)]^-/[OsBr_5(AN)]^{2-}$	0.02	70
$IrCl_6^-/IrCl_6^{2-}$	1.67	70
$IrCl_6^{2-}/IrCl_6^{3-}$	−0.04	63
Ce(IV)/Ce(III)[c]	1.07	150

[a] Reduction potentials vs. SCE, medium = 0.10 M TEAP in AN, scan rate = 50 mV/s, 24 °C. [b] Potential of the irreversible cathodic wave given. [c] Solution of $(NH_4)_2Ce(NO_3)_6$.

nm, was approximately first order in Os(V). The first-order rate constant at 25.0 °C was found to be $2.5 \times 10^{-5}\ s^{-1}$ or a half-life of about 8 h. The spectrum of the solution after decomposition was essentially identical with that of the $OsCl_6^{2-}$ ion, supporting a redox decomposition rather than aquation. Thus, the measured rate represents an upper limit to the rate of substitution and shows that the $OsCl_6^-$ ion can be characterized as robust.

The most striking chemical property of the $OsCl_6^-$ ion is its potency as an oxidizing agent. Cyclic voltammetry on either $(Et_4N)_2OsCl_6$ or I in 0.10 M TEAP in AN showed a fully reversible couple at +1.24 V vs. SCE. As can be seen in Table I, I is a better oxidant than the Ce(IV) ion and over a volt better oxidant than the $IrCl_6^{2-}$ ion in this medium. Measurements on $(Et_4N)_2IrCl_6$ uncovered an additional, nearly reversible wave at 1.67 V with currents comparable to the Ir(IV)–Ir(III) couple at −0.04 V. The wave is most likely the Ir(V)–Ir(IV) couple, and the assignment is supported by noting that the difference between the M(V)–M(IV) and M(IV)–M(III) couples is almost the same for Ir and Os.[18] The chemical oxidizing power of the $OsCl_6^-$ ion is demonstrated by its ability to react with a wide variety of organic molecules, including slow room temperature reactions with acetone and primary and secondary alcohols. In most cases the $OsCl_6^{2-}$ ion is produced, which suggests that an outer-sphere electron-transfer process is involved. A surprisingly rapid oxidation of olefins by I under mild conditions is currently under investigation.

Table II. Spectral Properties of Osmium Complexes in Acetonitrile

complex ion	λ, nm	energy[a]	$10^{-2}\epsilon$[b]	assignt
$OsCl_6^-$, $(Ph_4P^+$, 25 °C)	~1650	6.1	0.068	$\rightarrow b\Gamma_8(^2T_{1g})$
	1330	7.52	0.087	$\rightarrow \Gamma_6(^2T_{1g})$, $c\Gamma_8(^2E_g)$
	1295	7.72	0.122	
	1268	7.89	0.175	
	1248 sh	8.01	0.132	
	1233	8.11	0.220	
	1224 sh	8.17	0.132	
	1220	8.33	0.029	
	920	10.87	0.057	$\rightarrow \Gamma_7(^2T_{2g})$
	908	11.01	0.091	
	896	11.16	0.116	
	763	13.1	0.74	$\rightarrow c\Gamma_8(^2T_{2g})$[c]
	707	14.1	0.87	
	588	17.0	14.6	
	580 sh	17.2	14.3	$\pi(Cl) \rightarrow t_{2g}$[d]
	502	19.9	52	
	456 sh	21.9	88	
	450	22.2	89	
	442 sh	22.6	85	
	424 sh	23.6	84	
	414	24.2	86	
	401 sh	24.9	78	
$OsBr_6^-$, $(Et_4N^+$, 1 M HFTA, 0 °C	~770 sh	13.0		$\pi(Br) \rightarrow t_{2g}$[c]
	~690 sh	14.5		
	626	16.0		
	550	18.2		
	489	20.4		
	468 sh	21.4		$[OsBr_5(AN)]^-$
$[OsBr_5(AN)]^-$, $(Et_4N^+$, 25 °C)	584 sh	17.1	19.5	
	533	18.8	52	
	469	21.3	85	
	421	23.8	16.5	
	334	29.9	23	
	283	35.3	59	

[a] $10^3\ cm^{-1}$. [b] $M^{-1}\ cm^{-1}$. [c] See text. [d] Detailed assignments are given in Table III.

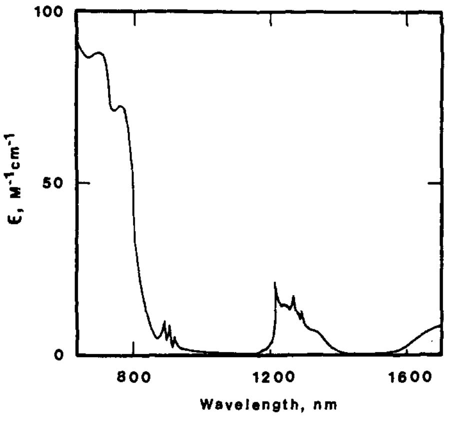

Figure 1. Low-energy spectrum of $(Ph_4P)OsCl_6$, 25 °C.

Oxidation of the $OsBr_6^{2-}$ Ion. Cyclic voltammetry measurements on $(Et_4N)_2OsBr_6$ showed a nearly reversible wave at +1.20 V, which can be attributed to the $OsBr_6^-/OsBr_6^{2-}$ couple. When a solution of $(Et_4N)_2OsBr_6$ in AN at −10 to 0 °C was oxidized with PbO_2/HTFA as described in the Experimental Section, new visible spectral bands appeared at lower energies than the absorptions of the $OsBr_6^{2-}$ ion, with no evidence of an intermediate species. This is interpreted as a simple oxidation of $OsBr_6^{2-}$ to $OsBr_6^-$, as has been demonstrated for the chloro analogue. When the solution was warmed to room temperature, further spectral changes occurred over a few minutes, indicating a fairly rapid decomposition of the $OsBr_6^-$ ion. Elemental analyses of the isolated decomposition product are in excellent agreement with its formulation as $(Et_4N)[OsBr_5(NCCH_3)]$ (II). The infrared spectrum of this material exhibits peaks attributable to the Et_4N^+ ion and weak absorptions at 2330, 2300 cm⁻¹ (KBr) in the C≡N stretching region of acetonitrile. The molar conductivity of II in AN, determined as 119 cm² Ω⁻¹ mol⁻¹ at 22 °C, is consistent with a 1:1 electrolyte. The visible spectrum of II in AN (Table II) closely matches the spectrum obtained by warming solutions of the $OsBr_6^-$ ion to room temperature. Further support for the sequence of oxidation of $OsBr_6^{2-}$ to $OsBr_6^-$ followed by decomposition to the $[OsBr_5(NCCH_3)]^-$ ion was found in electrochemical measurements. When the potential was held 300 mV above the oxidation wave of the $OsBr_6^{2-}$ ion for 2 min at 23 °C, and then a scan toward lower potentials was made, the cathodic wave was substanntially diminished a new reversible couple appeared at 0.02 V. Cyclic voltammetry scans of II exhibited a reversible couple at the same potential. The redox mode of decomposition of the $OsBr_6^-$ ion is reasonable, since the Os(V)–Os(IV) couple is 0.53 V above the irreversible anodic wave of Br⁻ ion.

Electrochemical reduction of the $OsBr_6^{2-}$ ion in AN was irreversible at normal scan rates. Again a new reversible couple appeared at 0.02 V, suggesting that rapid solvolysis occurred in the Os(III) oxidation state, affording the $[OsBr_5(NCCH_3)]^{2-}$ ion.

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[18] The spectrum of the $IrCl_6^-$ ion would be of interest; however, attempts to generate it by PbO_2 oxidation have not succeeded as yet.

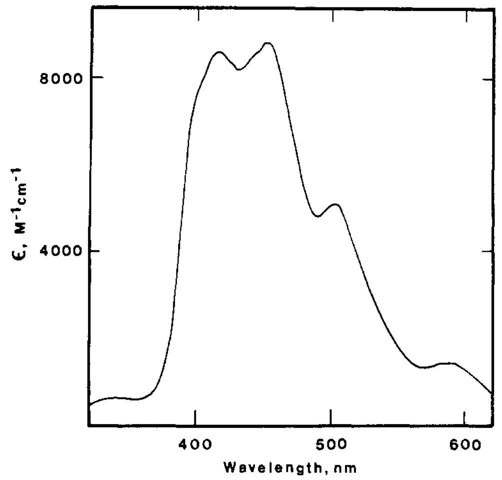

Figure 2. Visible spectrum of $(Ph_4P)OsCl_6$, 25 °C.

Electronic Spectral Properties. The solution absorption spectrum (Table II) of the $OsCl_6^-$ ion is quite intricate, as would be expected for a $5d^3$ hexahalogeno complex. It may be divided conveniently into two regions: weak absorptions extending well into the near-infrared (Figure 1) and visible absorptions with high extinction coefficients (Figure 2). The latter are surely associated with charge-transfer transitions and will be considered after the NIR bands.

The weak low-energy bands can be attributed to intraconfigurational transitions within the $(t_{2g})^3$ subset of the strong octahedral field. The spectrum possesses a very close resemblance to the solution spectrum of the isoelectronic $ReCl_6^{2-}$ ion[19] with a general shift of about 2000 cm^{-1} toward lower energies, and assignments in Table II are made by analogy with those of Jørgensen[9] and Eisenstein[19] for the Re(IV) complex. For 5d ions the octahedral field splitting between e_g and t_{2g} orbitals is sufficiently large that a nearly pure $(t_{2g})^3$ electron configuration is attained for a $5d^3$ ion, and this approximation is certainly appropriate for Os(V). However, electrostatic and spin–orbit interactions are comparable in energy, so that an intermediate coupling scheme is needed to describe the intraconfigurational electronic structure.[16] In the intermediate scheme, the ordering of the levels is $a\Gamma_8(^4A_{2g}) < b\Gamma_8(^2T_{1g}) < \Gamma_6(^2T_{1g}) \simeq c\Gamma_8(^2E_g) < \Gamma_7(^2T_{2g}) < d\Gamma_8(^2T_{2g})$.[20] The Γ_6 and $c\Gamma_8$ states are very nearly degenerate because of the large octahedral field potential. The complicated pattern of narrow peaks centered at about 7850 cm^{-1} in the $OsCl_6^-$ spectrum can be attributed to vibronic transitions into these two states. Another set of narrow peaks occurring at about 11 000 cm^{-1} is simpler in structure and can be assigned to vibronic transitions ($\nu \simeq 145$ cm^{-1}) to $\Gamma_7(^2T_{2g})$. As observed for the $ReCl_6^{2-}$ ion, transitions into the $b\Gamma_8(^2T_{1g})$ and $d\Gamma_8(^2T_{2g})$ do not show vibrational fine structure; moreover, the $d\Gamma_8(^2T_{2g})$ level is split into two components about 1000 cm^{-1} apart. For hexahalogenorhenate(IV) complexes, the splitting in solution is reported as 810, 480, and 340 cm^{-1} for F^-, Cl^-, and Br^- ions, respectively, and is rationalized as either a lowering of symmetry or a dynamic Jahn–Teller effect.[9] Unfortunately, for the $OsCl_6^-$ ion these transitions occur at the low-energy edge of the charge-transfer spectrum, and the possibility that the bands attributed to $d\Gamma_8$ are charge transfer in origin cannot be completely discounted at this time. Support for the tentative assignment to d–d transitions is found in estimates of Racah repulsion parameters. The energy of the middle of the $\Gamma_6(^2T_{1g})$ and $c\Gamma_8(^2E_g)$ absorptions may be used as an approximation of the Racah sum $3(3B + C)$,[9] leading to $3B + C = 2617$ cm^{-1}. The energy of the baricenter of the transitions to $\Gamma_7(^2T_{2g})$ and to $d\Gamma_8(^2T_{2g})$ is about $5(3B + C)$,[21] which, with the d–d assignment, gives $3B + C = 2551$ cm^{-1}, in very good agreement. It should be noted that corrections for configuration interactions with $(t_{2g})^2(e_g)^1$ levels are fairly small for this Os(V) complex, since the ratio B^2/Δ is small. If one follows Jørgensen[9] for determination of the nephelauxetic ratio, $\beta_{55} = (3B + C)/7B_{\text{free ion}}$, and uses a free ion value of 727 cm^{-1},[21] the ratio is readily calculated as 0.51. Allen's C/B ratio of 4.75 for Os(V)[21] gives the somewhat lower $\beta_{55} = 0.46$. Although the absolute magnitude of the nephelauxetic ratio may be debated, it cannot be doubted that an extremely low relative value must be assigned to the $OsCl_6^-$ ion and that a high degree of covalency is present in its bonding.[22] A choice of $\beta_{55} = 0.48$ is clearly in line with well-established trends in this parameter. Application of the procedure described above to the spectrum of the OsF_6^- ion[21] for comparison yields $\beta_{55} \simeq 0.65$. A significantly lower value for hexachloro complexes is a common feature, and the reduction can be seen, for example, in nephelauxetic ratios for RF_6^{2-} (0.83) and $ReCl_6^{2-}$ (0.68).[9] A lower β_{55} for $OsCl_6^-$ than $ReCl_6^{2-}$ is also in line with the decrease for isoelectronic ions as the atomic number is increased, for example, in the series ReF_6^{2-} (0.83) > OsF_6^- (0.65) > IrF_6 (0.47).

If the assignments of absorptions at 13 100 and 14 100 cm^{-1} to $d\Gamma_8(^2T_{2g})$ are correct, a rough estimate of the spin–orbit coupling constant for the $OsCl_6^-$ ion can be made.[9] With $B = 350$ cm^{-1}, a very reasonable value of $\zeta_{5d} \simeq 2800$ cm^{-1} is computed, which is somewhat higher than hexachlororhenate(IV) and -osmate(IV) complexes[9,23-25] and somewhat lower than the value of 3200 cm^{-1} attributed to the OsF_6^- ion,[21] as would be expected. When 4500 cm^{-1} is used as the Os^{5+} free ion spin–orbit coupling constant,[15] a relativistic nephelauxetic ratio, $\beta^*_{55} = \zeta_{\text{complex}}/\zeta_{\text{free ion}}$, of 0.62 is found. Once again this relatively low ratio reflects substantial delocalization in the bonding of the $OsCl_6^-$ ion.

The strong absorptions in the solution visible spectrum of the $OsCl_6^-$ ion (Figure 2, Table II) can be reasonably assigned to charge-transfer transitions on the basis of their high extinction coefficients and the general shift to lower energies from the charge-transfer transitions of the $OsCl_6^{2-}$ ion.[7,26-28] Superficially, the pattern of strong absorptions is quite simple and consists of four principal bands. However, closer inspection, particularly of the higher energy peaks, reveals a more complex substructure, as has been observed in the charge-transfer spectrum of the $ReCl_6^{2-}$ ion. The main features of charge-transfer spectra of hexahalogeno transition-metal ions has been successfully described by Jørgensen in terms of Laporte-allowed transitions from filled molecular orbitals of π symmetry, carrying predominantly ligand char-

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(19) Eisenstein, J. C. *J. Chem. Phys.* **1961**, *34*, 1628.

(20) One-electron orbitals at the metal will be designated as t_{2g} for the octahedral limit and $t_{3/2}$ or $t_{1/2}$ to emphasize the *j* value. Bethe double-group notation will be used to describe intermediate coupling metal-derived states, and lower case letters will distinguish states of the same symmetry in order of increasing energy, following Jørgensen.[9] The strong-field Russell–Saunders term to which the states are correlated will be given in parentheses. Ligand molecular orbital sets unsplit by spin–orbit coupling will be designated by $(\pi + \sigma)t_{1u}$ and $(\pi)t_{2u}$, while lower case Bethe notation will be used for spin–orbit split one-electron ligand levels.

(21) Allen, G. C.; El-Sharkawy, G. A. M.; Warren, K. D. *Inorg. Chem.* **1972**, *11*, 51.

(22) Allen, G. C.; Warren, K. D. *Coord. Chem. Rev.* **1975**, *16*, 227.

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(24) Allen, G. C.; Al-Mobarak, R.; El-Sharkawy, G. A. M.; Warren, K. D. *Inorg. Chem.* **1972**, *11*, 787.

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(26) Jørgensen, C. K. *Prog. Inorg. Chem.* **1970**, *12*, 101.

(27) Jørgensen, C. K. *Halogen Chem.* **1967**, *1*, 265.

(28) Piepho, S. B.; Dickinson, J. R.; Spencer, J. A.; Schatz, P. N. *Mol. Phys.* **1972**, *24*, 609.

acter, into empty orbitals at the metal center. In hexachloro complexes, transitions into the metal e_g orbitals are normally found well into the ultraviolet region, while transitions into the t_{2g} orbitals occur at substantially lower energies and often extend into the visible region.[7] The visible absorptions of the $OsCl_6^-$ ion are assigned to the latter type, and allowed transitions into e_g orbitals should appear below 33 000 cm^{-1} because of the large octahedral field splitting expected for Os(V).

The lower energy charge-transfer spectra of 5d^5 ions, such as $IrCl_6^{2-}$, are relatively simple, since the transition leads to a single state at the metal corresponding to $(t_{2g})^6$, so that the absorption pattern inverts the energies of the ligand π orbitals from which transitions occur. MCD measurements have shown that the strong absorptions can be ascribed to transitions from the spin–orbit split $(\pi + \sigma)t_{1u}$ and $(\pi)t_{2u}$ levels, with the baricenter of the latter lying 3000–4000 cm^{-1} below the former.[8] The strikingly similar spectra for 5d^4 complexes, such as the $OsCl_6^{2-}$ ion, have been rationalized by Jørgensen[7,26] on the basis of nearly pure *j–j* coupling in the charge-transfer state (and the resulting exclusion of some transitions as two-electron jumps). However, for 5d^3 complexes such a simple pattern does not exist, and the *j–j* rule has been discounted.[8-10,26] The complete description of possible charge-transfer states and calculation of their energies is a formidable task. It has been carried out in part for interpretation of absorption and MCD spectral properties of Re^{4+} doped into chloride and bromide cubic host crystals by Collingwood et al. Consideration of only Laporte-allowed transitions from the spin–orbit split ligand $(\pi + \sigma)t_{1u}$ and $(\pi)t_{2u}$ molecular orbitals to metal t_{2g} derived orbitals leads to 60 possible excited states, and all 60 transitions are symmetry allowed under the octahedral double group. Fortunately, several simplifying assumptions can be made, which reduce the problem to a tractable level, and as will be seen, the principal bands of the $OsCl_6^-$ charge-transfer spectrum can be projected surprisingly well.

(1) The ligand spin–orbit splitting of the $(\pi + \sigma)t_{1u}$ and $(\pi)t_{2u}$ levels is small for hexachloro complexes. It should be on the order of $(3/4)\zeta_{Cl}$ to $(3/2)\zeta_{Cl}$ theoretically, or less than 900 cm^{-1},[8] so that to a first approximation the splitting will be unresolved.

(2) Electrostatic splitting between holes in ligand molecular orbitals and metal states is small. They have been estimated to be substantially less than 1000 cm^{-1} for Mo^{4+} in cubic lattices.[29]

(3) The electrostatic and spin–orbit splittings of metal-derived terms of the ligand to metal charge-transfer state of a $(t_{2g})^n$ configuration are closely approximated by those of the $(t_{2g})^{n+1}$ one-electron-reduced metal center. This concept has been successfully applied to the 4d^2 Mo^{4+} ion and some of the lower energy transitions of the 5d^3 Re^{4+} ion in cubic host lattices.[8,29] In essence, this assumption allows one to map transitions from a particular ligand π orbital onto the d–d spectrum of the $(t_{2g})^{n+1}$ ion.

The intraconfigurational transitions of the $OsCl_6^{2-}$ ion have been very well studied by a number of techniques, and the recent report by Kozikowski and Keiderling[25] may be consulted. The energy states, in 10^3 cm^{-1}, are ordered: $a\Gamma_1(^3T_{1g})$, ground state; $\Gamma_4(^3T_{1g})$, 2.76; $a\Gamma_5(^3T_{1g})$, 4.88; $a\Gamma_3(^3T_{1g})$, 4.98; $b\Gamma_5(^1T_{1g})$, 10.5; $b\Gamma_3(^1E_g)$, 10.9; $b\Gamma_1(^1A_{1g})$, 17.1. The energy difference between the $(\pi + \sigma)t_{1u}$ and $(\pi)t_{2u}$ ligand orbitals may be taken as 2700 cm^{-1}, the difference observed for the $OsCl_6^{2-}$ ion.[10] If all possible $\pi \rightarrow t_{2g}$ transitions were to occur, the total spread of Laporte-allowed transitions should be about 20 000 cm^{-1} (the sum of 17 100 and 2700), as has been suggested by Jørgenson for the $ReCl_6^{2-}$ ion.[9] Yet the charge-transfer spectrum of the $OsCl_6^-$ ion extends only about 8000 cm^{-1} and *there are no bands with high extinction in the 26 000- to 31 000-cm^{-1} region*, where four Laporte-allowed transitions should appear if states obtained from $b\Gamma_3$ and $b\Gamma_5$ were accessible. The $OsCl_6^-$ ion provides a unique test case for the existence of these transitions because of the relatively low energy of the spectrum. Previous work on Re(IV) has been limited by the onset of host lattice absorptions and dispersion effects. Clearly, Jørgensen's rule based on *j–j* coupling, which had been dismissed for 5d^3 ions, must be reintroduced in modified form to account for the absence (or much lower oscillator strength) of these transitions in the $OsCl_6^-$ ion.

Table III. Calculated Charge-Transfer Spectrum of the $OsCl_6^-$ Ion

excited states[a]	calcd[b]	obsd[c]
$(\pi)t_{2u}^5 \times a\Gamma_5, a\Gamma_3$ (10)	24.7	24.9 sh, 24.2, 23.6 sh
$(\pi)t_{2u}^5 \times \Gamma_4$ (6)	22.6	22.6 sh, 22.2, 21.9 sh
$(\pi + \sigma)t_{1u}^5 \times a\Gamma_5, a\Gamma_3$ (10)	22.1	
$(\pi + \sigma)t_{1u}^5 \times \Gamma_4$ (6)	19.9	19.9
$(\pi)t_{2u}^5 \times a\Gamma_1$ (2)	19.8	
$(\pi + \sigma)t_{1u}^5 \times a\Gamma_1$ (2)	17.1	17.2 sh, 17.0

[a] Number of excited terms in parentheses. [b] Energy in 10^3 cm^{-1}. [c] Spectrum in AN.

(4) From a ground state described by $(t_{3/2})^3$ in the *j–j* coupling scheme, charge-transfer transitions to the $(t_{3/2})^4$ configuration and states derived from the $(t_{3/2})^3(t_{1/2})^1$ configuration are allowed, but transitions to states derived from $(t_{3/2})^2(t_{1/2})^2$ are forbidden as two-electron jumps.

The 8000-cm^{-1} spread of the strong visible absorptions of the $OsCl_6^-$ ion can now be understood as the sum of the energy difference between the $a\Gamma_3(^3T_{1g})$ and $a\Gamma_1(^3T_{1g})$ states of the charge-transfer configuration plus the difference between $(\pi + \sigma)t_{1u}$ and $(\pi)t_{2u}$. One further simplification can be made by noting that the $a\Gamma_3(^3T_{1g})$ and $a\Gamma_5(^3T_{1g})$ states on Os(IV) are practically degenerate at about 4900 cm^{-1} above the $a\Gamma_1(^3T_{1g})$ state. At this stage only a single parameter, ΔE, corresponding to the lowest energy Laporte-allowed transition, is necessary to calculate the charge-transfer spectrum of the $OsCl_6^-$ ion. An excellent fit occurs for the four major features by choosing ΔE = 17 100 cm^{-1}, as can be seen in Table III. The superficial simplicity of the spectrum apparently is the result of a near coincidence in the energy difference between ligand π-molecular orbitals and the difference between $a\Gamma_1(^3T_{1g})$ and $\Gamma_4(^3T_{1g})$ metal-centered states. The finer structure of the complex "clumps" of bands at about 24 200 and 22 200 cm^{-1} and perhaps the higher extinction coefficients are consistent with the large number of states expected from transitions into $a\Gamma_5$ and $a\Gamma_3$ derived terms.

The reasonability of the choice of ΔE as 17 100 cm^{-1} can be tested by calculation of the optical electronegativity for Os(V). Jørgenson has based the optical electronegativity scale for transition metals on the energy of the first Laporte-allowed transition, σ_{obsd}, after corrections for the spin-pairing energy, D, and spin–orbit coupling:

$$\sigma_{corr,rel} = (30\,000\ \mathrm{cm}^{-1})[\chi_{opt}(X) - \chi_{opt}(M)]$$

where $\chi_{opt}(X) = 3.0$ for Cl, and corrections for a d^3 ion are[9]

$$\sigma_{corr,rel} = \sigma_{obsd} - 2D + 2(\zeta_{nd}) - (\zeta_{nd})^2/35B$$

For the $OsCl_6^-$ ion, σ_{obsd} is identical with ΔE above. An estimate of D from the intraconfigurational transitions shows it to be virtually equal to the spin–orbit coupling constant (~2800 cm^{-1}). Thus, one obtains χ(Os(V)) = 2.45, which is clearly in line with general trends of optical electronegativities.[27] In particular, it may be compared with the value of 2.53 estimated from the unresolved high-energy charge-transfer bands of the OsF_6^- ion.[21]

The visible spectrum of the $OsBr_6^-$ ion in AN (Figure 3 and Table II) was obtained at about 0 °C as described above.

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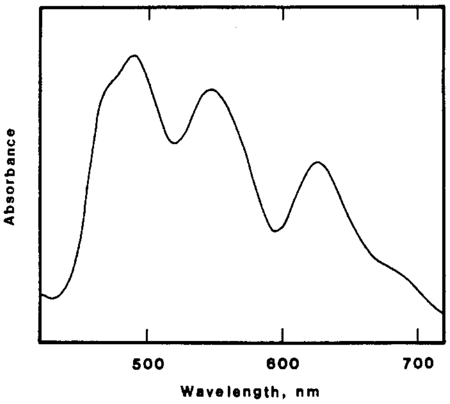

Figure 3. Visible spectrum of the $OsBr_6^-$ ion, 0 °C.

Although accurate measurements were hindered by decomposition, it is certain that the three strongest bands in the visible spectrum have extinction coefficients on the order of several thousand M^{-1} cm^{-1} by comparison with absorbancies of the decomposition product $[OsBr_5(NCCH_3)]^-$. The latter has a very strong absorption at 21 300 cm^{-1}, which most likely accounts for the higher energy shoulder appearing in the $OsBr_6^-$ spectrum. On the basis of the high extinction coefficients and the general shift to lower energies from the transitions of $OsBr_6^{2-}$,[10] the visible bands of $OsBr_6^-$ can be assigned to charge-transfer transitions from ligand π-molecular orbitals into the t_{2g} metal set. The charge-transfer spectrum of a $5d^3$ hexabromo ion is expected to be much more complicated than that of its hexachloro analogue because the spin-orbit splitting of the ligand orbitals by bromine is substantial (1800 to 3600 cm^{-1}) and cannot be ignored. The general framework has been laid out by Collingwood et al.[8] in discussion of Re^{4+} in a $CsZrBr_6$ host crystal. The $(\pi + \sigma)t_{1u}$ level is split by about 3900 cm^{-1} into γ_{6u} and γ_{8u} orbitals, while the lower energy $(\pi)t_{2u}$ level is split into γ_{8u} and γ_{7u} components about 1800 cm^{-1} apart.[28,29]

The higher energy portion of the visible spectrum of the $OsBr_6^-$ ion does not contain any absorptions with oscillator strengths comparable to the strong bands at 20 400 cm^{-1} and below, so that the selection rule developed for the $OsCl_6^-$ is confirmed. Even so, one would expect 12 allowed transitions into the states derived from the $(t_{3/2})^4$ and $(t_{3/2})^3(t_{1/2})^1$ charge-transfer configurations at the metal, compared to 6 for the $OsCl_6^-$ ion, and a detailed assignment of the relatively broad features observed in the $OsBr_6^-$ spectrum cannot be made with confidence. In the spectra of the $IrBr_6^{2-}$ and $OsBr_6^{2-}$ ions, the strongest charge-transfer absorptions have been assigned to transitions from γ_{8u} and γ_{7u} components of $(\pi)t_{2u}$ and γ_{8u} from $(\pi + \sigma)t_{1u}$,[28,29] and it may be that much of the oscillator strength of the bands at 20 400, 18 200, and 16 000 cm^{-1} is derived from transitions from these levels into excited states arising from $a\Gamma_3(^3T_{1g})$, $a\Gamma_5(^3T_{1g})$ at the metal. In any case, the highest energy absorption at 20 400 cm^{-1} can be attributed with some certainty to the transition from the γ_{8u} component of $(\pi)t_{2u}$ to the $a\Gamma_3(^3T_{1g})$, $a\Gamma_5(^3T_{1g})$ derived states. This assignment can be checked by calculation of the optical electronegativity, for which

$$\sigma_{corr,rel} = \sigma_{obsd} - 2D + 2\zeta_{nd} - \zeta_{nd}^2/35B - 4900 - (1/4)\zeta_{Br} - 3500$$

The 4900-cm^{-1} term is a correction for the energy difference between $a\Gamma_1$ and the $a\Gamma_3$, $a\Gamma_5$ states observed in the $OsBr_6^{2-}$ ion,[25] $(1/4)\zeta_{Br}$ is a correction to the baricenter of the $(\pi)t_{2u}$ level, and 3500 cm^{-1} is the energy difference between the baricenters of the $(\pi)t_{2u}$ and the reference $(\pi + \sigma)t_{1u}$ levels.[8,28,29] With χ_{opt} (Br) = 2.8,[27] $\chi_{opt}(Os(V))$ is found to be 2.44, which is fully consistent with the value of 2.45 obtained from the spectrum of the $OsCl_6^-$ ion.

As has been pointed out by Allen,[22] there is a correlation between the optical electronegativity of the metal center and the extent of delocalization. For both the $OsBr_6^-$ and $OsCl_6^-$ ions, the optical electronegativity difference $(\chi(M) - \chi(X))$ is quite small, which further emphasizes the importance of covalency in the bonding.

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Registry No. $(Ph_4P)OsCl_6$, 86365-50-6; $(C_2H_5)_4N[OsBr_5(NCCH_3)]$, 86365-52-8; $OsBr_6^-$, 86365-51-7; $(Ph_4P)_2OsCl_6$, 66200-11-1; $(Et_4N)_2OsBr_6$, 3787-55-1; $(Et_4N)_2OsCl_6$, 41119-82-8; $(Et_4N)_2IrCl_6$, 84699-86-5; $(NH_4)_2Ce(NO_3)_6$, 10139-51-2.