Table II. Bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)copper(II) (M_r = 387.882): Summary of Typical Combustion and Comparison Experiments[a]

	combustn expt	comparison expt
m(complex)[b]/g	0.293990	
m(cyclam)[c]/g		0.151833
$m(Cu(NO_3)_2 \cdot 3H_2O)$/g		0.1868
m(benzoic acid)/g	0.383733	0.381280
m(filter paper)/g	0.007629	0.007651
$\Delta R_{cor}/\Omega$	1.1370	1.1404
$n^i(H_2O)$/mol	1.3060	1.3060
$n^i(HNO_3)$/mol	0.0500	0.0500
$-\Delta R\epsilon$(calor)/kJ	−15.3800	−15.4257[e]
$-\Delta R\epsilon$(cont)/kJ	−0.3165	−0.3206
ΔE(ign)/kJ	0.0015	0.0016
ΔE_W[d]/kJ	0.0559	0.0555
$-m\Delta e_c^\circ$(benzoic acid)/kJ	10.1441	10.0792
$-m\Delta e_c^\circ$(cyclam)[c]/kJ		5.4857
$-m\Delta e_c^\circ$(filter paper)/kJ	0.1314	0.1318
$-m\Delta e_{soln}^\circ(Cu(NO_3)_2 \cdot 3H_2O)$/kJ		−0.0075
$m\Delta e_e^\circ$(complex)[b]/kJ	−5.3636	
Δe_c°(complex)[b]/kJ	−18.2442	

[a] The symbols and abbreviations are those of ref 10. [b] Complex = bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)copper(II). [c] Cyclam = 1,4,8,11-tetraazacyclotetradecane. [d] Items 81-85, 87-91, 93, and 94 of the computation form of ref 14; correction to standard states. [e] Value used to determine ϵ(calor) for the corresponding combustion experiment.

Table III. Summary of Experimental Results: Values of of Δe_c° at 298.15 K

$-\Delta e_c^\circ$/kJ g^{-1}	$-\Delta e_c^\circ$/kJ g^{-1}	$-\Delta e_c^\circ$/kJ g^{-1}
18.2473	18.2346	mean: 18.2412
18.2442	18.2408	std dev: 0.0018
18.2388	18.2416	

of Δe_c° = −7075.4 ± 4.0 kJ mol^{-1} and a corresponding standard molar enthalpy of combustion ΔH_c° = −7085.3 ± 4.0 kJ mol^{-1}. The uncertainties are twice the standard deviation of the mean and include the uncertainties in the determined energies of all the materials used. The values $\Delta H_f^\circ(CO_2(g))$ = −393.51 kJ mol^{-1},[17] $\Delta H_f^\circ(H_2O(l))$ = −285.830 kJ mol^{-1},[17] and $\Delta H_f^\circ(Cu(NO_3)_2 \cdot 3H_2O(c))$ = −1217.1 kJ mol^{-1} [16] were used to derive a standard enthalpy of formation $\Delta H_f^\circ(C_{10}H_{24}N_6O_6Cu(c))$ = −639.4 ± 4.0 kJ mol^{-1}.

Considering the thermochemical cycle (Figure 2) ΔH_2 represents the enthalpy of formation of the (1,4,8,11-tetraazacyclotetradecane)copper(II) ion in solution. This value can be calculated by combining ΔH_1 with the standard enthalpies of solution ΔH_3, ΔH_4, and ΔH_5, i.e., $\Delta H_2 = \Delta H_1 + \Delta H_5 - \Delta H_3 - \Delta H_4$. We have previously reported[8] ΔH_4 = −10.5 ± 0.7 kJ mol^{-1} and $\Delta H_f^\circ(L_1)$ = −115.9 ± 2.1 kJ mol^{-1}. Using a TRONAC calorimeter (Model 450), we have determined ΔH_3 = +9.6 ± 0.8 kJ mol^{-1} and ΔH_5 = +22.0 ± 0.8 kJ mol^{-1}. Hence ΔH_2 = −141.0 ± 5.0 kJ mol^{-1}. This value is in excellent agreement with that obtained by direct calorimetry,[6] ΔH_2 = −135.6 ± 2.5 kJ mol^{-1}. This study therefore strongly indicates the absence of any serious systematic errors in either the rotating-bomb combustion calorimetric method or the earlier reaction calorimetry. However, the presence of possible systematic errors within the assigned uncertainties cannot be excluded and could arise, for example, in the value used for the enthalpy of solution of CO_2 in the bomb liquid which has been taken as equal to that in pure water.

With reference to the macrocyclic effect, it can now be confirmed, at least for the copper complexes with L_1 and L_2 in aqueous solution, that both entropy and enthalpy terms contribute, almost equally, to the increased stability of the macrocyclic complex. This work has confirmed the value of the macrocyclic enthalpy term[4,6] by using an alternative calorimetric method. This in turn vindicates the earlier direct calorimetric method which was performed in strongly alkaline solutions and does not change our contention that the difference in hydration energies of the two ligands has a major influence on the magnitude of the macrocyclic enthalpy.

Wherever possible, we feel that enthalpy values should be determined calorimetrically, rather than indirectly, by the temperature dependence of stability constants. While the direct calorimetric method[4,6] is much simpler to perform, combustion calorimetry could be used with profit if the ligand proved to be essentially insoluble in water or on those occasions when complicated protonation equilibria in aqueous solution prevent the accurate description of the calorimetric reaction.

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(17) CODATA (key values for thermodynamics): *J. Chem. Thermodyn.*, **3**, 1 (1971); *CODTA Bull.*, **5** (1971).

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Characterization and Reactions of Osmium(IV) Ammines

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Cis and trans forms of $Os(NH_3)_4X_2^{2+}$ and of *mer*-$Os(NH_3)_3X_3$ (where X is Cl, Br, or I) were prepared by oxidizing the corresponding Os(III) complexes with Fe^{3+}(aq). Acidic solution aquation and disproportionation are sufficiently slow so that ion-exchange methods are applicable to separations and characterization. The osmium(IV) ammines in comparison to the corresponding Os(III) species show LMCT at lower energies and metal to halide stretching frequencies ca. 40 cm^{-1} higher. At high enough acidity the Os(IV)/Os(III) couples are reversible in cyclic voltammetry. Application of this method yielded E_f values for *trans*-$[Os(NH_3)_4Cl_2]$, *cis*-$[Os(NH_3)_4Cl_2]$, *mer*-$[Os(NH_3)_3Cl_3]$, and $OsNH_3Cl_5$ of 0.73, 0.83, 0.61, and 0.37 V, respectively. As the pH is raised, the values of E_f become acid dependent. A combination of electrochemical and spectrophotometric measurements yielded pK_a values for the four chloro complexes of 4.0, ~1, 4.9, and 6.5, respectively. The relatively higher acidity of the osmium(IV) ammines compared to that of Pt(IV) analogues is attributed to charge transfer from ligands to the unfilled π orbitals of Os(IV).

Introduction

Ammine complexes of metals in the oxidation state 4+ have received little attention, and of this class only those of Pt(IV) have thus far been described. A property of these species which alone makes them worthy of further attention is the high acidity of the coordinated ammonia. For ammonia complexes of metals in the oxidation state 3+, values of pK_a have been estimated for Ru,[1] Co,[2] Rh,[3] and Os[4] of which only that for

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Ru[1] purports to be accurate; in addition the powerful enhancement of the acidity of the Os(III)–NH_3 unit when a π-acid ligand is coordinated to the metal center has been demonstrated.[5] Values of pK_a have been reported for ammonia coordinated to Pt(IV);[6] similar measurement for Os(IV) which has a different electronic structure would add a dimension to the subject. The complexes of Os(IV) are interesting also in another context. Low-spin d^5 and d^6 ammine complexes have been much studied, but virtually nothing is known about the low-spin d^4 systems.

We have succeeded in preparing and characterizing a number of haloammines of Os(IV), but none with more than four ammonia molecules per metal center. These species are found to be at least kinetically stable in strongly acidic solution, but at higher pH, disproportionation takes place. In this paper we deal mainly with the foregoing aspects of the chemistry of the new species. Details on the very interesting reaction in which nitric oxide reacts with an osmium(IV) amido species converting it to a dinitrogen complex of Os(III) are deferred for a later paper.[7]

Experimental Section

A. Reagents and Materials. Osmium tetraoxide (99.8%) was purchased from Alfa Products in 1-g ampules. Dowex AG-50W-X2 cation-exchange resin from Bio-Rad was purified[8] and stored wet in the dark. SP-Sephadex C-25 cation-exchange resin was used as obtained from Pharmacia. Argon was passed through two chromous perchlorate bubbling towers before use. Water was doubly distilled, the second distillation being from an alkaline permanganate solution. All other chemicals were reagent grade and were used without purification.

B. Preparation of Known Compounds. Ammonium hexachloroosmate(IV) was prepared by the procedure of Dwyer and Hogarth;[9] those of Clifford and Kobayashi[10] were followed in preparing potassium nitridoosmate(VIII), $K[OsO_3N]$, and potassium pentachloronitridoosmate(VI), $K_2[OsCl_5N]$. Potassium osmate(VI), $K_2[OsO_2(OH)_4]$, was prepared by an adaptation of the synthesis reported by Fremy[11] and tetraamminedioxoosmium(VI) chloride by adaptation from the work of Gibbs.[12]

The dihalo species *cis*-$[Os(NH_3)_4X_2]X$ were prepared by the method of Allen and Stevens.[13] They were purified by ion-exchange chromatography on Dowex AG-50W-X2. The trihalotriammineosmium(III) complexes were prepared as described elsewhere.[7] Potassium ammonium amminepentachloroiridate(III) was synthesized according to the published procedure.[14]

Pentaammine(dinitrogen)osmium(II) Chloride, $[Os(NH_3)_5N_2]Cl_2$. The synthesis of this dinitrogen complex was adapted from the method of Allen and Stevens.[15,16] Six grams of ammonium hexachloroosmate was added slowly with stirring to 50 mL of hydrazine hydrate. After the mixture was refluxed for 10 h, the solid was collected, washed with ethanol and ether, and air-dried. The product was refluxed in 50 mL of hydrazine hydrate for 10 h, collected and washed as above, and then refluxed in another 50-mL portion of hydrazine hydrate for an additional 10 h. After 30 h at reflux, all of the *cis*-bis(dinitrogen)tetraammineosmium(II) chloride impurity had been removed. Shorter reflux times are referred to in published syntheses, but we found that they result in contamination by the bis(dinitrogen) complex. In some preparations, a black insoluble residue was present which was removed by filtration before the compound was allowed to react with other reagents. The yields were typically from 80 to 90%. The compound was characterized by its UV spectrum (λ_{max} = 208 nm, $\epsilon = 2.51 \times 10^4\ M^{-1}\ cm^{-1}$) and its IR spectrum ($\nu(N{\equiv}N)$ = 2035 cm^{-1}).

***cis*-Bis(dinitrogen)tetraammineosmium(II) chloride, *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$,** was prepared following Magnuson's modifications[17] of Scheidegger's procedure by the reaction between $Os(NH_3)_5N_2^{2+}$ and HNO_2.[18]

Pentaammineaquoosmium(III) perchlorate, $[Os(NH_3)_5(OH_2)](ClO_4)_3$, was prepared according to the Scheidegger procedure,[19] as follows. Pentaammine(dinitrogen)osmium(II) perchlorate (450 mg) (this compound can be detonated) was dissolved with warming, in a minimum volume of water (18 mL) containing 5 drops of 1 M $HClO_4$. An equivalent amount (1.8 mL) of a 0.5 M Ce(IV) solution (0.5 M $H_2Ce(ClO_4)_6$) obtained from G. F. Smith was added to the warm solution slowly with stirring. The mixture was heated to 50 °C for 10 min. Then the solution was cooled in an ice bath, and 5 g of $NaClO_4 \cdot H_2O$ was added. After 15 min at 0 °C, the precipitate was collected, washed with ethanol and ether, and air-dried. The yield was 90%. The compound was characterized by its UV spectrum (220 nm (sh), $\epsilon = 1.10 \times 10^3\ M^{-1}\ cm^{-1}$) and by its elemental analysis. The compound was judged to be pure when no dinitrogen stretch could be detected in the infrared spectrum.

Pentaamminechloroosmium(III) Chloride, $[Os(NH_3)_5Cl]Cl_2$. The cation was synthesized by either of two routes. The more facile and efficient method involved the reaction of chloride ion with pentaammineaquoosmium(III). Pentaammine(dinitrogen)osmium(II) chloride (800 mg, 2.15 mmol) was dissolved with warming in 120 mL of 0.07 M HCl, and the solution was filtered. One equivalent of a 0.5 M $H_2Ce(ClO_4)_6$ solution (G. F. Smith) was added and the resulting solution heated to 50 °C. After 5 min, 40 mL of concentrated HCl was added, and the solution was kept at 65 °C for 15 min. The chloro complex precipitated from the heated solution. (It should be noted that protracted heating will result in the production of a nitrido impurity which is difficult to remove.) The mixture was cooled in an ice bath and the solid collected, washed with ethanol and ether, and air-dried. The product was recrystallized from 50 mL of hot 0.1 M HCl. An additional quantity of pure compound was obtained by adding concentrated hydrochloric acid to the recrystallization liquor and recrystallizing the precipitate from 20 mL of hot 0.1 M HCl. The overall yield was between 85 and 90%. The compound was characterized by its ultraviolet spectrum (267 nm, $\epsilon = 2.00 \times 10^3\ M^{-1}\ cm^{-1}$). An alternative synthesis involving a 48-h reflux met with less success.[13]

Pentaamminebromoosmium(III) Bromide, $[Os(NH_3)_5Br]Br_2$. The monobromide complex was prepared in a manner analogous to that for the monochloro species. The most efficient synthesis involved generation of the pentaammineaquoosmium(III) ion. Eighteen milliliters of 0.005 M $HClO_4$ was used to dissolve 136 mg (0.27 mmol) of $[Os(NH_3)_5N_2](ClO_4)_2$. After addition of an equivalent amount of 0.5 M $H_2Ce(ClO_4)_6$ (G. F. Smith), the solution was heated to 50 °C for 5 min. Five milliliters of concentrated HBr was added and the solution heated at 65 °C for an additional 15 min. The solution was cooled in an ice bath for 15 min and the precipitate collected. Recrystallization from hot dilute HBr (35 mL) gave a pure product in 71% yield. The compound was characterized by its UV spectrum (314 nm, $\epsilon = 1.87 \times 10^3\ M^{-1}\ cm^{-1}$).[13]

Pentaammineiodoosmium(III) Iodide, $[Os(NH_3)_5I]I_2$. This complex was prepared by several routes, the most successful of which made use of pentaammineaquoosmium(III) as the starting material. Five hundred milligrams of $[Os(NH_3)_5OH_2](ClO_4)_3$ was dissolved in 25 mL of H_2O. Two grams of NaI and 0.5 mL of concentrated HI were added and the solution heated for 10 min at 80 °C. An additional 1 g of NaI was added and the heating continued for an additional 15 min. The mixture was cooled in an ice bath and the precipitate collected. Five milliliters of concentrated HI was added to the filtrate, and the mixture was heated for 30 min at 80 °C. After cooling of

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the mixture in an ice bath, a second crop of crystals was obtained. The compound was characterized by its UV–vis spectrum (407 nm, $\epsilon = 1.97 \times 10^3$ M^{-1} cm^{-1}). The yield was 67%. Alternate syntheses are described elsewhere.[13,20]

Hexaammineosmium(III) perchlorate, $[Os(NH_3)_6](ClO_4)_3$, was prepared by a modification of the procedure developed by Scheidegger as none of the published procedures[4,20,21] was found to be reproducible. To a solution of 137 mg of $[Os(NH_3)_5NO](ClO_4)_3$ dissolved in 20 mL of 0.1 M $HClO_4$ were added ten 1-cm pieces of amalgamated zinc, and the mixture was stirred for 0.5 h until it had decolorized. The hexaammine complex precipitated gradually during this time. The complex was collected, washed with ethanol and ether, and air-dried. The yield was 79%. The complex was characterized by its elemental analysis and UV spectrum (221 nm (760), 229 nm (759)). Anal. Calcd: N, 14.23; H, 3.07. Found: N, 13.30; H, 3.08.

***trans*-Tetraamminedichloroosmium(III) Chloride, *trans*-$[Os(NH_3)_4Cl_2]Cl$.** Tetraamminedioxoosmium(VI) chloride (0.55 g, 1.52 mmol) was dissolved in 30 mL of 6 M HCl, and 4 equiv of $SnCl_2 \cdot 2H_2O$ (0.687 g) was added. The mixture was cooled and heated at 70 °C for 12 h, after which it was cooled in an ice bath and the solid was collected, washed with ethanol and ether, and air-dried. For removal of contamination by the hexachlorostannate salt, the solid was dissolved in water and the perchlorate salt precipitated with perchloric acid, which was then converted to the chloride with the use of concentrated hydrochloric acid. The overall yield was 85%. The compound was characterized by its UV spectrum (271 nm, $\epsilon = 4.90 \times 10^3$ M^{-1} cm^{-1}). It was also prepared by isomerization of *cis*-$[Os(NH_3)_4Cl_2]Cl$,[13] a slow reaction occupying 72 h.

***trans*-Tetraamminedibromoosmium(III) bromide, *trans*-$[Os(NH_3)_4Br_2]Br$,** was prepared in an analogous manner to that for the *trans*-dichloro species. The osmyl chloride (0.439 g, 1.22 mmol) was dissolved in 30 mL of 6 M HBr and treated with 0.55 g of $SnCl_2 \cdot 2H_2O$. The solution was covered and heated for 5 h at 70 °C and then cooled in an ice bath to produce a solid. To rid the product of the $SnBr_6^{2-}$ impurity, we made the perchlorate salt by adding concentrated $HClO_4$ to a saturated aqueous solution of the dibromo complex. From this the dibromo salt was then made by metathesis. The overall yield was 86%. The compound was characterized by its UV spectrum (317 nm, $\epsilon = 4.69 \times 10^3$ M^{-1} cm^{-1}). This compound can also be made by isomerization of the *cis*-dibromo species.[13]

***trans*-Tetraamminediiodoosmium(III) Iodide, *trans*-$[Os(NH_3)_4I_2]I$.** Tetraamminedioxoosmium(VI) chloride (400 mg, 1.11 mmol) was dissolved in 35 mL of 4 M HI, and 300 g of iron wire (5.37 mmol) was added. The vessel was deaerated with argon, and the system was heated at 70 °C for 12 h. The compound was collected after cooling, washed with ethanol and ether, and air-dried. The yield was 90%. The compound was characterized by its UV–vis spectrum (418 nm, $\epsilon = 4.92 \times 10^3$ M^{-1} cm^{-1}). It was also prepared from *trans*-$[Os(NH_3)_4Cl_2]Cl$ by refluxing in hydriodic acid.[13] Purification by ion-exchange chromatography on Sephadex SP C-25 resin was found to be successful.

Cesium amminepentachloroosmate(III), $Cs_2[OsCl_5NH_3]$, was prepared by reducing $K_2[OsCl_5N]$ with Sn^{2+}, V^{2+}, or Eu^{2+} by using an excess of reducing agent on a concentrated solution of the nitrido species (100 mg in 5 mL) in 1 M HCl. When Sn^{2+} was used as the reductant, the solution was stirred for 15 min before being passed through a cation-exchange resin (AG-50W-X2). The solvent was stripped from the effluent by rotary evaporation. The residue was redissolved in 0.1 M HCl, and CsCl was added with stirring until precipitation occurred. The yellow solid was collected, washed with ethanol and ether, and air-dried. When Eu^{2+} or V^{2+} was used, the reduction took place under argon, and except for omission of the ion-exchange step, the procedure was that used with Sn(II). The yields were 50%. It should be noted that the osmium(III) complex is somewhat air sensitive.

The nature of the product formed in this reduction has been debated in the literature.[22,23] The species formed has been positively identified as amminepentachloroosmium(III) by the band at 269 nm with $\epsilon = 4.50 \times 10^3$ M^{-1} cm^{-1}.

C. Characterization of New Compounds. The syntheses and properties of new species are described in the Results. Each new compound is characterized by its UV–vis spectrum, IR spectrum, cyclic voltammogram, and elemental analysis (C, H, N determined). In addition, the charge for the complex was determined by its elution behavior on Sephadex C-25 and/or Dowex AG-50W-X2 ion-exchange column (proton form) by comparison with the elution behavior of known compounds. For the simple ammine complexes discussed here, the following guides to elution behavior were found to be infallible: on Dowex AG-50W-X2, 1+ ions eluted rapidly with 1 M H^+, 2+ ions with 2 M H^+, and 3+ ions with 3 M H^+; ~~while on~~ Sephadex C-25, 1+ ions eluted rapidly with 0.1 M H^+, 2+ ions with 0.2 M H^+, and 3+ ions with 0.3 M H^+. Commonly HCl was used as the eluant although HBr, HI, $HClO_4$, HO_3SCF_3, and HO_2CCF_3 were also used occasionally. The extreme substitution inertia of osmium(III) ammine species in acidic solution and of osmium(IV) ammines in strongly acidic solution facilitated characterization since substitution under usual experimental conditions did not occur (e.g., $k \approx 10^{-8}$ s^{-1} for the aquation of $[Os(NH_3)_5Cl]^{2+}$ in 0.1 M HO_3SCF_3: $[Os(NH_3)_5Cl]^{2+} + H_2O \rightarrow [Os(NH_3)_5OH_2]^{3+} + Cl^-$).

It was generally deemed unnecessary to analyze for the counterion or to determine conductivity since the charge was determined by ion exchange. Also, the $E_{1/2}$ values determined for the complexes are very sensitive to the halide content of the coordination sphere. The facile electron transfer coupled with substitution inertia in both oxidation states leads to a reversible cycle III → IV → III and thus, starting from an Os(III) compound of known composition and structures, serves to identify the Os(IV) species. The elemental analyses for N and H were adequate for determining the ammine content of the complex. The large extinction coefficients of the halo species discussed provide convenient means to assess the purity of isolated complexes. Impurities were readily discerned by UV–vis spectroscopy when present in amounts of ~1% or more.

D. Instruments and Techniques. Visible and ultraviolet absorption spectra were taken on a Cary 15, Beckman Acta MVII, or Beckman 5270 spectrophotometer. Near-infrared spectra were recorded on a Beckman Acta MVII or a Beckman 5270 instrument, and infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. Electrochemical experiments were made by using Princeton Applied Research equipment (Model 173 potentiostat and galvanostat, Model 175 universal programmer, Model 176 current follower).

Formal potentials, E_f, were obtained by cyclic voltammetry. The formal potentials were taken as the mean of the cathodic and anodic peak potentials at 20 °C measured with respect to the standard calomel electrode but referred to the SHE. Usually carbon-paste electrodes (Bioanalytical Systems) were used, and occasionally platinum-button electrodes were used. The formal potentials cited were measured at a scan rate of 100 mV s^{-1}. The electrochemical behavior was studied over a range of 20 mV s^{-1} to 50 V s^{-1} for complexes which exhibited irreversibility (peak-to-peak separations greater than 60 mV and/or cathodic current less than anodic current). Experiments were conducted with millimolar sample concentrations in 0.1 M electrolyte solutions (0.1 M HCl, 0.1 M KCl, 0.1 M NaOH, 0.1 M buffered aqueous solutions, or 0.1 M tetraethylammonium hexafluorophosphate in acetonitrile). The solutions were deaerated with argon prior to scanning.

Mass electrolytic oxidations were performed with a three-compartment cell in which the electrolysis (central) chamber was separated from the auxiliary electrode chamber by a 10-mm medium-porosity sintered-glass frit and from the reference chamber by a 10-mm fine-porosity sintered-glass frit. The main compartment could be deaerated with an inert gas. The working electrode was a platinum-gauze cylinder with a platinum wire attached, and the auxiliary electrode was a platinum wire. The solution to be oxidized was poured into the main compartment, and solvent (generally 0.1 M HCl) was added to the side compartments so that the liquid levels in all compartments were the same. The solution to be oxidized was as concentrated as was conveniently possible. Argon was bubbled through the solution, and occasionally a magnetic stirring bar was used to provide additional agitation. The potential was held 120 mV more positive than the formal potential of the substance to be oxidized unless this led to the formation of undesired oxidation products. The progress of the oxidation was monitored by a plot of current vs. time recorded on the X–Y plotter or by an electronic coulometer (PAR Model 179). The reaction was allowed to continue until at least 99.9% of the reactant had been consumed.

pH measurements were done by using a Metrohm 101 pH meter with a Metrohm combination microglass electrode (purchased from

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Brinkman Instruments). The pH meter was calibrated with National Bureau of Standards buffers supplied by Beckman Instruments, Inc.

pK_a Determinations. Several methods were used to obtain pK_a values for coordinated ammines and for other coordinated ligands, and wherever possible, at least two methods were used to corroborate a particular determination.

Acid–base titrations were performed in a specially designed cell, which consisted of a cylinder of 10-mL capacity, a buret, and pH-electrode ground-glass joint inlets and an inert-gas inlet at the bottom and an outlet at the top. Solutions to be studied were deaerated with argon and agitated with a magnetic stirring bar before and during the titration.

Cyclic voltammetry was one of the methods used to estimate acid dissociation constants. Plots of E_f vs. pH were constructed from data provided by voltammograms taken from two kinds of experiments. In the first a series of buffered solutions was prepared to which the substance to be studied was added immediately before recording the voltammograms. The reference compartment contained a blank solution of the buffer. The second method required a cell designed so that the pH could be monitored continuously while the solution was titrated with acid or base. Voltammograms were recorded periodically. The main compartment was deaerated with argon during the course of the experiment.

Spectrophotometric titrations were done by preparing a solution of the species of interest at known concentrations in each of a series of buffers immediately before spectrophotometric measurements. A graph of pH vs. molar absorption yielded the pK_a of the complex as the pH of the solution at which the absorption was the mean of the two terminal absorptions.

An empirical correlation was developed for the osmium ammine complexes studied. At a pH near or above the pK_a value for the coordinated ammine ligand on the oxidized metal center, the cyclic voltammogram indicated a cathodic current less than the anodic current, irrespective of the scan rate. Through correlation with other techniques, the pK_a value was found to be near the value of the pH at which the cathodic current is half the anodic current. This correlation was found to be accurate to well within ± 1 pH unit for all cases in which an alternative determination could be made.

Inert-Atmosphere Techniques. For reactions requiring an inert atmosphere, the most common vessel used was a round-bottom flask equipped with a j-shaped bottom-entry 2-mm capillary tube with a ball joint which could be joined to an argon manifold with a spring clamp. After fitting of the tube with a rubber serum stopper and stainless steel exit needle, argon was bubbled through the flask for at least 15 min before the reaction was started. Alternatively, flasks were fitted with gas-dispersion tubes and serum stoppers with exit needles, and the same procedure was followed.

For a reaction of long duration done at temperatures exceeding 50 °C, a cylinder was constructed with a large glass ball joint at the top. A greased socket joint equipped with a stopcock was fitted atop the flask with a screw-down clamp. The system was subjected to repeated cycles (>10) of vacuum and inert gas. The stopcock was closed and the reaction allowed to proceed.

Transfers were accomplished with platinum needles and all-glass or Teflon gas-tight syringes with Luer tips or with Teflon tubing. The syringes were flushed with inert gas a minimum of 5 times before contact with the solution.

Kinetic experiments were monitored by UV–vis spectroscopy in cuvettes of suitable path length sealed with tight-fitting serum stoppers. Reactant solutions were deaerated with argon before being mixed.

Ion exchange under argon was carried out in a modified chromatographic column. The column was jacketed, and many of the separations were performed at 0 °C. The column was equipped with a closeable-bypass tube which enabled the entire apparatus to be maintained under inert gas. The column was deaerated by passing an inert gas up the column from the bottom. Deaerated solutions were added by a platinum needle and syringe through a rubber septum at the top. The column could be pressurized to accelerate the ion-exchange procedure.

Results

Preparation of Osmium(IV) Ammines. Electrochemical studies of tetraamminedihaloosmium(III) complexes first suggested the existence of the osmium(IV) analogues in acidic solution. Further evidence for osmium(IV) ammines was provided by spectroscopic studies in which 1 equiv of oxidant was added to a solution of an osmium(III) species. They showed an end point at 1:1 stoichiometry, leading to a product which had a substantial bathochromic shift in the halide–metal charge-transfer absorption. A convenient high-yield synthesis for these new osmium(IV) complexes was developed in which an excess of $FeCl_3 \cdot 6H_2O$ is added to a saturated solution of the osmium(III) analogue in 0.1 M HCl. The syntheses of the *trans*-dihaloosmium(IV) compounds will be illustrated with the diiodo species.

A saturated solution of *trans*-$[Os(NH_3)_4I_2]Cl$ was prepared by dissolving 32 mg in 4 mL of 0.1 M HCl. A solution of Fe(III) (0.5 mL of 0.5 M $FeCl_3$) was added and the beaker placed in an ice bath. The solution immediately turned green, and a precipitate formed. After 15 min, the solid was collected, washed with ethanol and ether, and air-dried. The yield was 82%. The dipositive species was characterized as the chloride salt by its elemental analysis and by its UV–vis spectrum (634 nm, $\epsilon = 1.18 \times 10^4$ M^{-1} cm^{-1}). Anal. Calcd for $[Os(NH_3)_4I_2]Cl_2$: N, 9.61; H, 2.07. Found: N, 9.63; H, 2.37. The dibromo dichloride, 93% yield (Anal. Calcd: N, 11.46; H, 2.47. Found: N, 11.40; H, 2.47), and the dichloro dichloride, 91% yield (Anal. Calcd: N, 14.00; H, 2.02. Found: N, 13.97; H, 3.01), were similarly prepared.

The cis analogues were made in a similar manner. The diiodo complex was prepared as the chloride salt by adding a 10-fold excess of $FeCl_3 \cdot 6H_2O$ to a saturated solution of *cis*-$[Os(NH_3)_4I_2]Cl$ in 0.1 M HCl. This resulted in the immediate precipitation (60% yield) of the chloride salt of the dipositive osmium(IV) species. Anal. Calcd: N, 9.32; H, 2.35. Found: N, 9.36; H, 2.36. The dichloro and dibromo compounds, as chloride salts, were prepared in an analogous manner. The procedure was not entirely satisfactory because the solids were found, on the basis of UV–vis analysis, to be contaminated with a few percent Os(III) starting material.

The trihaloosmium(IV) ions also were prepared by oxidizing the osmium(III) analogues[7] with Fe(III). The preparation of the triiodo species will be described. Forty milligrams of *mer*-triamminetriiodoosmium(III) was dissolved in 400 mL of 0.1 M HCl, by warming the solution under argon. A solution of Fe^{3+} (20% in excess) was added, turning the yellow solution blue. The solution was concentrated by rotary evaporation until a precipitate appeared. The mixture was cooled in an ice bath and the solid collected, washed with ethanol and ether, and air-dried. The yield of the monopositive osmium(IV) complex was 30%. The compound $[Os(NH_3)_3I_3]Cl$ was characterized by its UV–vis spectrum (637 nm, $\epsilon = 8.76 \times 10^3$ M^{-1} cm^{-1}) and elemental analysis. Anal. Calcd: N, 6.39; H, 1.38. Found: N, 6.40; H, 1.51.

Cesium amminepentachloroosmate(IV), $Cs[Os(NH_3)Cl_5]$, was prepared by oxidizing the osmium(III) analogue with the use of Fe^{3+}, O_2, or mass electrolysis in 0.1 M HCl. After the oxidation was complete, the solution was concentrated by rotary evaporation. Cesium chloride was added to precipitate the brown solid which was characterized by its UV–vis spectrum ($\lambda_{max} = 352$ nm, $\epsilon = 4.89 \times 10^3$ M^{-1} cm^{-1}). The oxidized product was easily reconverted to the osmium(III) analogue by reduction (Cr^{2+}, Eu^{2+}, V^{2+}) as observed by UV–vis spectroscopy. Cyclic voltammetry experiments were used to demonstrate that only a single electron differentiates the oxidized and reduced forms of this amminepentachloroosmium ion.

UV–Visible Absorption Spectra. The charge-transfer absorptions in the UV–vis region are presented in Table I for both osmium(III) and osmium(IV) complexes. A regular increase in the energies of these bands is noted for the series I^-, Br^-, and Cl^- in analogous compounds. The spectra of the osmium(IV) species resemble those of the corresponding osmium(III) complexes, the major differences being that the

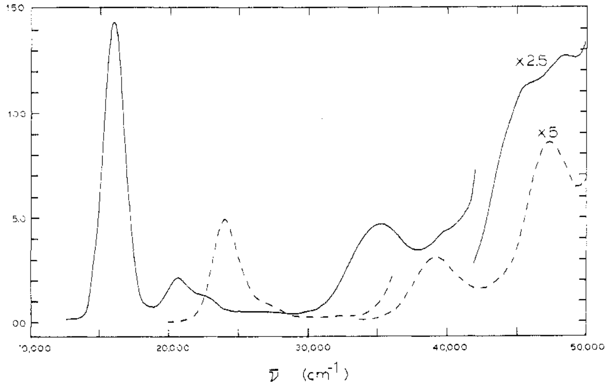

Figure 1. UV–vis spectra of *trans*-$[Os(NH_3)_4I_2]^{+,2+}$. For the segment in question, multiply ordinate reading by the scaling factor to obtain ε (solid line, Os(IV)).

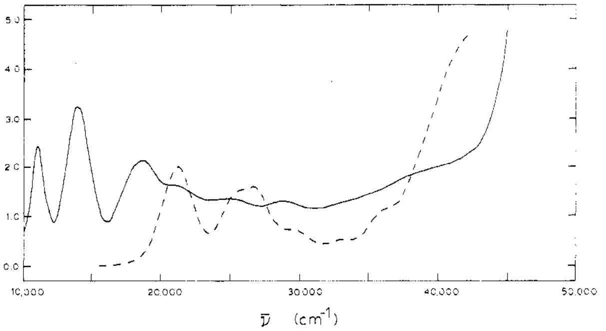

Figure 2. UV–vis spectra of *cis*-$[Os(NH_3)_4I_2]^{+,2+}$ (solid line, Os(IV)).

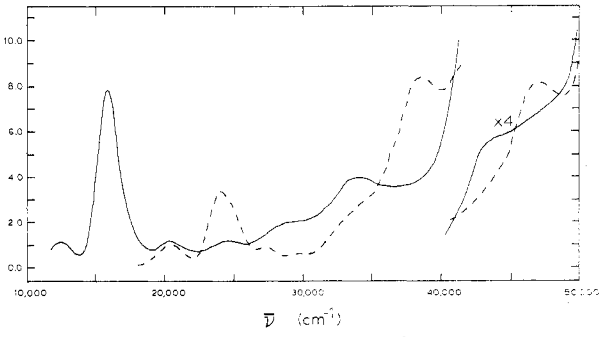

Figure 3. UV–vis spectra of *mer*-$[Os(NH_3)_3I_3]^{0,+}$ (solid line, Os(IV)).

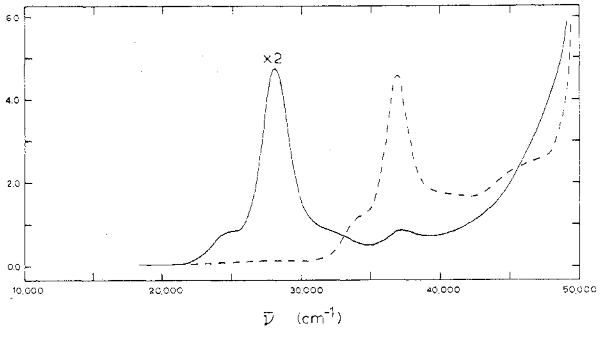

Figure 4. UV–vis spectra of *mer*-$[Os(NH_3)_3Cl_3]^{0,+}$ (solid line, Os(IV)).

osmium(IV) species have lower energies and higher extinction coefficients. The spectra of both osmium(III) and osmium(IV) forms of *trans*-$[Os(NH_3)_4I_2]$, *cis*-$[Os(NH_3)_4I_2]$, *mer*-$[Os(NH_3)_3I_3]$, and *mer*-$[Os(NH_3)_3Cl_3]$ are presented in Figures 1–4.

A perusal of Table I reveals that the absorption energy is rather insensitive to the number of halides present in the compound. The complexity of the bands and their number do depend on the halide content and configuration of the coordination sphere. For the monohalo and trans complexes, only a single principal absorption is observed (Figure 1). The *cis*-dihalo species, with the exception of the osmium(IV) diiodo complex (Figure 2), show two principal bands while the *mer*-trihalo ions feature a single principal absorption with two distinct shoulders (Figures 3 and 4).

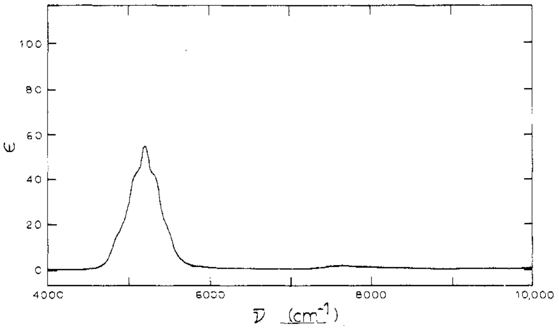

Figure 5. Near-IR spectrum of $[OsCl_6]^{2-}$.

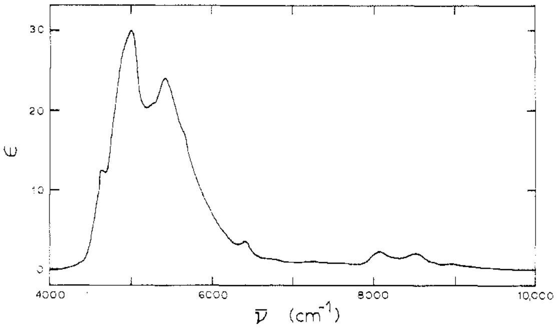

Figure 6. Near-IR spectrum of *trans*-$[Os(NH_3)_4I_2]^+$.

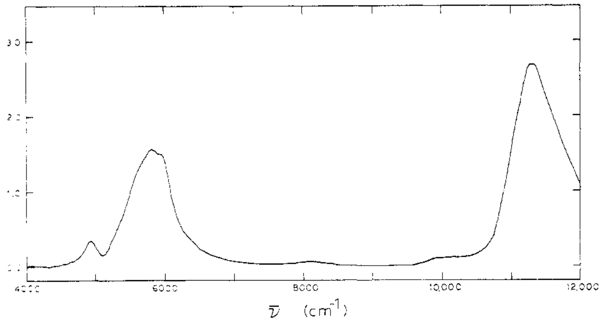

Figure 7. Near-IR spectrum of *trans*-$[Os(NH_3)_4I_2]^{2+}$.

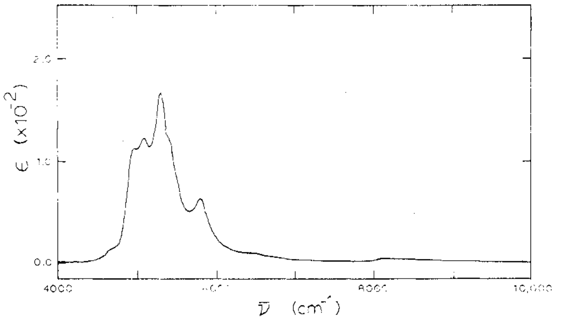

Figure 8. Near-IR spectrum of $[Os(NH_3)_5I]^{2+}$.

Near-Infrared Absorption. Near-infrared absorptions are found for all osmium(III), d^5, and osmium(IV), d^4, complexes. These absorptions are rather narrow with low extinction coefficients and often possess vibrational structure at room temperature. The near-IR transitions observed for a number of examples are shown in Table II, and representative spectra are illustrated in Figures 5–8. It is to be noted that both d^4 and d^5 ions have absorptions near 5000 cm^{-1} while d^4 species

Table I. Charge-Transfer Absorptions of Osmium Haloammines

species	$10^{-3}E^a$ ($10^{-3}\epsilon$)		$10^{-3} \times$ ΔE^b
	Os(III)	Os(IV)	
$[Os(NH_3)_5Cl]$	37.45 (2.01)^c		
$[Os(NH_3)_5Br]$	31.85 (1.84)^c		
$[Os(NH_3)_5I]$	24.57 (1.97)^c		
trans-$[Os(NH_3)_4Cl_2]$	36.90 (4.81)^c	28.01 (11.6)	8.89
trans-$[Os(NH_3)_4Br_2]$	31.50 (4.69)^c	23.57 (13.1)	8.93
trans-$[Os(NH_3)_4I_2]$	23.90 (4.92)^c	15.82 (11.8)	8.08
cis-$[Os(NH_3)_4Cl_2]$	39.22 (2.03)^c	28.57	10.65
	35.20 (1.68)^c	25.00	10.20
cis-$[Os(NH_3)_4Br_2]$	33.56 (1.60)^c	24.10	9.46
	29.07 (1.62)^c	19.61	9.46
cis-$[Os(NH_3)_4I_2]$	26.46 (1.68)^c	18.35 (1.56)	
	21.28 (2.07)^c	13.74 (3.22)	
		10.96 (2.48)	
mer-$[Os(NH_3)_3Cl_3]$	37.31 (4.60)	29.24 (9.40)	8.07
mer-$[Os(NH_3)_3Br_3]$	31.45 (4.20)	22.52 (7.85)	8.93
mer-$[Os(NH_3)_3I_3]$	23.58 (3.22)	15.67 (8.76)	7.91
$[Os(NH_3)Cl_5]$	37.17 (4.50)	28.41 (8.35)	9.72
$[OsCl_6]$	37.74	*d*	

^{a} In units of cm^{-1}. ^{b} $\Delta E = E(Os(III)) - E(Os(IV))$ (cm^{-1}). ^{c} Reference 13. ^{d} Several prominent bands.

Table II. Near-IR Transitions of Osmium Complexes^a

species	principal absorptions (ϵ)
$[OsCl_6]^{2-}$	5210 (53)
cis-$[Os(NH_3)_4Cl_2]^+$	4871 (40), 5444 (42), 5705 (50)
cis-$[Os(NH_3)_4Br_2]^+$	5909 (81), 5417 (105)
cis-$[Os(NH_3)_4I_2]^+$	4843 (299), 5236 (2420)
trans-$[Os(NH_3)_4I_2]^+$	5033 (30), 5464 (24)
trans-$[Os(NH_3)_4I_2]^{2+}$	5995 (135), 10940 (268)
trans-$[Os(NH_3)_3I_2(N_2)]^{+\ b}$	· · ·, 7840 (50)
$[Os(NH_3)_5I]^{2+}$	5325 (170)
cis-$[Os(NH_3)_4I(N_2)]^{2+\ b}$	4988 (40), 7564 (180)

^{a} All energies are reported in wavenumbers (cm^{-1}). ^{b} Reference 7.

have additional excitations at higher energies. No near-IR electronic transitions are observed for any mononuclear osmium compound in which the metal is in oxidation state II.

Infrared Spectra. Differences in the infrared spectra of the Os(III) and Os(IV) forms of the same compound are not as pronounced as those observed in the UV-vis spectrum, but they serve to distinguish the two oxidation states. Table III contains comparisons of the IR spectra for osmium compounds in both the III and IV oxidation states. The osmium-halide stretching frequency increases by ca. 40 cm^{-1} upon oxidation while δ-$(NH_3)_{sym}$ increases by ca. 25 cm^{-1}.

Electrochemistry. The electrochemical potentials as measured by cyclic voltammetry for the dihalo species are recorded in Table IV. The IV/III couples were studied in 0.1 M HCl at a scan rate of 100 mV s^{-1} and were found to be reversible under these conditions. Data are also presented for the reversible couples found for the triamminetrihalo species.

In contrast to these multihalo complexes, the pentaamminehaloosmium(III) species do not exhibit reversible behavior for the IV/III couples as studied by cyclic voltammetry. In no case with scan rates up to 100 V s^{-1} was a reduction current observed after the initial oxidation wave. Only in very strong acid do these monohalo complexes exhibit a slight cathodic current in the cyclic voltammograms, and apparently the life of the Os(IV) species, very short at low acidity, is prolonged as the acid concentration is raised. The oxidations of hexaammine- and pentaammineaquoosmium(III) ions are also irreversible at scan rates up to 100 V s^{-1} at any acid strength up to 6 M $HClO_4$.

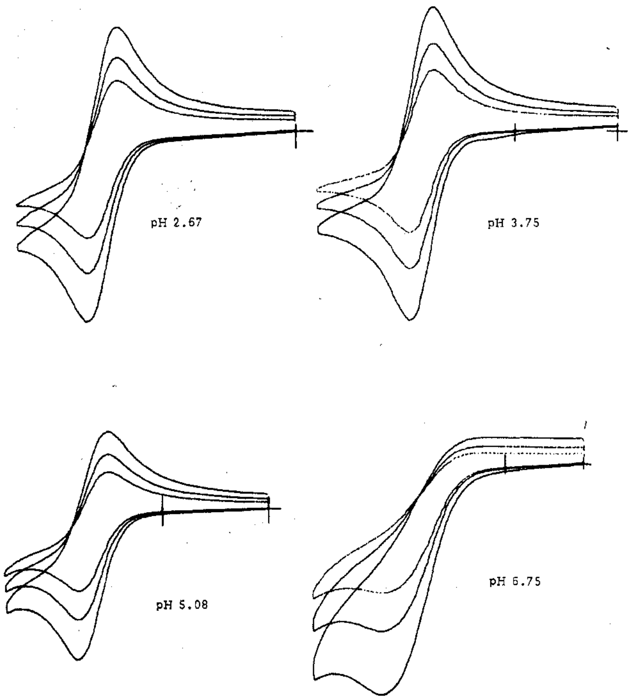

Figure 9. Cyclic voltammograms of *trans*-$[Os(NH_3)_4Cl_2]^+$. The pK_a of the Os(IV) analogue is ~4.0. Increasing amplitude of the voltammograms represents scan rates of 50, 100, and 200 mV s^{-1}.

As might be expected from the electrochemical results, the haloammineosmium(III) complexes exhibit increased sensitivity to oxidation by oxygen with increasing halide content. The hexachloroosmium(III) ion is air oxidized in solution in a few minutes to oxidation state IV.

Acidity. The interesting chemistry attributable to the osmium(IV) haloammines stems in part from the unusually low pK_a values of the coordinated ammine ligands. Osmium(IV) ammine complexes persist only in strongly acidic media. Studies were undertaken to determine the pK_a values for these coordinated ammines. Several methods were used to compile the data presented in Table V, and, where possible, each value was verified by a second method.

As shown in Table V, the osmium(IV) species are very acidic, more acidic by 5–6 orders of magnitude than the platinum analogues[6] but only slightly more acidic than the iridium(IV) analogues (the pK_a of $[Ir(NH_3)Cl_5]^-$ prepared by mass electrolytic oxidation of the Ir(III) complex was found to be ~7 by pH titration and by UV-vis titration).

Cyclic voltammetry was used to estimate the pK_a of the coordinated ammines of the osmium(IV) species. It is expected that the only manifestation of a simple deprotonation of the higher oxidation state will be a pH dependence of the $E_{1/2}$ values for the reversible couple. The osmium compounds exhibited anomalous behavior at solution pH values near or above the pK_a of the oxidized complex, in that cathodic currents were less than the anodic currents (Figure 9). The ratio of cathodic to anodic current was only slightly affected by scan rate, the ratio increasing with the rate. Usually the ratio varied from 1 to 0 over a change of 2 or 3 pH units with a value of ca. 0.5 when the pH of the solution was equal to the pK_a of the complex. This empirical correlation was found to be a reliable estimate of the ammine pK_a to within ±1.5 pH units.

Reaction with Nitric Oxide. The osmium(IV) haloammines (two or three halide ligands) were found to react rapidly with NO upon deprotonation, forming osmium(III) dinitrogen complexes. This diazotization reaction is discussed in the following paper.[7]

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(24) J. Gulens and J. A. Page, *J. Electroanal. Chem. Interfacial Electrochem.*, **55**, 239 (1974).

(25) J. Gulens and J. A. Page, *J. Electroanal. Chem. Interfacial Electrochem.*, **67**, 215 (1976).

Table III. Infrared Vibrational Frequencies for Osmium(III) and Osmium(IV) Haloammines[a,b]

species	$\delta(NH_3)_{deg}$	$\delta(NH_3)_{sym}$	$\rho(NH_3)$	ν(Os–N)	ν(Os–X)
trans-$[Os(NH_3)_4Cl_2]Cl$[c]	1617 m	1320 s, 1308 s	780 m	454 w	308 m
trans-$[Os(NH_3)_4Cl_2]Cl_2$	1615 m	1336 s	872 m	480 w	356 m
trans-$[Os(NH_3)_4Br_2]Cl$[c]	1608 m	1332 s, 1324 s, 1311 s	808 m	457 w	
trans-$[Os(NH_3)_4Br_2]Cl_2$	1612 m	1334 s	865 m	479 w	
trans-$[Os(NH_3)_4I_2]Cl$[c]	1618 m	1310 s	795 m	455 w	
trans-$[Os(NH_3)_4I_2]Cl_2$	1610 m	1340 s	835 m	472 w	
mer-$[Os(NH_3)_3Cl_3]$	1616 m	1307 s, 1300 s	780 m	475 w	310 m
mer-$[Os(NH_3)_3Br_3]$	1610 m	1315 sh, 1304 s, 1295 sh	770 m	463 w	
mer-$[Os(NH_3)_3I_3]$	1607 m	1320 sh, 1305 s, 1300 sh	760 m	445 w	
mer-$[Os(NH_3)_3I_3]Cl$	1605 m	1323 s	850 m	465 w	
$Cs_2[Os(NH_3)Cl_5]$[d]	1617 m	1326 m	775 w	410 w	290 m
$Cs[Os(NH_3)Cl_5]$	1644 m	1357 m	832 w	482 w	322 s

[a] All entries are in wavenumbers (cm^{-1}). [b] All ammine species feature several NH stretching bands near 3200 cm^{-1}. [c] Reference 13. [d] Reference 23.

Table IV. Cyclic Voltammetry Data (V) for Osmium Ammines[a]

species	IV/III couple	III/II couple
$[Os(NH_3)_6]$	1.25 irrev	−0.78[b]
$[Os(NH_3)_5OH_2]$	1.24 irrev	−0.73[b]
$[Os(NH_3)_5Cl]$	1.06 irrev	−0.85[c]
$[Os(NH_3)_5Br]$	1.05 irrev	
$[Os(NH_3)_5I]$	0.97 irrev	−0.77[c]
trans-$[Os(NH_3)_4Cl_2]$	0.73	
trans-$[Os(NH_3)_4Br_2]$	0.75	
trans-$[Os(NH_3)_4I_2]$	0.71	
cis-$[Os(NH_3)_4Cl_2]$	0.82	
cis-$[Os(NH_3)_4Br_2]$	0.81	
cis-$[Os(NH_3)_4I_2]$	0.74	
mer-$[Os(NH_3)_3Cl_3]$	0.61	
mer-$[Os(NH_3)_3Br_3]$	0.63	
mer-$[Os(NH_3)_3I_3]$	0.57	
$[Os(NH_3)Cl_5]$	0.37	
$[OsCl_6]$	0.22	

[a] All values (SHE) were recorded in 0.1 M HCl or 0.1 M $HClO_4$ with a carbon-paste electrode at a scan rate of 100 mV s^{-1} except for the III/II couples which were recorded at pH 7. All voltammograms were reversible except for those indicated. [b] Reference 24. [c] Reference 25.

Table V. pK_a Values for Osmium Ammines

species	pK_a	method[a]
$[Os(NH_3)_6]^{3+}$	>15	chem[b]
$[Os(NH_3)_6]^{4+}$	<0	CV
$[Os(NH_3)_5I]^{3+}$	~0	CV
trans-$[Os(NH_3)_4Cl_2]^{2+}$	4.0	CV, UV–vis, pH
trans-$[Os(NH_3)_4I_2]^{2+}$	3.9	CV
cis-$[Os(NH_3)_4Cl_2]^{2+}$	~1	CV
cis-$[Os(NH_3)_4Br_2]^{2+}$	~1	CV
cis-$[Os(NH_3)_4I_2]^{2+}$	~3	CV
mer-$[Os(NH_3)_3Cl_3]^+$	4.9	CV
mer-$[Os(NH_3)_3I_3]^+$	~5	UV–vis
$[Os(NH_3)Cl_5]^-$	~6.5	CV

[a] Key: CV, E_f vs. pH; pH, pH titration with 0.1 N NaOH; UV–vis, spectrophotometric titration vs. pH; chem, chemical evidence. [b] Reference 4.

Disproportionation. As indicated by the electrochemical behavior, solutions of osmium(IV) dihalotetraammines and trihalotriammines are unstable, increasingly so at higher pH. Spectrophotometric analysis demonstrated that a major product of the decomposition was the corresponding osmium(III) complex. The final concentration of the osmium(III) species was determined to be approximately 67% that of the initial osmium(IV) complex for a number of the dihalo species under varied pH conditions.

The *trans*-$[Os(NH_3)_4Cl_2]Cl_2$ complex was studied in some detail. The osmium(IV) ion was allowed to decompose in 0.1 M H_2SO_4 under argon, and the products were separated by ion-exchange chromatography. The osmium(III) species was identified as *trans*-$[Os(NH_3)_4Cl_2]Cl$ on the basis of cyclic voltammetry (CV), UV–vis measurements, and elemental analysis. The only other species isolated was determined to be the osmyl(VI) compound *trans*-$[Os(NH_3)_4O_2]Cl_2$ on evidence provided by CV, UV–vis, and IR experiments. These two products accounted for more than 95% of the total osmium present.

These results show that the net disproportionation reaction is

$$3\,trans\text{-}[Os(NH_2)(NH_3)_3Cl_2]^+ + 2H_2O = 2\,trans\text{-}[Os(NH_3)_4Cl_2]^+ + [Os(NH_3)_4O_2]^{2+} + H^+ + 2Cl^-$$

Kinetic studies were undertaken to probe the mechanism of the disproportionation. The reaction was found to be sensitive to the anion present as well as to ionic strength. For each anion (ClO_4^-, $O_2CCF_3^-$, $O_3SCF_3^-$) in a citrate buffered solution, the reaction is first order in [osmium(IV)] over a pH range from 0.3 to 4.3 in dilute solution. The specific rate was also found to be dependent on the initial concentration of *trans*-$[Os(NH_3)_4Cl_2]^{2+}$. In the 10^{-4} M range, first-order behavior was noted, but increasing the concentration to 10^{-3} M introduced a second-order component in the disappearance of Os(IV). A very slow acid-independent path was indicated by the results for strongly acidic solution. The rate constants for the disproportionation of this dichloro species and others studied are summarized in Table VI.

The ultraviolet spectrum of a freshly prepared solution of *trans*-$[Os(NH_3)_4Cl_2]Cl_2$ at pH 4, near the pK_a of the complex, features two absorptions. The first at 28.01×10^3 cm^{-1} corresponds to the protonated Os(IV) species while the second at 36.23×10^3 cm^{-1} is apparently due to the deprotonated osmium(IV) ion, *trans*-$[Os(NH_2)(NH_3)_3Cl_2]^+$. At higher pH

Table VI. Rate Constants for Osmium(IV) Disproportionation Reactions

complex	solvent	pH	μ	initial concn, M	k, s^{-1} (% accuracy)
trans-$[Os(NH_3)_4Cl_2]^{2+}$	citrate/NaTFMS	2.93	0.50	1.50×10^{-4}	7.9×10^{-5} (3)
trans-$[Os(NH_3)_4Cl_2]^{2+}$	citrate/NaTFMS	3.51	0.50	1.75×10^{-4}	1.1×10^{-4} (2)
trans-$[Os(NH_3)_4Cl_2]^{2+}$	citrate/NaTFMS	4.10	0.50	1.50×10^{-4}	3.5×10^{-4} (10)
trans-$[Os(NH_3)_4Cl_2]^{2+}$	citrate/NaTFMS	4.20	0.50	1.50×10^{-4}	4.0×10^{-4} (2)
trans-$[Os(NH_3)_4Cl_2]^{2+}$	citrate/NaTFMS	4.31	0.50	1.75×10^{-4}	5.1×10^{-4} (2)
trans-$[Os(NH_3)_4Cl_2]^{2+}$	0.1 M HCl	1.01	0.10	7.80×10^{-5}	5.3×10^{-5} (5)
trans-$[Os(NH_3)_4Br_2]^{2+}$	0.1 M HCl	1.01	0.10	1.68×10^{-4}	1.7×10^{-5} (5)
trans-$[Os(NH_3)_4I_2]^{2+}$	0.1 M HCl	1.01	0.10	1.54×10^{-4}	4.4×10^{-6} (5)
cis-$[Os(NH_3)_4I_2]^{2+}$	0.1 M HCl	1.01	0.10	2.93×10^{-4}	5×10^{-4} (20)

(>5), only the band at 36.23 × 10^3 cm^{-1} ($\epsilon \approx 2.9 \times 10^3$) is present initially, but the absorption shifts with time to 36.90 × 10^3 cm^{-1} characteristic of *trans*-$[Os(NH_3)_4Cl_2]^+$.

The *cis*-dichloro– and *cis*-dibromoosmium(IV) species offered an additional complexity because of their rapid isomerization to the trans configuration. This isomerization is pH dependent and appears to be characteristic of the deprotonated Os(IV) species. These isomerization reactions were faster than the disproportionation reactions below pH 1. In 6 M H_2SO_4, the rate constant for the isomerization of *cis*-$[Os(NH_3)_4Cl_2]^{2+}$ was observed to be 2.05 × 10^{-4} s^{-1} while in 1 M H_2SO_4 the reaction was found to be complete in a few seconds. No isomerization was observed for the *cis*-diiodo complex.

At pH 2 or above, the *cis*-dichloro and -dibromo species disproportionate in a manner similar to that observed for the trans isomers. The reactions are complete on dissolution in 0.01 M HCl.

One-electron oxidation of acidic solutions of hexaammine- and pentaamminehaloosmium(III) complexes resulted in the immediate generation of an osmium(VI) nitrido complex tentatively identified as *trans*-$[OsN(NH_3)_4(OH_2)]^{3+}$. The reaction transformed one-third of the osmium(III) starting material into the nitrido species. These observations may be summarized with

$$Ce^{IV} + Os(NH_3)_6{}^{3+} = Ce^{3+} + [Os(NH_2)(NH_3)_5]^{3+} + H^+$$

$$H^+ + H_2O + 3[Os(NH_2)(NH_3)_5]^{3+} = 2[Os(NH_3)_6]^{3+} + [OsN(NH_3)_4OH_2]^{3+} + NH_4{}^+$$

The amido species is expected to be the dominant form of the osmium(IV) ion in 0.1 M acid because the pK_a values of the hexaammine- and pentaamminehaloosmium(III) complexes are well below 1. It is not certain from our limited observations that the reaction follows the course indicated by the two equations. If Ce(IV) reacts much more rapidly with $[Os(NH_2)(NH_3)_5]^{3+}$ than with $[Os(NH_3)_6]^{3+}$, the same stoichiometry would be observed. Mass electrolytic oxidation of Os(III) in 0.1 M $HClO_4$ at potentials slightly more positive than the irreversible oxidation wave recorded in cyclic voltammograms revealed a 3.0 electron oxidation per osmium. The only product isolated from the mass electrolysis was the nitrido species.

The nitrido product has been reported in the literature[26] but has eluded complete characterization. The trans labilization by the nitrido ligand on osmium(VI) is well substantiated[27,28] so that in hydrochloric acid the dominant form may be $[OsN(NH_3)_4Cl]^{2+}$. The nitrido species is very difficult to characterize. When prepared in hydrochloric acid, the solid is rather insoluble, but the complex does not readily precipitate when the oxidation takes place in perchloric acid. The UV–vis spectra of the two compounds are identical. The electronic absorption spectrum of the complex is sensitive to the pH of the solution. A small change is noted on going from 0.1 M acid to water, but the absorption is altered totally when 0.1 M NaOH is used. In acidic solution, the spectrum shows the bands at 42.37 × 10^3 cm^{-1} ($\epsilon = 3.15 \times 10^3$ M^{-1} cm^{-1}), 37.04 × 10^3 cm^{-1} ($\epsilon = 1.35 \times 10^3$ M^{-1} cm^{-1}), 30.8 × 10^3 cm^{-1} (sh) ($\epsilon = 75$ M^{-1} cm^{-1}), and 24.39 × 10^3 cm^{-1} ($\epsilon = 25$ M^{-1} cm^{-1}) (the extinction coefficients were calculated by assuming a molecular weight of 378.7 for $[OsN(NH_3)_4Cl]Cl_2$). The electronic spectrum resembles that of the bridged nitrido species, $[(Os(NH_3)_4Cl)_2N]Cl_3$, except for the extinction coefficients which are lower for the monomer by a factor of 10.[29] The infrared spectrum suggests an ammine complex with a nitrido group present (ν(OsN) = 1090 cm^{-1}). The compound can be reduced (irreversibly) at −0.61 V (SHE). In a CV experiment, reduction of the nitrido species led to the appearance of an irreversible oxidation wave at +1.05 V similar to that observed for $[Os(NH_3)_5Cl]^{2+}$. Elemental analyses indicated that all solids obtained were mixtures, and further characterization is in order.

Discussion

Physical Properties. The charge-transfer absorptions observed for the Os(III) and Os(IV) halo complexes are described as arising through electron transfer from a ligand π orbital to a metal d orbital.[13,30] The energy of the metal receptor orbital is not expected to change much upon altering the halide ligand so that the attendant variation of the CT energy is attributable mainly to differences in the energy needed to remove electrons from the halide. As expected on the basis of the optical electronegativities of the halides,[31] the energy of the charge-transfer absorptions increases in the series I^-, Br^-, and Cl^-.

Upon oxidation of the central metal, the receptor orbital becomes more stable and the CT absorptions are shifted to lower energy. As the ligands are only slightly affected by this oxidation, an almost constant shift in the absorption is expected regardless of the nature of the halide. This is observed experimentally as summarized in Table I (ΔE values).

Verdonck and Vanquickenborne[30] have applied simplified molecular orbital theory to the charge-transfer spectra of osmium(III) ammines. They have met with considerable success in rationalizing the positions and intensities of the absorptions observed for the monohalo, *cis*-dihalo, and *trans*-dihalo species. Their arguments should also be applicable to the osmium(IV) species.

When $[OsNCl_5]^{2-}$ is reduced, a pentachloro complex of Os(IV) or Os(III) can be the product. By comparison with the position of the charge-transfer bands in other chloroosmium species, the complex absorbing near 37 000 cm^{-1} contains osmium(III), and that absorbing near 28 600 cm^{-1} contains osmium(IV) (Table I). This assignment was verified by simple redox and electrochemical experiments which demonstrate that the two species differ by only a single electron.

Arguments based on group theory show that when the number of halide ligands increases, additional charge-transfer transitions at near the same energy are possible. Unfortunately, few predictions can be made about their intensities. As mentioned earlier, the CT spectra of the monohalo (single band), *trans*-dihalo (single band), and *cis*-dihalo (two bands) species are well understood.[30] A similar analysis for triamminetrihalo ions has not been carried out. The appearance of three charge-transfer bands for these trihalo species is consistent with meridional geometry. A meridional configuration is strongly implied by chemical evidence since the species is formed from a *trans*-dihalo ion by replacing ammonia by halide through diazotization.[7] The lability to isomerization of dihaloosmium(IV) ammines has been demonstrated, the trans configuration having been found to be stable with respect to the cis configuration, except possibly in the diiodo case.[13]

Discussions of the near-IR spectra of third-row transition-metal hexahalo ions have appeared in the literature.[32-35] For

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both d^4 and d^5 (but not d^6) low-spin third-row metal centers, near-IR absorptions are cited. These absorptions are attributed to vibrationally coupled metal-centered intraconfigurational transitions. The states involved arise through the significant spin–orbit coupling ($\xi_{SO} \approx 2500$ cm^{-1}) of third-row metal ions which splits the $^2T_{2g}$ (d^5) or $^3T_{1g}$ (d^4) ground states. A transition is predicted at an energy slightly greater than $^3/_2\xi_{SO}$ or ca. 4000 cm^{-1} for each state. More transitions are expected in the near-IR region for d^4 ions due to the greater number of states arising from this configuration, but none for a low-spin d^6 ion. The singlet ground state arising from the πd^6 (t_{2g}^6) configuration is not split by spin–orbit coupling even in an environment which deviates from octahedral symmetry.

It is apparent from Figures 5–8 that the near-IR spectra observed for the haloammine complexes are of the same type as those observed for the hexahalo species. The same vibrational structure is found for the ammine ions, and the extinction coefficients have the same order of magnitude.

It is interesting to note that this type of transition may be responsible for the near-IR absorptions observed for the μ-dinitrogen (Os(II)–Os(III) and Os(III)–Os(III)) complexes which have a high intensity in both forms.[17] Previously, these absorptions were described as being intervalence transfer in origin, but recognizing that the systems are strongly delocalized. The absorptions show the same vibrational structure and occur in the same energy range as those observed for the monomeric d^5 ions. An important difference is the very large extinction coefficients ($\sim$5000 M^{-1} cm^{-1}) found for the μ-dinitrogen complexes as compared with those found for the monomeric entities ($\sim$50 M^{-1} cm^{-1}). It has been recognized that the intensity of a d–d[36,37] transition for an oscillator can be greatly enhanced by interaction with another metal center, often with minor effects on the energy. Thus the transitions for the μ-dinitrogen species are likely fundamentally the same as those found in the monomers with the increased intensity being ascribable to the second interacting center.

The electrochemical data presented in Table IV reveal several trends in the stabilization of the osmium(IV) centers by halide ligands. The number of halides present figures prominently in the reduction of the IV/III couple. Each ammine replaced by a halide lowers the oxidation potential by approximately 150 mV. Comparable behavior is observed for ruthenium III/II couples ([Ru(NH$_3$)$_5$Cl], −40 mV; *trans*-[Ru(NH$_3$)$_4$Cl$_2$], −180 mV[38]) and is expected on the basis that the halide ligands, being negatively charged and acting as π-electron donors, will interact more strongly with the higher oxidation state.

The nature of the halide also influences the value of the redox couple. Iodide, though the largest of the halides, stabilizes osmium(IV) relative to osmium(III) more than bromide or chloride. The stabilization varies from 10 to 20 mV per halide.

Configurational differences also control the stabilization provided by the halide ligands. For the dihalo species, trans geometry lowers the redox couple by $\sim$90 mV relative to the cis configuration, except in the iodide case. The same ordering is also found for the III/II couples of the ruthenium analogues.[38]

The highly acidic nature of the osmium(IV) ammines is not unexpected. The low pK_a values may be attributed to the high oxidation state of the central metal and to the high electron affinity of the d^4 t_{2g} orbitals which stabilize the amide formed on deprotonation by double-bond formation. The effect of charge is clearly important. On comparison of the pK_a values of coordinated ammonia for the hexaammine complexes of Rh(III)[3] and Pt(IV)[6] (both t_{2g}^6), at least an 8 pK_a unit decrease upon one-electron oxidation is noted. The considerably larger decrease in pK_a, at least 15 units, observed upon oxidizing [Os(NH$_3$)$_6$]$^{3+}$ by one electron, demonstrates the importance of stabilizing the amido species.

A comparison of osmium(IV) and platinum(IV) ammines is enlightening in assessing the heightened acidity due to stabilization of the amide. The pK_a for *trans*-[Pt(NH$_3$)$_4$Cl$_2$]$^{2+}$ is reported to be 11.2[6] which is 7 units less acidic than recorded for the analogous osmium complex. Iridium(IV) ammines are also expected to be more acidic than platinum(IV) ammines due to their high oxidation state and t_{2g}^5 electronic configuration, and this is borne out by the pK_a of 7 determined for [Ir(NH$_3$)Cl$_5$]$^-$. Distortion of the coordination spheres, leading to nonequivalence of similar ligands, can also have a profound effect on acidity. Such distortions are expected to be greater for Os(IV) than Ir(IV) and for this in turn than for Pt(IV). It is noteworthy in this connection that [Os(NH$_3$)Cl$_5$]$^-$ is only slightly more acidic than the iridium analogue.

An increase in the number of halides would be expected to decrease the ammine acidity because of the decreased overall charge of the complex. A comparable trend is observed for platinum(IV) haloammines.[6] Another factor responsible for the pK_a dependence on the number of halide ligands is the increased t_{2g} electron density donated by the halides which destabilizes the amido complex.

The *cis*-dihalo complexes are invariably more acidic than the trans isomers although the difference is much smaller for the diiodo species. The variation in acidity can be correlated with the difference in IV/III couples for the cis and trans isomers. The potential for the cis isomer exceeds that of the trans by ca. 80 mV except for the diiodo case in which they are quite close. The same trend in acidity of the cis and trans isomers is also found for [Pt(NH$_3$)$_4$Cl$_2$]$^{2+}$.[6] A critical factor in trying to understand the acidities is the position from which the proton is lost. This important issue is not illuminated by the kind of work we have reported.

The irreversible behavior observed in the cyclic voltammograms in solutions with pH values near or above the pK_a value of the osmium(IV) species was not anticipated (Figure 9). The sensitivity of this phenomenon to scan rate is consistent with a chemical step succeeding the oxidation such as a slow structural reorganization. Several explanations for this behavior were considered. The oxidized, deprotonated species are known to disproportionate (see below), but the changes observed in homogeneous solutions are slower than those accompanying the electrode process. It is possible that the d^4 ion is altered structurally by Jahn–Teller distortions accompanied by proton loss.

Chemistry. Turning now to the disproportionation of the osmium(IV) ammines, we note that the oxidized product of the reaction is one of the two forms of osmium(VI) depending on the number of ammine ligands present initially. For the hexaammine and pentaammine halo ions, the osmium(VI) species formed contains a nitrido ($\equiv$N) ligand created from one of the ammines. When four or fewer ammines are present in any configuration, the osmium(VI) product contains the *trans*-dioxo moiety, O=Os=O.

The rates of disproportionation reflect the reorganization necessary to form the osmium(VI) product. The nitrido species requires only the loss of three protons, and its formation was observed to be very rapid by the irreversible nature of the cyclic voltammetry experiment at scans up to 100 V s^{-1} in 1 M HCl. The osmyl species was observed to be produced more slowly

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because two positions must aquate before the oxo ligands can form.

The kinetic studies done on the disproportionation of *trans*-tetraamminedichloroosmium(IV) indicate that a variety of paths are involved. Components both first and second order in [Os(IV)] are observed, and the rate increases as the acidity decreases through a pH range from 0 to 4.

The rate of disproportionation was found to depend on the halide present. Table VI indicates an increase in the rate constant by a factor of 12 for the *trans*-dihalo compounds over the series I^-, Br^-, and Cl^-.

The rate is more sensitive to the configuration of the complex than to a change in the halide. A 100-fold increase in rate was recorded on comparing the *trans*-diiodo species to the *cis*-diiodo ion even though the pK_a values for the complex differ by less than 1 unit. This rate difference is most likely attributed to the ease of loss of the ligand trans to the amido group. For the *trans*-diiodo species a strongly held ammine group occupies this position while for the cis analogue a more labile iodide can be the trans ligand.

The facility with which the d^4 configuration undergoes isomerization as compared to d^5 or d^6 is remarkable. At solution pH less than 2, the *cis*-dibromo and -dichloro complexes isomerize to the trans configuration more rapidly than they disproportionate while for pH values of 2 or greater the disproportionation reaction is faster. The pH dependence found for the rates of isomerization of the *cis*-dichloro and *cis*-dibromo species may be ascribed to the trans-labilizing property of the amido group. This characteristic of the amide ligand is well documented in cobalt chemistry.[39] In the context of the behavior of the dichloro and dibromo speices, the failure of the *cis*-diiodo complex to isomerize is remarkable. The explanation for the lack of isomerization of *cis*-$[Os(NH_3)_4I_2]^{2+}$ is not yet clear. A bonding cis ligand–ligand interaction may be responsible in part.

The isomerization observed for the dichloro- and dibromo- but not for the diiodoosmium(IV) complexes has implications concerning the mechanism of the isomerization reported by Allen and Stevens for the *cis*-dichloro- and *cis*-dibromoosmium(III) ions.[13] Reflux conditions for protracted periods (48–72 h) are required for this transformation. Their findings parallel those for the osmium(IV) species. It is consistent with all the observations to attribute the isomerization of the cis osmium(III) complexes to a reaction of an osmium(IV) amide. When the osmium(III) reaction mixture is exposed to the air under reflux conditions, it is observed that small quantities of osmium(IV) are produced. Under anaerobic conditions the generation of small quantities of osmium(IV) is still likely through the disproportionation $2Os^{III} = Os^{II} + Os^{IV}$. This means of osmium(IV) production would explain the low yields reported by Allen and Stevens as Os(II) complexes are known to lose halide ligands.[25]

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Registry No. $[Os(NH_3)_5N_2]Cl_2$, 20611-50-1; $[Os(NH_3)_5(OH_2)](ClO_4)_3$, 73531-74-5; $[Os(NH_3)_5Cl]Cl_2$, 39176-94-8; $[Os(NH_3)_5Br]Br_2$, 41099-80-3; $[Os(NH_3)_5N_2](ClO_4)_2$, 20611-53-4; $[Os(NH_3)_5I]I_2$, 39733-97-6; $[Os(NH_3)_6](ClO_4)_3$, 42055-56-1; *trans*-$[Os(NH_3)_4Cl_2]Cl$, 73531-73-4; *trans*-$[Os(NH_3)_4Br_2]Br$, 41099-83-6; *trans*-$[Os(NH_3)_4I_2]I$, 41099-84-7; $Cs_2[OsCl_5NH_3]$, 73531-72-3; *trans*-$[Os(NH_3)_4I_2]Cl$, 73531-71-2; *cis*-$[Os(NH_3)_4I_2]Cl$, 73544-64-6; *cis*-$[Os(NH_3)_4I_2]Cl_2$, 73531-70-1; *cis*-$[Os(NH_3)_4Cl_2]Cl_2$, 73573-35-0; *cis*-$[Os(NH_3)_4Br_2]Cl_2$, 73531-69-8; *trans*-$[Os(NH_3)_4Cl_2]Cl_2$, 73531-68-7; *trans*-$[Os(NH_3)_4Br_2]Cl_2$, 73573-40-7; *trans*-$[Os(NH_3)_4I_2]Cl_2$, 73573-39-4; *mer*-$[Os(NH_3)_3I_3]Cl$, 73531-79-0; $Cs[Os(NH_3)Cl_5]$, 73531-78-9; ammonium hexachloroosmate(IV), 12125-08-5; $[Os(NH_3)_5NO](ClO_4)_3$, 73531-77-8; *trans*-$[Os(NH_3)_4O_2]Cl_2$, 12055-01-5; $K_2[OsCl_5N]$, 39553-99-6; $[Os(NH_3)_5Cl]^{2+}$, 43031-57-8; $[Os(NH_3)_5Br]^{2+}$, 43031-58-9; $[Os(NH_3)_5I]^{2+}$, 43031-59-0; *trans*-$[Os(NH_3)_4Cl_2]^+$, 43112-00-1; *trans*-$[Os(NH_3)_4Cl_2]^{2+}$, 73531-76-7; *trans*-$[Os(NH_3)_4Br_2]^+$, 43112-01-2; *trans*-$[Os(NH_3)_4Br_2]^{2+}$, 73573-38-3; *trans*-$[Os(NH_3)_4I_2]^+$, 43112-02-3; *trans*-$[Os(NH_3)_4I_2]^{2+}$, 73573-37-2; *cis*-$[Os(NH_3)_4Cl_2]^+$, 43111-97-3; *cis*-$[Os(NH_3)_4Cl_2]^{2+}$, 73573-36-1; *cis*-$[Os(NH_3)_4Br_2]^+$, 43065-21-0; *cis*-$[Os(NH_3)_4Br_2]^{2+}$, 73531-75-6; *cis*-$[Os(NH_3)_4I_2]^+$, 43111-98-4; *cis*-$[Os(NH_3)_4I_2]^{2+}$, 73531-88-1; *mer*-$[Os(NH_3)_3Cl_3]$, 73573-41-8; *mer*-$[Os(NH_3)_3Cl_3]^+$, 73531-87-0; *mer*-$[Os(NH_3)_3Br_3]$, 73531-86-9; *mer*-$[Os(NH_3)_3Br_3]^+$, 73531-85-8; *mer*-$[Os(NH_3)_3I_3]$, 73531-84-7; *mer*-$[Os(NH_3)_3I_3]^+$, 73531-83-6; $[Os(NH_3)Cl_5]^{2-}$, 73531-82-5; $[Os(NH_3)Cl_5]^-$, 73531-81-4; $[OsCl_6]^{3-}$, 62792-05-6; $[OsCl_6]^{2-}$, 16871-52-6; $[Os(NH_3)_6]^{3+}$, 48016-91-7; $[Os(NH_3)_5OH_2]^{3+}$, 53222-99-4; *trans*-$[OsN(NH_3)_4Cl]Cl_2$, 73531-80-3.

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Dinitrogen Complexes of Osmium(III) Haloammines

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The reaction of nitrous acid with a number of amminehaloosmium(III) complexes proceeds in two well-defined stages: oxidation of Os(III) by HNO_2 to an Os(IV) complex and subsequent reductive diazotization of the latter by the nitric oxide produced in the first stage. The reaction depends for its success on the deprotonation of coordinated ammonia; this is significant for osmium(IV) ammines even in quite acidic solution. The conversion of $[Os(NH_3)_5N_2]^{2+}$ to $[Os(NH_3)_4(N_2)_2]^{2+}$ takes an analogous course: HNO_2 oxidizes Os(II) to the corresponding Os(III) complex which is sufficiently acidic so that at pH >3 it undergoes reductive diazotization by the nitric oxide produced in the first stage. The kinetic stability to loss of dinitrogen from Os(III) is enhanced by partial replacement of NH_3 by halide: the first-order specific rates for aquation of $[Os(NH_3)_5N_2]^{3+}$, *cis*-$[Os(NH_3)_4I(N_2)]^{2+}$, and *trans*-$[Os(NH_3)_3I_2(N_2)]^+$ at 25 °C are 2×10^{-2}, 1.7×10^{-3}, and 2×10^{-3} s^{-1}, respectively. Quite remarkable is the enhancement by N_2 as ligand of the acidity of NH_3 coordinated to Os(III): the pK_a values of $[Os(NH_3)_6]^{3+}$ and $[Os(NH_3)_5N_2]^{3+}$ are ~16 and 6.6, respectively. In alkaline solution, the dinitrogen complexes of Os(III) disproportionate quite rapidly, producing the corresponding osmium(II) dinitrogen complex and an osmium(VI) species.

Introduction

Metal complexes of dinitrogen have been the subject of considerable interest since the first dinitrogen compound was isolated in 1965.[1] Investigations have focused on elucidating the metal–dinitrogen interaction with particular emphasis on the activation of N_2 toward reduction (nitrogen fixation). Only

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