

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 species, the failure of the *cis*-diiodo complex to isomerize is remarkable. The explanation for the lack of isomerization of *cis*-[Os(NH₃)₄I₂]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*-dibromo-

osmium(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(NH₃)₅N₂]Cl₂, 20611-50-1; [Os(NH₃)₅(O-H₂)](ClO₄)₃, 73531-74-5; [Os(NH₃)₅Cl]Cl₂, 39176-94-8; [Os(NH₃)₅Br]Br₂, 41099-80-3; [Os(NH₃)₅N₂](ClO₄)₂, 20611-53-4; [Os(NH₃)₅I]₂, 39733-97-6; [Os(NH₃)₆](ClO₄)₃, 42055-56-1; *trans*-[Os(NH₃)₄Cl]Cl, 73531-73-4; *trans*-[Os(NH₃)₄Br₂]Br, 41099-83-6; *trans*-[Os(NH₃)₄I₂]I, 41099-84-7; Cs₂[OsCl₅NH₃], 73531-72-3; *trans*-[Os(NH₃)₄I₂]Cl, 73531-71-2; *cis*-[Os(NH₃)₄I₂]Cl, 73544-64-6; *cis*-[Os(NH₃)₄I₂]Cl₂, 73531-70-1; *cis*-[Os(NH₃)₄Cl₂]Cl₂, 73573-35-0; *cis*-[Os(NH₃)₄Br₂]Cl₂, 73531-69-8; *trans*-[Os(NH₃)₄Cl₂]Cl₂, 73573-68-7; *trans*-[Os(NH₃)₄Br₂]Cl₂, 73573-40-7; *trans*-[Os(NH₃)₄I₂]Cl₂, 73573-39-4; *mer*-[Os(NH₃)₃I₃]Cl, 73531-79-0; Cs-[Os(NH₃)Cl₅], 73531-78-9; ammonium hexachloroosmate(IV), 12125-08-5; [Os(NH₃)₅NO](ClO₄)₃, 73531-77-8; *trans*-[Os(NH₃)₄O₂]Cl₂, 12055-01-5; K₂[OsCl₅N], 39553-99-6; [Os(NH₃)₅Cl]²⁺, 43031-57-8; [Os(NH₃)₅Br]²⁺, 43031-58-9; [Os(NH₃)₅I]²⁺, 43031-59-0; *trans*-[Os(NH₃)₄Cl₂]⁺, 43112-00-1; *trans*-[Os(NH₃)₄Cl₂]²⁺, 73531-76-7; *trans*-[Os(NH₃)₄Br₂]⁺, 43112-01-2; *trans*-[Os(NH₃)₄Br₂]²⁺, 73573-38-3; *trans*-[Os(NH₃)₄I₂]⁺, 43112-02-3; *trans*-[Os(NH₃)₄I₂]²⁺, 73573-37-2; *cis*-[Os(NH₃)₄Cl₂]⁺, 43111-97-3; *cis*-[Os(NH₃)₄Cl₂]²⁺, 73573-36-1; *cis*-[Os(NH₃)₄Br₂]⁺, 43065-21-0; *cis*-[Os(NH₃)₄Br₂]²⁺, 73531-75-6; *cis*-[Os(NH₃)₄I₂]⁺, 43111-98-4; *cis*-[Os(NH₃)₄I₂]²⁺, 73531-88-1; *mer*-[Os(NH₃)₃Cl₃], 73573-41-8; *mer*-[Os(NH₃)₃Cl]⁺, 73531-87-0; *mer*-[Os(NH₃)₃Br₃], 73531-86-9; *mer*-[Os(NH₃)₃Br]⁺, 73531-85-8; *mer*-[Os(NH₃)₃I₃], 73531-84-7; *mer*-[Os(NH₃)₃I]⁺, 73531-83-6; [Os(NH₃)Cl₅]²⁻, 73531-82-5; [Os(NH₃)Cl₅]⁻, 73531-81-4; [OsCl₆]³⁻, 62792-05-6; [OsCl₆]²⁻, 16871-52-6; [Os(NH₃)₆]³⁺, 48016-91-7; [Os(NH₃)₅OH₂]³⁺, 53222-99-4; *trans*-[OsN(NH₃)₄Cl]Cl₂, 73531-80-3.

(39) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Chemistry", Wiley, New York, 1967, Chapter 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 HNO₂ 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(NH₃)₅N₂]²⁺ to [Os(NH₃)₄(N₂)₂]²⁺ takes an analogous course: HNO₂ 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 NH₃ by halide: the first-order specific rates for aquation of [Os(NH₃)₅N₂]³⁺, *cis*-[Os(NH₃)₄I(N₂)₂]²⁺, and *trans*-[Os(NH₃)₃I₂(N₂)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 N₂ as ligand of the acidity of NH₃ coordinated to Os(III): the pK_a values of [Os(NH₃)₆]³⁺ and [Os(NH₃)₅N₂]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 N₂ toward reduction (nitrogen fixation). Only

(1) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

complexes with metals in low oxidation states have been reported, suggesting that donation of π -electron density by the metal center to dinitrogen² is important for stability.

One reaction pathway which would accomplish nitrogen fixation is the internal disproportionation $L_5Os^{III}N \equiv NOs^{III}L_5 \rightarrow 2L_5Os^{VI} \equiv N$.³ This reaction can reasonably be expected to proceed with the appropriate choice of auxiliary ligands. Osmium(VI) nitrido species are well characterized⁴ and show no tendency to undergo coupling reactions yielding N_2 .⁵ Binuclear dinitrogen-bridged osmium ammine complexes have been prepared.⁶ Those of the Os(III)–Os(III) unit are unstable with respect to metal–dinitrogen bond scission, but if this reaction becomes sufficiently slow, the desired reaction may predominate.⁷ Studies of the stability of osmium(III) dinitrogen complexes are thus essential to the investigation of the above proposed nitrogen fixation reaction.

In this article, we report the characterization of a new class of mononuclear dinitrogen compounds containing a metal in oxidation state III. Nitric oxide reacts rapidly with deprotonated osmium(IV) haloammines (two or three halides),⁸ forming osmium(III) dinitrogen complexes. Alternatively, nitrous acid reacts with osmium(III) haloammines (one, two, or three halides), producing osmium(III) dinitrogen species. These diazotization reactions are described along with the properties of the dinitrogen complexes formed.

Experimental Section

A. Reagents and Materials. Osmium tetroxide (99.8%) was purchased from Alfa Products in 1-g ampules. Dowex AG-50W-X2 cation-exchange resin from Bio-Rad was purified⁹ 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. Preparations. This section contains the procedures, some original, used to prepare known osmium complexes employed in this research.

Ammonium hexachloroosmate(IV) was prepared by the procedure of Dwyer and Hogarth,¹⁰ those of Clifford and Kobayashi¹¹ 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 Freymy¹² and tetraamminedioxoosmium(VI) chloride by adaptation from the work of Gibbs.¹³

The dihalo species $cis-[Os(NH_3)_4X_2]X$ were prepared by the method of Allen and Stevens.¹⁴ They were purified by ion-exchange chromatography on Dowex AG-50W-X2. Magnuson's modification⁷ of Scheidegger's synthesis¹⁵ was used to prepare $cis-[Os(NH_3)_4-$

$(N_2)_2]Cl_2$. The compounds $[Os(NH_3)_5N_2]Cl_2$, $[Os(NH_3)_5OH_2](ClO_4)_3$, $[Os(NH_3)_5X]X_2$ ($X = Cl^-, Br^-, I^-$), $trans-[Os(NH_3)_4X_2]X$ ($X = Cl^-, Br^-, I^-$), $trans-[Os(NH_3)_4X_2]Cl_2$ ($X = Cl^-, Br^-, I^-$), $cis-[Os(NH_3)_4X_2]Cl_2$, $Cs[Os(NH_3)_3Cl_3]$, and $mer-[Os(NH_3)_3L_3]Cl$ are described elsewhere.⁸ $[Ir(NH_3)_5Cl]Cl_2$ ¹⁶ and $K(NH_4)[Ir(NH_3)Cl_3]$ ¹⁷ were prepared by the literature methods.

Pentaammine(dinitrogen)osmium(III) Bromide, $[Os(NH_3)_5N_2]Br_3$. The osmium(III) dinitrogen complex was prepared by oxidizing the osmium(II) analogue. Pentaammine(dinitrogen)osmium(II) chloride (126 mg) was dissolved in a minimum volume of 0.1 M CF_3SO_3H at 0 °C. An equivalent amount of Ce(IV) (0.1 M $Ce(NO_3)_4 \cdot 2N-H_4NO_3$, Bio-Rad) was added rapidly with stirring. After 5 s, hydrated LiBr was added, with rapid stirring, to precipitate the yellowish solid. The product proved to be 80% osmium(III) ($\nu(N \equiv N) = 2212 \text{ cm}^{-1}$) with the remaining fraction, as judged by infrared spectroscopy, being comprised of unoxidized osmium(II).

***cis*-Tetraamminecarbonyl(dinitrogen)osmium(II) chloride, $cis-[Os(NH_3)_4(CO)N_2]Cl_2$,** was prepared by diazotizing $[Os(NH_3)_5CO]Cl_2$. Pentaamminecarbonylosmium(II) chloride (114 mg) was dissolved in 20 mL of 0.05 M HCl, and 52 mg of KNO_2 was added with stirring. The solution turned yellow and then colorless over a 15-min period. After concentration of the solution by rotary evaporation to 5 mL, 2 mL of concentrated HCl was added, and the resulting solution was placed in an ice bath. The white solid was collected, washed with ethanol and ether, and air-dried. The yield was over 80%. The compound was characterized by its IR spectrum ($\nu(NN) = 2179 \text{ cm}^{-1}$, $\nu(CO) = 1952 \text{ cm}^{-1}$) and its UV spectrum (207 nm, $\epsilon = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$; 257 nm (sh), $\epsilon = 1.69 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$; 280 nm (sh), $\epsilon = 1.05 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁸

C. Characterization of New Compounds. The synthesis and properties of compounds containing new complexes are presented in the Results. The extreme substitution inertia of osmium haloammines in acidic solution (with the exception of N_2 ligated to Os(III)) greatly facilitated product identification since substitution under the usual reaction conditions was not significant.

The charge of each complex was determined by its elution behavior on SP-Sephadex C-25 and/or Dowex AG-50W-X2 (proton form) ion-exchange columns. The elution behavior of known complexes of similar size was used as a standard. The elution behavior as function of charge has been outlined in a related paper.⁸

The substitution inertia of these osmium species was used to considerable advantage in characterizing the oxidized or reduced analogue of a complex which had been well characterized by other means. Thus in many cases cyclic voltammetry served to demonstrate that two species were related by simple electron abstraction or addition. By recourse to ultraviolet and visible spectroscopy, it could be shown that pairs of complexes could be readily interconverted by a redox process.

With the charge of the complex specified, elemental analyses for N and H suffice to determine the ammine content of the compound. Possible complications arising from replacement of halide by H_2O were eliminated by the $E_{1/2}$ value, which is very sensitive to the halide content of the inner coordination sphere, and by the infrared spectrum recorded in a Nujol mull.

The large extinction coefficients of the halo species dealt with provide a convenient means for assessing the purity of the compounds. Impurities were readily discerned by UV-vis spectroscopy even when present in amounts of less than 1%.

D. Instruments and Techniques. The determination of spectra, of formal potentials, and of values of pK_a and the procedures followed in mass electrolytic oxidations, in maintaining an inert atmosphere, and in doing ion-exchange separations are described elsewhere.⁸ There remain to be described here only a few additional operations. Mass electrolytic reductions were done over a mercury pool in a two-compartment cell. The auxiliary electrode chamber was separated from the main section by a 10-mm fine-porosity glass frit. The main compartment was fitted with a glass joint to provide connection to a salt bridge containing the reference electrode. The main compartment was sealed by using a serum stopper and the solution deaerated with argon. The level of solvent in the auxiliary chamber was adjusted to that of the main compartment. The various cells used

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- (17) F. Bottomley, S. G. Clarkson, and S. B. Tong, *J. Chem. Soc., Dalton Trans.*, 2344 (1974).
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ranged in capacity from 5 to 200 mL. Hydrazine hydrate was added to the auxiliary electrode compartment to provide a readily oxidizable species at the counter electrode. A constant voltage was applied by using a potentiostat at a potential 120 mV more negative than the formal reduction potential of the substance to be reduced. The progress of the reaction was again monitored by the current passing through the cell. This technique was found especially useful for the generation of zinc-free chromium(II) solutions.

Owing to the sensitivity of many of the reactions of nitric oxide to oxygen, a specialized apparatus containing only standard taper joints and stopcocks was designed and constructed. Nitric oxide was introduced into a reaction mixture only after purging with argon for at least 0.5 h.

Kinetic experiments were monitored by UV-vis spectroscopy in cuvettes of suitable path length sealed with tight-fitting serum stoppers. Reactant solutions were degassed with argon before mixing. Reactions of NO were studied in a specially designed apparatus in which an NO-saturated solution was mixed with a deaerated reactant solution and the resultant solution transferred to a cuvette while a closed system was maintained.

Part I. Nitrosation Reactions of Osmium Amines

Results

Nitric Oxide on Os(III) Complexes. Nitric oxide has been shown to react at higher pHs with $\text{Ru}(\text{NH}_3)_6^{3+}$ to produce $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$ essentially quantitatively.¹⁹ The analogous reaction with $[\text{Os}(\text{NH}_3)_6]^{3+}$ requires much more highly alkaline solutions²⁰ and is by no means as clean as that for hexaammineruthenium(III). With the use of osmium(III) haloammines, the only reactions thus far reported involve the reductive displacement of ammonia or halide, producing nitrosylosmium(II) complexes.²¹ The differences in behavior described above can reasonably be attributed to differences in the tendency for protons to dissociate from coordinated ammonia. The reaction to produce the dinitrogen complex, but not that to produce a nitrosyl, requires that an unshared electron pair be exposed by proton dissociation. We have somewhat amplified the observations made on the interaction of NO with osmium(III) haloammines. All of the following results were obtained at 0 °C in acidic solution ($[\text{H}^+] = 0.1 \text{ M HCl, CF}_3\text{CO}_2\text{H, CF}_3\text{SO}_3\text{H}$) with osmium complex concentrations of 10^{-3} M or less. The solutions were deaerated with argon for 1 h prior to admitting nitric oxide (purified by passing through columns of concentrated sulfuric acid and 5 M potassium hydroxide). It was found essential to maintain strictly anaerobic conditions for reproducible results.

(1) The monohalo complexes ($[\text{Os}(\text{NH}_3)_5\text{X}]^{2+}$, $\text{X} = \text{Cl}^-, \text{I}^-$) react with NO within ~1 h to yield *trans*- $[\text{Os}(\text{NH}_3)_4\text{X}(\text{NO})]^{2+}$ essentially quantitatively. The product was identified by ion-exchange chromatography and by IR and UV spectroscopy. The differences in this experiment from that reported previously²¹ are likely due to the different reaction conditions in the two experiments. When the reaction is allowed to proceed at room temperature, a mixture of products is obtained ($[\text{Os}(\text{NH}_3)_4\text{X}(\text{NO})]^{2+}$ and $[\text{Os}(\text{NH}_3)_5\text{NO}]^{3+}$).

(2) The *trans*-dihalo species (*trans*- $[\text{Os}(\text{NH}_3)_4\text{X}_2]^{2+}$, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) were found to react with nitric oxide in a few hours, producing mainly $[\text{Os}(\text{NH}_3)_4\text{X}(\text{NO})]^{2+}$ (>75%) with the remainder being $[\text{Os}(\text{NH}_3)_3\text{X}_2(\text{NO})]^+$ (the halide ligands presumably remaining *trans* to each other). The UV and infrared spectra of the two products are similar, and the assignment was based on their charge determined by ion-exchange chromatography.

(3) Nitric oxide interacts with *cis*-dihaloosmium complexes (*cis*- $[\text{Os}(\text{NH}_3)_4\text{X}_2]^{2+}$, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) in several hours, producing primarily $[\text{Os}(\text{NH}_3)_3\text{X}_2(\text{NO})]^+$ (>90%). The reaction

mixture was contaminated with a small amount of $[\text{Os}(\text{NH}_3)_4\text{X}(\text{NO})]^{2+}$ which could be removed by ion exchange. The dihalo products were analyzed by ion-exchange chromatography, by UV and IR spectroscopy, and by elemental analysis on the chloride salts. The geometry of the complex was not determined, but it seems likely that the halides remain *cis* to each other with the NO *trans* to one of the halides. Isomerization of the halides¹⁴ under the reaction conditions seems unlikely, and the preferential replacement of a ligand *trans* to a halide group under these conditions has been observed in sections 1 and 2 above. It was noted that, as the temperature was raised from 0 to 25 °C, an increasing amount of $[\text{Os}(\text{NH}_3)_4\text{X}(\text{NO})]^{2+}$ was produced.

(4) Triamminetrichloroosmium(III) upon treatment with NO for several hours produced only $[\text{Os}(\text{NH}_3)_3\text{X}_2(\text{NO})]^{2+}$ as judged by UV and IR spectroscopy, ion-exchange behavior, and elemental analysis. The geometry of the product is unknown but the similarity of the properties of this compound and that derived from *cis*- $[\text{Os}(\text{NH}_3)_4\text{Cl}_2]^+$ implies that the two are probably identical.

In contrast to the behavior cited, when solid $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Br}_3$ is added to an aqueous solution buffered between pH 3 and 6 and saturated with NO, a good yield of the bis(dinitrogen) complex is obtained (~75% isolated as *cis*- $[\text{Os}(\text{NH}_3)_4(\text{N}_2)_2]\text{Br}_2$). The diazotization is much less rapid at lower pH. In 0.1 M HCl only a small amount of the diazotized product is formed ($\leq 5\%$); rather, $[\text{Os}(\text{NH}_3)_5\text{OH}_2]^{3+}$ and $[\text{Os}(\text{NH}_3)_5\text{NO}]^{3+}$ are formed preferentially, the former by loss of N_2 from $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$ (see Part II) and the latter by the action of NO on the former. The reactivity to NO is very sensitive to the composition of the osmium-containing complex. It was observed that *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^{2+}$ does not react with NO even under basic conditions over a period of several hours.

Diazotization by Nitrous Acid. Somewhat to our astonishment, the reactions of HNO_2 with amminehaloosmium(III) complexes take place with great facility. Their study led to the discovery of a new class of reactions to be described presently, those of NO with osmium(IV) haloammines producing osmium(III) dinitrogen species, and to an understanding of how HNO_2 converts dinitrogen complexes of an osmium(II) ammine to the bis(dinitrogen) form.¹⁵

When HNO_2 is added to any of a number of amminehaloosmium(III) complexes containing two or three halides, the first reaction, usually quite rapid, is the oxidation of the Os(III) complex to the corresponding Os(IV) species. This was demonstrated spectrophotometrically, by making use of the spectrum of the Os(IV) complex which had been prepared by an alternative route.⁸

A cuvette containing a solution of *trans*- $[\text{Os}(\text{NH}_3)_4\text{I}_2]\text{Cl}$ ($1.0 \times 10^{-4} \text{ M}$) in 0.1 M HCl was deaerated with argon, and the cell was then placed in a spectrophotometer. On addition of an equimolar quantity of HNO_2 in H_2O , the yellow solution ($\lambda_{\text{max}} = 23\,900 \text{ cm}^{-1}$) immediately turned green ($\lambda_{\text{max}} = 15\,820 \text{ cm}^{-1}$). The spectrum of the green solution was identical with that observed with an authentic sample of *trans*- $[\text{Os}(\text{NH}_3)_4\text{I}_2]^{2+}$ with the exception that a small amount of starting material was left. Following this step, there is a second one, still rather rapid, in which the green solution turns blue. As has been demonstrated independently, this stage corresponds to the transformation by NO of the Os(IV) complex to a dinitrogen complex of Os(III). Then follows a third much slower change in which the yellow color is restored. In this stage, the Os(III)- N_2 species aquates to produce $[\text{Os}(\text{NH}_3)_3(\text{H}_2\text{O})\text{I}_2]^+$ which is expected to have and does have an absorption spectrum very close to that of the starting material.

The reaction of HNO_2 with Os(III) complexes provides ready access to a variety of complexes of dinitrogen with

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(21) F. Bottomley and S. B. Tong, *J. Chem. Soc., Dalton Trans.*, 217 (1973).

Os(III). Detailed observations on the reactions and preparations follow. Though, as shown above, the reactions take place in steps, if the NO formed in the first step is retained, good yields are obtained in a single-stage process.

When $[\text{Os}(\text{NH}_3)_5\text{I}]^{2+}$ reacts at 0 °C with a slight excess of HNO_2 in 0.1 M HCl, a nearly quantitative yield of *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^{2+}$ is produced. The reaction is rapid enough so that it is virtually free from complications attributable to loss of N_2 from the Os(III) complex—the half-life for this loss is several hours at 0 °C. The identity of the product as a dinitrogen species was confirmed by labeling studies with K^{15}NO_2 . The reduction in the infrared dinitrogen stretching frequency from 2198 to 2160 cm^{-1} is consistent with that predicted for the difference in $\nu(\text{NN})$ between $^{14}\text{N}^{14}\text{N}$ and $^{14}\text{N}^{15}\text{N}$, respectively. The geometry of the complex was established by analysis of the diiodo product formed on loss of dinitrogen and further reaction of the resulting aquo ion with hydriodic acid. Only the *cis*-diiodoosmium(III) species was formed upon warming the solution containing the aquo ion in 1 M HI for 15 min. Since reflux conditions for 24 h are required to effect the *cis* → *trans* isomerization of tetraamminediiodoosmium(III) ions,¹⁴ *cis* geometry for the iodo-dinitrogen complex is inferred.

A detailed procedure for the preparation of *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]\text{Br}_2$ is herewith described. A saturated solution of $[\text{Os}(\text{NH}_3)_5\text{I}]\text{Cl}_2$ (50 mg) in 0.1 M HO_2CCF_3 was prepared at 0 °C. Potassium nitrite (13.5 mg) was added, whereupon the solution turned purple. After 2 min, hydrated LiBr was added to the solution, resulting in nearly quantitative precipitation of the complex (but often containing a small amount of a nitrosyl complex as impurity). Alternatively, the violet solution was diluted by 2 volumes of ice-cold water and charged onto an ion-exchange column (AG-50W-X2) maintained at 0 °C. The resin was washed with 1 volume of cold 0.1 M HCl, and the purple band was then rapidly eluted under pressure (5 lb/in²) with 3 M HCl. Sodium bromide was added to the eluate at 0 °C with stirring, resulting in a 60% yield of the bromide salt. The properties of the complex are summarized in Table I.

The osmium(II) analogue of this compound was prepared by the reduction of the diazotized product. Pentaammineiodoosmium(III) chloride (200 mg) was dissolved in 100 mL of 0.1 M HCl in a bubbling flask. The flask was attached to an argon manifold, cooled in an ice bath, and deaerated. Potassium nitrite was added (1.5 equiv, 54 mg), immediately turning the yellow solution purple. Argon bubbling was continued for several minutes. A twofold excess of electrogenerated $\text{Cr}^{\text{II}}(\text{aq})$ (4.26 mL, 0.2 M in Cr(II) in 0.1 M HCl) was added by a syringe fitted with a platinum needle. After 5 min under argon, the air-sensitive yellow solution was concentrated under argon to ca. 0.5 mL by rotary evaporation. The solid was collected by rapid filtration under argon. The yield for this crop was 40%. An additional 30% yield was obtained on addition of an equal volume of deaerated ethanol to the filtrate. Data for this complex are summarized in Table I.

The reactions of the osmium(III) dihalo species with nitrous acid were not clean, but, when an excess of NO was passed through the solution containing the osmium complex and nitrous acid, a good yield of the dinitrogen product was obtained. The reactions were performed in an ice bath to reduce the rate of dinitrogen loss leading to nitrosyl-containing contaminants. The bromide salt of the diazotized dinitrogen product arising from the interaction of HNO_2 and the *trans*-dihaloosmium(III) ions was isolated but was found to be contaminated with *trans*- $[\text{Os}(\text{NH}_3)_4\text{X}_2]\text{Br}_2$. The preparation of the iodo complex will be outlined. A saturated solution of 30 mg of *trans*- $[\text{Os}(\text{NH}_3)_4\text{I}_2]\text{Cl}$ was prepared in

0.01 M HCl at 0 °C. After deaeration, HNO_2 was added and NO was passed through the solution for 5 min. Hydrated LiBr was added after purging the system rapidly with argon. The dark solid was collected, washed with ethanol and ether, and air-dried. The yield of $[\text{Os}(\text{NH}_3)_3\text{I}_2(\text{N}_2)]\text{Br}$ was 50%. The osmium(II) analogues of these dinitrogen complexes with two halide ligands in a *trans* configuration could be isolated as pure neutral solids. The synthesis of the iodo complex will be described.

trans-Tetraamminediiodoosmium(III) chloride (115 mg, 0.21 mmol) was dissolved in a minimum volume of 0.05 M HCl. The yellow solution was deaerated with argon in a bubble flask and brought to 0 °C in an ice bath. Potassium nitrite (26.7 mg) was added, producing a green color, and nitric oxide was bubbled through the solution for 5 min whereupon the solution rapidly turned from green to blue. After purging the system with argon, we added a twofold excess of 0.2 M electrogenerated aqueous Cr(II) (0.1 M HCl solution), immediately producing a yellow color. The solution was concentrated by rotary evaporation under argon until 3 mL remained and a golden precipitate formed. The solution was filtered in air. The neutral solid was washed with ethanol and ether and dried in a vacuum desiccator. The yield of *trans*- $[\text{Os}(\text{NH}_3)_3\text{I}_2(\text{N}_2)]$ was 73%. Physical properties for this compound and for the bromo and chloro analogues are entered in Table I. These properties will be discussed in Part II.

The geometry of the dinitrogen complexes derived from *trans*-dihalo species is assumed to be meridional with the dinitrogen ligand oriented *cis* to both halides. This seems warranted since, although isomerization in a haloamine of Os(IV) can be facile,⁸ the *trans*-dihalo form is stable with respect to the *cis* form.

The osmium(III) dinitrogen complexes derived from *cis*-tetraamminediiodoosmium(III) species by diazotization with HNO_2 can be prepared in the same manner as those from the *trans* analogues. We again failed to obtain pure samples; the bromide salt was always contaminated with *cis*- $[\text{Os}(\text{NH}_3)_4\text{X}_2]\text{Br}_2$. For preparation of the diiodo analogue, a 20-mg sample of *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}_2]\text{Cl}$ was dissolved in 0.1 M HCl to form a saturated solution at 0 °C. The solution was then deaerated. A twofold excess of HNO_2 (6.2 mg) was added, and NO was passed through the vessel for 5 min. After rapid purging with argon, we added hydrated LiBr, resulting in a precipitate. The compound was characterized by its infrared spectrum ($\nu(\text{NN}) = 2180 \text{ cm}^{-1}$). Alternatively, the chloride salt was prepared by freeze-drying the solution after purging with argon.

The osmium(II) dinitrogen compounds arising from *cis*- $[\text{Os}(\text{NH}_3)_3\text{X}_2(\text{N}_2)]^+$ were prepared in pure form in the same manner as those made from the *trans*-dihalo species. To prepare the iodo analogue, 45 mg of *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}_2]\text{Cl}$ was dissolved in 15 mL of 0.1 M HCl at 0 °C. Potassium nitrite (10.5 mg) was added, immediately turning the orange solution violet, and NO was bubbled through the solution for 5 min, producing a green solution. After purging with argon, we added 1 mL of 0.2 M electrogenerated $\text{Cr}^{\text{II}}(\text{aq})$ (0.1 M HCl) by a syringe. After 5 min, the yellow solution was concentrated by rotary evaporation under argon to ~2 mL. Deaerated ethanol (5 mL) was added, and a 77% yield of the neutral species was collected. The properties of the neutral compound are described in Table I together with the chloro and bromo analogues.

Two isomers formed by diazotizing *cis*-dihalotetraammine complexes are possible with the assumption of no isomerization. Facial geometry would place the diazotized ammine *cis* to both halides, while for meridional geometry, the diazotized ammine would lie *trans* to one halide and *cis* to the second. This aspect of the structures of the species has not been settled.

Table I

complex ^a	charge ^b	oxidn state	CT abs ^c (10 ⁻³ ε, L mol ⁻¹ cm ⁻¹)	ν(N≡N) (salt), cm ⁻¹	E _{1/2} (III/II), d V	% N, % H	
						calcd	found
cis-[Os(NH ₃) ₄ (N ₂)] ²⁺	+1	II	48.30 (12.5)	2028 (Cl ⁻)	0.37	18.72, 2.67	18.00, 2.64
cis-[Os(NH ₃) ₄ (N ₂)] ²⁺	+2	III	18.25 (2.48)	2198 (Br ⁻)		14.67, 2.11 (Br ⁻) ^k	14.77, 2.20
trans-[Os(NH ₃) ₃ I(N ₂)] ⁺	0	II	48.78 (45.0), 42.02 (12.0)	2024	0.19	13.39, 1.73	13.33, 1.72
trans-[Os(NH ₃) ₃ I ₂ (N ₂)] ⁺	+1	III	17.30	2174 (Br ⁻)			
trans-[Os(NH ₃) ₃ Br ₂ (N ₂)] ⁺	0	II	46.30 (24.2)	2027, 2003	0.18	16.32, 2.11	16.04, 2.23
trans-[Os(NH ₃) ₃ Br ₂ (N ₂)] ⁺	+1	III	24.75	2200 (Br ⁻)			
trans-[Os(NH ₃) ₃ Cl ₂ (N ₂)] ⁺	0	II	46.51 (15.5)	2029, 2004	0.15	20.59, 2.67	20.22, 2.63
trans-[Os(NH ₃) ₃ Cl ₂ (N ₂)] ⁺	+1	III	30.21	2205 (Br ⁻)			
cis-[Os(NH ₃) ₃ I ₂ (N ₂)] ⁺	0	II	45.45 (24.0)	2014	0.26	13.39, 1.73	13.00, 1.74
cis-[Os(NH ₃) ₃ I ₂ (N ₂)] ⁺	+1	III	15.29	2010			
cis-[Os(NH ₃) ₃ Br ₂ (N ₂)] ⁺	0	II	45.87 (12.2)	2010	0.33, 0.25 ^e	16.32, 2.26	16.35, 2.24
cis-[Os(NH ₃) ₃ Br ₂ (N ₂)] ⁺	+1	III		2003	0.32, 0.20 ^e	20.58, 2.67	19.85, 2.90
cis-[Os(NH ₃) ₃ Cl ₂ (N ₂)] ⁺	0	II	47.17 (10.0)	2035 (Cl ⁻) ^g	0.58 (0.53) ^j		
cis-[Os(NH ₃) ₃ Cl ₂ (N ₂)] ⁺	+1	III	29.85, 28.41 (sh) ^e	2212 (Br ⁻) ^h	1.12 ^j		
cis-[Os(NH ₃) ₃ Cl ₂ (N ₂)] ⁺	0	III	16.89	2114 (Br ⁻) ⁱ	0.92		
mer-[Os(NH ₃) ₂ I ₃ (N ₂)] ⁺	+2	II	48.10 (25.1) ^f		1.5 irrev		
[Os(NH ₃) ₅ N ₂] ²⁺	+2	II	42.25 (20.8) ^e				
[Os(NH ₃) ₅ N ₂] ²⁺	+3	III					
[Ru(NH ₃) ₅ N ₂] ²⁺	+2	II					
[Os(NH ₃) ₅ CO] ²⁺	+2	II					
cis-[Os(NH ₃) ₄ (N ₂)] ²⁺	+2	II					

^a The *cis*, *trans*, and *mer* prefixes indicate the geometry of the halides present. ^b The charge was determined by ion-exchange chromatography (see Experimental Section (C)). ^c All values are reported in wavenumbers (cm⁻¹). ^d All values (SHE) were reversible waves as determined by cyclic voltammetry with a carbon-paste electrode in 0.1 M HCl at a scan rate of 100 mV s⁻¹. ^e May be due to two isomers. ^f References 15 and 18. ^g Reference 18. ^h An erroneous value of 2130 cm⁻¹ was reported in ref 24. ⁱ Reference 25. ^j Reference 26. ^k Salt.

Table II. Infrared Spectra (cm⁻¹) of Dinitrogen Complexes^a

assignment	ν(N-H)				species	rate of loss, s ⁻¹
	A	B	C	D		
ν(N-H)	3266 s	3250 s	3297 s	3245 s	[Ru(NH ₃) ₅ N ₂] ²⁺ , ^b	2 × 10 ⁻⁶
	3184 s	3150 s	3280 s	3200 s	[Os(NH ₃) ₅ N ₂] ²⁺ , ^c	<10 ⁻⁶
			3231 s	3135 s	[Ru(NH ₃) ₅ N ₂] ³⁺ , ^d	>>50
			3177 s		[Os(NH ₃) ₅ N ₂] ³⁺ , ^d	2 × 10 ⁻²
ν(NN)	2028 vs	2198 vs	2024 vs	2174 vs	<i>cis</i> -[Os(NH ₃) ₄ (N ₂)] ²⁺	1.7 × 10 ⁻³
δ(NH ₃) _{deg}	1620 m	1626 m	1617 m	1604 m	<i>cis</i> -[Os(NH ₃) ₄ (N ₂)] ²⁺	<9 × 10 ⁻⁵
δ(NH ₃) _{sym}	1321 s	1344 s	1310 s	1339 s	<i>trans</i> -[Os(NH ₃) ₃ I ₂ (N ₂)] ⁺	3 × 10 ⁻³
			1273 s		<i>trans</i> -[Os(NH ₃) ₃ I ₂ (N ₂)] ⁺	2 × 10 ⁻³
ρ(NH ₃)	802 m	846 m	766 m		<i>trans</i> -[Os(NH ₃) ₃ Br ₂ (N ₂)] ⁺	2 × 10 ⁻³
ν(Os-N)	540 w	509 w	524 w		<i>trans</i> -[Os(NH ₃) ₃ Cl ₂ (N ₂)] ⁺	6 × 10 ⁻³
	521 vw	477 w	502 w		<i>cis</i> -[Os(NH ₃) ₃ I ₂ (N ₂)] ⁺	~2 × 10 ⁻³
		448 w	417 w	398 w	<i>mer</i> -[Os(NH ₃) ₂ I ₃ (N ₂)]	
		384 w				

^a All values were recorded in 0.1 M HCl, 0.1 M HClO₄, or 0.1 M HO₂CCF₃ at ca. 25 °C. ^b Reference 28. ^c Reference 29. ^d Reference 26. ^e This value represents an upper limit for loss of N₂.

Earlier in this section, the conversion by NO of $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$ to $[\text{Os}(\text{NH}_3)_4(\text{N}_2)_2]^{2+}$ at pH values between 3 and 6 was mentioned as well as the fact that, when the pH is low, e.g., 1, the diazotization does not succeed. In the Scheidegger method¹⁵ for converting $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{2+}$ to the bis(dinitrogen) complex, acid is added gradually to a solution containing the Os(II) complex and NO_2^- , so that strong-acid conditions prevail only after reaction NO_2^- rather complete. The preparation does not succeed when the mineral acid is added rapidly. Under these circumstances, although oxidation of $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{2+}$ to the 3+ ion takes place, the second step, the reaction of the latter with NO, is so slow in strong acid that aquation of $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$ to $[\text{Os}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ intervenes. In contrast to the behavior cited, HNO_2 converts $[\text{Os}(\text{NH}_3)_5\text{CO}]^{2+}$ efficiently to $[\text{Os}(\text{NH}_3)_4(\text{CO})\text{N}_2]^{2+}$ even in 0.10 M HCl. The difference between $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$ and $[\text{Os}(\text{NH}_3)_5\text{CO}]^{3+}$ lies in the respective values of $\text{p}K_a$, 6.6 for the former and 2 for the latter.

In an effort to extend the scope of the HNO_2 diazotization, the reaction with iridium amines was studied. No reaction between $[\text{Ir}(\text{NH}_3)_5\text{Cl}_2]^{2+}$ or $[\text{Ir}(\text{NH}_3)_5\text{Cl}]^{2+}$ and nitrous acid was found. When the iridium(IV) analogue of $[\text{Ir}(\text{NH}_3)_5\text{Cl}_2]^{2+}$, prepared by mass electrolytic oxidation, was allowed to react with NO, only the aminopentachloroiridium(III) ion was produced presumably by oxidizing nitric oxide.

The diazotization reaction was attempted in methanol, triethyl phosphate, dimethyl sulfoxide, and acetonitrile by using nitrosyl tetrafluoroborate. Addition of the nitrosyl salt to solutions of osmium(III) amines resulted only in oxidation to osmium(IV). Dinitrogen compounds were not formed, and the addition of a base, CH_3O^- or F^- , did not change the observations. Additional experiments were tried in which HCl was passed through the solvent before and after addition of NO^+ with no effect on the course of the reaction.

Reaction of Nitric Oxide with Osmium(IV) Amines. Nitric oxide has been found to react rapidly with *cis*- and *trans*-tetraamminedihaloosmium(IV) species,⁸ producing osmium(III) dinitrogen complexes. The reaction is pH sensitive and proceeds rapidly in solutions of pH 1 or greater but very slowly in 6 M HCl.

For verification of the identity of the agent effecting the diazotization, the relative reaction rates were compared for NO and HNO_2 reacting with Os(IV). The reaction of $[\text{Os}(\text{NH}_2)(\text{NH}_3)_3\text{I}_2]^+$ with NO proceeds rapidly in 0.1 N HCl while that with HNO_2 occurs slowly at a rate presumably limited by the disproportionation $3\text{HNO}_2 = 2\text{NO} + \text{NO}_3^- + \text{H}_3\text{O}^+$.

The diazotization reaction with NO was also observed for the triamminehaloosmium(IV) complexes.⁸ While the reaction with the dihalo species is quite rapid and complete on a preparative scale at 0 °C in a few minutes, the trihalo ions react considerably more slowly under any pH conditions. For the triammine complexes, the rate of diazotization is only slightly faster than the rate of dinitrogen loss from the dinitrogen product under optimum conditions (pH 2–3), and in fact disproportionation of the Os(IV) species⁸ also interferes. In aqueous solutions at 0 °C buffered at pH 3 and saturated with NO ($[\text{NO}] = 2 \times 10^{-3}$ M), the pseudo-first-order rate constant for diazotization of *mer*- $[\text{Os}(\text{NH}_3)_3\text{I}_3]^+$ was $\sim 1 \times 10^{-3} \text{ s}^{-1}$ while that for loss of N_2 was $\sim 2 \times 10^{-4} \text{ s}^{-1}$. The slow rate of diazotization precluded isolation of the $[\text{Os}(\text{NH}_3)_2\text{I}_3(\text{N}_2)]$ species.

The diazotization is by no means general for all osmium(IV) amines. The isolation of hexaammineosmium(IV) and pentaamminehaloosmium(IV) proved impossible as 1 e oxidation of the corresponding Os(III) complexes leads to an extremely rapid disproportionation reaction as discussed elsewhere.⁸ No reaction was observed when solutions of

$[\text{Os}(\text{NH}_3)\text{Cl}_5]^-$ were treated with NO over a pH range from 1 to 13.

Discussion

The reductive nitrosation by NO of osmium(III) amines in acidic solution proceeds in a manner analogous to that with ruthenium(III) amines under the same conditions.²² The rapidity of this compared to an ordinary substitution is a consequence of the difference in mechanism. The proposal²² that NO attacks at the face of the octahedron forming an electron-pair bond with the πd^5 center, finally ejecting an ammine ligand to restore octahedral geometry, still seems reasonable.

The trans-directing properties of the coordinated halide in this NO reductive substitution have not been recognized previously. For the pentaamminehaloruthenium(III) ion, a mixture of pentaamminenitrosyl and tetramminehalonitrosyl products were obtained by others upon interaction with nitric oxide. This distribution of products has also been reported for the osmium analogue in concentrated acid with 24-h reaction times.²¹ In contrast, we find that when dilute solutions of $[\text{Os}(\text{NH}_3)_5\text{I}]^{2+}$ in 0.1 M HCl at 0 °C are exposed to NO, the only product obtained is *trans*- $[\text{Os}(\text{NH}_3)_4(\text{NO})]^{2+}$.²¹ We also find that *cis*- $[\text{Os}(\text{NH}_3)_4\text{X}_2]^+$ under similar conditions leads to replacement by NO of an ammonia rather than halide. This is rather surprising in view of the fact that in normal substitution reactions halides rather than amines are replaced, exclusively.¹⁴ The reaction in which halide ion is replaced has a higher activation energy than that involving ammine replacement and is observed, as in the work of others, at higher temperatures.

All of the observations on reductive diazotization by NO are consistent with the idea that exposure of at least one electron pair by loss of a proton from coordinated ammonia is a requirement. The measurements on the $\text{p}K_a$ values of osmium(IV) amines⁸ show that they are acidic enough so that significant concentrations of the amido forms are present even in strongly acidic solution. Even with the realization that one of the conditions necessary for the reductive diazotization was fulfilled, the occurrence of the reaction with a metal in the oxidation state 4+, being unprecedented, was at first astonishing, though it became less so when evidence for back-bonding in Os(III) complexes began to accumulate (see Part II).

The fact that the reductive diazotization by NO, which thus far has been observed only for Ru(III), Os(III), and Os(IV), is so limited in scope becomes understandable when the requirements for the process are examined together. These involve (a) the redox potential for the metal complex, (b) the ammine acidity of the oxidized species, and (c) the back-bonding capacity of the reduced form.

(a) If E° for the HNO_2/NO couple (1.00 V) is exceeded by the metal couple, oxidation of NO, rather than reductive diazotization, can ensue. This kind of failure is apparently encountered in the $[\text{IrCl}_5\text{NH}_3]^- + \text{NO}$ system. On the other hand, if the reduction of the metal complex to the lower oxidation state is too difficult, reductive diazotization will again not occur (e.g., $[\text{Os}(\text{NH}_2)\text{Cl}_5]^{2-} + \text{NO}$ does not produce a dinitrogen complex).

(b) Coordinated ammonia must be acidic enough so that a significant fraction of the oxidized complex is deprotonated. In specific terms, the $\text{p}K_a$ of the coordinated amines must be less than ca. 17 in aqueous media. Double-bond formation can enhance the acidity of transition-metal ammine complexes. If, as is the case with Ru(II), Os(III), and Os(IV), there is a vacancy in a t_{2g} orbital, and if there is significant overlap

(22) J. N. Armor, H. S. Scheidegger, and H. Taube, *J. Am. Chem. Soc.*, **90**, 5928 (1968).

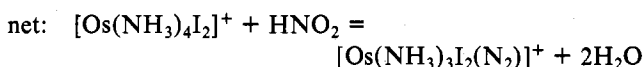
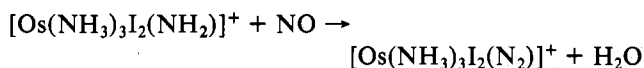
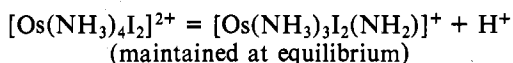
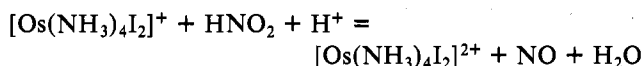
with the nitrogen p orbital, the electron-withdrawing power of the metal is increased.

(c) Inherent in the stability of the product dinitrogen complexes is the back-bonding provided by the central metal. It appears that the stability of the product dinitrogen complex may provide some of the driving force for the diazotization. The redox couple for the dinitrogen product correlates with the ease of reaction: the higher the couple, the more facile the reaction. Evidence for significant back-bonding in dinitrogen complexes of Os(III) will be adduced in Part II.

These criteria appear to restrict the diazotization to ruthenium and osmium among metals for which ammine chemistry has been extensively developed. Cobalt(III) amines are very weakly acidic, and the d^7 Co(II) electronic configuration is not conducive to the binding of dinitrogen. Rhodium amines in the III state are too resistant to reduction, and attaining the IV state requires a potential in excess of 1 V. Iridium(IV) amines are sufficiently acidic in the IV state, but the IV/III couples lie above 1.1 V. It seems probable that the reactions will also fail with chromium(III) amines. Chromium(II), the product of the reaction, would likely be in a high-spin state in which case the electron added to it by NO would be antibonding. Thus, the needed stabilization arising from back-bonding would not be forthcoming. Molybdenum(III) or molybdenum(IV) amines appear to have some promise (Mo(II) would almost certainly be low spin in species such as $[\text{Mo}(\text{NH}_3)_5\text{N}_2]^{2+}$), but the amines, particularly of Mo(IV), are not well characterized. Technetium(III) amines and technetium(II) π -acid amines may well undergo diazotization with nitric oxide. Observations²³ reported on *trans*- $[\text{Tc}(\text{NH}_3)_4(\text{H}_2\text{O})\text{NO}]^{2+}$ include characterization of the acidic oxidized analogue ($E_f = 0.80$ V), suggesting that the preparation of a dinitrogen nitrosyl species may be feasible.

It is possible that the failure to observe reductive diazotization of halo complexes when more than three halo ligands are coordinated in Os(IV) is the result of E_f for the IV/III couple being too low. A decrease of 150 mV in the IV/III and dinitrogen III/II couples is recorded between the dihalo and trihalo species. All of the known NO diazotizations occur with complexes which have redox potentials between 0.5 and about 1.0 V whether Os(III) or Os(IV) is involved. No diazotization is observed for deprotonated *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^{2+}$ with $E_f = 0.36$ V even though this species does not disproportionate rapidly (see Part II).

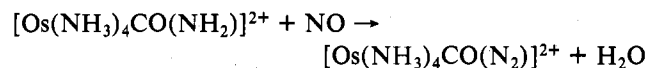
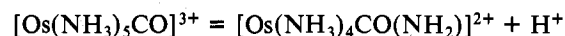
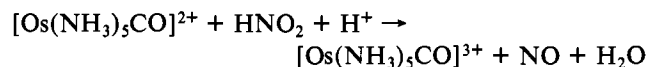
The stepwise nature of diazotization of Os(III) complexes by HNO_2 has been unambiguously demonstrated for some systems and is confirmed by the study of the reaction of NO with Os(IV) complexes prepared by an alternate route. The steps for the reaction of *trans*- $[\text{Os}(\text{NH}_3)_4\text{I}_2]^+$ with HNO_2 are



Owing to the low concentration of NO, under ordinary conditions the third reaction is rate determining. Alternative reactions for the Os(IV) species, which include disproportionation,⁸ can occur and account for reduced yields in some cases.

In the context of these considerations, the fact that $[\text{Os}(\text{NH}_3)_5\text{I}]^{2+} + \text{HNO}_2$ produces $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^{2+}$ quantitatively even under a vigorous inert-gas purge takes on special significance. The product of the oxidation of $[\text{Os}(\text{NH}_3)_5\text{I}]^{2+}$ is known to disproportionate rapidly, and it is unlikely that NO produced in a stepwise process could compete with this disproportionation reaction, particularly when the NO is being removed. Thus it appears that some type of concerted process, the nature of which is obscure, can occur instead of the stepwise one outlined above.

The stepwise mechanism proposed above for diazotization by nitrous acid applies equally well to the osmium(II) π -acid complexes as illustrated by



The 3+/2+ couple for this carbonyl complex is 0.92 V, and the pK_a of the 3+ ion is ca. 2 (see Part II); as expected, the reaction is essentially quantitative in 0.1 M HCl. The dinitrogen analogue, $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$, has a III/II couple of 0.58 V and a pK_a of 6.6 (Part II). In view of the high pK_a , this complex is not expected to undergo diazotization in 0.1 M HCl, and instead loss of N_2 from the osmium(III) dinitrogen complex is observed. In the Scheidegger procedure,¹⁵ acid is added gradually to the $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{2+} + \text{NO}_2^-$ mixture, and thus the system is for part of the reaction course at a pH high enough to deprotonate $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$.

The scope of the diazotization reaction with nitrous acid may be summarized as follows: (a) The reaction requires acid (a solution pH of 4 or less) to bring about the initial oxidation of the substrate. (b) The first step of the reaction involves oxidation of the metal complex which places an upper limit on its oxidation potential about equal to that of the HNO_2/NO couple (1.00 V). (c) The pK_a of the oxidized metal complex must be sufficiently low so that coordinated ammonia deprotonates to a significant extent in solutions of pH 4 or lower. (d) The reactions proceed more readily when the redox couple for the unreacted metal complex lies above 0.7 V. Because the metal center is reduced in the diazotization by NO, a relation is expected between the rate and the driving force for this reduction.

The nitrous acid diazotization reaction proceeds in good yield for $[\text{Os}(\text{NH}_3)_4\text{I}_2\text{N}_2]^{2+}$,⁷ $[\text{Os}(\text{NH}_3)_5\text{I}]^{2+}$, *cis*- $[\text{Os}(\text{NH}_3)_4\text{X}_2]^+$, *trans*- $[\text{Os}(\text{NH}_3)_4\text{X}_2]^+$, $[\text{Os}(\text{NH}_3)_5\text{CO}]^{2+}$, and $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{2+}$. All of these have the characteristics summarized above. The chloro- and bromopentaammine-osmium(III) ions do yield some dinitrogen product upon interaction with HNO_2 , though their high oxidation potentials (>1.05 V) apparently slow the reaction sufficiently so that competition by NO substitution is significant. The trihalo-triammineosmium(IV) species also undergo diazotization but only slowly. Iridium(III) amines do not undergo diazotization because the IV/III couples lie well above 1 V.

It was hoped that the scope of this reaction could be extended to complexes with redox couples up to +1.45 V by the use of nonaqueous solvents and NO^+ . Though various solvents such as methanol, acetonitrile, dimethyl sulfoxide, and triethyl phosphate were tried, the only reaction observed was oxidation of the metal complex. The diazotization did not occur with

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(26) C. M. Elson, J. Gulens, I. J. Itzkovitch, and J. A. Page, *Chem. Commun.*, 875 (1970).

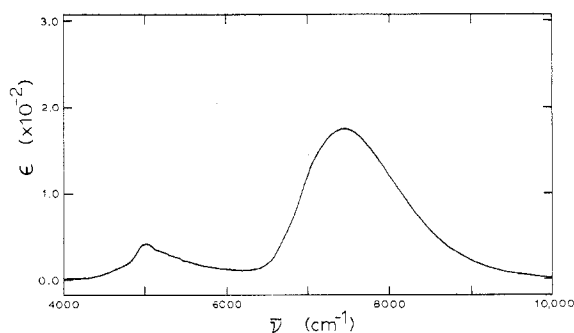


Figure 1. Near-IR spectrum of *cis*-[Os(NH₃)₄I(N₂)]²⁺.

or without the addition of a base (CH₃O⁻, F⁻) or an acid (HCl).

Part II. Characterization of Dinitrogen Complexes of Osmium(III) Amines

Results

Preparations. These have been described for some of the complexes in Part I. Others are prepared by analogous routes.

Electrochemistry. In Table I are listed the III/II couples for the monomeric osmium dinitrogen compounds known. Increasing replacement of ammine ligands by halides lowers the couple by approximately 150 mV per halide. These dinitrogen III/II couples lie approximately 500 mV toward more negative values than the ammine IV/III couples⁸ with the same number of halides and are 1.5 V more positive than the amines III/II couples.

Spectra. The charge-transfer absorptions observed for these dinitrogen complexes are compiled in Table I. Only a single band is found irrespective of the number or disposition of the halide ligands present. When comparisons are possible, this band lies to the high-energy side of that found for the comparable osmium(IV) complex by approximately 1500 cm^{-1} . Ratios of the charge-transfer energies of the corresponding chloride, bromide, and iodide compounds of these two classes are similar.

As is the case for other Os(III) complexes, those containing dinitrogen as a ligand show absorptions in the near-infrared (near-IR) region. A spectrum is shown in Figure 1. Observations for Os(III) and Os(IV) complexes are summarized in the preceding paper.⁸

The dinitrogen stretching frequencies for both the osmium(II) and osmium(III) forms of the known dinitrogen complexes of osmium amines are listed in Table I. Other values are included for comparison. The stretching frequency is observed to be very sensitive to the oxidation state of the metal but only moderately sensitive to the halide content of the coordination sphere. The osmium(II) complexes exhibit dinitrogen stretching frequencies near 2025 cm^{-1} . The osmium(III) analogues have absorptions near 2200 cm^{-1} , a significant reduction from the free-ligand value of 2331 cm^{-1} . The IR spectra are recorded in Table II for a variety of these dinitrogen compounds in both oxidation states II and III. Two representative spectra are presented in Figures 2 and 3.

Chemistry. While the osmium(II) dinitrogen species are extremely stable with respect to loss of dinitrogen, the osmium(III) analogues undergo loss of N₂ readily. The rates of dinitrogen loss for various species are summarized in Table III. The halide content of the coordination sphere does affect the rate at which dinitrogen is lost. A single iodide *cis* to the dinitrogen molecule retards the rate of loss by a factor of 10. However, further replacement of amines by iodide does not appear to augment the kinetic stability of the complex.

The facile loss of dinitrogen from osmium(III) dinitrogen complexes leading to aquo species was exploited synthetically. Pentaammineaquoosmium(III) leads to good yields of [Os-

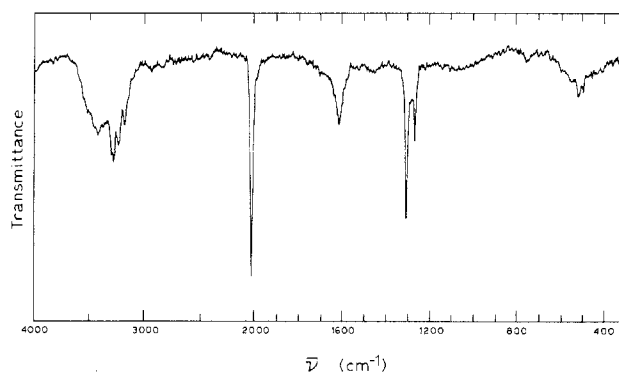


Figure 2. Infrared spectrum of *trans*-[Os(NH₃)₃I₂(N₂)].

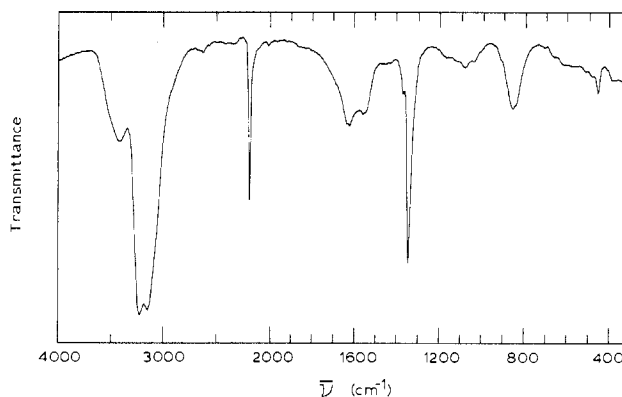


Figure 3. Infrared spectrum of *cis*-[Os(NH₃)₄I(N₂)]Br₂.

(NH₃)₅X]²⁺ upon warming it in the appropriate hydrohalic acid.⁸ This aquo ion also affords NO, SO₂,²⁷ and SCN⁻ species.

The dinitrogen complex derived from *trans*-tetraammine-dihaloosmium(III) provided ready access to the trihalo-triammine species with meridional geometry. The neutral compound [Os(NH₃)₃I₃] was prepared in the following manner. *trans*-Tetraamminediiodoosmium(III) chloride (270 mg) was dissolved in 80 mL of 0.05 M HCl. The solution was deaerated with argon and cooled to 0 °C. Potassium nitrite (150 mg) was added, and NO was bubbled through the solution for 5 min. After this time, the NO was removed by rapid purging with argon for 1 min. The solution was diluted with 20 mL of ice-cold water and charged onto 15 mL of AG-50W-X2 cation-exchange resin in a jacketed column maintained at 0 °C. Ten milliliters of 0.1 M HI was passed over the column and discarded. The [Os(NH₃)₃I₂(N₂)]⁺ ion was rapidly eluted under pressure of 5 lb/in.² with 1.5 M HI. The blue solution was deaerated with argon and left at 0 °C for 12 h. It was concentrated by rotary evaporation, and the reddish product (yield 75%) was collected, washed with ethanol and ether, and air-dried. The compound was characterized by its elemental analysis and by its UV-vis spectrum (414 nm, $\epsilon = 3.22 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). Anal. Calcd: H, 1.46; N, 6.76. Found: H, 1.43; N, 6.74. The analogous trichloro [Os(NH₃)₃Cl₃] (Anal. Calcd: N, 12.09; H, 2.61. Found: N, 12.07; H, 2.57) and tribromo compound [Os(NH₃)₃Br₃] (Anal. Calcd: N, 8.74; H, 1.87. Found: N, 8.66; H, 1.88) were prepared similarly. Their properties are discussed in the preceding paper.⁸

The aquo ions arising from *trans*-[Os(NH₃)₃X₂(N₂)]⁺ also led to the dihalo complexes containing NO, SO₂, SO₃H⁻, SO₃²⁻, and SCN⁻ ligands.³⁰ These aquo ions also provide

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(28) J. N. Armor and H. Taube, *J. Am. Chem. Soc.*, **92**, 6170 (1970).

(29) Borje Folkesson, *Acta Chem. Scand.*, **26**, 4157 (1970).

Table IV. Ammine pK_a Values of Dinitrogen Complexes^a

species	pK_a	method
$[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$	6.6	CV
$\text{cis-}[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^{2+}$	~8	UV-vis
$\text{trans-}[\text{Os}(\text{NH}_3)_3\text{I}_2(\text{N}_2)]^+$	~10.5	UV-vis
$[\text{Os}(\text{NH}_3)_5\text{CO}]^{3+}$	~2	CV

^a Key: CV, E_f vs. pH; UV-vis, spectrophotometric titration vs. pH.

access to mixed halotriammine complexes.

Diazotization of the *cis* isomers of the tetraamminedihalo ions did not as readily lead to isolable trihalo complexes as did the *trans*-dihalo species. The product of diazotization of a *cis*-dihalo ion can lead to either the meridional or facial isomer. Upon loss of dinitrogen and heating in hydrohalic acid, a number of species were observed, but no attempt was made to characterize them.

Diazotization of the trihalotriammines gave spectral changes analogous to those observed for the dihalotetraammines, and we infer that diamminetrihalo(dinitrogen)osmium(III) ions were formed. It was not feasible to use the aquo ions arising from these for further synthesis since they could not be obtained in pure form. The slow rate of diazotization with respect to the rate of N_2 loss leads unavoidably to nitrosyl-containing impurities. Thus it did not prove possible to produce tetrahalo species in significant yield.

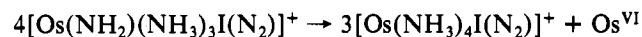
As might be expected from the π -acceptor characteristics of the dinitrogen ligand, the acidities of the coordinated amines were found to be quite high. In Table IV are summarized the pK_a values for several examples. They lie approximately 7 units above the values for the osmium(IV) analogues⁸ with dinitrogen replaced by NH_3 . The effect of N_2 relative to NH_3 on the acidity of the coordinated amines is demonstrated by a comparison of the pK_a values for $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$ (6.6) and $[\text{Os}(\text{NH}_3)_6]^{3+}$ (>14),²⁰ a difference of at least 8 units. Increasing the halide content of the coordination sphere of the osmium(III) dinitrogen complexes raises the pK_a of the complex as is also true for the osmium(IV) amines. Much of the chemistry of these dinitrogen complexes may be ascribed to the acidic nature of the coordinated amines.

Solutions of deprotonated osmium(III) dinitrogen compounds were observed to be unstable. When *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]\text{Br}_2$ is added to deaerated 0.1 M NaOH, yellow solutions are formed from the purple solid. Complete deprotonation is expected in strong base because the pK_a for the complex is ca. 8. No absorption maximum could be detected for *cis*- $[\text{Os}(\text{NH}_2)(\text{NH}_3)_3\text{I}(\text{N}_2)]^+$. The concentration of this amido species was shown to decrease with time. This was done by monitoring the concentration of *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^{2+}$ ($\lambda_{\text{max}} = 17300 \text{ cm}^{-1}$) in acidified aliquots extracted periodically from the 0.1 M NaOH solution.

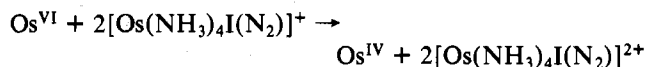
Logarithmic plots of absorbance of $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^{2+}$ contained in the acidified aliquots indicated a first-order process which continued until half the initial concentration of the dinitrogen complex remained. At this point the reaction was complete. At 23.5 °C, the first-order rate constant for the process was $(9 \pm 4) \times 10^{-5} \text{ s}^{-1}$ in millimolar solution.

It was surmised that although the reactant Os(III) species is consumed by disproportionation in base, it is partially restored when the product solution is acidified. An experiment was done in which 1, 2, and 3 mol of *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]\text{Cl}$ were added per mole of $[\text{Os}(\text{NH}_3)_4\text{O}_2]^{2+}$ in both basic and acidic solution. No reaction was observed in base, but upon acidification, 2 mol of *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^{2+}$ was generated per mole of osmium(VI) ion.

Thus, it seems likely that the disproportionation reaction for the osmium(III) ion in basic solution is



The osmium(VI) species has not yet been identified, but it is most probably an osmyl ion. In acidic solution, Os(VI) is reduced to Os(IV), regenerating the violet osmium(III) dinitrogen complex from the osmium(II) analogue. When the reaction is complete in basic solution, half the initial concentration of $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^{2+}$ will be regenerated upon acidification:



In all cases, disproportionation of the dinitrogen complexes of Os(III) in base was observed to be rapid compared to loss of N_2 from Os(III).

Discussion

Osmium(II) has long been recognized for its pronounced back-bonding properties. It is now apparent that osmium(III) as well is capable of significant back-donation, though not to as great a degree as the ion of lower oxidation state. In this respect osmium(III) is to be contrasted with ruthenium(III) which exhibits no significant propensity for back-bonding. The fact that back-bonding is minor for Ru(III) is nicely illustrated by infrared data on some nitrile complexes.³¹ The pentaammineruthenium(II) complexes with a number of nitrile ligands have CN stretching frequencies ca. 40 cm^{-1} lower than those in the free ligands, while the analogous Ru(III) species have stretching frequencies ca. 40 cm^{-1} higher than in the free ligands. The coupling of the M-N and N-C stretching modes and hybridization changes induced by coordination are expected to increase $\nu(\text{CN})$ while transfer of electron density to the π^* ligand orbital from the metal is expected to decrease it. By the same token, the decrease in $\nu(\text{NN})$ when dinitrogen is coordinated to Os(III) is evidence for back-donation by Os(III) to the ligand (see Table I). As in the case of the nitrile ligand, an increase in $\nu(\text{NN})$ is expected if no back-bonding occurs; the increase can be ascribed to engagement on coordination of the slightly antibonding electron lone pair on the nitrogen.

The effect on $\nu(\text{NN})$ of replacing ammonia by halide was anticipated because donation by the halide of π -electron density is expected to enhance donation to dinitrogen by the metal. The more polarizable iodide ligand lowers the N_2 stretching frequency to a greater extent than either bromide or chloride. As is expected, these effects are more noticeable in the III state since the inherent back-bonding capability of osmium(III) is much less than that of the Os(II) state, and Os(III) should, therefore, be more sensitive to ligand electron density donation.

The kinetic stability of the Os(III)- N_2 complexes compared to those of Ru(III) is in line with greater back-bonding to N_2 for the former. The enhancement in kinetic stability observed on replacing an ammonia by a halide is not surprising, but the fact that additional halide ligands do not further diminish the rate of loss of N_2 is surprising. The reason for this is not understood, but since effects on the energy of the activated complex relative to the ground state are involved, the behavior need not be simple.

Perhaps the most striking observations bearing on the interaction of N_2 with Os(III) is the decrease in pK_a for the coordinated ammine ligands when one NH_3 molecule is replaced by N_2 . The comparison of $[\text{Os}(\text{NH}_3)_6]^{3+}$ ($pK_a > 14$)

(30) John Buhr, research in progress.

(31) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970), and references contained therein.

and $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$ shows a decrease of at least 8 orders of magnitude. The electron-withdrawing power of dinitrogen on Os(III) is very great and, as reflected in the values of pK_a , approaches that of increasing the oxidation state by 1 unit.⁸

Though coordination of N_2 stabilizes Os(III), it stabilizes Os(II) much more. This follows from the enormous increase in E_f on changing from $[\text{Os}(\text{NH}_3)_6]^{3+/2+}$ to $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+/2+}$, which results in an increase in E_f of 1.4 V. The effect of adding a second dinitrogen (forming *cis*- $[\text{Os}(\text{NH}_3)_4(\text{N}_2)_2]^{2+}$) is not additive, but it does increase E_f by 1 V or so.

It is clear from the energies of the charge-transfer absorptions involving the halides that the relevant acceptor orbitals on the osmium center have been stabilized by interaction with dinitrogen to positions close to those in the osmium(IV) amines. Replacement of an ammine group with dinitrogen causes a bathochromic shift in the halide-to-metal charge-transfer absorption of ca. $6.5 \times 10^3 \text{ cm}^{-1}$. The ligated dinitrogen has effectively withdrawn charge density totaling almost one electron from the metal center.

Although for *cis*- $[\text{Os}(\text{NH}_3)_4\text{X}_2]^{2+}$ two bands are observed, there is only a single absorption for the diazotized product. If the dinitrogen complex has meridional geometry, an explanation for the existence of only one band comes to mind: the π orbitals of the halide trans to the dinitrogen would not overlap with the unfilled metal t_{2g} orbital because the electron vacancy is expected to be in the d_{xy} orbital (Os-N₂ as the z axis). Perhaps this may be construed as evidence for the assignment of the meridional configuration of the complex.

The data we have collected make it possible to compare the properties of dinitrogen as a π acid with those of carbon monoxide. The stability of the vast number of carbonyl complexes known is attributed to the effective π -acid properties of CO. The π -acceptor strength of CO is exceeded only by that of NO^+ , at least among ligands in common use. Dinitrogen, although not as effective as carbon monoxide, is seen to approach CO in its π -acid character.

A comparison of the oxidation couples of the pentaammineosmium(II) moiety with different ligands demonstrates the similar abilities of N_2 and CO to stabilize the osmium(II) center. The hexaammineosmium $3+/2+$ couple lies at -0.78 V (SHE).³² Introducing N_2 raises E_f to $+0.58 \text{ V}$ ($\Delta E_f = 1.36 \text{ V}$) while substituting CO for NH_3 raises it to $+0.92 \text{ V}$ ($\Delta E_f = 1.70 \text{ V}$). Carbon monoxide clearly stabilizes osmium(II) relative to osmium(III) to a greater extent than does N_2 , but the change in E_f for N_2 with respect to NH_3 is nearly as large as the change observed for CO.

A further indication of the similarity of the π -acceptor properties of CO and N_2 is the effect of each on the ammine acidity of the osmium(III) center. Studies of $[\text{Os}(\text{NH}_3)_6]^{3+}$

suggest that the ammine pK_a lies near 16^{20} and is certainly greater than 14. As already noted, the pK_a of $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$ has been determined to be ~ 6.6 , a decrease of at least 8 units relative to $[\text{Os}(\text{NH}_3)_6]^{3+}$. The pK_a for $[\text{Os}(\text{NH}_3)_5\text{CO}]^{3+}$ is estimated from electrochemical studies to be between 2 and 3, an acidity increase of coordinated ammine of at least 12 orders of magnitude compared to that of the hexaammine.

None of the properties of the pentaammine(dinitrogen)osmium(III) ion provides a ready means for analysis, and thus *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^{2+}$ was selected to study the decomposition of π -acid complexes of osmium(III) amines in alkaline solution. The characteristics of the iodide ligand provide a convenient probe for the system; although no absorption maximum appears in the UV-vis spectrum in basic solution for osmium(II) dinitrogen or amidoosmium(III) dinitrogen complexes, *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^{2+}$ in acidic solution has a strong absorption at $17.30 \times 10^3 \text{ cm}^{-1}$ due to LM charge transfer.

The driving force for the disproportionation of ammine-(dinitrogen)osmium(III) complexes in alkaline solution is the greater acidity of NH_3 on Os(VI) as compared to Os(III), assisted by the fact that N_2 is inherently a better ligand on Os(II) than on Os(III). The first-order behavior can be attributed to loss of N_2 as the rate-determining step. Once a molecule of N_2 is lost, the resulting Os(III) complex is oxidized in a rapid step to Os(VI) by remaining (dinitrogen)osmium(III). The reaction taking place on acidifying is described in the Results. It is a point of some interest that the facile reduction of the Os(VI) species to an Os(IV) ammine was demonstrated.

Acknowledgment. Support of this research by the National Institutes of Health under Grant No. GM22045-02 is gratefully acknowledged.

Registry No. *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]^+$, 73557-93-4; *cis*- $[\text{Os}(\text{NH}_3)_4(\text{N}_2)]^{2+}$, 73557-94-5; *trans*- $[\text{Os}(\text{NH}_3)_3\text{I}_2(\text{N}_2)]$, 73610-21-6; *trans*- $[\text{Os}(\text{NH}_3)_3\text{I}_2(\text{N}_2)]^+$, 73557-95-6; *trans*- $[\text{Os}(\text{NH}_3)_3\text{Br}_2(\text{N}_2)]$, 73557-96-7; *trans*- $[\text{Os}(\text{NH}_3)_3\text{Br}_2(\text{N}_2)]^+$, 73557-97-8; *trans*- $[\text{Os}(\text{NH}_3)_3\text{Cl}_2(\text{N}_2)]$, 73609-69-5; *trans*- $[\text{Os}(\text{NH}_3)_3\text{Cl}_2(\text{N}_2)]^+$, 73610-22-7; *cis*- $[\text{Os}(\text{NH}_3)_3\text{I}_2(\text{N}_2)]$, 73557-98-9; *cis*- $[\text{Os}(\text{NH}_3)_3\text{I}_2(\text{N}_2)]^+$, 73609-70-8; *cis*- $[\text{Os}(\text{NH}_3)_3\text{Br}_2(\text{N}_2)]$, 73609-71-9; *cis*- $[\text{Os}(\text{NH}_3)_3\text{Br}_2(\text{N}_2)]^+$, 73609-72-0; *cis*- $[\text{Os}(\text{NH}_3)_3\text{Cl}_2(\text{N}_2)]$, 73609-73-1; *cis*- $[\text{Os}(\text{NH}_3)_3\text{Cl}_2(\text{N}_2)]^+$, 73557-99-0; *mer*- $[\text{Os}(\text{NH}_3)_2\text{I}_3(\text{N}_2)]$, 73558-00-6; $[\text{Os}(\text{NH}_3)_5\text{N}_2]^{3+}$, 22840-90-0; $[\text{Os}(\text{NH}_3)_5\text{CO}]^{2+}$, 70528-08-4; $[\text{Os}(\text{NH}_3)_5\text{CO}]^{3+}$, 73558-01-7; *cis*- $[\text{Os}(\text{NH}_3)_4(\text{N}_2)_2]^{2+}$, 41099-85-8; *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]\text{Cl}$, 73558-02-8; *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}(\text{N}_2)]\text{Br}_2$, 73558-03-9; *trans*- $[\text{Os}(\text{NH}_3)_3\text{I}_2(\text{N}_2)]\text{Br}$, 73558-04-0; *trans*- $[\text{Os}(\text{NH}_3)_3\text{Br}_2(\text{N}_2)]\text{Br}$, 73587-36-7; *trans*- $[\text{Os}(\text{NH}_3)_3\text{Cl}_2(\text{N}_2)]\text{Br}$, 73609-74-2; $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]\text{Br}_3$, 73558-05-1; *cis*- $[\text{Os}(\text{NH}_2)(\text{NH}_3)_3\text{I}(\text{N}_2)]^+$, 73558-06-2; $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2$, 20611-50-1; *cis*- $[\text{Os}(\text{NH}_3)_4(\text{CO})(\text{N}_2)]\text{Cl}_2$, 39176-88-0; $[\text{Os}(\text{NH}_3)_3\text{CO}]\text{Cl}_2$, 39176-85-7; $[\text{Os}(\text{NH}_3)_5\text{I}]\text{Cl}_2$, 67202-28-2; *trans*- $[\text{Os}(\text{NH}_3)_4\text{I}_2]\text{Cl}$, 73531-71-2; *cis*- $[\text{Os}(\text{NH}_3)_4\text{I}_2]\text{Cl}$, 73544-64-6; *cis*- $[\text{Os}(\text{NH}_3)_3\text{I}_2(\text{N}_2)]\text{Br}$, 73609-75-3; *cis*- $[\text{Os}(\text{NH}_3)_3\text{I}_2(\text{N}_2)]\text{Cl}$, 73609-76-4; $[\text{Os}(\text{NH}_3)_3\text{I}_3]$, 73609-77-5; $[\text{Os}(\text{NH}_3)_3\text{Cl}_3]$, 73609-78-6; $[\text{Os}(\text{NH}_3)_3\text{Br}_3]$, 73609-79-7; HNO_2 , 7782-77-6.

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