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Photochemistry of Osmium(II) Ammine Complexes. The Dinitrogen Species $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ and *cis*- $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$

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Reported are quantum yields for photolysis of the osmium(II) dinitrogen complexes $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ and *cis*- $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ in aqueous chloride solution. The *cis*-dinitrogen ion undergoes photoaquation only over the wavelength range 365–214 nm to give $\text{Os}(\text{NH}_3)_4(\text{H}_2\text{O})\text{N}_2^{2+}$. Direct excitation of the metal-to-ligand charge-transfer (MLCT) band (λ_{max} 223 nm) gave smaller quantum yields than longer wavelength excitation. This indicates deactivation from the MLCT state(s) directly to the ground state competitive with internal conversion to lower energy state(s) which are precursors to ligand substitution pathways. The $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ ion gives only Os(III) species as final photolysis products but analysis of the product distributions indicates that significant photoaquation to give $\text{Os}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ is occurring over the excitation wavelength range 365–229 nm. Thermal oxidation of Os(II) species by solvent accounts for the Os(III) final products. Photooxidation directly to Os(III) may be competitive with photoaquation over this wavelength range, but at 214 nm photooxidation is the overwhelmingly dominant photoreaction pathway. In analogy to ruthenium(II) photochemistry, it is argued that a charge-transfer to solvent state is a likely precursor to primary photooxidation while ligand field states are the likely precursors to primary photoaquation.

Introduction

The photochemistry of hexacoordinate d^6 transition-metal complexes has been an active area of mechanistic investigation.³ Among the group 8 elements, most of oxidation states having the d^6 configuration have received considerable attention; however, among the exceptions are the complexes of osmium(II). Quantitative photochemical studies of Os(II) are very few, the only examples being a study of the dihalogeno species $\text{Os}(\text{py})_4\text{X}_2$ (py = pyridine, X = Cl⁻, Br⁻ or I⁻) in nonaqueous solvent⁴ and the demonstration that the bipyridine complex $\text{Os}(\text{bpy})_3^{2+}$ may serve as a photosensitizer.⁵ Somewhat more attention has been paid the luminescence properties of Os(II) when coordinated to such π -acceptor ligands as aromatic heterocycles or phosphines.⁶ Reported here is a study of the products and quantum yields of the dinitrogen complexes $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ and *cis*- $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$. This study is a continuation of our interest in the quantitative photochemistry of other d^6 Werner-type complexes with the goal of establishing the patterns of generality that extend from one metal ion system to another.

In contrast to the ruthenium(II) homologues,⁷ the chemistry of the Os(II) amines is quite limited. The only stable pentaammine complexes known are those of N_2 , CO, and NO^+ , and as yet, only a few tetraammines have been reported.^{8,9} In each case the stable complexes include a relatively good π -acceptor ligand (e.g., N_2). Without such ligands, the Os(II) amines are powerful reducing agents capable of reaction with water, and the only information regarding their properties has come from the electrochemical studies.¹⁰ In this context the photochemical studies reported here are of interest as the photolabilization of dinitrogen from the Os(II) coordinative sphere may serve as a mild and selective route to the production of new or only transiently stable Os(II) species.

Experimental Section

Dinitrogenpentaammineosmium(II) chloride [$\text{Os}(\text{NH}_3)_5\text{N}_2$]Cl₂ was synthesized according to the method of Allen and Stevens.¹¹ In aqueous solution, the electronic spectrum of the product displayed a shoulder at 208 nm with an extinction coefficient of $2.41 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in agreement with literature values.^{10a,11} *cis*-Bis(dinitrogen)-tetraammineosmium(II) chloride, [*cis*- $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2$]Cl₂, was prepared by the procedure of Magnuson.¹² In aqueous solution, the UV spectrum of this material displays an absorption maximum at 223 nm with an extinction coefficient of $1.86 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (lit. 221 nm, $\epsilon 1.85 \times 10^4$).¹² Chloropentaammineosmium(III) chloride, [$\text{Os}(\text{NH}_3)_5\text{Cl}$]Cl₂, was synthesized by oxidation of [$\text{Os}(\text{NH}_3)_5\text{N}_2$]Cl₂. A 50-mg sample of [$\text{Os}(\text{NH}_3)_5\text{N}_2$]Cl₂ (1.3×10^{-4} mol) was dissolved in 5 mL of 2 M aqueous HCl and an equivalent amount of cerium(IV)

Table I. Electronic Spectra of Osmium Reactions and Some Potential Products^a

Complex	Spectral feature, λ_{max} ^b (ϵ) ^c
$\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$	$\sim 355^d$ (172), $\sim 320^d$ (335), $\sim 295^d$ (490), $\sim 257^d$ (1.36×10^3), $\sim 208^d$ (2.20×10^4)
<i>cis</i> - $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$	$\sim 290^d$ (2.46×10^3), 223 (1.86×10^4)
$\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$	267 (2.02×10^3)
$\text{Os}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$	$\sim 260^d$ (345), 220 (1.10×10^4)

^a In 25 °C, 0.001 M HCl/0.199 M NaCl aqueous solution. ^b In nm. ^c In $\text{M}^{-1} \text{ cm}^{-1}$. ^d Shoulder.

was added as cerium ammonium sulfate dihydrate (83 mg). After refluxing the solution overnight, yellow powder precipitated upon the adding of 3 mL of concentrated HCl and cooling the solution in ice. The crude material was collected by filtration. Further purification was accomplished by elution from acid form BioRad AG50W-X2 (200–400 mesh) ion-exchange resin. The aliquots containing $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$ eluted with 1.5 M aqueous HCl. These were concentrated by rotary evaporation to a 5 mL volume from which the product precipitated upon addition of concentrated HCl. The light yellow powder was collected by filtration, washed with ethanol and then ether, and dried overnight under vacuum. Yield 25 mg (49%). The electronic spectrum in aqueous solution exhibited a peak at 267 nm ($\epsilon 2.02 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) in agreement with literature values.^{13,14} Aquopentaammineosmium(III) ion, $\text{Os}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, was prepared in situ by the oxidation of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$. A weighed portion (5 mg) of [$\text{Os}(\text{NH}_3)_5\text{N}_2$]Cl₂ was dissolved in 10 mL of aqueous sulfuric acid and 3 equiv of silver sulfate (obtained by dissolution of silver oxide in dilute aqueous sulfuric acid) was added. The Ag/AgCl precipitate was filtered off and rinsed with dilute sulfuric acid. The filtrant and wash solutions were combined and then diluted to a desired volume (25 mL) in a volumetric flask. The electronic spectrum of this solution exhibited a peak at 220 nm ($\epsilon 1100 \text{ M}^{-1} \text{ cm}^{-1}$) in agreement with the literature.^{10a}

Photolyses were carried out in argon-deaerated aqueous solution (0.001 M HCl/0.199 N NaCl) at 25 °C. The photolysis sources and techniques for irradiation at 214, 229, 254, 313, 334, and 366 nm are described elsewhere.^{15,16} Spectral changes were monitored periodically on a Cary 118C recording spectrophotometer and quantum yields were calculated from these as described in the Results section. Analogous dark reactions were run but showed no evidence of measurable thermal reaction under the photolysis conditions.

Results

$\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$. Photolysis of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ in deaerated aqueous chloride solution (0.001 M HCl/0.199 M NaCl) in the wavelength region 229–366 nm consistently leads to spectral changes such as illustrated in Figure 1. The photolysis is accompanied by decreased absorption of the intense metal-to-ligand charge-transfer (MLCT) band ($\lambda_{\text{max}} \sim 208$ nm, Table I¹¹) characteristic of the $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ ion and the

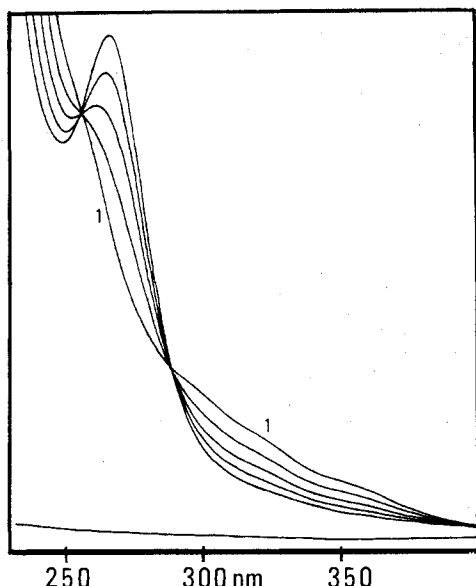
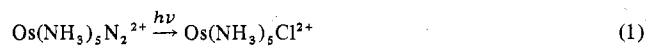


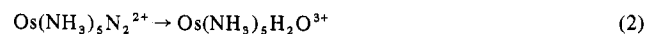
Figure 1. Spectral changes observed for the 313-nm photolysis of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ in deaerated aqueous solution (0.001 M HCl/0.199 M NaCl). The starting material spectrum is indicated by 1.

development of a new band at ~ 267 nm. This corresponds to the λ_{max} of the Os(III) species $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$ (Table I), and the isosbestic points (287 and 255 nm) correspond to the wavelengths where $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ and $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$ have identical extinction coefficients. These data and the observation that long term 313-nm photolysis gives an absorbance at 267 nm equal to 98% conversion to $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$ constitute strong evidence for the transformation



However, for some runs, spectra obtained after very short periods of photolysis showed only a general absorbance decrease over the entire UV region although subsequent points indicated the formation of $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$. Since this induction period for $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$ formation was seen only intermittently and the reproducibility was poor, it appears to be the result of trace impurity inhibition of steps, subsequent to the primary photochemical reaction, which lead to $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$ formation (see Discussion). Nonetheless, calculations carried out using the incremental method¹⁷ to analyze spectral data and assuming eq 1 for the disposition of the osmium species gave very reproducible quantum yield values for the photolyses in the wavelength range 229–366 nm (Table II). Photolysis (313 nm) of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ in N_2 -deaerated solution gave the same products and quantum yields as argon-deaerated solutions (Table II).

Photolyses of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ in the identical 0.001 M HCl/0.199 M NaCl aqueous solution which has not been deaerated lead to very different spectral consequences. Instead of absorbance increases at ~ 270 nm, decreases throughout the spectral region were observed. The product spectra are similar to that of $\text{Os}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, a logical product under these circumstances (see Discussion). Thus the quantum yields listed in Table II for this experiment were calculated from spectral data based on this assumption (eq 2). Since any



Os(II) complex containing dinitrogen (e.g., $\text{Os}(\text{NH}_3)_4(\text{H}_2\text{O})\text{N}_2^{2+}$) would be expected to have MLCT absorption bands similar to those of the starting material, since chloroammineosmium(III) products apparently are not formed in significant yields, and since aquoammineosmium(III) complexes would have spectral properties similar to those of

Table II. Quantum Yields^a for Photolysis of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$

λ_{irr} , nm	Φ , ^b mol einstein ⁻¹	λ_{irr} , nm	Φ , ^b mol einstein ⁻¹
366	0.19 ± 0.01^c (6)	254	0.18 ± 0.01^c (4)
334	0.20 ± 0.03^c (5)	229	0.15 ± 0.01^c (5)
313	0.21 ± 0.01^c (8)	214	0.16 ± 0.02^e (4)
	$0.20 \pm 0.01^{c,d}$ (3)		$0.17 \pm 0.01^{e,h}$ (3)
	$0.19 \pm 0.01^{e,f}$ (2)		
	$0.21 \pm 0.04^{e,g}$ (2)		
	$0.20 \pm 0.01^{d,e,g}$ (3)		

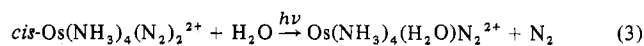
^a Measured in 0.001 M HCl/0.199 M NaCl deaerated aqueous solution at 25.0 °C, except where noted. ^b Mean value and average deviation reported, number of independent determinations in parentheses. ^c Calculation based on assumption that $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$ is the only product. ^d Deaerated with N_2 . ^e Calculations based on assumption that $\text{Os}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ is the sole product. ^f Aerated solution. ^g Measured in 0.001 M HCl. ^h Measured in 0.0001 M HCl/0.200 M NaCl.

$\text{Os}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, the quantum yield so calculated represents the depletion of osmium(II) dinitrogen complexes from the photolysis solution. Notably, the quantum yield calculated for 313-nm photolysis in aerated solution and based on eq 2 is very close to that for 313-nm photolysis in deaerated solution and based on eq 1 (Table II).

When 313-nm photolysis of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ is carried out in deaerated solutions which have a very low chloride concentration (0.001 M HCl), the spectral changes are consistent with the transformation indicated in eq 2. Quantum yields of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ disappearance calculated with the assumption that $\text{Os}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ is the sole product are identical with those seen in the presence of chloride and in aerated solution. Again no significant differences between quantum yields measured in argon-deaerated solution and in dinitrogen-deaerated solution was seen (Table II).

Photolysis at 214 nm in deaerated solution leads to spectral changes like those seen for the photolysis in aerated solution above. Hence the quantum yields listed are based on eq 2 as the disposition of the osmium species. No quantum yield difference was noted between reactions in pH 3 and pH 4 solutions (Table II). The values listed in Table II vary little with λ_{irr} , although a small decrease barely outside the experimental uncertainties is apparent at the shorter wavelengths.

cis- $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$. Photolysis of *cis*- $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ in deaerated aqueous solution (0.001 M HCl/0.199 M NaCl) leads to spectral changes as illustrated in Figure 2. The same pattern including the isosbestic point at 216 nm was observed for all irradiation wavelengths (λ_{irr}) between 214 and 366 nm up to about a 20% decrease in the intensity of the starting material MLCT band (223 nm). However, prolonged irradiation leads to a breakdown of the isosbestic point, a decrease of the absorption below 211 nm, and a corresponding buildup of an absorption band at ~ 270 nm. The latter observation suggests formation of chloroammineosmium(III) species as secondary photolysis products since $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$ (Table I) and *cis*- and *trans*- $\text{Os}(\text{NH}_3)_4\text{Cl}_2^+$ display ligand to metal absorption bands in this spectral region.¹⁴ Similarly the initial absorbance decreases at 223 nm and corresponding increases at wavelengths shorter than 216 nm (Figure 2) strongly suggest photoaquation of N_2 (eq 3) as the primary photoreaction, since



$\text{Os}(\text{NH}_3)_4(\text{H}_2\text{O})\text{N}_2^{2+}$ should have spectral properties similar to those of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$.

In order to characterize better the reaction products, a 7.5-mg sample of *cis*- $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ in 10^{-3} M HCl was irradiated at 313 nm until >75% of the starting material had been consumed. This solution was then dried to a solid by rotary evaporation. An IR spectrum of this material displayed a single strong absorption at 2020 cm^{-1} plus two weak bands

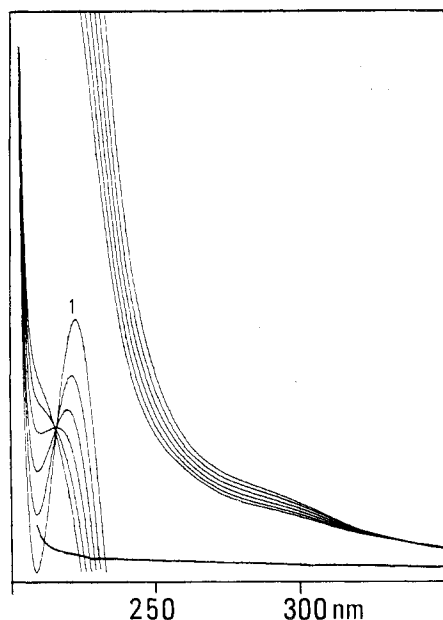


Figure 2. Spectral changes observed for the 254-nm photolysis of *cis*-Os(NH₃)₄(N₂)₂²⁺ in deaerated aqueous solution (0.001 M HCl/0.199 M NaCl). The starting material spectrum is indicated by I.

from residual [*cis*-Os(NH₃)₄(N₂)₂]Cl₂ in the dinitrogen stretching region. The ν_{NN} bands for [*cis*-Os(NH₃)₄(N₂)₂]Cl₂ occur at 2105 (s) and 2170 cm⁻¹ (s) while that of [Os(NH₃)₅N₂]Cl₂ occurs at 2025 cm⁻¹ (s). Cation exchange of the product from Dowex 50W-X2 (200–400 mesh) using hydrochloric acid as the eluent resolved four reaction components but gave incomplete separation. The spectral properties were the following: I, $\lambda_{\text{max}} \sim 270$ nm (eluted with 1.00 M HCl); II, $\lambda_{\text{max}} 209$ nm (eluted with 1.25 M HCl); III, $\lambda_{\text{max}} \sim 270$ nm (eluted with 1.25 M HCl); IV, $\lambda_{\text{max}} \sim 222$ nm (eluted with 1.5 M HCl). Based on the spectral properties, I and III are probably chloroammineosmium(III) species, while II and IV are *cis*- and/or *trans*-Os(NH₃)₄(H₂O)N₂²⁺ and the starting material, respectively.

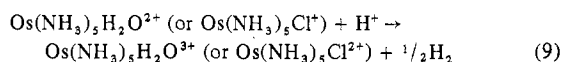
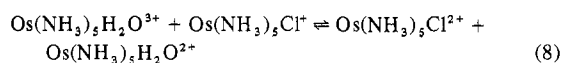
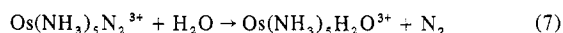
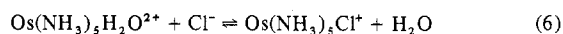
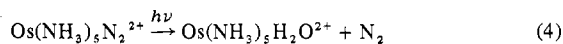
Attempts to isolate a pure sample of Os(NH₃)₄(H₂O)N₂²⁺ were unsuccessful; thus we were unable to determine accurate extinction coefficients for this product, and quantum yields could be only approximated from spectral data. The approximation was based on the assumption that the spectra of Os(NH₃)₅N₂²⁺ and Os(NH₃)₄(H₂O)N₂²⁺ are quantitatively very similar. Thus the product extinction coefficients in the regions of the starting material MLCT band were assumed to equal those of Os(NH₃)₅N₂²⁺, and concentration changes were calculated from the assumed $\Delta\epsilon$ values. The approximation appears relatively good since quantum yields calculated at several different wavelengths in the MLCT regions are in agreement, but some systematic error is inevitable.

Photolysis of Os(NH₃)₄(N₂)₂²⁺ in air-equilibrated solutions gave the same initial spectral changes as shown for deaerated solution. Quantum yields were also unaffected by air in the solution.

Discussion

The photolysis results for Os(NH₃)₅N₂²⁺ can be interpreted in terms of competing primary photosubstitution and photoredox steps and subsequent thermal substitution and redox reactions (Scheme I). A complicating factor is the thermal oxidation of Os(NH₃)₅H₂O²⁺ and Os(NH₃)₅Cl⁺ by water to give Os(III) species.¹⁰ Thus even if photosubstitution (eq 4) were the sole primary photolysis pathway, the combination of (eq 4, 6, 8, and 9) would give Os(NH₃)₅Cl²⁺ as the osmium reaction product.¹⁶ However, according to this scheme,

Scheme I



production of the Os(NH₃)₅Cl²⁺ requires formation of at least catalytic quantities of Os(NH₃)₅H₂O²⁺, a species which has proved somewhat elusive in studies of the thermal chemistry of the osmium ammine complexes. Since Os(NH₃)₅N₂²⁺ undergoes relatively rapid thermal aquation to Os(NH₃)₅H₂O³⁺ (eq 7),¹⁹ photooxidation (eq 5) alone should give Os(NH₃)₅H₂O³⁺ as the principal reaction products (eq 5 and 7).

Analogy for Scheme I can be drawn from photochemical studies of the Ru(II) compounds: Ru(NH₃)₅N₂²⁺ and Ru(NH₃)₅CH₃CN²⁺.¹⁵ In the former case photooxidation to Ru(III) species (with concomitant formation of H₂) is the predominant photoreaction at 254-nm irradiation, and subsequent pathways analogous to eq 7, 8, and 9 are argued to give Ru(NH₃)₅Cl²⁺ as the predominant product in aqueous chloride solution. However, the more extensively studied acetonitrile complex showed both photoaquation and photooxidation with the former dominating at longer wavelengths (>254 nm) and the latter dominating at shorter wavelengths (≤ 254 nm). The redox paths have been attributed to higher energy charge transfer to solvent (CTTS) states, and the photoaquation reactions to the population of ligand field (LF) states.¹⁵

The observation of Os(NH₃)₅Cl²⁺ as the exclusive photoproduct from Os(NH₃)₅N₂²⁺ at $\lambda_{\text{irr}} \geq 229$ nm in deaerated solution implies some photoaquation to give Os(NH₃)₅H₂O²⁺. When oxygen is present, Os(NH₃)₅Cl²⁺ is not formed, and spectral changes are consistent with the formation of Os(NH₃)₅H₂O³⁺ instead. This implies that any Os(NH₃)₅H₂O²⁺ formed is rapidly oxidized to Os(III) thus preventing the substitution step (eq 6) required in the catalytic formation of Os(NH₃)₅Cl²⁺. A similar argument can be used to explain the induction period intermittently seen for Os(NH₃)₅Cl²⁺ formation in deaerated solutions; i.e., traces of oxidizing impurities (O₂?) deplete the first Os(NH₃)₅H₂O²⁺ formed by eq 4. The similarity of Os(NH₃)₅N₂²⁺ disappearance quantum yields in dinitrogen-deaerated solution to those measured in argon-deaerated solution suggests that trapping of any transient Os(NH₃)₅H₂O²⁺ by N₂ to re-form starting material is slow relative to other reactions depleting Os(NH₃)₅H₂O²⁺ (eq 6 and 9). A factor influencing this slow rate is the low concentration of N₂ ($\sim 10^{-3}$ M) even in a saturated solution. Lastly, the failure to see Os(NH₃)₅Cl²⁺ as a product of 214-nm photolysis in deaerated solution argues for the overwhelming predominance of photooxidation at this λ_{irr} .

The *cis*-Os(NH₃)₄(N₂)₂²⁺ photolysis results are the more easily interpreted. The spectral changes in the early stages of the reactions are consistent with N₂ photoaquation (eq 3) as the sole process leading to spectral changes. Thus, it appears that photoaquation is the predominant reaction for each λ_{irr} studied. The presence of a dinitrogen remaining in the coordination sphere of the previously unreported Os(NH₃)₄(H₂O)N₂²⁺ ion stabilizes the +2 oxidation state and thermal oxidation to Os(III) is not seen. Secondary photolysis of the initial product Os(NH₃)₄(H₂O)N₂²⁺ apparently gives oxidation

Table III. Approximate Quantum Yields^a for the Photochemical Reaction: $cis\text{-Os}(\text{NH}_3)_5(\text{N}_2)_2^{2+} + \text{H}_2\text{O} \rightarrow \text{Os}(\text{NH}_3)_4(\text{H}_2\text{O})\text{N}_2^{2+} + \text{N}_2$

λ_{irr} , nm	Φ , ^b mol einstein ⁻¹	λ_{irr} , nm	Φ , ^b mol einstein ⁻¹
366	0.48 ± 0.03 (4)	229	0.30 ± 0.01 (2)
313	0.51 ± 0.04 (3)	214	0.29 ± 0.03 (2)
254	0.31 ± 0.02 (2)		

^a Measured in 0.001 M HCl/0.199 M NaCl deaerated aqueous solution at 25.0 °C. Calculated from spectral changes assuming the product extinction coefficients are the same as $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ under analogous conditions. ^b Mean value and average deviation reported, number of independent determinations in parentheses.

to $\text{Os}(\text{III})$ as expected in analogy to the photoreactions of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$. Quantum yields listed in Table III for $cis\text{-Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ are significantly higher at 366 and 313 nm than at the $\lambda_{\text{irr}} \leq 254$ nm. Since the primary photoreaction remains the same, the decreased quantum yields at the shorter wavelengths indicate that higher energy states may deactivate by pathways independent of the excited state responsible for the photoreactions at longer λ_{irr} .

Examination of the spectra of $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ and $cis\text{-Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ (Figures 1 and 2, Table I) indicates considerable absorption in the forms of broad shoulders to the long-wavelength sides of the principal MLCT bands. For example $cis\text{-Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ displays a shoulder centered ~290 nm with a large extinction coefficient. Since LF bands in pentaammineiridium(III) complexes have considerably smaller absorbancies,²⁰ it can be argued that this shoulder is a charge-transfer band (the "triplet" of the more intense MLCT band at 223 nm?). Similar arguments might be applied to the $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ spectrum; however, given the number of shoulders seen, it appears likely that some of these have a LF origin. LF absorption very likely contributes to the long-wavelength absorption of the $cis\text{-Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ ion as well. Attempts confirm the CT nature of the $\text{Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ shoulder using solvent effects gave ambiguous results. Although some modest band shape changes in the 290-nm region were noted in 90% ethanol/10% water and in 90% acetonitrile/10% water (v/v), there was no clear-cut shift in the position of the shoulder. Similarly the MLCT λ_{max} is also unresponsive to these solvents, shifting only 2 nm to the red from aqueous solvent to 90% aqueous ethanol.

The photolysis results are consistent with models proposed for $\text{Ru}(\text{II})$ analogues, namely, that CTTS states are responsible for the primary photooxidation steps and lower energy LF states are responsible for the primary photoaquation steps. For $\text{Os}(\text{NH}_3)_5\text{N}_2^{2+}$ photooxidation and photoaquation are competitive except at 214-nm irradiation where photooxidation is the only process seen. Problems in differentiating the separate contributions of photooxidation and photoaquation preclude pinpointing the λ_{irr} where oxidation becomes the dominant pathway and any estimate of CTTS state energies

from the continuous-photolysis experiments. However, results at 214 nm indicate that the MLCT state initially populated with this wavelength irradiation either undergoes direct reduction of the solvent or interconverts to a redox-active CTTS competitive with direct deactivation to the ground state from these upper levels. The failure to see $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$ as a product strongly suggests that significant internal conversion to substitution-active LF states is not occurring. In contrast, for $cis\text{-Os}(\text{NH}_3)_4(\text{N}_2)_2^{2+}$ photooxidation is at most a minor primary pathway even at 214-nm irradiation, a result consistent with the greater difficulty in oxidizing an $\text{Os}(\text{II})$ center coordinated to two π -acceptor ligands.⁹ Thus in this case the CTTS state must be sufficiently high in energy that irradiation into the MLCT state(s) leads only to direct deactivation to the ground state competitive with internal conversion to substitution-active LF states at lower energy.

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Registry No. $[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$, 20611-50-1; $[cis\text{-Os}(\text{NH}_3)_4(\text{N}_2)_2]\text{Cl}_2$, 54477-45-1; $[\text{Os}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, 39176-94-8; $\text{Os}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, 53222-99-4; $\text{Os}(\text{NH}_3)_4(\text{H}_2\text{O})\text{N}_2^{2+}$, 66027-76-7.

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