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Oxidation of $[Os(NH_3)_5CO]^{2+}$ to $[(Os(NH_3)_4CO)_2N_2]^{4+}$

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Received December 6, 1978

The oxidation of $[Os(NH_3)_5CO]^{2+}$ in acidic solution by Ce(IV) when the molar ratio of the two reagents is 1.0 or slightly less yields the μ-dinitrogen species $[(Os(NH_3)_4CO)_2N_2]^{4+}$, almost quantitatively. Under these concentration conditions, $[Os(NH_3)_5CO]^{3+}$ first forms rapidly and quantitatively and then disproportionates to the binuclear product and $[Os(NH_3)_5CO]^{2+}$ at a rate which is second order in [Os(III)] and inverse in $[Os(NH_3)CO^{2+}]$. This evidence points to an irreversible first-order change in an Os(IV) species as being rate determining but leaves open the question of whether the coupling occurs in the Os(IV) product of the rate-determining step or in an Os(V) state which might result from the oxidation of the Os(IV) by $[Os(NH_3)_4CO]^{3+}$. It is suggested that deprotonation of coordinated ammonia keeps the Os–CO bond intact, in spite of the increase in oxidation state for osmium. The yields of the binuclear species are high also on oxidation at an anode or using $K_2S_2O_8$, and the last named reagent leads to a simple high-yield preparation of the binuclear ion.

Introduction

Considerable effort in these laboratories has been devoted to the search for a composition in which the disproportionation reaction

$$L_5Os^{III}N{\equiv}NOs^{III}L_5 = 2L_5Os^{VI}N$$

would occur. In the course of this work, we have encountered a remarkable example of coupling of the nitrogen of coordinated ammonia by oxidation to produce dinitrogen. The coupling takes place in a higher oxidation state of osmium, and the reaction is therefore closely related to the kind of process we are trying to realize.

Experimental Section

Reagents. Osmium tetroxide (99.8%) and potassium hexachloroiridate(IV) (99.9%) were used as purchased from Alfa Products.

Standard solutions of 0.100 M $Ce(NO_3)_4{\cdot}2NH_4NO_3{\cdot}2H_2O$ were prepared by diluting samples purchased from BioRad. Cerium(IV) perchlorate, 0.5 M in 6 M $HClO_4$, was purchased from G. Frederick Smith. Cerium(IV) sulfate solutions, 0.10–0.50 M, were prepared from $Ce(HSO_4)_4$ dissolved in 1 M H_2SO_4 or from $Ce(DSO_4)_4$ dissolved in 1 M D_2SO_4 or 1 M CF_3CO_2D (the latter from trifluoroacetic anhydride (Aldrich) and D_2O).

The water used in preparing solutions was doubly distilled, the second distillation being from an alkaline potassium permanganate solution. All other chemicals were reagent grade and were used without further purification.

Sephadex SP C-25 anion-exchange resin was used as purchased from Pharmacia Fine Chemicals, Inc.

All microanalyses were done by the Stanford Microanalytical Laboratory, Stanford, Calif.

Osmium Complexes. Pentaamminedinitrogenosmium(II) Chloride, $[Os(NH_3)_5N_2]Cl_2$. The synthesis of this dinitrogen complex was adapted from the method of Allen and Stevens.[1] Ammonium hexachloroosmate(IV) (6 g) was added slowly with stirring to hydrazine hydrate (50 mL) and the mixture was refluxed for 10 h. The pale yellow product was collected, washed with ethanol and ether, and air-dried. The solid was then added to 50 mL of $N_2H_4{\cdot}H_2O$ and refluxed for 10 h. After collection and washing of the product as above, the reflux was repeated in another 50 mL of $N_2H_4{\cdot}H_2O$. After a total of 30 h at reflux, all of the *cis*-bis(dinitrogen)tetraammineosmium(II) chloride impurity had been removed. (A shorter reflux time is referred to in the published syntheses but was found to result in contamination by the bis(dinitrogen) complex.) The solid contains a black component, which was removed by filtering a solution in water. The yields ranged from 80 to 90%. The compound was characterized by its UV spectrum ($\lambda_{max} = 208$ nm, $\epsilon = 2.51 \times 10^4$) and its IR spectrum ($\nu(N{\equiv}N) = 2022$ cm^{-1}).

Pentaamminechloroosmium(II) Chloride, $[Os(NH_3)_5Cl]Cl$. Pentaamminedinitrogenosmium(II) chloride (800 mg, 2.15 mmol) was dissolved with warming in 120 mL of 0.07 M HCl and the solution was filtered. An equivalent amount of Ce(IV), 0.5 M solution in 6 M $HClO_4$, was added and the resulting mixture heated to 50 °C. After 5 min, 40 mL of concentrated HCl was added and the solution was heated at 65 °C for 15 min. The chloro complex precipitated from the heated solution. The mixture was cooled in an ice bath and the solid collected, washed with ethanol and ether, and air-dried. The product was recrystallized from 50 mL of hot 0.1 M HCl. An additional quantity of pure compound was obtained by adding concentrated hydrochloric acid to the recrystallization liquor and then recrystallizing the precipitate from 20 mL of hot 0.1 M HCl. The overall yield was between 85 and 90%. The compound was characterized by its ultraviolet spectrum (267 nm, $\epsilon = 2.00 \times 10^3$).[2]

Pentaamminecarbonylosmium(II) Chloride, $[Os(NH_3)_5CO]Cl_2$. This osmium(II) complex was prepared by the method of Allen and Stevens.[1]

Pentaamminecarbonylosmium(III) Hexachloroiridate(III) Monohydrate, $[Os(NH_3)_5CO](IrCl_6)$. Eight milligrams of $[Os(NH_3)_5CO]Cl_2$ was dissolved in 20 mL of 0.1 M CF_3CO_2H. An equivalent amount of K_2IrCl_6 (10.3 mg) was added with stirring, resulting in the nearly quantitative precipitation of a fine lavender solid. The compound was collected on a fine porosity frit, washed with ethanol and ether, and air-dried. The carbonyl complex was characterized by its IR spectrum ($\nu(CO) = 2058$ cm^{-1}) and by its elemental analysis (Calcd: C, 1.65; H, 2.36; N, 9.64. Found: C, 1.60; H, 2.24; N, 9.65).

μ-Dinitrogen-bis(*cis*-tetraamminecarbonylosmium(II)) Chloride Monohydrate, $[(Os(NH_3)_4CO)_2N_2]Cl_4{\cdot}H_2O$. A principal concern of the research described in this paper was to understand the reactions leading to the title compound. For convenience to others, a preparative procedure is outlined here. The complex was prepared by oxidizing $[Os(NH_3)_5CO]^{2+}$. Fifty milligrams of $[Os(NH_3)_5CO]Cl_2$ was dissolved in 25 mL of 0.1 M HCl. A 1.3-fold excess of $K_2S_2O_8$ (72 mg) was dissolved in 5 mL of H_2O and added to the carbonyl complex with stirring. After 1 h, the reaction mixture was charged onto Sephadex ion exchange resin. The resin was washed with 0.2 M HCl before eluting the binuclear species with 0.4 M HCl. After the solvent had been removed from the eluate by rotary evaporation, the product was redissolved in a minimum volume of 0.01 M HCl and reprecipitated by adding concentrated HCl to the solution. The white powder (80% yield) was collected, washed with ethanol and ether, and air-dried. Anal. Calcd: C, 3.16; H, 3.45; N, 18.42. Found: C, 3.19; H, 3.44; N, 18.37. The compound was further characterized as will be described later.

Instrumentation and Techniques. Visible and ultraviolet spectra were recorded on a Beckman Acta MVII, a Beckman 5270, or a Cary 15 spectrophotometer. A Perkin-Elmer Model 621 spectrophotometer was used for infrared spectra and a Spex Industries Ramalog Raman Spectrophotometer Model 1401 (argon laser, 5145-Å exciting line) for Raman spectra. Electrolytic oxidations were made with electronic equipment supplied by Princeton Applied Research (Model 173 potentiostat and galvanostat, Model 175 universal programmer, Model 176 current follower).

Kinetic studies were carried out by using a stopped-flow apparatus in which mixing was provided by synchronized manual depression of two jacketed syringes. The reaction mixture was forced into a demountable cell (Barnes Engineering Co.) with CaF_2 windows and polyethylene spacers (25–100 μm). This cell was used for IR and UV spectrophotometric studies.

Results

A. Characterization of μ-[(*cis*-$Os(NH_3)_4CO)_2N_2]Cl_4$. The analytical results cited earlier conform closely to the formula given for the new compound. This evidence is buttressed by

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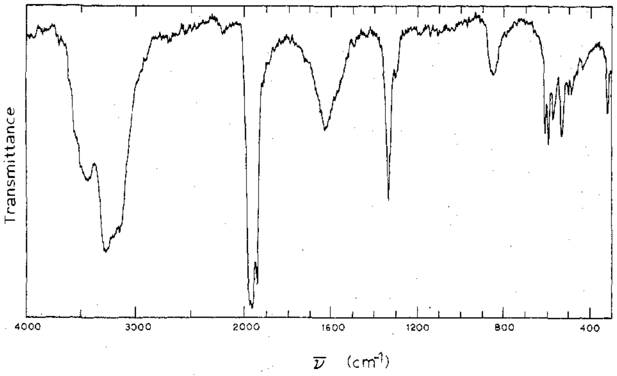


Figure 1. Infrared spectrum of $[(Os(NH_3)_4CO)_2N_2]Cl_4{\cdot}H_2O$.

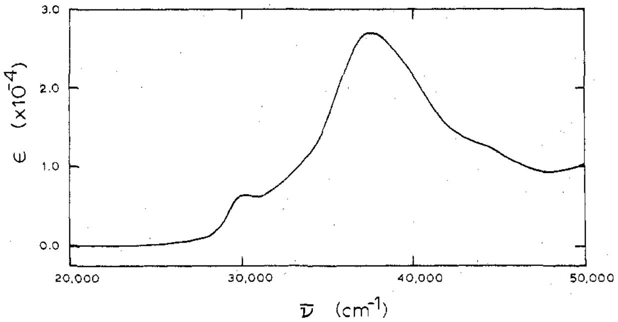


Figure 2. Electronic absorption spectrum of $[(Os(NH_3)CO)_2N_2]^{4+}$ in water.

the fact that the product cation is eluted from a Sephadex SP (C-25) column with 0.4 M HCl, thus suggesting a 4+ charge, and by the stoichiometry of the oxidation reaction as determined in a mass electrolysis experiment. The solution to be oxidized was ca. 5×10^{-3} M in $[Os(NH_3)_5CO]Cl_2$ and 0.1 M in HCl; platinum electrodes were used and the potential was adjusted to 1.02 V vs. NHE. Coulometric measurements showed that each osmium center had been oxidized by 3.0 electrons. As shown by ion-exchange separation, the major product was the title complex; the only other product was an osmium(VI) nitrido species, formed in no more than 5% yield.

In Figure 1 is shown the infrared spectrum, and in Figure 2 the UV-visible absorption spectrum of the new compound. The UV absorption with respect to both position and intensity is consistent with having N_2 coordinated to Os(II). In this connection, the fact that no absorption assignable to an N_2 stretch appears in the infrared region but a strong band at 2125 cm^{-1} appears in the Raman spectrum is especially significant. The observations are accounted for by assigning the N_2 to a bridging position and by requiring the molecule to be symmetrical about the N_2 bridging group. This leaves unanswered the question of the disposition of the two CO molecules, whether cis or trans to μ-N_2. The absorption at 1970-cm^{-1} is assignable to CO stretch, and the fact that it is complex suggests that CO is cis to the N_2 ligand. This assignment is supported by the medium intensity infrared bands between 500 and 600 cm^{-1} which are similar to those observed between 400 and 500 cm^{-1} for *cis*-$[Os(NH_3)_4(N_2)_2]^{2+}$ and which are assigned to ν(Os–N). The most convincing evidence is chemical in nature. When the complex is oxidized by MnO_4^-, *cis*-$[Os(NH_3)_4CO(N_2)]^{2+}$ is important among the products formed. Oxidation of one end of the molecule would release a dinitrogen-containing moiety without any necessity for rearrangement.

The fact that both CO and N_2 are held in such stable (at least in the kinetic sense) combination in the molecule is strong evidence for assigning to osmium the oxidation state 2+. The molecule is not oxidizable in a cyclic voltammetric experiment until a potential of 1.49 V (vs. NHE) is reached (water as solvent, 0.1 M $HClO_4$), and the oxidation when it occurs is irreversible, there being no complementary reducing wave in the trace.

B. Observations Bearing on the Mechanism of Formation. The oxidation reactions to be described were all done in acidic solution. Though persulfate, for example, does oxidize $[Os(NH_3)_5CO]^{2+}$ in neutral solution, the μ-dinitrogen species is not produced.

Cerium(IV) produces the binuclear species in yields greater than 95% when added in a 1:1 molar ratio to concentrated solutions of $[Os(NH_3)_5CO]^{2+}$, i.e., 1×10^{-2} M at 25 °C. A series of experiments were run with $[Os(NH_3)_5CO]^{2+}$ at 8.4×10^{-3} M (0.1 M CF_3CO_2H, 25 °C), but changing the amounts of Ce(IV) added. The production of the binuclear species was efficient (85%) with up to 2.0 equiv of Ce(IV)/mol of Os(II); above this ratio, there was a continued decrease in yield (66% with 2.5 equiv and 48% with 3.0). In another experiment with Os(II) at 9.1×10^{-3} M, 5 °C, Ce(IV) was added in the molar ratio Ce(IV)/Os(II) = 3.0. The oxidizing agent was observed to be consumed in less than 5 s, but the binuclear product appeared at a slower rate, the slower reaction approximately obeying second-order kinetics. The yield of the binuclear product was quite low however, ca. 50%.

The experiment just described shows that Ce(IV) is consumed very rapidly by the Os(II) species, even at the 3:1 molar ratio. The experiment, however, does not establish that the Os(II) species is fully consumed in the initial phase of the reaction. This point was investigated in a stopped flow experiment using infrared absorption to monitor the concentration of $[Os(NH_3)_5CO]^{2+}$. The carbonyl absorbance at 1895 cm^{-1} was followed in a demountable cell (BaF_2 plates, 0.1-nm path length). A Ce(IV) solution was prepared by dissolving $Ce(DSO_4)_4$ in 1 M CF_3CO_2D/D_2O and standardized by titration with $Na_2C_2O_4$. The solution of $[Os(NH_3)_5CO]^{2-}$ was at 0.028 M in 0.1 M CF_3CO_2D; Ce(IV) and Os(II) were mixed in a 1:1 molar ratio. It was found that more than 95% of the Os(II) had been consumed in the mixing time, ca. 1 s. Following this initial phase in which Os(II), and thus, of necessity, Ce(IV), had been consumed, the original Os(II) species reappeared gradually, to about 50% of the original amount.

The foregoing experiment demonstrated that Ce(IV) reacts more rapidly with Os(II) than with Os(III), which according to the 1:1 stoichiometry observed must be the first osmium-containing product of the reaction. This conclusion is important for the interpretation of the experiments now to be described.

In this series, the initial molar ratio of $[Os(NH_3)_5CO]^{2+}$ to Ce(IV) varied from 3 to 41, the initial concentration of the latter remaining constant at 1.0×10^{-3} M. The one-to-one reaction occurs on mixing; hence the ratio of Os(II)/Os(III) in the series varies from 2 to 40. The reaction was followed spectrophotometrically at 30.59×10^3 cm^{-1}, where among the species produced after Ce(IV) is consumed only the μ-dinitrogen species absorbs strongly. At the highest ratio of $[Os(II)]_0/[Ce(IV)]_0$, the formation of the binuclear product takes place very slowly. Increasing the ratio decreases the rate at which the binuclear product appears and for high ratios of Os(II)/Os(III) the yield of the product is diminished. For experiments with $[Os(II)]_0/[Ce(IV)] = 3$ and 5 (corresponding to $[Os(II)]/[Os(III)] = 2$ and 4 after the consumption of Ce(IV) which takes place immediately on mixing) the reaction to form the binuclear species is much more rapid, and in each case was found to follow second-order kinetics. The specific rates at 25 °C were determined from second-order plots as 2.2 and 1.1 M^{-1} s^{-1}.

With persulfate ion as oxidant, the yield of the binuclear product is high even when a slight excess is used. Thus, in one experiment at 25 °C, with $[Os(NH_3)_5CO^{2+}]_0 = 4.73 \times 10^{-3}$ M in 0.10 M HCl with 2.0 mol of $S_2O_8^{2-}$ for each of the carbonyl complex, the binuclear species was formed in 94% yield. In contrast to the case with Ce(IV), with Os(II) in excess, $S_2O_8^{2-}$ does not disappear immediately on mixing. In an experiment with $[Os(NH_3)_5CO^{2+}]$ at 5.63×10^{-3} M, 0.08 M in trifluoroacetic acid, and with Ba^{2+} present, $S_2O_8^{2-}$(aq) was added to bring the initial concentration to 4.64×10^{-3} M in osmium and 6.96×10^{-3} M in $S_2O_8^{2-}$. Barium sulfate was seen to form immediately on mixing, but continued to form thereafter for a considerable period of time.

An experiment was done by adding a solution of $K_2S_2O_8$ to a rather concentrated solution ($>5 \times 10^{-2}$ M) of $[Os(NH_3)_5CO]^{2+}$ in 0.10 M CF_3CO_2H to bring the molar ratio of $S_2O_8^{2-}$/Os(II) to 1.5. A precipitate started forming immediately as the $K_2S_2O_8$ dissolved. The solid was collected after 2 to 3 min and dried, and the infrared spectrum was taken. It showed SO_4^{2-} to be the major anion with a slight contamination by $S_2O_8^{2-}$. In the carbonyl absorption region, the major band was at 2025 cm^{-1}, but there was also a minor one at 2338 cm^{-1}. This solid was redissolved in 0.1 M CF_3CO_2H, and the solvent stripped by rotary evaporation. The infrared spectrum of the dried solid was again taken. The infrared spectrum in the carbonyl region now showed only bands at 1970 and 1900 cm^{-1}, corresponding to $[(Os(NH_3)_4CO)_2N_2]^{4+}$ and $[Os(NH_3)_5CO]^{2+}$.

Permanganate ion acting on $[Os(NH_3)_5CO]^{2+}$ in acidic solution produced the binuclear species but not as cleanly as the other three oxidizing agents thus far dealt with—anode, Ce(IV), and $S_2O_8^{2-}$. Bromine in acidic solution is consumed by $[Os(NH_3)_5CO]^{2+}$ but without producing the binuclear complex.

Experiments were done on the oxidation of $[Os(NH_3)_5CO]^{2+}$ with thiourea present. The conditions were $[[Os(NH_3)_5CO]^{2+}] = 3 \times 10^{-3}$ M, $[S_2O_8^{2-}] = 1 \times 10^{-3}$ M, [thiourea] = 1×10^{-3} M, and 0.1 M CF_3CO_2H. Blanks showed that the reaction of thiourea with $S_2O_8^{2-}$ is very slow and that thiourea does not react with $[Os(NH_3)_5CO]^{2+}$. The yield of the binuclear product was less than 5%. The solution turned brown (λ_{max} at 29×10^3 cm^{-1}) but the species responsible for the color was not identified. Thiourea was observed to interfere with the formation of the binuclear complex also when Ce(IV) was used as oxidant (1×10^{-3} M).

A tracer experiment using ^{18}O was performed to learn whether CO undergoes oxygen exchange when $[Os(NH_3)_5CO]^{2+}$ is converted to the binuclear ion. In this experiment, $K_2S_2O_8$ was added (1.5 mol/mol of Os(II)) to a solution 2.2×10^{-2} M in $[Os(NH_3)_5CO]Cl_2$ and 0.10 M in CF_3CO_2H. The solvent contained 48.9 atom % ^{18}O and 10.5 atom % ^{17}O. After a reaction time of 1 h, the solid was collected and dried and the infrared spectrum was taken. Incorporation of solvent oxygen into CO was less than 1%.

With $IrCl_6^{2-}$ as oxidant, the reaction takes a different course from that observed for the other systems dealt with. Under conditions as described in the Experimental Section, precipitation of an osmium-containing species is immediate. The solid obtained has a strong infrared band at 2058 cm^{-1}. This is close to the value (2044 cm^{-1}) extrapolated for $[Os(NH_3)_5CO]^{3+}$ from free CO and $[Os(NH_3)_5CO]Cl_2$ by assuming shifts analogous to those observed for ν(N–N) in N_2, $[Os(NH_3)_5N_2]Br_2$,[1] and $[Os(NH_3)_5N_2]Br_3$.[3] The hexachloroiridate(III) salt of $[Os(NH_3)_5CO]^{2+}$ was prepared to assess the effect of the anion: ν(C–O) was observed to be at 1887 cm^{-1} which is close to the value of 1895 cm^{-1} observed for the chloride salt.

Discussion

Basolo and co-workers[4-8] have reported the results of an imaginative series of studies in which bond formation by coordinated nitrogen is featured. They have chosen to discuss many of their results in terms of the chemistry of coordinated nitrene, though they do acknowledge that the formulas themselves do not lead to a distinction between the designation they elect and an alternative involving a higher oxidation state of the metal.[4] The choice of which formalism to adopt is of course arbitrary, and no difficulties should arise if more is not read into the descriptions than they are competent to handle. Nevertheless, it seems worthwhile to point out that some advantages are lost in adopting the "nitrene" rather than the orthodox "nitrido" description for ground-state species. Chief among them is that the analogy between the new chemistry uncovered for the "nitrido" or "nitrene" ligand and the extensive chemistry involving reduction of oxy species by oxygen transfer is lost sight of. There is a large body of observations for such systems which have been dealt with without invoking coordinated "oxenes" to describe it. In such reactions, bond formation takes place before bond breaking in the oxidant is complete and, in certain cases, for example, in the reaction of OsO_4 with olefins, species can be identified[9] in which coordinated oxygen makes bonds to carbon in much the same sense that coordinated nitrogens makes bonds. The simple analogy between oxygen and nitrogen transfer in redox processes has been resourcefully exploited by Sharpless and co-workers.[10] Their results serve to demonstrate that the formation of new bonds by coordinated nitrogen is a ground-state property of the nitrogen complexes they have dealt with. There is of course an important quantitative difference between O^{2-} and N^{3-} which is that transfer of electron density (multiple bond formation) in the latter case is much more extensive than in the former. (It is on this account that it is not unreasonable to expect a considerable lifetime for a NOs^{V}–CO species.) A second point is that the "nitrene" description suggests an exotic excited-state property, whereas nitrogen transfer, just as in the case for oxygen, is an expected ground-state property of nitrido complexes, which, though "intermediates" in certain chemical contexts, are simply reagents in others. Finally, as is recognized by Basolo et al., since excited states of the species, with still higher reactivity, might be formed thermally as well as photochemically, it might be advantageous to reserve the "nitrene" description for an appropriate one among the electronically excited states.

Because the oxidation of coordinated ammonia is so strongly dependent on the identity of the central metal ion—thus compare the difficulty of oxidizing NH_3 when it is coordinated to Co(III)[11] to the ease of oxidation on Os(III)—we see no merit in discussing the chemistry we have encountered as that of coordinated nitrene. In particular, the high yield of the binuclear product in reactions involving dilute reagents and extending over long periods of time, where of necessity the steady-state concentrations of intermediates is low, militates against the coupling reaction involving electronically excited species. We believe we are dealing with ground-state properties and thus choose the orthodox higher oxidation state designation for the reactive intermediates. This does not deny the possibility that in other circumstances where electronic excitation energy can be stored, the chemistry would be more aptly described as that of coordinated nitrene.

Though the overall stoichiometry for the formation of the binuclear species, according to the usual assignments of oxidation state, corresponds to oxidation of coordinated ammonia:

$$2[Os(NH_3)_5CO]^{2+} = [(Os(NH_3)_4CO)_2N_2]^{4+} + 6H^+ + 6e^-$$

it appears from the observations made on the reaction with Ce(IV) that an osmium-containing intermediate of oxidation state at least as high as 4+ is involved. The experiments which lead to this conclusion are those with $[Os(NH_3)_5CO]^{2+}$ in excess, which show that the disappearance of $[Os(NH_3)_5CO]^{3+}$ is inhibited by $[Os(NH_3)_5CO]^{2+}$ and is approximately at least second order in Os(III). This behavior is accounted for by the mechanism:

$$2[Os(NH_3)_5CO]^{3+} = [Os(NH_3)_5CO]^{2+} + Os(IV)$$
rapidly established equilibrium, K_{eq}

$$Os(IV) \rightarrow$$
slow step, k_1

This leads to the observed rate law with $k_{obsd} = K_{eq}k_1$. No effort has been made to incorporate proton dependencies into the mechanism. Other work[3] has shown that CO enhances the acidity of NH_3 coordinated to Os(III) enormously and that Os(IV) tetraammines have pK_a values for coordinated ammonia in the range 2–4. Osmium(V) is expected to be very acidic, with an ammonia probably being deprotonated to the nitrido stage.

According to the rate law, the coupling must take place after the k_1 step. The nature of the k_1 step is obscure, but it should be noted that in the study of other osmium(IV) ammine complexes,[3] disproportionation has been observed, controlled by a reaction first order in Os(IV). It is possible that also in the present system further disproportionation ensues, or oxidation of the product of the k_1 step by Os(III), and that the coupling takes place in the 5+ oxidation state. In any event, it seems likely that a high oxidation state is involved, in which protons are released from coordinated ammonia, to make N to N bonding possible. That nitride coordinated to Os in a high oxidation state is electrophilic has been demonstrated by Griffith and Pauson.[12] When the product of the reaction of $OsNCl_4^-$ with triphenylphosphine in acetone is treated with acid, $[Ph_3PNH_2]Cl$ is formed. In the course of our work, we found that $OsCl_5N^{2-}$ in water reacts with thiourea, without producing $[OsNH_3Cl_2]^-$ or $[OsNH_3Cl_5]^{2-}$. It is likely that a product was formed by nucleophilic attack by sulfur on coordinated nitrogen, as has been demonstrated for triphenylphosphine by Griffith and Pauson.

A remarkable feature of the chemistry is that the bond to CO is retained even when Os is in an oxidation state of 4+ or 5+. The possibility that in this reaction CO is converted to formate, which then regenerates CO in the coupling reaction is eliminated by the tracer experiment. Nitride ion (N^{3-}) is an extremely polarizable ligand so that as oxidation number rises, the effective charge on the metal rises much less rapidly with oxidation number than when NH_3, H_2O, or even O^{2-} is the ligand. Nitride is not qualitatively different in kind from oxide, but it is rather an extreme in a quantitative sense. The diminished yield of the binuclear product when the ratio of $[Os(NH_3)_5CO]^{2+}$ to $[Os(NH_3)_4CO]^{3+}$ is high, so that the lifetime of $[Os(NH_3)_5CO]^{3+}$ is much prolonged, may be the result of the release of CO from $[Os(NH_3)_5CO]^{3+}$.

Experiments not reported in detail were done with other pentaammine Os(II) complexes of π-acid ligands (SO_2 and NO^+) to learn whether N to N coupling takes place when they are oxidized, but without success, nor is coupling observed when $[Os(NH_3)_5H_2O]^{3+}$ is oxidized. There are probably different reasons for failure in each of these cases. When SO_2 is the ligand, an obvious one is that the ligand itself may be oxidized.

The chemistry with $S_2O_8^{2-}$ as oxidant is much less clear than that with Ce(IV). In this case, the simplification obtaining with Ce(IV), namely, that the oxidizing agent is rapidly and completely consumed in a clean conversion of $[Os(NH_3)_5CO]^{2+}$ to $[Os(NH_3)_5CO]^{3+}$, does not occur. However, with an excess of $S_2O_8^{2-}$ and with [Os(II)] high, it appears that $[Os(NH_3)_5CO]^{3+}$ is precipitated as the sulfate salt. Consistent with what has already been discussed, the cation of this salt when dissolved disproportionates, restoring in part the starting osmium complex.

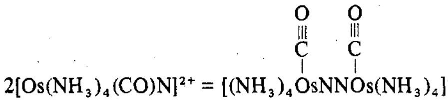
$$3[Os(NH_3)_5CO]^{3+} = 2[Os(NH_3)_5CO]^{2+} + {}^1/_2[(Os(NH_3)_4CO)_2N_2]^{4+} + 3H^+$$

The infrared frequency in the carbonyl region for the sulfate salt in question is close enough to that observed when $IrCl_6^{2-}$ is the oxidant to make it rather certain that the solid contained $[Os(NH_3)_5CO]^{3+}$.

In this solid, a weak absorption was observed at 2338 cm^{-1} and has been noted in approximately this region in other experiments. Unfortunately, the material producing the band was not identified. The high value suggests a species in which CO is attached to the metal in a high oxidation state, and the species in question may be an intermediate in the coupling reaction.

The striking difference in chemistry of the μ-dinitrogen species introduced by replacing saturated ligands on Os(II) by CO merits mention. In the species $[(Os(NH_3)_4Cl)_2N_2]^{2+}$, the first oxidation takes place at <–0.2 V vs. NHE to yield a mixed valence species, which then requires a much stronger oxidant for the second stage ($E_f = 0.69$).[13] As a consequence of this difference in the redox potentials, the mixed valence oxidation state is very stable with respect to disproportionation. When Cl^- is replaced by CO, there is no evidence for a mixed oxidation state, and when oxidation does occur, it results in destruction of the molecular framework.

The relation of the observations made to the desired goal of bringing about a disproportionation of a bridging dinitrogen remains to be considered. Assuming that the coupling takes place in the 5+ oxidation state (this is consistent with but not demanded by the data), we learn from the observations that the reaction



$$2[Os(NH_3)_4(CO)N]^{2+} = [(NH_3)_4\overset{CO}{Os}NN\overset{CO}{Os}(NH_3)_4]^{4+}$$

is strongly exoergic and that the reaction path is facile. A driving force for the coupling obviously is the stabilization by CO of osmium in the lower or 2+ oxidation state. In the absence of such stabilization, namely, in the species $[(NH_3)_5OsNNOs(NH_3)_5]^{4+}$, disproportionation to $Os^V(N^{3-})$ might be expected. The fact that it does not occur for this or related species,[13] in view of the conclusion about accessibility of the path, argues that the disproportionation is strongly endoergic. This constitutes an argument for focusing on disproportionation in $Os^{III}NNOs^{III} \rightarrow 2Os^{VI}(N^{3-})$ as a more promising alternative. In this alternative, stabilization by back-bonding in the reactant is reduced, and advantage is taken of the fact that Os(VI) is inherently more stable than Os(V).

Acknowledgment. Support of this research by NIH (Grant No. GM22045) is gratefully acknowledged.

Registry No. $[(Os(NH_3)_4CO)_2N_2]Cl_4$, 70562-08-2; $[Os(NH_3)_5CO](IrCl_6)$, 70528-09-5; $[Os(NH_3)_5Cl]Cl$, 39176-94-8; $[Os(NH_3)_5N_2]Cl_2$, 20611-50-1; $[Os(NH_3)_5CO]Cl_2$, 39176-85-7.

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Ruthenium Ammine Disulfides

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Received December 6, 1978

The complex of 1,2-dithiane with pentaammineruthenium(II) can be prepared by direct substitution on the pentaammineaquo ion, but with the analogous five-membered ligand, preparation by this route is not successful. The disulfide complexes can, however, be prepared by starting with $Ru(NH_3)_5OH_2^{2+}$ and 1,4-butanedithiol or 1,3-propanethiol. The products of these substitution reactions undergo one-electron oxidations to the Ru(III)–thiol state and, on further one-electron oxidation, produce the cyclic disulfides coordinated to Ru(II). This can be further oxidized, in a process which in the case of the six-membered ring was shown to be reversible on the cyclic voltammetric time scale (E_f = 630 mV vs. NHE at 25 °C), to the Ru(III) complex. In contrast to a simple thioether complex of Ru(III) which shows ligand to metal charge transfer at ca. 450 nm, the ruthenium(III) disulfide (six-membered ring) has a band at 618 nm with a second band discernible as a shoulder at 360 nm. The splitting is analogous to that observed with 1,5-dithiocane as ligand, which has been ascribed to sulfur lone-pair interactions. As expected on this basis, the splitting observed in the Ru(III) complex of the five-membered disulfide is even greater, owing to the fact that the dihedral angle between the sulfur lone pairs is smaller in the five-membered than in the six-membered ring.

In a previous paper, some manifestations in ligand-to-metal charge-transfer spectra of sulfur lone-pair interactions in the spectra of cyclic dithioether complexes of pentaammineruthenium(III) were described.[1] Such interactions have been well documented in the photoelectron spectra[2] of the ligands themselves, and after the fact at least, their influence on the charge-transfer spectra is not astonishing. The interactions are expected to be particularly prominent in disulfide complexes, and the work to be described was undertaken to investigate the electronic absorption of disulfide complexes of Ru(III). Disulfide complexes of metals are unusual, and since the desired species have not previously been prepared, their synthesis seemed a worthy goal in its own right.

Experimental Section

The procedures for handling air-sensitive solutions made use of argon as a blanketing gas and have been described elsewhere.[3]

Distilled water was further purified by redistilling from alkaline permanganate in an all-glass still. Acetone used as solvent was Baker Analyzed reagent grade.

Cerium(IV) sulfate was commonly used for quantitative oxidations. The salt $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ was purchased from G. F. Smith and was standardized by using primary-standard grade sodium oxalate.

The ligands 1,2-ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, and 1,6-hexanedithiol were purchased from Aldrich and were used without further purification.

Lipoamide (racemic) was purchased from Sigma Chemical Co. and used without further purification. Hydrochloric acid (Baker) was titrated against Titrisol–0.1 N NaOH.

The compound 1,2-dithiane used in the direct synthesis of a disulfide complex was prepared by the procedure of Claeson et al.[4] 1,4-Butanedithiol (21.6 g, 0.171 mol) was dissolved in 2 L of 50% ethanol. A 5% alcoholic iodine solution was then introduced dropwise with stirring until a faint yellow color persisted. A few drops of 1% $Na_2S_2O_3$ in water were then added to decolorize the solution. After the addition of 3 L of water, the mixture was extracted with two 150-mL portions of petroleum ether. The extracts were combined and dried over anhydrous $MgSO_4$. On cooling of the solution to −80 °C, crystals of 1,2-dithiane were deposited, but these rapidly polymerized to a petroleum ether-insoluble rubbery solid when dried. Accordingly, no further purification was attempted, and the ligand was stored as a solution in petroleum ether in the absence of light at −5 °C. Under these conditions, the disulfide is stable for extended periods of time (>1 year).

The compounds $[(NH_3)_5RuXC_6H_5](PF_6)_2$ (X = S, Se), referred to in Table I, were incidental to the main purpose of this investigation, and the method of preparation is described here. Diphenyl disulfide or diphenyl diselenide (220 mg) was dissolved in 5 mL of acetone, and the mixture was degassed in a stream of argon. Solid $[(NH_3)_5RuOH_2](PF_6)_2$ was then added, and within 3 min the mixture had changed from orange to brown to red (sulfur) or orange to green to blue (selenium). After 10 min the product was precipitated by adding the solution to 50 mL of ether. The yield was >95%.

Analyses were not performed on the sulfur derivative, but the quality of the preparation was established by comparing the properties with those of a material made by an alternate procedure, with excellent agreement. In the alternate preparation, benzenethiol reacted with $[(NH_3)_5RuOH_2]^{2+}$ in aqueous solution, and the product was then oxidized by air. Anal. Calcd for $[(NH_3)_5RuSeC_6H_5](PF_6)_2$: C, 11.36; H, 3.34; N, 11.06; Se, 12.47; Ru, 15.97. Found: C, 11.51; H, 3.01; N, 10.54; Se, 12.0; Ru, 15.69.

Results

Preparation of Pentaammine(1,2-dithiane)ruthenium(II) Hexafluorophosphate by Substitution. Synthesis by simple substitution is possible when 1,2-dithiane is the ligand. Owing to the instability of the unsubstituted five-membered analogue,[5] the preparation of the corresponding Ru(II) complex was not undertaken with it. The description of the successful synthesis by substitution follows.

One hundred milligrams of $[(NH_3)_5RuOH_2](PF_6)_2$ was added to approximately a threefold excess of 1,2-dithiane dissolved in petroleum ether and then the mixture was placed in 5 mL of degassed acetone, whereupon the solution turned red over the course of 30 min. The mixture was then added to an equal volume of 0.2 M HCl and loaded on a column containing Dowex 50W-X2 ion-exchange resin (acid form), and a yellow product was eluted with 2 M HCl. By addition of NH_4PF_6, the dipositive ion was precipitated as the yellow salt $[(NH_3)_5Ru(1,2\text{-dithiane})](PF_6)_2$ (I) in 30% overall yield. Anal. Calcd for $C_4H_{23}N_5S_2RuP_2F_{12}$: C, 8.05; H, 3.87; N, 11.74; S, 10.75; Ru, 16.95; F, 38.22. Found: C, 8.06, H, 3.89;

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