977 (1966); (d) A. McAuley and R. Shanker, *J. Chem. Soc., Dalton Trans.*, 2321 (1973).
(30) T. J. Lane, J. A. Ryan, and L. J. Walter, *J. Am. Chem. Soc.*, **78**, 5560 (1956).
(31) R. Curci and J. O. Edwards, "Organic Peroxides", Vol. 1, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1970.
(32) R. Hiatt and C. McColeman, *Can. J. Chem.*, **49**, 1712 (1971).
(33) L. Cattalini, "Inorganic Reaction Mechanisms", Part I, J. O. Edwards, Ed., Wiley-Interscience, New York, N.Y., 1970, p 266.
(34) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).
(35) (a) J. H. Krueger, P. F. Blanchet, A. P. Lee, and B. A. Sudbury, *Inorg. Chem.*, **12**, 2714 (1973); (b) P. F. Blanchet and J. H. Krueger, *ibid.*, **13**, 719 (1974); (c) J. H. Krueger, B. A. Sudbury, and P. F. Blanchet, *J. Am. Chem. Soc.*, **96**, 5733 (1974).

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Reactivity of Coordinated Nitrosyls. 6. Preparation, Characterization, and Reduction of Nitrosylpentaaquoruthenium(3+) and Reduction of Various Ruthenium Ammine Nitrosyls

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A new nitrosyl complex, nitrosylpentaaquoruthenium(II), has been prepared in acidic solution by the direct nitrosylation of $Ru(H_2O)_6^{3+}$ and characterized. The $Cr(H_2O)_6^{2+}$ reductions of $Ru(H_2O)_5NO^{3+}$, $Ru(NH_3)_5NO^{3+}$ in the absence of Cl^-, and several *cis*- and *trans*-tetraammine nitrosyls were found to proceed with a 4:1 stoichiometry to yield stable complexes which have been tentatively formulated as imido-bridged heterometallic dimers: $[(H_2O)L_4Ru-\underset{\cdot\cdot}{N}H-Cr(H_2O)_5]^{5+}$, L = NH_3, H_2O. The formulation of the latter structure is based upon UV-vis and IR spectra, ion-exchange chromatography, and microanalyses. The product analysis indicates that the nitrosyl nitrogen is retained in the bridge, and the presence of Cr(III) in the product suggests that inner-sphere attack by chromium(II) occurs via the nitrosyl entity at some point during the reduction. The chemistry of this new nitrosyl complex, $Ru(H_2O)_5NO^{3+}$, has been compared with that of previous complexes which we have studied; and we have discovered a striking difference in the nature of the products by simply replacing ruthenium for chromium as the metal center. In the reduction of $Ru(NH_3)_5NO^{3+}$ by $Cr(H_2O)_6^{2+}$, the presence of excess Cl^- changes the stoichiometry, rate, and products of the reduction. By replacing ammine with aquo ligands a large rate increase is observed and formation of dimer is unaffected by Cl^-. These observations have been discussed in terms of a possible nitrene intermediate.

Introduction

Transition-metal nitrosyl complexes have been extensively investigated because of the often unique chemical–physical properties of the nitrosyl ligand. Studies of the oxidation–reduction behavior of these nitrosyl complexes provide insight into the reactivity of a ligand capable of undergoing successive stages of reduction through several potentially stable intermediate oxidation states (i.e., $\dot{N}O$, NO^-, N_2, NH_3OH^+, N_2H_4, NH_3).

A decade ago Fraser[3] and Griffith[4] began to delve into the redox behavior of coordinated nitrogen oxides. Griffith[5] first described the reduction of ruthenium nitrosyls with Sn(II) in Cl^- medium. Subsequent investigations of these reductions[6,7] led to the isolation and characterization of novel binuclear nitrido-bridged complexes of ruthenium(IV). A similar study by Mukaido[8] resulted in complexes containing coordinated $SnCl_3^-$ and provided sketchy evidence for a nitrosyl-bridged binuclear ruthenium complex as well as a nitrido-bridged ruthenium(IV) dimer.

More recently, upon reduction of several metal nitrosyls with the common reductant chromium(II) in acidic aqueous solution, we have found that the nitrosyl does indeed react in a variety of ways. Although the mechanisms of reduction appear dissimilar, reduction of $Cr(H_2O)_5NO^{2+}$ [9] and $Cr(NH_3)_5NO^{2+}$ [10] by $Cr(H_2O)_6^{2+}$ resulted in the consumption of 2 equiv of reductant and the formation of 1 equiv of free hydroxylamine. On the other hand, the reduction of $Ru(NH_3)_5NO^{3+}$ [11] in Cl^- medium results in the immediate formation of $Ru(NH_3)_6^{2+}$ via a six-electron reduction.

In this paper, we describe the preparation of a new compound, $Ru(H_2O)_5NO^{3+}$, and detail another mode of reduction in which the $Ru(H_2O)_5NO^{3+}$ consumes 4 equiv of chromium(II) to form a novel chromium–ruthenium dimer. An identical stoichiometry with the formation of a heteronuclear dimer containing a similar chromaphore is also reported herein for the chromium(II) reduction of $Ru(NH_3)_5NO^{3+}$ (in the absence of Cl^-) and *cis*- and *trans*-nitrosyltetraammineruthenium(II) complexes.

Experimental Section

Analyses. Chromium was analyzed spectrophotometrically at 372 nm (ε 4815 M^{-1} cm^{-1})[12] after oxidation in alkaline peroxide. In the presence of ruthenium, chromium was analyzed in acidic solution by employing 1,5-diphenylcarbazide (540 nm, ε 4 × 10^4 M^{-1} cm^{-1}).[13,14] Our previously mentioned procedure[15] based on the ruthenate–perruthenate method of Woodhead and Fletcher[16] was used for all ruthenium assays. When both chromium and ruthenium were present, a correction for chromium(VI) was made on the basis of the 1,5-diphenylcarbazide analysis for chromium (417 nm, ε 680 M^{-1} cm^{-1}).[17] Hydroxylamine was analyzed spectrophotometrically (λ_{max} 368, ε 1.4 × 10^4 M^{-1} cm^{-1})[18] after forming the *p*-nitrobenzaldoxime. Ammonium ion was separated from the product mixtures by ion-exchange methods[19] and spectrometrically analyzed as the indophenol (λ_{max} 628, ε ~6.6 × 10^4 M^{-1} cm^{-1}) as described previously.[10] Nitrite content was determined by the standard method.[20] Nitrous oxide production was determined by the previously described gas chromatographic procedure.[21] The solubility of N_2O in aqueous solution was accounted for by preparing standard solutions of N_2O.

Preparations. Solutions of $Cr(H_2O)_6^{3+}$ in $TFMS^-$ medium were prepared by the peroxide reduction of CrO_3 in the presence of HTFMS.[22] The corresponding $Cr(H_2O)_6^{2+}$ solutions were prepared and standardized as previously reported.[9] Trifluoromethylsulfonic acid (HTFMS) (3M Corp.) was distilled under vacuum at 10 Torr at 62 °C and diluted immediately to a concentration of 3 M and stored in a polyethylene bottle. NaTFMS was prepared by the procedure of Scott.[22]

Complexes. **$[Ru(NH_3)_5NO]Cl_3$** was prepared either by reaction of NO(g) with solutions of $[Ru(NH_3)_6]Cl_3$ [23] or by the procedure of Gleu.[24] In order to exclude Cl^- impurity, $[Ru(NH_3)_5NO](TFMS)_3$ was prepared by the following method. Fifty milligrams of $[Ru(NH_3)_5NO]Cl_3$ was completely dissolved in approximately 50 mL of H_2O and placed on a $^1/_2$ in. × 1 in. SP Sephadex C25 cation-exchange column resulting in an orange band. The column was washed with water until several drops of $AgNO_3$ added to the rinse no longer indicated the presence of Cl^-. The $Ru(NH_3)_5NO^{3+}$ was then quickly removed from the column with 25 mL of 1.0 M NaTFMS (0.1 M

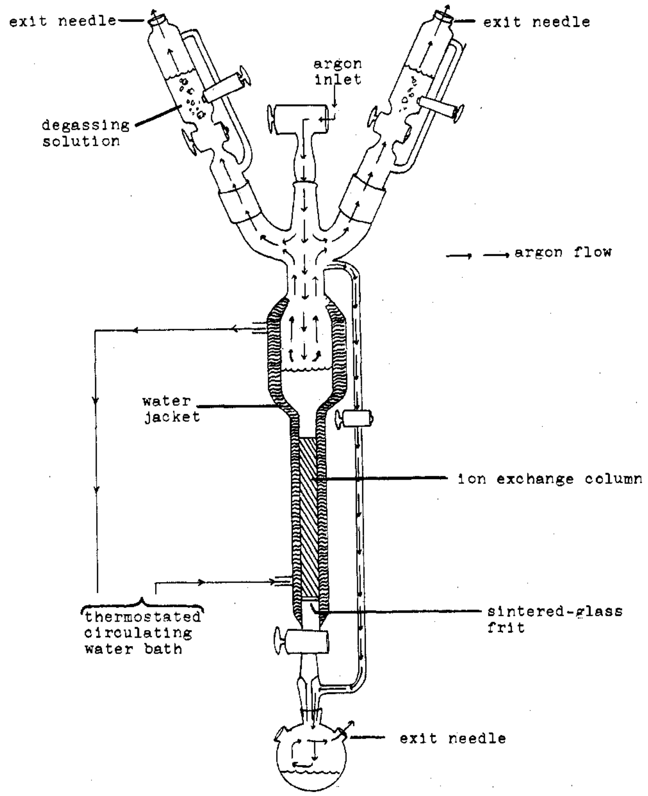


Figure 1. Apparatus used for the ion exchange of air-sensitive solutions at low temperature.

HTFMS) solution by forcing the solution through with air pressure to prevent precipitation of the complex on the column. Several drops of neat HTFMS were added to the orange solution, and after 1 h, the very soluble $[Ru(NH_3)_5NO](TFMS)_3$ was filtered and dried in a vacuum desiccator.

$K_2[RuCl_5(H_2O)]$ was prepared by the procedure of Mercer and Buckley[25] in which $RuCl_3 \cdot 3H_2O$ (1.87 g, 7.2 mmol) was refluxed for 2.5 h in 70 mL of concentrated HCl before adding a stoichiometric amount of KCl (1.07 g, 14.3 mmol) and then elemental mercury. The mixture was stirred until a slight green color developed at the Hg-solution interface and then was filtered. The clear red filtrate was rotary evaporated to dryness and recrystallized from 6 M HCl.

$Ru(H_2O)_6^{2+}$. Following the procedure of Creutz and Taube,[26] 0.544 g of $K_2[RuCl_5(H_2O)]$ was dissolved in a two-neck, 250-mL, round-bottom flask and then degassed with H_2. After 15 min, a platinum gauze, freshly blackened by electrolysis in chloroplatinic acid, was dropped into the stirred solution. Over several hours, the red-brown solution gradually turned deep blue at which point it was ion exchanged under argon at 4 °C on the apparatus shown in Figure 1. The lower charged chlororuthenium complexes[27] were removed before 1.0 M HTFMS and 1.5 M HTFMS rinses were used to elute pink $Ru(H_2O)_6^{2+}$ (λ_{max} 535, ϵ 10.8) and yellow $Ru(H_2O)_6^{3+}$ (λ_{max} 392, ϵ 30 M^{-1} cm^{-1}),[28] respectively.

$Ru(H_2O)_5NO^{3+}$. After O_2 oxidation of $Ru(H_2O)_6^{2+}$ to $Ru(H_2O)_6^{3+}$ over a period of ~1 h, the $Ru(H_2O)_5NO^{3+}$ was prepared by the reaction of NO(g) with $Ru(H_2O)_6^{3+}$ in 1.0 M HTFMS using the nitric oxide flow-line described earlier.[9] The nitrosyl complex was purified by placing the solution on a column of Dowex 50W-X8 ion-exchange resin, washing with H_2O and 0.5 M HTFMS, and removing the complex with a 1.0 M HTFMS solution. Anal. Calcd for 1 mol of N/mol of Ru: Ru, 0.386 mg/mL; N, 0.054 mg/mL. Found: Ru, 0.386 mg/mL; N, 0.0604 mg/mL.

$K_2[RuCl_5NO]$. Following the procedure of Mercer and Cox,[29] 2.2 g of $RuCl_3 \cdot 3H_2O$ was dissolved in 200 mL of concentrated HCl and the solution was heated near boiling while NO was bubbled through. After dissolved NO(g) was removed from the solution by purging with argon, the solution was cooled and a stoichiometric amount of KCl was added. The solution was reduced in volume to about 15 mL by heating on a steam bath overnight. Upon cooling, red crystals appeared which were collected by filtration and washed with acetone and ether.

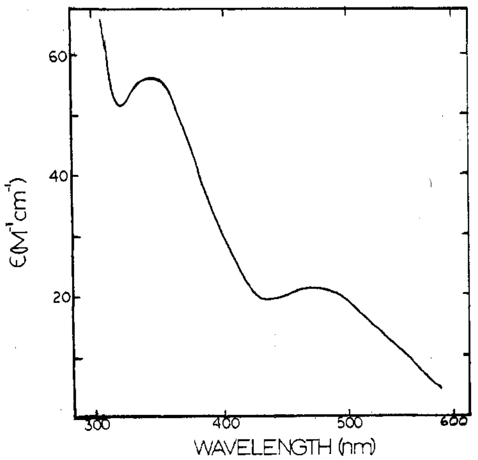


Figure 2. Electronic spectrum of $Ru(H_2O)_5NO^{3+}$ in a 1.0 M HTFMS solution.

The filtrate from the last step was reduced to a smaller volume, and a second group of crude crystals was recovered. The complex was recrystallized from 6 M HCl. The visible spectrum was identical with that reported for $[RuCl_5NO]^{2-}$ with λ_{max} 519 nm, ϵ 50.4 M^{-1} cm^{-1}.[30]

The preparation of *cis*- and *trans*-$[Ru(NH_3)_4(NO)X]Y_2$, where $X^- = OH^-$ or Cl^- and $Y^- = Cl^-$ or ClO_4^-, has been described elsewhere.[24,31]

Instrumentation. All visible and ultraviolet spectra were recorded on either a Cary 14 or a Cary 118 recording spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrophotometer. Complexes were suspended in a KBr matrix and the spectra were calibrated with polystyrene. A S+L Model 810 gas chromatograph was used to detect the presence of gaseous products. A Durrum-Gibson stopped-flow spectrophotometer was employed to measure rates of reactions.

Product Analysis. The product-study procedures were outlined previously[9,10] including the ion-exchange behavior expected for cationic complexes on Dowex 50W-X8, 200-400 mesh and SP Sephadex C25, 100-200 mesh ion-exchange resins. Both resins were employed in the present study.

Kinetics. Most kinetic studies were performed under pseudo-first-order conditions. With the aid of a Zwickel flask,[32] the reaction products were mixed and transferred to a spectrophotometer cell and then to the Cary 14 where the rate data were collected. The operation of the Zwickel flask was described in part 2.[9] For the measurements using the stopped-flow spectrophotometer, argon-saturated solutions of the two reactants were withdrawn via 20-mL syringes, the needles were removed, and the syringe was coupled to the storage syringe parts of the Durrum-Gibson instrument. The reservoir syringe, 2-mm cell, and stop-syringe were repeatedly flushed (at least four times with argon-saturated water and then with our reactants) before any data were collected. Trial runs on Cr^{2+} + $Ru(NH_3)_5Cl^{2+}$ indicated this procedure was sufficient to avoid trace oxidation by air.[33] The reactant solutions were thermostated and degassed in the same circulating water bath used to control the temperature of the stop-syringes and mixing chamber.

Results

Preparation and Characterization of $Ru(H_2O)_5NO^{3+}$. From earlier studies on the rapid uptake of NO by $Ru(NH_3)_6^{3+}$ or $Ru(NH_3)_5H_2O^{3+}$,[23] it was anticipated that the recently discovered $Ru(H_2O)_6^{2+}$ when oxidized to $Ru(H_2O)_6^{3+}$ would react similarly with NO(g). Solutions containing up to 0.01 M $Ru(H_2O)_5NO^{3+}$ could be prepared from the reaction of NO(g) and $Ru(H_2O)_6^{3+}$ in an acidic aqueous medium. Purification and the assignment of 3+ as the charge of the complex was achieved by ion-exchange chromatography using Dowex 50W-X2, 200-400 mesh cation-exchange resin. Its elution properties were matched to those of other 1+, 2+, and 3+ aquo-metal ion complexes. In acidic solution, the complex appears to be indefinitely stable, a property characteristic of the highly stable $[Ru^{II}-NO^+]$ entity.[34]

Figure 2 shows the UV-vis spectrum of $Ru(H_2O)_5NO^{3+}$ in 1.0 M HTFMS. The spectrum of $Ru(H_2O)_5NO^{3+}$ (λ_{max} 470

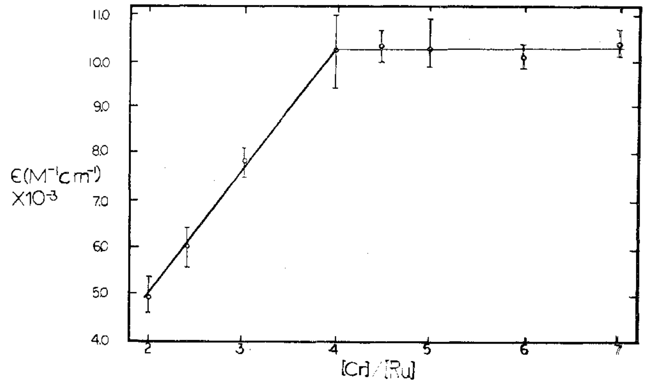


Figure 3. Extinction coefficient at 280 nm (based on total ruthenium concentration) vs. the ratio of the equivalents of Cr^{2+} per equivalent of $Ru(H_2O)NO^{3+}$ in 1.0 M HTFMS.

Table I. Product Analysis for the Reduction of 1 equiv of $Ru(H_2O)_5NO^{3+}$ by 4 equiv of $Cr(H_2O)_6^{2+}$ in 1.0 M HTFMS

[Fraction],[a,b] M	Color	λ_{max}, nm	% Ru[c,e]	% Cr[c,e]
0.2	Pink	388 281 216	7	3
0.5	Blue	574 408		67 ± 10
1.0	Orange	510 sh[d] 446 392 280	50 ± 10	12 ± 3
1.5	Green	460 310 sh 255	5	6
2.0[f]	Light green	440 320 sh 253	3	3
	Yellow	260	6	3
	Brown	450 sh 330 sh 254 sh	10	5

[a] Sp Sephadex C25 cation-exchange resin. [b] $NaClO_4$ solutions at pH 1. [c] Percentage of initial reaction (25% Cr = 100% Ru). [d] Shoulder. [e] Larger errors are associated with solutions containing both Ru and Cr. Thus, it appears that essentially all of the Ru and Cr have been recovered. [f] Three bands are separated with the 2.0 M eluent.

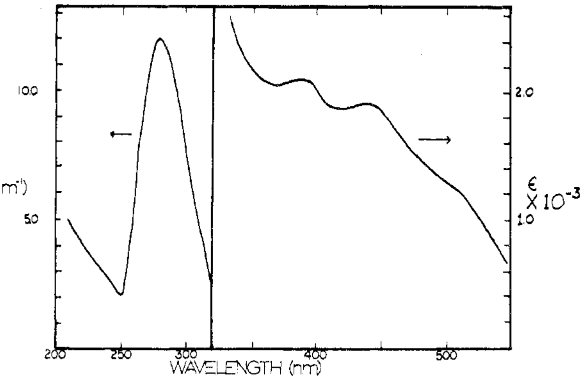


Figure 4. Electronic spectrum of $[(H_2O)_5Ru{-}\ddot{N}H{-}Cr(H_2O)_5]^{5+}$ in 1.0 M $NaClO_4$ (0.1 M H^+).

nm, ϵ 23 M^{-1} cm^{-1}; λ_{max} 345 nm, ϵ 57 M^{-1} cm^{-1}) is similar in shape and intensity to those of other ruthenium nitrosyls.[35] Shreiner et al.[35] have suggested that for complexes of the general formula $Ru(NH_3)_4(NO)L^{n+}$ (L = NH_3, NCO^-, N_3^-, OAc^-, Cl^-, OH^-, Br^-) the lower energy band possesses both "d–d" and charge-transfer ($t_{2g} \rightarrow \pi^*(NO)$) components and a similar assignment can probably be made for $Ru(H_2O)_5NO^{3+}$.

The $Ru(H_2O)_5NO^{3+}$ could be converted to *trans*-$[Ru(NH_3)_4NO(H_2O)]Cl_3$ by slowly adding pentaaquonitrosylruthenium(3+) in 1 M HTFMS to liquid ammonia,[36] allowing the excess ammonia to evaporate at room temperature, acidifying, adding NaCl, and filtering the precipitate. The orange complex produced in this manner exhibited an infrared spectrum similar to that of *trans*-$[Ru(NH_3)_4NO(H_2O)]Cl_3$[37] with the characteristically intense ν_{NO} at 1922 cm^{-1} and ν_{Ru-NO} at 610 cm^{-1}.

$Ru(H_2O)_5NO^{3+}$ + $Cr(H_2O)_6^{2+}$: Stoichiometry and Product Analysis. Treatment of acidic aqueous solutions of $Ru(H_2O)_5NO^{3+}$ with Cr^{2+} leads to an immediate color change from orange to brown. A rapid rise in the absorbance is observed from 500 to 200 nm, and the dominant feature becomes an intense maximum at 280 nm. Figure 3 shows that the intensity at 280 nm (based on total ruthenium present) increases linearly until the $[Cr^{2+}]/[RuNO^{3+}]$ ratio reaches 4 and then levels off even when large excesses of Cr^{2+} ($[Cr^{2+}]/[RuNO^{3+}] > 4$)[38] are present. Except for the expected change in absorbance due to reaction of excess Cr^{2+} with O_2, the product solutions are insensitive to oxygen. The presence of chloride ion in either the reaction medium or the coordination sphere of the ruthenium appears to have little effect on the stoichiometry of the reaction. Solutions containing chloride ion were obtained by removing $Ru(H_2O)_5NO^{3+}$ from Dowex 50W-X8 resin with 1.0 M HCl eluent and then quickly reduced with $Cr(H_2O)_6^{2+}$. The stoichiometry and spectral results are identical with those of the reduction in 1.0 M HTFMS medium. The reduction of $K_2[RuCl_5NO]$ with chromium(II) in 0.5 M HCl also consumes approximately 4 equiv of the reductant and results in a product spectrum containing an intense maximum at 280 nm.

Table I lists the eluent concentrations, spectrum, color, percent chromium, and percent ruthenium of each fraction separated via ion-exchange chromatography from the 4-equiv reduction of $Ru(H_2O)_5NO^{3+}$ by $Cr(H_2O)_6^{2+}$ in 1.0 M HTFMS.

Approximately 70% of the initial chromium(II) is oxidized to $Cr(H_2O)_6^{3+}$ which can be identified from the color, charge, and visible spectrum (λ_{max} 408 nm, ϵ 13.3 M^{-1} cm^{-1}; λ_{max} 574 nm, ϵ 15.8 M^{-1} cm^{-1}).[39] One equivalent of ruthenium (50% of the initial) per equivalent of chromium (12% of the initial) is separated as an orange 4+ or 5+ charged complex. On the basis of the sum of the absorbances of separated products at 280 nm (which is equal to that of the reaction mixture), the orange product comprises ~65% of the total absorbance at this wavelength.

Four additional highly charged complexes are also separated. These contain varying ratios of chromium and ruthenium in lower yields and were not characterized further. The total chromium and ruthenium recovered after ion exchange accounts for essentially all of the starting material.

Hydroxylamine analyses of the product solution and each ion-exchanged fraction as a function of either the ratio of $Cr^{2+}:RuNO^{3+}$ = 2,3,4,6:1 or time were negative. Only a small amount of NH_4^+ (<10%) could be detected in the reaction solution or ion-exchanged fractions. Neither N_2 nor N_2O was detected as a gaseous product. The notable absence of free nitrogen species suggests that the nitrosyl nitrogen is retained in the products. Inasmuch as the orange product is composed of ~50% of the original ruthenium and is mainly responsible for the intense absorption at 280 nm, our efforts were focused on characterizing this species. Figure 4 shows the UV–vis spectrum of the orange product (from ion exchange) which has the spectral characteristics of the original product solution. While the absorbance near 500 nm (ϵ ~100 M^{-1} cm^{-1}) is unusual for ruthenium(II) or ruthenium(III) complexes containing simple ligands, the spectra of ruthenium(IV), existing in dimeric complexes, commonly are red and contain strong bands in the visible region.[40,41] Furthermore, the nitrido-bridged Ru(IV) dimer isolated by Griffith[42] absorbs strongly ($\epsilon \sim 20000$ M^{-1} cm^{-1}) in the ultraviolet region.

An extremely hygroscopic and difficult-to-handle brown solid was obtained by evaporating the solvent. Microanalysis[43] was obtained for the orange product in aqueous HTFMS medium or in the presence of KCl. (1) In HTFMS: obsd: Ru, 0.42 mg/mL; Cr, 0.210 mg/mL, which corresponds to 1 mol of Ru/mol of Cr. (2) In KCl after correcting for K = Cl: obsd: Ru, 4.75%; N, 0.53%; Cl, 3.77%, which corresponds to a 1:1 mole ratio of Ru:NCl_5. Repeated ruthenium and chromium analysis in our laboratory on the orange product solution also yielded 1 mol of ruthenium/mol of chromium. On the basis of its electronic spectrum, charge, and microanalysis, one possible structure of the orange complex is $[(H_2O)_5Ru^{IV}-\ddot{N}H-Cr^{III}(H_2O)_5]^{5+}$, I. This structure is also consistent with a 4:1 Cr:Ru stoichiometry, Figure 3. However, since this product only accounts for $\simeq$50% of the initial ruthenium nitrosyl, it must be assumed that most of the remaining ruthenium (and chromium) is in the form of polymers in which the nitrosyl has also undergone a net four-electron reduction. Given the high charge of these complexes and the absence of free nitrogen species, this is not altogether unreasonable.

Kinetics of $Ru(H_2O)_5NO^{3+}$ + $Cr(H_2O)_6^{2+}$. The rapid rise in absorbance from 500 to 200 nm due to the formation of the chromium–ruthenium dimer prevented any observations of the kinetics of the decay of the nitrosyl complex. Rates were obtained on the Durrum–Gibson stopped-flow spectrophotometer under pseudo-first-order conditions for the treatment of $Ru(H_2O)_5NO^{3+}$ with excesses of $Cr(H_2O)_6^{2+}$ by monitoring the formation of the dimer at 280.5 nm at 25.9 °C. Three consecutive reactions were observed all of which gave linear first-order plots through 3 half-lives. Specific rate constants of ($[Cr^{2+}]$ = 8 mM) 90.9 ± 0.3, 1.23 ± 0.02, and (3.2 ± 0.9) × 10^{-2} s^{-1} were obtained from these plots. The reactions were only approximately first order in $Cr(H_2O)_6^{2+}$ as indicated by the proportional increase in k_{obsd} with an increase in the chromium(II) concentration. The rate law for the reaction becomes

$$d[\text{Cr-Ru dimer}]/dt = k_2[Cr^{2+}][(H_2O)_5RuNO^{3+}]$$

in 1.0 M HTFMS. However, because of (1) the 4:1 stoichiometry, (2) the less than 100% yield of the aquo RuCr dimer, and (3) the less than strict first-order behavior of $Cr(H_2O)_6^{2+}$, a more detailed study of the kinetics of the reaction is warranted. The rate constants will serve as a comparison with the corresponding rate of reduction of $Ru(NH_3)_5NO^{3+}$ by Cr^{2+}, which will be discussed in the following sections.

$Ru(NH_3)_5NO^{3+}$ + $Cr(H_2O)_6^{2+}$. Earlier[11] we reported that the reduction of $Ru(NH_3)_5NO^{3+}$ with $Cr(H_2O)_6^{2+}$ in Cl^- medium consumes 6 equiv of chromium(II) and nearly quantitatively yields $Ru(NH_3)_6^{2+}$. At that time, preliminary studies showed that in the absence of chloride ion, hexaammineruthenium(II) is not the only product generated from this same reaction; an air-stable product is also formed which strongly absorbs with λ_{max} near 280 nm. Although there are significant differences, we have found the $Ru(NH_3)_5NO^{3+}$–$Cr(H_2O)_6^{2+}$ reduction (in the absence of Cl^-) to be quite similar to that in the $Ru(H_2O)_5NO^{3+}$–$Cr(H_2O)_6^{2+}$ system.

By monitoring the absorbance at 280 nm, Figure 5 shows that the reduction of $Ru(NH_3)_5NO^{3+}$ in acidic TFMS$^-$ medium consumes approximately 4 equiv of $Cr(H_2O)_6^{2+}$ and that the absorbance remains stable in excess chromium(II). The absorbance at 280 nm also remains stable upon bubbling the reaction solution with O_2.

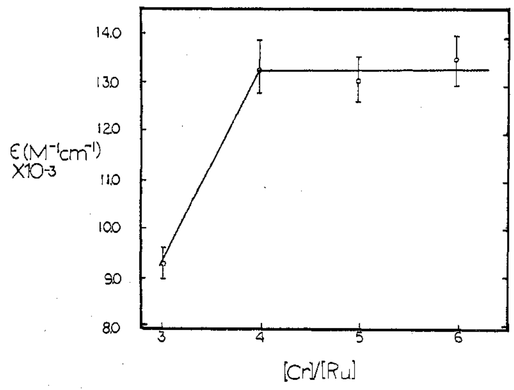


Figure 5. Extinction coefficient at 280 nm (based on total ruthenium concentration) vs. the ratio of the equivalents of Cr^{2+} per equivalent of $[Ru(NH_3)_5NO]^{3+}$ present in the reaction solution ($[H^+]$ = 0.5 M, μ = 1.0 (TFMS$^-$)).

Table II. Separation of the Reaction Products of the Reduction of 1 equiv of $Ru(NH_3)_5NO^{3+}$ by 4 equiv of $Cr(H_2O)_6^{2+}$ in Acidic TFMS$^-$ Medium and the Percentage of Chromium and Ruthenium in Each Fraction[a]

[Fraction],[b] M	Color	Species	% Ru[c,d]	% Cr[c,d]
Rinse				
0.2				
0.5	Blue	$Cr(H_2O)_6^{3+}$		60 ± 10
1.0[e]	Yellow	$[Ru(NH_3)_5OH_2]^{3+}$	20 ± 5	
	Green	$[Cr_2(OH)_2]^{4+}$		15 ± 3
1.5	Orange	RuCr dimer	70 ± 10	15 ± 5

[a] A greater than 5+ species remained on the column. [b] $NaClO_4$ solutions at pH 1. [c] Distribution error determined from the results of three product studies. [d] Percent of initial amount of reactant; there are 4 equiv of Cr^{2+}/equiv of $Ru(NH_3)_5NO^{3+}$ (25% Cr = 100% Ru). [e] Two bands are separated with the 1.0 M eluent.

Table II gives the product separation, color, identity, and percent of Ru and Cr of each fraction collected. Chromium(III),[39] aquopentaammineruthenium(III),[44] and chromium(III) dimer[45] were identified by comparing their UV–vis spectra with those previously reported. In addition to the spectral identification, $Ru(NH_3)_5OH_2^{3+}$ (λ_{max} 268 nm) was converted to $Ru(NH_3)_5Cl^{2+}$ (λ_{max} 327, ϵ 1.9 × 10^3 M^{-1} cm^{-1}).[44] This was accomplished by reducing the former complex in acidic Cl^- medium with Zn(Hg), removing the Hg amalgam, and then bubbling the solution with O_2.[46,47]

Figure 6 shows the UV–vis spectrum of the bright orange 5+ charged product which follows the Cr(III) dimer[45] off the ion-exchange column. This product contains approximately 70 ± 10% of the initial ruthenium and 1 equiv of chromium/equiv of ruthenium. A shoulder at 510 nm and inflection at 430 nm precede maxima at 340 nm (ϵ 234 M^{-1} cm^{-1}) and 280 nm (ϵ 1.36 × 10^4 M^{-1} cm^{-1}). As mentioned earlier, red color and visible absorptions are characteristic of Ru(IV) complexes.[40-42]

A comparison of the spectra of all the products shows that this orange product accounts for approximately 80% of the absorbance at 280 nm. The color, charge, spectrum, and metal analysis are nearly identical with those of the dimer (I) obtained from the chromium(II) reduction of $Ru(H_2O)_5NO^{3+}$.

Analysis of the separated complexes accounted for approximately all the initial chromium and ruthenium. A small amount of a highly charged gray product remained on the ion-exchange column and was not characterized further.

Product analysis also indicated free ammonia (the amount of which depended on the age of the reaction solution). For aliquots removed at different times from a reaction mixture

Table III. Vibrational Frequencies (cm^{-1}) for $[(H_2O)(NH_3)_4Ru\text{-}NH\text{-}Cr(H_2O)_5]Cl_5$ (A) and the Deuterated Analogue (B) in a KBr Matrix

Compd	ν_{NH}	ν_{NH_3}(asym)	ν_{NH_3}(sym)	ρ_{NH_3}	$\nu_{Ru\text{-}NH_3}$	Others
A	3200 s, b 2990 vw, sh 1410 w	1610 s, sh	1295 s, sh	779 m	440 w	982 w 866 w 533 w
B	2460 m, b 2310 m, b	1190 m	990 s	575 w, b	435 w	1423 m 1150 m 865 vw 510 sh 328 vw

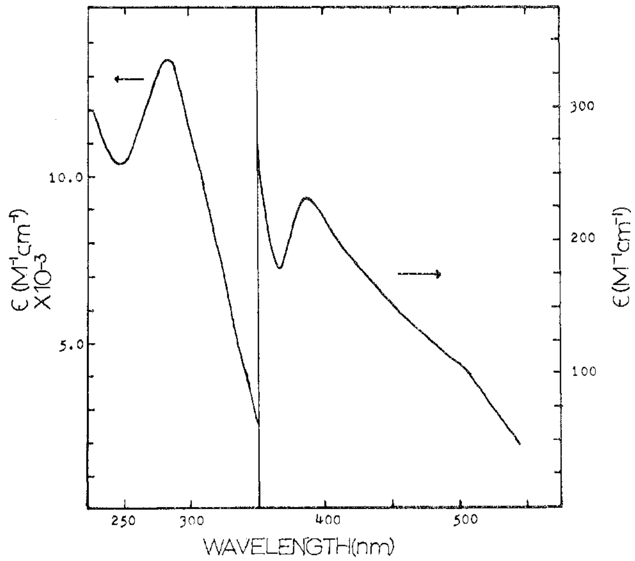


Figure 6. Electronic spectrum of $[(H_2O)(NH_3)_4Ru\text{-}H\underset{..}{N}\text{-}Cr(H_2O)_5]^{5+}$ in 2.0 M HCl.

initially containing 9.2×10^{-3} M $[Ru(NH_3)_5NO](TFMS)_3$ and 3.65×10^{-2} M $Cr(H_2O)_6^{2+}$ in 0.5 M HTFMS, approximately 1 equiv of free ammonia/equiv of ruthenium was recovered after 20 h and remained at this level for at least 3 days. Given the approximate 4:1 stoichiometry and the fact that the absorbance at 280 nm reaches a stable value much more rapidly than the release of ammonia, the appearance of ammonia must be due, at least in part, to the aquation of the ruthenium products.

The detection of 1 equiv of NH_3/initial equiv of $Ru(NH_3)_5NO^{3+}$ along with the separation of 20% of the initial complex as $Ru(NH_3)_5OH_2^{3+}$ suggests that this fraction of the original nitrosyl has been reduced to ammonia which would require 6 equiv of Cr^{2+}. Assuming that the remaining 70% is reduced by 4 equiv, the effect of this 20% on the overall stoichiometry would be within error of the spectral technique employed (which gives an approximate 4:1 value for the overall stoichiometry). In any event, it is apparent from the above that the major orange ruthenium product is formed via a 4:1 stoichiometric reduction of the nitrosyl and this product, once formed, slowly loses NH_3.

A brown noncrystalline solid is obtained by roto-evaporating to dryness the orange 2.0 M HCl fraction obtained from ion exchange on Dowex 50W-X8 which yielded the following elemental analysis (%): Ru, 19.17; Cr, 9.99; N, 13.89; Cl, 31.95; H, 4.77. This analysis leads to an empirical formula of $RuCrN_5H_{25}$. On the basis of the stoichiometry charge, UV–vis spectrum, and microanalysis the following heteronuclear dimer can be formulated: $[(H_2O)(NH_3)_4Ru^{IV}\text{–}\underset{..}{N}H\text{–}Cr^{III}(H_2O)_5]Cl_5$, II. The calculated elemental analysis for this complex yields the following (%): Ru, 19.38; Cr, 9.94; N, 13.44; Cl, 34.03; H, 4.79. It was also found that the dimer slowly decomposed in concentrated HCl and upon standing overnight turned from orange to green and yielded the orange precipitate $Ru(NH_3)_5Cl_3{\cdot}H_2O$ for which the following microanalysis was obtained. Anal. Calcd: Ru, 32.5; N, 22.5; Cl, 34.3; H, 4.83. Found: Ru, 31.79; N, 22.5; Cl, 36.0; H, 4.85. Also, the UV–vis spectrum of the orange precipitate shows a maximum at 327 nm which is characteristic of $Ru(NH_3)_5Cl^{2+}$.[44] The filtrate, which was not analyzed further, probably contained green chlorochromium species. It is important to note that decomposition occurs only slowly and redissolution of the solid dimer obtained by roto-evaporation, which also gives concentrated HCl, shows a UV–vis spectrum indicating some slight decomposition.

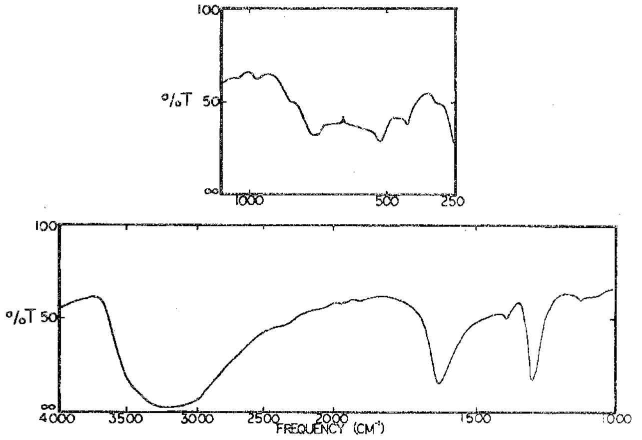


Figure 7. Infrared spectrum of $[(H_2O)(NH_3)_4Ru\text{–}H\underset{..}{N}\text{–}Cr(H_2O)_5]Cl_5$ in a KBr matrix.

In an attempt to determine the exact nature of the bridging ligand, the infrared spectrum of the solid (II) was obtained in a KBr matrix, Figure 7. Table III gives the band maxima for this compound and the deuterated analogue along with assignments for those bands readily identified as ammine or aquo in origin.

It is evident that the dimer obtained in this study does not contain an O^{2-} or OH^- bridge which is characterized by strong maxima (assigned to the Ru–X–Ru vibration) located near 1070, 880, and 570 cm^{-1} respectively, for the several known homometallic dimeric complexes.[48] Medium-strong bands at 558 and 525 cm^{-1} occur for known imido- and amido-bridged complexes, respectively.[48] Because of the large background-coordinated H_2O absorption,[49] this region is not definitive for the dimer isolated in this study. However, one cannot rule out either possibility.

Kinetics of $Ru(NH_3)_5NO^{3+}$ + $Cr(H_2O)_6^{2+}$. The reduction of $Ru(NH_3)_5NO^{3+}$ in 0.5 M $[H^+]$, $\mu = 1.0$ (adjusted with NaTFMS), at 25.0 °C under pseudo-first-order conditions with excesses of chromium(II) is slow and could be monitored on the Cary 14 by following the rate of formation of the chromium–ruthenium ammine dimer at the 280-nm maximum. A linear first-order plot was obtained through 1 half-life before upward and then downward deviations from linearity appear. For the first half-life no marked pH dependence was observed in the range $[H^+] = 0.1\text{–}0.9$ M HTFMS. Figure 8 shows the good first-order dependence on $[Cr^{2+}]$ and yields the second-order rate constant $k_2 = 2.18 \times 10^{-3}$ M^{-1} s^{-1} and

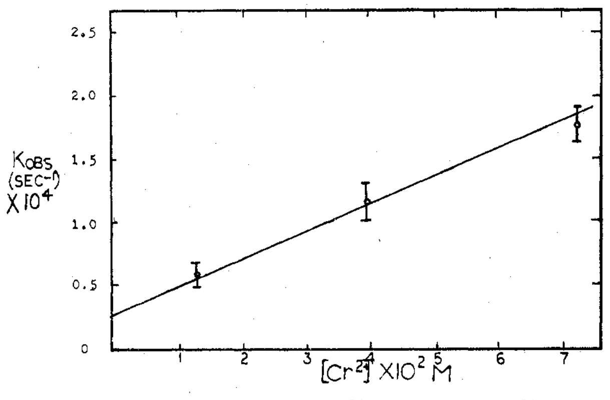


Figure 8. Dependence of K_{obsd} upon Cr^{2+}; $[Ru(NH_3)_5NO^{3+}] = 1.35 \times 10^{-4}$ M at 25 °C, $\mu = 1.0$.

intercept of 2.6×10^{-5} s^{-1}. The rate law for this step in the reduction can be written

$$d[\text{Ru-Cr dimer}]/dt = k_2[Cr^{2+}][Ru(NH_3)_5NO^{3+}]$$

in 0.5 M HTFMS. Because of the deviation from strict pseudo-first-order behavior, a more detailed picture of the kinetics was not obtained at this time.

***cis*- and *trans*-$Ru(NH_3)_4NO(L)^{2+}$ + $Cr(H_2O)_6^{2+}$, Where L^- = Cl^- or OH^-.** Preliminary data for the chromium(II) reduction of *trans*-$[Ru(NH_3)_4NO(Cl)]^{2+}$, *trans*-$[Ru(NH_3)_4NO(OH)]^{2+}$, and *cis*-$[Ru(NH_3)_4NO(Cl)]^{2+}$ were also collected. In the absence of Cl^-, reduction of the trans complexes gave a stoichiometry plot identical with Figure 5 indicating a 4:1 Cr:Ru stoichiometry. A product study of the reduction of the *trans*-$[Ru(NH_3)_4NO(Cl)]^{2+}$ was nearly identical with that obtained for the $Ru(NH_3)_5NO^{3+}$ reduction except that only a small amount of free NH_3 was recovered in the product studies. These results are consistent with the proposed formula of the dimer (II) in which the bridging ligand originates from the nitrosyl ligand. For the *cis*-$Ru(NH_3)_4NO(Cl)^{2+}$, the production of the orange chromium–ruthenium dimer also occurs suggesting that cis–trans isomerization occurs during reduction by $Cr.^{2+}$

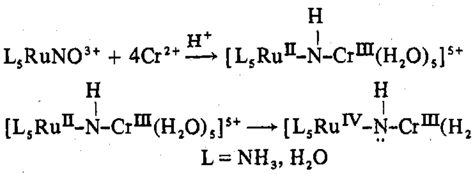
Discussion

The μ-imido ruthenium–chromium dimers isolated in this study are the first known stable single-atom-bridged complexes containing these metals. Bimetallic dimers of chromium and ruthenium have been observed with complex bridging groups.[50] As in previous studies, the dimers are evidence for inner-sphere electron transfer (in this instance involving the nitrosyl or a reduced fragment thereof).

We have previously found[9,10] that several chromium nitrosyls undergo a $2e^-$ reduction to form hydroxylamine. The chromium nitrosyls, on the basis of the d–d spectrum and ν_{NO} (which occurs at 1730 cm^{-1} for $[Cr(NH_3)_5NO](ClO_4)_2$), are considered to formally contain the $[Cr^{III}\text{–}NO^-]$ entity,[51] while the ruthenium complexes based on their characteristic d–d spectrum and ν_{NO} (which occurs at 1908 cm^{-1} for $[Ru(NH_3)_5NO]Br_3$)[31] are considered to formally contain the $[Ru^{II}\text{–}NO^+]$ moiety.[52] Consequently, the $2e^-$ reduction for the chromium nitrosyls to form hydroxylamine is analogous to the $4e^-$ reduction of the ruthenium nitrosyls. However, by simply replacing ruthenium for chromium as the metal center, there is a striking difference in the nature of the products.

Given the complexity of the reaction, a simple but plausible reaction scheme is one which involves reduction of the nitrosyl ligand to a nitrene intermediate[53] (reactions 1 and 2).

Basolo and co-workers[54a,b] have postulated ruthenium nitrene intermediates for reactions involving azide. The species represented in reaction 2 are actually valence resonance



$$L_5RuNO^{3+} + 4Cr^{2+} \xrightarrow{H^+} [L_5Ru^{II}\text{-}\overset{H}{N}\text{-}Cr^{III}(H_2O)_5]^{5+} \quad (1)$$

$$[L_5Ru^{II}\text{-}\overset{H}{N}\text{-}Cr^{III}(H_2O)_5]^{5+} \longrightarrow [L_5Ru^{IV}\text{-}\overset{H}{\ddot{N}}\text{-}Cr^{III}(H_2O)_5]^{5+} \quad (2)$$

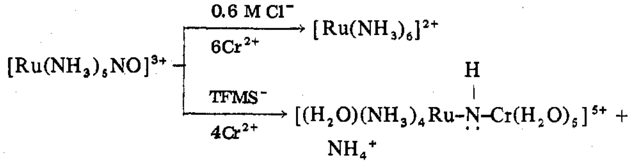
$$L = NH_3, H_2O$$

structures, whereby stabilization of the highly electrophillic nitrene occurs by an internal transfer of electrons from ruthenium(II). The stability of the resulting dimer is the result of the inherent substitution inertia of chromium(III) and the multiple-bond character of ruthenium–imido bond. Stable Ru(IV) dimeric complexes containing π-donor nitrido bridges have been reported,[7] and it is important to note that these complexes are prepared by the reduction of ruthenium nitrosyls with Sn^{2+}. As in the present study, these data indicate that the $[Ru^{IV}\text{–}\ddot{N}\text{–}M]$ framework ($M = Ru^{IV}, Cr^{III}$) is usually stable toward further reduction.

The absence of a nitride band in the infrared spectrum as well as the charge analysis and microanalysis requires that the dimers isolated in this study contain an imido bridge. Since the π donation in the chromium–ruthenium dimer is directed toward one Ru(IV) center (as opposed to two in the $Ru^{IV}{}_2N$ dimers) greater electron density on the nitride may lead to protonation. The slow aquation of the ammine dimer results from the trans-labilizing effect of the strong σ- and π-donor imido bridge. A similar effect results in trans aquo ligands for a number of bridged Ru(IV) dimers (i.e., $K_3[Ru_2NCl_8(H_2O)_2]$[7]), and the crystal structure of the diamido-bridged "ruthenium black" reveals lengthening of the trans metal–ammine bonds.[55]

Central to the issue of postulating a nitrene intermediate is the effect of Cl^- on the nature of the reaction products for the reduction of $Ru(NH_3)_5NO^{3+}$ by Cr^{2+}. In the presence of excess Cl^-, the reduction results in rapid and quantitative production of $Ru(NH_3)_6{}^{2+}$.[11] This study has shown that in the absence of Cl^-, the reaction is much slower and mainly produces the heterometallic dimer. These results are to be compared to the reduction of azide and organic azides by Cr^{2+}.[56,57] In addition to N_2, small amounts of $(CrN(R)Cr)^{4+}$ ($R = H$,[56] CH_3, C_2H_5, $n\text{-}C_3H_7$[57]) are produced in the absence of Cl^-, as opposed to the quantitative formation of ammonia or amines in excesses of Cl^-. As in the present study, these reactions are quite complicated; however, they all suggest the Cl^- may react directly with an electron-deficient intermediate which inhibits dimerization and promotes reduction to coordinated ammonia and/or organoamines.

In the present study, the effect of Cl^- on the stoichiometry and products as well as the rate suggests a similar role of Cl^-. Scavenging of nitrene intermediates by Cl^- has been reported.[54] Hence, it appears that two pathways exist for the reduction:



The overall rate law may be modified to include the chloride term

$$-d[Ru(NH_3)_5NO^{3+}]/dt = k[Ru(NH_3)_5NO^{3+}][Cr^{2+}] + k'[Ru(NH_3)_5NO^{3+}][Cr^{2+}][Cl^-]$$

We have also observed this same effect of Cl^- with the powerful outer-sphere reductant Zn(Hg) which reduces $Ru(NH_3)_5NO^{3+}$ to $Ru(NH_3)_6{}^{2+}$ in high yield in the presence of Cl^- but not in the presence of the $TFMS^-$ anion.[58] Finally, the replacement of ammine with aquo ligands results in an increase in the rate of formation of the dimer by a factor of

10^4. This rate enhancement may explain the absence of a Cl^- effect on the $Ru(H_2O)_5NO^{3+}$–Cr^{2+} reduction.

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Registry No. I, 64294-49-1; II, 64294-50-4; $[(NH_3)_5Ru\text{-}NH\text{-}Cr(H_2O)_5]^{5+}$, 64294-51-5; $[Ru(NH_3)_5NO](TFMS)_3$, 64200-43-7; $K_2[RuCl_5(H_2O)]$, 14404-33-2; $Ru(H_2O)_6^{2+}$, 30251-71-9; $Ru(H_2O)_6^{3+}$, 30251-72-0; $Ru(H_2O)_5NO^{3+}$, 56586-57-3; $K_2[RuCl_5NO]$, 14854-54-7; $[Ru(NH_3)_5OH_2]^{3+}$, 25590-52-7; $[Cr_2(OH)_2]^{4+}$, 12323-96-5; $Ru(NH_3)_5Cl_3$, 18532-87-1; *trans*-$[Ru(NH_3)_4NO(Cl)]^{2+}$, 20094-12-6; *trans*-$[Ru(NH_3)_4NO(OH)]^{2+}$, 52720-69-1; *cis*-$[Ru(NH_3)_4NO(Cl)]^{2+}$, 52707-08-1; $Cr(H_2O)_6^{3+}$, 14873-01-9; $Cr(H_2O)_6^{2+}$, 20574-26-9.

References and Notes

(1) Abstracted in part from the Ph.D. thesis of R. P. Cheney, Boston University, 1976.
(2) To whom correspondence should be addressed at Allied Chemical Corp., P.O. Box 1021 R, Morristown, N.J. 07960.
(3) R. T. M. Fraser, *J. Chem. Soc.*, 3641 (1965).
(4) W. P. Griffith, *J. Chem. Soc.*, 3286 (1963).
(5) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals", Interscience, New York, N.Y. 1967.
(6) M. J. Cleare and W. P. Griffith, *Chem. Commun.*, 1302 (1968).
(7) M. J. Cleare and W. P. Griffith, *J. Chem. Soc. A*, 1117 (1970).
(8) H. Mukaida, *Bull. Chem. Soc. Jpn.*, **43**, 3805 (1970).
(9) J. N. Armor and M. Buchbinder, *Inorg. Chem.*, **12**, 1086 (1973).
(10) J. N. Armor, M. Buchbinder, and R. Cheney, *Inorg. Chem.*, **13**, 2991 (1974).
(11) J. N. Armor, *Inorg. Chem.*, **12**, 1959 (1973).
(12) G. W. Haupt, *J. Res. Natl. Bur. Stand.*, **48**, 414 (1952).
(13) B. E. Saltzman, *Anal. Chem.*, **24**, 1016 (1952).
(14) P. F. Urone, *Anal. Chem.*, **27**, 354 (1955).
(15) J. N. Armor, R. Furman, and, M. Z. Hoffman, *J. Am. Chem. Soc.*, **97**, 1734 (1975).
(16) J. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 5039 (1961).
(17) Determined in our laboratory at the ruthenate–perruthenate isosbestic point.
(18) D. P. Johnson, *Anal. Chem.*, **40**, 646 (1968).
(19) J. N. Armor, H. Scheidegger, and H. Taube, *J. Am. Chem. Soc.*, **90**, 3263 (1968).
(20) P. F. Boltz, Ed., "Colormetric Determination of Non-Metals", Interscience, New York, N.Y., 1958, p 124.
(21) J. N. Armor and H. Taube, *Chem. Commun.*, 287 (1971).
(22) A. C. Scott, M.S. Thesis, Stanford University, 1969.
(23) J. N. Armor, H. Scheidegger, and H. Taube, *J. Am. Chem. Soc.*, **90**, 5928 (1968).
(24) K. Gleu and I. Buddecker, *Z. Anorg. Allg. Chem.*, **268**, 202 (1952).
(25) E. E. Mercer and R. R. Buckley, *Inorg. Chem.*, **4**, 1692 (1965).
(26) C. Creutz and H. Taube, *Inorg. Chem.*, **10**, 2664 (1971).
(27) E. E. Mercer and P. E. Dumas, *Inorg. Chem.*, **10**, 2755 (1971).
(28) T. W. Kallen and J. E. Early, *Inorg. Chem.*, **10**, 1149 (1971).
(29) E. E. Mercer and A. B. Cox, *Inorg. Chim. Acta*, **6**, 577 (1972).
(30) E. E. Mercer, W. M. Campbell, Jr., and R. M. Wallace, *Inorg. Chem.*, **3**, 1018 (1964).
(31) S. Pell and J. N. Armor, *Inorg. Chem.*, **12**, 873 (1973).
(32) C. C. Kuehn and H. Taube, *J. Am. Chem. Soc.* **98**, 689 (1976).
(33) J. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).
(34) B. F. G. Johnson and J. A. MCleverty, *Prog. Inorg. Chem.*, **7**, 277 (1966).
(35) A. F. Schreiner, S. W. Lin, P. J. Hauser, E. A. Hopcus, D. J. Hamm, and J. D. Gunter, *Inorg. Chem.*, **11**, 330 (1972).
(36) M. B. Fairley and R. J. Irving, *J. Chem. Soc. A*, 475 (1966).
(37) J. N. Armor, Ph.D. Thesis, Stanford University, 1970.
(38) $\epsilon(Cr^{2+})$(at 280 nm) 18 M^{-1} cm^{-1}.
(39) L. B. Anderson and R. A. Plane, *Inorg. Chem.*, **3**, 1470 (1964).
(40) D. F. P. Rudd and H. Taube, *Inorg. Chem.*, **10**, 1543 (1971).
(41) R. M. Wallace and R. C. Propst, *J. Am. Chem. Soc.*, **91**, 3779 (1969).
(42) M. J. Cleare, F. M. Lever, and W. P. Griffith, *Adv. Chem. Ser.*, **No. 98**, Chapter 5 (1971).
(43) Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.
(44) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).
(45) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).
(46) J. N. Armor and H. Taube, *J. Am. Chem. Soc.*, **92**, 6170 (1970).
(47) P. C. Ford, D. F. P. Rudd, R. G. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).
(48) D. J. Hewkin and W. P. Griffith, *J. Chem. Soc. A*, 472 (1966).
(49) K. Nakamato, "Infrared Spectra of Inorganic and Coordination Complexes", Wiley, New York, N.Y., 1963, p 156.
(50) R. G. Gaunder and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970).
(51) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1497 (1971).
(52) R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8**, 26, (1975).
(53) "Nitrene" refers to the coordinated, electron-deficient radical $\ddot{N}H\cdot$.
(54) (a) P. S. Sheridan and F. Basolo, *Inorg. Chem.*, **11**, 2721 (1972); (b) L. A. P. Kane–Maguire, P. S. Sheridan, F. Basolo, and, R. G. Pearson, *J. Am. Chem. Soc.*, **92**, 5865 (1970); (c) B. C. Lane, J. W. MacDonald, F. Basolo, and, R. Pearson, *ibid.*, **94**, 3786 (1972).
(55) M. T. Flood, R. F. Ziolo, J. E. Earley, and H. B. Gray, *Inorg. Chem.*, **12**, 2153 (1973).
(56) M. Ardon and B. E. Meyer, *J. Chem. Soc.*, 2816 (1962).
(57) E. J. Kaufmann and R. C. Thompson, *J. Am. Chem. Soc.*, **99**, 1824 (1977).
(58) R. P. Cheney, Ph.D. Thesis, Boston University, 1975.

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Kinetics of Reduction of $Ru(NH_3)_6^{3+}$ and of $Ru(NH_3)_5Cl^{2+}$ by Ti(III)

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Both $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ (in Cl^- and $CF_3SO_3^-$ media) are reduced by Ti(III) in second-order reactions. Rate constants for both reactions are inversely proportional to $[H^+]$, indicating that $TiOH^{2+}$, not Ti^{3+}, is the reductant. Rate constants (at 25 °C) for reduction by $TiOH^{2+}$ are 35 and 12 M^{-1} s^{-1}; corresponding activation enthalpies are 41 and 33 kJ/mol. Outer-sphere electron transfer is indicated for both reactions. The relative values of the rate constants accord with expectations based on the free-energy changes involved.

Since Ti^{3+} is a d^1 ion and Ru(III) complexes are low-spin d^5, Ti(III)–Ru(III) redox reactions involve t_{2g} orbitals both as donor and as acceptor orbitals. In the expectation that this circumstance would lead to interesting redox behavior, we have studied reduction of $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ by Ti^{3+}. Since both Ti^{3+} and Ru(II) reduce ClO_4^-, we used Cl^- and $CF_3SO_3^-$ media.

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