Studies on the Rate of Reduction of Ruthenium(III) Complexes by Chromium(II) and Vanadium(II)

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Abstract: The rates of reduction of $Ru(NH_3)_5Cl^{2+}$, *cis*-$Ru(NH_3)_4Cl_2^+$, *cis*-$Ru(NH_3)_4H_2OCl^{2+}$, *trans*-$Ru(NH_3)_4Cl_2^+$, and *trans*-$Ru(NH_3)_4H_2OCl^{2+}$ by Cr(II) and V(II) were measured. The Cr(II) reductions of $Ru(NH_3)_5Cl^{2+}$ and the *cis* complexes proceed by a mechanism involving a chloride-bridged intermediate, within which there is reversible electron transfer prior to decomposition of the intermediate to products. The Cr(II) reduction of *trans*-$Ru(NH_3)_4Cl_2^+$ follows second-order kinetics. The V(II) reductions are outer sphere and follow second-order kinetics. The rates of the V(II) reductions do not parallel the trend observed for Co(III) complexes as the complexes are varied. Data are presented concerning the aquation rates of several Ru(II) complexes that were observed as secondary reactions following the above reductions. An equilibrium constant for the formation of a chloride-bridged binuclear intermediate prior to electron transfer is calculated.

Although the effect on the rate of transition metal oxidation–reduction reactions with a change in the nonbridging ligands is an area of research that has attracted considerable interest,[1-9] most studies have been concerned with complexes of Co(III) and Cr(III). These complexes are quite inert to substitution and are relatively easily synthesized. This concentration of effort on Cr(III) and Co(III) complexes has resulted, on one hand, in the accumulation of a considerable amount of data on the effect of nonbridging ligands on the rate of these reductions, but on the other hand, has led to a situation in which advantage of a significant variation in the electronic structure of the oxidant has not been taken. Such a variation could prove helpful in understanding the nature of the nonbridging ligand effect.

There is a striking correlation between the rates of reduction of variously substituted Co(III) complexes and similarly substituted Cr(III) complexes. This correlation can be understood as a reflection of the similar electronic properties of the two metal-ion systems. Reducing a Co(III) complex requires population of an orbital of e_g symmetry (in pseudooctahedral notation); it seems likely that such an orbital is also initially populated upon reduction of Cr(III) complexes since the t_{2g}^4 configuration of Cr(II) is generally unstable. It was suggested several years ago[10] that in cases such as these a specific effect on the rate of reduction as the nonbridging ligands were varied might be expected. Benson and Haim[1] extended this argument in one manner, while Bifano and Linck[5] took a somewhat different approach. This latter approach was to use the relative energy of the e_g orbital to be populated as a measure of the relative energy necessary to bring about the distortion of the complex to that proper nuclear geometry in which electron transfer could take place. The higher the energy of this orbital, the more energy is necessary to distort the complex properly, and hence the slower the rate of reaction. In the case of Co(III) and Cr(III) complexes the symmetry of the lowest lying empty orbital is such that the σ-bonding power of the ligands is the proper bonding interaction of concern in an estimate of relative energies. In a complex in which the orbital to be populated is of t_{2g} symmetry, the π-bonding power of the ligands would be the bonding interaction of importance. A system to test this latter suggestion is available. Complexes of Ru(III), t_{2g}^5, are sufficiently inert to allow synthesis of complexes of fixed stereochemistry, which, when reduced, yield product complexes of Ru(II) of t_{2g}^6 electronic configuration. We wish to report here the kinetics of the Cr(II) and V(II) reduction of variously substituted Ru(III)–chloroammine complexes.

Our studies with Cr(II) as a reductant have not led to an answer to the original question posed. In these cases, the substitution behavior of the reagents completely dominates the electron-transfer process. Nevertheless, these experiments are of value for they shed light on the aquation rates of several of the Ru(II) complexes which are products of the reduction. Such information, important in its own right in that it helps elucidate the substitution reactivity of a d^6 system in the 2+ valence state, is significant in another context also. We have found that from these data we can obtain information concerning the energetics of formation of a binuclear intermediate with two metal-ion centers bridged by a chloride ion. Such information is of value if one is to understand the detailed energies involved in formation of inner-sphere electron-transfer transition states.

On the other hand, the results of the V(II) reduction of chloroamine–Ru(III) complexes has shed light on the question concerning the role played by electronic structure in the determination of nonbridging ligand effects.

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Experimental Section

The complexes, $[Ru(NH_3)_5Cl]Cl_2$,[11,12] $[$*cis*-$Ru(NH_3)_4Cl_2]Cl \cdot {}^2/_3H_2O$,[13,14] $[$*trans*-$Ru(NH_3)_4Cl_2]Cl \cdot H_2O$,[15-17] and $[$*cis*-$Ru(bipy)_2Cl_2]Cl \cdot 2H_2O$[18] were prepared by standard literature methods. Ruthenium analyses[19-21] agree with theoretical expectations and the spectra agree with literature values, where the latter are known. The spectrum of $[$*trans*-$Ru(NH_3)_4Cl_2] \cdot H_2O$ is reported here for the first time. *Anal.* Calcd for $[Ru(NH_3)_5Cl]Cl_2$: Ru, 34.6. Found: Ru, 35.7. λ, Å (ϵ, l. mol^{-1} cm^{-1}), 3300 (1860); lit.[22] 3280 (1930). *Anal.* Calcd for $[$*cis*-$Ru(NH_3)_4Cl_2]Cl \cdot {}^2/_3H_2O$: Ru, 35.2. Found: Ru, 35.2. λ (ϵ), 3530 (1580), 3100 (1350), 2620 (500); lit.[22] 3520 (1640), 3100 (1380), 2620 (520). *Anal.* Calcd for $[$*trans*-$Ru(NH_3)_4Cl_2]Cl \cdot H_2O$: Ru, 34.5. Found: Ru 35.3. λ (ϵ), 5150 (14), 4550 (sh), 4130 (22), 3330 (4700). λ (ϵ) for $[$*cis*-$Ru(bipy)_2Cl_2]Cl \cdot 2H_2O$: 3690 (5550), 3120 (28,800), 3010 (26,300), 2530 (23,700); lit.[23] 3790 (5100), 3110 (27,000), 2990 (28,000), 2520 (28,000).

***cis*-Chloroaquotetraammineruthenium(III) *p*-toluenesulfonate monohydrate, $[$*cis*-$Ru(NH_3)_4ClH_2O](C_7H_7SO_3)_2 \cdot H_2O$,** was prepared in analogy to the corresponding ethylenediamine compound.[24] In 10 ml of water were suspended 0.299 g of $[$*cis*-$Ru(NH_3)_4Cl_2]Cl \cdot {}^2/_3H_2O$ (1.04 mmol) and 0.580 g of silver *p*-toluenesulfonate (2.08 mmol), prepared from Ag_2O and *p*-toluenesulfonic acid. This mixture was heated near boiling for 10 min. The precipitated AgCl was filtered out while hot (yield, 0.296 g; calcd, 0.298 g). Upon cooling the yellow filtrate, light yellow needles were deposited, which were filtered and dried *in vacuo*. The complex was recrystallized from hot water (yield, 0.314 g, 54%; λ (ϵ), 3250 (1110)). *Anal.* Calcd for $C_{14}H_{30}ClN_4O_8RuS_2$: C, 28.83; H, 5.10; Cl, 6.09; Ru, 17.38. Found: C, 29.22; H, 5.16; Cl, 6.20; Ru, 17.12. Additional product could be obtained from the filtrate by addition of *p*-toluenesulfonic acid but was contaminated with acid.

***trans*-Chloroaquotetraammineruthenium(III) *p*-Toluenesulfonate Monohydrate, $[$*trans*-$Ru(NH_3)_4ClH_2O](C_7H_7SO_3)_2 \cdot H_2O$.** In 8 ml of water were suspended 0.305 g of $[$*trans*-$Ru(NH_3)_4Cl_2]Cl \cdot H_2O$ (1.04 mmol) and 0.580 g of silver *p*-toluenesulfonate (2.08 mmol). This mixture was heated near boiling for 25 min, during which the solution turned dark brown. (The 10-min heating time used in the synthesis of the *cis* complex was not sufficient to precipitate all of the AgCl.) The solution was filtered while hot (yield of AgCl, 0.291 g; calcd, 0.298 g). Upon cooling the filtrate, light yellow flakes with a green tinge were deposited; these were filtered, washed with acetone, and dried *in vacuo*. The complex was recrystallized from hot water (yield, 0.296 g, 51%; λ (ϵ), 3230 (2010)). *Anal.* Calcd for $C_{14}H_{30}ClN_4O_8RuS_2$: C, 28.83; H, 5.10; Cl, 6.09; Ru, 17.38. Found: C, 28.52; H, 5.15; Cl, 6.52; Ru, 16.75. The spectrum of the dark brown filtrate showed that it contained no appreciable quantities of product.

Chromium(II) solutions were prepared from chromium metal and *p*-toluenesulfonic acid solutions. Reaction was initiated with a small quantity of zinc metal. Chromium(II) solutions in chloride media were prepared by reducing green $CrCl_3 \cdot 6H_2O$ with amalgamated zinc in HCl solution. These solutions were analyzed by syringing an aliquot into deaerated excess known iodate, adding excess iodide, and titrating with thiosulfate.

Vanadium(II) solutions were prepared by amalgamated zinc reduction of solutions of vanadyl *p*-toluenesulfonate; the latter solution was prepared from vanadyl sulfate, barium carbonate, and *p*-toluenesulfonic acid. The concentration of V(II) was analyzed by syringing the V(II) solution into deaerated solutions of excess $[Co(NH_3)_5N_3](ClO_4)_2$, allowing the reaction to proceed to completion,[25] and observing the spectrum at 5180 Å, a maximum for the Co(III) complex. Solutions of $[Co(NH_3)_5N_3](ClO_4)_2$ were kept in dark containers to obviate photodecomposition.[26,27] From the spectrum and known molar absorptivities of $Co(NH_3)_5N_3{}^{2+}$,[28] Co^{2+},[29] and V^{3+},[30] the V(II) concentration was calculated.

All kinetic measurements were made in 0.10 *M* *p*-toluenesulfonic acid solution and at 25° unless otherwise stated. *p*-Toluenesulfonic acid monohydrate was obtained from Eastman and was recrystallized from diethyl ether before use. Mixed solutions of sodium *p*-toluenesulfonic acid and sodium *p*-toluenesulfonate were prepared from 0.1 *M* *p*-toluenesulfonic acid and sodium carbonate. All water was doubly distilled. All solutions were freed of dissolved oxygen by deaerating using N_2 or Ar as the carrier gas. The results of the kinetic experiments were independent of the nature of the carrier gas. Standard syringe techniques were used throughout with no loss of titer observed upon transfer of air-sensitive solutions. Transmittance *vs.* time curves were obtained on a Durrum–Gibson stopped-flow spectrometer.

Results

Stoichiometry. Stoichiometries for the Cr(II) reduction of $Ru(NH_3)_5Cl^{2+}$[31] and *cis*-$Ru(NH_3)_4Cl_2{}^+$[19] have been reported previously and involve 1 mol of Ru(III) complex per mole of Cr(II); $Cr(H_2O)_5Cl^{2+}$ is the Cr(III) product. No proof is extant on the nature of the Ru(II) product, although the results of Ford and Sutton[32] would imply that the stereochemistry of the ruthenium center is maintained, with water molecules replacing chlorides. We have established this same stoichiometry for the Cr(II) reduction of *cis*-$Ru(NH_3)_4ClH_2O^{2+}$. A solution of this complex, 1.23×10^{-3} *M*, was made 9.5×10^{-4} *M* in Cr(II), and then inspected spectrophotometrically in the region 7000–3000 Å. A peak with λ_{max} 6030 Å, ϵ 15 ± 2 M^{-1} cm^{-1}, based on total chromium concentration, was observed. Literature values[33] for $Cr(H_2O)_5Cl^{2+}$ are λ_{max} 6070 Å, ϵ 16.4 M^{-1} cm^{-1}.

Similar experiments with *trans*-$Ru(NH_3)_4Cl_2{}^+$ and *trans*-$Ru(NH_3)_4ClH_2O^{2+}$ do not give interpretable results. The presence of a broad band in the region 5700–6100 Å failed to confirm the sole existence of either $Cr(H_2O)_6{}^{3+}$ or $Cr(H_2O)_5Cl^{2+}$ by simple spectroscopic techniques. In an ion-exchange experiment, a solution of *trans*-$Ru(NH_3)_4Cl_2{}^+$ was prepared in 0.1 *M* HCl and reacted with less than one equivalent of Cr(II). After reaction was complete, oxygen was bubbled through the solution. (At this point, the color of the solution became an intense green; the nature of the species responsible for this color is not known.) The solution was charged onto a cation-exchange resin, Dowex 50W-X8, 20–50 mesh in the H^+ form, washed with dilute acid, and then eluted with 1.0 *M* HCl. Spectra of these eluents identified the Cr(III) species as $Cr(H_2O)_5Cl^{2+}$. At least 60% of the total Cr(II) added was recovered as $Cr(H_2O)_5Cl^{2+}$. Further experiments with both *trans* complexes demonstrated that under the second-order conditions necessary to determine stoichiometry, the Ru(II)-catalyzed loss

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Table I. Rate Data for the Cr(II) Reduction of *cis*-$Ru(NH_3)_4Cl_2^+$, *cis*-$Ru(NH_3)_4ClH_2O^{2+}$, and $Ru(NH_3)_5Cl^{2+}$ [a]

Complex	[Ru(III)] × 10^4, *M*	[Cr(II)] × 10^3, *M*	k_{obsd}, sec^{-1}	k_{calcd}, sec^{-1} [b]
cis-$Ru(NH_3)_4Cl_2^+$ [c]	1.66	2.75	78	86.5
	1.66	1.66	73	67.2
	0.62	1.04	48	50.3
	0.50	6.28	116	115
	1.32	6.80	120	117
	2.71	14.8	132	134
	2.71	4.86	106	107
	0.64	0.66	36	36.2
	1.18	8.69	127[d]	124
	1.18	3.42	96[d]	94.6
cis-$Ru(NH_3)_4ClH_2O^{2+}$ [e]	1.74	14.8	102	98.7
	1.74	8.21	82	87.6
	0.52	1.57	42	42.5
	0.52	2.78	58	58.8
	1.50	5.32	77	77.1
	1.38	4.14	71	70.3
	1.38	1.90	47	47.8
	1.44	3.34	67[d]	64.2
	1.44	9.14	90[d]	90.0
$Ru(NH_3)_5Cl^{2+}$ [f]	1.23	2.92	81	78.5
	1.23	1.87	54	53.5
	0.96	2.16	61	60.7
	0.76	2.51	69	69.1
	0.92	7.00	145	152
	0.92	1.88	53	53.8
	0.92	4.92	121	118
	0.92	4.01	101	101

[a] Temperature = 25°; $[H^+] = \mu = 0.10$ *M* *p*-toluenesulfonic acid. [b] Calculated from eq 2 and the parameters in Table II. [c] For wavelength of observation, see ref 19. Last two runs are observed at 4500 Å. [d] *p*-Toluenesulfonic acid, 0.05 *M*, ionic strength 0.01 *M* with sodium *p*-toluenesulfonate. [e] Wavelength of observation 4300 Å. [f] Wavelength of observation 3300 Å.

of chloride from Ru(III)[31,34,35] is competitive in rate with Cr(II) reduction. Addition of less than one equivalent of Cr(II) or Ru(II) (generated by treating the Ru(III) complex with amalgamated zinc) to solutions of *trans*-$Ru(NH_3)_4Cl_2^+$ or *trans*-$Ru(NH_3)_4ClH_2O^{2+}$ led to a loss of *all* color in the regions where the Ru(III) chloro complexes absorb strongly. The complex, *trans*-$Ru(NH_3)_4(H_2O)_2^{3+}$, is essentially colorless in this region, and its reduction by Cr(II) would presumably lead to $Cr(H_2O)_6^{3+}$. Since no deviations are noted in the kinetic plots under pseudo-first-order conditions for the Cr(II) reduction of *trans*-$Ru(NH_3)_4Cl_2^+$, we believe that the result of the stoichiometry experiments are best interpreted in terms of Ru(II)-catalyzed aquation, and that the stoichiometry of the reaction is similar to that for the other complexes for the [Cr(II)] used in the kinetic runs. The Cr(II) reduction of *trans*-$Ru(NH_3)_4ClH_2O^{2+}$ under pseudo-first-order conditions does not yield simple kinetics, rendering the determination of stoichiometry (and kinetics) unclear.

Chromium(II) Reduction of $Ru(NH_3)_5Cl^{2+}$ and the *cis*-Ru(III)-Ammine Complexes. As we have reported earlier,[19] the rate of the Cr(II) reduction of *cis*-$Ru(NH_3)_4Cl_2^+$ does not obey a second-order rate law. Instead there is a saturation of the pseudo-first-order rate constant as the [Cr(II)] is increased. The same results pertain to the Cr(II) reductions of $Ru(NH_3)_5Cl^{2+}$ and *cis*-$Ru(NH_3)_4ClH_2O^{2+}$. In all cases we have been successful in fitting the data to a rate expression of the type

$$\frac{-d[Ru(III)]}{dt} = k_{obsd}[Ru(III)] \tag{1}$$

$$k_{obsd} = \frac{kK[Cr(II)]}{1 + K[Cr(II)]} \tag{2}$$

The success of this fit is shown by comparing the values of k_{obsd} in Table I with those of k_{calcd} calculated from parameters *k* and *K* and eq 2. The best values for *k* and *K* are listed in Table II. In the cases of *cis*-$Ru(NH_3)_4Cl_2^+$ and *cis*-$Ru(NH_3)_4ClH_2O^{2+}$, additional experiments have been performed at 0.05 *M* *p*-toluenesulfonic acid (ionic strength maintained with sodium *p*-toluenesulfonate), in order to verify that the dominant term in the rate law is indeed independent of $[H^+]$. For $Ru(NH_3)_5Cl^{2+}$ Stritar and Taube's data[35] establish this independence.

Table II. Kinetic Parameters for the Cr(II) Reduction of *cis*-$Ru(NH_3)_4Cl_2^+$, *cis*-$Ru(NH_3)_4ClH_2O^{2+}$, and $Ru(NH_3)_5Cl^{2+}$ [a]

Complex	*k*, sec^{-1}	*K*, M^{-1}
$Ru(NH_3)_5Cl^{2+}$	460 ± 50	70 ± 8
$Ru(NH_3)_4ClH_2O^{2+}$	117 ± 4	362 ± 25
$Ru(NH_3)_4Cl_2^+$	154 ± 8	465 ± 40

[a] Temperature = 25°; $[H^+] = \mu = 0.10$ *M* *p*-toluenesulfonic acid.

Additional information relevant to the failure of these systems to obey second-order kinetics can be obtained by extrapolating the kinetic plots back to zero time. These zero-time intercepts do not give values of the absorbance predicted from the spectra of reactants. The zero-time spectra for experiments with *cis*-$Ru(NH_3)_4ClH_2O^{2+}$ and $Ru(NH_3)_5Cl^+$ show strong bands in the visible region not due to reactants or products and are the same, within experimental error, as that previously reported for the reaction with *cis*-$Ru(NH_3)_4Cl_2^+$.[19] Following the reduction of *cis*-

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(35) J. A. Stritar and H. Taube, *ibid.*, **8**, 2281 (1969).

$Ru(NH_3)_4Cl_2^+$ a slow reaction of small absorbance change was observed, independent of [Cr(II)] with rate constant about 4 sec^{-1}.

Chromium(II) Reduction of *trans*-$Ru(NH_3)_4Cl_2^+$. Upon addition of Cr(II) to a solution of *trans*-$Ru(NH_3)_4Cl_2^+$ in 0.10 *M* *p*-toluenesulfonic acid, the absorbance at the maximum in absorptivity of the Ru(III) complex decreases. However the resulting pseudo-first-order rate plots are not linear. The problem has been identified as the formation of a precipitate in these mixtures. Examination of the solutions in sunlight after reaction clearly shows scattering. This problem can be avoided, however, by performing the reduction in 0.10 *M* HCl. That such precipitation did not occur in HCl is demonstrated by the complete absence of any indication of light scattering by visual examination and by the very good fits of the data to linear first-order kinetic plots: typical plots were linear to four half-lives. In addition, the data, listed in Table III, fit a second-order rate law very well. The last two experiments in Table III demonstrate the dominance of the [H$^+$]-independent term in the rate law. The change in medium from *p*-toluenesulfonic acid to hydrochloric acid does not materially affect the rate, for the slopes of kinetic plots of experiments run in *p*-toluenesulfonic acid either before precipitation has begun or after it has ceased yield an estimate of the second-order rate constant of 120 ± 10 M^{-1} sec^{-1}.

Table III. Experimental Data for the Cr(II) Reduction of *trans*-$Ru(NH_3)_4Cl_2^+$ [a]

$[\mathrm{Ru(III)}_4 \times 10^4$, *M*	$[\mathrm{Cr(II)}_4 \times 10^3$, *M*	k_{obsd}, sec^{-1}	k_2, M^{-1} sec^{-1}
0.79	7.66	0.938	122
0.79	3.76	0.469	125
0.75	16.6	2.13	128
0.72	2.96	0.376	127
0.72	2.05	0.268	130
0.65	7.87	0.974	124[b]
0.65	1.92	0.246	128[b]
		Av	126 ± 3

[a] Temperature = 25°; [H$^+$] = μ = 0.10 *M* *p*-toluenesulfonic acid. [b] [H$^+$] = 0.05 *M* HCl, ionic strength 0.10 with NaCl.

Chromium(II) Reduction of *trans*-$Ru(NH_3)_4ClH_2O^{2+}$. Pseudo-first-order rate plots for the Cr(II) reduction of *trans*-$Ru(NH_3)_4ClH_2O^{2+}$ in *p*-toluenesulfonic acid are also not linear. But precipitation is not the problem, as evidenced by visual examination, the shape of the kinetic plots, and the fact that changing the medium to 0.1 *M* HCl does not change the shape of the plots but does affect the rate. The shape of the kinetic plots appears to be near that of a two-step process with the plots concave upward—the rate of change of the logarithm of absorbance decreases with time. The slower "step" has a second-order rate constant on the order of 100 M^{-1} sec^{-1} and the faster greater than that by a factor of about 10 although these numbers were far from constant over the [Cr(II)] range used (1×10^{-3}–3×10^{-2}). Repeated recrystallization of the Ru(III) complex in no way affected the plots. Absorbances extrapolated back to zero time do not correspond to those of reactants and, as is the case for the Cr(II) reductions of the *cis* and the pentaammine complexes, peaks at zero time are observed in the visible region of the spectrum which are not due to products or reactants; however, they are of low intensity. Because of the highly complex nature of this reaction, no further attempt was made to elucidate the kinetics of this reduction.

Chromium(II) Reduction of *cis*-$Ru(bipy)_2Cl_2^+$. Extrapolation to zero time of kinetic plots of the reaction between Cr(II) and *cis*-$Ru(bipy)_2Cl_2^+$ yields a spectrum far different from that of reactants. There is a large peak in the visible region at about 4800 Å and molar absorptivity of about 9000 l. mol^{-1} cm^{-1}; $Ru(bipy)_2Cl_2^+$ has a molar absorptivity of only 1000 here. This species then decays in two steps, both independent of [Cr(II)] over the range 2×10^{-3}–1×10^{-2} *M*, to a species with λ_{max} about 5000 Å and ϵ also about 9000. Although the small absorbance change made the determination of accurate kinetic parameters difficult, four experiments did yield the rate constants, 6.2 ± 0.4 sec^{-1} and 0.10 ± 0.03 sec^{-1}.

Vanadium(II) Reductions. The V(II) reduction of the complexes, *trans*-$Ru(NH_3)_4Cl_2^+$, *trans*-$Ru(NH_3)_4H_2OCl^{2+}$, and *cis*-$Ru(NH_3)_4Cl_2^+$, has been assumed to proceed with 1:1 stoichiometry. The Ru(II)-catalyzed aquation of chloro–Ru(III) complexes precludes spectroscopic proof of stoichiometry at wavelengths where Ru(III) absorbs. Kinetic experiments were performed in the region of the first intense absorption band, in which region Ru(II), V(II), and V(III) absorb much less strongly. Each complex followed a second-order rate law quite well as shown in Table IV. Following the reduction of each complex a much slower reaction of small absorption change independent of [V(II)] is observed. The values of k_{obsd} in Table IV have been corrected for this slow absorptivity change. The rate of this slower step is 16 ± 8 sec^{-1} for *cis*-$Ru(NH_3)_4Cl_2^+$ and less than 0.1 sec^{-1} for *trans*-$Ru(NH_3)_4Cl_2^+$ and *trans*-$Ru(NH_3)_4ClH_2O^{2+}$.

Pseudo-first-order kinetic plots of the vanadium(II) reduction of *cis*-$Ru(NH_3)_4ClH_2O^{2+}$ are not linear but concave downward—the rate of change of the logarithm of the absorbance increases with time. After what appears as an induction period, the kinetic plots straighten out and assume a long-term rate on the order of 7000 M^{-1} sec^{-1}, the length of the induction period being about the length of the final reaction time. We have found no satisfactory explanation for this phenomenon.

Discussion

Before discussing the implications our results have on the interpretation of the nonbridging ligand effect, it is necessary to inquire into the mechanistic scheme that will yield the rate law observed for the Cr(II) reduction of *cis*-$Ru(NH_3)_4Cl_2^+$, *cis*-$Ru(NH_3)_4ClH_2O^{2+}$, and $Ru(NH_3)_5Cl^{2+}$. These three systems obey a rate law of the form given in eq 1 and 2. A mechanism consistent with this rate law is

$$\mathrm{Cr(II)} + \mathrm{Ru(III)\text{-}Cl} \rightleftharpoons \underset{\mathbf{1}}{[\mathrm{Cr\text{-}Cl\text{-}Ru}]^{n+}} \qquad K \tag{3}$$

followed by one of the following steps

$$[\mathrm{Cr\text{-}Cl\text{-}Ru}]^{n+} \xrightarrow{k} \mathrm{CrCl^{2+}} + \mathrm{Ru(II)} \tag{4}$$

$$\mathrm{Cr(II)} + \mathrm{Ru(III)\text{-}Cl} \xrightarrow{k_2} \mathrm{CrCl^{2+}} + \mathrm{Ru(II)} \tag{5}$$

Table IV. Experimental Data for the Vanadium(II) Reduction of Ruthenium(III)-Amine Complexes[a]

Complex	[Ru(III)] × 10^4, *M*	[V(II)] × 10^3, *M*	k_{obsd}, sec^{-1}	k_2, $M^{-1}\ sec^{-1}$
trans-$Ru(NH_3)_4Cl_2^+$ [b]	0.92	18.5	15.4	833
	0.92	3.91	3.16	809
	0.78	14.7	13.0	885
	0.78	6.06	4.85	800
				Av 830 ± 30
trans-$Ru(NH_3)_4ClH_2O^{2+}$ [c]	1.17	8.90	12.5	1400
	0.76	20.0	29.0	1450
	0.76	4.42	5.92	1340
	1.34	12.5	18.4	1470
	1.34	5.56	7.98	1430
				Av 1420 ± 50
cis-$Ru(NH_3)_4Cl_2^+$ [d]	1.74	5.39	52.4	9720
	2.70	9.08	78.8	8680
	2.70	3.50	34.5	9850
	1.94	11.3	121	10700
	1.94	5.45	55.5	10200
				Av 9800 ± 800

[a] Temperature = 25°; $[H^+] = \mu = 0.10$ *M* *p*-toluenesulfonic acid. [b] Wavelength of observation 3330 Å. [c] Wavelength of observation 3300 Å. [d] Wavelength of observation 3530 Å.

We prefer reaction 4 because reaction 5 requires **1**, a complex involving a chloride bridge between the two metal ions, to decompose to Cr(II) and Ru(III)–Cl, which then re-form a distinct chloride bridged species—**1** is not found anywhere on the reaction coordinate of reaction 5. The mechanism, eq 3 and 4, is also consistent with the anomalous spectra observed at zero time, which is assigned to **1**. The absence of maxima in the kinetic plots at wavelengths where **1** absorbs strongly, even with the lowest [Cr(II)] used, verifies that **1** is indeed in equilibrium with reactants. The observed values of *K* and *k* are listed in Table II.

We have previously presented arguments[19] to indicate that the preferred assignment of the formal oxidation states to the metal atoms in the intermediate is **3** rather than **2**. This assignment of formal oxidation

[Ru(III)–Cl–Cr(II)]
2

[Ru(II)–Cl–Cr(III)]
3

states can be understood on the basis of substitution chemistry of the various metal-ion constituents. Apparently in these systems the electron-transfer step, **2** $\rightleftharpoons$ **3**, is in rapid equilibrium, even though configuration **3** is favored over that of **2**. The rapid electron-transfer process within the bridged complex gives rise to some "Cr(II) character" in the bridged intermediate, and because of the high rate of substitution on Cr(II),[36] gives rise to a rapid path to reactants. In contradistinction the lability of Ru(II), a d^6 low-spin system, is probably considerably less; therefore the lifetime of the intermediate with respect to disappearance to products is sufficiently long to allow the intermediate to achieve equilibrium with reactants.[36b] Such a situation does not arise in the reduction of Co(III) complexes because the lability of Co(II) effectively competes with reversion to the bridged complex having the oxidation states of reactants.

The data previously reported by Stritar and Taube[35] for the Cr(II) reduction of $Ru(NH_3)_5Cl^{2+}$ are consistent with that reported here. Deviation from second-order kinetics is small in their data because a smaller range of [Cr(II)] was used than in this study. Because *K* is smaller for this complex than for the *cis* complexes, much larger values of [Cr(II)] are needed before deviation from second-order kinetics becomes significant.

The mechanism, eq 3 and 4, is also consistent with the results for the Cr(II) reduction of *cis*-$Ru(bipy)_2Cl_2^+$. The experimental value of *K* is very large, which is consistent with a greatly increased overall driving force for the reaction relative to the ammine systems, as deduced from a comparison of the $Ru(NH_3)_6^{2+,3+}$ [34] and $Ru(bipy)_3^{2+,3+}$ [37] couples, as most of this increase should be incorporated into the step, reactants $\rightleftharpoons$ **3**. The two observed kinetic steps are then the losses of $Cr(H_2O)_5Cl^{2+}$ and Cl^- from the first coordination sphere of Ru(II). It could not be determined if this reaction is indeed inner sphere, as the highly absorbing nature of ruthenium–bipyridine complexes precluded detection of $Cr(H_2O)_5Cl^{2+}$.

There are two circumstances under which the Cr(II) reduction of *trans*-$Ru(NH_3)_4Cl_2^+$ would obey second-order kinetics and yet follow mechanism 3 and 4. The first is if the rate of electron transfer is slow with respect to *k*, as is the case with reductions of Co(III) complexes. Then the observed second-order rate constant is indeed the electron-transfer rate. The other circumstance occurs if the value of *K* is small. Then the electron-transfer rate would be rapid, and the observed second-order rate constant would be equal to *kK*. This is the situation approached in the reduction of $Ru(NH_3)_5Cl^{2+}$, in which system *K* has a value of only 70 M^{-1}. The data for *trans*-$Ru(NH_3)_4Cl_2^+$ require an upper limit on *K* of 15 M^{-1} and a lower limit on *k* of 9 sec^{-1}. Distinction between these two kinetic schemes is not possible with the available data. Thus for the Cr(II)-reduced systems, no information is gained concerning the effect of nonbridging ligands of the oxidant on the rate of electron transfer, for the rate of reduction is not necessarily related to the rate of electron transfer for any of the complexes, substitution on Ru(II) being the dominant factor.

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(36) (a) C. W. Merideth and R. E. Connick, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, Paper 106M. (b) A similar system has been reported since submission of this manuscript: see D. Seewald, N. Sutin, and K. O. Watkins, *J. Amer. Chem. Soc.*, **91**, 7307 (1969).

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We have circumvented the difficulty of slow substitution on Ru(II) by studying reductions with V(II). The rate constants listed in Table IV are too fast to be consistent with the relatively slow rate of exchange of water from $V(H_2O)_6^{2+}$.[38–40] The reactions of interest are therefore either outer-sphere or proceed by a mechanism involving expansion of the coordination number of one of the reagents.[41] In Table V are listed the rates of V(II) reduction of the Ru(III) complexes measured in this work, the rate of V(II) reduction of $Ru(NH_3)_5Cl^{2+}$ previously measured by Stritar and Taube,[35] and the rates of reduction by V(II) and Fe(II) of various Co(III) complexes.[1,8,9,42] The complexes are arranged in order of increasing rate of reduction of the Co(III) complexes, an order that has been found to be independent of reductant, except for minor reversals. Even reactions known to be outer sphere, $Ru(NH_3)_6^{2+}$ + Co(III)–Cl systems, show similar relative rates as the "nonbridging" ligand is varied. The conditions necessary for this correlation have been outlined previously.[8,9] It is to be noted, however, that the rates of reduction of the Ru(III) complexes do not at all parallel those of Co(III). Compare especially the rates of reduction for $Ru(NH_3)_5Cl^{2+}$, *trans*-$Ru(NH_3)_4H_2OCl^{2+}$, and *trans*-$Ru(NH_3)_4Cl_2^+$ with those for the corresponding Co(III) complexes. At the least, this comparison implies that a difference in the electronic structure of the oxidant, d^6 for Co(III) and d^5 for Ru(III), is of major importance in determining the reactivity pattern produced by a change in nonbridging ligands. Moreover, this change in order is that predicted on the basis of the model of the importance of the orbital to be populated. In the case of Ru(III) complexes, this orbital is of t_{2g} symmetry and is raised in energy by ligands with π-donor ability, such as H_2O and, even more so, Cl^-. The higher the energy of this orbital, the more energy is needed in the transition state to distort the complex to a configuration compatible with electron transfer, and hence the slower the rate. Extension of this model to *cis*-$Ru(NH_3)_4Cl_2^+$ is not possible without doing more detailed numerical calculations, for the ligand axes and symmetry axes are no longer coincident. Extending such a one-electron model to numerical calculations is of doubtful value.

Table V. Rate Constants for the Reduction of Ru(III) and Co(III) Complexes at 25°

Oxidant ligands	V(II) reduction of Ru(III)	V(II) reduction of Co(III)[c]	Fe(II) reduction of Co(III)[d]
cis-$(en)_2H_2OCl$		10.1	0.00045
$(NH_3)_5Cl$	3050[a]	7.58	0.00135
cis-$(en)_2Cl_2$		24.0	0.0016
trans-$(en)_2Cl_2$		128	0.032
cis-$(NH_3)_4H_2OCl$		57.6	0.0353
cis-$(NH_3)_4Cl_2$	9800[b]		*e*
trans-$(en)_2H_2OCl$		259	0.24
trans-$(NH_3)_4Cl_2$	830[b]		2.21
trans-$(NH_3)_4H_2OCl$	1420[b]	~460	~10

[a] See ref 35. [b] This work. [c] See ref 9. [d] See ref 1, 8, and 42. [e] This complex aquates much too rapidly to allow evaluation of its reduction rates. However, its position as to relative rate of reduction could be estimated by comparison with the analogous ethylenediamine complex. See ref 8.

The data presented here also allow us to make some comments about the substitution of d^6 systems. Although much of this evidence is indirect in nature because of the ephemeral nature of the Ru(II) complexes, the dominant role that Ru(II) substitution plays in several of the electron-transfer reactions of Ru(III) complexes warrants attempts to obtain information about Ru(II) substitution rates. It is reasonable to believe that the slow reactions of small absorbance change following all the V(II) reductions and the Cr(II) reduction of *cis*-$Ru(NH_3)_4Cl_2^+$ are due to the loss of chloride ion from the first coordination sphere of the appropriate Ru(II) complex. These rate constants are listed in Table VI along with those corresponding to the leaving group $CrCl^{2+}$; the latter data were obtained from Table II.

Table VI. Rate Constants for Aquation of Ruthenium(II) Amine Complexes[a]

Complex	Leaving group X: Cl^-	Leaving group X: $CrCl^{2+}$
trans-$(NH_3)_4ClRu^{II}X$	<0.1	
trans-$(NH_3)_4H_2ORu^{II}X$	<0.1	
$(NH_3)_5Ru^{II}X$		460 ± 50
cis-$(NH_3)_4H_2ORu^{II}X$	4 ± 2	117 ± 4
cis-$(NH_3)_4ClRu^{II}X$	16 ± 8	158 ± 8
cis-$(bipy)_2ClRu^{II}X$		6.2 ± 0.4

[a] Rate constants have units of sec^{-1}. Temperature = 25°; $[H^+] = \mu = 0.10\ M$ *p*-toluenesulfonic acid.

For the loss of chloride, the general trend noticed in Co(III)[43] and Rh(III)[44] substitutions that *cis* complexes are more labile than the corresponding *trans* complexes is followed, although the magnitude of this difference cannot be evaluated. When consideration is given to the parallel nature of loss of Cl^- and $HgCl^+$ from various Co(III)–Cl^- species,[45] and the smaller affinity for Cl^- of Cr(III) compared to Hg(II),[46] the crude data for the loss of Cl^- are strongly supported by the more accurate data for loss of $CrCl^{2+}$. The rate of water substitution on $Ru(NH_3)_5OH_2^{2+}$ by N_2[47,48] is also consistent with the order of magnitude of our data.

One further item of interest can be derived from the data in Table II. To the best of our knowledge, no one has yet been able to estimate the value of the equilibrium constant for the formation of the bridged species formed before inner-sphere electron transfer takes place. The existence of such a step in the achievement of the transition state has been argued indirectly, first by Taube,[49] on the basis of the very low values for $\Delta H^{\ddagger}$ in the Cr(II) reduction of a number of species. Others have subsequently developed this subject.[50–52]

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Our data allow the evaluation of this equilibrium constant for the reductant, $Ru(NH_3)_5OH_2^{2+}$, and the oxidant, $Cr(H_2O)_5Cl^{2+}$. From our value of the equilibrium constant for the process

$$Ru(NH_3)_5Cl^{2+} + Cr(H_2O)_6^{2+} \rightleftharpoons (NH_3)_5Ru^{II}ClCr^{III}(H_2O)_5^{4+} \quad (6)$$

literature values for the electrode potential of the couple, $Ru(NH_3)_5H_2O^{2+,3+}$,[53] and the affinity of $Cr(H_2O)_6^{3+}$ [54] and $Ru(NH_3)_5H_2O^{3+}$ [34] for chloride ion, we have calculated the equilibrium constant for the process

$$Ru(NH_3)_5H_2O^{2+} + Cr(H_2O)_5Cl^{2+} \rightleftharpoons (NH_3)_5RuClCr(H_2O)_5^{4+} + H_2O \quad (7)$$

to be $4 \times 10^{-5}\ M^{-1}$. The small value of this equilibrium constant indicates that direct kinetic observations of such a preequilibrium step in chloride bridged reactions will not be feasible except at high concentrations.

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Steric Factors in the Kinetics of Ligand Exchange with Copper(II)–Triglycine ($CuH_{-2}L^-$)

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Abstract: The reaction of $CuH_{-2}L^-$ (where L^- is the triglycinate ion and two protons are ionized from the peptide nitrogens) with multidentate ligands proceeds by two general mechanisms. (1) In a general acid catalysis mechanism a proton is transferred to a peptide nitrogen to assist the dissociation of the triglycine. The conjugate acid of the multidentate ligand may be a reactant in this mechanism. (2) In a nucleophilic mechanism the displacing ligand coordinates to copper and speeds the breaking of the copper–peptide nitrogen bonds. The peptide nitrogens add protons only after the rate-determining step. Polyamines and aminocarboxylates in which a nitrogen donor can coordinate to copper react much faster in the second mechanism than in the first. However, steric effects are very important and the structure of the multidentate ligand can easily block the nucleophilic mechanism. Triethylenetetramine and ethylenediaminediacetate ion react by the second mechanism while N,N′,N″,N‴-tetramethyltriethylenetetramine, ethylenediaminetetraacetate ion, and nitrilotriacetate ion do not.

In a previous report it was shown that the reaction of ethylenediaminetetraacetate ion (EDTA) with $CuH_{-2}L^-$ (see Figure 1) is general acid catalyzed[3] with EDTA reacting only after a proton had been transferred to $CuH_{-2}L^-$. On the other hand, the reaction is catalyzed by triethylenetetramine (trien) which greatly speeds the conversion of copper–triglycine to copper–EDTA.[4]

In the present work, the kinetics of the direct reaction of trien with $CuH_{-2}L^-$ is studied. Trien reacts as a nucleophile in a completely different type of mechanism than the EDTA reaction. Other ligands are tested and also follow either the acid-catalyzed or nucleophilic mechanism depending on the structure of the ligand.

Experimental Section

The copper(II)–triglycine complex was prepared from twice-recrystallized copper perchlorate and from triglycine (chromatographically homogeneous, Mann Research Laboratories, N. Y.). The copper peptide solutions were freshly prepared before each series of reactions. Boric acid or sodium tetraborate solutions were used as buffering agents (total borate was $6.0 \times 10^{-3}\ M$). Ionic strength was maintained at 0.10 *M* with $NaClO_4$. The hydrogen ion concentrations were calculated from pH measurements by the relationship $-\log[H^+] = pH - 0.11$.[5] In the pH range used (7.5–9.3) the predominant copper–triglycine species present is $CuH_{-2}L^-$.[6–8]

Trien solutions were prepared from the twice-recrystallized sulfate salt (Baker Analyzed Reagent). Solutions of ethylenediaminediacetate ion (EDDA) were freshly prepared from basic solution in order to avoid cyclization of the ligand.[9] The N,N′,N″,N‴-tetramethyltriethylenetetramine was obtained from the Ames Laboratories, Inc., Milford, Conn. All exchanging ligands were standardized either by acid–base titration or by a mole-ratio method using a standard copper solution and an acetate buffer.

Kinetic runs were followed spectrophotometrically at 235 mμ using a modified Durrum-Gibson stopped-flow, Durrum Instrument Corporation, Palo Alto, Calif. Data were recorded on Polaroid film. A typical kinetic run had a $CuH_{-2}L^-$ concentration of $4 \times 10^{-5}\ M$ and a displacing ligand concentration equal to or greater than this concentration. Each rate constant is the average of at least four kinetic runs at 25.0°. Individual rate constants, under first-order or second-order (unequal concentrations) condi-

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