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(16) The reactions are balanced only with respect to chromium and chlorine. The formulation for the higher charged product is speculative. [See (a) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **20**, 3564 (1959); (b) G. Thompson, Ph.D. Dissertation, University of California, Berkeley, Calif., June 1964; (c) R. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).] However, slow ion-exchange experiments on the products of reactions 3 and 4 (with excess oxidant initially present) with $Al(ClO_4)_3$ and $Ba(ClO_4)_2$ as eluting agents indicate that primarily one higher charged product is formed and that it elutes in the same manner as reported for $Cr(OH)_2Cr^{4+}$.
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(24) Ignored, however, are outer-sphere reactions of the types (a) $CrOClO_2^{2+} + Cr^{2+} = CrOClO^{3+} + (H_2O)_6Cr^{3+}$ and (b) $CrOClO_2^{2+} + Cr^{2+} = CrOClO^{2+} + Cr^{4+}$, $Cr^{2+} + Cr^{4+} = Cr(OH)_2Cr^{4+}$. This serves to illustrate how difficult it is to elucidate even the initial step in multistage reactions with numerous possibilities throughout. However, the stoichiometric and oxygen-18 results on the Cr^{2+}–ClO_3^- system require extensive inner-sphere reactions. Also, reaction a would probably lead to the production of more $(H_2O)_6Cr^{3+}$ than is observed. Reaction b is unpalatable to us in that it invokes the formation of the very strong oxidant Cr(IV) whereas other reasonable schemes are available that do not require its participation.
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Chromium(II)-Catalyzed Aquations of the Nicotinamide- and the Thioisonicotinamide-Bridged Ruthenium(II)-Chromium(III) Complex Ions

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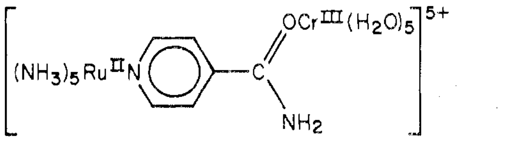
The chromium(II)-catalyzed aquation reaction of the ligand-bridged ruthenium(II)–chromium(III) species formed as a result of the inner-sphere reduction of $(NH_3)_5RuL^{3+}$ by chromium(II) was studied for L = nicotinamide and thioisonicotinamide in perchlorate medium under pseudo-first-order conditions. The observed rate constant for the aquation reactions is described by the expression $k_{obsd} = k_0 + k_1/[H^+] + k_2[Cr^{2+}]_{excess}/[H^+]$ where $k_0 \approx 10^{-7}$ sec^{-1}, $k_1 = (1.95 \pm 0.01) \times 10^{-7}$ M sec^{-1}, and $k_2 = (4.05 \pm 0.26) \times 10^{-5}$ sec^{-1} for the nicotinamide-bridged species at 25 ± 0.1° and $\mu = 0.10$ and $k_0 = (3.94 \pm 0.27) \times 10^{-4}$ sec^{-1}, $k_1 = (8.97 \pm 0.21) \times 10^{-5}$, and $k_2 = 0.271 \pm 0.005$ sec^{-1} for the thioisonicotinamide-bridged species at 2.0 ± 0.1° and $\mu = 0.01$. The significantly larger values of the rate constants reported for the aquation of the thioisonicotinamide-bridged species compared to those for the aquation of the nicotinamide-bridged species are interpreted to result from the aquation of an activated complex with a protonated sulfur atom. The aquation of the nicotinamide-bridged species was studied in bromide medium. Results indicate the aquation reaction to be catalyzed by the presence of bromide ion and to have complex acid dependence.

Introduction

The chemistry of $(H_2O)_5Cr^{III}X$ has been of interest for some years because the formation of such complexes often comes as a result of an inner-sphere electron-transfer reaction[1] and also the complexes represent a simple system to study the kinetics of chromium(III)–ligand bond cleavage. Reactions have been studied in which X is a halogen or a more complex ligand with chromium(III) coordination through nitrogen, oxygen, or sulfur.[2] In the case of X being a halogen or a nitrogen- or oxygen-bound ligand not only has the spontaneous aquation of the Cr^{III}–X species been investigated but also the chromium(II)-catalyzed aquation reaction has been studied.[3-5] Results of these studies indicate the chromium(II) catalysis is due to an inner-sphere electron transfer from the attacking chromium(II) to the chromium(III) center labilizing the chromium ligand bonds.

The chromium(II)-catalyzed aquation reaction of I in HClO$_4$–LiClO$_4$ medium resulting in the formation of isonicotinamidepentaammineruthenium(II) and hexaaquochromium(III) has been reported earlier.[6] Efforts to elucidate the nature of the chromium(II) catalysis and the effect of changing the basicity of the ruthenium(II)–ligand system on the rate of aquation led us to investigate the chromium(II)-catalyzed aquation of the reaction intermediates formed as a result of the inner-sphere chromium(II) reduction of the pentaammineruthenium(III) complex ions of nicotinamide and thioisonicotinamide. Although the kinetics of some chromium(III)–thiolato complexes have been investigated in detail by Deutsch et al.,[7-9] there has been no report to date of a chromium(II)-catalyzed aquation of a chromium(III)–sulfur bond.



I

Experimental Section

Reagents. Tap distilled water was redistilled from alkaline potassium permanganate before using in synthetic, chromatographic, and kinetic experiments. All chemicals used were of reagent grade. The reaction mixtures were adjusted to the desired ionic strength using lithium perchlorate or lithium bromide. The lithium perchlorate obtained from G. F. Smith Co. was prereduced with chromium(II) and then recrystallized from water twice before use. The lithium bromide from Fisher Scientific Co. was recrystallized twice from water. Hydrobromic acid was purified by double distillation of 48% hydrobromic acid. Hexaaquochromium(III) was prepared by reduction of potassium dichromate with hydrogen peroxide in the presence of excess perchloric acid. Chromium(II) perchlorate solutions were prepared by reducing aliquots of the hexaaquochromium(III) stock solution over freshly prepared zinc amalgam under a blanket of argon gas. Isonicotinamidepentaammineruthenium(III) perchlorate and nicotinamidepentaammineruthenium(III) perchlorate were prepared as previously described.[10] Thioisonicotinamide from Aldrich Co. was recrystallized from acetone before use in synthesis.

Preparation of $[(NH_3)RuL](ClO_4)_2$ and $[(NH_3)_5RuL](ClO_4)_3$

Where L = Thioisonicotinamide. Chloropentaammineruthenium(III) chloride was prepared by the method of Vogt, Katz, and Wiberly.[11] A 0.200-g portion of chloropentaammineruthenium(III) chloride was added to a solution of Ag(I) made by dissolving 0.149 g of silver oxide in 2.0 ml of hot water with dropwise addition of trifluoroacetic acid. The silver chloride formed was removed by filtration. The pH of the solution was then adjusted to approximately 6 by dropwise addition of 1.0 *M* $NaHCO_3$ using pH paper as an indicator. The solution was transferred to a modified Zwickel[12] flask stoppered with syringe caps. After the solution had been deoxygenated for 20 min, several pieces of zinc amalgam were added and the solution was left in contact with the zinc amalgam for 5–6 min. The solution, now containing Ru(II), was transferred to a two-necked bubbling flask which contained an excess of thioisonicotinamide dissolved in acetone; the acetone solution of the ligand had been deoxygenated with argon for 30–40 min before the addition of the Ru(II) solution. After a reaction time of 45 min, the solution containing $[(NH_3)_5RuL]^{2+}$ was exposed to air and excess ligand was removed by filtration followed by two 200-ml extractions with ether. A saturated solution of $NaClO_4$ was added to induce precipitation. The crude product was recrystallized from 40° water, washed with ether, and stored in an evacuated glass container suspended in a mixture of Dry Ice and acetone. Yields of 60% were obtained. Anal. Calcd for $[(NH_3)_5Ru(C_6H_6N_2S)](ClO_4)_2$: C, 13.8; H, 4.1; S, 6.2. Found: C, 13.4; H, 4.1; S, 6.4.

The Ru(III) complex was prepared by Ce(IV) oxidation of $[(NH_3)_5RuL](ClO_4)_2$. A 0.100-g amount of the Ru(II) complex was dissolved in a minimum of water. Ceric perchlorate (ca. 0.5 *M* in 6 *M* $HClO_4$) was added dropwise until a yellow-orange color persisted. Orange crystals formed on cooling. The crude product was recrystallized from 40° water and washed with ether. The recrystallized salt was stored under vacuum at temperatures of Dry Ice–ethanol mixture. Anal. Calcd for $[(NH_3)_5Ru(C_6H_6N_2S)](ClO_4)_3$: C, 11.55; H, 3.37; S, 5.14. Found: C, 11.34; H, 3.37; S, 4.95.

Analysis. Microanalyses of the ruthenium salts were performed by Galbraith Laboratories, Knoxville, Tenn.

Perchlorate ion concentration was determined by the method of Gould and Taube[13] as modified by Deutsch.[3] The total chromium concentration of a solution was measured by oxidizing aliquots with hydrogen peroxide in a basic solution and determining the chromate produced spectrophotometrically.[14]

The concentration of free acid in hexaaquochromium(III) perchlorate solutions was determined by potentiometric titration after first converting the Cr(III) to the tris(oxalato)chromate(III) ion.[15]

Apparatus and Techniques. Visible and uv spectroscopic measurements were made using a Cary 17I spectrophotometer. A thermostated cell compartment was used in kinetic experiments. Ir spectra were measured using a Perkin-Elmer 257 grating spectrophotometer. The pK_a of thioisonicotinamidepentaammineruthenium(II) perchlorate was determined by potentiometric titration using a Beckman Model 1019 pH meter. Chromatographic studies of reaction products were carried out using an all-glass apparatus such that the column and eluent (1.5 M $LiClO_4$, 0.1 *M* $HClO_4$) could be deoxygenated with argon.

All kinetic experiments were carried out under pseudo-first-order conditions and were followed using conventional spectrophotometric techniques. For kinetic studies involving the reaction of nicotinamidepentaammineruthenium(III) with Cr(II), an all-glass apparatus consisting of a Cr(II) preparation flask and a Zwickel flask was used to prepare, mix, and sample. For aquation reactions of the product of the Cr(II) reduction of thioisonicotinamidepentaammineruthenium(III), a special all-glass apparatus was designed such that mixing and sampling was complete within a few seconds. In each apparatus argon gas was used to deoxygenate and transfer solutions.

Treatment of Data. All kinetic data were interpreted on the basis of a pseudo-first-order reaction. Absorbance–time data for the reactions involving the thioisonicotinamidepentaammineruthenium(III) complex ion were plotted using the Guggenheim method.[16] Statistical treatment of all kinetic data included using a nonlinear least-squares computer program provided by Lietzke[17] to fit raw absorbance–time data and the resulting observed rate constants as a function of the reaction conditions. The standard error of fit was used to calculate weighted averages of the rate constants reported.

Table I. Spectral Properties of Pentaammineruthenium Complexes of Thioisonicotinamide

Compd	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}
$(NH_3)_5Ru^{II}$(thioisoamide)	521	7.53 ± 0.1[a]
	270	5.93 ± 0.2[a]
	645	6.17 ± 0.02[b]
	267	6.75[b]
$(NH_3)_5Ru^{III}$(thioisoamide)	472	2.67 ± 0.1[a]
	320	1.52 ± 0.1[a]
	425	2.64 ± 0.1[b]
	270	5.00 ± 0.1[b]

[a] Measurement made in water solution. [b] Measurement made in 0.01 *M* $HClO_4$.

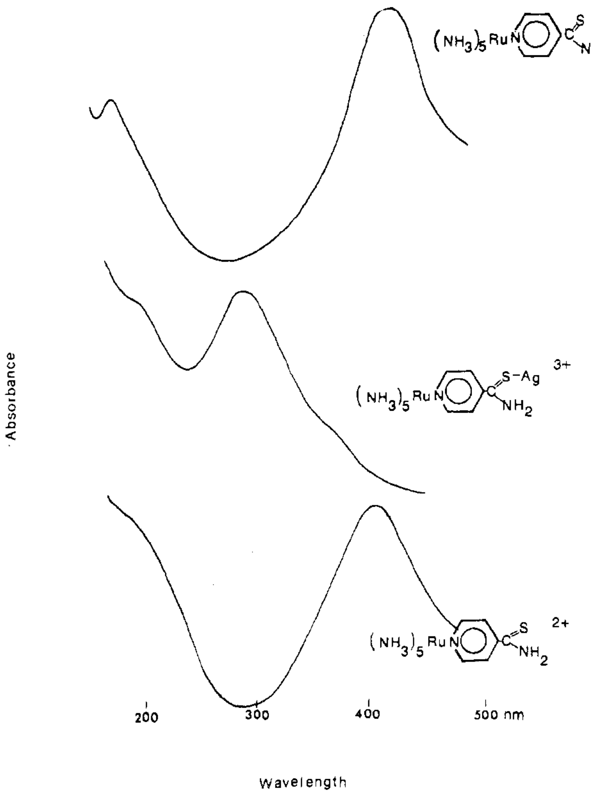


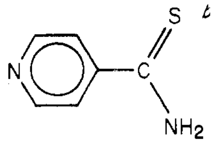
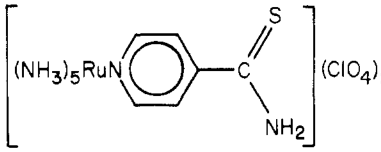
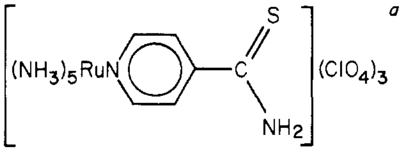
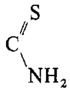
Figure 1. Spectral shifts of the visible absorbance band of $(NH_3)_5Ru^{II}$(thioisoamide) in water, in the presence of Ag(I), and after addition of excess Br^- ion.

Results and Discussion

Characterization and Structure of the $(NH_3)_5Ru^{II}L$ and $(NH_3)_5Ru^{III}L$ Species Where L = Thioisonicotinamide. The uv–visible spectral characteristics for the pentaammineruthenium(II) and pentaammineruthenium(III) complex ions of isonicotinamide and nicotinamide[18] have been previously reported.[10] The uv–visible spectral characteristics of $(NH_3)_5Ru^{II}$(thioisoamide) and $(NH_3)_5Ru^{III}$(thioisoamide) species are summarized in Table I. As in the case of other ruthenium(II) complexes with heterocyclic ligands,[19] the visible spectrum of $(NH_3)_5Ru^{II}$(thioisoamide) in water solution is characterized by an intense metal-to-ligand charge-transfer band. As shown in Figure 1, addition of Ag(I) ion to a solution of $(NH_3)_5Ru^{II}$(thioisoamide) results in a blue shift of the visible absorbance band, an effect characteristic of a complex containing a free sulfur[20–22] and due to formation of a S–Ag^I adduct. Addition of bromide ion results in recovery of the original spectral features. Ir spectral shifts on ligand coordination are summarized in Table II. Little or no change in carbon–sulfur or carbon–sulfur–nitrogen stretches occurs on coordination to ruthenium. The ir data and spectral shifts on addition of Ag(I) support coordination of thioisonicotinamide to ruthenium through the pyridine nitrogen.

Unlike the analogous isonicotinamide system, in 0.01 *M*

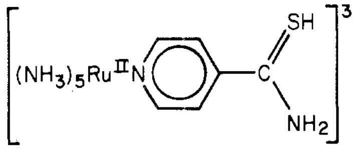
Table II. Infrared Spectral Shifts (μ) of Stretching Modes in Thioisonicotinamide on Coordination to Ruthenium(II) and Ruthenium(III) Metal Ions

Mode[c,d]	 [b]	 [a]	 [a]
C=S str	5.98, 6.23	5.98, 6.22	6.22
N in ring str	7.66	7.74	7.74
 $C(=S)NH_2$ str	7.04	7.05	

[a] Data taken from mulls in Nujol and hexachlorobutadiene spectra. [b] Data taken from KBr pellet spectrum. [c] K. Jensen and P. Halfdannielsen, *Acta Chem. Scand.*, 20, 597 (1966). [d] J. H. Karchmer, Ed., "The Analytical Chemistry of Sulfur and Its Compounds", Wiley-Interscience, New York, N.Y., 1972.

$HClO_4$ the charge-transfer band of $(NH_3)_5Ru^{II}$(thioisoamide) is shifted to longer wavelength as indicated in Table I. Also the absorbance band is noticeably asymmetric. Addition of $NaHCO_3$ solution to a pH of 6.8 restores the visible spectral pattern to that observed in water solution. At high acid concentration (>0.1 *M* $HClO_4$) the visible absorbance band decreases in intensity with time until the uv–visible spectral features resemble those of $(NH_3)_5Ru^{III}$(thioisoamide) suggesting an oxidation process.

The shift of the charge-transfer band to longer wavelength in acid solution is due to protonation of the thioisonicotinamide ligand forming



Charge effects of protonation would be expected to lower the energy of the metal-to-ligand charge transfer. The value of the pK_a of $(NH_3)_5Ru^{II}$(thioisoamide) was found to be 4.04 ± 0.13.

The uv–visible spectral features of $(NH_3)Ru^{III}$(thioisoamide) are of interest. The spectrum of the free ligand as shown in Figure 2 is characterized by three absorbance bands:[23] $\pi^* \leftarrow$ n thiocarbonyl, λ 350 nm; $\pi^* \leftarrow \pi$ thiocarbonyl, λ 232 nm; $\pi^* \leftarrow \pi$ pyridine, $\lambda \sim 260$ nm. The visible spectrum of the Ru(III) complex ion also shown in Figure 2 has in addition to these three absorbances of the ligand an absorbance in the region 400–500 nm which shifts to shorter wavelength on addition of acid; this shift is reversible and the measured molar extinction coefficient is pH dependent. The magnitude of the extinction coefficient at λ_{max} for the visible absorbance band, the fact that this absorbance band is not present in the free ligand, and the acid spectral shift suggest the absorbance band is due to a ligand-to-metal charge transfer. In the corresponding oxygen-containing complex, $(NH_3)_5Ru(isoamide)^{3+}$, there is no absorbance band of this nature detected in the visible or near-uv spectrum. The sulfur atom is larger than the oxygen atom and seems to possess some d character[24] in its atomic orbitals. If this is the case, then charge transfer could be attributed to the transfer of a nonbonding electron of sulfur from an orbital of d character into a vacant orbital of the ruthenium(III) metal center.

Aquation Reaction of the Product of the Chromium(II) Reduction of $(NH_3)_5Ru(amide)^{3+}$. The chromium(II) reduction of $(NH_3)_5Ru(amide)^{3+}$ as previously reported[10] proceeds by two parallel paths resulting in the formation of $(NH_3)_5Ru(amide)^{2+}$ from an outer-sphere electron-transfer pathway and in the formation, from an inner-sphere pathway, of a bridged species which undergoes slow aquation represented by the equation

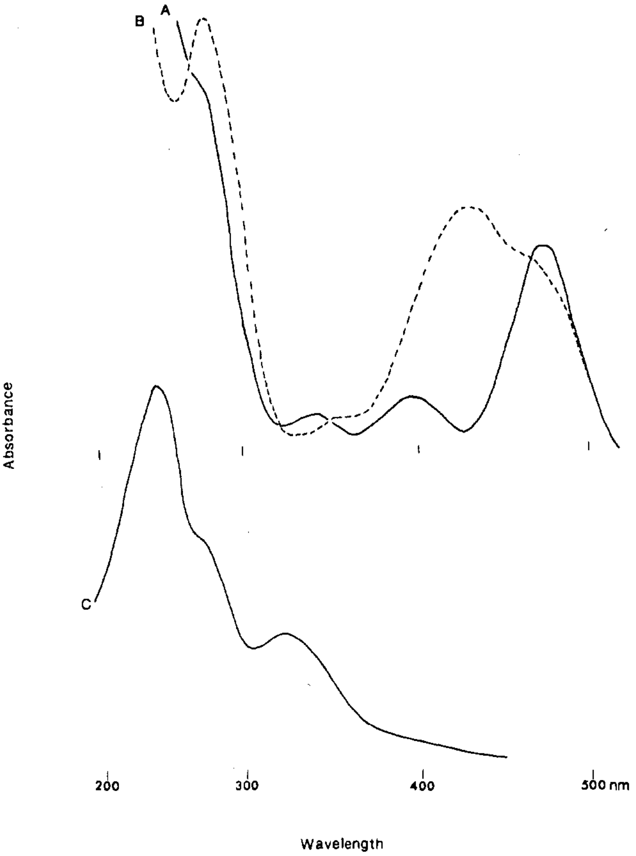
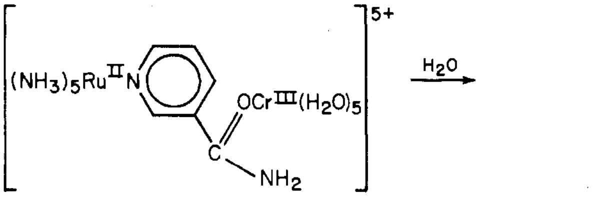


Figure 2. Visible–uv spectra of the $(NH_3)_5Ru^{III}$(thioisoamide) complex ion in water (A) and 0.01 *M* $HClO_4$ (B) and the thioisonicotinamide ligand in 0.01 *M* $HClO_4$ (C).



II

$(NH_3)_5Ru(amide)^{2+} + Cr(H_2O)_6^{3+}$

Results of kinetic experiments for the aquation of II in $HClO_4$–$LiClO_4$ medium are summarized in Table III. Plots of k_{obsd} *vs.* $[Cr^{2+}]_{excess}$ at fixed $[H^+]$ and k_{obsd} vs. $[H^+]^{-1}$ at fixed $[Cr^{2+}]_{excess}$ are linear and as in the case of the aquation

Table III. Observed Rate Constants for the Aquation of Ru^{II}-(amide)-Cr^{III} Bridged Species in the Presence of Excess Cr(II)[a]

10^4 [Ru(III)], *M*	10^3 $[Cr^{2+}]_{excess}$, *M*	$[H^+]$, *M*	$10^7 k_{obsd}$, sec^{-1}
A. Data at $\mu = 0.10$ in $HClO_4$-$LiClO_4$			
2.07	3.32	0.10	8.78
1.83	2.32	0.10	4.90
1.88	3.98	0.10	10.7
1.93	3.23	0.10	8.78
2.26	2.80	0.10	6.21
2.05	2.84	0.10	6.23
1.79	2.00	0.10	4.00
2.31	3.32	0.10	8.80
2.12	3.42	0.10	9.77
2.32	2.32	0.09	6.60
1.84	2.32	0.085	7.75
1.96	2.32	0.093	5.80
2.32	2.80	0.090	9.20
2.01	2.80	0.085	11.5
1.87	2.80	0.093	7.10
2.30	3.35	0.085	14.5
2.07	3.35	0.095	9.8
2.01	3.35	0.10	9.00
1.97	3.35	0.090	11.5
B. Data at $\mu = 0.10$ in HBr-LiBr Medium			
1.87	3.63	0.10	74.8
1.75	1.50	0.10	42.2
1.84	2.21	0.10	55.6
1.92	2.98	0.10	66.4
2.00	0.646	0.10	27.6
1.97	4.30	0.10	90.5
2.01	2.32	0.10	57.6
1.90	2.32	0.075	19.9
1.73	2.32	0.025	11.5
1.85	2.32	0.090	40.7
1.25	3.32	0.090	41.5
1.42	3.32	0.090	40.6
1.47	3.32	0.10	72.5
1.57	3.32	0.080	24.9
1.60	3.32	0.075	20.4
1.58	3.32	0.050	8.83
1.60	3.32	0.250	7.28
1.57	3.32	0.085	33.8
1.61	3.32	0.065	14.5
1.54	3.32	0.060	9.98

[a] Reactions followed at 410 nm at 25°.

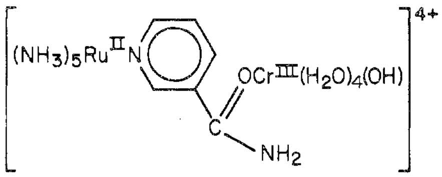
of I can be interpreted on the basis of the rate law

$$-\frac{d[II]}{dt} = \left\{ k_0 + \frac{k_1}{[H^+]} + \frac{k_2[Cr^{2+}]}{[H^+]} \right\} [II]$$

The values of the rate constants k_0, k_1, and k_2 are reported in Table IV.

Only an estimate of k_0 can be made from the experimental data. The aquation reaction of II is complicated after a period of about 1 half-life by the buildup of significant amounts of $(NH_3)_5Ru(amide)^{2+}$; there is the possibility of interference from both an aquation reaction of $(NH_3)_5Ru(amide)^{2+}$ and the perchlorate oxidation of the Ru(II)-containing species to Ru(III)-containing species. More important is the fact that there is a very small difference in the visible absorbance between II and $(NH_3)_5Ru(amide)^{2+}$ (60 M^{-1} cm^{-1} at the maximum difference in molar extinction coefficients). The change observed in the absorbance over 1 half-life was only 0.03 absorbance unit. Data were obtained using a 0.1 full-scale slide-wire. The error contribution is evident in the negative intercepts of the data plots; the error appears to affect all k_{obsd} values to the same extent as indicated by the fact that the intercepts of the lines for k_{obsd} vs. $[H^+]^{-1}$ at fixed $[Cr^{2+}]_{excess}$ are the same within the standard error of fit. The experimental data fit to an equation using a fixed value of $k_0 = 10^{-7}$ sec^{-1} resulted in a change of less than 10% in the values of k_2 compared to that reported in Table IV.

The rate law indicates three pathways for the aquation of the bridged species. The k_0 path corresponds to the spontaneous aquation of species II resulting in the formation of $(NH_3)_5Ru(amide)^{2+}$ and Cr(III) ions. The k_1 path corresponds to the spontaneous aquation of species III formed by



III

the ionization of a coordinated water of the chromium(III). The chromium(II)-catalyzed path described by k_2 is the result of an inner-sphere electron transfer from an attacking chromium(II) through the hydroxide bridge of III labilizing the chromium-carbonyl oxygen bond.

Comparison of the values of k_2 for the aquation of II to that of the aquation reaction of the protonated nicotinamidepentaaquochromium(III) complex ion[4] is of interest. Increased reactivity of protonated nicotinamidepentaaquochromium(III) ($k_2 = 1.3 \times 10^{-3}$ sec^{-1}) compared to that of the hexaaquo- ($k_2 = 1.2 \times 10^{-4}$ sec^{-1})[25] and acetatopentaaquochromium(III) ions ($k_2 = 2.5 \times 10^{-5}$ sec^{-1})[3] has been attributed to the presence of a postive charge on the ligand producing an increased acidity of protonated nicotinamidechromium(III).[4] According to this argument the presence of Ru(II) should effect a still greater reactivity in the aquation of II. The reverse reactivity, i.e., the value of k_2 for the aquation of II is nearly 2 orders of magnitude smaller than the value of k_2 reported for the protonated nicotinamidechromium(III) ion, is direct evidence for significant Ru(II)-to-ligand charge transfer which was suggested by the earlier reported aquation reaction of I.[6]

Bromide Ion Catalysis of the Aquation Reaction of I and II. In HBr-LiBr medium the aquation reactions of both I and II are at least 10 times faster than the aquation reactions studied under similar conditions of $[Cr^{2+}]_{excess}$, $[H^+]$, and temperature in $HClO_4$-$LiClO_4$ medium. The final products of the reaction in HBr-LiBr are the same as those in perchlorate medium.

Since the aquation reaction of I is sensitive to light, the aquation of II in bromide medium was studied in more detail. The values of k_{obsd} are reported in Table III. Plots of k_{obsd} vs. $[Cr^{2+}]_{excess}$ at fixed $[H^+]$ and k_{obsd} vs. $[H^+]$ at fixed $[Cr^{2+}]_{excess}$ are shown in Figures 3 and 4, respectively.

The acid dependence was somewhat unexpected. The acid dependence is best described in terms of variance of fit and

Table IV. Rate Data for the Aquation of the Ru^{II}-L-Cr^{III} Bridged Species Where L is Isonicotinamide, Nicotinamide, or Thioisonicotinamide[a]

Bridged species	k_0, sec^{-1}	k_0', sec^{-1}	k_1, *M* sec^{-1}	k_2, sec^{-1}
I	$(3.07 \pm 0.18) \times 10^{-6}$ [b]		$(2.77 \pm 0.29) \times 10^{-7}$ [b]	$(4.74 \pm 0.05) \times 10^{-4}$ [b]
	$(1.7 \pm 0.9) \times 10^{-6}$ [c]		$(2.72 \pm 0.50) \times 10^{-7}$ [c]	$(3.41 \pm 0.06) \times 10^{-4}$ [c]
II	$\sim 10^{-7}$		$(1.95 \pm 0.01) \times 10^{-7}$	$(4.05 \pm 0.26) \times 10^{-5}$
IV		$(3.94 \pm 0.27) \times 10^{-4}$ [d]	$(8.97 \pm 0.21) \times 10^{-5}$ [d]	0.271 ± 0.005[d]

[a] All data at 25° and $\mu = 0.10$ in $HClO_4$ except where noted. [b] $\mu = 1.0$. [c] $\mu = 0.40$. [d] All rates at 2.0° and $\mu = 0.01$.

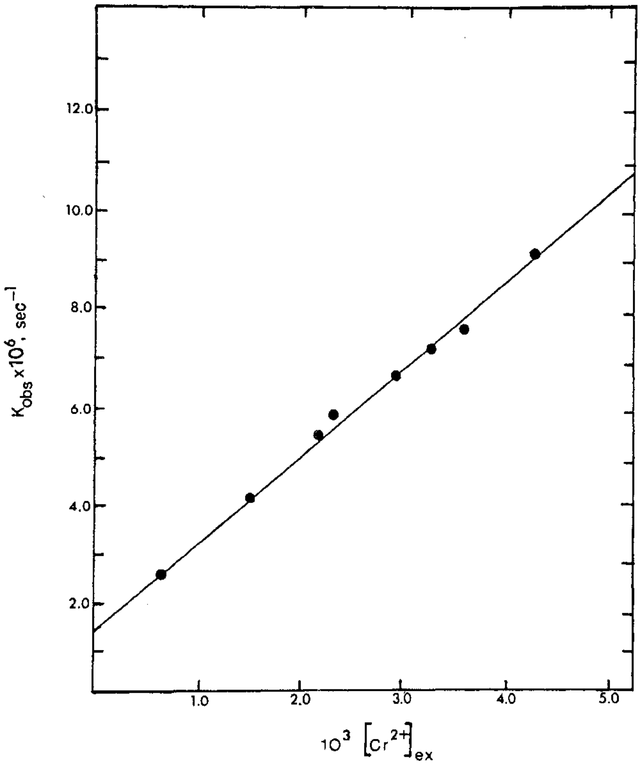


Figure 3. Plot of k_{obsd} for the aquation of $(NH_3)_5Ru^{II}$-(amide)-Cr^{III} species as a function of the concentration of excess Cr(II) at 25.0 ± 0.1°, $[H^+] = 0.10\ M$, and $\mu = 0.10$ in HBr-LiBr medium.

the number of parameters by the expression

$$k_{obsd} = k_0 + \frac{B}{[H^+]} + k'[H^+]$$

where $k_0 \approx 10^{-7}$, $B = (2.2 \pm 0.8) \times 10^{-7}$, and $k' = (1.49 \pm 0.32) \times 10^{-4}$.

It would be expected that the term B is defined by the expression $B = k_1 + k_2[Cr^{2+}]$ since both these terms show inverse acid dependence. The value of B and the value of k_2 observed in $HClO_4$-$LiClO_4$ medium indicate, although not conclusively, the terms

$$k_0 + \frac{k_1}{[H^+]} + \frac{k_2[Cr^{2+}]}{[H^+]}$$

are independent of bromide ion concentration and that in the overall rate law there are additional terms to describe the bromide ion catalysis and the direct acid dependence. Earlier work by Pennington and Haim indicated bromide ion catalysis and direct acid dependence in the chromium(II)-catalyzed path for the substitution of the iodide ion by the bromide ion in iodopentaaquochromium(III) ion.[26] The exact nature of the bromide ion catalysis, i.e., the extent of a trans effect or actual electron transfer through a bromide bridge instead of an hydroxide bridge, is not clear. Studies of the effect of changing bromide ion concentration at zero chromium(II) excess may clarify the nature of the bromide ion catalysis.

Aquation Reaction of the Product of the Chromium(II) Reduction of $(NH_3)_5Ru^{III}$(thioisoamide). On addition of Cr(II) to a solution containing $(NH_3)_5Ru^{III}$(thioisoamide) the color changes rapidly from yellow to violet. The initial reaction product has an intense absorption band centered about 610–615 nm which shifts to longer wavelength with time. The results of chromatographic studies at 4° indicate highly charged species are formed initially which rapidly ($t_{1/2} \approx 1.5$ min) undergo aquation resulting in the formation of $(NH_3)_5Ru^{II}$(thioisoamide) and Cr(III) ions.

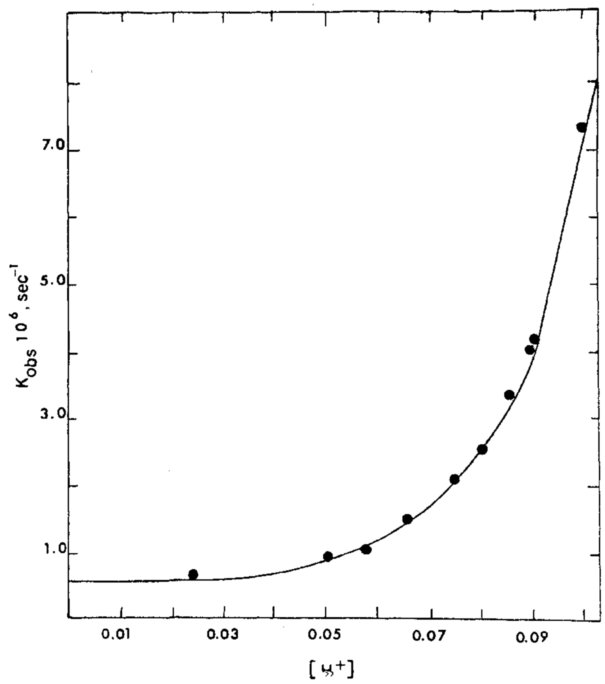
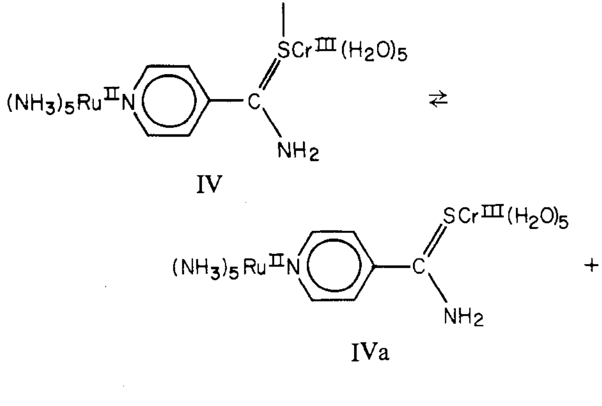


Figure 4. Plot of k_{obsd} for the aquation of $(NH_3)_5Ru^{II}$-(amide)-Cr^{III} species as a function of the acid concentration at 25.0 ± 0.1°, $\mu = 0.10$ in HBr-LiBr, and $[Cr^{2+}]_{excess} = 3.32 \times 10^{-3}\ M$.

The uv spectrum of the initial reaction product mixture is of more interest and importance in determining the nature of the initial products of the electron-transfer reaction. A very intense absorbance (ϵ ~9000 M^{-1} cm^{-1}) in the region around 270 nm is present; the intensity of the absorbance band decreases rapidly with time, and measurements of the extinction coefficient made at proportional intervals of the half-life at different acid concentrations indicate a direct relationship between the intensity of the absorbance and the acid concentration. For example, in 0.40 M HBr ϵ is 10,439 M^{-1} cm^{-1} while in 0.1 M HBr ϵ is 8884 M^{-1} cm^{-1}. Although the absorbance is in the region of the aromatic $\pi^* \leftarrow \pi$ transition, it is far too intense to be due to the $\pi^* \leftarrow \pi$ transition alone. Also the $\pi^* \leftarrow \pi$ transition should not decrease rapidly with time or show pH dependence. There is a second uv spectral feature at 350 nm. This absorbance also decreases with time, but the dependence of extinction coefficient on pH is completely opposite to that of the band at 270 nm. These two absorbance features may be explained as resulting from a sulfur-to-chromium(III) charge transfer, a characteristic feature of chromium(III)–sulfur bonds.[7-9] The absorbance at 350 nm may be attributed to the charge transfer of the unprotonated product species, while the band at 270 nm is due to the protonated species. On the basis of this evidence the Cr(II) reduction of $(NH_3)_5Ru^{II}$(thioisoamide) results in the formation of the bridged species related by the equilibrium



IV

IVa

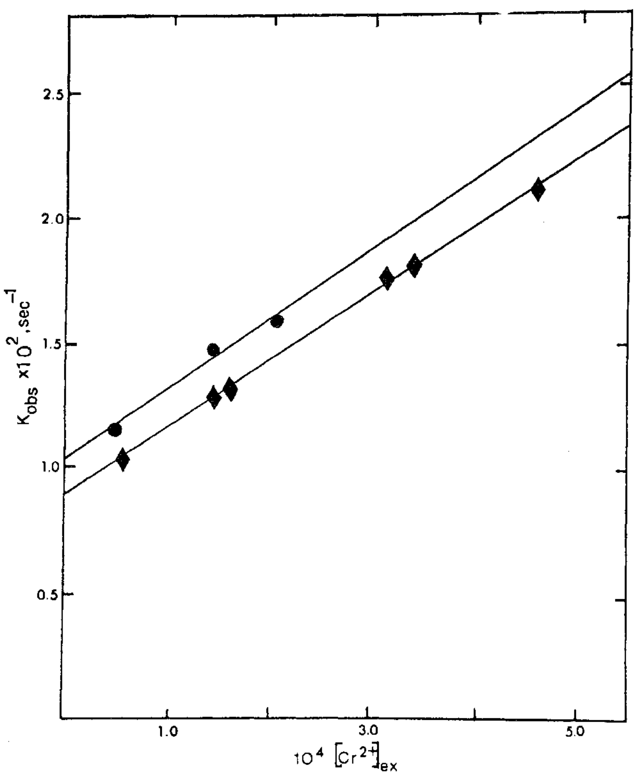


Figure 5. Plot of k_{obsd} for the aquation of $(NH_3)_5Ru^{II}$-(thioisoamide)-Cr^{III} as a function of the concentration of excess Cr(II) at $[H^+] = 0.009$ *M* (circles) and $[H^+] = 0.01$ *M* (diamonds). All data are at 2.0 ± 0.10° and $\mu = 0.01$.

The results of the kinetic experiments for the aquation of the Ru(II)-(thioisoamide)-Cr(III) species are summarized in Table V. Under the reaction conditions the bridged species is predominantly in the form of IV. The range of acid concentrations and $[Cr^{2+}]_{excess}$ is admittedly limited in order that the rate of aquation could be followed by conventional methods. The rate of the aquation reaction precluded any temperature dependence studies without stopped-flow methods. Plots of k_{obsd} vs. $[Cr^{2+}]_{excess}$ at fixed $[H^+]$ and k_{obsd} vs. $[H^+]^{-1}$ at fixed $[Cr^{2+}]_{excess}$ are shown in Figures 5 and 6, respectively. The data can be interpreted by a rate law similar to that observed in the case of the aquation of I and II, i.e.

$$\text{rate} = \left\{ k_0' + \frac{k_1}{[H^+]} + \frac{k_2[Cr^{2+}]}{[H^+]} \right\} [IV]$$

The values of the rate constants k_0', k_1, and k_2 are summarized in Table IV.

The argument of Nordmeyer and Taube[4] used in accounting for the enhanced reactivity of protonated nicotinamidepentaaquochromium(III) compared to that of the aquo and the acetato complexes is of value here. The enhanced reactivity of the protonated nicotinamidechromium(III) complex was explained as the effect of the presence of a positive charge on the ligand. The enhanced reactivity of the chromium(III) center in IV compared to I and II can be satisfactorily explained on the basis of protonation of the thioisonicotinamideruthenium(II) ligand. The presence of a proton on the sulfur atom in a position immediate to the chromium(III) should decrease the strength of the Cr^{III}-S bond, enhance the acidity of the pentaaquochromium(III) center, and increase the ease of the electron transfer to Cr(III); thus, the values of k_0', k_1, and k_2 would be expected to be greater due to protonation.

Table V. Observed Rate Constants for the Aquation of Ru^{II}-(thioisoamide)-Cr^{III} Bridged Species in the Presence of Excess Cr(II)

$10^4[Ru^{3+}]$, *M*	$10^4[Cr^{2+}]$, *M*	$[H^+]$,[a] *M*	10^2k_{obsd}, sec^{-1}
2.17	4.64	0.010	2.10
2.13	1.55	0.010	1.35
2.18	3.02	0.010	1.80
2.13	3.33	0.010	1.85
2.12	0.00	0.010	0.90
2.10	1.50	0.010	1.26
2.12	0.530	0.010	1.02
2.10	1.40	0.010	1.32
2.10	1.40	0.0085	1.59
2.10	1.40	0.0085	1.56
2.10	1.40	0.009	1.48
2.10	1.40	0.0095	1.41
2.10	1.40	0.0095	1.42
2.09	2.04	0.0091	1.54
2.11	2.04	0.010	1.42
2.10	2.04	0.0095	1.48
2.10	2.04	0.0095	1.46
2.11	2.04	0.0085	1.64
2.10	2.04	0.0091	1.58
2.11	0.404	0.010	1.01
2.10	0.404	0.0083	1.19
2.12	0.404	0.0093	1.02
2.09	0.404	0.0088	1.15

[a] All data at $\mu = 0.01$ in $HClO_4$-$LiClO_4$. Reaction followed at 580 nm at 2.0°.

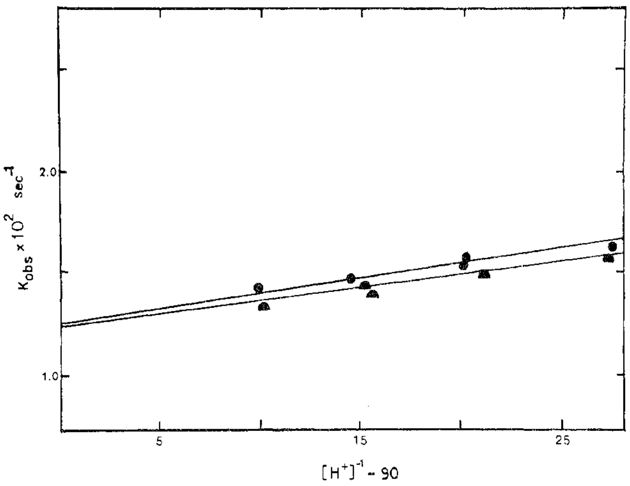


Figure 6. Plot of k_{obsd} for the aquation of $(NH_3)_5Ru^{II}$-(thioisoamide)-Cr^{III} as a function of $[H^+]^{-1} - 90$ at $[Cr^{2+}]_{excess} = 2.04 \times 10^{-4}$ *M* (circles) and $[Cr^{2+}]_{excess} = 1.40 \times 10^{-4}$ *M* (half-circles). All data are at 2.0 ± 0.1° and $\mu = 0.01$.

Recent studies of the spontaneous aquation of chromium(III)-sulfur bonds have been conducted by Deutsch et al.[7-9] The rate law which seems characteristic for these reactions is

$$\text{rate} = (k_0 + k[H^+])[\text{Cr(III) species}]$$

There is generally very little contribution from a $k_1/[H^+]$ path.

The detection of the k and k_1 paths depends upon the level of acid concentration used; at low acid concentrations the k_1 path would be easier to observe. The enhanced rate of the aquation reaction and the oxidation of $(NH_3)_5Ru^{II}$(thioisoamide) by perchlorate ion at increased ionic strength made observation of the aquation reaction at higher acid concentrations by conventional kinetic techniques impractical.

Although there is no direct proof, the k_0' term may well correspond to the expression

$$k_0' = k_0 + k[H^+]$$

A study of the aquation reaction of IV over a large range of acid concentration is needed to detect the presence of the k

path with confidence. No conclusion can be drawn as to the nature of the k_0 path, but the strongly basic nature of the sulfur suggests the possibility of the "tautomeric" mechanism[7] in which the leaving group is a protonated ligand, the proton coming from an intermolecular transfer instead of a simple aquation. The activation parameters of the k_0' path may elucidate the mechanism present.[3] Also at higher excesses of Cr(II) a "tautomeric" path of the form $k_3[Cr^{2+}]$ may well be observed.

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Registry No. I, 50639-78-6; II, 50639-79-7; IV, 54642-85-2; Cr^{2+}, 22541-79-3; Br^-, 24959-67-9; $[(NH_3)_5Ru(C_6H_6N_2S)](ClO_4)_2$, 54566-87-9; $[(NH_3)_5Ru(C_6H_6N_2S)](ClO_4)_3$, 54566-89-1.

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Manganese–Schiff Base Complexes. VI. Synthesis and Spectroscopy of Aquo[*N*,*N*'-ethylenebis(4-*sec*-butylsalicylaldiminato)]manganese(III) Perchlorate and μ-Dioxo-bis[*N*,*N*'-ethylenebis(4-*sec*-butylsalicylaldiminato)]dimanganese(IV) and the Related *N*,*N*'-Trimethylenebis(4-*sec*-butylsalicylaldimine) Complexes

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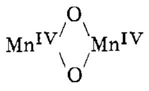
The new five-coordinate cationic complexes of Mn(III), $[Mn(SB)H_2O]ClO_4$, where SB is the dianion of the tetradentate Schiff base *N*,*N*'-ethylenebis(4-*sec*-butylsalicylaldimine) (BuSalen) and *N*,*N*'-trimethylenebis(4-*sec*-butylsalicylaldimine) (BuSaltm) have been synthesized and characterized. Mild base hydrolysis of chloroform solutions of these complexes in air yielded the new six-coordinate species $[Mn_2(BuSalen)_2O_2]\cdot H_2O$ and $[Mn_2(BuSaltm)O_2]\cdot 2H_2O$. The Mn(IV) complexes are dimeric in chloroform solution and show reduced room-temperature magnetic moments, $\mu = 2.5$ BM. Ir and visible spectral properties are also consistent with the presence of the ring



in these complexes.

Rapid progress has been made toward a detailed understanding of the important reaction of oxygen with metal ions in biological systems. Work on naturally occurring iron complexes and model compounds has revealed the complexities of the processes.[1] In order to assess the unique role of the metal atom, comparisons have been made between the behavior of the iron complexes and that of the complexes of the similar metals like cobalt and manganese. The bulk of the work to date has been carried out with cobalt[2] while the manganese system has been the subject of scattered reports. The reaction of a divalent metal complex with oxygen can lead to reversible oxygen binding or irreversible oxidation of the metal. In general, the latter process ultimately leads to the formation of tri- and tetravalent metal complexes which occur as dimeric and polymeric materials with oxo, peroxo, or hydroxo bridges between the metal ions. For manganese(II) complexes, the reaction with oxygen appears to lead to oxidation of the metal. For example, the reaction of oxygen with phthalocyaninemanganese(II) yields a dimeric complex with the linear unit $Mn^{III}–O–Mn^{III}$.[3] It should be pointed out that the reactant is a rare example of an intermediate-spin manganese complex.

A number of manganese complexes of the tetradentate Schiff bases *N*,*N*'-ethylenebis(salicylaldimine), H_2Salen, and *N*,*N*'-trimethylenebis(salicylaldimine), H_2Saltm, have been prepared. Recent reports indicate that the high-spin Mn(II) complexes react with oxygen irreversibly to yield various oxidation products. The crystal structure of the major reaction product for $Mn(Saltm)H_2O$ is a dimer with bridging oxygen