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Registry No. $Co(NH_3)_5SCN^{2+}$, 15005-69-3; $Co(NH_3)_5NCS^{2+}$, 14970-18-4.

References and Notes

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(22) The fact that the ratio of the quantum yields of Co^{2+} and $Co(NH_3)_5NCS^{2+}$ is essentially independent of excitation wavelength is consistent with the interpretation that no $Co(NH_3)_5NCS^{2+}$ is formed in the primary radical recombination.
(23) The formation of thiocyanate in the photolysis of complexes of this type is not without precedent.[8,24] It has been proposed[8] that the thiocyanate arises through hydrolysis of $(NCS)_2$ or through scavenging of $\cdot NCS$ or $(NCS)_2^-$ by dissolved species.
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(26) Presumably the memory arises from the absence of rotational relaxation in the primary cage.
(27) Calculations described in ref 17 indicate that electron transfer within the $Co(NH_3)_5ONO^{2+}$ precursor complex should be more rapid than within the $Co(NH_3)_5NO_2^{2+}$ precursor complex. Despite the fact that these calculations "predict" the desired result, they are open to question on at least two grounds. The first objection concerns the assumption that the charge on NO_2^- is centered on the *nitrogen* atom. Actually, although the latter assumption is incorrect, this error is of little consequence since the important factor is not where the net charge lies in NO_2^- but where the electron is added when NO_2 radical is reduced to NO_2^-. In the case of free NO_2, the reduction process can at least formally be regarded as electron addition to the nitrogen atom (which in NO_2 carries a formal positive charge).[28] The second objection is more fundamental. In calculating the solvent reorganization terms for the $(NH_3)_5CoONO^{2+}$ and $(NH_3)_5CoNO_2^{2+}$ precursor complexes, an equation derived for spherical ions was used[17] to predict the behavior of these systems. It is thus assumed that the solvent reorganization energy varies as $(1/a_1 + 1/a_2 - 1/r)$, where a_1 and a_2 are the radii of the reactant ($Co(NH_3)_5^{2+}$, NO_2, or ONO) spheres. There is, unfortunately, no sensible way to define the radius of the reactant sphere when the reactant is V shaped and the precursor complex is of the inner-sphere variety. Although it is clear that r is greater for $(NH_3)_5CoONO^{2+}$ (thus favoring formation of this isomer), the value of the $1/a_2$ term is *not* negligible and, depending on the a_2 values used, the formation of either isomer may be predicted.
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(29) Although we have postulated an inner-sphere electron-transfer reaction, an outer-sphere reaction in which the electron-transfer products $Co(NH_3)_5^{3+}$ and SCN^- combine to form only $Co(NH_3)_5NCS^{2+}$ (and $Co(NH_3)_5^{3+}$ and NO_2^- form only $Co(NH_3)_5ONO^{2+}$) is, of course, also consistent with the observations.
(30) Above it was tacitly assumed that the charge-transfer *singlet* state is responsible for the observed photochemistry and that this excited state produces a geminate radical pair of net *singlet* multiplicity upon dissociation. In a more detailed treatment it would be necessary to consider the possible formation of a geminate radical pair of triplet spin multiplicity and to allow for possible changes in the spin state of the cobalt(II).[7,17]
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Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Reactions of Chloraminepentaammineiridium(III) Ion. Evidence for a Coordinated Nitrene Intermediate

EDWARD D. JOHNSON and FRED BASOLO*

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The kinetics of the reaction of $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ with bromide ion and hydroxide ion have been investigated in acetic acid–sodium acetate buffers. The reactions are both first order in iridium complex. The reaction with hydroxide ion is first order in hydroxide ion, whereas the reaction with bromide ion is zero order in bromide ion. The hydrolysis reaction is inhibited by chloride ion. The mechanism proposed involves a coordinated nitrene intermediate. The kinetics of the reaction of iodide ion with $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ and with $[Ir(NH_3)_5(NH_2OSO_3)]^{2+}$ were also studied. The reaction of $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ is interpreted as two consecutive reactions, both first order in iodide ion. The reaction of $[Ir(NH_3)_5(NH_2OSO_3)]^{2+}$ is first order in complex and first order in iodide ion. A coordinated iodamine intermediate is postulated.

Introduction

Nitrene intermediates are well-known in organic chemistry and are postulated for aryl azide[1] and sulfonylchloramine[2] decompositions. Coordinated nitrene intermediates have been reported for the reactions of some azido–metal complexes. Photochemical generation of nitrenes are reported for $[Rh(NH_3)_5N_3]^{2+}$ [3] and for $[Ir(NH_3)_5N_3]^{2+}$.[4] Coordinated nitrene intermediates are also postulated for some thermal reactions of azido–metal complexes of ruthenium(III)[5] and iridium(III).[6,7] These coordinated nitrenes react with various nucleophiles.[6,7] This paper reports a kinetic study of the reactions of the chloraminepentaammineiridium(III) ion with bromide ion, hydroxide ion, and iodide ion. The results obtained suggest the formation of a nitrene intermediate in the reaction with bromide ion and with hydroxide ion. The intermediate behaves similarly to the intermediate generated from $[Ir(NH_3)_5N_3]^{2+}$, which is believed to be the nitrene $[Ir(NH_3)_5NH]^{3+}$.

The reactions of iodide ion with $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ and with $Ir(NH_3)_5(NH_2OSO)_3]^{2+}$ are first order in iodide ion, and for these reactions the intermediate is believed to be $[Ir(NH_3)_5(NH_2I)]^{3+}$.

Experimental Section

Synthesis and Reactions. The compounds $[Ir(NH_3)_5(NH_2Cl)](ClO_4)_3$, $[Ir(NH_3)_5N_3](ClO_4)_2$, and $[Ir(NH_3)_5(NH_2OH)](ClO_4)_3$

were prepared by published methods[6,8] and characterized by ultraviolet spectra, infrared spectra, and elemental analyses.

Bromaminepentaammineiridium(III) perchlorate, $[Ir(NH_3)_5(NH_2Br)](ClO_4)_3$, was prepared by adding 3 ml of concentrated H_2SO_4 to 0.52 g of $[Ir(NH_3)_5N_3](ClO_4)_2$ in 8 ml of water, keeping the mixture at room temperature for 45 min and then cooling it to 0 °C. The white precipitate, $[Ir(NH_3)_5(NH_2OSO_3)]SO_4$, was collected on a fritted filter and then suspended in a solution of 1.1 g of $BaBr_2$ in 20 ml of 0.1 M HBr. After 1 h at 25 °C, the $BaSO_4$ precipitate was removed, and 20 ml of 70% $HClO_4$ was added to the filtrate. The precipitated perchlorate was collected on a filter, washed with ethanol and then with ether, and then air-dried; yield 0.23 g, 35%. Anal. Calcd for $[Ir(NH_3)_5(NH_2Br)](ClO_4)_3$: N, 12.51; H, 2.55. Found: N, 12.75; H, 2.66.

It was also possible to prepare $[Ir(NH_3)_5(NH_2Br)](ClO_4)_3$ by starting with $[Ir(NH_3)_5(NH_2Cl)]^{3+}$. To a solution of 0.10 g of $[Ir(NH_3)_5(NH_2Cl)](ClO_4)_3$ in 20 ml water was added 0.6 g of NaBr and 2 drops of 50% HBr solution. After 30 min at room temperature, 30 ml of 70% $HClO_4$ was added to the reaction mixture to precipitate the product. After cooling of the mixture in an ice bath, the product which crystallized was collected on a frit, washed with ethanol, and air-dried; yield 0.069 g, 60%. Anal. Calcd for $[Ir(NH_3)_5(NH_2Br)](ClO_4)_3$: N, 12.51; H, 2.55. Found: N, 12.62; H, 2.84.

The corresponding bromide salt $[Ir(NH_3)_5(NH_2Br)]Br_3$ was prepared by adding 5 ml of 50% HBr to a solution of 0.20 g of $[Ir(NH_3)_5(NH_2Br)](ClO_4)_3$ in 20 ml of water. Upon cooling of the mixture to 0 °C the crystalline product separated from solution; yield 47%.

An additional method for the preparation of $[Ir(NH_3)_5(NH_2Br)]Br_3$ involved the direct decomposition of $[Ir(NH_3)_5N_3]^{2+}$. A solution of 0.40 g of $[Ir(NH_3)_5N_3](ClO_4)_2$ in 6 M HBr (20 ml) was heated for 1 h at 80 °C. The solution was cooled to room temperature, and 60 ml of methanol was added to precipitate the desired product. The product was twice recrystallized from 0.01 M HBr, collected on a filter, and air-dried; yield 0.20 g, 42%.

The titration of an aqueous solution of $[Ir(NH_3)_5(NH_2Br)]Br_3$ with silver ion showed 3 equiv of bromide ion. A solution of $[Ir(NH_3)_5(NH_2Br)]Br_3$, which had been made basic by the addition of a sodium hydroxide solution (to a pH of 9) and then after 15 min made acidic with $HClO_4$, showed 4 equiv of bromide ion when titrated with silver ion. Solutions of $[Ir(NH_3)_5(NH_2Cl)]Cl_3$ show analogous behavior when titrated with silver ion.[6]

Salts of the complex $[Ir(NH_3)_5(NH_2Br)]^{3+}$ oxidize iodide ion to iodine with the formation of $[Ir(NH_3)_6]^{3+}$. The salt $[Ir(NH_3)_6]Cl_3$ was isolated from such a reaction mixture and identified by its UV spectrum and elemental analyses. This reaction of the bromamine complex with iodide ion is similar to that of free NH_2Br,[9] NH_2Cl,[10] and $[Ir(NH_3)_5(NH_2Cl)]^{3+}$,[6] all of which also oxidize I^- to I_2.

The ultraviolet spectrum of $[Ir(NH_3)_5(NH_2Br)]^{3+}$ salts contain a strong band at 270 nm (ϵ 1600) (Figure 1). This atypical $[Ir(NH_3)_5L]^{3+}$ spectrum can be attributed to the same transition that gives rise to a band at 278 nm[11] in bromamine itself.

Kinetic Studies. Kinetic data were obtained in aqueous solutions for reactions 1–4. All kinetic studies were carried out using approximately 10^{-3} M solutions of complexes.

$$[Ir(NH_3)_5(NH_2Cl)]^{3+} + Br^- \rightarrow [Ir(NH_3)_5(NH_2Br)]^{3+} + Cl^- \quad (1)$$

$$[Ir(NH_3)_5(NH_2Cl)]^{3+} + OH^- \rightarrow [Ir(NH_3)_5(NH_2OH)]^{3+} + Cl^- \quad (2)$$

$$[Ir(NH_3)_5(NH_2Cl)]^{3+} + 2I^- + H^+ \rightarrow [Ir(NH_3)_6]^{3+} + I_2 + Cl^- \quad (3)$$

$$[Ir(NH_3)_5(NH_2OSO_3)]^{2+} + 2I^- + H^+ \rightarrow [Ir(NH_3)_6]^{3+} + I_2 + SO_4^{2-} \quad (4)$$

Pseudo-first-order reaction conditions were employed using at least a tenfold excess of reagent over the complex concentration. First-order rate constants were calculated from plots of ln $(A_t - A_\infty)$ vs. time, which were linear for at least 3 half-lives. Duplicate kinetic runs gave rate constants with a better than 10% precision.

The rate of reaction 1 in buffered solutions of sodium phosphate–sodium hydrogen phosphate or acetic acid–sodium acetate were followed by monitoring the increase in absorbance at 270 nm. The rates of reaction 2 in acetic acid–sodium acetate buffer solutions, with added chloride ion, were followed by the decrease in absorbance at 258 nm. Initial rates (first 3% of the reaction) were used to determine the rates of reaction 2 in the absence of chloride ion and to determine the hydrogen ion dependence of the reaction. The rate of reaction 3 was measured at an ionic strength of 0.1 M ($NaClO_4$) and was determined by monitoring the increase in absorbance at both 400 and 353 nm. The rate of reaction 4 was determined by following the increase in absorbance at 400 nm. Reaction 1 was followed with a Cary 14 spectrometer. Reactions 2 and 4 were studied both on a Cary 14 and an Applied Physics Model 1705 stopped-flow spectrometer. Reaction 3 was followed with the stopped-flow instrument.

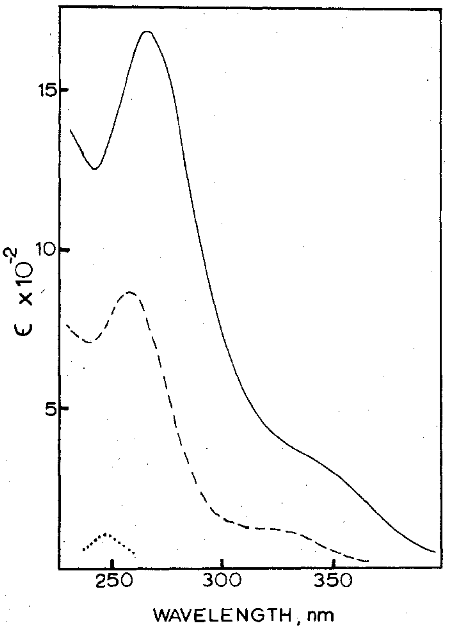


Figure 1. Absorption spectra of $[Ir(NH_3)_5(NH_2Br)](ClO_4)_3$ (—), $[Ir(NH_3)_5(NH_2Cl)](ClO_4)_3$ (- - -), and $[Ir(NH_3)_5(NH_2OH)](ClO_4)_3$ (· · · ·).

Results

The formation of $[Ir(NH_3)_5(NH_2Br)]^{3+}$ from $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ is found to be first order in $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ and independent of bromide ion in the range 0.02 M $< [Br^-] <$ 0.1 M (Table I). However, the rate of formation is pH dependent, and kinetic studies were carried out at 2×10^{-5} M $< [H^+] < 14 \times 10^{-5}$ M. A plot of $1/k_{obsd}$ vs. $[H^+]$ is linear over the range studied.

The formation of $[Ir(NH_3)_5(NH_2OH)]^{3+}$ from $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ is first order in iridium complex concentration when additional chloride ion is present. In the absence of additional chloride ion, the ln $(A - A_\infty)$ vs. time plot (Figure 2) deviated from linearity. Reaction 2 is inversely dependent on chloride ion concentration and inversely dependent on hydrogen ion concentration. A plot of $1/k_{obsd}$ vs. $[H^+]$ (obtained from initial rates) is linear.

A plot of ln $(A - A_\infty)$ vs. time (Figure 3) for the reduction of $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ by iodide ion did not yield a straight line. However, treatment of the data according to the theory of consecutive first-order reactions[12] yields two pseudo-first-order rate constants, k_{slow} and k_{fast} (Table II). Plots of k_{slow} vs. $[I^-]$ and k_{fast} vs. $[I^-]$ are linear and give respective second-order rate constants of 10 and 45 M^{-1} s^{-1}, respectively. The reaction was independent of hydrogen ion in the range 10^{-2}–10^{-4} M.

The reaction of iodide ion with $[Ir(NH_3)_5(NH_2OSO_3)]^{2+}$ is first order in $[Ir(NH_3)_6(NH_2OSO_3)]^{2+}$ concentration. Values of k_{obsd} for reaction 4 are given in Table II. A plot k_{obsd} vs. $[I^-]$ is a straight line and yields a second-order rate constant of 0.01 M^{-1} s^{-1}.

Discussion

A mechanism for the formation of $[Ir(NH_3)_5(NH_2Br)]^{3+}$ consistent with the results is given by eq 5–8. Equations 9 and 10 give two forms of the expression for the observed rate

Table I. Pseudo-First-Order Rate Constants for the Formation of $[Ir(NH_3)_5(NH_2Br)]^{3+}$ and of $[Ir(NH_3)_5(NH_2OH)]^{3+}$ from $[Ir(NH_3)_5(NH_2Cl)]^{3+}$

Effect of Hydrogen Ion on the Formation of $[Ir(NH_3)_5(NH_2Br)]^{3+}$ ($[Br^-] = 0.05$ M, $T = 25$ °C, Eq 1)

$10^5[H^+]$, M	10^3k_{obsd}, s^{-1}	$10^5[H^+]$, M	10^3k_{obsd}, s^{-1}
1.99	3.48, 4.11	6.68	1.25, 1.24, 1.28
4.26	1.79, 1.81	14.10	0.609, 0.617

Effect of Bromide Ion on the Formation of $[Ir(NH_3)_5(NH_2Br)]^{3+}$ Ion ($[H^+] = 1.4 \times 10^{-5}$ M, $T = 25$ °C, Eq 1)

$10^2[Br^-]$, M	10^3k_{obsd}, s^{-1}	$10^2[Br^-]$, M	10^3k_{obsd}, s^{-1}
2.30	6.21, 6.25	7.50	6.95, 6.44
5.00	6.68, 6.47, 6.81	10.00	7.08, 6.87

Effect of Chloride Ion on the Hydrolysis of $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ ($[H^+] = 3.72 \times 10^{-6}$ M, 25 °C, Eq 2)

$10^2[Cl^-]$, M	10^3k_{obsd},[a] s^{-1}	$10^2[Cl^-]$, M	10^3k_{obsd},[a] s^{-1}
1.00	7.33	7.00	1.92
3.00	3.90	10.0	1.39
5.00	2.43		

Effect of Hydrogen Ion on the Hydrolysis of $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ (k_{obsd} from Initial Rates, 25 °C, Eq 2)

$10^5[H^+]$, M	10^3k_{obsd},[b] s^{-1}	$10^5[H^+]$, M	10^3k_{obsd},[b] s^{-1}
2.82	3.71	9.04	1.61
5.64	2.28	11.22	1.33

[a] Each k_{obsd} is the average of three runs. [b] Each k_{obsd} is the average of several runs.

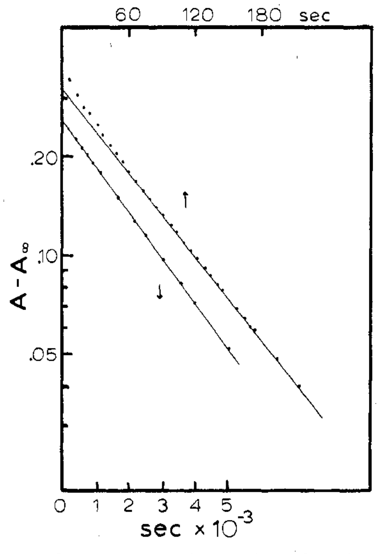


Figure 2. Plot of ln ($A - A_\infty$) vs. time for the hydrolysis of $[Ir(NH_3)_5(NH_2Cl)](ClO_4)_3$, eq 2, with added chloride ion (0.05 M) (lower curve), and with no added chloride ion (upper curve); $[H^+] = 3.72 \times 10^{-6}$ M, 25 °C.

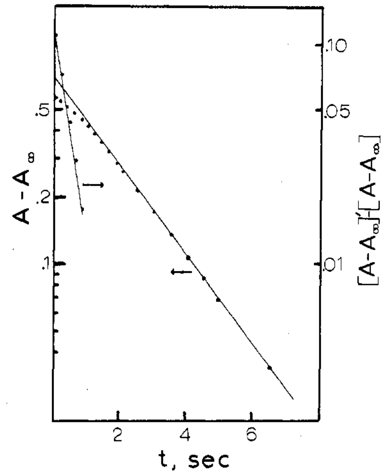


Figure 3. Plot of ln ($A - A_\infty$) and ln [$(A - A_\infty)' - (A - A_\infty)$] for the reaction of $[Ir(NH_3)_5(NH_2Cl)](ClO_4)_3$ with iodide, eq 3, at 25 °C.

Table II. Pseudo-First-Order Rate Constants for the Reduction of $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ and of $[Ir(NH_3)_5(NH_2OSO_3)]^{2+}$ by Iodide Ion

Effect of Iodide Ion on Reduction of $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ ($T = 25$ °C, eq 3)

$10^2[I^-]$, M	$10k_{slow}$,[a] s^{-1}	$10k_{fast}$,[a] s^{-1}
0.50	1.24, 1.18, 1.25, 1.15	5.9, 5.5, 5.8, 5.2
1.0	1.64, 1.66, 1.70, 1.68	7.7, 8.0, 8.0, 7.5
3.0	3.69, 3.49	17.0, 16.0
4.0	4.48	21.0
5.0	5.55, 5.84, 5.69	25.0, 27.0, 27.0

Effect of Iodide Ion on Reduction of $[Ir(NH_3)_5(NH_2OSO_3)]^{2+}$ ($T = 20$ °C, eq 4)

$10^2[I^-]$, M	10^3k_{obsd}, s^{-1}	$10^2[I^-]$, M	10^3k_{obsd}, s^{-1}
1.35	2.61, 2.65	4.02	5.66, 5.50, 5.34
2.22	3.54, 3.50, 3.61	5.34	6.77, 6.61, 6.68

[a] See Figure 3 for meaning of k_{slow} and k_{fast}.

$$[Ir(NH_3)_5(NH_2Cl)]^{3+} \overset{K_1}{\rightleftharpoons} [Ir(NH_3)_5(NHCl)]^{2+} + H^+ \tag{5}$$

$$[Ir(NH_3)_5(NHCl)]^{2+} \xrightarrow{k_2} [Ir(NH_3)_5NH]^{3+} + Cl^- \tag{6}$$

$$[Ir(NH_3)_5NH]^{3+} + Br^- \rightarrow [Ir(NH_3)_5(NHBr)]^{2+} \tag{7}$$

$$[Ir(NH_3)_5(NHBr)]^{2+} + H^+ \rightarrow [Ir(NH_3)_5(NH_2Br)]^{3+} \tag{8}$$

$$k_{obsd} = \frac{k_2K_1}{K_1 + [H^+]} \tag{9}$$

$$1/k_{obsd} = \frac{[H^+]}{k_2K_1} + \frac{1}{k_2} \tag{10}$$

constant derived from the mechanism (5)–(8). Earlier studies reported[6] the acid ionization constant $K_1 = 1.26 \times 10^{-6}$, from a titration of a solution of $[Ir(NH_3)_5(NH_2Cl)]^{3+}$. The value of k_2 is obtained from a plot of $1/k_{obsd}$ vs. $[H^+]$ which is a straight line.

This rate law is of the same form as that reported[6] for the hydrolysis of $[Ir(NH_3)_5(NH_2Cl)]^{3+}$. Also the limiting rates are similar, 0.025 s^{-1} compared with 0.05 s^{-1} found in this study. However the earlier study[6] did not distinguish between a nucleophilic attack by hydroxide ion (eq 2) and a unimolecular chloride ion release of the deprotonated chloramine (eq 6). The work reported here on the bromamine suggests that a unimolecular process may also be occurring with the hydrolysis of the chloramine. If the hydrolysis also goes by a unimolecular decomposition (i.e., a coordinated nitrene intermediate), then chloride ion should react with the coordinated nitrene intermediate.[4,6] In such a case reactions run with added excess chloride ion should be slower than those run with initially no chloride ion present. Experiments do indeed show that the reactions run with excess chloride ion were much slower than those with no added chloride ion (Table I). This observation, along with the earlier results[6] of inverse hydrogen ion concentration dependence, supports the mechanism (11)–(13). The rate law derived from the above mechanism

$$[Ir(NH_3)_5(NH_2Cl)]^{3+} \overset{K_1}{\rightleftharpoons} [Ir(NH_3)_5(NHCl)]^{2+} + H^+ \tag{11}$$

$$[Ir(NH_3)_5(NHCl)]^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Ir(NH_3)_5NH]^{3+} + Cl^- \tag{12}$$

$$[Ir(NH_3)_5NH]^{3+} + H_2O \xrightarrow{k_4} [Ir(NH_3)_5(NH_2OH)]^{3+} \tag{13}$$

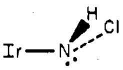
is given by eq 14.

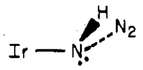
$$k_{\text{obsd}} = \frac{k_4k_3K_1}{(k_4 + k_{-3}[\text{Cl}^-])([\text{H}^+] + K_1)} \qquad (14)$$

This is consistent with the rate law previously reported[6] for studies at low chloride ion concentration. Under these conditions $k_4 \gg k_{-3}[\text{Cl}^-]$ and $k_{\text{obsd}} = k_3K_1/([\text{H}^+] + K_1)$. For the proposed mechanism, both hydrolysis (eq 2) and the formation of bromamine complex (eq 1) have the loss of chloride ion as the rate-determining step. This requires that the two reactions proceed at the same rate (i.e., $k_3 = k_2$). However, bromamine formation from $[\text{Ir(NH}_3)_5(\text{NH}_2\text{Cl})]^{3+}$ is faster than the rate reported for its hydrolysis.

Using the values reported[4] of $k_4 = 2 \times 10^3$ s^{-1} and $k_{-3} = 3.5 \times 10^6$ M^{-1} s^{-1}, one can estimate the $k_4 + k_{-3}[\text{Cl}^-]$ term in the rate expression (eq 14). Under the conditions of this study, 10^{-3} M complex, the chloride ion concentration will vary from 0.0 to 10^{-3} M during the course of hydrolysis. The $k_4 + k_{-3}[\text{Cl}^-]$ term will then vary from 2×10^3 s^{-1} at $[\text{Cl}^-] = 0.0$ to 5.5×10^3 s^{-1} at $[\text{Cl}^-] = 1.0 \times 10^{-3}$ M. For a change of this magnitude, a factor of 2 in k_{obsd}, one does not expect simple first-order kinetic behavior for the hydrolysis of the chloramine complex with no added chloride ion. Upon reexamination of the hydrolysis of $[\text{Ir(NH}_3)_5(\text{NH}_2\text{Cl})]^{3+}$, with no excess chloride ion in a sodium acetate–acetic acid buffer, a deviation from first-order behavior was observed (Figure 2). The initial portion of a plot ln $(A - A_\infty)$ vs. time was curved, and as the reaction proceeded, the rate decreased and the plot approached linearity. Further investigation of the hydrolysis using initial rates gave a limiting rate of 0.04 s^{-1} for the hydrolysis which compares with 0.05 s^{-1} for the formation of bromamine. (The initial rates covered less than the first 3% of the reaction, so any chloride ion produced is negligible.) The similarity of the limiting rates ($k_3 \approx k_2$) is further evidence that both reactions go by the same coordinated nitrene intermediate.

Much has been written[4-6] on the stability of the coordinated nitrene intermediate. This enhanced stability of coordinated nitrene compared with free nitrene is attributed to dπ–pπ bonding (from a filled d orbital on the metal to the empty p orbital of the electron-deficient NH). One resonance form of the protonated azido group, $\text{Ir(N}_3\text{H)}$, is similar to that of the coordinated chloramide.





In both cases the leaving group would take with it a pair of bonding electrons leaving an electron-deficient nitrogen capable of interacting with a filled d_{xz} or d_{yz} orbital of the metal. This stabilization of the nitrene intermediate may allow the hydrolysis of the coordinated chloramine to proceed via a nitrene intermediate, whereas the hydrolysis of free chloramine involves an $\text{S}_\text{N}2$ process.[13]

The reaction of $[\text{Ir(NH}_3)_5(\text{NH}_2\text{Cl})]^{3+}$ with iodide ion is an order of magnitude faster than either the reaction with bromide ion or the hydrolysis reaction. The reaction with iodide ion is not a simple first-order reaction but is consistent with two consecutive reactions. This behavior suggests a nucleophilic attack by iodide ion on the chloramine producing an iodamine intermediate, which subsequently reacts with another iodide ion to form iodine (eq 15–17).

$$[\text{Ir(NH}_3)_5(\text{NH}_2\text{Cl})]^{3+} + \text{I}^- \xrightarrow{k_5} [\text{Ir(NH}_3)_5(\text{NH}_2\text{I})]^{3+} + \text{Cl}^- \qquad (15)$$

$$[\text{Ir(NH}_3)_5(\text{NH}_2\text{I})]^{3+} + \text{I}^- \xrightarrow{k_6} [\text{Ir(NH}_3)_5(\text{NH}_2)]^{2+} + \text{I}_2 \qquad (16)$$

$$[\text{Ir(NH}_3)_5(\text{NH}_2)]^{2+} + \text{H}^+ \rightarrow [\text{Ir(NH}_3)_6]^{3+} \qquad (17)$$

Monoiodamine (NH_2I) has been demonstrated to be an intermediate in the iodination of aqueous ammonia.[14] Krueger et al.[15] have also postulated monoiodamine to be an intermediate in the oxidation of hydroxylamine-*O*-sulfonic acid ($\text{NH}_2\text{OSO}_3\text{H}$) by iodide ion.

The reaction of iodide ion with $[\text{Ir(NH}_3)_5(\text{NH}_2\text{OSO}_3)]^{2+}$ is first order in complex and iodide ion. A mechanism analogous to that of the reaction of the chloramine complex is proposed (eq 18–20).

$$[\text{Ir(NH}_3)_5(\text{NH}_2\text{OSO}_3)]^{2+} + \text{I}^- \xrightarrow{k_7} [\text{Ir(NH}_3)_5(\text{NH}_2\text{I})]^{3+} + \text{OSO}_3^{2-} \qquad (18)$$

$$[\text{Ir(NH}_3)_5(\text{NH}_2\text{I})]^{3+} + \text{I}^- \rightarrow [\text{Ir(NH}_3)_5(\text{NH}_2)]^{2+} + \text{I}_2 \qquad (19)$$

$$[\text{Ir(NH}_3)(\text{NH}_2)]^{2+} + \text{H}^+ \rightarrow [\text{Ir(NH}_3)_6]^{3+} \qquad (20)$$

In this case, however, there is no evidence for an iodamine intermediate. The iodamine intermediate is included because of the similarity of this reaction to the reaction of iodide ion in the chloramine system and because NH_2I is postulated as an intermediate in the reduction of $\text{NH}_2\text{OSO}_3^-$ by iodide ion.[15] The iodamine intermediate is not observed in the reaction of $[\text{Ir(NH}_3)_5(\text{NH}_2\text{OSO}_3)]^{2+}$ with iodide ion because reaction 18 is slower than reaction 19. As a result, the concentration of the intermediate iodamine remains small relative to the reaction of iodide ion with the chloramine complex.

Finally it is of interest to note that the reaction of this coordinated $\text{NH}_2\text{OSO}_3^-$ group (eq 4) is slightly faster (0.10 M^{-1} s^{-1}) than the reaction of iodide ion with uncoordinated $\text{H}_2\text{NOSO}_3^-$ (eq 21) (0.069 M^{-1} s^{-1}),[15] and faster than the

$$\text{H}_2\text{NOSO}_3^- + 3\text{I}^- + 2\text{H}^+ \rightarrow \text{I}_3^- + \text{NH}_4^+ + \text{SO}_4^{2-} \qquad (21)$$

reaction with H_3NOSO_3 (0.023 M^{-1} s^{-1}).[15] The greater reactivity of coordinated $\text{H}_2\text{NOSO}_3^-$ is further demonstrated by the reaction of chloride with $[\text{Ir(NH}_3)_5(\text{NH}_2\text{OSO}_3)]^{2+}$ (eq 22),[6] whereas chloride ion does not react with the uncoordinated hydroxylamine-*O*-sulfonate anion.[15]

$$[\text{Ir(NH}_3)_5(\text{NH}_2\text{OSO}_3)]^{2+} + \text{Cl}^- \rightarrow [\text{Ir(NH}_3)_5(\text{NH}_2\text{Cl})]^{3+} + \text{SO}_4^{2-} \qquad (22)$$

Krueger et al.[15] explained the greater reactivity observed for $\text{H}_2\text{NOSO}_3^-$ than for the molecular form, H_3NOSO_3, by involving the lone pair of electrons on the nitrogen of the anion in π bonding with low-lying unfilled orbitals on the iodide ion.

The positively charged ion $[\text{Ir(NH}_3)_5(\text{NH}_2\text{OSO}_3)]^{2+}$ would be expected to react much faster with iodide ion than the anion $\text{NH}_2\text{OSO}_3^-$. Since the reactivity is increased only slightly, the charge factors appear to be compensated by another factor, perhaps that of π bonding described by Krueger[15] (vide supra). Since the lone pair of electrons of the nitrogen ligand atom are involved in bonding to the iridium, they are not available (as is also true for H_3NOSO_3) to participate in π bonding with the entering iodide ion. Thus, the similarity of reactivity of $\text{NH}_2\text{OSO}_3^-$ and $[\text{Ir(NH}_3)_5(\text{NH}_2\text{OSO}_3)]^{2+}$ can be understood if the charge effect counterbalances the π-overlap effects.

Conclusion

The reaction of $[\text{Ir(NH}_3)_5(\text{NH}_2\text{Cl})]^{3+}$ with bromide ion and hydroxide ion has been shown to go by a nitrene intermediate, $[\text{Ir(NH}_3)_5\text{NH}]^{3+}$, which is the same intermediate that is postulated for the reaction of $[\text{Ir(NH}_3)_5\text{N}_3]^{2+}$ with concentrated acids. The reduction of $\text{Ir(NH}_2\text{X)}$ compounds (X = Cl, OSO_3) with iodide ions has been shown to go by an $\text{Ir(NH}_2\text{I)}$ intermediate.

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Registry No. $[\text{Ir(NH}_3)_5(\text{NH}_2\text{Br})](\text{ClO}_4)_3$, 61128-91-4; $[\text{Ir(NH}_3)_5(\text{NH}_2\text{Cl})]^{3+}$, 44627-60-3; $[\text{Ir(NH}_3)_5(\text{NH}_2\text{OSO}_3)]^{2+}$, 45020-90-4; $[\text{Ir(NH}_3)_5\text{N}_3](\text{ClO}_4)_2$, 38552-10-2; I^-, 20461-54-5; H^+,

12408-02-5; Br⁻, 24959-67-9; Cl⁻, 16887-00-6.

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Contribution from the Department of Chemistry and Division of Biochemistry,
University of Wyoming, Laramie, Wyoming 82071

Properties of Metal Complexes in the Interphase of an Oil Continuous Microemulsion. 2. Interaction of Copper(II) with the Side Chains of Lysine, Glutamine, and Methionine[1]

GARLAND D. SMITH, B. B. GARRETT,[2] SMITH L. HOLT, and ROLAND E. BARDEN*[3]

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Complexes of Cu(II) and the side chains of N^α-dodecanoyl-L-lysinol, N^α-dodecanoyl-L-glutaminol, and N-dodecanoyl-L-methioninol were investigated in the interfacial domain of an oil continuous microemulsion. The microemulsion consisted of water solubilized in a hexane continuous phase by hexadecyltrimethylammonium perchlorate and 2-propanol. Potentiometry and/or absorption and electron paramagnetic resonance spectroscopy were used to determine the nature of the complexes. In the Cu(II)/N^α-dodecanoyl-L-lysinol system, the limit species is a $\mathrm{CuL_4}^{2+}$ complex in which four ϵ-amino groups are bound to Cu(II) in a square-planar geometry. The calculated formation constants are log $K_1 = 6.13$, log $K_2 = 5.66$, log $K_3 = 4.97$, and log $K_4 = 3.93$. The measured values for $g_\parallel$, $A_\parallel$, $g_\perp$, and $A_\perp$ are respectively 2.25, 170 G, 2.07, and 15 G. The side chains of glutamine and methionine contain functional groups which are very weak ligands for Cu(II). These two side chains were "forced" to interact with Cu(II) by significantly decreasing the amount of water in the microemulsion. In the Cu(II)/N^α-dodecanoyl-L-glutaminol system, the limit species is a CuL^{2+} complex (log $K = 0.23$), for which $g_\parallel = 2.36$ and $A_\parallel = 140$ G. The carbonyl oxygen of the amido group is believed to be the ligand site. CuL^{2+} and $\mathrm{CuL_2}^{2+}$ complexes were observed in the Cu(II)/N-dodecanoyl-L-methioninol system, but a limit species was not identified.

Introduction

The influence of surfactant systems on chemical phenomena has been a subject of considerable investigation in recent years. To date, surfactant solutions containing micelles[4] or inverse micelles[5] have been used most commonly for these studies. We recently initiated a project which employs a different kind of surfactant solution, namely, an oil continuous microemulsion.[6,7a] A primary objective of this research is to determine the effect, if any, of an interfacial environment on transition metal complexes. We are presently investigating the interaction of transition metals with the side chains of certain amino acids. Both the metal and the ligand are microencapsulated in the aqueous droplets of the dispersed phase. The ligand is introduced into the system as a surface-active derivative, an N^α-dodecanoyl amino alcohol, and, consequently, the side chains (and their metal complexes) are located within the interfacial domain of the droplet. This system is potentially suitable for characterizing complicated metal–ligand interactions, such as those which occur in metalloproteins and other complexes of biological interest.

Recently, a few investigators have studied systems in which metal complexes were incorporated into inverse micelles. Fendler and his co-workers have studied systems of this type.[5] In addition, Klein and Miller have investigated the tetrachlorocuprate(II) complex, and Kitahara et al., a Mn(II)-surfactant complex in such a system.[7b]

This paper describes the interaction of Cu(II) with N^α-dodecanoyl-L-lysinol, N^α-dodecanoyl-L-glutaminol, and N^α-dodecanoyl-L-methioninol. The host system is a hexane continuous microemulsion stabilized by hexadecyltrimethylammonium perchlorate and 2-propanol. Of particular interest is our observation that the metal can be "forced" to interact with very weak ligands by making certain adjustments in the composition of the microemulsion.

Experimental Section

Materials. All organic solvents were reagent grade. Amino acids were purchased from Sigma and the other chemicals from Aldrich. Water was twice-distilled with a Pyrex still. Hexadecyltrimethylammonium perchlorate and β-hydroxyethyl dodecanoate were prepared as previously described.[6] The N^α-dodecanoyl derivatives of L-lysinol, L-glutaminol, L-methioninol, and glycinol were synthesized following the general procedure previously outlined for the synthesis of N^α-dodecanoyl-L-histidinol.[6] Relevant modifications on the general procedure are described below for the pertinent derivatives.

In the synthesis of N^α-dodecanoyl-L-glutaminol the reaction times for the acylation and reduction steps were relatively short (~60 min). This procedure avoided the formation of significant amounts of undesirable side products, but the overall yield (8%) was significantly decreased.

The synthesis of N^α-dodecanoyl-L-lysinol was quite tedious, since the ϵ amino group had to be blocked while the α amino group was acylated.[8] The Cu(II) complex of 25 g (0.137 mol) of L-lysine monohydrochloride was prepared by the procedure of Kjaer and Larsen.[9] Subsequently, 12.9 g (0.137 mol) of freshly distilled benzaldehyde and 11 g (0.27 mol) of NaOH were added to the reaction mixture, which was then stirred vigorously for 30 min at 0 °C.[10] The ϵ Schiff base formed as a pale blue precipitate. The precipitate was dispersed in water, and thioacetamide (10.3 g, 0.137 mol) was added, the mixture was heated to boiling, and CuS was removed by filtration. The solution of N^ϵ-benzylidene-L-lysine was treated with dodecanoyl