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Reactions of Hydrogen Sulfite and Sulfite Ions with Coordinated Nitrene. Synthesis of Sulfamatopentaammineiridium(III) Salts

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Research in our laboratory has provided evidence for the formation of coordinated nitrene intermediates in three different metal systems. These involve the reaction of $[Ru(NH_3)_5N_3]^{2+}$[1] and of $[Ir(NH_3)_5N_3]^{2+}$[2] with acid and the photochemical[3] reaction of the latter[4] and of its analogous rhodium(III) complex.[5] For all of these complexes, the coordinated nitrene in $[M(NH_3)_5NH]^{3+}$ behaves like a singlet nitrene, being very susceptible to nucleophilic attack. Since its properties are that of a soft Lewis acid, it was felt that sulfite ion should be an efficient trapping agent for such a coordinated nitrene in aqueous solution. This was found to be correct, and it also provided a method for the synthesis of salts of the new complex $[Ir(NH_3)_5NH_2SO_3]^{2+}$.

Experimental Section

Materials. Iridium trichloride and ruthenium trichloride were a loan from Matthey Bishop Co. Other chemicals were readily available commercially and were used without further purification. Salts of the complexes $[Ir(NH_3)_5H_2O]^{3+}$,[6] $[Ir(NH_3)_5N_3]^{2+}$,[6,7] $[Ir(NH_3)_5NH_2OSO_3]^{2+}$,[6] $[Ru(NH_3)_5Cl]^{2+}$,[8] and $[Ru(NH_3)_5H_2O]^{3+}$[9] were prepared by slight modifications of the literature methods. Since salts of $[Ru(NH_3)_5N_3]^{2+}$ are not stable,[10] this complex was prepared *in situ* and used immediately as described below.

Sulfamatopentaammineiridium(III) Chloride, $[Ir(NH_3)_5NH_2SO_3]Cl_2$. This complex was prepared by three different methods.

Method 1. Aquopentaammineiridium(III) perchlorate (0.50 g, 8.4×10^{-4} mol) was dissolved in H_2O (50 ml) containing sulfamic acid (0.971 g, 10^{-2} mol) and NaOH (0.20 g, 5×10^{-3} mol). The resulting solution was sealed in a polymer pressure bottle and heated in an oil bath at 105–110° for 8 hr. The solution was cooled and 12 *M* $HClO_4$ (5 ml) and saturated $NaClO_4$ solution (20 ml) was added. This solution was cooled at 0° for a few hours and the white solid formed was collected by suction filtration. This product was a mixture of the perchlorate salts of $[Ir(NH_3)_5(OH_2)]^{3+}$ and the desired product $[Ir(NH_3)_5(NH_2SO_3)]^{2+}$.

The cation sulfamatopentaammineiridium(III) was purified by the following steps. The solid was dissolved in a minimum amount of H_2O and washed onto a cation-exchange column in the proton form (Dowex 50W-X2, 20:1 excess of exchange capacity). After the column had been washed with several portions of water, the cation $[Ir(NH_3)_5(NH_2SO_3)]^{2+}$ was eluted with 4 *M* H_2SO_4. Several fractions were collected and those exhibiting an uv absorption at 255 nm were retained, the rest being discarded. An equal volume of 12 *M* $HClO_4$ was added to the combined fractions, and this solution was cooled at 0° overnight. The solid formed was collected by suction filtration. This solid was dissolved in the minimum amount of H_2O required and washed onto an anion-exchange column in the chloride form (Dowex 1-X8, 20:1 excess exchange capacity). The eluent was collected and combined with two water washings of the column, both being larger than the predetermined dead volume of the column. The solution was evaporated to near dryness at about 60° with a rotary evaporator. The solid was washed with several portions of methanol and then diethyl ether and dried *in vacuo*. The yield was 0.090 g, or 24% of theoretical. *Anal.* Calcd for $[Ir(NH_3)_5(NH_2SO_3)]Cl_2$: N, 18.91; H, 3.86. Found: N, 18.93; H, 4.07.

Method 2. Hydroxylamine-*O*-sulfamatopentaammineiridium(III) perchlorate,[6] $[Ir(NH_3)_5NH_2OSO_3](ClO_4)_2$, (0.15 g) was dissolved in 60 ml of a solution 0.10 *M* in both $HClO_4$ and Na_2SO_3. This solution was stirred for 6 hr and 12 *M* $HClO_4$ (30 ml) was added. This operation was carried out in a hood, due to the evolution of SO_2 upon addition of acid. The solution was cooled at 0° for 1 hr. The white solid formed, principally the desired product, was collected by suction filtration and washed with methanol and diethyl ether, and air-dried. This solid was purified and converted to the chloride salt by the ion-exchange techniques described in method 1. Yields ranged around 75% of theoretical. *Anal.* Calcd for $[Ir(NH_3)_5(NH_2SO_3)]Cl_2$: Ir, 43.25; N, 18.91; H, 3.86; O, 10.80; S, 7.22; Cl, 15.96. Found: Ir, 43.20; N, 18.81; H, 3.79; O, 10.74; S, 7.20; Cl, 15.82.

Method 3. A solution 0.1 *M* in Na_2SO_3 and 0.01 *M* in $HClO_4$ was prepared, and $[Ir(NH_3)_5(N_3)](ClO_4)_2$ (0.25 g) was dissolved in 250 ml of this solution. The resulting solution was irradiated in a preparative-scale photochemical apparatus. The lamp used was a 100-W medium-pressure mercury lamp, the Hanovia 8A36. A cooled filter solution, 5% benzene in methanol, was circulated through the apparatus. The filter solution was replaced by a fresh solution for every 20 min of irradiation. The uv spectrum of aliquots of the irradiated solution was checked periodically. After 40 min, the band at 280 mm due to the azide complex had completely disappeared and the irradiation was stopped. The resulting solution was charged onto a cation-exchange column in the proton form (Dowex 50W-X2, 30:1 excess exchange capacity), and the product was eluted and purified as in method 1. The yields of this reaction varied but were generally about 50–60%. *Anal.* Calcd for $[Ir(NH_3)_5(NH_2SO_3)]Cl_2$: N, 18.9; H, 3.86. Found: N, 18.16; H, 4.19.

The gas evolved by this photochemical reaction was determined by normal Toepler pump techniques. The reaction was carried out in a sealed 1-cm quartz test tube attached to the reactor. The ultraviolet spectrum of the irradiated solution could be observed in the sealed tube, and the gas evolved was measured when the spectrum showed the reaction to be complete, as above.

Sulfimatopentaammineiridium(III) Perchlorate, $[Ir(NH_3)_5(NHSO_3)]ClO_4$. Solid $[Ir(NH_3)_5(NH_2SO_3)]Cl_2$ (0.053 g) was dissolved in 0.1 *M* NaOH (20 ml) and washed onto a cation-exchange column in the Li^+ form (Dowex 50W-X2, 100:1 excess exchange capacity). The column was then washed several times with 0.02 *M* NaOH solution. The product was then eluted with a solution 0.5 *M* in $LiClO_4$ and 0.02 *M* in NaOH. The eluent was collected in several fractions and those exhibiting an uv absorption at 230 nm were retained, the rest being discarded. The eluent containing the product was evaporated to dryness with a rotary evaporator at 600°. Methanol (80 ml) was added to the solid, and the mixture was well stirred to dissolve the $LiClO_4$, $NaClO_4$, and NaOH in the solid. The solution was cooled overnight at 0°, and the white solid formed was collected by filtration. The solid was washed with several 15-ml portions of methanol and then diethyl ether and air-dried. This compound was identified by its uv and ir spectra.

Azidopentaammineruthenium(III), $[Ru(NH_3)_5(N_3)]^{2+}$. This complex is very difficult to isolate pure because it is not too stable.[10] Therefore, it was prepared *in situ* and used immediately. In a typical preparation, $[Ru(NH_3)_5(OH_2)](ClO_4)_3$ (0.500 g) was dissolved in 15 ml of H_2O, and this solution was filtered and neutralized with a dilute LiOH solution. Lithium azide (1.25 g) was dissolved in water (10 ml), and enough 12 *M* $HClO_4$ added to lower the pH to 7.0. This solution was cooled to room temperature, and the two solutions were mixed. This mixture was stirred at room temperature for 10 min and then placed in a water–ice slush bath to prevent decomposition of the azido complex formed.

For spectroscopic studies of the formation of $[Ru(NH_3)_5(NH_2SO_3)]^{2+}$, cold solutions prepared as above containing $[Ru(NH_3)_5(N_3)]^{2+}$ were pipetted into test solutions using pipets cooled in the freezer for several hours prior to use. The reactions were given a few minutes to go to completion, then the reaction mixtures were neutralized, and the amount, if any, of the sulfamato complex formed was determined by observing the absorbance of the band at 398 nm (ϵ 5.15×10^3 M^{-1} cm^{-1})[11] due to $[Ru(NH_3)_5(NHSO_3)]^+$. A series of solutions was prepared 0.1 *M* in SO_3^{2-} with varying amounts of acid

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added. A second series of solutions was prepared containing no sulfite ion, but only enough acid added to reproduce the measured pH of each of the sulfite-containing solutions. Aliquots (1.0 ml) of a solution of $[Ru(NH_3)_5(N_3)]^{2+}$ were pipetted into each of these solutions. After each reaction was complete, the solution was neutralized, and the electronic absorption spectrum was measured for each solution. Identical experiments were carried out using solutions containing $[Ru(NH_3)_5(OH_2)]^{2+}$ only, or N_3^- only, in place of solutions of $[Ru(NH_3)_5(N_3)]^{2+}$.

Sulfimatopentaammineruthenium(III), $[Ru(NH_3)_5(NHSO_3)]^+$. A solution 0.10 *M* in Li_2SO_3 was prepared by washing a solution of Na_2SO_3 through a cation-exchange column in the lithium form (Dowex 50W-X8, 50:1 excess exchange capacity). An equivalent amount of 12 *M* $HClO_4$ (2 ml, 0.025 moles) was added to 250 ml of this solution, converting the majority of the sulfite ion to the form HSO_3^-. A freshly prepared and cooled solution of $[Ru(NH_3)_5(N_3)]^{2+}$ (see above) was added slowly, 1 ml at a time, to this solution with constant stirring at room temperature. Following each addition, a few drops of concentrated $HClO_4$ was added to keep the pH of the solution at 2. After the addition was complete, stirring was continued for 15 min; then the solution was carefully neutralized with 1 *M* LiOH. This solution was poured through a cation-exchange column in the lithium form (Dowex 50W-X2, 10:1 excess exchange capacity based on the number of moles of ruthenium present in all forms). The cation concentration of this solution is high enough that the 1+ charged product, $[Ru(NH_3)_5(NHSO_3)]^+$, is washed off the column. This leaves most of the ruthenium, in the form of higher charged complexes, on the column. This solution was passed through an anion-exchange column in the chloride form to convert all of the anions in the solution to chloride ion. When necessary, the eluent was neutralized. Because of the low concentrations, the product could not be isolated. However, the solutions were studied spectrophotometrically under both neutral and acid conditions.

Results and Discussion

The major goal of this investigation was to test further the mechanism proposed for the reaction of $[Ru(NH_3)_5N_3]^{2+}$ with acid[1] and for the photochemical[3,4] reaction of $[Ir(NH_3)_5N_3]^{2+}$. The mechanism proposes the formation of coordinated nitrene intermediates as the first step of these reactions (eq 1 and 2).

$$[(NH_3)_5RuN_3]^{2+} + H^+ \rightarrow [(NH_3)_5Ru(NH)]^{3+} + N_2 \tag{1}$$

$$[(NH_3)_5IrN_3]^{2+} + H^+ \xrightarrow[\text{(or acid)}]{h\nu} [(NH_3)_5Ir(NH)]^{3+} + N_2 \tag{2}$$

It was further shown[1] that the coordinate nitrene behaves like a very reactive soft electrophile. This, therefore, suggests that sulfite ion should fit the requirements of an efficient "nitrene trap" for these aqueous systems. The reaction of the coordinate nitrene with sulfite ion (or hydrogen sulfite ion) should produce the corresponding sulfamato complexes (eq 3 and 4). Both of these complexes were prepared by

$$[(NH_3)_5Ru(NH)]^{3+} + H^+ + SO_3^{2-} \rightarrow [(NH_3)_5RuNH_2SO_3]^{2+} \tag{3}$$

$$[(NH_3)_5Ir(NH)]^{3+} + H^+ + SO_3^{2-} \rightarrow [(NH_3)_5IrNH_2SO_3]^{2+} \tag{4}$$

these reactions, lending further credence to the proposed nitrene mechanism. The ruthenium(III) complex had been previously prepared,[11] but the iridium(III) complex had not been reported previously.

The complex $[Ir(NH_3)_5NH_2SO_3]^{2+}$ was prepared by the irradiation, with uv light, of $[Ir(NH_3)_5N_3]^{2+}$ in the presence of excess sulfite ion in neutral or slightly acid solutions (eq 5).

$$[Ir(NH_3)_5N_3]^{2+} + 2H^+ + SO_3^{2-} \xrightarrow{h\nu} [Ir(NH_3)_5(NH_2SO_3)]^{2+} + N_2 \tag{5}$$

The stoichiometry of this reaction was established by identification of the iridium(III) product and by the fact that 1 mol of nitrogen gas was produced per mole of azido complex (average of three runs gave 95% of one mole of gas evolved per mole of complex). A benzene-methanol filter solution was used which prevented irradiation of the product. The photochemical properties of the product were not studied, but salts of the product are stable for many months with no protection from light.

For the purpose of characterization of the product of this photochemical reaction (eq 5), the complex $[Ir(NH_3)_5NH_2SO_3]^{2+}$ was also prepared by two other methods. One of these involved the reaction of the aquo complex with sulfamate ion (eq 6), and the other employed the reaction of

$$[Ir(NH_3)_5H_2O]^{3+} + NH_2SO_3^- \rightarrow [Ir(NH_3)_5NH_2SO_3]^{2+} + H_2O \tag{6}$$

the hydroxylamine-*O*-sulfato complex with sulfite ion (eq 7).

$$[Ir(NH_3)_5NH_2OSO_3]^{2+} + SO_3^{2-} \rightarrow [Ir(NH_3)_5(NH_2SO_3)]^{2+} + SO_4^{2-} \tag{7}$$

The chemical and physical properties are identical for each of the three products prepared by these three different methods (eq 5–7). This in itself is very good evidence identifying the complex prepared as $[Ir(NH_3)_5(NH_2SO_3)]^{2+}$. It is difficult to conceive of another complex being prepared by all of these methods.

Additional support that this complex is correctly formulated as the sulfamato complex is provided by many of its properties which resemble that of known sulfamato complexes. For example, nitrogen-bonded sulfamato complexes commonly exhibit an acidic proton, as is also true of this iridium(III) product (eq 8). Armor and Taube[11] have isolated both

$$[Ir(NH_3)_5(NH_2SO_3)]^{2+} \rightleftharpoons [Ir(NH_3)_5(NHSO_3)]^+ + H^+ \tag{8}$$

$[Ru(NH_3)_5(NH_2SO_3)]Br_2$ and $[Ru(NH_3)_5(NHSO_3)]Cl$ and have determined a pK_a of 2.6 for the acid dissociation in this system. Similarly, a pK_a = 5.38 was measured[12] for the acid dissociation of $[Co(NH_3)_5(NH_2SO_3)]^{2+}$. We have also determined a pK_a of 7.1 for the acid dissociation reaction (eq 8) by titration with dilute NaOH solutions and isolated and identified the conjugate base $[Ir(NH_3)_5(NHSO_3)]ClO_4$. Complexes prepared by each of the three methods were titrated, and all showed equivalent weights within 5% of the calculated molecular weight.

Both $[Ir(NH_3)_5(NH_2SO_3)]Cl_2$ and $[Ir(NH_3)_5(NHSO_3)]ClO_4$ are white diamagnetic solids, as expected. Iridium(III) complexes always have low-spin d^6 electronic configurations and are diamagnetic. The amine complexes of iridium(III) generally exhibit only high-energy electronic absorptions and are therefore colorless or pale yellow. The uv spectra of $[Ir(NH_3)_5(NH_2SO_3)]^{2+}$ and $[Ir(NH_3)_5(NHSO_3)]^+$ are shown in Figure 1. Three bands are observed for the $NH_2SO_3^-$ complex at 254 nm (ϵ 125 M^{-1} cm^{-1}), 221 nm (ϵ 125), and 208 nm (ϵ 165). The sulfimato complex, $[Ir(NH_3)_5(NHSO_3)]^+$, exhibits one considerably stronger band at 225 nm (ϵ 320).

The ir spectra of the sulfamato and sulfimato complexes are very informative. There are at least seven distinctive bands for each of these ligands in the 1300-400-cm^{-1} region of the ir spectrum. These complexes can be largely identified by their ir spectra alone. The spectra are very different from those of any of the starting materials, or any combination thereof. The ir spectra of $[Ir(NH_3)_5(NH_2SO_3)]^{2+}$ and $[Ir(NH_3)_5(NHSO_3)]^+$ are almost identical with those of the corresponding ruthenium and cobalt complexes.[11] Table I lists group frequencies for the coordinated sulfimato and

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[11] J. N. Armor and H. Taube, *Inorg. Chem.*, **10**, 1570 (1971).

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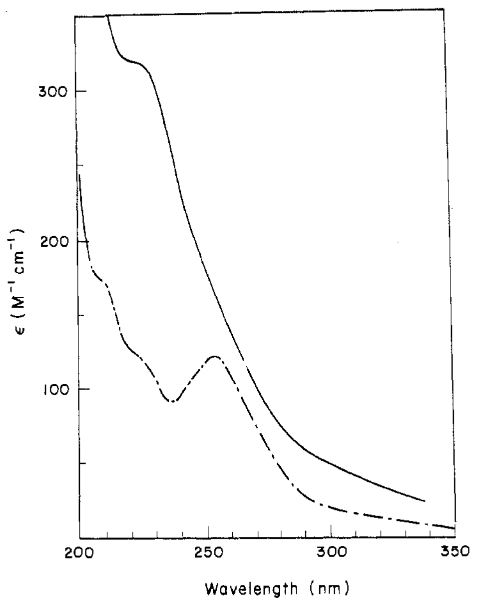

Figure 1. Ultraviolet absorption spectra of 0.002 *M* solutions of $[Ir(NH_3)_5NH_2SO_3]^{2+}$ (in H_2O) (– · –) and of $[Ir(NH_3)_5NHSO_3]^+$ (in 0.02 *M* NaOH) (—).

Table I. Infrared Frequencies (cm^{-1}) of Pentaamminesulfamatometal(III) and Pentamminesulfimatometal(III) Complexes of Iridium, Ruthenium, and Cobalt

$[M(NH_3)_5(NH_2SO_3)]^{2+}$			$[M(NH_3)_5NHSO_3]^+$		
Ir	Ru	Co	Ir	Ru	Co
			1347		1343
1355	1318	1345	1337	1320	1320
			1322		1283
1200	1190	1198			
1049	1053	1049	1022	1025	1010
			909	885	874
729	725	720			
			638	628	642
586	584	585	577	573	576
537	549	538	527	510	521
496	505	497	505	482	475
			467	440	452

sulfamato ligands. All other absorbances in the ir spectra can be assigned to common metal-ammine vibrations.

Qualitative observations on the chemistry of $[M(NH_3)_5NH_2SO_3]^{2+}$ (where M(II) = Co, Ru, Ir) indicate that their stability is at least equal to or greater than that of the corresponding halogenopentaammine complexes but less than the hexaammines. The iridium complexes are very stable in the solid state and in solution. These iridium complexes can be heated to near boiling for several hours in the presence of aqueous halogen acids, without significant ligand substitution, and are stable indefinitely in acidic or basic solution at room temperature. Their stability is very much greater than that of other products of nitrene reactions for this system.[2,3]

Investigations of the reaction of $[Ru(NH_3)_5N_3]^{2+}$ with acid in the presence of sulfite ion were carried out by comparing the uv spectra of the reaction products with the published spectra of $[Ru(NH_3)_5(NH_2SO_3)]^{2+}$ and $[Ru(NH_3)_5(NHSO_3)]^+$. The azido complex, prepared *in situ*, was allowed to react with solutions of sodium sulfite under a variety of conditions. The solutions were neutralized, and the amount, if any, of the sulfamato complex formed was determined by observing the abosrbance of the band at 398 nm (ϵ 4.15 × 10^3 M^{-1} cm^{-1}) due to $[Ru(NH_3)_5(NHSO_3)]^+$. Because of the low pK_a of the sulfamato complex, all of this complex is in the deprotonated or sulfimato form in neutral solution. By selectively leaving out reactants, it was possible to show that all three key reactants, azide ion, aquopentaammineruthenium(III), and sulfite ion, were necessary to produce this band. No other strong bands at this position in neutral solution were observed for this system.

The ratio of $[Ru(NH_3)_5(N_2)]^{2+}$ to $[(NH_3)_5Ru(N_2)Ru(NH_3)_5]^{4+}$ formed by the reaction of $[Ru(NH_3)_5(N_3)]^{2+}$ at various conditions has been determined.[1] The formation of the dinitrogen-bridged dimer is favored by higher acid concentrations and lower concentrations of the reacting azide complex. We tested the effect of varying these conditions on the formation of sulfamato complexes. Within the rather large limits of experimental error, the amount of sulfamato complex formed was proportional to the amount of dinitrogen-bridged dimer formed (as indicated by the absorbance of the band at 260 nm due to this complex) in a solution of equal pH but with no sulfite ion. No sulfamato complex was formed in neutral solution, where the azido complex decomposes to give only the monomer $[Ru(NH_3)_5(N_2)]^{2+}$; and the amount of sulfamato complex formed was at a maximum under the conditions of low pH and low concentration of azido complex, which are also conditions most conducive to formation of the dinitrogen-bridged dimer, $[(NH_3)_5Ru(N_2)Ru(NH_3)_5]^{4+}$.

Sulfamatopentaammineruthenium(III) was prepared, *in situ*, by making use of this information. A freshly prepared solution of $[Ru(NH_3)_5(N_3)]^{2+}$ was added slowly to an acidified solution of sulfite ion, so as to keep the concentration of azide ion in the reacting solution at any time quite small. A pH under 2 could not be used, due to the decomposition of the sulfite ion solution. Acid was added to the sulfite ion solution after each addition of azido complex to keep the pH at 2 by offsetting the effect of the excess azide ion in solution. The solution was neutralized when the additions were complete. The yields of sulfamato complex (determined spectrophotometrically) produced by this reaction were only 5–10%, the majority of the ruthenium azide being converted to the dinitrogen complex. The product in neutral solution, $[Ru(NH_3)_5(NHSO_3)]^+$, eluted from an anion-exchange column as a 1+ cation. The eluent exhibited a strong band at 398 nm in neutral solution. When acidified, this band disappeared and a weaker band appeared at 280 nm. The complex $[Ru(NH_3)_5(NH_2SO_3)]^{2+}$ exhibits a band at 280 nm (ϵ 510 M^{-1} cm^{-1}).[11] The absorbances of these two bands were in the proper ratio, and the spectra could be interconverted by neutralization or acidification of the solution. Because of the small yields, attempts to isolate the sulfamato or sulfimato complexes proved fruitless. However, the spectrophotometric evidence is overwhelming for the formation of $[Ru(NH_3)_5(NH_2SO_3)]^{2+}$ by the reaction of $[Ru(NH_3)_5(N_3)]^{2+}$ with acid (eq 9).

$$[Ru(NH_3)_5(N_3)]^{2+} + H^+ + HSO_3^- \rightarrow [Ru(NH_3)_5(NH_2SO_3)]^{2+} + N_2 \qquad (9)$$

These results indicate that sulfite ion interferes with the formation of $[(NH_3)_5Ru(N_2)Ru(NH_3)_5]^{4+}$ from the reaction of $[Ru(NH_3)_5(N_3)]^{2+}$ in acid solution but not with the formation of $[(NH_3)_5Ru(N_2)]^{2+}$. This provides further evidence that the formation of the dinitrogen-bridged dimer proceeds by a nitrene mechanism, but it does not support such a mechanism for the formation of $[Ru(NH_3)_5(N_2)]^{2+}$. It could not be determined if the nitrene mechanism does not hold for the formation of $[Ru(NH_3)_5(N_2)]^{2+}$ or if sulfite ion cannot compete kinetically in the formation of this species by the nitrene mechanism.[1]

Finally, sulfite ion would seem to be a fairly good nitrene trap for aqueous systems, but it has some serious drawbacks. It cannot be used in very acidic solution, and irradiation of any band at a wavelength lower than 260 nm cannot be carried out in its presence. However, the sulfamato complexes produced by the reaction of coordinated nitrene with sulfite ion are much more stable than the corresponding chloramine or hydroxylamine complexes prepared by this same type of reaction.[2] Also, the identification of the sulfamato complexes formed is assisted by the ability to prepare these compounds by other methods, and by the fingerprint characteristics of their ir spectra.

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Registry No. $[Ir(NH_3)_5(NH_2SO_3)]Cl_2$, 51202-26-7; $[Ir(NH_3)_5(NHSO_3)]ClO_4$, 51202-28-9; $[Ru(NH_3)_5(N_3)]^{2+}$, 28223-30-5; $[Ru(NH_3)_5(NHSO_3)]^+$, 51259-39-3; $[Ir(NH_3)_5H_2O](ClO_4)_3$, 31285-82-2; $[Ir(NH_3)_5(N_3)](ClO_4)_2$, 38552-10-2; $[Ir(NH_3)_5NH_2OSO_3](ClO_4)_2$, 34412-12-9; SO_3^{2-}, 14265-45-3; $[Ru(NH_3)_5(NH_2SO_3)]^{2+}$, 51259-40-6.

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Exchange of Oxygen-18 between Aquopentaammineiridium(III) Ion and Solvent Water. Pressure Effect and Mechanism

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Borghi, Monacelli and Prosperi[1] have shown that the anation of $Ir(NH_3)_5OH_2^{3+}$ by chloride ion in acidic aqueous perchlorate solution proceeds by an interchange mechanism

$$Ir(NH_3)_5OH_2^{3+} + Cl^- \overset{K}{\rightleftharpoons} \{Ir(NH_3)_5OH_2^{3+}, Cl^-\} \xrightarrow{k_i} Ir(NH_3)_5Cl^{2+} + H_2O \qquad (1)$$

such that the rate of formation of the product is pseudo first order (rate coefficient k_{obsd}) in aquo complex at a given concentration of Cl^- in large excess, according to the relationship

$$k_{obsd} = \frac{k_i K[Cl^-]}{1 + K[Cl^-]} \qquad (2)$$

The rate coefficient k_i was significantly greater than that (k_{ex}) for the aquo exchange

$$Ir(NH_3)_5{}^{18}OH_2^{3+} + H_2O \xrightarrow{k_{ex}} Ir(NH_3)_5OH_2^{3+} + H_2{}^{18}O \qquad (3)$$

even when the influence of ion pairing on k_{ex} was considered, which suggests that $Ir(NH_3)_5OH_2^{3+}$ reacts by an associative interchange (I_a) mechanism.

The ion $Rh(NH_3)_5OH_2^{3+}$ behaves in a closely similar fashion,[2,3] and we have shown[4] that the measured volume of activation ΔV^* for aquo exchange in $Rh(NH_3)_5OH_2^{3+}$ confirms an associative mode of activation for simple aquo substitution in this complex.

Table I. First-Order Rate Coefficients k_{ex} for the Exchange of $H_2{}^{18}O$ between $Ir(NH_3)_5{}^{18}OH_2^{3+}$ and Solvent Water at 70.5° in 0.010 *M* $HClO_4$[a]

Pressure, kbars	10^5k, sec^{-1}	Pressure, kbars	10^5k, sec^{-1}
0.001	3.82 ± 0.08,[b] 3.96[b,c]	2.02	4.95 ± 0.23
0.059	4.01 ± 0.22	3.31	5.79 ± 0.41, 5.76 ± 0.21
1.027	4.56 ± 0.10	4.00	6.00 ± 0.29

[a] [Ir(III)] = 0.041 mol kg^{-1}. [b] In ordinary glass vessels. [c] Interpolated from data of ref 6.

Table II. Activation Parameters for Aquo Exchange of $M(NH_3)_5OH_2^{3+}$ in 0.01-0.10 *M* $HClO_4$

M	ΔV^*, cm^3 mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}	ΔH^*, kcal mol^{-1}
Co[a]	+1.2 ± 0.2	+6.7 ± 1.0	26.6 ± 0.3
Rh[b]	−4.1 ± 0.4	+0.8 ± 1.1	24.6 ± 0.3
Ir	−3.2 ± 0.1[c]	+2.7 ± 1.0[d]	28.1 ± 0.3[d]
Cr[b]	−5.8 ± 0.1	0.0 ± 1.6	26.2 ± 0.3

[a] H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, 80, 2642 (1958). [b] Reference 4. [c] This work. [d] Recalculated from data of ref 6.

The primary objective of the present work was to seek support for the I_a mechanism, assigned by Monacelli, *et al.*,[1] to reaction 1, by evaluation of ΔV^* for reaction 3.

Experimental Section

Materials. $[Ir(NH_3)_5Cl]Cl_2$ was prepared from $K_3IrCl_6 \cdot 3H_2O$ (Alfa Inorganics) by the method of Basolo,[5] and the recrystallized product was converted to $[Ir(NH_3)_5OH_2](ClO_4)_3$ as described by Borghi and Monacelli.[6] The spectrum of the recrystallized product (maximum absorption at 258 nm, ϵ 85 M^{-1} cm^{-1}, and a shoulder at 333 nm, ϵ 12) agreed with that reported in the literature.[7] *Anal.* Calcd for $[Ir(NH_3)_5OH_2](ClO_4)_3$: N, 11.80. Found: N, 11.78. $[Ir(NH_3)_5OH_2](ClO_4)_3$ was recovered from the $[Ir(NH_3)_5Br]Br_2$ residues by the same procedure.

The oxygen-18-labeled aquo complex was prepared by maintaining a solution of the perchlorate salt in the minimum of water (1.7% $H_2{}^{18}O$, Bio-Rad Laboratories) at 94° for 24 hr, filtering, concentrating the filtrate, and allowing the product to crystallize at 0°.

Perchloric acid (71%, Baker Analyzed) was used without further purification. Distilled water was passed through Barnstead deionizer and organic removal cartridges before use.

Kinetics. A weighed amount of $[Ir(NH_3)_5OH_2](ClO_4)_3$ was dissolved in 30 g of 0.010 *M* $HClO_4$, quickly brought to the thermostat temperature, and placed in a preheated glass syringe which was promptly connected into the thermostated pressure assembly (±0.02°) described previously;[8] a Hastelloy B capillary outlet tube was used in these experiments, it having been established that aqueous iridium(III) ammines (unlike Co(III)[9]) do not react with this alloy. About 40-60 min was allowed after pressurization to ensure full thermal equilibration. Pressures were constant to within ±5 bars in the course of a run, except during sample withdrawal. Samples (3.0 ml, plus 1.0-ml "hold-up" which was rejected) were treated at once with 48% HBr (3.0 ml) at 0°, and the filtered $[Ir(NH_3)_5OH_2]Br_3$ was washed with acetone, dried *in vacuo*, and deaquated at temperatures *not exceeding 200°* on the vacuum line (higher temperatures led to general decomposition, evidently with evolution of N_2O). The liberated water was converted to CO_2 as described previously[4] and the ${}^{12}C^{16}O^{18}O$ content was determined relative to ${}^{13}C^{16}O_2$ (mean of 6–15 determinations, corrected for background; standard error *ca.* ±0.1%) using either a modified Nier isotope ratio spectrometer[10] or a Varian/MAT CH-5 mass spectrometer.

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