Notes

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Proton Magnetic Resonance Spectra of Cobalt Ammine Complexes in Sulfuric Acid

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Clifton and Pratt[2] have shown that, in the proton magnetic resonance spectra of cobalt ammine complexes, separate resonances are observed for the ammine groups that occupy geometrically different sites. Because of interference of the strong solvent peak in ordinary water solutions, deuterium oxide was used as the solvent. Although acidic solutions were used, the ammine resonances gradually disappeared because of hydrogen exchange with the solvent.

We have found certain advantages and interesting features in the use of concentrated sulfuric acid as a solvent for n.m.r. studies[3] of cobalt ammine complexes. Practically all the complexes that we have studied are soluble in sulfuric acid at least to the extent of 1 *M*, whereas their solubilities in water are generally less than 0.2 *M*. The H_2SO_4 solvent peak is far removed from the ammine peaks; therefore the undeuterated solvent can be used, and the ammine resonances do not disappear because of hydrogen exchange. Several of the cobalt ammine complexes undergo solvolytic reactions and *cis–trans* isomerizations. These reactions can be readily followed by observing the disappearance and appearance of various ammine resonances which, in most cases, do not overlap seriously.

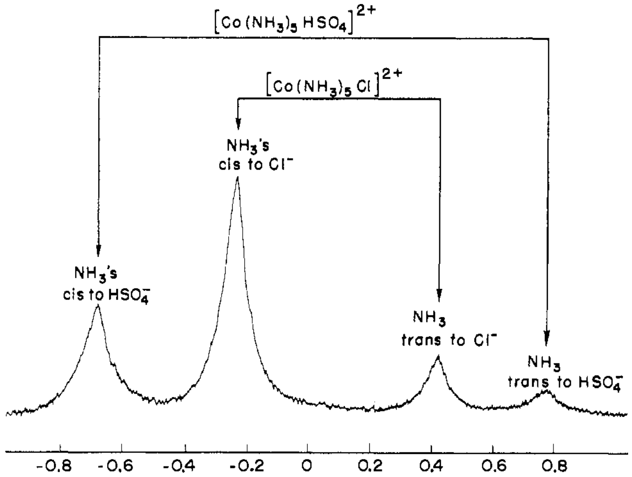

Figure 1.—The proton magnetic resonance spectrum of a solution (~1 *M*) of $[Co(NH_3)_5Cl]Cl_2$ in 97% H_2SO_4. A large fraction of the $[Co(NH_3)_5Cl]^{2+}$ ions have been converted to $[Co(NH_3)_5HSO_4]^{2+}$ ions. The chemical shifts are relative to $[Co(NH_3)_6]^{3+}$.

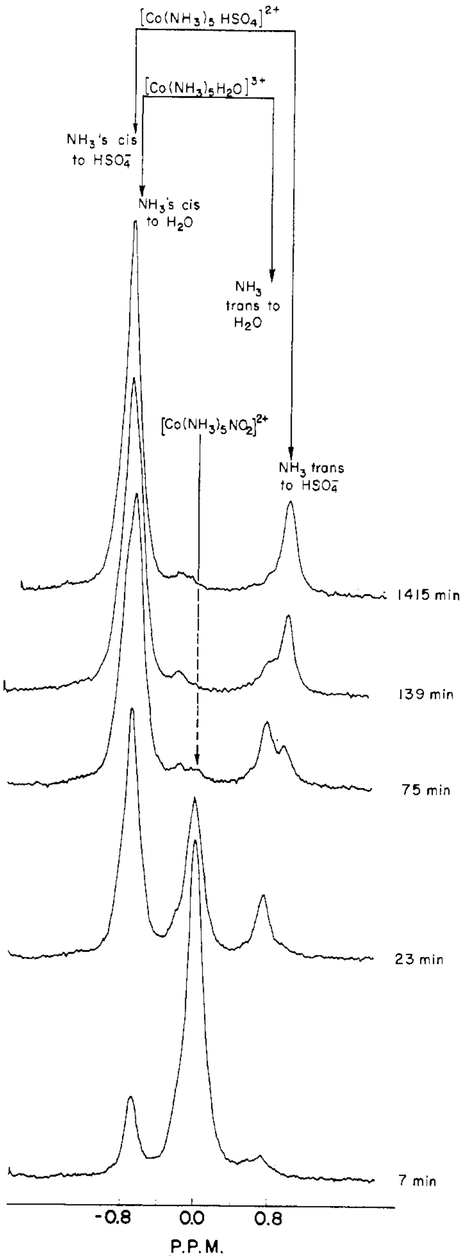

Figure 2.—Proton magnetic resonance spectra of a solution initially 0.184 *M* $[Co(NH_3)_5NO_2]SO_4$ in 80% H_2SO_4. The chemical shifts are relative to $[Co(NH_3)_6]^{3+}$.

Cobalt(III) pentaammine complexes, in which the sixth ligand was SO_4^{2-}, F^-, or I^-, dissolved in 97% sulfuric acid to give solutions having identical n.m.r. spectra. The spectra consisted of two peaks with a 4:1 intensity ratio; we assume that the $[Co(NH_3)_5HSO_4]^{2+}$ ion was rapidly formed in each case.

The spectra of solutions of $[Co(NH_3)_5Cl]^{2+}$ and

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[1] National Science Foundation High School Teacher Fellow, 1964.

[2] P. Clifton and L. Pratt, *Proc. Chem. Soc.*, 339 (1963).

[3] A Varian A-60 n.m.r. spectrometer was used in this research.

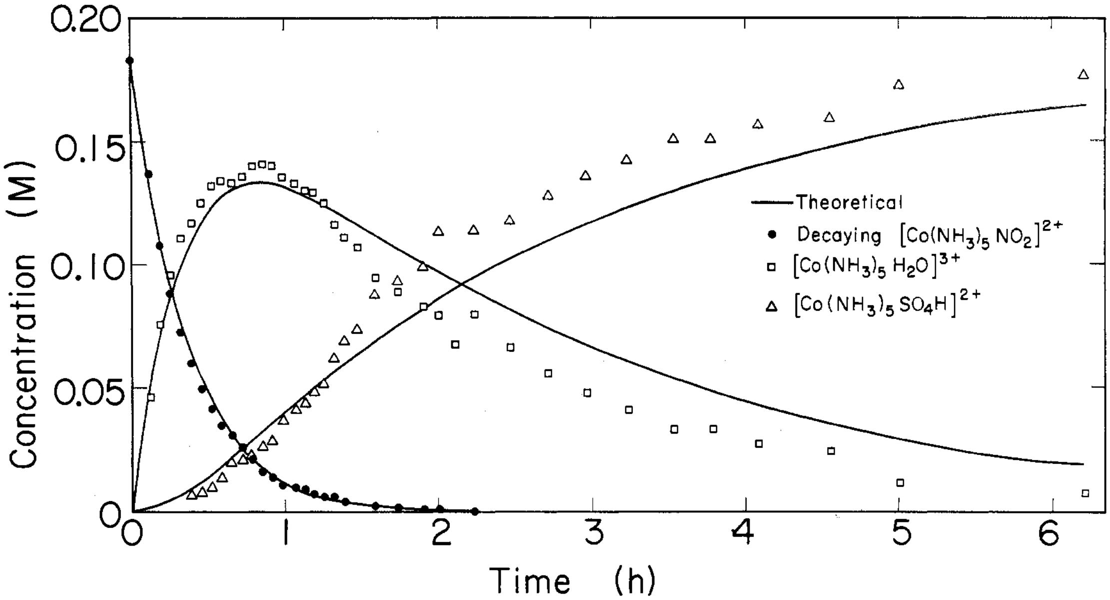

Figure 3.—Concentrations of $[Co(NH_3)_5NO_2]^{2+}$, $[Co(NH_3)_5H_2O]^{3+}$, and $[Co(NH_3)_5HSO_4]^{2+}$ as a function of time in a solution initially 0.184 M $[Co(NH_3)_5NO_2]^{2+}$ in 80% H_2SO_4.

$[Co(NH_3)_5Br]^{2+}$ salts in 97% sulfuric acid consisted of two 4:1 pairs of peaks, of which one pair corresponded to the $[Co(NH_3)_5HSO_4]^{2+}$ ion (see Figure 1). When these latter solutions were kept in open or loosely-capped n.m.r. tubes, the $[Co(NH_3)_5HSO_4]^{2+}$ peaks gradually increased in intensity as the other peaks correspondingly decreased in intensity. In sealed n.m.r. tubes, the spectra did not change with time; apparently equilibria of the type

$$[Co(NH_3)_5Cl]^{2+} + H_2SO_4 \rightleftharpoons [Co(NH_3)_5HSO_4]^{2+} + HCl$$

were achieved. By bubbling dry air through a solution of the chloro complex, the substitution reaction, rather than the escape of HCl from the solution, was made the rate-determining step. The reaction was observed to be first order, with a half-time of 4 hr. The rate showed a strong dependence on the sulfuric acid concentration and on the bisulfate concentration. Thus, in 100% H_2SO_4, in 100% H_2SO_4 which was 2 M in $NaHSO_4$, and in 115% H_2SO_4, the half-times were 2 hr., 23 hr., and less than 5 min., respectively. When account is taken of the bisulfate introduced with the salt, it appears probable that the reaction rate follows the Hammett acidity function h_0 (or, less likely, the activity of SO_3). Probably the mechanism is of type SE2, in which the coordinated ligand is plucked from the cobalt ion by a proton.[4]

The $[Co(NH_3)_5H_2O]^{3+}$ ion was converted to the $[Co(NH_3)_5HSO_4]^{2+}$ ion with a half-time of approximately 25 min. in 97% H_2SO_4 and with a half-time of approximately 100 min. in 80% H_2SO_4. The reaction rate appears to be proportional to the activity of H_2SO_4. In the range 55–75% H_2SO_4, measurable equilibria between the two complexes were achieved; approximately equimolar amounts of the complexes formed in 63% H_2SO_4. Below 55% H_2SO_4, the bisulfato complex was essentially quantitatively converted to the aquo complex.

Cobalt(III) pentaammine complexes, in which the sixth ligand was CO_3^{2-}, NO_3^-, ONO^-, or NO_2^-, reacted so rapidly with 97% H_2SO_4 that the spectra corresponding to these species could not be observed.[5] The first observed products of the reactions were mixtures of the aquo and bisulfato complexes. Thus a 4-min. old solution of the nitro complex consisted of a 5:1 mixture of the aquo and bisulfato complexes. In 80% H_2SO_4, $[Co(NH_3)_5NO_2]^{2+}$ reacted relatively slowly, according to two consecutive pseudo-first-order reactions, to form first $[Co(NH_3)_5H_2O]^{3+}$ and then $[Co(NH_3)_5HSO_4]^{2+}$. N.m.r. spectra of a solution corresponding initially to 0.184 M $[Co(NH_3)_5NO_2]SO_4$ in 80% H_2SO_4, taken at selected times, are presented in chronological order in Figure 2. The concentrations of the three complexes, calculated from the areas of the appropriate n.m.r. peaks, are plotted as a function of time in Figure 3. The smooth curves correspond to the consecutive rate constants $k_1 = 7.7 \times 10^{-4}$ sec.$^{-1}$ and $k_2 = 1.1 \times 10^{-4}$ sec.$^{-1}$ at ~35°.

Both *trans*-$[Co(NH_3)_4Cl_2]^+$ and *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ reacted in 97% H_2SO_4 to give *cis*-$[Co(NH_3)_4(HSO_4)_2]^+$ as the final product. The latter species was recognized by two well-separated peaks of equal intensity, one for the ammonias *cis, cis* to the bisulfates and one for the ammonias *cis, trans* to the bisulfates. In both reactions, two intermediates were observed. In each case, the first intermediate had a single-peak n.m.r. spectrum and the second intermediate had a three-peak (2:1:1 intensity ratio) n.m.r. spectrum. We believe the data may be explained by the sequences

$$\begin{tikzcd}
\textit{trans}\text{-}[Co(NH_3)_4Cl_2]^+ \arrow[r] & \textit{trans}\text{-}[Co(NH_3)_4(HSO_4)Cl]^+ \arrow[d] \\
\textit{cis}\text{-}[Co(NH_3)_4(HSO_4)_2]^+ & \textit{cis}\text{-}[Co(NH_3)_4(HSO_4)Cl]^+ \arrow[l]
\end{tikzcd}$$

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(4) Other examples of this type of mechanism are discussed by F. Basolo, W. R. Matoush, and R. G. Pearson [*J. Am. Chem. Soc.*, **78**, 4883 (1956)] and S. C. Chan [*J. Chem. Soc.*, 2375 (1964)].

(5) By fast manipulation, it was just barely possible to detect a peak attributable to the $[Co(NH_3)_5NO_2]^{2+}$ ion in 97% H_2SO_4.

$$\begin{tikzcd}
trans\text{-}[Co(NH_3)_4(NO_2)_2]^+ \arrow[r] & trans\text{-}[Co(NH_3)_4(NO_2)H_2O]^{2+} \arrow[d] \\
cis\text{-}[Co(NH_3)_4(HSO_4)_2]^+ & cis\text{-}[Co(NH_3)_4(HSO_4)H_2O]^{2+} \arrow[l]
\end{tikzcd}$$

The identification of the intermediates in these reactions is based not only on the number and relative intensities of the n.m.r. peaks, but also on the chemical shifts, which are discussed below. It is noteworthy that when a solution of *cis*-$[Co(NH_3)_4(HSO_4)_2]^+$ in 97% H_2SO_4 was diluted with water to make the solvent 75% H_2SO_4, the resulting solution contained both *cis*-$[Co(NH_3)_4(HSO_4)_2]^+$ and *cis*-$[Co(NH_3)_4(HSO_4)H_2O]^{2+}$.

We have calculated the chemical shifts relative to that for the hexaamminecobalt(III) ion. (The peak for this ion lies 3.12 p.p.m. to low field of tetramethylsilane.) The chemical shifts for the two kinds of ammonia molecules in the pentaammine complexes are given in Table I, and the chemical shifts for the various kinds of ammonia molecules in the tetraammine complexes are given in Table II. If we assume that the chemical shift for a coordinated ammonia molecule is the sum of five terms characteristic of the other five ligands and their positions, then it is possible, using the data of Table I, to estimate the chemical shift values for ammonia molecules in tetraammine complexes.[6] These estimated chemical shifts are presented alongside the experimental values in Table II. The close agreement of the experimental and estimated values gives us confidence in our structural assignments.

TABLE I

CHEMICAL SHIFTS, RELATIVE TO THE HEXAAMMINECOBALT(III) ION, FOR SEVERAL PENTAAMMINECOBALT(III) IONS IN CONCENTRATED H_2SO_4

Acido ligand	Chemical shift, p.p.m.
cis-HSO_4^-	−0.65
trans-HSO_4^-	0.84
cis-H_2O	−0.57
trans-H_2O	0.67
cis-Cl^-	−0.17
trans-Cl^-	0.49
cis-Br^-	−0.06
trans-Br^-	0.42
cis- and *trans*-NO_2^-	0.00

TABLE II

CHEMICAL SHIFTS, RELATIVE TO THE HEXAAMMINECOBALT(III) ION, FOR SEVERAL TETRAAMMINECOBALT(III) IONS IN CONCENTRATED H_2SO_4

Acido ligands	Chemical shift, p.p.m. Observed	Chemical shift, p.p.m. Estimated
cis-HSO_4^-, *cis*-HSO_4^-	−1.30[a]	−1.30
cis-HSO_4^-, *trans*-HSO_4^-	0.22	0.19
cis-HSO_4^-, *cis*-H_2O	−1.10[a]	−1.22
cis-HSO_4^-, *trans*-H_2O	−0.07	−0.02
trans-HSO_4^-, *cis*-H_2O	0.24	0.27
cis-HSO_4^-, *cis*-Cl^-	−0.91,[a] −1.16[b]	−0.82
cis-HSO_4^-, *trans*-Cl^-	−0.29	−0.16
trans-HSO_4^-, *cis*-Cl^-	0.66	0.67
cis-H_2O, *cis*-NO_2^-	−0.52[b]	−0.57

[a] *cis* complex. [b] *trans* complex.

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[6] For example, we take the chemical shift contributions of *cis*-NH_3, *trans*-NH_3, *cis*-HSO_4^-, and *trans*-HSO_4^- as 0, 0, −0.65, and 0.84 p.p.m., respectively. Thus in the complex *cis*-$[Co(NH_3)_4(HSO_4)_2]^+$ we calculate a chemical shift of $2(-0.65) = -1.30$ p.p.m. for the ammonia molecules which are *cis* to two HSO_4^- ions and a chemical shift of $0.84 - 0.65 = 0.19$ p.p.m. for the ammonia molecules which are *cis* to one HSO_4^- ion and *trans* to the other.

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Intermediates in the Oxidation of Water by Perxenate[1]

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Octavalent xenon in acid solution is one of the few substances that rapidly oxidize water to molecular oxygen.[3] We may write the reactions that take place when we dissolve solid sodium perxenate in water and subsequently acidify the solution

$$Na_4XeO_6(s) + H_2O \longrightarrow HXeO_6^{-3} + OH^- + 4Na^+ \quad (1)$$

$$HXeO_6^{-3} + 3H^+ \longrightarrow XeO_3 + {}^1/_2O_2 + 2H_2O \quad (2)$$

The product is a stable solution of hexavalent xenon.[3]

The xenon(VI)–xenon(VIII) electrode potential is about 3 v.,[3] making a number of mechanisms possible for reaction 2. Among these are processes involving the direct transfer of one or more electrons to the xenon(VIII) from one of its ligand oxygens or from a solvent water molecule. Transfer of a single electron leads to the formation of an OH radical and a transient Xe(VII) intermediate, while a double electron transfer from a single donor results in an oxygen atom and Xe(VI).

In the gas phase, atomic oxygen is known to bring about isotopic "scrambling" of the atoms in O_2 molecules by means of the chain reaction[4]

$$O^{16} + O^{18}O^{18} \rightleftharpoons O^{16}O^{18} + O^{18} \quad (3)$$

In aqueous solution the situation may be more complicated, but it still seems likely that by one mechanism or another atomic oxygen will bring about "scrambling" of the atoms of dissolved O_2. If this is true, we may look for the formation of oxygen atoms by allowing reaction 2 to proceed in a solution that is saturated with oxygen containing $O^{16}O^{16}$ and $O^{18}O^{18}$, but containing very little $O^{16}O^{18}$. If oxygen atoms are formed, we should observe the production of $O^{16}O^{18}$ molecules.

We may check our method by using ozone instead of perxenate. In the gas phase, ozone forms atomic oxygen by dissociation, and the O atoms then participate in reaction 3.[4] Thus we would expect appreciable "scrambling" to occur in a solution containing $O^{16}O^{16}$, $O^{18}O^{18}$, and ozone. However, even if we find that

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] On Sabbatical leave from the Weizmann Institute of Science, Rehovoth, Israel.

[3] E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

[4] R. A. Ogg and W. T. Sutphen, *Discussions Faraday Soc.*, **17**, 47 (1954).