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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

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

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 nmr studies[3] of cobalt

(3) A Varian A-60 NMR Spectrometer was used in this research.

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.

Cobalt(III) pentammine complexes, in which the sixth ligand was SO_4^{2-}, F^- or I^-, dissolved in 97% sulfuric acid to give solutions having identical

nmr 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 $[Co(NH_3)_5Br]^{2+}$ 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 Fig. 1) When these latter solutions were kept in open or loosely-capped nmr tubes, the $[Co(NH_3)_5HSO_4]^{2+}$ peaks gradually increased in intensity as the other peaks correspondingly decreased in intensity. In sealed nmr tubes, the spectra did not change with time; apparently equilibria of the following type were achieved:

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

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 hours. 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 hours, 23 hours, and less than 5 minutes, 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_o (or, less likely, the activity of SO_3). Probably the mechanism is of type S_E2, in which the coordinated ligand is plucked from the cobalt ion by a proton.[4]

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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)].

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 minutes in 97% H_2SO_4 and with a half-time of approximately 100 minutes 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) pentammine 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

(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.

observed products of the reactions were mixtures of the aquo and bisulfato complexes. Thus a 4-minute-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 $[CO(NH_3)_5HSO_4]^{2+}$. Nmr 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 Fig. 2. The concentrations of the three complexes, calculated from the areas of the appropriate nmr peaks, are plotted as a function of time in Fig. 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 nmr spectrum and the second intermediate had a three-peak (2:1:1 intensity ratio) nmr spectrum. We believe the data may be explained by the following sequences:

$$\begin{array}{ccc}
\text{trans-}[CO(NH_3)_4Cl_2]^+ & \longrightarrow & \text{trans-}[CO(NH_3)_4(HSO_4)Cl]^+ \\
 & & \downarrow \\
\text{cis-}[CO(NH_3)_4(HSO_4)_2]^+ & \longleftarrow & \text{cis-}[CO(NH_3)_4(HSO_4)Cl]^+ \\
\text{trans-}[CO(NH_3)_4(NO_2)_2]^+ & \longrightarrow & \text{trans-}[CO(NH_3)_4(NO_2)H_2O]^{2+} \\
 & & \downarrow \\
\text{cis-}[CO(NH_3)_4(HSO_4)_2]^+ & \longleftarrow & \text{cis-}[CO(NH_3)_4(HSO_4)H_2O]^{2+}
\end{array}$$

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 hexamminecobalt(III) ion. The chemical shifts for the two kinds of ammonia molecules in the pentammine complexes are given in Table I, and the chemical shifts for the various kinds of ammonia molecules in the tetrammine 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 tetrammine complexes.[6] These estimated

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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 ppm, respectively. Thus in the complex cis-$[CO(NH_3)_4(HSO_4)_2]^+$ we calculate a chemical shift of 2(-0.65) = -1.30 ppm for the ammonia molecules which are cis to two HSO_4^- ions and a chemical shift of 0.84- 0.65 = 0.19 ppm for the ammonia molecules which are cis to one HSO_4^- ion and trans to the other.

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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.

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Table I

Chemical Shifts, Relative to the Hexamminecobalt(III) Ion, for Several Pentamminecobalt(III) Ions in Concentrated H_2SO_4

Acido Ligand	Chemical Shift, ppm.
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 Hexamminecobalt(III) Ion, for Several Tetramminecobalt(III) Ions in Concentrated H_2SO_4

Acido Ligands	Chemical Shift, ppm. Observed	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^-	-0.33[b]	-0.57

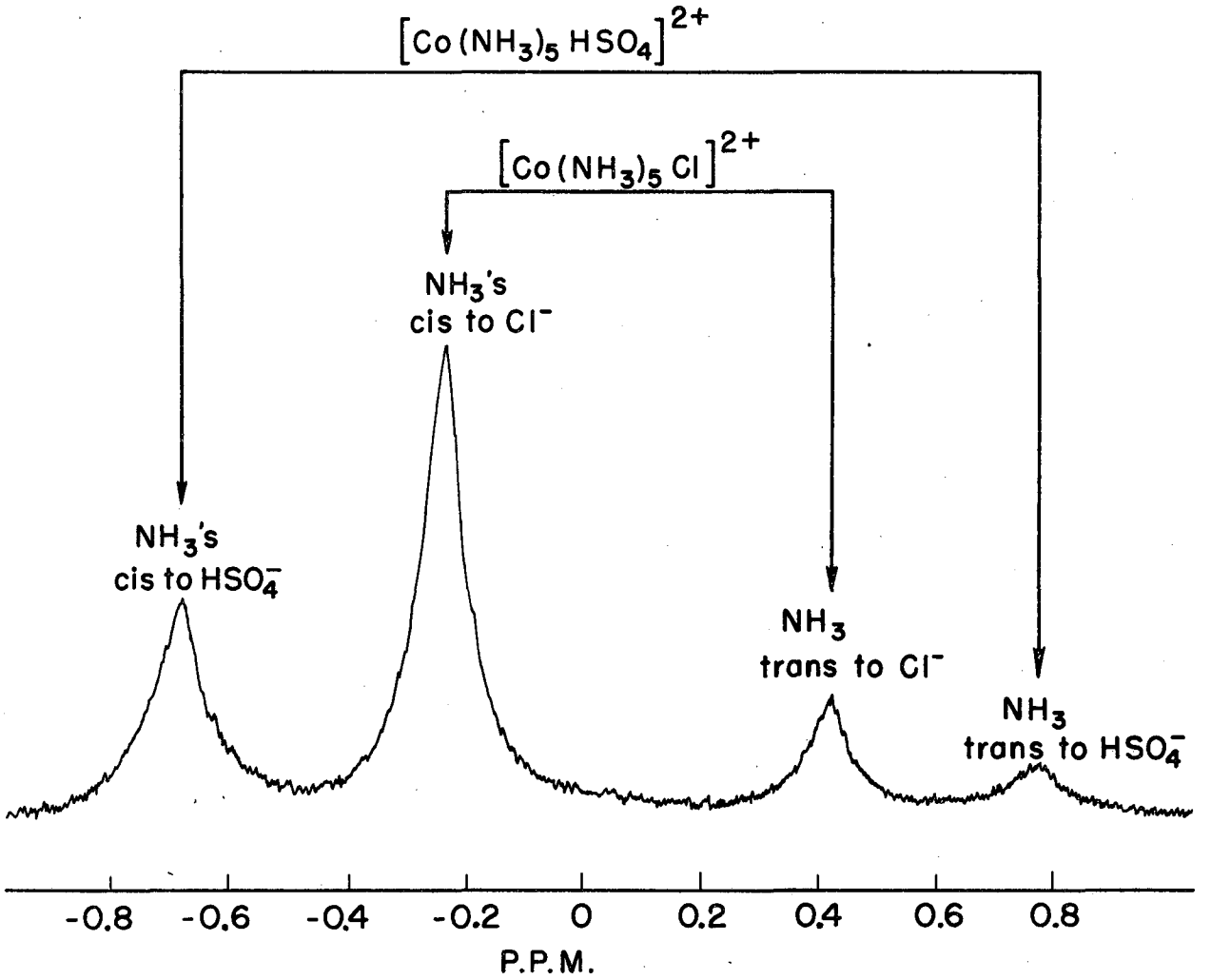
(a) cis- complex (b) trans- complex

Figure Captions

Fig. 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 $[Co(NH_3)_6]^{3+}$.

Fig. 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 $[Co(NH_3)_6]^{3+}$.

Fig. 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(NH3)5 HSO4]2+
[Co(NH3)5 Cl]2+
NH3's cis to Cl−
NH3's cis to HSO4−
NH3 trans to Cl−
NH3 trans to HSO4−
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
P.P.M.

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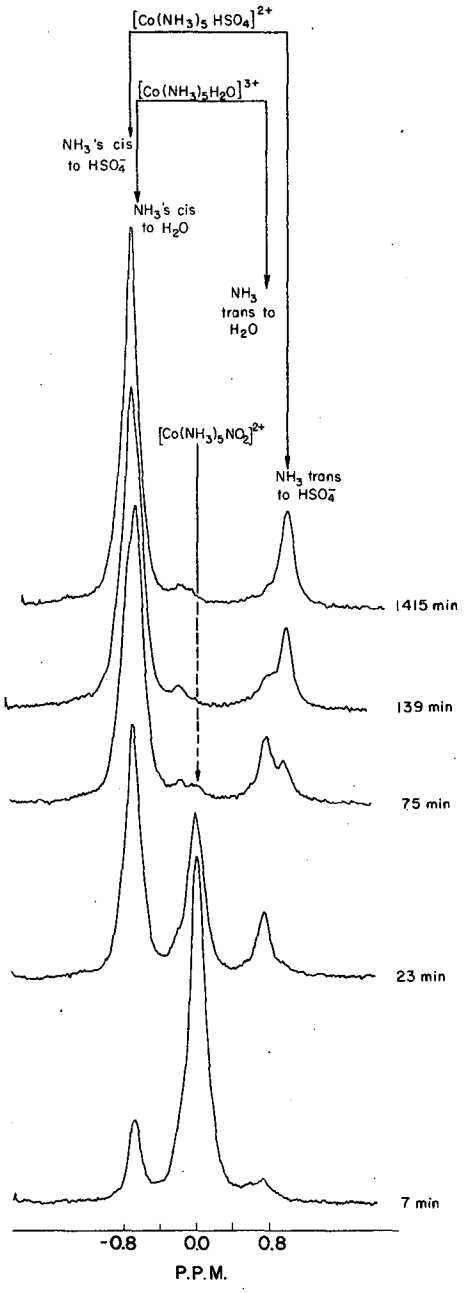
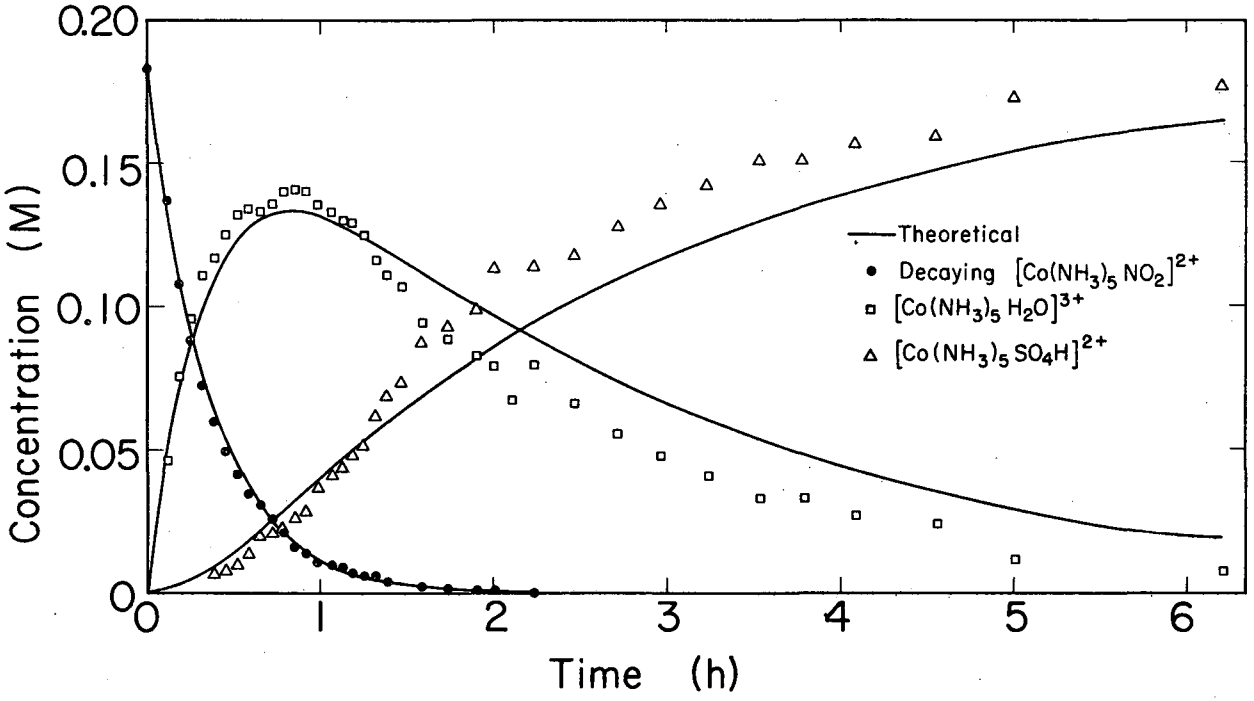

[Co(NH3)5 HSO4]2+
[Co(NH3)5H2O]3+
NH3's cis to HSO4−
NH3's cis to H2O
NH3 trans to H2O
[Co(NH3)5NO2]2+
NH3 trans to HSO4−
1415 min
139 min
75 min
23 min
7 min
-0.8
0.0
0.8
P.P.M.

MUB-4928


0.20
0.15
0.10
0.05
0
Concentration (M)
0
1
2
3
4
5
6
Time (h)
Theoretical
Decaying $[Co(NH_3)_5NO_2]^{2+}$
$[Co(NH_3)_5H_2O]^{3+}$
$[Co(NH_3)_5SO_4H]^{2+}$

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