Proton Magnetic Resonance Study of Some Cobalt(III) Complexes with Ethylenediamine. Evidence for Secondary Coordination Shell

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Abstract: The proton magnetic resonance spectra of tris(ethylenediamine)cobalt(III) chloride and *trans-* and *cis-*dichlorobis(ethylenediamine)cobalt(III) chloride in dimethyl sulfoxide-d_6 and D_2O–D_2SO_4 are reported. The appearance of different axial and equatorial NH proton signals is explained by the "freezing" of the motion of the ethylenediamine ring due to hydrogen bonding with the solvent. The formation of secondary coordination shell is also evidenced by the change of the NH proton chemical shift of $[Co(en)_3]Cl_3$ with the composition of the D_2O–D_2SO_4 solvent system. The activation energy for the inversion of the ring formed by ethylenediamine and cobalt in $[Co(en)_3]Cl_3$ dissolved in dimethyl sulfoxide-d_6 was found to be +10.5 ± 0.5 kcal/mole.

In the solution of a coordinated compound, the complex ions or molecules may have specific interactions with the environment. For a positively charged complex ion, "outer-sphere complexes" may be formed between the solvated cation and anions.[1] Although there are evidences for the interaction between complex cations and added anions in the ion aggregates in solution,[1,2] not very much is known about the interaction between a complex ion and the solvent molecules in its solvation shell.[3] Since the interaction of the latter type is very weak except in certain specific cases, detailed information about the nature of the second coordination shell is difficult to obtain. However, if the ligands in the complex are capable of forming hydrogen bonding with the solvent or another solute, a definitive secondary coordination shell around the complex could be formed. The interaction may then be strong enough to bring about some observable changes in the properties of the system.

Nuclear magnetic resonance has been successfully applied to the study of hydrogen bonding.[4] The proton magnetic resonance of some cobalt(III) complexes with ammonia[5,6] and diamines[7–11] has been studied, but no particular emphasis has been put on the possible formation of hydrogen bonding between the coordinated amine and the solvent. In connection with the study of protonation and coordination shifts of ammonia and some amines, we have examined the proton magnetic resonance spectra of some cobalt(III) complexes with ethylenediamine (en) in several solvents. The results have indicated that an ethylenediamine molecule coordinated to Co(III) can form hydrogen bonds of different strength with the solvent. Such an interaction may lead to the formation of a definitive secondary coordination shell, which in turn could have considerable influence on the conformational equilibrium of the ethylenediamine ring. The establishment of a second coordination shell around the complex *via* the formation of hydrogen bonding is not only important in determining the structure of metal complexes, but also may be found interesting in the kinetic studies of ligand substitution processes.[12,13]

Experimental Section

The Co(III) complexes were prepared according to standard methods[14] and carefully recrystallized from water. Dimethyl sulfoxide-d_6 ((DMSO)-d_6) (99.5% D), D_2O (99.8% D), and D_2SO_4 (99% D) were purchased from Stohler Isotope Chemicals. The proton in (DMSO)-d_5, which exists as impurity in (DMSO)-d_6, shows a quintet signal at −2.52 ppm from tetramethylsilane (TMS). H_2O also appears as impurity and absorbs at *ca.* −3.34 ppm. The position of the proton absorption in D_2O–D_2SO_4 solutions depends upon the acid concentration. Proton magnetic resonance spectra were taken with a Varian A-60A spectrometer at 35° unless otherwise specified.

Results

The proton resonance spectra of $[Co(en)_3]Cl_3$, *cis-*$[Co(en)_2Cl_2]Cl$, and *trans-*$[Co(en)_2Cl_2]Cl$ in DMSO-d_6 and D_2O–D_2SO_4 solutions are shown in Figures 1–5.

For $[Co(en)_3]Cl_3$ in DMSO-d_6 there are two broad and superimposed peaks for the NH protons at −5.40 and −5.80 ppm from TMS (Figure 1a). The peak at lower field is broader than the one at higher field. They seem to have equal intensity. The CH protons absorb at near −2.65 ppm. It is not clear whether there are two separate peaks or not in this region because of the superposition of the solvent signal. The two kinds of magnetically different NH protons are in slow exchange, as shown by the change in the line shape with temperature (Figure 2). The appearance of two NH absorptions for the tris(en) complex was also observed in a D_2O–D_2SO_4 solution (concentration not specified) at 100 MHz.[9] At 60 MHz, the NH protons showed

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Figure 1. Proton nmr spectra of three Co(III) complexes in DMSO-d_6 at 60 MHz: (a) $[Co(en)_3]Cl_3$, (b) *trans*-$[Co(en)_2Cl_2]Cl$, (c) *cis*-$[Co(en)_2Cl_2]Cl$. On the upper left side of each spectrum, an accumulation of 25 scans on a Varian C-1024 Computer Average of Transients (CAT) of the same spectrum is shown.

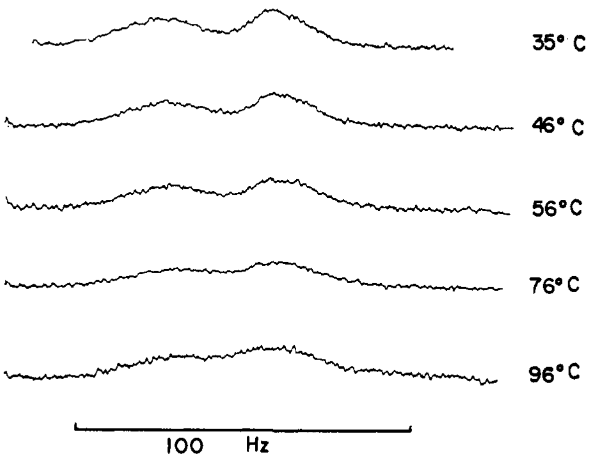

Figure 2. The variation of the nmr signal of the NH protons of $[Co(en)_3]Cl_3$ in DMSO-d_6 with temperature. Each spectrum is an accumulation of 25 scans on C-1024.

only one broad absorption in D_2O–D_2SO_4 solutions because of lower resolution. However, the line width of the NH absorption and its chemical shift with respect to the absorption of the CH protons did change with the composition of the solvent (Figure 3). In a solution of 0.0175 mole fraction (mf) of D_2SO_4, the NH absorption has a chemical shift of −2.01 ppm from the CH absorption, and it moves upfield with the increase of the D_2SO_4/D_2O ratio (Table I and Figure 6). The line width seems to be smaller for intermediate concentrations of D_2SO_4 and becomes very large in 100% acid. The spectra did not change at all when the temperature was lowered from 35 to 15°.

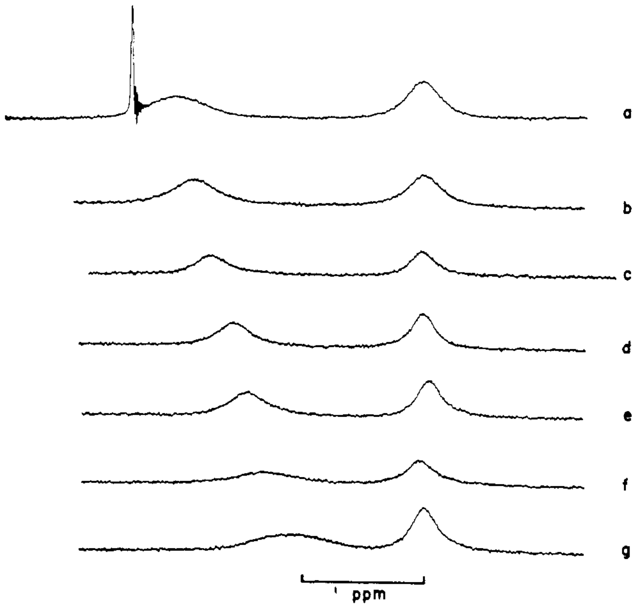

Figure 3. Proton nmr spectra of $[Co(en)_3]^{3+}$ in D_2O–D_2SO_4 solutions at 60 MHz. The solvent compositions are in mole fraction of D_2SO_4: (a) 0.0175, (b) 0.077, (c) 0.144, (d) 0.239, (e) 0.308, (f) 0.564, (g) 1.00. The H_2O peak of the solvent appeared at much lower field and is not shown in the spectra except in (a).

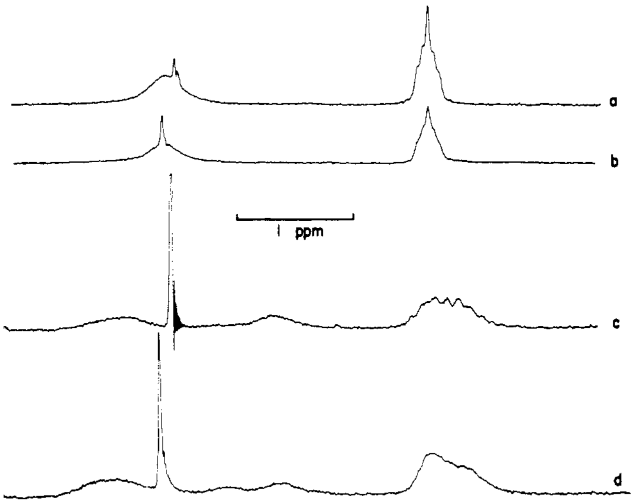

Figure 4. Proton nmr spectra of $[Co(en)_2Cl_2]^+$ in acidified D_2O solutions (0.0175 mole fraction in D_2SO_4) at 60 MHz: (a) the *trans* isomer at 35°, (b) the *trans* isomer at 25°, (c) the *cis* isomer at 35°, (d) the *cis* isomer at 25°. The sharp peak is due to H_2O in the solvent.

For *trans*-$[Co(en)_2Cl_2]Cl$ in DMSO-d_6, there is only one absorption for the NH protons at −5.29 ppm; the CH absorption appears at −2.84 ppm (Figure 1b). In a solution of 0.0175 mole fraction of D_2SO_4 in D_2O, the chemical shift of the NH protons from the CH protons is −2.27 ppm and does not change with temperature (Figure 4a,b). The CH absorption shows fine structure. Although not well resolved, it appears to be a characteristic five-line pattern, which arises from an $A_2A'_2X_2X'_2$ coupling in ethylenediamine and is similar to tetrahydrothiophene.

For *cis*-$[Co(en)_2Cl_2]Cl$ in DMSO-d_6, there are two peaks at −4.00 and −5.59 ppm, respectively (Figure 1c). The intensity ratio of these two absorptions is 1:3. Both of the signals can be assigned to the NH protons for reasons to be discussed. There are also two CH absorptions (−2.32 and −2.74 ppm) with

Table I. Proton Magnetic Resonance Data for Three Co(III) Complexes

Complex	Solvent	$\delta_{\text{NH-CH}}$, ppm	Remarks
$[Co(en)_3]Cl_3$	DMSO-d_6	−2.75, −3.15 (av −2.95)	Intensity ~1:1; merge together with the increase of temperature
	0.0175 mf D_2SO_4 in D_2O	−2.01	
	0.077 mf D_2SO_4	−1.87	
	0.144 mf D_2SO_4	−1.72	
	0.239 mf D_2SO_4	−1.53	No temperature dependence from 35 to 15°
	0.308 mf D_2SO_4	−1.41	
	0.564 mf D_2SO_4	~ −1.22	
	1.00 mf D_2SO_4	~ −1.03	
trans-$[Co(en)_2Cl_2]Cl$	DMSO-d_6	−2.45	No temperature dependence
	0.0175 mf D_2SO_4	−2.27	CH protons appeared as quintet
cis-$[Co(en)_2Cl_2]Cl$	DMSO-d_6	−1.26 −2.85	Intensity ~1:3; there is another CH absorption at a higher (0.42 ppm) field; solvent substitution occurred above 50°
	0.0175 mf D_2SO_4	−1.50 −2.77	35°, intensity ~1:1
		−1.42, −1.91, −2.88	25°, intensity ~1:1:2

different intensities. The intensity ratio of these absorptions cannot be measured accurately because of the superposition of the solvent absorption. Although solvolysis is negligible at 35°, ligand substitution occurred when the temperature was raised,[15] and a new absorption at −5.22 ppm grew at the expense of the one at lowest field (Figure 5). In an acidified D_2O solution (0.0175 mole fraction of D_2SO_4) at 35° the CH absorption showed some fine structure which is probably the superposition of two or more multiplets but is difficult to analyze unequivocally. The NH protons gave rise to two absorptions of equal intensity at −1.50 and −2.77 ppm, respectively, from the center of the CH absorption (Figure 4c). When the temperature was reduced to 25° and lower, the structure of the CH absorption was smeared and became asymmetrical, while a new NH peak appeared at the expense of the one at higher field. The three NH absorptions, which appear at −1.42, −1.91, and −2.88 ppm, respectively, from the center of the CH absorption, have intensity ratios approximately 1:1:2 (Figure 4d).

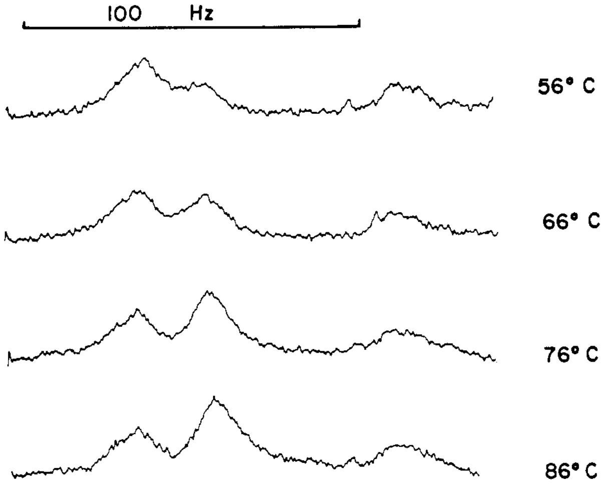

Figure 5. The variation of the nmr signal of the NH protons of *cis*-$[Co(en)_2Cl_2]Cl$ in DMSO-d_6 with temperature. Each spectrum is an accumulation of 25 scans on C-1024.

The results discussed above are summarized in Table I.

Discussion

The hydrogen atoms attached to the nitrogen in an amine are capable of forming hydrogen bonds with proton acceptors.[4] Upon the coordination to a metal ion, the tendency of the amine to form hydrogen bonding would increase because of the decrease of electron density on the nitrogen. Thus, for some sterically favored metal–amine complexes in basic solvents, hydrogen bonding between the ligands and the solvent molecules may be formed. This would result in a definite second coordination shell around the complex. The formation of the second coordination shell may cause some observable change of certain properties of the amino group.

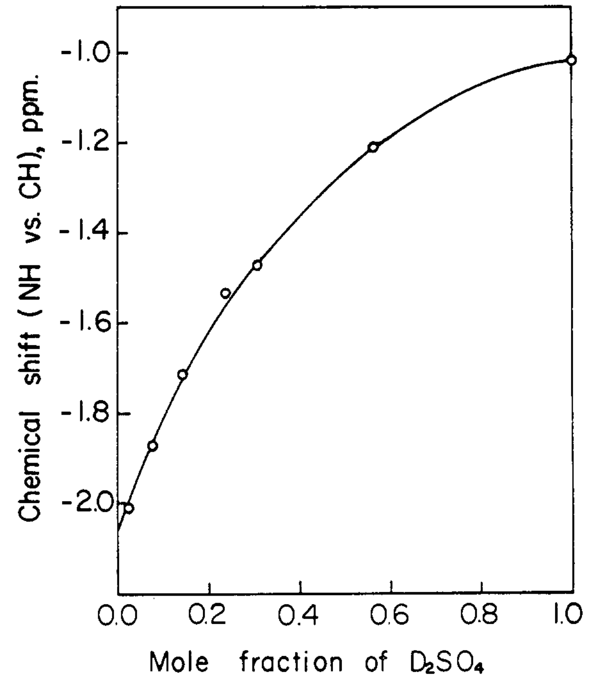

Figure 6. The chemical shift of the NH protons of $[Co(en)_3]^{3+}$ in D_2O-D_2SO_4 solutions.

In a metal–ethylenediamine complex, the five-membered ring formed by the diamine and the metal has a nonplanar conformation.[16] As a result, the protons

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attached to both the carbon and the nitrogen atoms may assume approximately axial and equatorial positions. The axial hydrogens and the equatorial hydrogens are interconvertible upon the motion of the ring. If the motion is slow, these hydrogens may show different chemical shifts in the proton magnetic resonance spectrum, as for cyclohexane[17] and its derivatives.[18] In solvents of considerable basicity, if the sterical factors are favorable, the motion of the ring would indeed slow down owing to the formation of the second coordination shell. In such cases, the change of conformation requires either the breakage of hydrogen bonds followed by the motion of the ring, or the secondarily coordinated molecules being carried together in the motion. Both processes would require additional energy to the normal activation energy for the conversion between the two conformations. As a result, there may exist "frozen" conformers. Separate resonance signals for the axial and equatorial positions would then be observable.

The above conditions are fulfilled for $[Co(en)_3]^{3+}$ in DMSO-d_6, a strong proton acceptor. Therefore, the two NH signals at -2.75 and -3.15 ppm can be assigned to the axial and the equatorial protons, respectively, in analogy to the assignment for cyclohexane.[17] The larger line width for the equatorial protons probably arises from dipolar broadening, because in the most stable conformation each equatorial N–H bond is approximately parallel to the C_3 axis and quite close to two other equatorial N–H bonds in the other two rings.[19,20] The temperature dependence of the NH absorption has been shown in Figure 2. The theoretical line shape of two exchanging species with unequal transversal relaxation times[21] can be programmed to fit the experimental data. The lifetime, τ, of the NH protons for the ring inversion at different temperatures was obtained by fitting the computed spectra into the experimental spectra (Figure 2). The computation was performed on an IBM 7090 computer. An Arrehenius plot based upon the data thus obtained is given in Figure 7. The activation energy was found to be $+10.5 \pm 0.5$ kcal/mole. The relatively large value for the conformational change of the ethylenediamine ring is not too surprising in view of the reasons discussed above.

The probable existence of a second coordination shell in the solution of $[Co(en)_3]^{3+}$ is further exemplified by the composition and temperature dependence in the D_2O–D_2SO_4 solvent system. As shown in Figure 3, δ_{NH-CH} decreases with the increase of the concentration of D_2SO_4. Because the exchange rate of D for H in the amine is inversely proportional to the D^+ concentration,[22] the chemical shift in pure D_2O could not be measured directly. An extrapolated value of δ_{NH-CH} for $Co(en)_3{}^{3+}$ at infinite dilution of D_2SO_4 is -2.06 ± 0.02 ppm (Figure 6). The corresponding value in DMSO-d_6 is -2.95 ± 0.02 ppm, averaged for the axial and equatorial protons. The difference of 0.89 ppm can be explained by the change in the strength of the hydrogen bond between the NH proton and the solvent molecule, because water is a weaker proton acceptor than dimethyl sulfoxide. In the presence of D_2SO_4, the acid molecule, the DSO_4^- ion, and the SO_4^{2-} ion may enter the second coordination shell in replacement of D_2O. The replacement would, of course, change the strength of the hydrogen bonding and the NH proton chemical shift. The higher field shift of the NH resonance in D_2SO_4 is again due to weaker hydrogen bonding between the NH proton and the acid molecules or anions. Nevertheless, we could not determine the value of the chemical shift of various secondarily coordinated species accurately, because there are too many possible ionization products in D_2SO_4.[23] The temperature dependence for the proton nmr spectra of $[Co(en)_3]^{3+}$ in D_2O–D_2SO_4 solutions is very small, as we have already noted. The line width of the NH absorption seems to be smaller for intermediate concentration of D_2SO_4 in the temperature range studied. These facts indicate that the exchange of secondary "ligands" is probably a simple diffusion-controlled process.

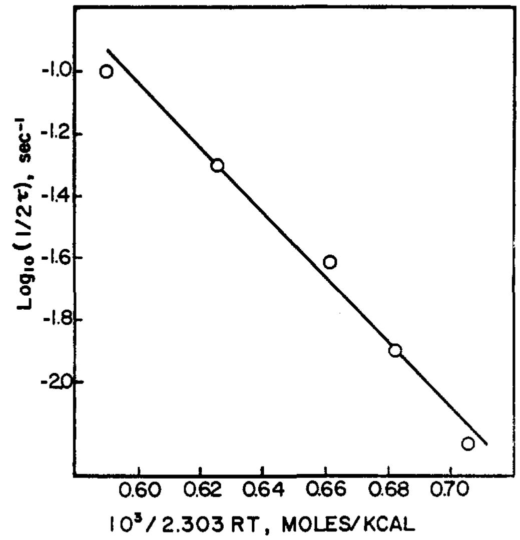

Figure 7. The Arrhenius plot for the conformational equilibrium of the ethylenediamine rings in $[Co(en)_3]Cl_3$ in DMSO-d_6.

In a D_2SO_4–D_2O solution at 100 MHz, Spees, Durham, and Sargeson observed that the NH protons in $[Co(en)_3]^{3+}$ showed two superimposed signals with a peak-to-peak separation of 0.30 ppm.[9] They explained these as signals of two conformers. However, we do not see why the chemical shifts of all the NH protons in a conformer would be the same but different in different conformers. On the other hand, the two signals can be explained as due to equatorial and axial hydrogens in the ethylenediamine ring, just as in DMSO-d_6. The smaller peak-to-peak separation in D_2O is probably due to a larger overlapping of the signals, or a small difference in the strength of hydrogen bonding for the axial and equatorial protons in different solvents due to steric factors. Yoneda and Morimoto showed that the two NH signals of the cobalt complex in trifluoroacetic acid behave as an AB pair,[10] which rules out the

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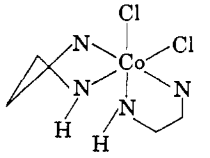

Figure 8. Schematic diagram showing the two least sterically hindered NH protons (designated as H_c in text) in the *cis*-dichlorobis(ethylenediamine)cobalt(III) ion. All other NH protons are adjacent to either one or two chlorine atoms.

possibility that they arise from protons in different molecules.

For *trans*-$[Co(en)_2Cl_2]Cl$, the steric hindrance due to the large size of the chlorine atoms would prevent the formation of a stable secondary coordination shell. The two stable conformations of each ethylenediamine ring may then be in rapid equilibrium. Therefore, we can no longer differentiate between axial and equatorial hydrogens. As a result, there is only one broadened NH signal in both DMSO-d_6 and D_2O–D_2SO_4. The appearance of an overlapped five-line signal for the CH proton in D_2O further confirms the rapid equilibrium between the conformers of the ethylenediamine ring. A small difference (0.18 ppm) for δ_{NH-CH} in the two kinds of solvents suggests the existence of a very weak second coordination shell for the *trans* complex in DMSO-d_6.

In each of the ethylenediamine rings in *cis*-$[Co(en)_2Cl_2]Cl$ there are two NH hydrogens (designated by H_a) *cis* to two Cl atoms and two NH_2 groups, and two NH hydrogens *cis* to one Cl atom and three NH_2 groups. Of the latter two NH hydrogens, one is adjacent to one Cl and one NH_2 group (designated as H_b); the other is adjacent to two NH_2 groups (designated as H_c) (Figure 8). As in the case of the *trans* complex, the two H_a hydrogens and the H_b hydrogen would not form stable second coordination bonds because of steric hindrance. However, H_c is capable of forming a definite hydrogen bond with a solvent molecule. In D_2O at 35°, the hydrogen bonding is probably not very strong so that H_b and H_c appeared as unresolved absorptions (-1.50 ppm from the center of the CH absorption); the H_a protons absorbed at a lower field (-2.77 ppm) because of the influence of two *cis* Cl atoms.[5] When the temperature was lowered, the H_c absorption appeared as a separate peak because of the formation of more definitive hydrogen bonding (Figure 4d). The CH protons showed some fine structure, but were not well resolved. (Three peaks of 1:1:2 ratio for the NH protons in *cis*-$[Co(en)_2(NH_3)_2](ClO_4)_3$ were also observed in acidified D_2O with the H_a peak at a higher field than the H_b and H_c peaks.[9]) In DMSO-d_6, the solvent molecule can form a stronger hydrogen bond with the H_c hydrogens in *cis*-$[Co(en)_2Cl_2]Cl$. As a result, the H_c signal moved further downfield; in the case we studied, this signal superimposed on the H_a signal. Therefore, the intensity of the two peaks at δ_{NH-CH} -1.26 and -2.85 ppm have the ratio 1:3. The difference in the chemical shift for the H_c proton in D_2O (with 0.0175 mole fraction of D_2SO_4) and in DMSO-d_6 is 0.94 ppm, which is the same as that for the NH protons of $[Co(en)_3]^{3+}$ in the two solvents. This may serve as another evidence for the existence of secondary coordination due to hydrogen bonding between the ligands in a complex and the solvent molecules.

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Electron Transfer through Organic Structural Units. IV. N-Coordinated Pyridines as Bridging Groups in Oxidation–Reduction Reactions[1]

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Abstract: The specific rates of reduction of six substituted pyridinepentaamminecobalt(III) complexes, and the pyrazolepentaamminecobalt(III) complex, with Cr^{2+} have been measured. In these complexes, acetyl- and benzoylpyridines coordinate through the ring nitrogen, as does N,N-dimethylnicotinamide; 2- and 4-hydroxypyridine coordinate through oxygen. Rate constants for the unsubstituted pyridine and pyrazole complexes, and for the 2-OH-, 4-OH-, and 3-$(CH_3)_2NCO$-substituted pyridine derivatives, lie in the range 0.002–0.03 l. mole^{-1} sec^{-1} (24.5°, $\mu = 1.2$), whereas the acetyl and benzoyl derivatives have values in the range 10^2–10^4 l. mole^{-1} sec^{-1}. The 4-benzoylpyridine complex is reduced more rapidly than any other organic pentaamminecobalt(III) derivative thus far reported, except for a few which form chelated Cr(III) products. These rates are not acid dependent. The ketopyridine complexes, like the unsubstituted pyridine complex, give $Cr(H_2O)_6^{3+}$ as the sole isolable Cr(III) product, but the very striking accelerations (five to six powers of ten) resulting from incorporation of the carbonyl substituent strongly indicate direct participation of the carbonyl group in the electron-transfer process, *i.e.*, reduction by remote attack. Surprisingly, rate increases for 3-keto substitution in Co(III)-bound pyridine are nearly as great as for 4-keto substitution.

The reduction, with Cr(II), of pentaamminecobalt(III) complexes may be substantially accelerated by introducing an appropriately substituted pyridine as a sixth ligand at the Co(III) center. Earlier papers in this

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