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A Spectrophotometric Investigation of Iron(III) Chloride in Pyridine

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The incorporation of the solvent pyridine into the Coordination Model for non-aqueous solvents is most illuminating with regards to the importance of non-specific solvation. This is a strongly coordinating solvent with poor solvating properties. The species formed when $FeCl_3$ *is dissolved in pyridine have been investigated in both dilute and concentrated solutions over a mole ratio range of 0 to 10 moles of chloride per mole of iron(III). It has been shown that the three species formed which can be detected by ultraviolet-visible spectroscopy and molar conductance techniques are* $FeCl_4^-$, *(*$FeCl_3.nC_5H_5N$*), and a metastable species of low* Cl^-/Fe^{III} *ratio.*

Introduction

The Coordination Model[2,5] was proposed to rationalize the solvation reactions occurring in non-aqueous solvents. By constructing a thermodynamic cycle for the reaction:

$$MX_{(soln)} + S_{(soln)} \rightarrow MS^+_{(soln)} + X^-_{(soln)}$$

we were able to show that specific and non-specific solvent properties were important. The specific effects include the donor strength of the solvent toward cations or its acceptor strength toward anions. The non-specific effects include interactions outside the primary coordination sphere and dieletric properties of the solvents. Various criteria were proposed to enable estimation of donor strength and for evaluating the combined solvents acceptor strength and dielectric property. In addition to rationalizing the extent of chloride ion dissociation of $FeCl_3$ in various solvents, these considerations have also been shown to be of importance in determining the mechanism of chloride ion substitution in square planar platinum(II) complexes.[6]

The Coordination Model has now become widely accepted. Recently Gutmann *etal.*, have[7,8] applied these considerations to a large number of transition metal compounds in many of the solvents previously studied in this laboratory.[5] The have been reporting consistent confirmations of the predictions of the Coordination Model.

The importance of non-specific solvating properties of the solvents has been nicely illustrated by studies in N, N-dimethylacetamide and N-methylacetamide.[4] The ease with which $(CH_3)_3NO$ displaces halides from $Co[(CH_3)_3NO]_2X_2$ was also shown[9] to be a function of the solvent employed and of the anion in the primary coordination sphere.

We report here some very interesting behavior of $FeCl_3$ in the solvent pyridine. This is the first exhaustive study in a solvent of low solvating ability with strong donor strength. The results emphasize the importance of non-specific solvation energies from both the thermodynamic and kinetic standpoints.

Experimental Section

Materials. *(*$C_2H_5)_4NFeCl_4$. Tetraethylammonium tetrachloroferrate(III) was prepared as described previously.[4]

Anal. Calcd. for $C_8H_{20}NFeCl_4$: C, 29.30; H, 6.15; N, 4.27. Found: C, 29.40; H, 6.28; N, 3.91.

($C_2H_5)_4NCl$. Tetraethylammonium chloride was obtained commercially from Eastman Organic Chemicals Company. The white solid was dried in an Abderhalden drying pistol at 100°C for 12 hrs. *in vacuo* and stored in a closed glass container in a dry box under a dry air atmosphere. The material is slighthly hygroscopic.

Anal. Calcd. for $C_8H_{20}NCl$: C, 57.98; H, 12.17; N, 8.45. Found: C, 58.04; H, 12.23; N, 8.14. Attempts to recrystallize the compound from acetone and/or to dry it for longer periods of time at 100°C caused decomposition.

($C_2H_5)_4NC1O_4$. Tetraethylammonium perchlorate was obtained commercially from Eastman Organic Chemicals Company. No drying procedure was employed, as the white solid is not hygroscopic.

Anal. Calcd. for $C_8H_{20}NC1O_4$: C, 41.83; H, 8.78. Found: C, 41.86; H, 8.62.

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$FeCl_3$. Ferric chloride was obtained as a resublimed anhydrous solid from Matheson, Coleman, and Bell. No further purification was carried out. The material is very hygroscopic.

2,2-Dimethoxypropane. Dimethoxypropane (DMP) was obtained in practical grade purity from Eastman Organic Chemicals Company, and used without further purification.

CH_3OH. Methanol was obtained in reagent grade puritp from Mallinckrodt Chemical Company and used without further purification.

C_5H_5N. Baker and Adamson Reagent Grade pyridine was refluoxed under reduced pressure at 40°C over barium oxide for four hours, distilled, and stored in a dry box. An infrared spectrum of pyridine purified by this procedure showed no water bands at 3400 cm^{-1}.

$(C_2H_5)O_2$. Reagent grade anhydrous ether was stored over Linde 4A molecular sieve pellets in a dry box.

$Fe(H_2O)_6(ClO_4)_3$. Hexaquo iron(III) perchlorate was obtained from the G. F. Smith Chemical Company and used without further purification.

$[Fe(C_5H_5N_5)(ClO_4)](ClO_4)_2$. Hexaquo iron(III) perchlorate (5 g.) was stirred with CH_3OH (23 ml.) and DMP (100 ml.) for 4 1/2 hrs. A solution of pyridine (50 ml.) and DMP (50 ml.) was also stirred for the same length of time and then slowly added to the iron-containing solution. Stirring was continued for 14 hrs., during which time an egg-shell white colored powder appeared. The solid was filtered on a medium grade sintered glass funnel, washed with ether four times, dried for 45 hours under vacuum over P_4O_{10}, and stored in a screwcap bottle in a dry box. The material is slightly hygroscopic. Its characterization is described later.

Anal. Calcd. for $C_{25}H_{25}N_5FeCl_3O_{12}$: C, 40.05; H, 3.36; N, 9.34. Found: C, 40.22; H, 3.34; N, 9.39.

Spectra. Ultraviolet and Visible. Spectra in the 305 mμ range were recorded on a Cary Model 14M spectrophotometer, utilizing either 1 cm. or 0.007 cm. path length quartz cells. A Thermoboy constant temperature recirculating bath was used in conjunction with a jacketed cell mount which could accommodate a 1 cm. cell. Temperature settings of 20.00 ± 0.11°C and 30.00 ± 0.11°C were determined by a National Bureau of Standards thermometer.

Infrared. Infrared spectra in the 4000 cm^{-1} to 250 cm^{-1} region were recorded on a Perkin Elmer Model 521 spectrometer, and were calibrated by the use of polystyrene bands superimposed at 5.495μ and 11.035μ. Nujol mulls were made using a Wig-L-Bug grinder.

Conductance. Molar conductance measurements were made with an Industrial Instruments Conductivity Bridge Model R 16B2, operated at 1000 cps. The cell was calibrated with an aqueous solution of KCl.

Experimental Procedure. Transfers of solids and solutions were carried out in a dry box under an atmosphere of dry air. Weighings were accomplished when necessary by addition of the desired material to a preweighed glass stoppered flask in the dry box, followed by a final weighing of the stoppered flask plus contents in air. The concentrations of $[Fe(C_5H_5N)_5(ClO_4)](ClO_4)_2$ listed in the caption under Figure 1 were obtained by this procedure. All glass apparatus was usually dried overnight at 160°C, and never less than four hours at this temperature prior to use, then cooled to room temperature in a dry box under a dry air atmosphere.

Results and Discussion

Infrared analysis of a Nujol mull of $[Fe(C_5H_5N)_5(ClO_4)](ClO_4)_2$ indicated the presence of coordinated perchlorate[10] and the absence of uncoordinated pyridine.[11] The molar conductance of a 10^{-3}M solution of this species was initially about twice that of a comparable $(C_2H_5)_4NClO_4$ solution and increased with time over a period of 7 weeks to a value slightly less than 3/2 the initial value. The molar conductance of $(C_2H_5)_4NClO_4$ in pyridine remained constant with respect to time, and showed variations due only to temperature effects.

The molar conductance of a 2.15×10^{-3} *M* $FeCl_3$ pyridine solution showed that the solution is essentially a non-electrolyte upon initial preparation when compared with a comparable solution of $(C_2H_5)_4NClO_4$. Very small changes in the molar conductance were observed with time, and can be attributed to temperature effects.

Solutions for spectral studies were prepared by addition of varying amounts of $(C_2H_5)_4NCl$ to $[Fe(C_5H_5N)_5(ClO_4)_2$ in pyridine, such that the final ratio of chloride to iron varied from 0/1 to 10/1. In the dilute solutions, the final iron concentration was *ca.* 2.7×10^{-4} M, whereas in the more concentrated solutions, a concentration of *ca.* 4×10^{-2} M was utilized. Solutions of $(C_2H_5)_4NFeCl_4$ and $FeCl_3$ were prepared in an analogous manner. Initially, the 0/1 molar ratio dilute solution was yellow in color, while other molar ratio dilute solutions and the $FeCl_3$ dilute solution appeared yellow-brown. The dilute $(C_2H_5)_4NFeCl_4$ solution was initially light green in color. The concentrated solutions initially appeared to be burgundy colored.

The visible and ultraviolet spectra of these solutions were found to vary with time, the most pronounced change in the dilute solutions occurring within one week. Changes in the more concentrated solutions occurred at a slower rate. All dilute solutions gradually became light burgundy in color.

Composite spectra obtained from the dilute pyridine solutions taken over a five-week period are shown in Figures 1-3, inclusive.

A composite spectrum of a 3/1 molar ratio solution in which $[Fe] = 4.49 \times 10^{-2}$ is shown in Figure

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(10) J. Hathaway and A. Underhill, *J. Chem. Soc.*, 3091 (1961).

(11) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, *18*, 79 (1961).

4, and a 3.08 $\times 10^{-2}$ M $FeCl_3$ solution is shown in Figure 5.

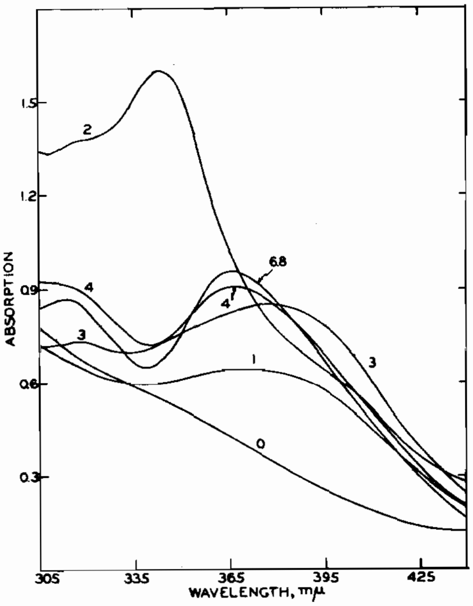

Figure 1. Initial spectral composite of pyridine solutions of $[Fe(C_5H_5N)_5ClO_4](ClO_4)_2$ and $(C_2H_5)_4NCl$ in the following Cl^-/Fe^{III} molar ratios: 0/1 (0); 1/1 (1); 2/1 (2); 3/1 (3); 4/1 (4); 6.8/1 (6.8). The molar concentrations of iron(III)$\times 10^4$ in each solutions is (0), 2.51; (1), 2.67; (2), 2.69; (3), 2.69; (4), 2.64; (6.8), 2.51.

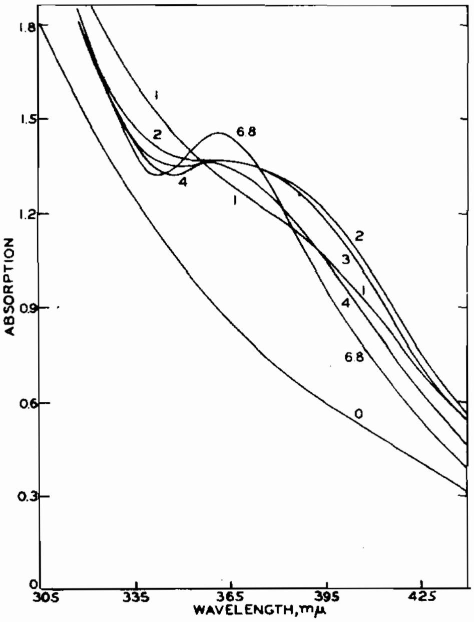

Figure 2. One week spectral composite of pyridine solutions described in Figure 1.

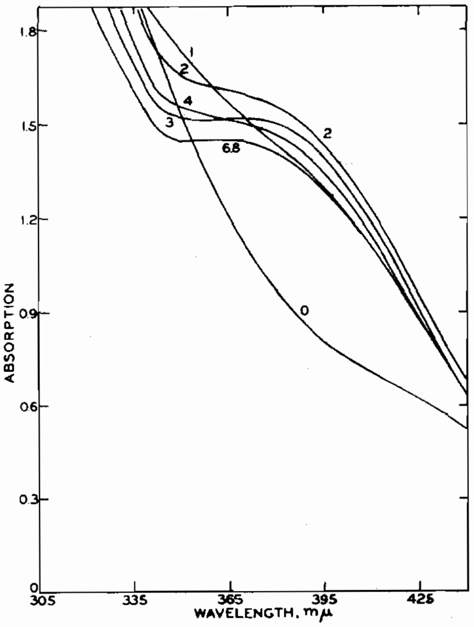

Figure 3. Five week spectral composite of pyridine solutions described in Figure 1.

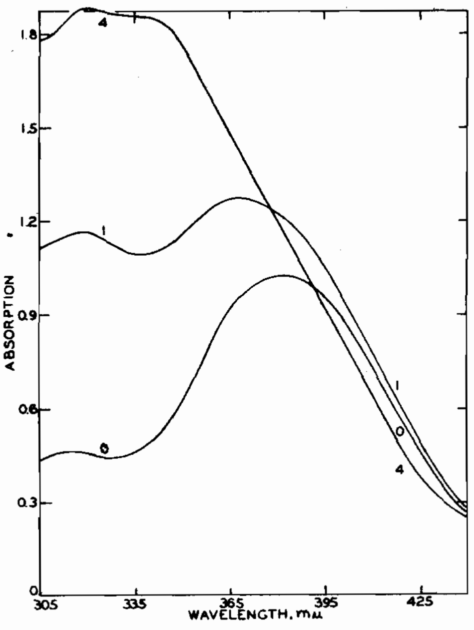

Figure 4. Composite spectrum of a 3/1 Cl^-/Fe^{III} molar ratio pyridine solution with time. $[Fe] = 4.49 \times 10^{-2}$. Solution age in weeks is indicated on each spectrum.

Temperature variation of dilute $(C_2H_5)_4NFeCl_4$, 2.7/1 molar ratio, and $FeCl_3$ solutions from 20°C to 30°C produced no changes in band maxima and less than a 2.5% variation in absorption. Hence, no precautions were taken to thermostat the solutions.

The purpose of this investigation is an elucidation of the species formed when $FeCl_3$ is dissolved in pyridine in order to correlate the behavior of this solvent with that previously reported for other solvents.[3,5,8]

A typical spectrum obtained upon initial dissolution of $FeCl_3$ in pyridine at a concentration of 3.08×10^{-2} M is shown in the curve labelled « 0 » in Figure 5. Maxima are present in this spectrum at 320 mμ and 349 mμ, and a shoulder is present at approximately 380 mμ. The spectrum of a more dilute soltuion shows a somewhat different ratio of band intensities, and will be discussed below. A $FeCl_4^-$ spectrum in a variety of solvents[12] shows maxima at

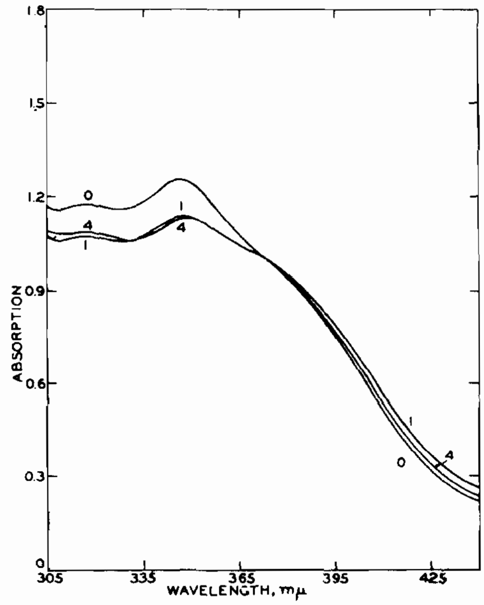

Figure 5. Composite spectrum of a 3.08×10^{-2} *M* $FeCl_3$ pyridine solution behavior with time. Solution age in weeks is indicated on each spectrum.

approximately 320 mμ and 363 mμ, as well as a shorter wavelength absorption maximum at 240 mμ which is not observable here because of the pyridine charge transfer cut-off at 295 mμ. The 363 mμ maximum exhibits a somewhat larger extinction coefficient than the 320 mμ absorption maximum. Since the extinction coefficient of the 363 mμ $FeCl_4^-$ absorption is larger than that of the 320 mμ absorption maximum its presence should be observed in the spectrum labelled « 0 » in Figure 5. The total amount of $FeCl_4^-$ present is so small, however, that the 363mμ band maximum cannot be distinguished in the rather broad shoulder at approximately 380 mμ. The maxima of other chloro-containing species containing various coordinated ligands are not well enough defined to allow specific wavelength assignments for monochloro, etc., species. Therefore, the maximum in the initial spectrum of Figure 5 at 349 mμ and the shoulder at 380 mμ are of interest here. The maximum at 320 mμ can be assigned to $FeCl_4^-$.

In order to identify the species producing the maximum at 349 mμ and the shoulder at 380 mμ, an attempt was made to prepare $[Fe(C_5H_5N)_6](ClO_4)_3$ so that the change in spectrum as a function of added chloride ion could be used to identify the chloro species in solution. A similar approach was used successfully in earlier studies.[3]

The compound which resulted analyzed for $Fe(C_5H_5N)_5(ClO_4)_3$. The infrared spectrum exhibited coordinated perchlorate absorptions and no uncoordinated pyridine absorptions in a Nujol mull spectrum, and can therefore be formulated as $[Fe(C_5H_5N)_5(ClO_4)](ClO_4)_2$. When this substance is dissolved in pyridine, the value of the molar conductance is found to increase with time, as described above. It is presumed that this increase reflects the slow replacement of the coordinated perchlorate ion by pyridine. Such an increase parallels the spectrophotometric results as well. The spectra of this 0/1 solution, in Figures 1 - 3, inclusive, show the behavior of a 2.51×10^{-4} *M* pyridine solution of this solid with respect to time. The general increase in absorption which parallels the conductance behavior in the more concentrated solution is believed to be due to the slow replacement of coordinated ClO_4^- by pyridine to form $[Fe(C_5H_5N)_6]^{3+}$. Since only an absorption edge is observed in these spectra, the extinction coefficient of the pyridine iron charge transfer band in the hexakis-pyridine species must be very large. Only a relatively small change in the concentration of the hexakis-pyridine species would produce large changes in its absorption. This gradual change has been observed over a five week period. The greatest change occurs during the first week, and the gradual changes occurring thereafter appear to taper off only slightly during an additional month. It is estimated that this slow reaction would require several months at room temperature to reach a point at which the spectral changes would be unobservable.

Figure 1 indicates a composite of the spectra taken on the freshly prepared solutions. Whenever a solution is described in terms of a certain molar ratio, it is implied that this solution is prepared from $[Fe(C_5H_5N)_5(ClO_4)](ClO_4)_2$ and $(C_2H_5)_4NCl$. The species present in the 2/1 molar ratio exhibit a spectrum with maxima similar to those shown in Figure 5, the primary difference lying in the relative intensities of the 349 mμ versus the 320 mμ absorption maxima as well as the broad shoulder around 380 mμ and the appearance of a small maximum near 405 mμ. This latter absorption is quite weak, and appears to be due to the same species that produced the 349 mμ maximum. In Figure 5, these two maxima are much less intense, the 405 mμ band being lost in the large shoulder around 380 mμ.

It is reasonable to expect, since both Cl^- and pyridine are better bases than ClO_4^-, that one or both of these species should displace the coordinated ClO_4^- in the primary coordination sphere of Fe^{III}. Since both conductance experiments and the 0/1 spectra of Figures 1 -3 indicate only a slow replacement of coordinated ClO_4^- by *pyridine*, the changes observed in the 2/1 and other ratio solutions compared with the 0/1 solution are attributed to a reaction between $[Fe(C_5H_5N)_5(ClO_4)]^{2+}$ and Cl^-. The species exhibiting absorption maxima at 349 mμ and 405 mμ will be referred to as I, and the species exhibiting an absorption maximum at approximately 380 mμ will be referred to as II. The species absorbing at 320 mμ has been identified as $FeCl_4^-$. The remaining spectra in Figure 1 indicate that there is a tendency to form both $FeCl_4^-$ and II at low Cl^-/Fe^{III} ratios and that the trend shifts in favor of $FeCl_4^-$ at higher Cl^-/Fe^{III} ratios. There appear to be several rapid reactions in these freshly prepared dilute solutions, therefore, which favor the formation of II in low ratio solutions and which shift to the preferred formation of $FeCl_4^-$ in higher ratio solutions. This trend is interrupted at the 2/1 ratio by the favored formation of I.

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(12) See, for example, G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.* 1435 (1953).

In all dilute solutions represented in Figures 1 - 3, incl., there is also a slow reaction in which coordinated Cl^- is slowly replaced by pyridine, forming $[Fe(C_5H_5N)_6]^{3+}$. This is evidenced by the general increase in the absorption edge in Figures 2 and 3.

We can conclude from Figure 1, the composite spectra taken of the freshly prepared dilute solutions, that there is a multicomponent system set up by the addition of Cl^- to $[Fe(C_5H_5N)_5(ClO_4)]^{2+}$. It appears that the coordinated ClO_4^- is rapidly displaced by addition of the coordinating anion Cl^-, that species II, which must contain Cl^-/Fe^{III} in a ratio less than 4/1 as evidenced by the favored formation of $FeCl_4^-$ at Cl^-/Fe^{III} ratios of 4: 1 and higher, is favored in solutions 1/1 and 3/1, that formation of $FeCl_4^-$ is favored in 4/1 and 6.8/1 solutions and that species I is favored only in the 2/1 solution.

Figure 2 indicates that I is a metastable species in dilute solution. The 349 mμ band maximum present in the spectrum of the 2/1 solution upon initial preparation has disappeared and a general trend in the maxima exists after one week in solutions of $(C_2H_5)_4$-NCl and $[Fe(C_5H_5N)_5(ClO_4)](ClO_4)_2$ in pyridine. In the 1/1, 2/1, and 3/1 solutions, species II, and $FeCl_4^-$ both exist as the band maximum is a composite of 363 mμ and 380 maxima. Formation of of $FeCl_4^-$ predominates in the 4/1 and 6.8/1 solutions as evidenced by the presence of the 363 mμ $FeCl_4^-$ maximum. Also evidenced after one week is the gradual formation of $[Fe(C_5H_5N)_6]^{3+}$ as the absorption edge has increased significantly compared with Figure 1.

After five weeks (Figure 3), as pyridine slowly replaces the coordinated Cl^- of $FeCl_4^-$ and II, the spectra indicate that at least $[Fe(C_5H_5N)_6]^{3+}$ and some II exist in solution, as the absorption edge has increased significantly and a rather well defined shoulder exists at approximately 380 mμ. A small amount of $FeCl_4^-$ may also be present, but is lost under the absorption edge.

Species II can be assigned the formula $[FeCl_3 \cdot nC_5H_5N]_x$. As indicated above, the ratio of Cl^- to Fe^{III} in species II must be less than 4/1. The 1/1, 2/1, and 3/1 solutions exhibit a well defined maximum near 380 mμ in Figure 2. This maximum is best defined in the 3/1 solution, and although the 2/1 solution shows a higher absorption in this region than the 3/1 solution in Figure 3, the increase is due to the absorption edge, not to the species with an absorption maximum at 380 mμ. Conductance studies, *vide infra,* support this assignment.

In more concentrated solutions, the behavior of $[Fe(C_5H_5N)_5(ClO_4)]^{2+}$ plus added Cl^- is somewhat different. Spectra of a 3/1 solution taken immedediately upon preparation, aften one week, and after four weeks, where the initial concentration of $[Fe(C_5H_5N)_5(ClO_4)]^{2+}$ has been increased to 4.49×10^{-2} *M*, are shown in Figure 4. The spectrum labelled « O », taken on a freshly prepared solution, indicates the presence of $FeCl_4^-$ and II as evidenced by the 320 mμ and 380 mμ maxima, respectively. A larger fraction of the Fe^{III} in this solution exists as the molecular species than in the 3/1 dilute solution, as indicated by the large, well defined, maximum at 380 mμ in this spectrum. That only a negligible amount of the hexakis-pyridine species has formed in this solution at this time can be inferred from the small absorption at 305 mμ. In Figure 1, where the concentration of Fe^{III} in the corresponding 3/1 solution is only 2.69×10^{-4} *M,* the presence of $[Fe(C_5H_5N)_6]^{3+}$ contributes to a total absorption of 0.75 at this wavelength. In this solution, where the concentration of Fe^{III} is approximately 200 times as great, the total absorption at 305 mμ is only approximately 0.45. Evidently, the higher the concentration of Fe^{III}, the greater the tendency towards formation of uncharged species in this solvent of low dieletric strength (12.3 at 25°C).

Over a period of four weeks, as shown by the spectra labelled 1 and 4 in Figure 4, there is a gradual increase in absorption due to I as $[Fe(C_5H_5N)_6]^{3+}$. The concentration of $FeCl_4^-$ remains constant over this time, however, as the 360 mμ maximum is retained.

Using the information obtained from Figures 1 - 4. inclu., it can be concluded that the species formed in a freshly prepared 3.08×10^{-2} *M* solution of $FeCl_3$ in pyridine, as shown in Figure 5, are $[FeCl_3 \cdot nC_5H_5N]_x$, $FeCl_4^-$, and I. This solution is quite stable with respect to time.

If all reactions had proceeded to the same extent after four weeks, spectra labelled « 4 » in Figures 4 and 5 should be superimposable. It is evident from a comparison of these two spectra, however, that the reactions have not proceeded to the same extent in each solution. The major difference in the two spectra can be accounted for on the basis of the difference in concentration of Fe^{III} in the two solutions. The remaining difference appears to be a slightly larger formation of $[Fe(C_5H_5N)_6]^{3+}$ in the solution represented in Figure 4. This is expected in view of the slowness of the replacement of Cl^- by pyridine and in view of the fact that the solution prepared from $[Fe(C_5H_5N)_5(ClO_4)](ClO_4)_2$ and Et_4NCl, Figure 4, has a higher ionic strength, thus facilitating the formation of a highly charged $[Fe(C_5H_5N)_6]^{3+}$ species.

In a dilute solution, however, $FeCl_3$ exhibits a somewhat different behavior. A 2.0×10^{-4} *M* $FeCl_3$ solution in pyridine initially gives a spectrum virtually identical to that of the freshly prepared 2/1 solution shown in Figure 1. After one week, the spectrum of this solution is virtually identical to that of the 3/1 dilute solution of Figure 2. Apparently the reactions procede at a much faster rate in these dilute solutions than in the concentrated solutions.

As all these absorption bands overlap significantly, quantitative measurements of concentrations cannot be obtained from spectra alone. The extent of formation of II in freshly prepared $FeCl_3$-pyridine concentrated solutions can, however, be qualitatively inferred from conductance measurements. Since pyridine has a low dielectric constant, optimum values for molar conductances have been measured using solutions of concentration 2×10^{-3} *M*. The 1/1 electrolyte $(C_2H_5)_4NClO_4$ was utilized as a standard. A 2.15×10^{-3} *M* $FeCl_3$ solution exhibited a molar conductance which indicated only a very small amount of ionization when compared to this standard. It can therefore be concluded that in $FeCl_3$-pyridine solutions of this concentration (and above), $FeCl_3$ must be largely present initially as the molecular species. The concentrated solution spectral data of Figure 5 also indicate that the dissociation of this species is very slow.

Species other than $FeCl_3$ also exhibit a slow rate of dissociation in pyridine. A 2.6×10^{-4} *M* $(C_2H_5)_4NFeCl_4$ solution initially exhibits band maxima at 363 mμ and 320 mμ. These maxima also disappear with time, however, and a new maximum appears in the 375-380 mμ region, indicating the gradual decomposition of $FeCl_4^-$ and formation of $[FeCl_3 . nC_5H_5N]_x$. The band maximum at 320 mμ becomes masked by the generally increasing absorption edge of $[Fe(C_5H_5N)_6]^{3+}$. A week by week spectral comparison of a 4/1 vs. a dilute $FeCl_4^-$ solution shows that in both cases the band maxima are the same, and the intensities almost identical after one week. The slight difference between the spectra in these two systems is manifested in the shorter wavelength region where the perchlorate-containing solution shows a larger absorption than that not containing perchlorate ions. It appears that the perchlorate-containing solution contains more of the cationic $[Fe(C_5H_5N)_6]^{3+}$ species. Since the extinction coefficient of the hexakis-pyridine species is very large, only a very small difference in its concentration between the two solutions would produce the observed result. The additional ionic strength of the 4/1 solution may cause the state of the system to be shifted very slighthly in the direction of more highly charged species since charge separation is facilitated by higher ionic strength. It can be concluded, then, that $FeCl_4^-$ is not stable in dilute pyridine solution, but instead gradually forms $[Fe(C_5H_5N)_6]^{3+}$ and $[FeCl_3 \cdot nC_5H_5N]_x$.

It is interesting to note that Swanson and Laurie[13] in an e.p.r. study of $FeCl_3$ in several non aqueous solvents postulate that the following equilibrium is established in $FeCl_3$-pyridine solutions in the concentration range ca. 10^{-2} to 10^{-1} *M* Fe^{III}:

$$2FeCl_3 \rightleftharpoons FeCl_2^+ + FeCl_4^- \qquad (1)$$

The authors[13] report that $k_C = 0.028$ for this reaction at 25°C. Their conclusions are based on detection of $FeCl_4^-$ by e.p.r., however, and as such do not specifically support the formation of $FeCl_2^+$. It is tempting for us to conclude that species I in our study is also $FeCl_2^+$ (or $[Fe(C_5H_5N)_4Cl_2]^+$. The sudden appearance of the 349 mμ maximum in the 2/1 solution and its behavior with time leads one to expect that it is a metastable species, possibly containing a 2/1 ratio of chloride ion to Fe^{III}, but that the simple equilibrium represented above is not correct. Unfortunately, electronic spectra and molar conductance measurements do not support a more definite asignment of formula for this species or for its decomposition products.

In conclusion, $FeCl_3$, when dissolved in pyridine forms three species detectable by ultraviolet-visible spectra and molar conductance techniques. These species are $FeCl_4^-$, $FeCl_3 . nC_5H_5N$, and I. In this regard, pyridine is a very interesting solvent to add to those previously reported.[3,5,8] In spite of its strong donor properties, extensive chloride ion dissociation does not occur in concentrated solutions because of the poor solvating properties of this solvent. Instead, the uncharged addition compound is the predominant species and equilibrium is only slowly attained in this poorly solvating medium when anion displacement is involved. The slow perchlorate displacement that occurs when $[Fe(C_5H_5N)_5ClO_4]^{2+}$ is dissolved in pyridine is also consistent with this solvent property.

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