(**G**) **N.m.r. Spectra.**—The F^{19} n.m.r. spectra of $(FSO_2)_2NF$ and FSO_2NF_2 were obtained on a Varian Model V4310A spectrometer operating at 40 Mc. Samples were measured neat at 25° for $(FSO_2)_2NF$ and $-50°$ for FSO_2NF_2. Trichlorofluoromethane was used as an external reference.

Additional Characterization of $(FSO_2)_2NH$.—In addition to the physical constants of $(FSO_2)_2NH$ given by Appel and Eisenhauer,[14] a single sharp F^{19} resonance was found at $-56.9\ \phi$ and a proton resonance at -9.0 p.p.m. (neat *vs.* TMS). Infrared bands were observed at 3.3, 3.5, 3.7, 6.8, 7.3, 8.5, 8.9, 11.7, 12.6, and 13.2 μ.

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CONTRIBUTION FROM BELL TELEPHONE LABORATORIES,
INCORPORATED, MURRAY HILL, NEW JERSEY

The Structure of Ferric Chloride in Neutral and Acid Solutions

BY G. W. BRADY, M. B. ROBIN, AND J. VARIMBI

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X-Ray diffraction and spectral studies demonstrate that the structure of a concentrated solution of $FeCl_3$ in water is strongly influenced by the presence of H^+ ions. While the coordination about the Fe^{+3} is largely octahedral in concentrated, neutral solutions, the addition of acid results in the formation of a polymer consisting of alternating $FeCl_4$ (tetrahedral) and $FeCl_4(H_2O)_2$ (octahedral) units, with adjacent units sharing a chloride ion. It is also pointed out that the polymerization phenomenon is found only in the concentrated solutions (*ca.* 5 *M* in $FeCl_3$) and not in the dilute solutions normally investigated. About 75% of the Fe^{+3} in neutral solution appears to be $FeCl_4(H_2O)_2$ as deduced from its spectral similarity to the octahedral species in acid solution.

We wish to discuss some further observations on the structure of concentrated (*ca.* 5 *M*) $FeCl_3$ solutions. Earlier X-ray diffraction work[1] was taken to indicate that a significant part of the iron in concentrated aqueous $FeCl_3$ solutions exists as $FeCl_6^{-3}$ in octahedral coordination. On the other hand, Standley and Kruh[2] studied "neutral"[3] and concentrated HCl solutions of $FeCl_3$ using the same technique and claimed that the principal species in *both* solutions is tetrahedral $FeCl_4^-$. In agreement with our work, Standley and Kruh also found that there does not appear to be any iron–water peak in the radial distribution function (RDF) of these solutions. Long before the X-ray work was performed, it already had been determined that in dilute (0.68 *M*) solutions of $FeCl_3$ in concentrated HCl more than 90% of the iron is present as $FeCl_4^-$.[4] Unlike the results found in dilute solution and in contrast to the conclusion reached by Standley and Kruh, who based their analysis mainly on the first peak in the RDF, our recent study of the RDF and optical spectra of concentrated solutions of $FeCl_3$ in H_2O and concentrated HCl leads us to the conclusion that octahedral and tetrahedral forms exist in equilibrium in the solution with octahedral predominating in neutral solution and both octahedral and tetrahedral present in about equal amounts in strongly acidic solutions. In this publication we present the evidence for this and offer an interpretation of our experiments, which is preliminary, but nonetheless of sufficient interest to present at this time.

The RDF curves and the Cl : Fe ratios of the "neutral" and HCl solutions are shown in the upper portion of Fig. 1. The Fe^{+3} mole fractions in the three solutions are equal, the compositions being $Fe_{0.067}Cl_{0.201}(H_2O)_{0.731}$, $Fe_{0.067}Cl_{0.201}(H_2O)_{0.698}(HCl)_{0.034}$, and $Fe_{0.067}Cl_{0.201}(H_2O)_{0.656}(HCl)_{0.078}$ in solutions 1, 2, and 3, respectively. In the water solution (curve 1), the strong Cl–Cl peak at 3.2 Å., consistent with the 3.25 Å. separation expected for *cis* interaction in octahedral coordination, is evident. While the Cl–H_2O peak is also expected in the 3.2 Å. region, the observed intensity is much too high to be explained solely by this interaction.[1,5] The peak at 2.3 Å. is due to Fe–Cl bonding and a consideration of its area shows that there are,

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[1] G. W. Brady, *J. Chem. Phys.*, **26**, 1371 (1958).

[2] G. L. Standley and R. F. Kruh, *ibid.*, **34**, 1450 (1961).

[3] The "neutral" solutions are prepared by the addition of $FeCl_3 \cdot 6H_2O$ to pH 7 water and have a pH of 2 due to a slight hydrolysis.

[4] H. L. Friedman, *J. Am. Chem. Soc.*, **74**, 5 (1952).

[5] Standley and Kruh in their analysis of the "neutral" solution RDF dismissed any contribution of the octahedral Cl–Cl interaction to the peak area at 3.2 Å. Considering the position and the area (490 electrons^2 (el.^{2})) of this peak, we conclude that a strong Cl–Cl contribution is involved. The only other interactions of any possible importance at this distance are the H_2O–H_2O and H_2O–Cl contacts. Standley and Kruh's attempt to account for a large part of the 3.2 Å. area by postulating that 100% of the water participates in tetrahedral H_2O–H_2O interactions (2.9 Å.) is of questionable value because this necessitates an extended solvent structure wherein the presence of the ions is ignored. Since the ratio of ions (Fe^{+3} + $3Cl^-$) to H_2O at the concentration studied is 1 : 2.6, there is barely enough solvent for the necessary hydration of the ions, and the tetrahedral water structure cannot possibly exist. This is further evidenced by the lack of a definite peak at 2.9 Å. As pointed out in an earlier paper,[1] we could not detect any Fe–H_2O interaction (expected at 2.0 Å.) and conclude that the H_2O forms a hydration sheath around the Cl atoms, contributing 192 el.^{2} to the area at 3.2 Å. and leaving 298 el.^{2} to be accounted for. Assuming that there are 3.6 H_2O groups about each Cl results in each H_2O having about two H_2O neighbors with a resultant contribution of 72 el.^{2} to the scattering at 3.2 Å. The remaining 226 el.^{2} is then most logically assigned to the *cis* Cl–Cl interaction in an octahedral complex.

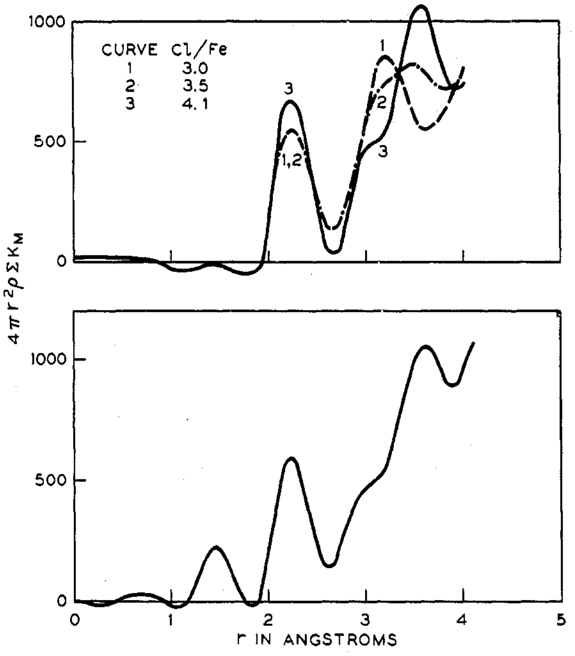

Fig. 1.—The radial distribution functions (upper) for (1) $FeCl_3 \cdot 6H_2O$ in H_2O, (2) $FeCl_3 \cdot 6H_2O$ in 50% H_2O–50% concentrated HCl, (3) $FeCl_3 \cdot 6H_2O$ in concentrated HCl and (lower) for $FeCl_3 \cdot 6H_2O$ in 70% $HClO_4$. The compositions by mole fraction are given in the text.

on the average, three Fe–Cl bonds per ferric ion.[6] The absence of a peak at 2.0–2.1 Å. or a shoulder on the 2.3 Å. peak at smaller r indicates that there are fewer than two Fe–H_2O bonds per ferric ion in the neutral solution.

On increasing the HCl concentration two effects are noticed. First, the Fe–Cl peak at 2.3 Å. increases in area, indicating that the average number of Fe–Cl bonds is increasing, while the peak shifts to about 2.2 Å., consistent with a change of coordination number from six to four. Second, simultaneously with the increase of intensity at 2.2 Å., there is a broadening of the peak at 3.2 Å., with an apparent shift toward larger r. In fact, the curve for the intermediate concentration (curve 2) gives the appearance in this region of being composed of two peaks, one centered at 3.2 Å. and the other at 3.6 Å. At the highest HCl concentration (12 *M* HCl as solvent), the 2.3 Å. peak intensity has increased by 25% over that in the neutral solution. The peak at 3.2 Å., consistent with the Cl–Cl distance in the tetrahedral $FeCl_4^-$ ion, is the predominant feature of the distribution curve in the 3–4 Å. region. Since the Cl^-–H_2O contribution to the peak at 3.2 Å. would be expected to increase on increasing the Cl^- concentration, we are led to the conclusion that the decrease of the intensity of this peak is due to the decrease of the octahedral Cl^-–Cl^- interaction as the ion transforms into the tetrahedral configuration. We also mention that the peak at 4.6 Å. found earlier[1] in the neutral solution is also prominent in the acid solution RDF. The 4.6 Å. spacing is in agreement with that expected for a *trans* Cl–Cl interaction in an octahedral complex.

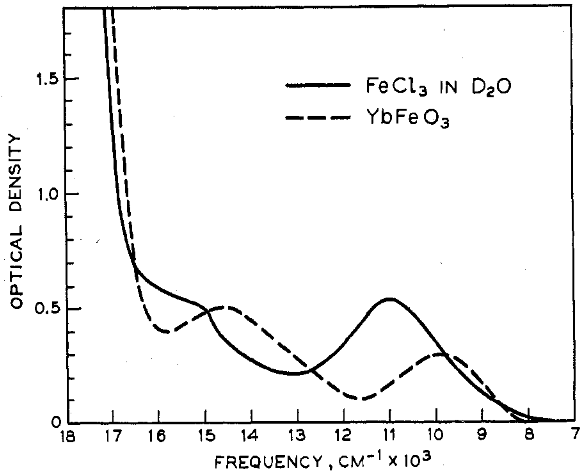

Fig. 2.—The optical absorption spectra of the Fe^{+3} ion in the octahedral sites of $YbFeO_3$[4] (– – – –) and of anhydrous $FeCl_3$ dissolved in D_2O (————).

The X-ray diffraction experiments demonstrate then that the configuration around the Fe^{+3} ion in a neutral H_2O solution is essentially different from that in a solution in which either the Cl^- anion is present in excess or the H^+ cation is present in high concentration, or both. It would seem surprising that an excess of Cl^- would reduce the coordination number from six to four, because of mass action considerations. It must be remembered, however, that in these concentrated solutions the $H_2O/FeCl_3$ ratio is very low and that, therefore, we are dealing with a system in which the solvent, H_2O, may play an important role in the coordination scheme, and the change in its environment also must be taken into account. To determine whether it is the Cl^- or the H^+ ion that is promoting the octahedral to tetrahedral change of coordination, we repeated the X-ray experiments using 70% $HClO_4$ instead of concentrated HCl as solvent, working on the assumption that it would be unlikely that the ClO_4^- ion would complex the Fe^{+3} ion. The composition of the $HClO_4$ solution was $Fe_{0.073}Cl_{0.218}(H_2O)_{0.595}(HClO_4)_{0.114}$. As can be seen from the lower curve in Fig. 1, the radial distribution curve is of the same form in concentrated $HClO_4$ as in concentrated HCl, with the tetrahedral peak at 3.6 Å. being clearly evident. Thus, it appears that it is the H^+ ion that is the agent promoting the transformation to the tetrahedral form of the complex ion, rather than the excess Cl^- ions. As an additional feature, we notice a clearly resolved peak at 1.55 Å., characteristic of the Cl–O bond of the ClO_4^- ion. The perchlorate

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(6) From the evaluation of the area of the 2.3 Å. peak, we arrive at a value of three for the average number of Cl atoms coordinated to Fe^{+3}. Standley and Kruh assign a value of four to this average coordination number. The results of the two experiments check very closely and the difference lies in the methods used to treat the data. Standley and Kruh included the two H atoms with too much weight in the form factor for H_2O, whereas we claim that the contribution of the H atoms is small and can be ignored. In a later publication, these authors acknowledge this point.[7] The second difference arises in the evaluation of the electron numbers to be assigned to the different species in the scattering system. Standley and Kruh use an extension of the Waser–Schomaker[8] treatment of amorphous scattering, while we have used the Warren method,[9] feeling that the Waser–Schomaker technique leads, too often, to electron numbers which are too low.

(7) R. F. Kruh and C. L. Standley, *Inorg. Chem.*, **1**, 941 (1962).

(8) J. Waser and V. Schomaker, *Rev. Mod. Phys.*, **25**, 671 (1953).

(9) B. E. Warren, H. Krutter, and O. Morningstar, *J. Am. Ceram. Soc.*, **19**, 202 (1936).

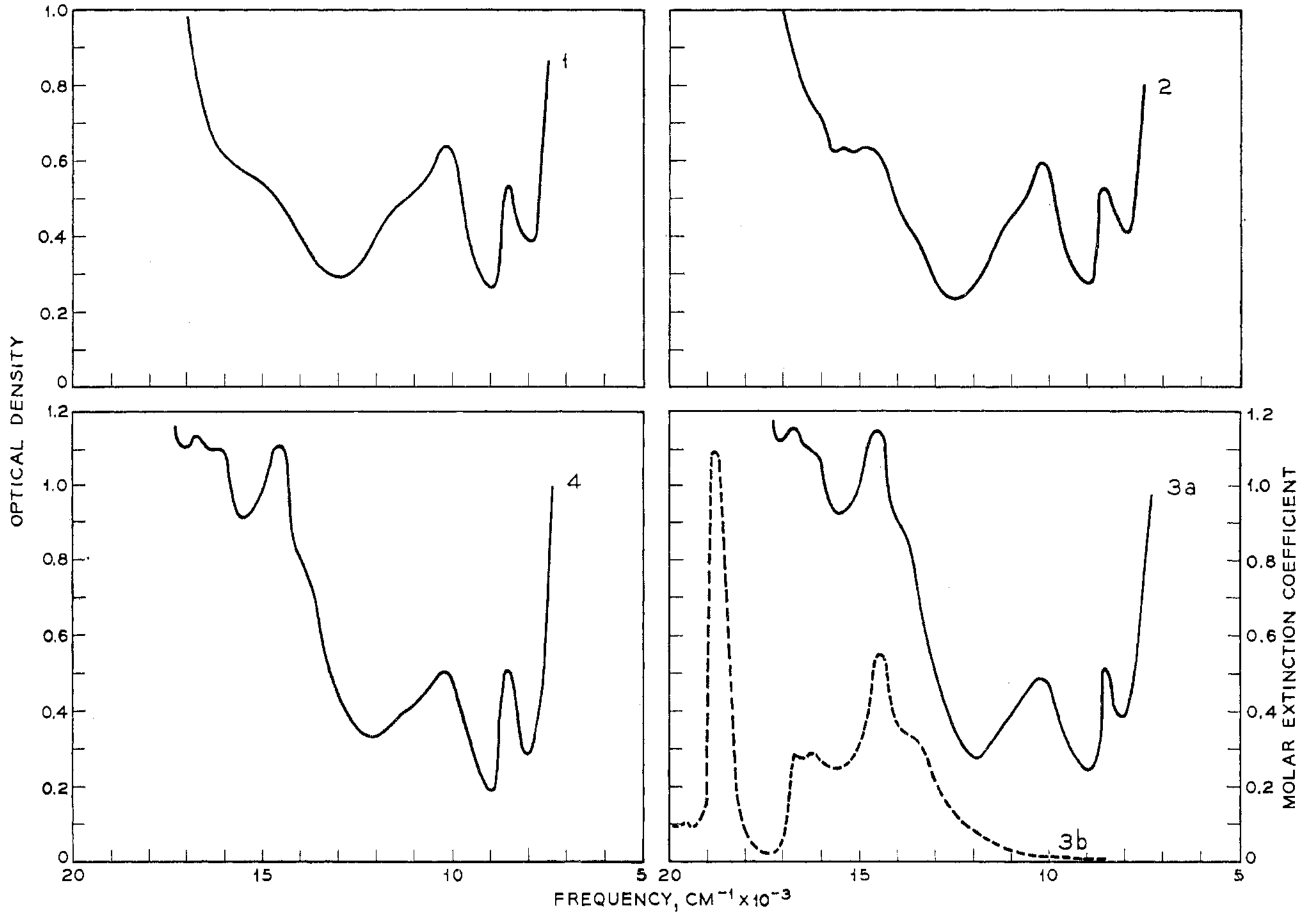

Fig. 3.—The optical absorption spectra of (1) $FeCl_3 \cdot 6H_2O$ in H_2O; (2) $FeCl_3 \cdot 6H_2O$ in 50% concentrated HCl–50% H_2O; (3a) $FeCl_3 \cdot 6H_2O$ in concentrated HCl; (3b) $(C_2H_5)_4NFeCl_4$ in acetone; and (4) $FeCl_3 \cdot 6H_2O$ in 70% $HClO_4$. The concentrations are given in the text and are the same as those used in the X-ray experiments.

O–O peak is expected to be centered at 2.5 Å. and is probably responsible for the asymmetry of the 2.2 Å. Fe–Cl peak.

In order to obtain confirmation of the above RDF interpretation, we measured the optical absorption spectra of the concentrated solutions in 1-cm. cells on a Cary Model 14 spectrophotometer. The solutions for this study were prepared by dissolving a weighed amount of reagent grade $FeCl_3 \cdot 6H_2O$ in the appropriate solvent and then filtering the solution even though there was no apparent residue. A D_2O solution was prepared by dissolving freshly sublimed $FeCl_3$ in D_2O and centrifuging the solution, the supernatant of which was used for the determination of the spectrum. All spectra were determined at 27° with an empty 1-cm. cell in the reference beam. In the neutral, aqueous solution (Fig. 2), the $FeCl_3$ spectrum is similar to that observed by Wickersheim and Lefever[10] for Fe^{+3} octahedrally coordinated in oxide crystals, the essential features of the solution spectrum being a band at 11,100 cm.$^{-1}$ and a shoulder at about 15,000 cm.$^{-1}$. Jørgensen's[11] compilation of the spectra of transition metal complexes shows that these two bands in the region 11,000–20,000 cm.$^{-1}$ are to be found in all octahedral weak-field Fe^{+3} species, regardless of the explicit identity of the ligands. Thus, it seems reasonable that the spectra of Fe^{+3} in an oxide lattice and in a chloride ion solution are comparable.

That the 11,100 cm.$^{-1}$ band is not due to solvent absorption was demonstrated by the unchanged frequency of this band in solutions of $FeCl_3$ in D_2O and H_2O. The similarity between the $FeCl_3$ solution and the $YbFeO_3$ crystal spectra was not as clear if the $FeCl_3$ was dissolved in H_2O instead of D_2O, for in the former case, there is an interference from the 8500 and 10,250 cm.$^{-1}$ H_2O vibrational transitions (Fig. 3, curve 2). Though no quantitative information can be gleaned from the spectrum of Fig. 2, the optical spectrum does support the RDF claim that there is a large amount of octahedrally coordinated Fe^{+3} present in neutral solutions of $FeCl_3$.

The spectrum of $FeCl_3 \cdot 6H_2O$ in 50% H_2O–50% concentrated HCl solution (Fig. 3, curve 2) shows essentially the same features as the spectrum in H_2O (curve 1); however, with a strong indication of a new group of bands appearing in the 13,000–17,000 cm.$^{-1}$ region. As expected from the form of RDF curve 2, the spectral curve 2 is also signaling an incipient transformation of coordination. Like their RDF curves, the spectra of solutions of $FeCl_3$ in concentrated HCl and in 70% $HClO_4$ (Fig. 3, curves 3a and 4) are identical, showing

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[10] K. A. Wickersheim and R. A. Lefever, *J. Chem. Phys.*, **36**, 844 (1962).

[11] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford. 1962.

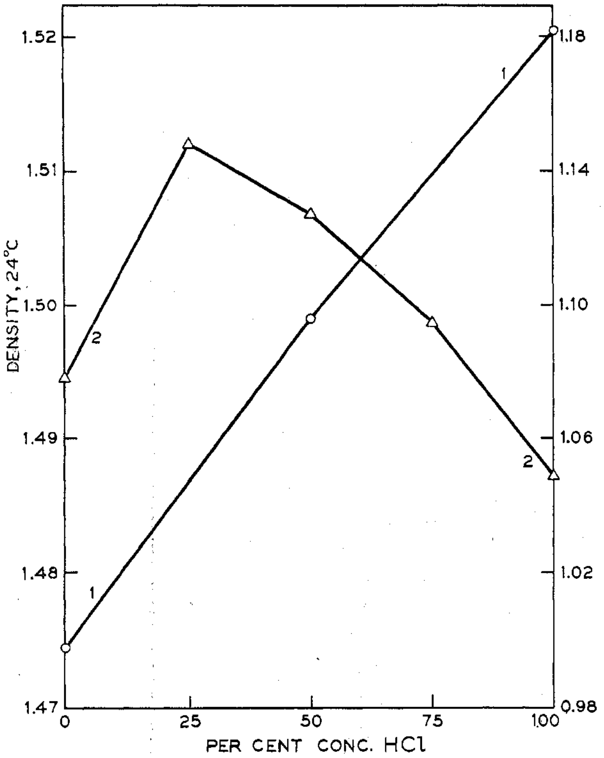

Fig. 4.—The mass density of HCl solutions as a function of the volume per cent of concentrated HCl in the solution, curve 1, right ordinate, and of the same solutions with 30.5 g. of $FeCl_3 \cdot 6H_2O$ added per 10 ml. of solvent, curve 2, left ordinate.

four well-defined peaks at 13,900, 14,500, 16,250, and 16,600 cm.$^{-1}$, which are just those frequencies observed at room temperature for the $FeCl_4^-$ ion in $(C_2H_5)_4NFeCl_4$ (Fig. 3, curve 3b).[12] The rapid rise of the optical densities of the acid solutions at the higher frequencies is thought to be due to the charge-transfer absorption edge of the octahedral species present in the acid solution. While it must be pointed out that a faint trace of the tetrahedral bands can be observed in the aqueous octahedral spectrum and the octahedral band at 11,100 cm.$^{-1}$ appears prominently in the acid spectra, there appears to be little doubt that the addition of H^+ to concentrated $FeCl_3$ solutions causes the amount of tetrahedrally bound Fe^{+3} to increase approximately 100-fold at the expense of the octahedral species.

In Fig. 4, we show how the densities of water and of aqueous $FeCl_3$ solutions vary as the HCl concentration is increased from 0 to 12 *M*. Whereas the densities of water solutions of HCl rise monotonically with increasing HCl concentration (curve 1), we find that in the presence of $FeCl_3$ (curve 2) the density reaches a maximum and then decreases to a value in concentrated HCl which is *lower* than that of $FeCl_3$ in pure water.

Discussion

In a previous paper[1] we speculated on the absence of a peak in the distribution function characteristic of the Fe^{+3}–H_2O bond in neutral aqueous $FeCl_3$ solutions. It was concluded that the H_2O groups were taking up a place around $FeCl_6^{-3}$ ions, with the remaining Fe^{+3} ions occupying the interstices in such a fashion that their average coordination with the H_2O groups was too small to give a well-defined peak in the distribution function. Though the absence of the Fe^{+3}–H_2O peak in both the neutral and acid solution RDF curves is still disturbing, with the added evidence now available we are able to present a more reasonable and detailed rationalization of the RDF results for the acid solution, which in turn sheds some light on the nature of the neutral solution.

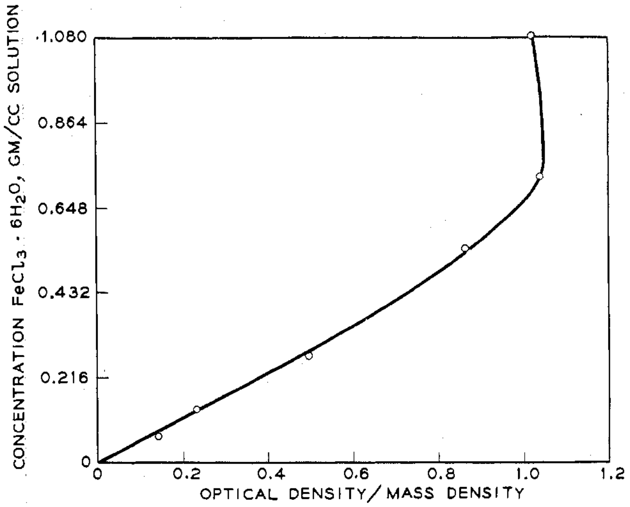

Fig. 5.—A Beer's law plot of the 14,500 cm.$^{-1}$ optical density: mass density ratio *vs.* concentration of $FeCl_3 \cdot 6H_2O$ in concentrated HCl.

A comparison of the absorption intensities of the 14,500 cm.$^{-1}$ tetrachloroferrate band in the concentrated HCl and $HClO_4$ solution spectra leads to the conclusion that the ratio of the fraction of Fe^{+3} present in concentrated HCl solution as $FeCl_4^-$ to the fraction of Fe^{+3} present in 70% $HClO_4$ solution as $FeCl_4^-$ is 1.022, *i.e.*, the amount of $FeCl_4^-$ in strongly acid solutions of $FeCl_3$ does not depend upon the Cl^- ion concentration. A check of the RDF's in Fig. 1 shows that indeed the Fe–Cl peak intensity, as well as the tetrahedral Cl–Cl peak intensity, is no higher in concentrated HCl than in $HClO_4$ solution in spite of the 40% higher Cl^- concentration in the HCl solution. Moreover, a comparison of the intensity of the 14,500 cm.$^{-1}$ band in the HCl and $HClO_4$ solution spectra with that of the same band of $(C_2H_5)_4NFeCl_4$ in acetone (Fig. 3) shows that 48% of the Fe^{+3} is present as $FeCl_4^-$ in the acid solutions. Thus we find only about half the iron in concentrated $FeCl_3$–concentrated acid solutions is present as $FeCl_4^-$, whereas in the more dilute solution, Friedman finds nearly 100% of the iron is present as $FeCl_4^-$.

In confirmation of the above stated difference, a Beer's law plot of the optical density/mass density ratio of the 14,500 cm.$^{-1}$ band of the $FeCl_4^-$ species in concentrated HCl solutions of $FeCl_3 \cdot 6H_2O$ *vs.* g. of $FeCl_3 \cdot 6H_2O$/ml. of solution is presented in Fig. 5. There appears to be normal Beer's law behavior at low concentrations up to about 0.4 g. of $FeCl_3 \cdot 6H_2O$/ml. of solution, as would be expected from Friedman's[4] earlier work, but at the high concentrations used in the X-ray

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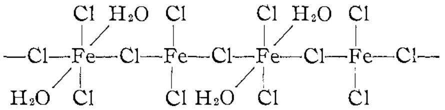
(12) A. P. Ginsberg and M. B. Robin, *Inorg. Chem.*, **2**, 817 (1963).

experiments there is seen to be a strong deviation from linearity, indicative of association. Extrapolation of the low concentration, linear portion of the curve to the highest concentration used predicts an optical density/mass density ratio of 1.9 ± 0.1 while we observe only 1.023. Thus, while all of the Fe^{+3} in concentrated HCl is in the form of $FeCl_4^-$ in solutions dilute in $FeCl_3$, increasing the concentration of $FeCl_3$ is again seen to result in solutions in which only half of the iron appears to assume the tetrahedral configuration. Contrary to its behavior in HCl solutions, the $FeCl_4^-$ species obeys Beer's law in $HClO_4$ solutions in that concentration range reported for the HCl solutions (Fig. 5).

Since the 11,100 and 15,000 $cm.^{-1}$ octahedral absorptions are also present in the acidic concentrated solutions, we will assume that an octahedral species accounts for the 50% of the Fe^{+3} that is not tetrahedral. From the large number of possibilities imaginable for the coordination of the two types of iron, only one seems to be in agreement with both the X-ray and spectrophotometric results. By elimination, we are led to suggest that a polymeric species in acid solution having alternately octahedral and tetrahedral coordination with a sharing of corners



is the iron species present in concentrated solutions of $FeCl_3$ in concentrated acids. We now present our reasons for having decided that the polymeric structure is the one most compatible with our evidence.

First, since $FeCl_3$ furnishes all of the Cl^- required for the stoichiometry of the above polymer, addition of further Cl^- would not be expected to raise above 50% the amount of tetrahedral $FeCl_4$ formed. Thus $HClO_4$ and HCl might well be expected to lead to the formation of the polymeric species in identical amounts, as observed. Again, the polymer has an average of four Fe–Cl bonds per Fe^{+3} as observed in the RDF, but only one Fe–H_2O bond per Fe^{+3}. It is clear now why there is no Fe–H_2O peak in the acid solution RDF (expected at 2.0 Å.) for we estimate that a configuration with only one Fe–H_2O bond per Fe^{+3} would not be a sufficiently strong scatterer to give a peak in the RDF with an observable intensity. The presence of the two H_2O groups in the octahedral coordination sphere is necessitated by the low average number of Fe–Cl bonds observed in the RDF and by the fact that the observed octahedral absorption frequencies do not agree with those reported for either $FeCl_6^{-3}$ or $FeCl_5H_2O^{-2}$.[13]

Again, all dimer or polymer species sharing more than one ligand between adjacent irons are ruled out because this would demand that the tetrahedral ligand–ligand distance equal the octahedral *cis* ligand–ligand distance, and neither the X-ray nor the spectrophotometric experiments show these normally unequal distances to be changed.

The effect of diluting concentrated HCl solutions of $FeCl_3$ with concentrated HCl can be represented chemically by the equation

$$[FeCl_4FeCl_2(H_2O)_2]_x + 2xCl^- \rightarrow 2xFeCl_4^- + 2xH_2O$$

from which it is clear how the degradation of the polymer upsets the Beer's law behavior of the $FeCl_4^-$ species. However, since there is no excess Cl^- in $HClO_4$ solutions with which to form monomeric $FeCl_4^-$, it may be understood then that the $HClO_4$ solutions do not degrade and that Beer's law is therefore obeyed.

As a test of the polymer model of the structure of $FeCl_3$ in concentrated solutions of concentrated acids, we determined the magnetic moment of the iron in such an HCl solution hoping to find a depression from the free-spin value characteristic of exchange coupling. Though the observed moment of 5.63 B.M. per Fe (27°, corrected for diamagnetism) is quite close to the spin-free value, earlier work on chloride-bridged dimers[12] shows that the exchange coupling energy due to association can be quite small in such systems and that depressed moments may appear only at much lower temperatures in spite of extensive association. Nevertheless, we feel that both the RDF and the spectral data strongly support the polymeric species of alternating coordination postulated above for concentrated solutions of $FeCl_3$ in concentrated acids.

Unfortunately, it is not nearly as clear as to what the species is in neutral solution; the facts are at odds with one another for any conventional coordination scheme and we must turn to an explanation which is admittedly unusual but consistent with the data. First, a pH measurement of the "neutral," 5 *M* $FeCl_3$ in water solution shows that the hydrogen ion concentration is only 10^{-2} *M* and that hydrolysis therefore is not of any importance at this high $FeCl_3$ concentration. Since the first absorption band of the neutral $FeCl_3$ solution falls at just the wave length found for the species assigned as octahedral in the acid solution, we assume that the neutral solution contains the octahedral species $FeCl_4(H_2O)_2^-$. As pointed out above, the neutral solution RDF can also be interpreted assuming the presence of an octahedral species. Consideration of the area of the 3.2 Å. *cis* Cl–Cl peak with due allowance for overlapping Cl–H_2O interactions shows that the amount of Fe^{+3} present in the neutral solution as $FeCl_4(H_2O)_2^-$ must be maximal, *i.e.*, 75%. Now the RDF (Fig. 1), curve 1, demands that there be on the average only three Fe–Cl bonds and at the most two Fe–H_2O bonds per Fe^{+3}, a condition fulfilled only if the 25% of the Fe^{+3} as yet unaccounted for is not coordinated with any Cl^- ions. If the above were true, then the optical density of the 11,100 $cm.^{-1}$ octahedral peak of $FeCl_3$ in neutral solution would be 1.5 times that of an equivalent amount of $FeCl_3$ in HCl solution. Experiments do suggest that this ratio is about 1.5, although overlapping H_2O bands render an exact quantitative evaluation difficult. Thus, the RDF and spec-

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[13] W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 265 (1963).

tral data lead to the tentative picture of the concentrated, neutral $FeCl_3$ solution as being an array of $FeCl_4(H_2O)_2^-$ ions surrounded by a hydration sheath about a molecule thick and interstitial Fe^{+3} ions with very low coordination numbers. As for the exact coordination of the interstitial iron, 25% of the total, we do not feel that the data are sufficiently compelling to warrant saying anything more quantitative than that the coordination number is less than four. Again we have disregarded small amounts of other species such as $FeCl_4^-$ which while undoubtedly present would not contribute enough to the X-ray or spectral data to affect the results.[14]

Reasoning from the above we may suppose that one factor essential to the stability of the neutral solution structure is the hydration sheath which surrounds the $FeCl_4(H_2O)_2^-$ ions. We can regard the role of the H^+ ion as being a competitor for these H_2O molecules, in effect stripping them away from the octahedral ion to complete its own hydration sphere. The small size of H^+ makes it an extremely effective competitor in this process. We found also that in neutral concentrated $LiClO_4$ solutions of $FeCl_3$ the tetrahedral spectrum was again prominent, as would be expected in the presence of such a small ion. The formation of the tightly bound hydration layers around the small ions would lower the H_2O activity considerably and we could in fact look on this process as increasing the concentration of $FeCl_3$ and thus favoring the formation of polymer which, naturally, only would form in highly concentrated solution.

The octahedral to tetrahedral transformation is no doubt responsible for the maximum observed in the mass density of solutions of increasing HCl concentration (Fig. 4). It is, of course, extremely difficult to correlate mass densities with liquid structures because of their complexity, and we only cite the density data as giving qualitative support to the transformation.

It must be admitted that these models are speculative, and while a reasonably detailed structure of the acid solution can be postulated, that for the neutral solution is not as satisfactory. However, the important thing is that both the spectrophotometric and X-ray diffraction methods indicate unquestionably that the octahedral–tetrahedral transformation is caused by H^+ and Li^+ ions and that there is a fundamental structural difference between concentrated neutral and acid solutions of $FeCl_3$ and even between dilute and concentrated solutions of $FeCl_3$ in acid.

Acknowledgments.—We wish to acknowledge the technical assistance of N. A. Kuebler in the spectral work, and G. Wertheim for his measurements of the Mössbauer spectra. We also thank A. Ginsberg for some stimulating discussions.

(14) The presence of two different ion species in significant quantity in the neutral solution might be expected to yield two separate lines in the Mössbauer spectrum, if the solutions can be frozen. We found that all of the solutions, neutral and acid, freeze to clear, green glasses having the octahedral coordination spectrum. The Mössbauer spectra of the rigid glasses show a broad line which could be consistent either with two peaks indicating different isomer shifts for two different iron entities, or a very large quadrupole splitting. Unfortunately, little is known about the Mössbauer spectra of glasses and the results, while not inconsistent with our picture of the solutions, are not unambiguous.

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Chloro–Aquo Complexes of Vanadium(III)

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Preparations hitherto thought to be substances of stoichiometry $K_2VCl_5 \cdot nH_2O$ are shown by X-ray powder patterns to be fortuitous, equimolar mixtures of $KVCl_4 \cdot nH_2O$ and KCl. Two distinct substances are characterized, a green 6-hydrate and a red 1.5-hydrate, either capable of synthesis from the other by simple hydration or dehydration procedures. It appears to be impossible to dehydrate either completely to a simple chlorovanadate(III) complex. The green 6-hydrate has absorption bands at 16,050 and 22,990 cm.$^{-1}$, and the red 1.5-hydrate has bands at 19,300 and 12,580 cm.$^{-1}$. The compound $VCl_3 \cdot 4H_2O$ has been prepared by the dehydration of $VCl_3 \cdot 6H_2O$, both compounds exhibiting absorption spectra identical with that of $KVCl_4 \cdot 6H_2O$.

Introduction

Several red salts of $VCl_5 \cdot H_2O^{2-}$ were reported by Stahler,[1] and recently a green compound, $K_2VCl_5 \cdot 4H_2O$, was reported by Crayton and Thompson.[2] The latter workers also reported that the green compound dehydrates at 100–125° to pink anhydrous K_2VCl_5. When attempts to duplicate this dehydration failed, we undertook a study of these hydrates.

Experimental

Preparation of Compounds. (A) General Procedure for Preparing the Starting Solutions.—Anhydrous VCl_3 and KCl were dissolved in 150 ml. of 12 *M* HCl, such that the resulting solution was 0.5 *M* in VCl_3 and 1.0 *M* in KCl. Such solutions, being of the correct composition to produce $K_2VCl_5 \cdot nH_2O$, invariably produced $KVCl_4 \cdot nH_2O$ contaminated with KCl.

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(1) A. Stahler, *Ber.*, **37**, 4411 (1904).

(2) P. H. Crayton and W. A. Thompson, *J. Inorg. Nucl. Chem.*, **25**, 742 (1963).