atoms are reduced to 88.3° (X = H) and to 85.1° (X = F). Again reflecting the coordination, the Be–X_1 bonds are lengthened compared to the Be–X_2 bonds. In addition to Snelson's structure IV (X = F), VII is also a possible candidate for the C_{2v} Li_2BeF_4 isomer.

On the basis of the structural details found for IV, V, and VII, it is easy to understand why isomers VI and VIII are higher in energy. The C_{3v} structures (VI, X = H or F) (E_{rel} = 27 kcal/mol for Li_2BeH_4 and 34 kcal/mol for Li_2BeF_4) are unfavorable because one of the lithium atoms is only attached to only a single X atom. The $LiBeX_3$ forms, I, similar in this respect, are also high in energy. VI was examined by imposing C_{3v} symmetry, but this structure is more likely to be a saddle point than a mimimum on the potential energy surface. The structural alternative VIII (X = H or F), obtained by imposing D_{2h} symmetry, was highest in energy (E_{rel} = 46 kcal/mol for Li_2BeH_4 and 43 kcal/mol for Li_2BeF_4). Compared to the corresponding D_{2d} isomers V, the BeX bonds in VIII are lengthened considerably: Be–H, 1.60; Be–F, 1.64 Å. In addition to the unfavorable four-membered ring (also present in V), structure VIII suffers from the planar BeX_4^{2-} arrangement. However, lithium coordination *reduces* the tetrahedral/planar energy difference from about 60 kcal/mol for both BeH_4^{2-} and BeF_4^{2-} to about 40 kcal/mol (V vs. VIII).

The pπ–pπ STO-3G overlap populations for planar Li_2BeF_4 structures IV and VI are 0.16 (terminal F–Be) and 0.06–0.08 (bridging F to Be or Li).

D. Dissociation and Ionization Reactions. Mass spectroscopic studies[3b] of $LiBeF_3$ and Li_2BeF_4 suggest the possibility of thermal dissociation of these species in the gas phase. The calculated heats of dissociation for Li_2BeH_4, $LiBeH_3$, Li_2BeF_4, and $LiBeF_3$ (based on the lowest energy structures for each species) are summarized in Table VI, along with comparison data for $(LiH)_2$ and $(LiF)_2$.

Similarly large energies (40–47 kcal/mol at 6-31G*//4-31G) are needed to dissociate the lithium hydride dimer (D_{2h}) or to remove a LiH molecule from either $LiBeH_3$ or Li_2BeH_4. The fluoride complexes are even more stable toward dissociation; about 70 kcal/mol (4-31G//4-31G) is needed to split off LiF from D_{2h} Li_2F_2,[22] $LiBeF_3$, or Li_2BeF_4.[9a,10c] These data suggest that equilibria involving BeX_2 and LiX should lie entirely on the side of the complexes. Except at extremely high temperatures, the vapor pressure of BeX_2 in the presence of LiX should not be measurable.

The complexes might dissociate into ions under mass spectroscopic conditions. We calculated the heats of ionization only for the $LiBeX_3$ species (Table VI); the energies for ionization of Li_2BeX_4 into Li^+ and $LiBeX_4^-$ are expected to be of similar magnitude. Such ionic dissociations are highly endothermic; the 4-31+G//4-31+G values are 147 kcal/mol for $LiBeH_3$ and 148 kcal/mol for $LiBeF_3$. Nevertheless, some stabilization by charge delocalization in the complex anions is shown by the comparison of the data for the dissociation of LiH and LiF into ions, indicated experimentally to require 163 and 183 kcal/mol, respectively. (The calculated values at the 4-31+G level are in very good agreement.) The electronegative fluorine atoms in BeF_3^- accept and distribute the extra charge somewhat better than the hydrogen atoms in BeH_3^-. Thus, the difference in ionization energies between LiF and $LiBeF_3$, 31 kcal/mol, is larger than the 15 kcal/mol difference calculated for LiH vs. $LiBeH_3$ (4-31+G).

Conclusions

Several factors compete in determining the most stable structures. Higher coordination is favorable, but this is often achieved at the expense of smaller angles and longer distances. For tetracoordination, tetrahedral, rather than planar, arrangements around beryllium are preferred; for tricoordination, trigonal planar is better than pyramidal. Metal–metal interaction is indicated in many of the structures, despite expectations based on simple electrostatic considerations.

Structure II for $LiBeX_3$ is most favorable both for X = H and X = F. Insertion of an additional LiX unit into a LiX bond to give planar IV combines the favorable features of I with better angular arrangements. Despite the lower coordination of all the metal atoms in IV, this structure competes well against the best alternatives based on tetrahedral tetracoordinate beryllium, V and VII. Li_2BeH_4 is indicated to prefer structure IV at the MP2/6-31G*//4-31G level; the Li_2BeF_4 ordering is IV (best) > V > VII (4-31G//4-31G), but higher levels of theory are needed to verify this conclusion. Although we have emphasized the energies of various forms, these molecules are likely to have fluxional character.

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Registry No. $LiBeH_3$, 25282-11-5; $LiBeF_3$, 15552-34-8; Li_2BeH_4, 19321-21-2; Li_2BeF_4, 13874-36-7.

Supplementary Material Available: Listings of Mulliken analysis data (dipole moments, charges, overlap populations (STO-3G)) and calculated total energies needed to determine the values in Table VI (2 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98195

Vaporization Characteristics of Ammonium Tetrachloroferrate(III). The Monoammine of Iron(III) Chloride in the Vapor Phase

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The behavior of NH_4FeCl_4 on heating is found to be complex. The iron(III) tends to be reduced by ammonia; however as HCl, a product of the reduction reaction, accumulates, the system stabilizes sufficiently to permit the study of vaporization equilibria. Absorption spectroscopy, mass spectrometery, and diaphragm gauge measurement of total pressures have been used to determine the composition of the vapor phase, and thermodynamic data for the reactions $NH_4FeCl_4(C) = NH_3FeCl_3(g) + HCl(g)$ and $NH_4FeCl_3(C) = FeCl_2(s) + NH_3(g) + HCl(g)$ are reported. The UV–visible absorption spectrum of NH_3FeCl_3 between 240 and 500 nm is given.

Ammonium tetrachloroferrate(III) is easily prepared by reaction of ammonium chloride and ferric chloride and has been studied by a number of investigators.[1-7] In the present work, the molecular composition of the vapor phase formed

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when NH_4FeCl_4 is heated and the stability of the complex at elevated temperatures have been examined. Fireman reported that $NH_4Cl–FeCl_3$ mixtures decompose slowly around 400–420 °C, releasing gas assumed to be nitrogen and hydrogen chloride.[5] Thermodynamic properties indicate such a mixture to be unstable relative to these gases and $FeCl_2(s)$, even at room temperature.[8] However, the rate of decomposition is sufficiently slow that Hachmeister[6] was able to study the phase diagram; he reported a congruent melting point for NH_4FeCl_4 (the only intermediate compound detected) at 297 °C, miscibility (from 30 to 100 mol % $FeCl_3$) in the liquid range, and a sharp maximum in the boiling point curve around 380 °C at a composition close to that of the 1:1 compound. Friedman and Taube[9] have shown that the similar compound NH_4GaCl_4 vaporizes to NH_3GaCl_3 and HCl; and Laughlin and Gregory[10] found NH_4AlCl_4 to vaporize to NH_3AlCl_3 and HCl. No report of experimental evidence for molecules containing ammonium ion in the vapor phase has been found for any system. Thermodynamic constants are well-known for the vaporization of NH_4Cl.[8]

$$NH_4Cl(s) = NH_3(g) + HCl(g) \qquad (1)$$

In the UV–visible region of the spectrum, iron(III) halide vapor molecules have strong charge-transfer absorbance bands, which can be used to follow changes in concentration.[11-15] Vapor-phase absorption spectroscopy, together with mass spectrometry and diaphragm gauge measurement of total pressures, has been used in the present work to examine the $FeCl_3–NH_3–HCl$ system. An initial summary of conclusions drawn from the combined results will facilitate discussion of each of these independent studies.

Between 200 and 475 °C, the principal molecules detected in the vapor phase generated by NH_4FeCl_4 are HCl, NH_3, N_2, and NH_3FeCl_3. In appreciable partial pressures of HCl, the overall reaction producing nitrogen is believed to be

$$^1/_3NH_3(g) + FeCl_3 = FeCl_2(s) + {}^1/_6N_2(g) + HCl(g)$$

or equivalently

$$NH_4FeCl_4(C) = FeCl_2(s) + {}^2/_3NH_3(g) + 2HCl(g) + {}^1/_6N_2(g) \qquad (2)$$

((C) represents either solid or liquid; the melting point lies in the range of interest.) $FeCl_2(s)$ may be converted to or equilibrate with a condensed iron(II) complex, NH_4FeCl_3,[16] (the present study would not distinguish NH_4FeCl_3 from $(NH_4)_2FeCl_4$ etc.) and equilibrium 3 must also be considered.

$$NH_4FeCl_3(C) = FeCl_2(s) + NH_3(g) + HCl(g) \qquad (3)$$

The change indicated by (2) appears irreversible, as may be expected on thermodynamic grounds; however, as the partial pressure of HCl increases, the rate of reduction is greatly reduced and the vaporization equilibrium (4) can be studied.

Table I. Sample Characteristics

	mol × 10^7			cell path, cm	cell vol, cm³
sample	n°_{HCl}	$n^\circ_{NH_3}$	n°_{Fe}		
	Initial Reactants: NH_4Cl, $FeCl_3$				
1	(183)	(183)	20.0	2	7.97
2	(88)	(88)	7.84	5	15.6
3	(69)	(69)	24.9	5	15.1
4	(59)	(59)	15.0	10	30.1
7	(94)	(94)	61.4	5	15.8
	Initial Reactants: NH_3, HCl, $FeCl_3$				
9	487	15.8	1.70	5	15.2
10	486	4.58	9.49	1	4.28
11	447	10.0	15.9	2.5	9.11
12	2971	159.2	15.4	10	30.2
13	18 (22)	467.2	12.8	10	29.8
14	465	465	33.7	5	15.7
15	70.6 (65)	70.6	45.1	5	15.2
D-1	1824	1824	1791		26.3
D-2	1000	1000	1791		31.0
D-3	(482)	(482)	1791		29.8
	Initial Reactants: NH_3, $FeCl_3$				
5	0	93	19.6	1	4.32
16	0	1400	?	2.5	9.1
17	0	3500	?	10	30
18	0	305	?	2.5	9.1
19	0	2080	?	10	30
D-5	0	1791	1791		26.2
	Initial Reactants: NH_3, NH_4Cl, $FeCl_3$				
6	(139)	?	23.1	5	15.4
	Initial Reactants: HCl, NH_4Cl, $FeCl_3$				
8	(353)	?	9.81	5	15.4
	Initial Reactants: NH_3, HCl, $FeCl_2$				
D-4	1660	1660	2000		26.0
	Initial Reactants: NH_3, $FeCl_2$				
D-6	0	2160	2210		26.0

$$NH_4FeCl_4(C) = NH_3FeCl_3(g) + HCl(g) \qquad (4)$$

The stabilized system can be held for several hours between 200 and 475 °C, as repeated on successive days, with reproducible total pressures. Further reduction will occur if samples are heated after removal of excess HCl. The ammine in the stabilized system is not appreciably dissociated into ammonia and ferric chloride. To correlate equilibrium preessures observed for various mixtures with reactions 3 and 4, it is necesssary to assume that NH_4FeCl_3 and NH_3FeCl_3 form a condensed solution in which NH_4FeCl_4 is not appreciably soluble. Evidence leading to these conclusions and other aspects of the behavior of the system will now be discussed.

Vapor Phase Absorbance Spectra

Absorbances of vapors in equilibrium with a condensed NH_4FeCl_4 phase were studied first and were found, at a given temperature, to vary inversely with the partial pressure of HCl. This was established by comparison of absorbances of samples prepared with widely different partial pressures of HCl and of samples prepared from different starting materials (see groupings in Table I) and corresponds to a mode of vaporization like reaction 4, as opposed, for example, to the behavior expected if NH_4FeCl_4, or NH_2FeCl_2, etc. were the dominant absorbing species. However, additional features were observed that could not be explained until the effects of the reduction process (2) and formation of the iron(II) complex NH_4FeCl_3, and solutions of the latter with NH_3FeCl_3, were recognized from results of the diaphragm gauge experiments.

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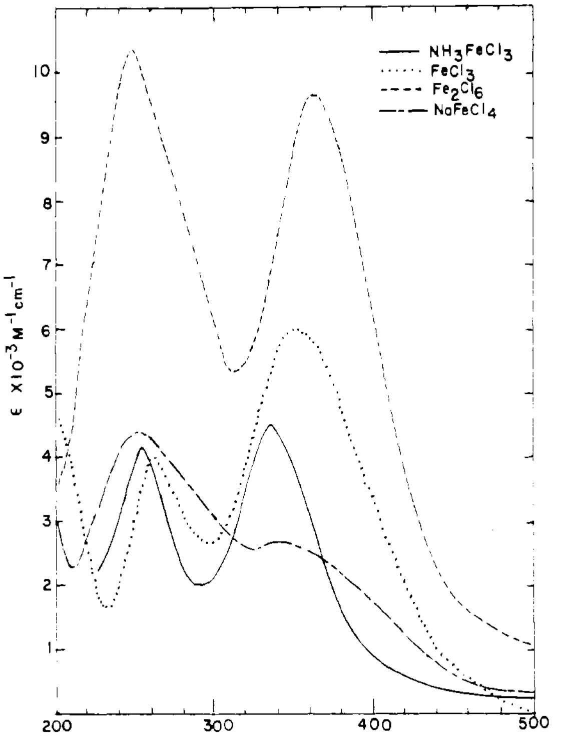

Figure 1. Tracing of the absorption spectrum of the vapor generated by NH_4FeCl_4 (attributed to NH_3FeCl_3) in comparison with $FeCl_3(g)$, $Fe_2Cl_6(g)$, and $NaFeCl_4(g)$.

Experimental Section

The Cary 14H spectrophotometer quartz absorption cells were cylindrical (ca. 20-mm o.d., path lengths 1–10 cm). Temperatures at the tips of side arms (T_3), 5–10 cm long and attached at the cell center, were kept a few degrees lower than at the cell windows (T_2) and cell centers (T_1) to reduce the tendency of volatile condensable matter to collect on the windows. This problem was exacerbated when substantial partial pressures of HCl (and/or N_2 or NH_3) were present and was particularly troublesome when measurements were made in a sequence of decreasing temperatures.

Sample characteristics are listed in Table I. For the preparation of samples 1–4 and 7, small quantites of NH_4Cl were first added to the cell side arms, attached to the Pyrex vacuum system. In these initial studies, the amount of NH_4Cl introduced was not measured. The equivalent quantites of NH_3 and HCl, shown in parentheses in Table I, were fixed by comparison with later experiments according to the method described in the Results and Discussion. (This also applies to the other quantities placed in parentheses in the table. Otherwise, the quantities are based on direct experimental measurement.) The NH_4Cl crystals were flamed and partially sublimed under vacuum to help remove traces of moisture. $FeCl_3$, prepared in an attached assembly by reaction of chlorine (released by heating $CuCl_2$) with iron wire, was sublimed into the cell and the mixture isolated by flame vacuum seal-off. A thin red film of $FeCl_3$ condensed on ammonium chloride became yellow (the color of NH_4FeCl_4) in a few hours at room temperature.

For samples 5 and 16–19 only NH_3 was added to $FeCl_3$. In sample 6, NH_3 was condensed into a mixture of NH_4Cl and $FeCl_3$, and similarly, for sample 8, HCl was added. Samples 9–15 were prepared by first subliming $FeCl_3$ into the cell and then freezing in (with liquid nitrogen) measured aliquots of HCl(g) and, separately, NH_3(g). Amounts of $FeCl_3$ could be estimated by visual observation of the condensed film and were finally determined by atomic absorption analysis. In six instances the amount was appropriate to permit complete vaporization of the volatile iron(III) compound while the absorbances were measured; in three additional cases complete vaporization was achieved after removing some of the sample by seal-off of part of the side arm.

Results and Discussion

A trace of a representative absorption spectrum is shown in Figure 1, together with spectra reported for Fe_2Cl_6, $FeCl_3$, and $NaFeCl_4$ vapors.[13] The general shape resembles that of the ferric chloride molecules. The peak maximum at the longer wavelength (ca. 335 nm) is shifted toward shorter wavelengths from the peak observed for Fe_2Cl_6 (360 nm) and is somewhat higher than the peak at 255 nm, contrary to the comparative heights of peaks for Fe_2Cl_6. The maximum at 255 nm is intermediate between corresponding peaks for Fe_2Cl_6 (245 nm) and $FeCl_3$ (260 nm). No unusul change in shape with temperature was observed, and no differences were detected on comparison of the various samples. Below 230 nm, absorbance of NH_3[17] and/or HCl[18] could be observed when either gas was present at sufficient concentrations; neither absorbs appreciably in the 230–600-nm range. The minimum temperature at which absorbance could be seen varied: around 210 °C for sample 5; near 300 °C for samples with a substantial partial pressure of HCl. The vapor concentration of $FeCl_2$ below 475 °C is too low to contribute measurably to the absorbance.[19]

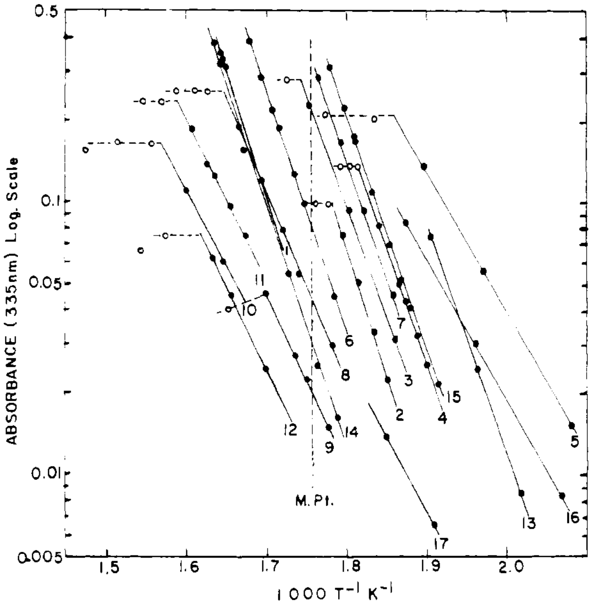

Figure 2. Temperature dependence of vapor-phase absorbances (as A_{obsd}/path length) for various mixtures identified in Table I.

Absorbances at the peak maximum near 335 nm from 17 different samples are shown at various temperatures in Figure 2. When the concentration of the absorbing species is fixed by equilibration with a condensed phase, absorbances increase exponentially with temperature (solid circles). The open circles indicate the absorbing species has completely vaporized. The solid circles for a given sample show a linear relationship (straight line drawn) on the ln A vs. $1/T_3$ plot; however, lines for the various samples are displaced, and differences in slope are noted. The displacements correlate with HCl pressures, which differ in the various samples by as much as a factor of 10^3, when it is assumed that equilibrium 4 controls the concentration of the absorbing species. This, with supporting mass spectral and diaphragm gauge evidence, leads to the proposal that the absorption of light is associated with charge-transfer transitions in NH_3FeCl_3 molecules.

After some of the samples were fully vaporized, the absorbance fell slowly with time, indicating a slow continuation of the reduction (of NH_3FeCl_3) process. The falloff rate varied: e.g., for sample 8 no perceptible change in 1 h, whereas for sample 5, at a lower temperature but with lower HCl

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Table II. Thermodynamic Constants Derived for Reaction 4[a]

		$\Delta H°$ (SD, %)	$\Delta S°$ (SD, %)			$\Delta H°$ (SD, %)	$\Delta S°$ (SD, %)
equil with liq phase	a	38 614 (5.1)	47.7 (7.0)	equil with solid phase	e	46 450	61.4
	b	39 185 (4.6)	48.6 (6.1)		f	46 767 (0.76)	62.3 (1.0)
	c	39 421 (3.1)	49.1 (4.2)				
	d	43 474 (1.2)	56.0 (1.6)				
NH_4AlCl_4		37 700	53.5	NH_4AlCl_4		43 900	64.0[10]

[a] ΔH in cal mol^{-1}; ΔS in cal mol^{-1} deg^{-1}.

pressure, about 20% in 20 min. In regions corresponding to the solid circles (Figure 2), no change was observed during measurement of a series of "equilibrium" absorbances in periods of a few hours. Except for those of NH_3–$FeCl_3$ samples, absorbances were also measured after reducing the temperature, with good concordance. One concludes that the reduction process does not change the activity of NH_4FeCl_4 signficantly and vapor–condensed phase equilibration keeps the concentration of $NH_3FeCl_3(g)$ constant. In those samples with negligible falloff rates the HCl concentration was large relative to small additional amounts expected from reduction. However, samples 2 and 4, with relatively small HCl pressures, did show, when reheated the following day, a slight parallel shift (decrease as expected if P_{HCl} increased) of the ln A vs. $1/T_3$ lines. No difference was seen in the falloff rate when sample illumination (quartz–iodine lamp) was continuous during thermal equilibration (ca. 30 min) or was limited to the time required to record the spectrum (5 min). This suggests that photolysis does not play a major role. The photochemical decomposition of NH_3 has been studied by many workers.[20]

When part of sample 1 was isolated and heated above 500 °C, the absorbance fell quickly below the observable range. Above 600 °C the spectrum of $FeCl_2$ vapor[19] was observed, as expected if reaction 2 correctly identifies the reduction product.

Comparison of the ratios of the absorbances (at the 335-nm peak) when vaporization of the ammine was complete to the total amounts of iron (expressed as a concentration) in the cells indicates that appreciably varying fractions of iron(III) are reduced to a nonabsorbing form prior to stabilization of the system: (2) 1950, (3) 1700, (4) 2700, (5) 500, (8) 4000, (9) 3600, (10) 700, (11) 1380, (12) 1500. All these ratios are presumed lower than the true molar absorptivity of NH_3FeCl_3; an estimated value of 4500 M^{-1} cm^{-1} (at 335 nm) was used to derive equilibrium constants and to construct Figure 1. Variation with temperature was neglected.

Data were correlated with reaction 4 as follows. In samples 9–12 and 14, the amount of HCl formed by reduction or removed by complex formation is small compared to the total, and to a good approximation $P_{HCl} = P°_{HCl} = n°_{HCl}RT_1/V$. P_{AM}, the partial pressure of NH_3FeCl_3, was taken as $ART_1/4500$, with $A = A_{obsd}$/path length. A least-squares solution of 21 values of ln K_4 vs. $1/T_3$, with $K_4 = P°_{HCl}P_{AM}$, gave result a, Table II. If $P_{AM(max)}$, the value of P_{AM} corresponding to the complete vaporization limit, represents the total iron(III) remaining in the cell, the amount reduced is known and P_{HCl} may be appropiately corrected. This gave result b, Table II, the same, within the standard deviations, as result a. With use of an interpolated absorbance (Figure 2) values of $n°_{HCl}$ for samples 1, 6, and 8 were assigned (parentheses, Table I) to make K_4 at a midrange temperature, 588 K, consistent with result b. Fifteen additional values of P_{HCL} and K_4 were then calculated from measured absorbances for these samples. A least-squares solution of the combined total of 36 gave result c, Table II.

Below the melting point insufficient information was known for direct evaluation of P_{HCl}, which must be relatively small to keep the absorbance in a measurable range. It was observed for sample 5, initially a mixture of NH_3 and $FeCl_3$, that a plot of ln K_4 vs. $1/T_3$, with P_{HCl} assumed equal to P_{AM}, extrapolated linearly to intersect result c at the melting point and gave result e, Table II. The enthalpy (7000 cal mol^{-1}) and entropy (12 cal deg^{-1} mol^{-1}) of fusion indicated by comparison of results e and c seem reasonable, slightly larger than reported for NH_4AlCl_4 (6000 cal mol^{-1}, 11 cal deg^{-1} mol^{-1})[10] and somewhat less than for $FeCl_3$ (10000 cal mol^{-1}, 14 cal deg^{-1} mol^{-1}).[8] $n°_{HCl}$ values for samples 2–4, 7, 13, and 17 were then fixed by choosing P_{HCl} so that $P_{HCl}P_{AM}$, with P_{AM} derived from an interpolated absorbance (Figure 2), at 540 K would be the same as K_4 from result e. Again, with allowance for changes in P_{HCl} associated with changes in P_{AM}, P_{HCl} and K_4 were calculated from each measured absorbance. A least-squares solution of the 34 values gave result f, Table II (data for NH_4AlCl_4 are included for comparison).[10] Figure 3 shows graphically all data used; the displaced linear absorbance plots in Figure 2 converge to a single line in Figure 3.

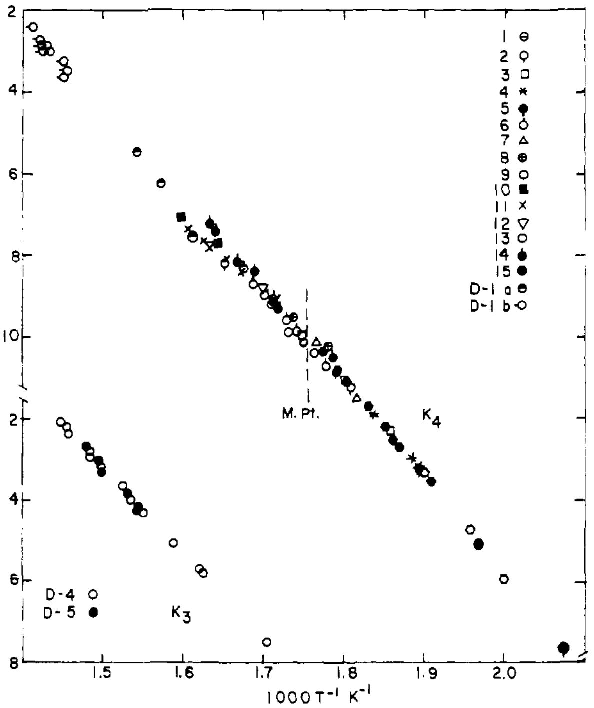

Figure 3. Temperature dependence of equilibrium constants for reactions 3 (K_3) and 4 (K_4) based on data from the various samples.

Hachmeister's phase diagram[6] shows an extended range of liquid miscibility around the 1:1 composition, and the effect of formation of solution in the absorbance samples above the melting point was considered. With $n°_{NH_3}$ and $P_{AM(max)}$ known, partial pressures of NH_3 can be derived. P_{NH_3} and P_{HCl} have quite different relative values in the various samples and, as expected for the model proposed, P_{NH_3} shows no direct correlation with absorbances. A calculation, assuming an ideal ionic solution (NH_4^+, $FeCl_4^-$, Cl^-) with K_1 for liquid NH_4Cl based on thermodynamic data for the solid[8] and an estimated enthalpy (5300 cal mol^{-1}) and entropy (8.6 cal K^{-1} mol^{-1}) of fusion, gave predicted X_{Cl^-} values of less than 0.03 for ten of 13 cases in which $n°_{NH_3}$ and $P_{AM(max)}$ were known (other

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(20) E.g.: Wiig, E. O. *J. Am. Chem. Soc.* **1935**, *57*, 1559.

values: 0.05, 0.06, 0.13). Estimated partial pressures of ammonia in the other samples gave a similar result. Also, in the NH_4Cl–$AlCl_3$ system, NH_3AlCl_3 was found to dissolve in NH_4AlCl_4.[10] However, in the present case NH_3FeCl_3 partial pressures are generally lower and temperatures higher. If vapor-pressure constants for NH_3FeCl_3 and NH_3AlCl_3 are assumed to be the same, the highest mole fraction of NH_3FeCl_3 predicted for the absorbance samples is 0.06. These estimates suggest that the activity of NH_4FeCl_4 will not be markedly lowered by solution formation. Lines drawn independently through points (Figure 3) for various samples above the melting point show slight parallel displacements in some cases. However, variations were not appreciably beyond experimental error, and the shifts did not correlate in a way expected from solution effects.

As the temperature was increased, no change in the wavelength of the maximum near 335 nm was seen, as might be expected if the ammine were appreciably dissociated into ammonia and ferric chloride. Small amounts of $FeCl_3(g)$ or $Fe_2Cl_6(g)$ would be difficult to detect because of the strong spectral overlap (Figure 1). If the expression $\Delta G° = 39900 - 36.3T$ cal mol^{-1}, reported for the reaction $NH_3AlCl_3(g) = NH_3(g) + AlCl_3(g)$, is used to estimate partial pressures of $FeCl_3$ and Fe_2Cl_6, concentrations in all samples are too low to give a measurable contribution to the vapor absorbance.[8,10,13]

In the absence of an appreciable partial pressure of HCl, NH_3 reduces $FeCl_3$ at lower temperatures, between 100 and 200 °C, and only irreproducibly small amounts of ammine vapor were observed when mixtures of NH_3 and $FeCl_3$ were heated. The sample 5 absorbances, Figure 2, were observed the first time the mixture was heated between 200 and 300 °C (over a 6-h period). After all the ammine had vaporized (open circles), the absorbance decreased relatively rapidly with time. When the sample was reheated the following day, no absorbance was detected. The cell windows were found covered with a small amount of grayish black deposit with a metallic sheen and appeared to contain iron; similar deposits were observed in other samples prepared with an excess of NH_3, but not when only NH_4Cl or NH_4Cl with HCl was used. With NH_3 in excess, a reduction reaction such as $4NH_3 + 4FeCl_3 = Fe + 3NH_4FeCl_4 + 0.5N_2$, together with reaction 4, could account for formation of iron and the apparent equivalency $P_{AM} = P_{HCl}$ in sample 5. However, a number of other reaction products which would disturb this relationship seem plausible. After being heated to higher temperatures, mixtures generally seemed, from sublimation behavior, to contain NH_4Cl and $FeCl_2$. In the presence of HCl one expects iron to be converted to $FeCl_2$. However, in a separate experiment an iron wire–NH_4Cl mixture gave no visual evidence of reaction after several hours at 400 °C.

None of the other four mixtures of NH_3 and $FeCl_3$ (Table I) duplicated the absorbance behavior of sample 5. Samples 18 and 19 showed no NH_3FeCl_3 absorbance; reduction of iron(III) was apparently complete before the temperature reached the measuring range. Small absorbances were observed in samples 16 and 17—lower, however, than expected from K_4 if $P_{AM} = P_{HCl}$—and the absorbance fell off rapidly above 270 °C.

After an initial heating sequence to ca. 300 °C, trace amounts of a purple-brown solid were observed in some of the NH_4Cl–$FeCl_3$ mixtures, which indicates that other intermediates may have transitory existence. This material, not isolated or identified, disappeared when samples were reheated and was not seen after mixtures stabilized. A similar observation was made in diaphragm gauge studies.

For an examination of the possibility that complexes of iron(II) chloride might contribute to the absorbance, the vapor spectrum of an equimolar (1×10^{-4} M) mixture of $FeCl_2$ and NH_4Cl was scanned between 240 and 600 nm at 50 °C intervals up to 480 °C; results were negative. Values of K_3 (following section) show that all the NH_3 and HCl should be in the vapor phase in this sample around 440 °C (total pressure ca. 860 torr). After the vapor was cooled, a deposit with sublimation characteristics of $FeCl_2$ was found on the cell windows. Transport of $FeCl_2$ at these temperatures suggests that a small partial pressure of an iron(II) complex may be generated in the system. Diaphragm gauge studies give no indication that such a species makes a major contribution to the total pressure, however. A mixture of 5.44×10^{-5} mol of NH_3 and 8.54×10^{-5} mol of $FeCl_2$ (1-cm cell, volume 4 cm^3) was examined similarly with no measurable absorbance detected.[21]

Diaphragm Gauge Pressures

Total pressures developed in sealed Pyrex diaphragm gauges (Daniels type)[22] by mixtures (see Table I) of NH_3, HCl, and $FeCl_3$ (samples D-1, D-2, and D-3) and of an NH_3–$FeCl_3$ mixture (D-5) were measured to ascertain the extent of the reduction reaction (as indicated by the amount of nitrogen produced) and to derive, where possible, independent values of K_4 for comparison with results based on the absorbance studies. A mixture of NH_3, HCl, and $FeCl_2$ (sample D-4) was also studied to derive values of K_3 (sample D-5 also gave information on this equilibrium), and a mixture of ammonia and $FeCl_2$ (sample D-6) was examined to see if condensed ammoniates of $FeCl_2$ were formed under conditions prevailing in either the diaphragm gauge or absorbance studies. Balancing pressures were measured manometrically (± 0.5 torr) and were observed at sample temperatures up to 475 °C. In the usual measuring range a temperature gradient, ca. 5°, developed along the gauges; cited values are an average. The various mixtures were prepared by first subliming $FeCl_3$ (or $FeCl_2$) into the evacuated gauge; then known quantities (derived from a measured temperature and pressure in a known volume) of HCl and/or NH_3 were frozen in by cooling the gauge with liquid nitrogen, after which the entrance tube was sealed off with a flame.

Sample D-1. $P_{23 °C}$ was initially zero. Pressures reached a measuring range (>20 torr for reasonable accuracy) around 310 °C and in series a were observed up to 375 °C. After the sample was cooled to 23 °C, a residual pressure of 12 torr ($HCl + N_2$) was observed. A light yellow solid was seen near the extremes of the gauge (cooler regions), and a thin white deposit and, separately, a small amount of a purple-brown solid were seen near the center. The mixture was then raised to 475 °C, after which variation of pressure, substantially higher than in series a, with temperature was reproducible—series b. Between 460 and 475 °C, the sample behaved as a perfect gas mixture with $n = 4.64 \times 10^{-4}$ mol. At 23 °C, $n = PV/RT = 1.82 \times 10^{-4}$ mol. If it is assumed that reaction 2 occurs to a limited degree after which the system stabilizes and that at the highest temperatures the remaining iron(III) is all vaporized by reaction 4, one predicts $n_{hi} = n_{N_2} + (n°_{HCl} + 6n_{N_2}) + (n°_{NH_3} - 2n_{N_2} - n_{AM}) + n_{AM}$, from which $n_{N_2} = 1.98 \times 10^{-5}$. This value corresponds to reduction of about two-thirds of the iron(III) and agrees well with $n_{23 °C}$ if the ammine is condensed (with HCl) to NH_4FeCl_4 and ammonia to NH_4Cl and/or NH_4FeCl_3; then $n_{23 °C} = n_{N_2} + (n°_{HCl} + 6n_{N_2}) - (n°_{NH_3} - 2n_{N_2} - n_{AM}) - n_{AM} = 9n_{N_2}$, from which $n_{N_2} = 2.02 \times 10^{-5}$. An average, 2.00×10^{-5}, also verified by observing the pressure with the gauge immersed in liquid nirogen (HCl condensed), was used to predict the nitrogen partial pressure at intermediate temperatures. After series b, the sample appeared uniformly light yellow.

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(21) Clark, R. J. H.; Williams, C. S. *J. Chem. Soc. A* **1966**, *10*, 1425.
(22) Daniels, F. *J. Am. Chem. Soc.* **1928**, *50*, 1115.

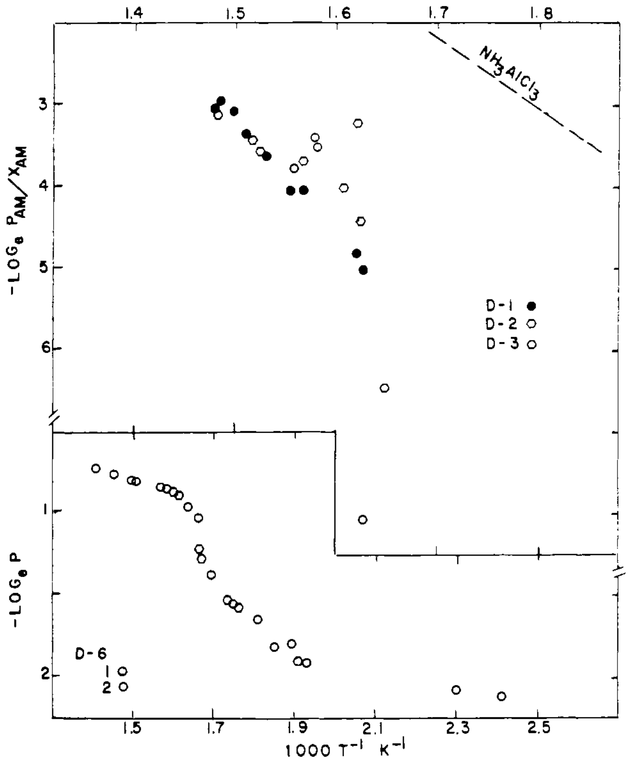

Figure 4. Top: Henry's law constants derived for NH_3FeCl_3 in NH_4FeCl_3-NH_3FeCl_3 solutions in comparison with vapor pressure reported for NH_3AlCl_3. Bottom: Variation of ammonia pressure with temperature in sample D-6 (pressure in atm).

Between 415 and 436 °C the total pressure varied with temperature as expected if controlled by equilibrium 4. On this basis, with $B = P_t - P_{N_2}$, $P_{HCl} = (P°_{HCl} - P°_{NH_3} - P°_{AM} + B)/2$ and $P_{AM} = P°_{AM} - P°_{HCl} + P_{HCl}$; $P°_{HCl} = 3.024 \times 10^{-4}\ RT/V$, $P°_{NH_3} = 8.33 \times 10^{-5}\ RT/V$, and $P°_{AM} = 5.91 \times 10^{-5}\ RT/V$, in which the respective numbers of moles correspond to $n°$ values (Table I) adjusted for changes accompanying the reduction reaction. Consistent with this interpretation the product $P_{HCl}P_{NH_3}$ in this temperature range is found to be less than K_1 or K_3. Values of $K_4 = P_{HCl}P_{AM}$ were also derived from the three highest pressures measured in series a, taking P_{N_2} as $P_{23°C}(T)/[9(296)]$. At high temperatures $P_{NH_3} = 4P_{N_2}$ if P_{NH_3} is below its condensation limit, and $P_{HCl} = 12P_{N_2} + P_{AM}$; P_{AM} may then be evaluated from P_t. The three K_4 values from series a and ten from series b are compared with absorbance data in Figure 3. The b values (at the high-temperature extreme) are slightly high compared with result c and "tilt" the least-squares solution of the combined 49 values, result d, Table II; an enthalpy of fusion based on c and f values seems more reasonable. The overall agreement is reassuring, however, considering assumptions, experimental errors, the uncertainty of the effects of solution formation, and the use of an estimated molar absorptivity.

Ten pressures observed between 340 and 405 °C correlated with the predicted behavior of K_3 and K_4 when it was assumed that the vapor equilibrates with both NH_4FeCl_4 and a solution of NH_4FeCl_3 and NH_3FeCl_3. If the ammine obeys Henry's law, a quartic equation in P_{HCl}, with constants fixed by $P°$ values, P_{N_2}, P_t, K_3, and K_4, may be derived. Mole fractions of ammine between 0.08 and 0.7 are predicted. Other models (separate phases, solution of NH_4FeCl_4, NH_4FeCl_3, and NH_3FeCl_3 and solution of NH_4FeCl_4 and NH_4FeCl_3) were unsatisfactory. A plot of the log of the ratio P_{AM}/X_{AM} (the Henry's law constant) vs. $1/T_3$ is shown in Figure 4 and is surprisingly consistent for sample D-1; $\Delta G° = 26770\ (\pm 4.7\%) - [33.7\ (\pm 5.7\%)]T$ cal mol^{-1}. Values are appreciably lower than the vapor pressure of NH_3AlCl_3 (dashed line), suggesting negative deviations. Independent evidence for formation of such a solution has not been obtained.

Sample D-2. An initial low-temperature series was not measured, and a region in which only NH_4FeCl_4 condensed was not observed; in other respects the behavior was similar to that of sample D-1. In this case $n_{hi} = 3.256 \times 10^{-4}$; $n_{23°C} = 2.38 \times 10^{-4}$, giving n_{N_2} values of 2.51×10^{-5} and 2.65×10^{-5}, respectively (average 2.59×10^{-5}). Five of the seven pressures correlated with the D-1 solution model; the other two (at the two highest temperatures) gave real roots only when it was assumed that $P_{HCl}P_{AM}$ was too low to form a condensed NH_4FeCl_4 phase. When equilibrium 4 is excluded, the expression for P_{HCl} reduces to a cubic.

Sample D-3. A break-seal attached to the D-2 gauge was ruptured to permit removal of HCl and N_2 remaining as residual gases at 23 °C. (The quantities in parentheses (Table I) were calculated from the amounts originally present and the amounts removed.) The gauge was resealed and after a heating cycle part of the remaining iron(III) was found to have been reduced. From n_{hi} and $n_{23°C}$, n_{N_2} was fixed at 1.26×10^{-6}. Between 308 and 368 °C pressures correlated on the basis of equilibrium with a solution of NH_3FeCl_3 and NH_4FeCl_3 with no NH_4FeCl_4 phase present. Henry's law constants derived for samples D-2 and D-3 (Figure 4) exhibit much larger scattering; experimental uncertainty is relatively large for these samples.

Determination of K_3. Sample D-4. $FeCl_2{\cdot}4H_2O$ (Baker Analyzed Reagent) was heated to 400 °C under 50 torr HCl; water, which condensed outside the furnace, was pumped out. $FeCl_2$ was sublimied into the gauge under vacuum and the measured quantities of HCl and NH_3 added. At 270 °C the pressure, which had increased to ca. 30 torr, fell rapidly, indicating formation of a condensed complex. Between 312 and 415 °C total pressures (reproduced on heating and cooling and on successive days) increased exponentially with temperature, and values (13) of $K_3 = P_{HCl}P_{NH_3}$ were derived by assuming $P_{HCl} = P_{NH_3} = P_t/2$. Between 430 and 475 °C, n_g remained constant at $n°_{HCl} + n°_{NH_3}$.

Sample D-5. As the mixture warmed to room temperature, some white solid was observed between the deposit of $FeCl_3$ and the tip into which NH_3 had been condensed. At 20 °C the pressure was about half the value expected from $n°_{NH_3}$ and fell slowly to $^1/_3$ in 30 min. As the temperature of the mixture reached 120 °C, the pressure fell virtually to zero. At 380 °C the pressure had increased to ca. 250 torr; after the mixture was cooled to 23 °C, a pressure of 26 torr was observed, which fell to 8 torr at liquid-nitrogen temperature, indicating that the gas was nitrogen.

After the sample was heated to 455 °C, total pressures (now higher) were found reproducible. Between 410 and 455 °C, n_{hi} was constant at 3.18×10^{-4} mol, and $n_{23°C}$ was found to be 8.09×10^{-5} mol. From the expressions described for sample D-1, n_{N_2} was found to be 2.85×10^{-5} mol ($n°_{HCl} = 0$), indicating that ca. 95% of the iron(III) had been reduced. The small amount remaining, 8.34×10^{-6} mol, was assumed to remain in the vapor phase between 370 and 410 °C as the ammine. From the seven measured values of P_t, values of K_3 were derived from the expressions $P_{HCl} = 6P_{N_2} - P_S$, $P_{NH_3} = P°_{NH_3} - 2P_{N_2} - P_{AM} - P_S$, and $P_t = P_{HCl} + P_{NH_3} + P_{N_2} + P_{AM}$; P_S is the pressure equivalent of the number of moles of NH_4FeCl_3 condensed. A combined least-squares treatment (20 values) of ln K_3 vs. $1/T_3$, Figure 3, gave $\Delta G° = 41841\ (\pm 0.88\%) - [56.42\ (\pm 1.0\%)]T$ cal mol^{-1}. This expression was used to calculate K_3 at various temperatures in the treatment of the tetrachloroferrate(III) samples described previously. In a separate experiment an equimolar mixture of $FeCl_2$ and NH_4Cl, heated in a sealed Pyrex tube, was observed to melt

Table III. Ions Observed in the Mass Spectrum of Vapors Generated by NH_4FeCl_4

mass no. range	species	% ion current scan 162	 scan 258
14–18	N^+, NH^+, O^+, NH_2^+, NH_3^+, H_2O^+	3.3	2.8
28	N_2^+	1.2	0.6
35–38	Cl^+, HCl^+	25.9	20.7
51–57	$NHCl^+$, NH_2Cl^+, Fe^+	5.8	13.0
91–93	$FeCl^+$	10.7	22.0
106–110	$NHFeCl^+$, NH_2FeCl^+, NH_3FeCl^+	12.7	7.5
126–130	$FeCl_2^+$	4.4	7.2
141–147	$NHFeCl_2^+$, $NH_2FeCl_2^+$, $NH_3FeCl_2^+$	8.5	3.7
161–167	$FeCl_3^+$	1.3	1.9
176–184	$NHFeCl_3^+$, $NH_2FeCl_3^+$, $NH_3FeCl_3^+$	4.2	1.1
217–221	$Fe_2Cl_3^+$	0.11	0.3
252–254	$Fe_2Cl_4^+$	0.13	0.9
287–293	$Fe_2Cl_5^+$	0.08	0.6
324–326	$Fe_2Cl_6^+$	0.01	0.02

between 440 and 455 °C. Hence it is assumed that these values of K_3 characterize the decomposition of $NH_4FeCl_3(s)$.

Sample D-6. As this mixture of ammonia and $FeCl_2(s)$ warmed to room temperature, the ammonia pressure fell to ca. 5 torr. Variation of P with T at higher temperatures is shown in Figure 4. Equilibration was slow below 100 °C. Between 100 and 160 °C the number of moles of gas remained constant at ca. 40% of the amount of NH_3 initially added. Above 370 °C the number of moles of gas corresponded to $n°_{NH_3}$. The curvature of the ln P vs. $1/T$ line (Figure 4) between 200 and 370 °C suggests that the condensed phase is a solid solution of changing composition. Partial pressures of ammonia in mixtures described above are appreciably less than values observed with this sample, and it has been assumed that condensed ammoniates of $FeCl_2$ need not be included in the treatment of those mixtures.

Mass Spectra

Mass spectrometric analysis of the vapors generated by heating a solidified melt of NH_4FeCl_4 was carried out to obtain direct evidence for the dominant molecular species generated in the vaporization process. Facilities available only permitted study of the free vaporization of the solid directly into the vacuum of the ion-source chamber.

The direct-insertion probe of a Hewlett-Packard 5985 GC mass spectrometer was used.[23] An equimolar mixture of NH_4Cl and $FeCl_3$ in an evacuated Pyrex tube was melted by gentle flaming, and the dark yellowish green liquid was driven along the walls into an attached thin-walled capillary (1.6-mm o.d.). The sample would not sublime readily, presumably inhibited by N_2 and HCl formed by the reduction reaction as the system stabilized. The solidified product (a block ca. 0.5 cm long) was isolated by flame seal-off and the 1-in. length of capillary was wedged into the mass spectrometer sample probe. At the moment of insertion the tip (away from the solid block) was snipped off. The brief exposure is assumed to have led to some hydrolysis at the surface; however, the bulk of the sample appeared unaffected.

With the probe in the ionization chamber, the temperature was increased at 30 °C/min to a maximum of 250 °C, and mass spectra were scanned repeatedly over a 20-min period (iv 70; mass range 0–400). At 60 °C $HCl^+ + Cl^+$ accounted for 25% of the total ion current (the rest was background; there were no peaks attributable to species expected from NH_3FeCl_3). This surge of HCl is assumed to have come from decomposition of surface hydrolysis products. Between 100 and 200 °C, the $HCl^+ + Cl^+$ current fraction fell to ca. 2% but increased again as the sample temperature approached 250 °C. The major ion peaks observed after several minutes at 250 °C (scan 162 as representative) are listed in Table III. Mass distributions in the various ranges were consistent with isotopic abundances for the species indicated. The overall result offers strong support for the conclusion that NH_4FeCl_4 vaporizes by reaction 4. Ion currents in mass range 196–224 (for species such as $FeCl_4^+$, $NH_4FeCl_4^+$, etc.) were at background level. On the last scan (258) the amount of material vaporizing appeared to be falling off (total ion current was one-fourth that of scan 162) and contributions, albeit very small, from species expected from ionization of Fe_2Cl_6 were relatively larger. Ion currents for these peaks in scan 162 were only slightly above background level. The presence of trace amounts of Fe_2Cl_6 may indicate a slight dissociation of the ammine, some solubility of ferric chloride in the NH_4FeCl_4 phase, or possibly disproportionation of oxychloride, formed by hydrolysis, into ferric chloride and ferric oxide.

Registry No. NH_4FeCl_4, 24411-12-9; NH_3FeCl_3, 78790-89-3.

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Role of Spin Change in the Stereomobile Reactions of Strong-Field d^6 Transition-Metal Complexes

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The isomerization, racemization, and stereomobile substitution reactions of low-spin d^6 complexes have been studied in the framework of a ligand field model. On the basis of orbital and state correlation diagrams for the different reaction mechanisms, it is concluded that stereomobility is only possible if a spin change takes place somewhere along the reaction coordinate. The lowest quintet state ($^5T_2$ octahedral parentage) plays an especially important role in this process. The ligand field expression for the activation energy is compatible with the experimentally observed negative correlation between $10Dq$ and the occurrence of stereomobility.

Introduction

Ever since the early fifties, ligand field theory has been applied to the kinetic and thermodynamic properties of transition-metal complexes.[1-3] Although the broad features of the relative stabilities and reactivities of the different d^n systems in solution can be rationalized in terms of ligand field theory,

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