modes are present, average values derived from a model which ignores them will be in error. It is not feasible to take such other modes into account in the analysis since a number of unknown parameters would be involved. It is felt, however, that while the absolute values of interionic distances predicted by the present model may be inaccurate, comparisons of sizes of related species obtained in this way are meaningful.

That the cation nuclear resonance shifts in systems like the present are of dipolar origin at all has recently been challenged. Burkert, *et al.*,[14] state that their ^{14}N resonance studies indicate that these shifts result from the Fermi contact interaction *via* direct counterion electron transfer. However, the fact that the protons of three different cations—$(C_4H_9)_4N^+$, $(C_6H_5)_4As^+$, and $C_4H_9(C_6H_5)_3P^+$—show, respectively, upfield and downfield shifts when ion paired to $Co(C_6H_5)_3PX_3^-$ and $Ni(C_6H_5)_3PX_3^-$ is unimpeachable evidence that they are predominantly dipolar in origin. Burkert, *et al.*,[14] offer no explanation for this decisive observation and in fact give no data or details of their own experiments. Their interpretation cannot be accepted.

[14] P. K. Burkert, H. P. Fritz, W. Gretner, H. J. Keller, and K. E. Schwartzhans, *Inorg. Nucl. Chem. Letters*, **4**, 237 (1968).

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Stabilization of the Hexachloroferrate(III) Anion by the Methylammonium Cation

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In 1963 Piper and coworkers[1] prepared several compounds which they postulated as containing the hexachloroferrate(III) anion, an ion whose existence had not previously been confirmed. X-Ray powder data for one of their compounds, $[Co(NH_3)_6][FeCl_6]$, were compared with similar data for $[Co(NH_3)_6][TlCl_6]$, where the octahedral $TlCl_6^{3-}$ is known to exist from a detailed X-ray study. The very similar powder patterns suggested that the two compounds were isomorphous. In the compounds prepared by Piper, *et al.*,[1] the $FeCl_6^{3-}$ species was stabilized in the crystal lattice by a cation of similar size and equal and opposite charge. This paper reports evidence that the $FeCl_6^{3-}$ entity can exist in the solid state in association with a smaller, univalent cation.

In the course of studying the reaction of methylammonium chloride with ferric chloride in concentrated hydrochloric acid, a compound with the stoichiometry $(CH_3NH_3)_4FeCl_7$ was obtained. Upon checking the literature, it was found that a compound corresponding to this stoichiometry was first prepared and reported by Remy in 1925.[2] We propose to show that this was the first reported synthesis of the hexachloroferrate(III) anion, where the complex exists as a double salt with the formula $[CH_3NH_3]_3[FeCl_6]\cdot CH_3NH_3Cl$.

Experimental Section

Compounds.—$(CH_3NH_3)_4FeCl_7$ was obtained by dissolving 5 g of anhydrous $FeCl_3$ and 8.4 g of CH_3NH_3Cl in 50 ml of concentrated HCl, concentrating the resulting solution over a water bath, and subsequently cooling in ice. The yellow-orange product obtained was recrystallized from absolute ethanol. The resulting crystals were very hygroscopic. *Anal.* Calcd for $(CH_3NH_3)_4FeCl_7$: Cl, 57.5; Fe, 12.9. Found: Cl, 57.0; Fe, 12.6.

The compounds prepared for comparative purposes were hexaamminecobalt(III) hexachloroferrate(III), $[Co(NH_3)_6][FeCl_6]$, and tris(1,2-propanediamine)rhodium(III) hexachloroferrate(III), $[Rh(pn)_3][FeCl_6]$. Both were prepared by the method outlined by Piper, *et al.*[1] The analysis of these compounds agreed with their theoretical composition within experimental error.

Magnetic Susceptibility Measurements.—Magnetic susceptibilities were obtained at 295°K by the Gouy method on a magnetic balance of standard design using $HgCo(NCS)_4$ as a calibrant. Diamagnetic corrections were made in the usual manner and the magnetic moments were calculated using the Curie law.

Ir Measurements.—Samples were prepared in pressed polyethylene disks and their spectra were obtained on a Beckman IR-11 spectrophotometer.

Mössbauer Measurements.—Spectra were taken using an Austin Science Associates drive unit and a 30-Mc source of ^{57}Co in chromium, which gave a line width of 0.28 ± 0.01 mm/sec with a thin nitroprusside absorber. Absorbers contained about 7 mg of iron/cm^2 and were mounted in a Teflon holder maintained at 78°K in a stainless steel dewar. The results were statistically analyzed, assuming Lorentzian line shapes, using an IBM 7040 computer.

Electronic Spectral Measurements.—The electronic spectra of KBr disks containing 5% sample were recorded by a Perkin-Elmer 450 spectrophotometer. Temperature of the sample disks was maintained at 78°K.

Results and Discussion

The data obtained for the $(CH_3NH_3)_4FeCl_7$ species and for the comparative compounds, $[Co(NH_3)_6][FeCl_6]$ and $[Rh(pn)_3][FeCl_6]$, are given in Tables I and II.

The magnetic data confirm that the ground state of the iron ion in $(CH_3NH_3)_4FeCl_7$ is the expected high-spin Fe(III). The positions of the peaks in the far-infrared region for ν_3 and ν_4 are identical within experimental error for the established hexachloroferrate species and for $(CH_3NH_3)_4FeCl_7$. The Mössbauer data show agreement between the isomer shifts for the established hexachloroferrates and $(CH_3NH_3)_4FeCl_7$ and are further proof of the existence of an octahedral arrangement of chloride ions about the central iron atom. The absence of detectable quadrupole splitting and the typical width Mössbauer lines indicate a symmetrical octahedral arrangement of the chlorides about the iron atom. The electronic spectrum of $(CH_3NH_3)_4FeCl_7$ consisted of a band at 18,700 cm^{-1} and a broader, more intense band with maximum intensity at 22,400 cm^{-1} which was unsymmetrical and trailed off toward the uv region. The band at 18,700 cm^{-1} for $(CH_3NH_3)_4FeCl_7$ agrees with the band at 18,730 cm^{-1} for

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

[2] H. Remy, *Chem. Ber.*, **58**, 1565 (1925).

TABLE I

SPECTRAL MEASUREMENTS

Compound	Ir abs freq, cm^{-1}		Electronic spectral data, λ_{max}, cm^{-1}
	ν_3	ν_4	
$[CH_3NH_3]_3[FeCl_6]\cdot CH_3NH_3Cl$	257 ± 4	182	18,700
$[Co(NH_3)_6][FeCl_6]$	251 ± 4	181	22,400
	248 ± 5[a]	181[a]	. . .
$[Rh(pn)_3][FeCl]_6$	252 ± 4	182	18,730[b] 22,080

[a] From D. M. Adams and D. M. Morris, *J. Chem. Soc.*, 694 (1968). [b] From ref 1.

TABLE II

MAGNETIC AND MÖSSBAUER DATA

Compound	μ_{eff}, BM	Isomer shift,[a] mm/sec	Absorption width at half-max, mm/sec
$[CH_3NH_3]_3[FeCl_6]\cdot CH_3NH_3Cl$	6.00[b]	+0.746 ± 0.01	0.478 ± 0.03
$[Co(NH_3)_6][FeCl_6]$	5.96[b]	+0.744 + 0.01	0.471 ± 0.03
$[Rh(pn)_3]]FeCl_6]$	. . .	+0.777 ± 0.01	0.430 ± 0.03

[a] Relative to a sodium nitroprusside standard. [b] Calculated spin-only moment is 5.92 BM.

the established hexachloroferrate. Piper, *et al.*,[1] assigned this band to the $^6A_1 \rightarrow {}^4T_2$ (^4G) transition. Our band at 22,400 cm^{-1} does not agree very well with that of 22,080 cm^{-1} reported for the $[Rh(pn)_3][FeCl_6]$ compound. Piper assigned this band to the $^6A_1 \rightarrow {}^4E$, $^4A_1$ (^4G) transitions. However, it is possible that this is a charge-transfer band rather than a d → d transition. We feel that the evidence presented confirms the existence of the hexachloroferrate ion in the compound $(CH_3NH_3)_4FeCl_7$ and that the formula should be written as $[CH_3NH_3]_3[FeCl_6]\cdot CH_3NH_3Cl$. The double salt formation must increase the crystal lattice energy to the level required for stabilization of the hexachloroferrate(III) ion.

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Dichloroboronation of Aromatic Hydrocarbons. Mechanistic Aspects

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Dichloroboronation of aromatic hydrocarbons was first reported in 1959[1] and was later established as a relatively general synthesis of aryldichloroboranes[2]

$$3C_6H_6 + 3BCl_3 + Al \longrightarrow 3C_6H_5BCl_2 + AlCl_3 + {}^3/_2H_2$$

Synthesis conditions varied from 25 to 150°; minimal temperature for reaction was shown to be sensitive to the aluminum surface activity and to the nature of aromatic hydrocarbon. Aromatic hydrocarbons, *e.g.*, durene and mesitylene, with all hydrogen atoms vicinal to two C-methyl groups did not react—at least without isomerization of the arene. It was noted that the distribution of isomers obtained from toluene and the three xylenes "was typical of a classical Friedel–Crafts system run in the presence of aluminum trichloride."[2] A speculative reaction sequence was postulated as

$$ArH + BCl_3 \longrightarrow ArHBCl_3 \xrightarrow{AlCl_3} ArHBCl_2{}^+AlCl_4{}^-$$
$$ArHBCl_2{}^+ \longrightarrow ArBCl_2 + H^+$$
$$3H^+AlCl_4{}^- + Al \longrightarrow {}^3/_2H_2 + 4AlCl_3$$

Recently Eggers and Kettle[3] investigated the thermal stabilities of certain aryldichloroboranes and the sensitivity of the dichlorides to isomerization in the presence of trichloroborane. From the observation of no *apparent* isomerization in the presence of trichloroborane, they concluded that the arylboron dichlorides *do not isomerize* once formed and that in the synthesis there is an intermediate or transition state of "finite" independent existence wherein the rearrangements occur within the intermediate or transition-state lifetime. The experimental observations are incomplete and do not permit conclusions of this nature. None of the tests of isomerization was made under reaction conditions, *i.e.*, in the presence of all possible reactants or products.

Aryldichloroboranes do not thermally isomerize at 150° although there is very minor decomposition with the formation of aromatic hydrocarbons. (Studies were restricted to 1-(dichloroboryl)-2,5-dimethylbenzene and 1-(dichloroboryl)-3,5-dimethylbenzene for direct relevance to the Eggers and Kettle investigation.) The same behavior prevails in presence of (1) iodine, (2) aluminum, (3) aluminum(III) chloride, (4) methyl iodide, (5) trichloroborane, (6) mercury(II) chloride, and (7) mixtures of the preceding reagents. Hence there is no catalytic rearrangement.[4] There is however synthesis reversibility. Hydrogen chloride, a product of the dichloroboronation reaction, cleaves aryldichloroboranes to give arenes and trichloroborane. This is the reversible aspect of the synthesis.[5] Aromatic hydrocarbons rearrange in the presence of HCl–$AlCl_3$.[6] Consistently we find that at 150° excess hydrogen chloride in the presence of catalytic amounts of alu-

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(1) E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 2597 (1959).

(2) E. L. Muetterties, *ibid.*, **82**, 4163 (1960).

(3) C. A. Eggers and S. F. A. Kettle, *Inorg. Chem.*, **6**, 1975 (1967).

(4) Previous papers[1-3] have carried the connotation that dichlorohoronation is a clean reaction. There are however by-products including methylated arenes and viscous oils. Hence these specific studies do not emulate synthesis conditions. Nothing is as yet known about the nature of the oils but these are under current investigation. Yields of the oils increase with synthesis temperature.

(5) The aryldichloroborane synthesis proceeds to completion presumably by the irreversible reaction of hydrogen chloride and aluminum.

(6) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, pp 717, 718.