procedure was followed using phosphorus trifluoride instead of phosphorus fluoride dichloride only a 0.26-g. sample of solid was isolated (based on the same amount of starting materials). The solid was shown to be the salt $FPCl_3SbCl_6$ by a comparison of its infrared and F^{19} n.m.r. spectra with those of an authentic sample.

Reaction of PBr_3 with $SbCl_5$.—Phosphorus tribromide, 10.6 mmoles, was allowed to react with 21.0 mmoles of antimony pentachloride in 50 ml. of methylene chloride at $-10°$. Precipitation of a white solid occurred as the components were mixed. The product, 5.07 g., was obtained by filtration. It was not stable and slowly turned first yellow and then red on standing at ambient temperature for several days. The same color changes occurred rapidly on melting, 152–154°, or upon attempted recrystallization from acetonitrile.

Anal. Calcd. for $PBr_3Cl_2 \cdot SbCl_5$: Sb, 20.3; Cl, 36.8; total halogen, 75.1. Found: Sb, 19.9; Cl, 37.6; total halogen, 76.0.

Preparation of $NOSbCl_6$.—Nitrogen oxide was purified by scrubbing with a 2 *N* NaOH solution and dried over phosphorus pentoxide before being bubbled through a solution containing approximately 20 mmoles of antimony pentachloride in 75 ml. of methylene chloride. A yellow precipitate formed after several minutes and the gas stream was shut off after 20 min. Nitrosonium hexachloroantimonate was isolated by filtration, and could be purified by vacuum sublimation.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by the normal microcombustion techniques. Antimony was determined by precipitation of antimony(III) sulfide with hydrogen sulfide, followed by dissolution in concentrated hydrochloric acid. The trivalent antimony was titrated with standard potassium bromate solution using a methyl orange indicator.[22] The salt, $FPCl_3SbCl_6$, was analyzed for fluorine by first degrading the sample with lithium in *n*-propylamine and isolating the fluoride ion by steam distillation.[23] Then the fluorine content was obtained by the conventional thorium nitrate titration procedure. Although hydrolysis of the samples with a saturated KOH–methanol solution was sufficient to remove all of the chlorine as chloride in the salts, fluorine could not be done this way. The liberated chloride ion was determined by the Volhard method. Chlorine in the presence of bromine was determined by the method of Berg[24] after hydrolysis of the sample.

Infrared Spectra.—The infrared spectra in the 2.5 to 25 μ range of the salts and the gases $FPCl_2$ and $FSiCl_3$ were obtained in Nujol mulls or in the gas phase using a Perkin-Elmer Model 21 spectrophotometer equipped with potassium bromide optics.

N.m.r. Spectra.—The proton n.m.r. spectra of the salts and phosphines were obtained on a 10–12% solution using a Varian Model A-60 spectrometer. Nitrobenzene was used as a solvent for the derivatives containing ethyl groups and nitromethane was used for those containing phenyl groups. Tetramethylsilane was used as an internal standard. The F^{19} n.m.r. spectrum was obtained on a saturated solution of $FPCl_3SbCl_6$ in acetonitrile using a Varian Model 4300B spectrometer operating at 40 Mc. Trifluoroacetic acid was used as a standard. This solution was not stable and darkened to a deep brown on standing at room temperature for several hours. Therefore, the solution was stored at $-78°$ until run.

Conductance.—The conductivity of the salts in nitrobenzene was determined at 25.0 ± 0.05° in a cell of conventional design which had a cell constant of 0.515 $cm.^{-1}$. An oscilloscope equipped with a high gain preamplifier was used to detect the null point in a 2-kc. sine wave signal. Decade load resistors and a variable air capacitor were used to balance the bridge and the cell leads, respectively.

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[22] W. W. Scott, "Standard Methods of Chemical Analysis," Vol. II, 5th Edition, D. Von Nostrand Co., New York, N. Y., 1939, p. 74.

[23] R. D. Strahm, *Anal. Chem.*, **31**, 615 (1959).

[24] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1947, p. 264.

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

The Structure, Spectra, and Magnetic Properties of Certain Iron Halide Complexes

BY A. P. GINSBERG AND M. B. ROBIN

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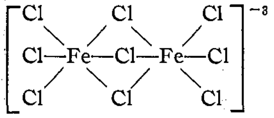
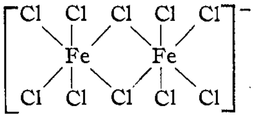
The magnetic susceptibilities, optical spectra, and Mössbauer spectra of the compounds $(pyH)_3Fe_2Cl_9$ and $(pyH)_3Fe_2Br_9$ indicate that they do not contain the μ-trihalo dimeric anion $(Fe_2X_9)^{3-}$ as suggested by several authors, but rather that the iron is entirely present as tetrahedral FeX_4^-. Two forms of $Cs_3Fe_2Cl_9$ have been prepared. One is probably like the pyridinium compounds, *i.e.*, $[CsFeCl_4]_2 \cdot CsCl$, while the other contains the μ-trichloro dimeric anion. Low temperature electronic spectra of the pyridinium iron halides are reported and the assignments of the bands are discussed.

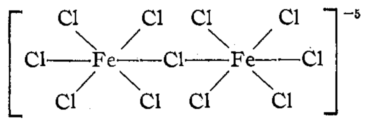
During the course of an investigation of metal–metal interactions in polynuclear transition metal complexes we examined the compounds $(pyH)_3Fe_2Cl_9$ and $(pyH)_3Fe_2Br_9$ (py = pyridine). As a result of this work we came to the conclusion, surprising in the light of earlier work, that the iron in these compounds is present entirely as a tetrahedrally coördinated monomeric anion. The enneachloride was first described by Weinland and Kissling,[1] who at the same time reported the compounds $(QH)_4Fe_2Cl_{10}$ (Q = quinoline) and $(pyH)_5Fe_2Cl_{11}$ and, on the basis of the stoichiometry, proposed that these substances contain the binuclear complex anions I, II, and III, respectively. In the above complexes, each iron is presumably surrounded octahedrally



I



II



III

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[1] R. F. Weinland and A. Kissling, *Z. anorg. allgem. Chem.*, **120**, 209 (1922).

by six chloride ions; in the μ-trichloro complex the octahedra share a face, an edge in the μ-dichloro, and a corner in the μ-monochloro complex. More recently Earnshaw and Lewis[2] determined the magnetic susceptibility *vs.* temperature curves for the above compounds between 300°K. and liquid nitrogen temperature. In an attempt to obtain a measure of the magnetic exchange energy between pairs of iron atoms, they fitted their results to the theoretical $\chi(T)$ equation for a system of spin $^5/_2$ centers interacting in pairs. It will be seen from our results that if the susceptibility measurements are carried below liquid nitrogen temperature, the fit to the $\chi(T)$ equation for a binuclear complex breaks down. The observed very weak exchange coupling in $(pyH)_3Fe_2Cl_9$ is simply a weak antiferromagnetic interaction similar to what we have found in $(C_2H_5)_4NFeCl_4$ and not a pairwise metal–metal interaction.

Experimental

$(pyH)_3Fe_2Cl_9$ was prepared as described by Weinland and Kissling[1] while $(pyH)_3Fe_2Br_9$ was prepared by the same procedure using the corresponding bromides. $(C_2H_5)_4NFeCl_4$ was obtained by precipitating a filtered ethanolic solution of anhydrous $FeCl_3$ with an excess of a concentrated solution of $(C_2H_5)_4NCl$ in ethanol. The product was recrystallized from hot ethanol and dried in a vacuum desiccator over P_2O_5. $(C_2H_5)_4NFeBr_4$ was obtained in a similar way from the corresponding bromides.

Anal. Calcd. for the enneachloride, $C_{15}H_{18}N_3Fe_2Cl_9$: Cl, 47.55; Fe, 16.64; C, 26.85; H, 2.70; N, 6.26. Found: Cl, 46.9; Fe, 16.3; C, 26.2; H, 3.2; N, 6.4. Calcd. for the enneabromide, $C_{15}H_{18}N_3Fe_2Br_9$: Br, 67.14; Fe, 10.43; C, 16.82; H, 1.69; N, 3.92. Found: Br, 67.2; Fe, 10.3; C, 17.1; H, 1.8; N, 3.9. Calcd. for the tetrachloride, $C_8H_{20}NFeCl_4$: Cl, 43.25; C, 29.30; H, 6.15; N, 4.27. Found: Cl, 43.0; C, 29.9; H, 6.3; N, 4.3. Calcd. for the tetrabromide, $C_8H_{20}NFeBr_4$: Br, 63.20; C, 19.00; H, 3.99; N, 2.77. Found: Br, 62.5; C, 19.2; H, 4.0; N, 2.8.

$Cs_3Fe_2Cl_9$ was prepared by first weighing out into a large quartz tube, in a drybox, 4.3633 g. of freshly sublimed $FeCl_3$ and 6.7930 g. of purified and fused CsCl. The tube was evacuated and sealed off and the mixture heated at 450° for 15 min. with occasional shaking. The tube was then quickly swirled to distribute part of the liquid on the walls and quenched by plunging into cold water. The material on the walls was orange in color and on grinding gave an orange powder (phase α). The lump in the bottom of the tube appeared brown, but on grinding gave a yellow powder (phase β). A chloride analysis confirmed the stoichiometry. *Anal.* Calcd. for $Cs_3Fe_2Cl_9$: Cl, 38.5. Found: Cl, 38.2. X-Ray powder diffraction patterns showed phase α to be isostructural with $Cs_3Cr_2Cl_9$, which contains the μ-trichloro dimeric anion.[3] Phase β has a different structure. Examination of the *d* spacings and relative intensities of the lines found in the powder patterns of the two phases (Table I) indicates that the phases are free of one another to within the sensitivity of the technique, *i.e.*, about 15%.

TABLE I

THE *d*-SPACINGS AND RELATIVE INTENSITIES OF THE POWDER PATTERN LINES OF THE TWO PHASES OF $Cs_3Fe_2Cl_9$

$Cs_3Fe_2Cl_9$ (α)	$Cs_3Fe_2Cl_9$ (β)
5.07 w	4.51 m
4.31 w	3.94 s
3.59 s	3.69 w
3.09 w	2.94 m
2.95 s	2.80 m
2.76 m	2.72 s
2.56 m	2.30 w
2.34 w	2.19 w
2.20 w	2.16 w
2.08 m	1.98 w
2.00 s	1.85 w
1.97 s	1.80 w
1.81 s	1.73 w
1.73 w	1.70 m
1.67 m	1.64 w
1.54 m	1.59 w
1.52 w	1.57 w
1.48 w	1.41 m
1.36 m	1.36 w
1.15 m	1.26 w
1.05 w	1.24 s
1.01 w	1.19 s
0.99 w	1.18 m
0.87 w	1.16 s
0.86 w	1.15 w
0.83 w	1.15 w

Magnetic susceptibility measurements were made between room temperature and 1.4°K. (pumped helium) on a pendulum magnetometer.[4]

Thin films of the compounds were obtained by melting the solid between quartz slides and then cooling to room temperature. The absorption spectra of the films were then measured at room temperature and 20°K. on a Cary Model 14 spectrophotometer in the range 0.5–2 μ. Acetone solutions of the compounds were measured at room temperature in 1-cm. cells.

Mössbauer spectra[5] were measured for us by Dr. G. K. Wertheim, of our Laboratories.

Results and Discussion

The magnetic susceptibility measurements are summarized in Table II. The susceptibility values χ_A' are per gram-atom of iron and include a diamagnetic correction. The effective magnetic moment μ_{eff} was calculated at each temperature from the expression

$$\mu_{eff} = 2.839[(\chi_A' - N\alpha)T]^{1/2}$$

with $N\alpha$, the temperature independent paramagnetism, taken to be zero.

Comparison of our results for $(pyH)_3Fe_2Cl_9$ with those of Earnshaw and Lewis, whose measurements only cover the range 90–300°K., shows substantial agreement. Using an exchange coupling constant of $J = -1.7°$ (-1.2 cm.^{-1}), a spectroscopic splitting factor $g = 2.09$, and taking $N\alpha = 0$, Earnshaw and Lewis found that their results fitted well to the χ_A' *vs.* T equation for two interacting $S = {}^5/_2$ centers

$$\chi_A' = \frac{3K}{T}\left[\frac{55 + 30\exp(10x) + 14\exp(18x) + 5\exp(24x) + \exp(28x)}{11 + 9\exp(10x) + 7\exp(18x) + 5\exp(24x) + 3\exp(28x) + \exp(30x)}\right] + N\alpha \qquad (1)$$

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(2) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).

(3) G. J. Wessel and D. J. W. Ijdo, *Acta Cryst.*, **10**, 466 (1957).

(4) R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.*, **103**, 572 (1956).

(5) "The Mössbauer Effect," H. Frauenfelder, Ed., W. A. Benjamin Company, New York, N. Y., 1962; A. J. F. Boyle and H. E. Hall, *Rept. Progr. Phys.*, **25**, 441 (1962).

TABLE II

EXPERIMENTAL ATOMIC SUSCEPTIBILITIES[a] (C.G.S./G.-ATOM OF IRON) AND EFFECTIVE MAGNETIC MOMENTS (B.M.)

$(pyH)_3Fe_2Cl_9$																					
T, °K.	298	274	253	233	214	194	180	153	131	90	70	52.5	40	31.5	18	12.5	8	4.2	1.4			
$10^2\chi_A'$	1.46	1.59	1.71	1.86	2.04	2.24	2.40	2.81	3.32	4.52	5.85	7.61	9.42	12.50	21.54	29.50	42.50	56.67	66.43			
μ_{eff}	5.92	5.92	5.91	5.91	5.92	5.92	5.91	5.89	5.91	5.73	5.73	5.68	5.51	5.65	5.62	5.45	5.24	4.37	2.74			
$(C_2H_5)_4NFeCl_4$																						
T, °K.	296	259	246	223	195	167	157	126	117	105	80	60	50	40	30	19	12	4.2	1.4			
$10^2\chi_A'$	1.50	1.72	1.81	1.99	2.27	2.68	2.86	3.56	3.77	4.23	5.39	7.12	8.48	10.42	14.20	22.48	34.65	70.36	81.05			
μ_{eff}	6.00	6.01	6.01	5.98	5.97	6.01	6.01	6.02	5.96	5.97	5.90	5.87	5.84	5.79	5.86	5.86	5.79	4.88	3.03			
α-$Cs_3Fe_2Cl_9$																						
T, °K.	287	270	238	216	194	171	157	125	100	80	60	50	40	30	20.5	16.5	10.5	4.2	1.4			
$10^2\chi_A'$	1.57	1.67	1.85	2.01	2.22	2.50	2.72	3.26	4.00	4.72	5.74	6.49	7.63	9.11	11.20	12.48	14.51	13.95	13.59			
μ_{eff}	6.03	6.02	5.96	5.91	5.90	5.87	5.87	5.73	5.68	5.52	5.27	5.11	4.96	4.68	4.28	4.04	3.52	2.17	1.24			
$(pyH)_3Fe_2Br_9$																						
T, °K.	299	281	258	231	218	187	165	151	141	110	81.5	60	50	40	31	26.5	20	14.5	9.1	7.3	4.2	1.4
$10^2\chi_A'$	1.52	1.60	1.74	1.92	2.05	2.36	2.66	2.93	3.11	3.84	4.88	6.68	7.64	9.04	11.19	12.66	15.49	18.83	23.23	24.90	25.55	27.21
μ_{eff}	6.04	6.02	6.02	5.96	6.00	5.96	5.95	5.96	5.95	5.84	5.66	5.68	5.54	5.39	5.30	5.22	4.99	4.68	4.12	3.82	2.94	1.75
$(C_2H_5)_4NFeBr_4$																						
T, °K.	298	282	234	201	163	140	100	80	60	50	40	30	20	14	9.3	6.7	4.2	1.4				
$10^2\chi_A'$	1.50	1.60	1.89	2.19	2.69	3.15	4.20	5.11	6.67	7.61	9.03	11.10	15.28	18.20	20.41	21.01	20.48	20.33				
μ_{eff}	6.02	6.03	5.97	5.96	5.95	5.96	5.82	5.73	5.68	5.54	5.40	5.18	4.97	4.54	3.91	3.38	2.64	1.52				

[a] Corrected for the diamagnetism of all the atoms in the molecule using corrections on pp. 78 and 92 of P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience, New York, N. Y., 1956.

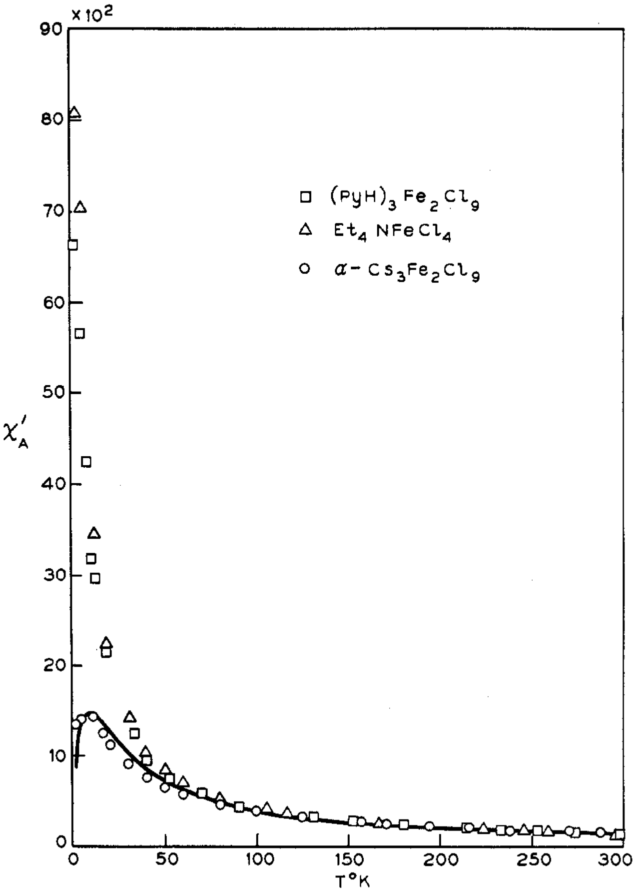

Fig. 1.—Magnetic susceptibility *vs.* temperature curves for $(pyH)_3Fe_2Cl_9$ (□), $(C_2H_5)_4NFeCl_4$ (△), and α-$Cs_3Fe_2Cl_9$ (○). The solid line is a plot of eq. 1 for $J = -1.6°$ and $g = 2.00$.

In expression 1 $x = -J/kT$, $K = g^2N\beta^2/3k$, N is the Avogadro number, β the Bohr magneton, and k the Boltzmann constant. Similarly, between 90 and 298°K. our results fit well to this equation with $J = -1.6°$ (-1.1 cm.$^{-1}$) and $g = 2.00$. This is demonstrated in Fig. 1, which contains a plot of eq. 1 for the above values of the parameters together with the χ_A' *vs.* T results for $(pyH)_3Fe_2Cl_9$. Figure 1 also shows, however, that below 90°K. the experimental points deviate from the theoretical curve, the measured values being very much higher than the theoretical at very low temperatures. The magnetic exchange interaction in $(pyH)_3Fe_2Cl_9$ is then much less than predicted by eq. 1 with $J = -1.6°$. We also note that the $(pyH)_3Fe_2Cl_9$ susceptibilities cannot be fitted to eq. 1 over the entire temperature range with any set of J and g values. The Weiss constant for $(pyH)_3Fe_2Cl_9$ is $\theta = 4°$ while for $(C_2H_5)_4NFeCl_4$, $\theta = 2°$, so that the exchange interaction in $(pyH)_3Fe_2Cl_9$ is of the same order of magnitude as in $(C_2H_5)_4NFeCl_4$ (Fig. 1). Figure 1 also contains the χ_A' *vs.* T data for the α form of $Cs_3Fe_2Cl_9$, which contains the μ-trichloro dimeric anion, and it can be seen that a fairly good fit to the theoretical curve over the entire temperature range is obtained. It is clear that the exchange interaction in dimeric $Cs_3Fe_2Cl_9$ ($\theta = 22°$) is much greater than in $(pyH)_3Fe_2Cl_9$.

Similar conclusions hold for $(pyH)_3Fe_2Br_9$. Thus in Fig. 2 we plot the χ_A' *vs.* T results for the pyridinium compound together with those for $(C_2H_5)_4NFeBr_4$.

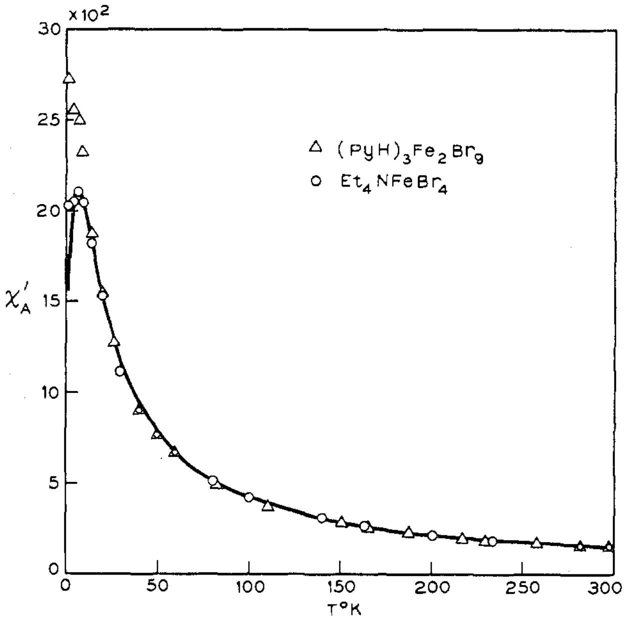

Fig. 2.—Magnetic susceptibility *vs.* temperature curves for $(pyH)_3Fe_2Br_9$ (△) and $(C_2H_5)_4NFeBr_4$ (○). The solid line is a plot of eq 1 for $J = -1.17°$ and $g = 2.05$.

The low temperature susceptibilities of $(pyH)_3Fe_2Br_9$ cannot be fitted by eq. 1 and they are higher than the corresponding susceptibilities of $(C_2H_5)_4NFeBr_4$, indicating a stronger exchange interaction in the latter compound (the Weiss constants are, respectively, 9 and 12°). Somewhat surprisingly, the susceptibilities for $(C_2H_5)_4NFeBr_4$ give a good fit to eq. 1 with $J = -1.17°$ (-0.81 cm.$^{-1}$) and $g = 2.05$. This suggests that there may be a pairwise interaction between $FeBr_4^-$ ions in the lattice.

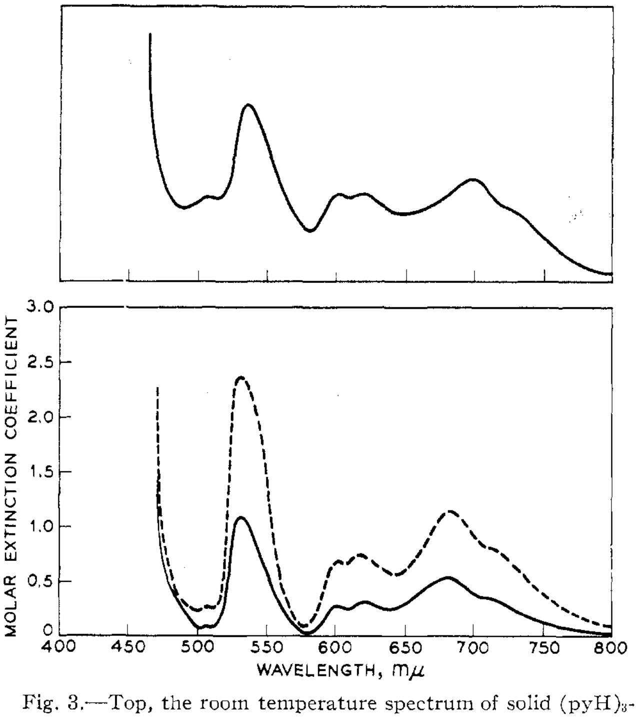

Fig. 3.—Top, the room temperature spectrum of solid $(pyH)_3Fe_2Cl_9$; bottom, the spectrum of $(pyH)_3Fe_2Cl_9$ (- - -) and $(CH_3)_4NFeCl_4$ (——) in acetone solution.

Table III

Isomer Shifts in the Mössbauer Spectra of Iron Halides

Compound	Isomer shift, cm./sec.[a]
$(pyH)_3Fe_2Cl_9$	0.047 ± 0.001
$(CH_3)_4NFeCl_4$	.045 ± .001
$(pyH)_3Fe_2Br_9$	.051 ± .001
β-$Cs_3Fe_2Cl_9$	.052 ± .002
α-$Cs_3Fe_2Cl_9$	.065[b] ± .002
$FeCl_3$ (octahedral)[c]	.069 ± .001
$FeBr_3$ (octahedral)[c]	.071 ± .002

[a] The shifts reported here are with respect to the resonance observed in a dilute solution of iron in chromium. All spectra were determined at 78°K. except that of β-$Cs_3Fe_2Cl_9$, which was run at 20°K. According to G. K. Wertheim (private communication) the isomer shift of β-$Cs_3Fe_2Cl_9$ at 78°K. is expected to be only very slightly different from that observed at 20°K. [b] The isomer shift of 0.065 is the average of two components observed at 0.049 and 0.081. The splitting presumably is due to the nuclear quadrupole coupling. [c] Unpublished work of D. N. E. Buchanan and G. K. Wertheim.

The most obvious conclusion to be drawn from the above discussion is that $(pyH)_3Fe_2Cl_9$ and $(pyH)_3Fe_2Br_9$ do not contain μ-trihalo dimeric anions. This is confirmed by the optical and Mössbauer spectra of these compounds. Figure 3 (top) shows the room temperature electronic spectrum of a thin film of $(pyH)_3Fe_2Cl_9$. The spectrum is unchanged on dissolving the compound in acetone (Fig. 3, bottom) and is identical with the spectrum of $(CH_3)_4NFeCl_4$ in acetone shown in the bottom of Fig. 3. This demonstrates that at least one of the iron atoms in $(pyH)_3Fe_2Cl_9$ is present as $FeCl_4^-$. The further fact, illustrated in the bottom of Fig. 3, that a solution of $(pyH)_3Fe_2Cl_9$ in acetone has an optical density in the $FeCl_4^-$ bands twice that of an equimolar solution of $(CH_3)_4NFeCl_4$ is only indirect evidence that *both* iron atoms are present as $FeCl_4^-$ anions in the solid. Corresponding results are obtained with $(pyH)_3Fe_2Br_9$ and $(CH_3)_4NFeBr_4$. An attempted assignment of the bands in the spectra of these compounds is presented in the Appendix.

The question as to the coördination of the second iron atom in the pyridinium salts is settled by their Fe^{57} Mössbauer spectra. In Table III we list the isomer shifts[6] and quadrupole splitting of the compounds of interest as well as $FeCl_3$ and $FeBr_3$. The occurrence of only a single resonance in $(pyH)_3Fe_2Cl_9$ and $(pyH)_3Fe_2Br_9$ and also in the β-phase of $Cs_3Fe_2Cl_9$ shows that both iron atoms in these compounds have similar coördination. The magnitude of the isomer shift (compare with $(CH_3)_4NFeCl_4$, $FeCl_3$, and $FeBr_3$) and the lack of quadrupole splitting indicates that the coördination about the iron atoms is tetrahedral. Thus the pyridinium salts, and also probably the β-phase of $Cs_3Fe_2Cl_9$, should be formulated as follows: $[(pyH)FeCl_4]_2\cdot(pyH)Cl$, $[(pyH)FeBr_4]_2\cdot(pyH)Br$, and $[CsFeCl_4]_2\cdot CsCl$. This is perhaps not too startling when one considers the great stability of the FeX_4^- anion. Also the structures of these compounds are in a way analogous with the structures of compounds such as $Cs_3As_2Cl_9$, which is known not to contain a dimeric anion, and Cs_3CoCl_5, which contains the $CoCl_4^-$ anion.

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(6) O. C. Kistner and A. W. Sungar, *Phys. Rev. Letters*, **4**, 412 (1960) L. R. Walker, G. K. Wertheim, and V. Jaccarino, *ibid.*, **6**, 98 (1961).

TABLE IV

THE FREQUENCIES AND POSSIBLE ASSIGNMENTS OF THE TRANSITIONS OF THE $FeCl_4^-$ AND $FeBr_4^-$ IONS

Free ion terms, cm.$^{-1}$ [a]	Frequency $FeCl_4^-$, cm.$^{-1}$	Frequency $FeBr_4^-$, cm.$^{-1}$	Assignment following Jørgensen	Assignment following Furlani and Furlani
$^6S \rightarrow {}^4G$, 32,000	13,700	11,950		$^6A_1 \rightarrow {}^4T_1$ (G)
$^6S \rightarrow {}^4P$, 35,100	14,600	12,650	$^6A_1 \rightarrow {}^4T_1$ (G)	$^6A_1 \rightarrow {}^4T_2$ (G)
$^6S \rightarrow {}^4D$, 38,500	15,650	13,250		$^6A_1 \rightarrow {}^4A_1$ (G), ^4E (G)
$^6S \rightarrow {}^4F$, 52,100	16,150	13,870	$^6A_1 \rightarrow {}^4T_2$ (G)	$^6A_1 \rightarrow {}^4T_2$ (D)[b]
	16,500	14,300		$^6A_1 \rightarrow {}^4E$ (D)[b]
	17,800	15,730		$^6A_1 \rightarrow {}^4T_1$ (P)[b]
	18,800	16,350	$^6A_1 \rightarrow {}^4A_1$ (G), ^4E (G)	$^6A_1 \rightarrow {}^4A_2$ (F)
	19,750	17,200	$^6A_1 \rightarrow {}^4T_2$ (D)	$^6A_1 \rightarrow {}^4T_1$ (F)
	22,100	(20,000)[c]	$^6A_1 \rightarrow {}^4E$ (D)	$^6A_1 \rightarrow {}^4T_2$ (F)

[a] C. E. Moore, "Atomic Energy Levels," Vol. II, United States Department of Commerce Circular No. 467, 1952, p. 65. [b] These bands could easily be interchanged. [c] While this band is not observed in $FeBr_4^-$ due to the strong edge absorption, it does appear that the $FeBr_4^-$ bands are uniformly displaced about 2000 cm.$^{-1}$ to lower frequency with respect to $FeCl_4^-$ and that the ninth band of $FeBr_4^-$ would probably come at 20,000 cm.$^{-1}$

We believe that the compounds $(QH)_4Fe_2Cl_{10}$ and $(pyH)_5FeCl_{11}$, which Earnshaw and Lewis found to have very similar magnetic properties to $(pyH)_3Fe_2Cl_9$, also contain only tetrahedrally coördinated iron rather than chloro-bridged binuclear anions.

The Mössbauer spectrum of the α-phase of $Cs_3Fe_2Cl_9$ shows two barely resolvable resonances of similar intensity. The occurrence of two resonances is believed to be due to quadrupole splitting of a single line. We rule out the possibility that the two resonances are due to iron ions in different coördinations since if the line at 0.81 cm./sec. is considered to be an unsplit resonance, it would lie outside the range observed for weak field ferric iron. This and the magnitude of the isomer shift (compare with $FeCl_3$) indicates that the iron atoms in α-$Cs_3Fe_2Cl_9$ are both equivalent and surrounded by a distorted octahedron of Cl^- ions, in agreement with the X-ray results.

Appendix

The fact that spectroscopic studies of iron tetrahalide complexes have so far been limited to poorly resolved room temperature solution spectra prompts us to present in this Appendix the low temperature (20°K.) spectra of thin films of $(pyH)_3Fe_2Cl_9$ and $(pyH)_3Fe_2Br_9$ (Fig. 4) together with an attempted assignment of the bands.

Table IV lists an assignment of the spectra in Fig. 4 analogous to Jørgensen's assignment[7] of the room temperature solution spectrum of $FeCl_4^-$ (Jørgensen assigned only one transition to the bracketed multiplets in Table IV). This assignment is based on the Orgel diagram for a d^5 ion in an octahedral or tetrahedral field (Fig. 5). The Jörgensen assignment leads to the strongest bands in the spectrum of $FeCl_4^-$ being assigned to transitions to states which are theoretically field independent, in a way reminiscent of the assignment of the bands in octahedral MnX_6^{-4}, where the sharpest but not necessarily the strongest bands are field independent.[8] The spectrum of $FeBr_4^-$ shows that this is probably not a very good criterion for assignment in tetrahedral molecules where bands can be orbitally allowed, for in this molecule the $^6A_1 \rightarrow {}^4T_1$ (G) (Jørgensen) field *dependent* band is the strongest in the spectrum.

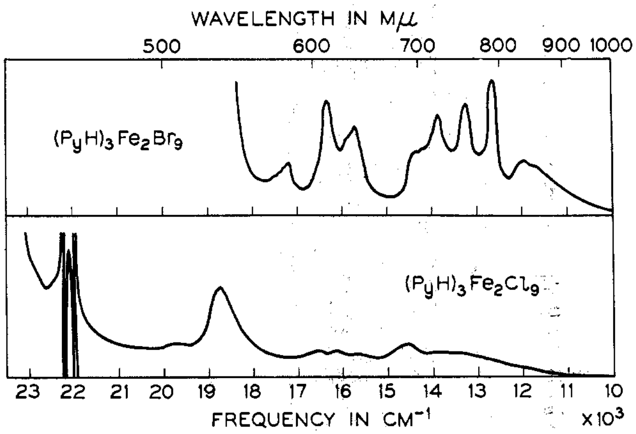

Fig. 4.—The absorption spectra of solid $(pyH)_3Fe_2Br_9$ (upper) and solid $(pyH)_3Fe_2Cl_9$ (lower) at 20°K.

The origin of the large splittings within each multiplet of the spectra of $FeCl_4^-$ and $FeBr_4^-$ is puzzling. The average splitting of 600–1000 cm.$^{-1}$ is much too large to be vibronic (estimated to be 200–400 cm.$^{-1}$) and one does not expect spin-orbit splittings of the free ion (estimated to be 200–300 cm.$^{-1}$ in Fe^{+3}) to be magnified in the complex.[9] That the splittings are due to a site symmetry lower than T_d seems improbable because the spectra of solid $(pyH)_3Fe_2Cl_9$ and of $FeCl_4^-$ in acetone solution are identical and there is no reason to suspect $FeCl_4^-$ in solution not to be tetrahedral.

An alternate assignment of the FeX_4^- spectrum can be made which parallels that made by Furlani and Furlani for MnX_4^{-2}.[10] In this alternate assignment each of the nine widely spaced bands of FeX_4^- is assigned in the way shown in Table IV to one of the nine sextuplet → quartet transitions predicted by Fig. 5. It is to be noticed that the orbitally allowed bands ($A_1 \rightarrow T_2$) in this assignment are among the strongest in the spectrum. The only unexplained splittings in this as-

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(7) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p. 292.

(8) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

(9) J. Owen, *Proc. Roy. Soc.* (London), **A227**, 183 (1955).

(10) C. Furlani and A. Furlani, *J. Inorg. Nucl. Chem.*, **19**, 51 (1960).

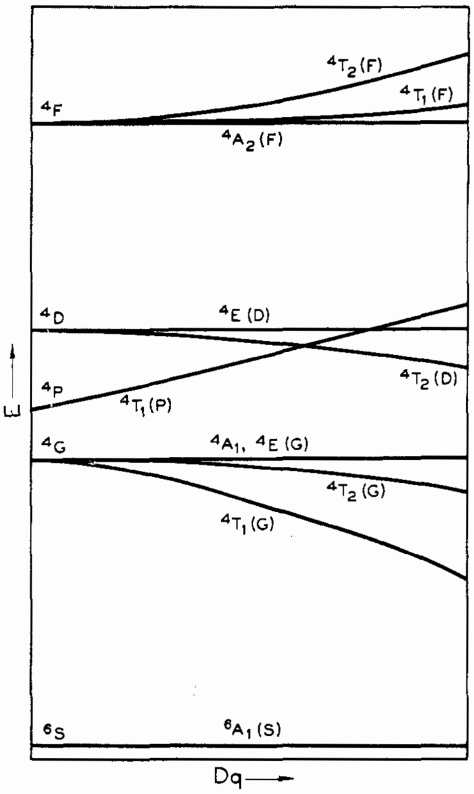

Fig. 5.—The Orgel diagram showing how the free ion terms of a d^5 ion in a tetrahedral crystal field are split as *Dq* increases.[10]

signment are 150–200 cm.$^{-1}$, which might be due to either vibrations or spin-orbit interaction.

It is interesting to note that the "field independent" bands $^6A_1 \rightarrow {}^4A_2$, ^4E (G), ^4E (D), $^4A_2$ (F) are actually shifted on going from $FeCl_4^-$ to $FeBr_4^-$. As a matter of fact, according to either assignment, there has occurred a tremendous shift of the field independent frequencies in the complexes as compared with the free ion energies (Table IV). Depressions of the free ion term values in complexes usually amount to 10–20% and are ascribed to the effect of covalent bonding on the values of the B and C integrals.[11] We apparently have in the iron tetrahalides depressions of the free ion term values of 50–70%, indicating powerful covalency, in contrast to the MnX_4^{-2} ion where the depressions of the free ion term values are 10–20%. This conclusion is further strengthened by the following reasoning. On replacing $4Cl^-$ with $4Br^-$ in the iron complexes, *Dq* decreases and the transitions are expected to move to slightly higher frequencies. However, the covalency also increases on replacing Cl^- with Br^- (Br^- is before Cl^- in the nephelauxetic series) so that all levels are lowered in frequency, and apparently this factor is the dominant one since the $FeBr_4^-$ spectrum is shifted ~2000 cm.$^{-1}$ to *lower* frequencies compared to that of $FeCl_4^-$.

Considering the two most prominent features of the splitting pattern, it is clear that neither of the above assignments based on the Orgel diagram can be made to yield even semiquantitative agreement with experiment. Thus, the largest split observed in the spectrum (2400 cm.$^{-1}$ between the 19,750 and 22,100 cm.$^{-1}$ bands of the tetrachloride) is predicted to be among the smallest in the Jørgensen assignment. In the Furlani assignment, while the split between the last two bands is predicted to be large, it should also be slightly smaller than that between the first two bands which are, in fact, split by only $^1/_3$ the frequency of the last two bands.

The value of the Orgel diagram in assigning the bands of $FeCl_4^-$ and $FeBr_4^-$ lies in its prediction of the number of ligand field bands to be expected and their symmetry in T_d and hopefully gives some idea as to their order. Similar difficulties in the quantitative assignment of the bands of tetrahedral $NiCl_4^{-2}$ and $CoCl_4^{-2}$ ions were experienced by Buffagni and Dunn.[12]

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(11) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, 1961, pp. 189–190.

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