680. Complex Halides of the Transition Metals. Part II.[1]
Tetrahedral Iron Complexes.

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The preparation of complex halides of the type $R_2[Fe^{II}Hal_4]$, where $R = [Et_4N]^+$ or $[Ph_3MeAs]^+$ and Hal = Cl, Br, or I, is reported. Conductivity, spectra, magnetic susceptibility, and crystal structure have been studied and comparison with those of similar complexes of other bivalent transition metals leads to the conclusion that $[Fe^{II}Hal_4]^{2-}$ ions have a tetrahedral structure. Spectra of $[Fe^{III}Cl_4]^-$ and $[Fe^{III}Br_4]^-$ are also reported.

CRYSTAL-FIELD theory predicts that spin-free Fe^{II} with six d-electrons will form tetrahedral complexes in which the ground state has the electronic configuration $d_\gamma{}^3 d_\epsilon{}^3$. The unsymmetrical filling of the d_γ-sub-level in such an arrangement of non-bonding electrons is expected to lead to slight distortion from a regular tetrahedral structure. However, if the ligand-field effects are of major importance in determining the stereochemistry of an Fe^{II} complex, then the crystal-field stabilisation energy will favour the formation of octahedral complexes rather than tetrahedral ones, although the difference in stabilisation is only small, being of the order of 3 kcal. mole^{-1}. In accordance with this prediction the existence of tetrahedral complexes of Fe^{II} has not yet been proved although recently complexes with triphenylphosphine [2,3] and triphenylarsine [2] have been described and this structure has been proposed for them. These complexes are of two types. The first are non-electrolytes of formula $FeX_2,2PPh_3$, where X = Cl, Br, or I, similar to the compounds $NiX_2,2PPh_3$ which have been shown to be tetrahedral in structure although greatly distorted.[4] The second are electrolytes which appear to contain the cations $[Fe(PPh_3)_4]^{2+}$ and $[Fe(AsPh_3)_4]^{2+}$, and the compound of empirical formula $FeI_2,2AsPh_3$, which is ionic in nitrobenzene solution, so that a possible structure is $[Fe(AsPh_3)_4][FeI_4]$.

TABLE 1. *Properties of tetrahalogeno-complexes of* Fe^{II}.

Compound	μ_{eff} at 20° (B.M.)	Molar conductivity in Ph·NO$_2$ at 25°	Compound	μ_{eff} at 20° (B.M.)	Molar conductivity in Ph·NO$_2$ at 25°
$[Ph_3MeAs]_2[FeCl_4]$ ...	5·33	58 (c = 0·0005M)	$[Et_4N]_2[FeBr_4]$ ...	5·46	—
$[Et_4N]_2[FeCl_4]$	5·40	—	$[Ph_3MeAs]_2[FeI_4]$...	5·40	53 (c = 0·001M)

In Part I [1] the preparation and properties of tetrahedral nickel halide complexes of the type $R_2[M^{II}Hal_4]$, where $R = [Et_4N]^+$ or $[Ph_3MeAs]^+$ and Hal = Cl, Br, or I, were described and the factors which influence the stereochemistry of complex ions discussed. It was shown that not only are ligand-field effects of importance in determining stereochemistry of complexes but also those arising from covalent bonding. Thus in circumstances favourable to the stability of the ions $[MHal_4]^{2-}$, *e.g.*, lowering of the solvation energy of the metal ion, such tetrahedral ions can be formed with certain bivalent metals of the first transition series and compounds containing them have been isolated. In this way, by using ethyl alcohol as solvent, salts of the anions $[FeHal_4]^{2-}$ have been prepared. The cations $[Et_4N]^+$ and $[Ph_3MeAs]^+$ were used but it was not possible to obtain each tetrahalogeno-complex with both; *e.g.*, $[Et_4N]_2[FeI_4]$ could not be prepared by the above method, only tetraethylammonium iodide crystallising from a mixture of this salt and ferrous iodide in ethyl alcohol. This was due, presumably, to the relative lattice energies of the required complex salt and tetraethylammonium iodide and the stability of the complex anion.

In Table 1 are given the properties of the compounds which have been prepared. All

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[1] Part I, Gill and Nyholm, *J.*, 1959, 3997.

[2] Naldini, *Gazzetta*, 1960, **90**, 361.

[3] Hieber and Floss, *Z. anorg. Chem.*, 1957, **291**, 314.

[4] Venanzi, *J.*, 1958, 719; Powell and Venanzi, *Proc. Chem. Soc.*, 1956, 6.

form cream-coloured crystals, and *X*-ray studies have shown that the arsonium salt of $[FeCl_4]^{2-}$ is isomorphous with those of $[MnCl_4]^{2-}$, $[MnBr_4]^{2-}$, $[CoCl_4]^{2-}$,$[CoBr_4]^{2-}$, $[NiCl_4]^{2-}$, and $[ZnCl_4]^{2-}$ as reported in Part I [5] and that the tetraethylammonium salt is isomorphous with those of $[MnCl_4]^{2-}$ and $[NiCl_4]^{2-}$, showing that $[FeCl_4]^{2-}$ is tetrahedral in the same way as these reference ions have been shown to be.[1,5] Similarly the tetraethylammonium salt of $[FeBr_4]^{2-}$ is isomorphous with that of $[MnBr_4]^{2-}$. The arsonium salt of $[FeI_4]^{2-}$ crystallises in leaflets as do the isomorphous series $[MnI_4]^{2-}$, $[CoI_4]^{2-}$, $[NiI_4]^{2-}$, $[ZnI_4]^{2-}$.[1] The crystal properties of the $[FeHal_4]^{2-}$ salts therefore undoubtedly show that these complex anions are all tetrahedral and a detailed study of them will be reported later by Dr. P. J. Pauling.

While the magnetic moments of bivalent iron complexes cannot be expected to prove their stereochemistry they are of interest. Fe^{2+} has a $^5D_4$ ground state which under the influence of the cubic field of a tetrahedral arrangement of ligands splits into a lower non-magnetic doublet (^5E) and an upper triplet ($^5T_2$), so that magnetic behaviour similar to that of octahedral Cu^{II} is to be expected.[6,7] Thus only a small orbital contribution to the magnetic moment above that of the spin-only value of 4·90 B.M. is predicted for a near-regular tetrahedral complex. The μ_{eff} values given in Table 1 show that the moments at room temperature are high even when "mixing-in" of the first excited level by spin–orbit coupling is allowed for by the formula $\mu = \mu_0 (1 - 2\lambda/\Delta)$, provided reasonable assumptions are made for the values of λ and Δ, of the order of -80 and 3000 cm.$^{-1}$, respectively, giving $\mu_{eff} = \sim 5{\cdot}20$ B.M. The moment of $[FeCl_4]^{2-}$ in the tetraethylammonium salt has been measured over the temperature range $-178°$ to $+22°$, giving a θ value of zero; the plot of magnetic susceptibility against temperature is shown in Fig. 1.

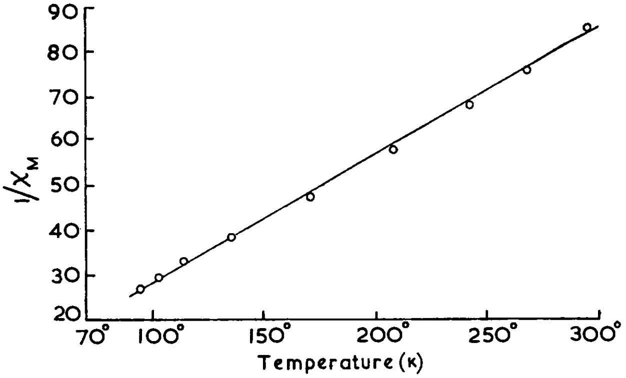


FIG. 1. *Plot of* $1/\chi_M$ *against temperature for* $[Et_4N]_2[FeCl_4]$.

It is also to be expected that there would be an increase in the magnetic moment in the order Cl < Br < I, as Δ decreases in this order and so increases the spin–orbit coupling. No trend of this kind was observed, the moments of the three complex ions being within the range of experimental error at room temperature. This seems to exclude an explanation of the high magnetic moments in terms of contribution from the $^5T_2$ triplet. Since spectroscopic measurements showed that there could be no more than traces of Fe^{III} complexes present in these Fe^{II} compounds, the only explanation of the high magnetic moments could be behaviour intermediate between that of tetrahedral Fe^{II} and that of the field-free Fe^{2+} ion. If the ligand field due to the halide ions were extremely weak it is feasible that the Fe^{II} atom would tend a little towards behaving as a field-free Fe^{2+} ion, for which the magnetic moment, calculated from the formula, $\mu = g\sqrt{J(J+1)}$, is 6·67 B.M., and the moment of the $[FeX_4]^{2-}$ would thus be raised above the value predicted by theory for a tetrahedral complex.

[5] Porai-Koshits, *Kristallografiya*, 1956, **1**, 291; Brehler, *Z. Krist.*, 1957, **109**, 68.
[6] Van Vleck, *Phys. Rev.*, 1932, **41**, 208.
[7] Figgis and Harris, *J.*, 1959, 855.

The conductivities of the $[FeCl_4]^{2-}$ and $[FeI_4]^{2-}$ salts show that they are uni-bivalent electrolytes in nitrobenzene, as expected. However, some dissociation of $[FeI_4]^{2-}$ must occur in organic solvents as the solutions have the characteristic dark colour of ferrous iodide in such solvents, presumably owing to formation of free iodine, although the conductivity in nitrobenzene shows that dissociation cannot occur to any large extent in that solvent.

FIG. 2. *Absorption spectra of* (1) $[FeCl_4]^{2-}$ (0·05M), (2) *as* (1) *but with* $10^{-1}\varepsilon$, (3) $[FeCl_4]^-$ (0·1M), *and* (4) *as* (3) *but with* $10^{-1}\varepsilon$, *all in dimethylformamide.*

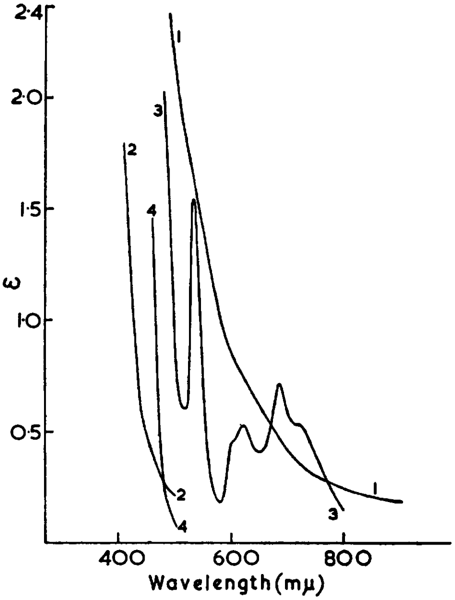
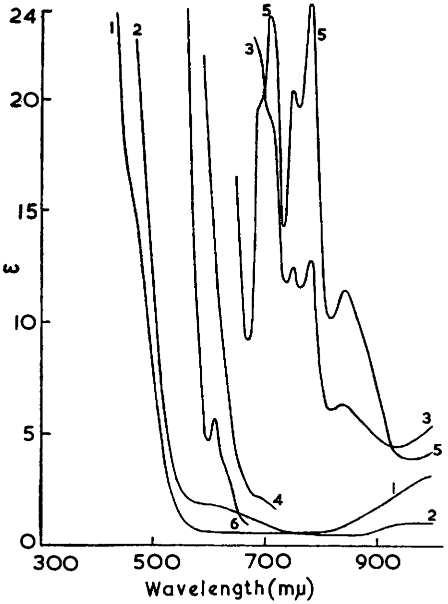


FIG. 3. *Absorption spectra of* (1) $[FeBr_4]^{2-}$ (0·01M), (2) *as* (1) *but with added* Br^-, (3) $[FeBr_4]^-$ (0·006M), (4) *as* (3) *but with* $10^{-1}\varepsilon$, (5) *as* (3) *but with added* Br^-, *and* (6) *as* (5) *but with* $10^{-1}\varepsilon$, *all in dimethylformamide.*



The spectra of $[FeCl_4]^{2-}$ and $[FeBr_4]^{2-}$* were measured in deoxygenated dimethylformamide and compared with those of $[FeCl_4]^-$ and $[FeBr_4]^-$ in the same solvent. The effect on the spectra of the addition of excess of halide ions necessary to obtain a constant value of ε was also studied; the observed results are shown in Fig. 2 and the values of $\varepsilon_{max.}$ and $\lambda_{max.}$ given in Table 2. In the spectrum of the octahedral hexa-aquo-complex of Fe^{2+} one band occurs at 10,400 cm.$^{-1}$ and three much weaker ones at 19,800—25,900 cm.$^{-1}$.[8] The former has been assigned to the transition $^5T_2 \longrightarrow {}^5E$ and thus in tetrahedral complexes of Fe^{II} the *d–d* band can be expected at long wavelengths well outside the visible

TABLE 2. *Spectra of tetrahalogeno-complexes of* Fe^{III} *in the visible region.*

Ion	$\varepsilon_{max.}$	$\lambda_{max.}$	Concn. of soln. in H·CO·NMe$_2$ (M)	Ion	$\varepsilon_{max.}$	$\lambda_{max.}$	Concn. of soln. in H·CO·NMe$_2$ (M)
$[FeCl_4]^-$	0·53	722	0·1				
	0·72	685					
	0·52	620					
	(sh.)	607					
	1·54	533					
$[FeBr_4]^-$	6·3	835	0·006	$[FeBr_4]^-$ + excess Br^-	11·4	844	0·006
	12·8	779			24·0	779	
	12·4	750			20·4	752	
	(sh.)	713			23·7	713	
	(sh.)	684			(sh.)	688	
					57·3	608	

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* As the tetraethylammonium salts.

[8] Jørgensen, *Acta Chem. Scand.*, 1954, **8**, 1502.

region. Examination of the spectrum of $[FeCl_4]^{2-}$ between 10,000 and 7000 cm.$^{-1}$ (in solution) and between 7800 and 3000 cm.$^{-1}$ in a Nujol mull showed that this transition occurs below 3000 cm.$^{-1}$. The other bands of $[Fe(H_2O_6)]^{2+}$ have not been definitely assigned because the energy levels of the ^3P, ^3H, and ^3F states are very close together. In the case of the tetrahedral complexes very intense charge-transfer bands occur beyond 20,000 cm.$^{-1}$; as large dilutions are necessary to measure them in solution it is considered that the results obtained are unlikely to be meaningful and they are not included in this paper.

Comparison of the spectra of the Fe^{II} complexes with those of the Fe^{III} complexes shows that the former are not oxidised in solution. Within the wavelength range studied halide ions had little or no effect on the spectra of $[FeCl_4]^{2-}$, $[FeBr_4]^{2-}$, and $[FeCl_4]^-$, but had considerable effect on that of $[FeBr_4]^-$. The lack of change produced in the spectra of the former ions and the increase in $\varepsilon_{max.}$ in that of the last are taken to indicate that no significant concentration of $[MX_6]^{x-}$ is formed under these conditions, as this should considerably decrease the value of the extinction coefficient. The change in the spectrum of $[FeBr_4]^-$ must then be due either to solvation of the complex ion or to displacement of Br^- by dimethylformamide, which is at least partially counteracted by the addition of excess of halide ions. The spectrum of $[FeBr_4]^-$ has not previously been reported; that of $[FeCl_4]^-$ in diethyl ether [9] and in di-isopropyl ether [10] has been studied but not interpreted. The spectra of $[FeCl_4]^-$ in these solvents and in dimethylformamide are very similar except that the band observed at 500 mμ in the ethers does not appear in dimethylformamide solution. A discussion of the spectra of both the chloro- and the bromo-complexes of Fe^{III} will be published by Dr. T. M. Dunn.

EXPERIMENTAL

Preparation of Ferrous Compounds.—All were prepared by mixing, in an atmosphere of nitrogen, fairly concentrated solutions of the calculated amounts of the appropriate ferrous halide and triphenylmethylarsonium or tetraethylammonium halide in ethyl alcohol which had been boiled to remove oxygen. The products crystallised immediately and no precautions to prevent oxidation of the chloro- and bromo-compounds were necessary if filtration was rapid. For the iodo-compound it was necessary to carry out all work in nitrogen. None of the compounds was recrystallised as decomposition occurred in hot alcohol. Thus were obtained: *bis(triphenylmethylarsonium) tetrachloroferrate*(II), cream needles stable to oxidation when dry (Found: C, 54·0; H, 4·6; Cl, 17·1. $C_{38}H_{36}As_2Cl_4Fe$ requires C, 54·3; H, 4·3; Cl, 16·9%); *bis(tetraethylammonium) tetrachloroferrate*(II), cream needles stable to oxidation when dry (Found: C, 42·4; H, 8·2. $C_{16}H_{40}Cl_4FeN_2$ requires C, 42·0; H, 8·8%); *bis(tetraethylammonium) tetrabromoferrate*(II), cream needles stable to oxidation when dry (Found: C, 30·2; H, 6·4. $C_{16}H_{40}Br_4FeN_2$ requires C, 30·0; H, 6·3%); *bis(triphenylmethylarsonium) tetraiodoferrate*(II), cream leaflets readily oxidised in air (Found: C, 38·1; H, 3·5; I, 41·1. $C_{38}H_{36}As_2FeI_4$ requires C, 37·9; H, 3·0; I, 42·2%).

Preparation of Ferric Compounds.—These were prepared in the same way as those of Fe^{II} except that no precautions against oxidation were necessary. Recrystallisation from ethyl alcohol gave *bis(tetraethylammonium) tetrachloroferrate*(III), yellow needles (Found: C, 29·8; H, 6·4. $C_8H_{20}Cl_4FeN$ requires C, 29·3; H, 6·1%), and *tetrabromoferrate*(III), brown needles (Found: C, 19·1; H, 4·2; Br, 63·2. $C_8H_{20}Br_4FeN$ requires C, 18·9; H, 4·0; Br, 63·2%).

Absorption Spectra.—Solutions of the Fe^{II} complexes were prepared by direct distillation, under nitrogen, of dimethylformamide into the cell containing a known weight of the compound. The spectra were obtained with a Unicam S.P. 500 spectrophotometer.

Magnetic susceptibilities were determined by the Gouy method.[11]

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[9] Friedman, *J. Amer. Chem. Soc.*, 1952, **74**, 5.

[10] Metzler and Myers, *J. Amer. Chem. Soc.*, 1950, **72**, 3776.

[11] Figgis and Nyholm, *J.*, 1959, **331**.