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Some Mixed-Ligand Iron(III) Complexes Produced by Reactions of Tris(acetylacetonato)iron(III) with Hydrogen Halides in Organic Solvents

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Tris(acetylacetonato)iron(III) $Fe(acac)_3$ reacts with an equimolar and double molar amounts of a hydrogen halide in dichloromethane to afford the mixed-ligand iron(III) complexes, $FeX(acac)_2$ and $FeX_2(acac)H_2O$, respectively, where X is Cl or Br. They are all high-spin iron(III) complexes and exist as monomeric five-coordinate molecules in non-coordinating solvents, but behave as uni-univalent electrolytes in methanol. Further reactions of $FeX_2(acac)H_2O$ with an excess of hydrogen halides in dichloromethane followed by the addition of twice as many moles of 1,10-phenanthroline produced $[FeX_2(phen)_2]X$. The reactions of $FeX_2(acac)H_2O$ with excesses of pyridine and 2,2′-bipyridine in tetrahydrofuran gave the six-coordinate complexes $FeX_2(acac)(py)_2$ and $FeX_2(acac)(bipy)$, respectively.

In the present series of studies on the reactions of metal acetylacetonates with bromine and hydrogen bromide in organic solvents, different kinds of products have previously been isolated and characterized.[1] For instance, dibromo(acetylacetone)cobalt(II) $CoBr_2(acacH)$, a novel complex containing an acetylacetone molecule as the bidentate ligand, was produced by the reaction of $Co(acac)_3$ with bromine in dichloromethane. However, an attempt to isolate the intermediary cobalt(III) complex, assumed to be a precursor of the cobalt(II) complex, was unsuccessful.[2] On the other hand, $Mn(acac)_3$ is reduced by hydrogen halides in organic solvents, ultimately resulting in manganese(II) chloride, bromide, or $Mn(acac)_2$, and the intermediary Mn(III) products, $MnX(acac)_2$, where X is Cl, Br, or I, could be isolated from the equimolar reactions.[3]

Collman[4] demonstrated that halogen substitution at the central carbon atom of metal acetylacetonate can be successfully carried out under electrophilic substitution reaction conditions. Thus, $Fe(acac)_3$ was directly brominated with *N*-bromosuccinimide in chloroform[5] or with bromine in buffered acetic acid.[6] On the contrary, one acetylacetonate ring of the acid labile tris-chelate was displaced in the reaction with picric acid in benzene–ethanol, affording the cationic iron(III) complex, $[Fe(acac)_2(H_2O)_2]$picrate.[7] The present paper reports some mixed-ligand iron(III) complexes which were isolated and characterized as intermediary products in the reactions between $Fe(acac)_3$ and hydrogen halides in organic solvents.[8]

Experimental

Materials. Tris(acetylacetonato)iron(III) was prepared and recrystallized according to Ref. 9. Found: Fe, 15.85; C, 51.12; H, 6.12%. Hydrogen chloride was generated by the reaction of hydrochloric acid with sulfuric acid, dried over calcium chloride, and dissolved in dichloromethane (*ca.* 0.2 mol/l). Hydrogen bromide was produced by the reaction between tetralin and bromine, dried over calcium bromide, and dissolved in dichloromethane (*ca.* 0.2 mol/l). Dichloromethane and acetonitrile were distilled twice over phosphorus pentaoxide. Benzene was distilled over metallic sodium. Nitromethane and methanol were also distilled.

The Reactions of Tris(acetylacetonato)iron(III) with Hydrogen Halides. A solution of $Fe(acac)_3$ in dichloromethane was placed in a three-necked flask equipped with a buret, a glass tube containing calcium chloride, and another outlet tube. A solution (*ca.* 0.1 mol/l) of hydrogen chloride or bromide in dichloromethane was added dropwise from the buret to the above solution with magnetic stirring. The usual precautions were taken for preventing moisture during filtration of the reaction product.

Isolation of Chlorobis(acetylacetonato)iron(III): To a solution of $Fe(acac)_3$ in dichloromethane was added a solution of an equimolar amount of hydrogen chloride in dichloromethane from the buret. After the reaction, a dark red precipitate was separated out by the addition of petroleum ether. The precipitate was filtered, washed with petroleum ether and dried *in vacuo*. Found: Fe, 19.88; Cl, 12.40; C, 41.43; H, 4.88%. Calcd for $FeCl(acac)_2=C_{10}H_{14}O_4ClFe$: Fe, 19.29; Cl, 12.25; C, 41.15; H, 4.87%.

Isolation of Bromobis(acetylacetonato)iron(III): A dichloromethane solution of $Fe(acac)_3$ was allowed to react with an equimolar amount of hydrogen bromide in dichloromethane. The initially red-brown solution turned to dark red. The solution was concentrated to a quarter of its original volume, whereupon a red-brown precipitate separated out. The precipitate was filtered, washed with petroleum ether and dried *in vacuo*. Found: Fe, 17.08; Br, 24.37; C, 35.67; H, 4.23%. Calcd for $FeBr(acac)_2=C_{10}H_{14}O_4BrFe$: Fe, 16.72; Br, 23.93; C, 35.96; H, 4.23%.

Isolations of Dichloro(acetylacetonato)aquairon(III) and Dibromo(acetylacetonato)aquairon(III): When a red-brown solution of $Fe(acac)_3$ in dichloromethane was forced to react with twice as many moles of hydrogen chloride or bromide in dichloromethane, its color turned to dark red. Petroleum ether was added slowly to the reaction mixture producing a dark red precipitate. This was filtered, washed with petroleum ether and dried *in vacuo*. Found for the chloro complex: Fe, 23.09; Cl, 28.86; C, 24.73; H, 3.77%. Calcd for $FeCl_2(acac)H_2O=C_5H_9O_3Cl_2Fe$: Fe, 22.90; Cl, 29.07; C, 24.62; H, 3.72%. Found for the bromo complex: Fe, 16.90; Br, 47.86; C, 18.19; H, 2.80%. Calcd for $FeBr_2(acac)H_2O=C_5H_9O_3Br_2Fe$: Fe, 16.78; Br, 48.02; C, 18.05; H, 2.73%. The same compounds were also produced from the equimolar reactions between $FeX(acac)_2$ and HX (X=Cl or Br) in dichloromethane in a manner similar to that described above.

Further Reactions of $FeCl_2(acac)H_2O$ and $FeBr_2(acac)H_2O$ with Excess Hydrogen Chloride and Bromide. Isolation of FeX_3 as $[FeX_2(phen)_2]X$, where X is Cl or Br: To a suspension of $FeX_2(acac)H_2O$ (X=Cl or Br) in dichloromethane was added an excess of hydrogen chloride or bromide dissolved in the same solvent, whereupon a transparent solution was

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produced. Twice as many moles of 1,10-phenanthroline as that of the iron(III) complex used were dissolved in a minimum quantity of dichloromethane and added to the above clean solutions to separate out the precipitates, which were yellow-brown (chloride) and red-brown (bromide), respectively. The precipitates were recrystallized from ethanol and dried *in vacuo*. Found for chloride: C, 51.13; H, 3.08; N, 9.94%. Calcd for $[FeCl_2(phen)_2]Cl = C_{24}H_{16}N_4Cl_3Fe$: C, 51.60; H, 2.89; N, 10.03%. Found for bromide: C, 44.08; H, 3.04; N, 8.21%. Calcd for $[FeBr_2(phen)_2]Br = C_{24}H_{16}N_4Br_3Fe$: C, 43.94; 2.46; N, 8.54%.

Preparation of $FeX_2(acac)(py)_2$ and $FeX_2(acac)(bipy)$, where X is Cl or Br. To tetrahydrofuran solutions of $FeX_2(acac)H_2O$ (X=Cl or Br) was added an excess of pyridine or 2,2′-bipyridine in tetrahydrofuran. The solution was stirred magnetically for about 1 hour, whereupon a precipitate gradually separated out. Found for the dichlorobispyridine complex: Fe, 14.43; Cl, 18.45; C, 46.89; H, 4.52; N. 7.09%. Calcd for $FeCl_2(acac)(py)_2 = C_{15}H_{17}O_2N_2Cl_2Fe$: Fe, 14.54; Cl, 18.46; C, 46.91; H, 4.46; N, 7.29%. Found for the dibromobispyridine complex: Fe, 11.29; Br, 33.51; C, 39.07; H, 3.79; N, 5.91%. Calcd for $FeBr_2(acac)(py)_2 = C_{15}H_{17}O_2N_2Br_2Fe$: Fe, 11.81; Br, 33.79; C, 38.10; H, 3.62; N, 5.92%. Found for the dichloro(2,2′-bipyridine) complex: Fe, 14.44; Cl, 18.46; C, 47.09; H, 4.25; N, 7.39%. Calcd for $FeCl_2(acac)(bipy) = C_{15}H_{15}O_2N_2Cl_2Fe$: Fe, 14.62; Cl, 18.56; C, 47.16; H, 3.96; N, 7.33%. Found for the dibromo(2,2′-bipyridine) complex: Fe, 12.09; Br, 34.06; C, 38.42; H, 3.28; N, 6.03%. Calcd for $FeBr_2(acac)(bipy) = C_{15}H_{15}O_2N_2Br_2Fe$: Fe, 11.86; Br, 33.93; C, 38.26; H, 3.21; N, 5.95%.

Analysis. Each compound was subjected to elemental analysis after drying *in vacuo* at room temperature. Iron was determined gravimetrically as iron(III) oxide, and chlorine and bromine as the silver salts. The concentrations of hydrogen chloride and bromide in dichloromethane were measured by the method reported previously.[1]

Measurements. The visible and ultraviolet absorption spectra were measured by means of a Hitachi EPS-3T autorecording spectrophotometer. The infrared spectra were taken in Nujol with JASCO IR-E (4000—700 cm^{-1}), Hitachi EPI-L (700—200 cm^{-1}) and FIS-3 (400—30 cm^{-1}) infrared spectrophotometers.

The magnetic susceptibility was measured at room temperature or at various temperatures down to 80 K by the Faraday method with an automatically recording magnetic balance MB-2 of the Shimadzu Seisakusho Co., Ltd. Mercury(II) tetraisothiocyanatocobaltate(II) (room temperature) and hexaammine chromium(III) chloride (lower temperature) were used as reference compounds.

The molecular weight was determined by vapor-pressure osmometry with an apparatus manufactured by the Knauer Co. of Germany. Benzene, nitromethane, acetonitrile and methanol were used as solvents, and benzil as a reference. The electric conductivity was measured in nitromethane or methanol by means of an MY-7 apparatus of the Yanagimoto Seisakusho, Ltd.

Results

Tris(acetylacetonato)iron(III) reacts in a stepwise manner with an equimolar amount or twice as many moles of hydrogen chloride or bromide to produce halogenobis(acetylacetonato)iron(III) or dihalogeno(acetylacetonato)aquairon(III), respectively.

Halogenobis(acetylacetonato)iron(III) Complexes. Chloro- and bromo-bis(acetylacetonato)iron(III) complexes were isolated from the equimolar reaction mixtures of $Fe(acac)_3$ and HX, where X is Cl or Br, by the addition of petroleum ether or the evaporation of the solution, respectively, and the composition of $FeX(acac)_2$ was confirmed by elemental analysis. As shown in Table 1, the compounds have magnetic moments typical of high-spin d^5 systems.

The molecular weights determined in benzene are close to the calculated values, indicating that each of the chloro and bromo complexes exists essentially as a discrete molecule in the non-coordinating solvent. The molar conductances in nitromethane at room temperature also indicate that the complexes are essentially non-electrolytes in this solvent.

In methanol, the complexes dissociate almost completely and the observed molecular weights are near to half of the formula weight. The molar conductances (λ_M) in the same solvent reveal that the complexes behave practically as uni-univalent electrolytes, although the values are smaller in comparison with 9.10 $\Omega^{-1}\,cm^2\,mol^{-1}$ of tetraethylammonium iodide in methanol. It may be presumed that the complexes are solvolyzed in methanol, affording a six-coordinate iron(III) cation and a halide ion:

$$FeX(acac)_2 + 2CH_3OH \rightarrow Fe(acac)_2(CH_3OH)_2^+ + X^-$$

Although the assumed compounds $[Fe(acac)_2(CH_3OH)_2]X$ could not be isolated, similar cationic complexes $[Fe(acac)_2(H_2O)_2]$picrate and $[Fe(acac)_2(TOPO)_2]ClO_4$ (TOPO=trioctylphosphine oxide) have been prepared by Aly[7] and Aggett.[10] The former is weakly dissociated in dichloromethane and the Λ_M value (31.3 $\Omega^{-1}\,cm^2\,mol^{-1}$) in the solvent is appreciably smaller

Table 1. Molecular weight, conductance and magnetic moment data of $FeX(acac)_2$ and $FeX_2(acac)H_2O$ (X=Cl or Br)[a]

Complex	Molecular weight				Molar conductance/ $\Omega^{-1}\,cm^2\,mol^{-1}$		Magnetic moment at 27°C/B.M.
	in C_6H_6	in CH_3NO_2	in CH_3OH	Calcd	in CH_3NO_2	in CH_3OH	
$FeCl(acac)_2$	304		140	290	17.6	61.1	6.11
$FeBr(acac)_2$	324		181	334	20.9	70.8	5.94
$FeCl_2(acac)H_2O$		224	95	244	35.6	65.1	5.76
$FeBr_2(acac)H_2O$		338	139	333	28.6	77.0	5.88

a) The molecular weight was measured at (1.0—5.0)×10^{-2} M, and the molar conductance at 1.0×10^{-2} M, both at room temperature.

than that observed for FeX(acac)$_2$ in methanol.

Puri and Mehrotra,[11] and Cox and his coworkers[12] prepared FeCl(acac)$_2$, either by refluxing the appropriate quantities of anhydrous iron(III) chloride and acetylacetone in benzene or by the reaction of stoichiometric amounts of anhydrous FeCl$_3$ and Fe(acac)$_3$ in chloroform. The complex has been shown [13] to possess a slightly distorted square-pyramidal structure, with the iron atom situated 0.51 Å above the basal plane.

Infrared Spectra: In a previous paper,[3] the present authors have discussed the infrared spectra of FeX(acac)$_2$ in comparison with those of MnX(acac)$_2$ in the 1600—700 cm^{-1} region, and therefore, only the far-infrared spectra are discussed here. There are one or two intense bands in the 400—250 cm^{-1} region as shown in Fig. 1. The band at 298 cm^{-1} in the parent complex, Fe(acac)$_3$, is isotopically assigned to the pure ν(Fe–O) vibration.[14] Thus, the peak around 310—300 cm^{-1} is readily attributed to the corresponding vibration in the two FeX(acac)$_2$ complexes.

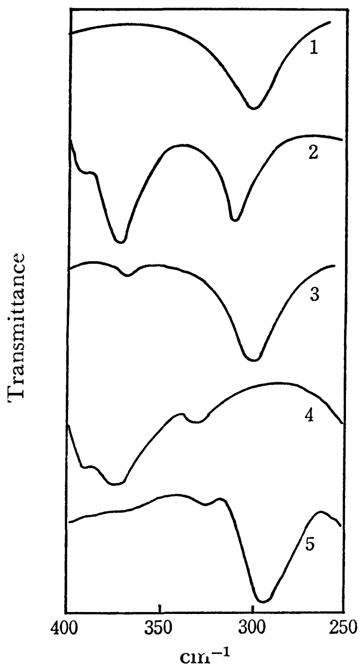


Fig. 1. Infrared spectra in the low-frequency region of Fe(acac)$_3$ (curve 1), FeX(acac)$_2$, where X=Cl (curve 2) or Br (curve 3), and FeX$_2$(acac)H$_2$O, where X=Cl (curve 4) or Br (curve 5).

The stretching band of the terminal Fe(III)–Cl bond of the five-coordinate iron(III) complexes is usually observed in the 300—400 cm^{-1} region and the exact position is affected by the coexisting ligands: 309 cm^{-1} for FeCl(S$_2$CNEt$_2$)$_2$[15], 355 and 375 cm^{-1} for FeCl$_3$(1,2-dimethoxyethane)[16], 380 cm^{-1} for FeCl$_3$(1,4-dioxane)[17] and 378 cm^{-1} for four-coordinate iron(III) ion FeCl$_4^-$.[18] Thus, the strong band observed at 373 cm^{-1} for FeCl(acac)$_2$ can be reasonably assigned to the ν_t(Fe–Cl) vibration. For the same metal, the ratio ν(M–Br)/ν(M–Cl) is usually 0.77—0.74,[19] and hence the corresponding ν_t(Fe–Br) absorption in the FeBr(acac)$_2$ complex appears to be incorporated in the ν(Fe–O) band at 300 cm^{-1}.

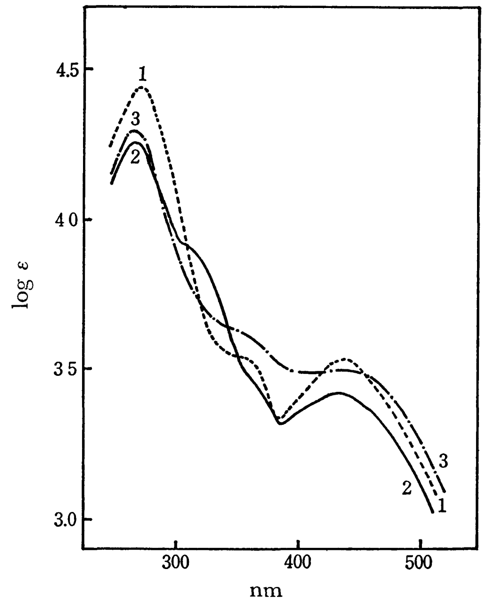


Fig. 2. Absorption spectra of Fe(acac)$_3$ (curve 1) and FeX(acac)$_2$ in CH$_2$Cl$_2$, where X=Cl (curve 2) or Br (curve 3).

Electronic Spectra: The electronic spectra of the present FeX(acac)$_2$ complexes in dichloromethane are shown in Fig. 2 together with the curve for the parent complex, Fe(acac)$_3$. The spectrum of Fe(acac)$_3$ has three absorption bands in the 200—600 nm region, and the most intense band at 270 nm is assigned to the intra-ligand π-π* transition. The other two bands in this region are assigned to a metal-to-ligand($t_{2g}\rightarrow\pi^*$) charge transfer (CT) at 353 nm and a ligand-to-metal ($\pi\rightarrow e_g$) charge transfer (CT) at 436 nm.[20] On the other hand, FeCl(acac)$_2$ exhibits a shoulder on the longer wavelength side (*ca.* 310 nm) of the π-π* transition band in addition to the original three bands. The new band can be feasibly assigned to a chlorine-to-metal CT transition. For the spectra of [FeCl$_2$(bipy)$_2$][FeCl$_4$]

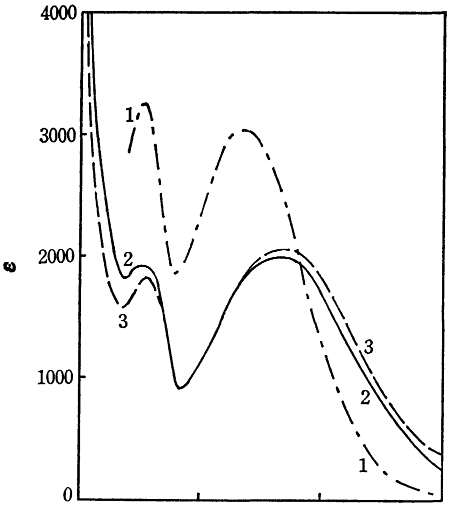


Fig. 3. Absorption spectra of Fe(acac)$_3$ (curve 1) and FeX(acac)$_2$ in methanol, where X=Cl (curve 2) or Br (curve 3).

in dichloromethane, a band at 365 nm is attributed to the same transition.[21] The corresponding bromine-to-metal CT band is not easy to assign in the spectrum of the bromo complex, $FeBr(acac)_2$, but an unusual increase in the absorption intensity is observed around 400 nm, as shown in Fig. 2. This may suggest that the band is obscured by the broad absorption at 435 nm.

The spectra of $FeCl(acac)_2$ and $FeBr(acac)_2$ in methanol are shown in Fig. 3. The measurements were made with 2×10^{-2} M solutions, of which the concentration was almost the same as those used in the molecular weight and molar conductance measurements, by the use of a cell with a 0.1 mm light path. The spectra of both the complexes show a pattern similar to that of the parent complex $Fe(acac)_3$ in methanol, and no absorption due to the halogen-to-metal CT transition was observed. This fact supports the assumed dissociation of a halide ion in methanol.

Dihalogeno(acetylacetonato)aquairon(III) Complexes. The complexes $FeX_2(acac)H_2O$ (X=Cl or Br) were produced by the reaction of $Fe(acac)_3$ with twice as many moles of HX or by the reaction of $FeX(acac)_2$ with an equimolar amount of HX in dichloromethane. The complexes are only slightly soluble in benzene, and hence the molecular weights were measured in nitromethane or in methanol. As shown in Table 1, the values determined in nitromethane are near to the formula weights, suggesting that each of the $FeX_2(acac)H_2O$ complexes also exists in the solvent essentially as a five-coordinate, monomeric complex. The Λ_M values obtained in the same solvent at room temperature also indicate that the complexes are practically non-electrolytes in this solvent, but the slightly large value for $FeCl_2(acac)H_2O$ may suggest some dissociation of a chloride ion.

In methanol, the molecular weights are one-half to one-third of the calculated values, while the Λ_M values imply that the complexes behave substantially as uni-univalent electrolytes in the same solvent. These results suggest that the $FeX_2(acac)H_2O$ complexes liberate only one of their two X^- ligands, and the resulting cations $FeX(acac)(H_2O)(CH_3OH)_2^+$ are partially solvolyzed to replace the aqua ligand with a solvent molecule:

$$\begin{aligned}&FeX_2(acac)H_2O + 2CH_3OH \rightarrow\\ &\qquad FeX(acac)(H_2O)(CH_3OH)_2^+ + X^-\\ &\qquad\qquad {\scriptstyle -CH_3OH}\Big\uparrow\!\Big\downarrow{\scriptstyle +CH_3OH}\\ &\qquad FeX(acac)(CH_3OH)_3^+ + H_2O\end{aligned}$$

The electronic spectra of the complexes in methanol also support this assumption. As shown in Fig. 4, a band due to the halogen-to-metal CT transition reappears at 330 nm in the spectrum of $FeCl_2(acac)H_2O$ and at 410 nm in that of the dibromo analog. Thus, it can be concluded that one halide ligand is still coordinated to the metal in the complex cation produced by the dissociation in methanol.

The magnetic susceptibilities were measured over the temperature range from 300—80 K. As shown in Table 1, the room-temperature moments are close to or slightly less than the 5.92 B.M. predicted by the spin-only formula and these values are independent of temperatures down to 77 K. The plots of χ_A^{-1} against T (Fig. 5) gave straight lines in accordance with the Curie-Weiss law $\chi_A=c/(T+\theta)$. The θ values were obtained from an extrapolation of the straight line and found to be 4 and 8 K for the dichloro and dibromo complexes, respectively. These facts show that each of the $FeX_2(acac)H_2O$ complexes exists as a magnetically dilute molecule in the solid state and that the complexes have no antiferromagnetic interactions with each other.

The infrared spectra of the dihalogeno complexes $FeX_2(acac)H_2O$ in the 4000—700 cm^{-1} region resemble those of the mono-halogeno complexes, except for additional absorption bands due to the coordination of an aqua ligand. As shown in Fig. 1, the strong band at 375 or 294 cm^{-1} in each spectrum of the dihalogeno

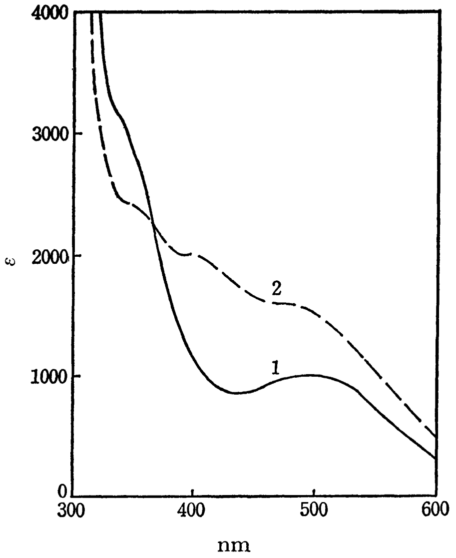


Fig. 4. Absorption spectra of $FeX_2(acac)H_2O$ in methanol, where X=Cl (curve 1) or Br (curve 2).

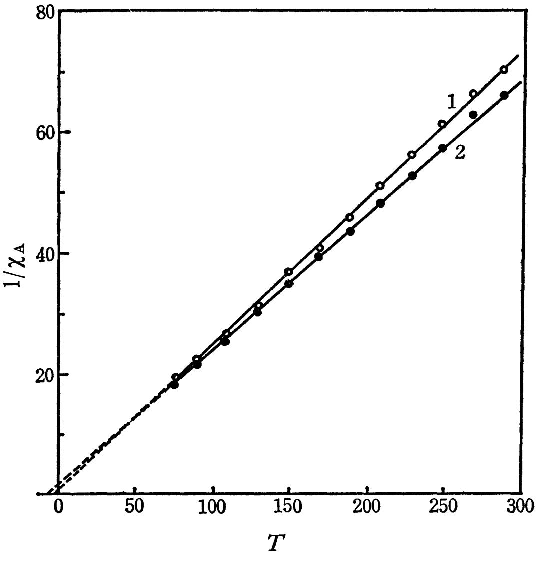


Fig. 5. Curie-Weiss plots for $FeCl_2(acac)H_2O$ (1) and $FeBr_2(acac)H_2O$ (2).

Table 2. Molecular weight, conductance and magnetic moment data of $FeX_2(acac)(py)_2$ and $FeX_2(acac)(bipy)$ (X=Cl or Br)[a]

Complex	Molecular weight				Molar conductance/ Ω^{-1} cm^2 mol^{-1}		Magnetic moment at 27 °C/B.M.
	in CH_3CN	in CH_3NO_2	in CH_3OH	Calcd	in CH_3NO_2	in CH_3OH	
$FeCl_2(acac)(py)_2$	330	178	130	384	28.7	105.6	5.96
$FeBr_2(acac)(py)_2$	385	259	158	473	38.9	150.6	5.82
$FeCl_2(acac)(bipy)$		193	136	382	7.1	66.6	5.85
$FeBr_2(acac)(bipy)$		272	156	471	22.1	84.8	5.77

a) The molecular weight was measured at $(1.0—5.0)\times10^{-2}$ M, and the molar conductance at 1.0×10^{-2} M, with both at room temperature.

complexes can be readily assigned to the stretching vibration of the terminal Fe(III)–X bond in comparison with the corresponding band of the monohalogeno complexes. In contrast to the Fe(III)–X stretching band, it is not easy to specify the band due to the Fe(III)–O(acac) stretching vibration because of its weak intensity. The weak band at 330 cm^{-1} for the dichloro complex and that at 326 cm^{-1} for the dibromo analog were tentatively assigned to the ν(Fe–O(acac)) vibration.

Puri and Mehrotra have also prepared $FeCl_2(acac)$ by the equimolar reaction of anhydrous iron(III) chloride and acetylacetone in benzene, but the compound does not contain an aqua ligand. Unfortunately, its properties and structure have not been reported.[11)]

The Six-coordinate Mixed Ligand Fe(III) Complexes. Further reactions of the $FeX_2(acac)H_2O$ complexes with excess hydrogen halides followed by an addition of twice as many moles of phen as that of the complex used gave the precipitate composed of $FeX_3(phen)_2$. A compound of the same composition, $FeCl_3(phen)_2$ was prepared as an acetic acid adduct by Harris and Lockyer[22)] and was formulated as a cationic iron(III) complex, $[FeCl_2(phen)_2]Cl\cdot2CH_3CO_2H$. Other similar compounds, $[FeCl_2(phen)_2]X\cdot nCH_3CO_2H$ ($X=ClO_4$, $n=1$; $X=FeCl_4$, $n=0.5$), containing the same cation were also prepared.

The five-coordinate complexes $FeX(acac)_2$ and $FeX_2(acac)H_2O$ have a vacant site to allow for the coordination of another monodentate base B. The former reacted with B to cause a disproportionation reaction, affording exclusively the dihalogeno complexes $FeX_2(acac)B_2$. Thus, the isolation of the six-coordinate complexes of the type $FeX(acac)_2B$ was not successful, whereas the neutral six-coordinate complexes $FeX_2(acac)(py)_2$ and $FeX_2(acac)(bipy)$ (X=Cl or Br) were isolated from the reaction of $FeX_2(acac)H_2O$ with excess pyridine or 2,2′-bipyridine, respectively, in tetrahydrofuran. Molecular weight, conductance and magnetic moment data of these mixed-ligand complexes are shown in Table 2. The magnetic moments at 27 °C lie in the range of 5.77—5.96 B.M., indicating that they are all high-spin Fe(III) complexes.

The molecular weights of the pyridine complexes in acetonitrile are slightly less than the formula weights, while they are close to half of the calculated values in nitromethane. The Λ_M values in nitromethane are not as large as expected for electrolytes. These results might indicate that the $FeX_2(acac)(py)_2$ complexes dissociate a pyridine molecule in this solvent. On the other hand, in methanol the molecular weights of both the pyridine complexes are about one-third of the formula weights, while the Λ_M values of the dichloro and dibromo complexes are comparable to or appreciably larger than that of a uni-univalent electrolyte, respectively. Hence, it may be presumed that both the complexes are solvolyzed in methanol in the following manner:

$$FeCl_2(acac)(py)_2 + 2CH_3OH \rightarrow FeCl(acac)(py)(CH_3OH)_2^+ + Cl^- + py$$

$$FeBr_2(acac)(py)_2 + 2CH_3OH \rightarrow Fe(acac)(py)_2(CH_3OH)_2^{2+} + 2Br^-$$

The affinity of iron(III) for the halide ions is in the order of F>Cl>Br>I. Such a trend might be reflected in the dissociation pattern of the second halide ion.

The electronic spectra of the $FeX_2(acac)(py)_2$ complexes in methanol are shown in Fig. 6. The absorption bands present at *ca.* 350 and *ca.* 450 nm are due to the metal-to-ligand(acac) and the ligand(acac)-to-metal CT transitions, respectively. As can be seen from the figure, in the spectrum of the dichloro complex a chlorine-to-metal CT band appears at *ca.* 330 nm as a

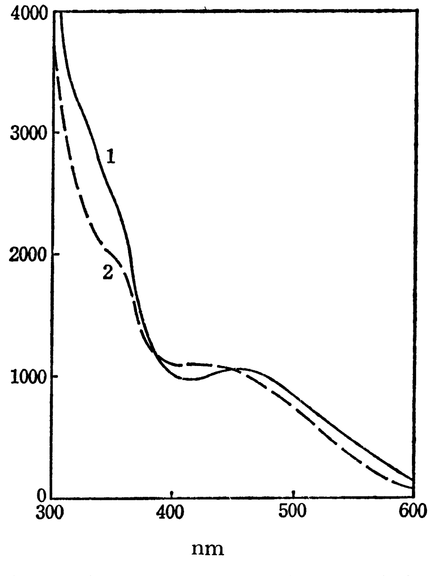


Fig. 6. Absorption spectra of $FeX_2(acac)(py)_2$ in methanol, where X=Cl (curve 1) and Br (curve 2).

discernible shoulder, while a corresponding bromine-to-metal CT band which is expected to appear around 410 nm is not observed for the bromo analog. This seems to reflect the dissociation patterns in methanol described above.

The behaviors of the 2,2′-bipyridine complexes $\mathrm{FeX_2(acac)(bipy)}$ in nitromethane and methanol are very similar to those of the $\mathrm{FeCl_2(acac)(py)_2}$ complex in the same solvents. Therefore, it can be concluded that they dissolve in nitromethane to dissociate a 2,2′-bipyridine molecule, but are solvolyzed in methanol to give a cation $\mathrm{FeX(acac)(CH_3OH)_3^+}$ and a halide ion in addition to a 2,2′-bipyridine molecule:

$$\mathrm{FeX_2(acac)(bipy) + 3CH_3OH} \rightarrow \mathrm{FeX(acac)(CH_3OH)_3^+ + X^- + bipy}$$

As shown in Fig. 7, the electronic spectra of the $\mathrm{FeX_2(acac)(bipy)}$ complexes in methanol show a band due to the halogen-to-metal CT transition at 340 nm for the dichloro complex and at 400 nm for the dibromo analog, respectively, in addition to the two CT metal-to-ligand(acac) and ligand(acac)-to-metal bands. Thus the spectral data are again in accord with the suggested dissociation pattern in methanol.

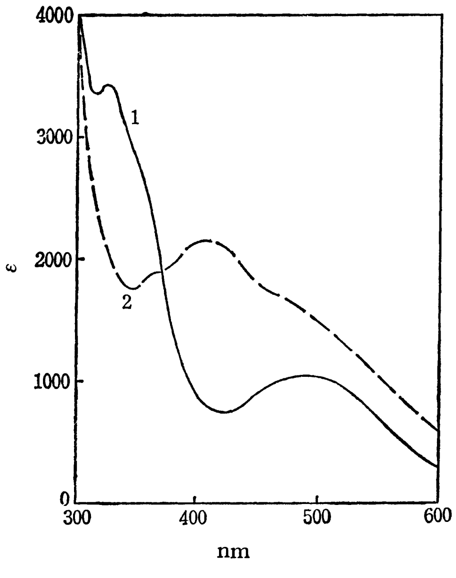
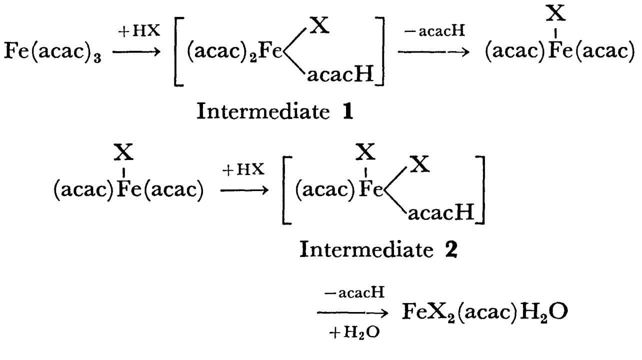


Fig. 7. Absorption spectra of $\mathrm{FeX_2(acac)(bipy)}$ in methanol, where X=Cl (curve 1) and Br (curve 2).

Discussion

Despite the biological importance of iron-containing systems, there is a comparative lack of interest in the coordination chemistry of iron, especially in the case of tervalent iron. This can largely be attributed to the properties of the d^5 ion.[23] The present work extends the studies[1–3] of the reactions of metal acetylacetonates with bromine and hydrogen halides in organic solvents to include the iron(III) complex. In some metal acetylacetonates previously studied, the oxidation state of the metal was finally reduced in the reactions with these reagents, but in the present case no reduction to an iron(II) complex occurred throughout the reactions of $\mathrm{Fe(acac)_3}$ with HX (X=Cl or Br) in dichloromethane. The detailed mechanism of these reactions could not be established in this investigation, but the reaction steps leading to the dihalogeno complex seem to proceed in the following sequence:



$$\mathrm{Fe(acac)_3} \xrightarrow{+\mathrm{HX}} \left[(\mathrm{acac})_2\mathrm{Fe}\begin{array}{l}\diagup\mathrm{X}\\ \diagdown\mathrm{acacH}\end{array}\right] \xrightarrow{-\mathrm{acacH}} (\mathrm{acac})\overset{\overset{\mathrm{X}}{|}}{\mathrm{Fe}}(\mathrm{acac})$$

Intermediate **1**

$$(\mathrm{acac})\overset{\overset{\mathrm{X}}{|}}{\mathrm{Fe}}(\mathrm{acac}) \xrightarrow{+\mathrm{HX}} \left[(\mathrm{acac})\overset{\overset{\mathrm{X}}{|}}{\mathrm{Fe}}\begin{array}{l}\diagup\mathrm{X}\\ \diagdown\mathrm{acacH}\end{array}\right]$$

Intermediate **2**

$$\xrightarrow[+\mathrm{H_2O}]{-\mathrm{acacH}} \mathrm{FeX_2(acac)H_2O}$$

Intermediates **1** and **2** have not been identified, but the latter has a composition similar to the chromium (III) complex $\mathrm{CrBr_2(acac)(acacH)}$, which has previously been isolated from the reaction of $\mathrm{Cr(acac)_3}$ with HBr in dichloromethane containing excess acetylacetone.[24] However, any attempts to isolate intermediate **2** in the present reactions were unsuccessful. This intermediate may be essentially labile, and change irreversibly to the insoluble complex, $\mathrm{FeX_2(acac)H_2O}$, upon the addition of petroleum ether to the reaction mixture of $\mathrm{Fe(acac)_3}$ and twice as many moles of hydrogen halides in dichloromethane.

In a preceding paper,[3] the present authors have reported that $\mathrm{Mn(acac)_3}$ reacted with excess HX to liberate some Mn(II) products, but no reduction occurred in the present case. Such a difference in reactivity could be due to a difference in the reduction potentials of Mn(III) (E=1.51 V) and Fe(III) (E=0.77 V). It was assumed that $\mathrm{FeX_3}$ was produced in the reaction mixture of $\mathrm{FeX_2(acac)H_2O}$ with excess HX in dichloromethane:

$$\mathrm{FeX_2(acac)H_2O} \xrightarrow[+(n-1)\mathrm{H_2O}]{+\mathrm{HX}} \mathrm{FeX_3}\cdot n\mathrm{H_2O} + \mathrm{acacH}$$

The existence of $\mathrm{FeX_3}$ in solution has not been confirmed directly, but $\mathrm{[FeX_2(phen)_2]X}$ was precipitated from the solution upon the addition of 1,10-phenanthroline:

$$\mathrm{FeX_3}\cdot n\mathrm{H_2O} + 2\mathrm{phen} \rightarrow \mathrm{[FeX_2(phen)_2]X} + n\mathrm{H_2O}$$

Although the base adducts $\mathrm{FeX_2(acac)B_2}$ were readily obtained from $\mathrm{FeX_2(acac)H_2O}$, $\mathrm{FeX(acac)_2}$ was disproportionated by the reaction with the base B to deposit the dihalogeno complex $\mathrm{FeX_2(acac)B_2}$ exclusively:

$$\mathrm{2FeX(acac)_2 + 2B} \rightarrow \mathrm{FeX_2(acac)B_2 + Fe(acac)_3}$$

Contrary to the Fe(III) complexes, it was noted previously[3] that $\mathrm{MnX(acac)_2B}$ (B=dioxane, 4-methylpyridine or pyridine oxide) are stable enough to be isolated in reactions of $\mathrm{MnX(acac)_2}$ with B, while $\mathrm{MnCl_2(acac)(O\text{-}py)_2}$ is unstable at room temperature and was obtained only at −78 °C.

All the complexes prepared in this work, with the exception of $\mathrm{FeCl_2(acac)H_2O}$ and $\mathrm{FeBr_2(acac)(bipy)}$, have magnetic moments of 5.82—6.11 B.M. at 27 °C, which are close to the calculated spin-only value of

5.92 B.M. The room-temperature magnetic moments (5.76 and 5.77 B.M.) of the complexes $FeCl_2(acac)H_2O$ and $FeBr_2(acac)(bipy)$ are slightly less than 5.92 B.M. Apparently the former complex retains the possibility of polymeric structure in the solid state, which induces the magnetic interaction between neighboring iron atoms. In practice, however, it obeys the Curie-Weiss law between room temperature and 80 K, and the θ value of 4 K is not so large as to indicate an antiferromagnetic interaction.

Frazer, Qureshi and Taylor[25] studied the reactions of 8-quinolinol or its iron(III) complex with iron(III) halides in organic solvents, and prepared $FeX(oxin)_2$ and $FeX_2(oxin)$ (oxin=8-quinolinolate ion and X=Cl or Br). These compounds were concluded to have a polymeric structure in the light of their insolubility and magnetic data. Only a small number of examples of high-spin iron(III) complexes which exist as five-coordinate monomers in solid state have been discovered up to now. They include adducts of $FeCl_3$ with 1,2-dimethoxyethane[16] and 1,4-dioxane,[17] *N*-substituted salicylideneamine complexes, $FeX(sal{=}NR)_2$ (X=Cl or Br),[26] *N,N'*-bis(salicylidene)ethylenediamine complexes, FeX(salen)monomer (X=Cl, Br, Ph or CH_2Ph)[27] and other Schiff-base iron(III) complexes[28] and some iron(III) porphyrins.[29] Both the present complexes, $FeX(acac)_2$ and $FeX_2(acac)H_2O$, are new examples of this group.

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