Basic iron (III) alkanoate complexes

Young Hee Kim

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BASIC IRON (III) ALKANOATE COMPLEXES

BY

YOUNG HEE KIM

A

THESIS

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W.P. \underline{T}affman (advisor)

\underline{\text{Ray Edwards}}

\underline{\text{Charles Hatfield}}
ABSTRACT

Much information appears in the literature concerning the preparation, properties and structure of the basic iron (III) acetates.

Initially Späth\(^1\) proposed a method for preparing iron (III) acetate and later Weinland and Reihlen\(^2\) indicated that it was impossible to prepare iron (III) acetate by this method but indicated that a basic acetate always resulted. Only early workers indicated the possible existence of three iron (III) ions per molecule attended with at least one or two hydroxide groups and other anions such as acetate groups—some of which may bridge between the iron (III) ions. Casey and Starke\(^3\) attempted to titrate the acetate groups of the basic iron (III) acetate molecule and found only a small percentage to titrate with HC\(_2\)O\(_4\) and proposed structures of the complex cation \([\text{Fe}_3(\text{OOOCR})_6(\text{OH})_2]^+\) with six bridging acetate groups between the iron (III) ions.

\(^1\)E. Späth, Monatsh, 33, 242 (1912).
Orgel recently projected on theoretical grounds the possibility that the unit may not contain hydroxide ions at all but have an oxide ion at the center of an equilateral triangular arrangement with the three iron (III) ions bound in such a structure and with the complex represented by the formula \([\text{Fe}_3\text{O}((\text{OCOCH}_3)_6]+\).

This study was initiated to prepare a number of the basic trinuclear iron (III) alkanoate complexes and to investigate the possibility of a common structure for all of these as suggested by the work of Orgel. The structural investigation was done on the basis of stoichiometric relationships, infrared spectra and magnetic moments.

Six basic trinuclear iron (III) alkanoate complexes were prepared having different anions, alkanoate units and/or solvated molecules. All six complexes have magnetic moments ranging between 3.52-3.68 B.M. for the cation indicating three unpaired electrons per iron (III) ion. The infrared spectra of these complexes as well as stoichiometric relationships were consistent with the concept of a common basic structure for all the compounds. This common structure involves a \(sp^2\) hybridized oxide ion at the center of an equilateral triangle with the three iron (III) ions on the vertices. Each iron (III) ion can be thought to be \(d^2sp^3\) hybridized, four hybrid lobes bonded onto the bridged acetate groups, one hybrid lobe bonded onto the \(sp^2\) hybridized oxide ion and one hybrid lobe occupied by a lone pair of electrons furnished by the iron (III) ion itself. This

---

leaves each iron (III) ion with three unpaired electrons in the unhybridized orbitals. Any solvated units in the complex are pictured as hydrogen bonded onto the central oxide ion.

FIGURE i

Fe
O
C
H
lone pair of electrons
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I. Introduction

The object of this study was to prepare and investigate the structure of iron (III) alkanoates isolated from the corresponding acid without recourse to standard X-ray methods. To initiate this study a number of these iron (III) alkanoates were prepared. In particular, iron (III) acetate, propionate and butyrate were prepared with the acetate being the one of primary interest. The iron (III) propionate and iron (III) butyrate have not previously been reported, but the preparations were made in order to obtain information on the effect of the different anions in these compounds.

Since several studies and reports on iron (III) acetate have been made and resulted in different views on the structure, our initial approach was to investigate the structure by various physical methods such as magnetic susceptibility, infrared spectra and the quantitative chemical stoichiometry of these compounds. A study was also made to determine the effect of a different source for the iron (III) (i.e. FeCl₃·6H₂O) from the one which was previously used (i.e. Fe(NO₃)₃·9H₂O). Also some modifications of the experimental conditions were made to see if there was any change in compositions of the final product.

Although each individual result does not provide absolutely conclusive results, the collective information can lead toward a possible interpretation of a recently proposed structure, that of a trinuclear iron (III) basic acetate complex which contains an oxide ion rather than a hydroxide ion, and is represented by the formula, $[\text{Fe}_3\text{O(OOCR)}_6]^+$. 
II. Review of Literature

In 1914 Weinland and Kessler (1) began their laboratory work for the synthesis of a number of iron (III) acetate chlorides with FeCl$_3$·6H$_2$O and either acetic acid or the acetates of alkali metals. Several different possible compounds were proposed for the various preparation conditions. These compounds have as a common structure the trinuclear iron (III) ion containing six acetates along with either two hydroxides and/or chlorides, and with different numbers of water molecules. One of the proposed compounds was $\left[\text{Fe}_3(\text{CH}_3\text{COO})_6\right]$ Cl$_3$ + 3H$_2$O produced from the direct reaction of FeCl$_3$·6H$_2$O and acetic acid. Another compound was $\left[\text{Fe}_3(\text{CH}_3\text{COO})_6(\text{OH})_2\right]^+\left[\text{FeCl}_4\right]^- + 6\text{H}_2\text{O}$ obtained from the reaction of FeCl$_3$·6H$_2$O and NaOOCCCH$_3$ in the presence of water, and prepared with different conditions from the former one. The experimental data on the chemical analysis for the compositions were presented in good agreement with the calculated ones.

Treadwell and Fisch (2) found the cation $\left[\text{Fe}_3(\text{CH}_3\text{COO})_6(\text{OH})_2\right]^+$ formed during the electrometric titration of FeCl$_3$ with NaOOCCCH$_3$ and proposed the ring structure of the complex shown in figure I,

![Figure I](image_url)

showing the iron with a coordination number of 4 or possibly 6.

Weelo (3) studied the magnetic susceptibilities of a group of
the trinuclear complexes of iron (III) and chromium (III) with different organic acids. He considered polynuclear salts of iron and chromium with a very large negative value of $\Theta$ in the Curie-Weiss law. $\chi = C/(T-\Theta)$. By measuring the susceptibilities at various temperatures he found a linear relationship between $\chi$ and temperature, $1/\chi = f(T)$. From the data, it appears that the values of $C$ for compounds of the type $[\text{Fe}_3(Y)_6\text{(OH)}_2X + n\text{H}_2\text{O}]$ where $Y$ represents $\text{CH}_3\text{COO}^-$, $\text{CCl}_3\text{COO}^-$, $\text{CH}_2\text{CNCOO}^-$ & $\text{CH}_2\text{ClCOO}^-$ and $X$ represents $\text{NO}_3^-$, $\text{Cl}^-$ & $\text{ClO}_4^-$, are quite similar. For compounds with different numbers of OH groups, however, he obtained different values of $C$ and $\Theta$. He interpreted these deviations as due to the lack of OH groups or the peculiar position of the oxygen in the compounds.

Casey and Starke (4) proposed the possible structure of a trinuclear iron complex from the result of their acidimetric titration of iron (III) acetate samples in glacial acetic acid with perchloric acid. Their experimental data for these samples showed only 11~12% purity of their sample on the basis of titratable acetates while the conventional chemical analyses gave near 100% purity. They suggested as an explanation that near the end point a definite species exist as a trinuclear complex $[\text{Fe}_3X_8]^+$ with nonionizable groups, either acetates or hydroxides, attached to the trinuclear iron (III) structure. The $[\text{Fe}_3X_8]^+$ resulting from the reaction of $[\text{Fe}_3X_8]^+$ $\text{CH}_3\text{COO}^-$ with $\text{HClO}_4$ during the titration.

Sommer and Pliska (5) made studies on the iron (III) acetate complexes spectrophotometrically, potentiometrically, electrophoretically, and also by measuring the magnetic susceptibilities of
the complex solutions. They proposed that the trinuclear acetate complex \([\text{Fe}_3(\text{CH}_3\text{COO})_6(\text{OH})_2]^+\) was isolated with \(\text{PtCl}_6^{-12\text{H}_2\text{O}}\) as the anion and with a different structural formula possible depending on the concentration of the components and the pH of the solution. A \(10^{-1} \sim 10^{-2}\) mole iron (III) solution forms trinuclear complexes, while a \(10^{-4}\) mole iron (III) solution at lower hydrogen ion concentration (pH > 4) forms the mononuclear complexes, \([\text{Fe}(\text{CH}_3\text{COO})]^+2\), \([\text{Fe}(\text{CH}_3\text{COO}_2)]^+1\), and \([\text{Fe(OH)}(\text{CH}_3\text{COO})]^+\).

Weinland and Reihlen (6) criticized the reaction recommended by Späth for the preparation of the iron (III) triacetate and proposed the existence of the hydroxo complex \([\text{Fe}(\text{CH}_3\text{COO})_6(\text{OH})_2]^+\) or \([\text{Fe}_3(\text{CH}_3\text{COO})_6\text{OH}]^+2\), where the anion can be acetate or some other anion.

Starke (7) continued to investigate the change in composition by varying the experimental conditions. The metal nitrate was treated at a low temperature in the presence of ethenol as a reducing agent for the nitrate. He proposed an unipositive acetato-hydroxo complex with nitrate as an anion as an intermediate whose composition is \([\text{Fe}_3(\text{CH}_3\text{COO})_7\text{OH} \cdot n\text{H}_2\text{O}]^+ n\text{NO}_3^-\) with \(n\) varying from 0 to 4. In the final state of the reaction, an additional acetato group replaces the nitrate ion while the hydroxo group is carried intact into the end product. In connection with the original attempt made by Späth to prepare the pure triacetates, Starke emphasized that the reaction had not been useful for this purpose. According to Starke, the complex proposed by him has low stability and the molecular weights are high and uncertain because of the varying amount of water of hydration retained after drying. From the
variations in composition of the complexes prepared by Späth, Weinland and Starke assumed that they must have been caused by the various amounts of water. In all cases, however, the concentration of water was low enough for the formation of a trinuclear complex with six acetato bridges as shown in figure II,

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{OC(CH}_3\text{)O} & \quad \text{OC(CH}_3\text{)O} & \quad \text{OH}_2^- \\
\text{HO}^- \quad \text{Fe}^- \quad \text{OC(CH}_3\text{)O} & \quad \text{Fe}^- \quad \text{OC(CH}_3\text{)O} & \quad \text{Fe}^- \quad \text{OH} \\
\text{H}_2\text{O} & \quad \text{OC(CH}_3\text{)O} & \quad \text{OC(CH}_3\text{)O} & \quad \text{OH}_2^-
\end{align*}
\]

Figure II

Upon further reaction of this complex with acetic acid, the water molecules and hydroxyl groups were still not completely removed. Although he obtained the intermediate reaction product in crystallized form, his analytical data could not definitely determine whether they are nitrates of heptaacetato complexes or mixtures of the hexa- and octaacetato complexes.

Recently Orgel (8) summarized the previous findings by postulating that the trinuclear complexes are formed only if the complex ion can be formulated to contain either hydroxyl group or water molecules. These hydroxyl groups cannot be replaced by halide ion and furthermore the majority of iron complexes contain six or more acetate groups for each group of three iron (III) ions. He further asserted that strong magnetic interactions occur between the metal ions. On the basis of all the information available he proposed a different structure for this iron complex, as shown in figure III,
Figure III. Proposed structure for the \([Fe_3(CH_3COO)_6O]^+\) ion:
(a) projected on to the Fe_3O plane; (b) seen along an Fe-O direction, the dotted line indicating the Fe_3O plane.

by introducing the assumption that each metal ion is octahedrally coordinated. This is the only type of coordination known for the chromium (III) ion which is supposed to form a similar complex with acetate groups as does iron (III) ion. Furthermore, he considered the magnetic interactions between metal atoms joined by one or more hydroxyl groups as compared to that between metal atoms joined through oxide ions. After considering the stronger interactions of the latter and the magnetic susceptibility data given by Welo (3), he oriented the metal-oxide bonds in such a way that the three metal atoms are arranged in an equilateral triangle about a central oxide ion. His proposed structure as shown in Figure III indicates that the six acetate groups complete the octahedral co-ordination about the metal ions with the position trans to the oxide ion occupied.
by any of the ligands such as water, amines, further acetate groups or halide ions. He emphasized strongly the possible existence of the oxide ion in his statement,

"The apparent requirement for at least one hydroxyl group in the complex is explained if it is assumed that it is really an oxide ion which is involved; if OH⁻ were really present as such it is difficult to see why it should not be replaced, for example, by halide ions." (8)

He suggested other possible structures such as the metal ions lying at the vertices of an equilateral triangle with the position trans to the oxide ion being occupied by two hydroxyl groups. He did not give high priority to a structure of this type.

The proposed structure shown in Figure III was supported by referring to the well known and very stable structure of the basic beryllium acetate stated by Moeller (9). Orgel in relating his proposed structure to the basic beryllium acetate pointed out the remarkable similarities such as the metal-oxide linkages through only the acetate groups, and the positions of oxide ions with the analogous roles within both structures. The difference is that the oxide ion in iron (III) basic acetate complex is trigonally co-ordinated while the one in the beryllium acetate complex is tetrahedrally co-ordinated. This well known structure of basic beryllium acetate is shown in figure IV. (9).
III. Experimental and Discussion

A. Compound Preparation

All melting points were determined in an open capillary tube by use of "Melt-Pointer" Vanderkamp. Infrared spectra were determined largely with a Beckman IR-5A spectrometer using Nujol and Fluorolube mulls. The use of these two mull systems were preferred since Fluorolube is transparent from 2.0 \( \mu \) to 7.7 \( \mu \) and Nujol is transparent from 7.9 \( \mu \) to 16 \( \mu \) except for one weak absorption band at 13.9 \( \mu \). A few infrared spectra were determined also by means of a Beckman IR-12 spectrometer for a wider scanning range using KBr discs.

Magnetic susceptibilities were determined by the use of a Gouy magnetic susceptibility balance which was calculated by the method described by Figgis and Nyholm (10). A sample tube of one mm. inside diameter was used.

Iron analyses were carried out according to the usual permanganate method. Nitrogen analyses were made through "the volumetric determination of nitrates with ferrous sulfate as reducing agent", described by Kolthoff, Sandell and Moskovitz (11). Chloride analyses were made by the usual gravimetric method. Microanalyses for carbon and hydrogen were performed by Huffman Laboratories, Inc., Wheatridge, Colorado.

Basic iron (III) acetate complex (1a).—This compound was prepared according to the procedure of Starke (7). The compound was dried over phosphorous pentoxide under vacuum at a temperature of 76.8° by use of an Abderhalden drying apparatus.
Recrystallization from acetic acid gave red brown water soluble crystals, mp 160± 2°.

**Anal.** Calcd for $\left[ \text{Fe}_3\text{O} (\text{CH}_3\text{COO})_6 \cdot (\text{HOCOCH}_3)\text{H}_2\text{O} \right]^+ \text{NO}_3^-$:

Fe, 24.7; C, 24.8; H, 3.54; N, 2.06.

Found: Fe, 23.89; C, 24.2; H, 4.00; N, 1.99.

**Basic iron (III) acetate complex (1b).**—A portion of 1a was dissolved in pure acetic acid by heating it until the solution reached saturation and allowing it to stand under reflux conditions for 10 days without contact to air. The crystals that deposited at the bottom of the container were collected, washed with acetic acid and then washed with petroleum ether and finally dried in the same manner as for 1a. Shiny, water soluble, deep red-brick, fine plate like crystals were obtained.

**Anal.** Calcd for $\left[ \text{Fe}_3\text{O} (\text{CH}_3\text{COO})_6 \cdot (\text{HOCOCH}_3)\text{H}_2\text{O} \right]^+ \text{CH}_3\text{COO}^-$:

Fe, 25.5; C, 29.2; H, 3.81; N, 0.0.

Found: Fe, 25.6; C, 29.2; H, 3.66; N, 0.0.

**Basic iron (III) propionate (2a).**—This compound was prepared according to the procedure of Stark (7) for acetate with minor modification. The reaction was slower than the case for the acetate. Recrystallization from propionic acid gave water soluble deep red-brick crystals, mp 114 ± 1°.

**Anal.** Calcd for $\left[ \text{Fe}_3\text{O} (\text{C}_2\text{H}_5\text{COO})_6 \cdot 2\text{H}_2\text{O} \right]^+ \text{NO}_3^-$:

Fe, 23.2; C, 30.0; H, 4.73; N, 1.90.

Found: Fe, 23.0; C, 27.0; H, 4.76; N, 1.89.

**Basic iron (III) propionate (2b).**—A portion of 2a was dissolved in propionic acid by heating and then letting it stand under reflux conditions for two weeks without contact to
air. The process of crystal formation was very slow and the crystals were collected from petroleum ether. The final product treated in the same manner as 2a gave a dark-brown, water soluble powder, mp 155 ± 1°.

**Anal.** Calcd for $\left[ \text{Fe}_3\text{O}(\text{C}_2\text{H}_5\text{COO})_6\text{HOCOC}_2\text{H}_5 \right]^{+} \text{C}_2\text{H}_5\text{COO}^{-}$:
- Fe, 21.8; C, 37.5; H, 5.34; N, 0.0.
- Found: Fe, 22.3; C, 39.3; H, 5.18; N, 0.0.

**Basic iron (III) butanoate (3a).**—This compound was prepared according to the procedure by Starke (7) for acetate. The reaction was so slow that the solution was distilled to eliminate some butyric anhydride and allowed to reflux overnight. A sticky oily solution appeared. The crystals (coal-tar like) were collected from petroleum ether. The deep brown crystals were water soluble, mp 86 ± 2° and gave negative result for a nitrogen test.

**Anal.** Calcd for $\left[ \text{Fe}_3\text{O}(\text{C}_3\text{H}_7\text{COO})_6\text{HOCOC}_2\text{H}_5 \right]^{+} \text{C}_2\text{H}_5\text{COO}^{-}$:
- Fe, 19.3; C, 44.1; H, 6.56; N, 0.0.
- Found: Fe, 19.4; C, ——; H, ——; N, 0.0.

**Basic iron (III) acetate (4a).**—This compound was prepared by the method used previously only with FeCl₃·6H₂O as the source for iron (III) instead of Fe(NO₃)₃·9H₂O. Recrystallization gave light brown water soluble fine plate like crystals, mp 190 ± 1°.

**Anal.** Calcd for $\left[ \text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6\text{HOCOC}_2\text{H}_5 \right]^{+}\text{FeCl}_4^{-}$:
- Fe, 26.10; C, 22.50; H, 3.04; Cl, 16.60.
- Found: Fe, 25.03; C, 23.59; H, 3.18; Cl, 15.60.
Basic iron (III) acetate (4b)—A portion of 4a was dissolved in acetic acid by heating to make a saturated solution. It was then allowed to stand for three weeks under reflux conditions but without boiling and without contact to air. The crystals were deposited along with what seems to be pure carbon. The separation process gave water soluble, light-brown fine needles, mp 190 ± 2° and the product was assumed to be the same as 4a.

Hexa-acetato-triferri-trichloride + 3H₂O (5a)—The preparation of this compound was attempted using the procedure described by Weinland, Kessler and Bayerl (1). Although the predicted red crystals were formed in the solution, a sudden change in the color and crystal form took place upon washing with acetic acid. A water soluble, light-brown powder, mp 188 ± 2° was obtained.

B. Measurements of Physical Properties

1. Magnetic Moments

The magnetic susceptibilities were studied by the use of a Gouey Balance and the gram susceptibilities were calculated directly from the experimental data according to the relationships,

\[ \chi_g = \frac{\beta (\Delta W - \delta)}{W} \]

\[ \chi_m = \chi_g \cdot (\text{mole weight}) \]

\[ \mu_{B.M} = 2.84 \sqrt{\chi_m \cdot T} \]

where

\[ \chi_g = \text{gram susceptibility} \]

\[ \chi_m = \text{molar susceptibility} \]

\[ \beta = \text{field strength constant} \]

\[ \delta = \text{tube correction factor} \]
\[ \mu_{\text{B.M.}} = \text{magnetic moment (Bohr Magnetian)} \]

\[ \Delta W = \text{change in weight} \]

\[ \Delta W = (\text{Wt. of tube + sample at a certain field strength}) - (\text{Wt. of empty tube with zero field}) \]

\[ W = \text{Sample weight} \]

\[ W = (\text{Wt. of tube + sample with zero field}) - (\text{Wt. of empty tube with zero field}) \]

\[ T = \text{absolute temperature at which the measurement was made.} \]

The measurement was carried out in a nitrogen atmosphere in a suspended sample tube at 1.0 and 1.5 amperes current for the electromagnet.

**TABLE I. Magnetic Moments data for basic iron (III) alkanoate complex**

<table>
<thead>
<tr>
<th>Proposed Compounds</th>
<th>(\chi_g(\times10^{-6}))</th>
<th>(\chi_m(\times10^{-6}))</th>
<th>(\mu_{\text{B.M.}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\left[ \text{Fe}_3\text{O} (\text{CH}_3\text{COO})_6 \cdot (\text{HOCOCH}_3) (\text{H}_2\text{O}) \right]^+ \text{NO}_3^- ) (1a)</td>
<td>22.64</td>
<td>5,115</td>
<td>3.52</td>
</tr>
<tr>
<td>(\left[ \text{Fe}_3\text{O} (\text{CH}_3\text{COO})_6 \cdot (\text{HOCOCH}_3) \right]^+ \text{CH}_3\text{COO}^- ) (1b)</td>
<td>25.79</td>
<td>5,645</td>
<td>3.68</td>
</tr>
<tr>
<td>(\left[ \text{Fe}_3\text{O} (\text{C}_2\text{H}_5\text{COO})_6 \cdot 2\text{H}_2\text{O} \right]^+ \text{NO}_3^- ) (2a)</td>
<td>21.32</td>
<td>5,115</td>
<td>3.52</td>
</tr>
<tr>
<td>(\left[ \text{Fe}_3\text{O} (\text{C}_2\text{H}_5\text{COO})(\text{HOCOC}_2\text{H}_5) \right]^+ \text{C}_2\text{H}_5\text{COO}^- ) (2b)</td>
<td>21.30</td>
<td>5,456</td>
<td>3.61</td>
</tr>
<tr>
<td>(\left[ \text{Fe}_3\text{O} (\text{C}_3\text{H}_7\text{COO})_6 \cdot \text{HOCOC}_3\text{H}_7^- \right]^+ \text{C}_3\text{H}_7\text{COO}^- ) (3a)</td>
<td>19.60</td>
<td>5,725</td>
<td>3.63</td>
</tr>
<tr>
<td>(\left[ \text{Fe}_3\text{O} (\text{CH}_3\text{COO})_6 \cdot 2(\text{HOCOCH}_3) \right]^+ \text{FeCl}_3^- ) (4a)</td>
<td>36.70</td>
<td>7,850</td>
<td>4.34</td>
</tr>
</tbody>
</table>
The magnetic moments for \( J_{\pi}, J_{\sigma}, \Lambda_a, \Lambda_{\sigma}, \Lambda_{\pi} \) and \( \Lambda_{\pi} \) are shown in Table I and fall in the range of 3.52 B.M. to 3.68 B.M. These magnitudes are then compared with the values calculated from \( \mu_s = \sqrt{n(n+2)} \), where \( n \) is the number of unpaired electrons in the compound. These data indicate the possible existence of three unpaired electrons per iron (III) ion in the compound. The existence of three unpaired electrons per iron (III) ion can be illustrated in terms of valence bond model assuming each iron (III) ion to have a position at the center of octahedral configuration, four corners being occupied by four oxygen atoms from bridging acetate groups. One corner is linked by an oxide ion situated at the center of its \( sp^2 \) configuration of which the three hybrid lobes and their electrons are shared with the three iron (III) ions. The sixth corner of the octahedral is occupied by a lone pair of electrons furnished by the iron (III) ions.

After the two electrons in the 3d-orbital are paired-up, four electrons from bridging acetate groups occupy four of the hybrid orbitals and one pair of electrons from the oxide ion occupy one other hybrid orbital. The sixth hybrid orbital will then be occupied by a lone pair of
electrons contributed by the iron (III) ion. This results in three unpaired electrons on each iron (III) ion.

2. Infrared Spectra

Some infrared spectra were obtained with the Beckman IR-12 spectrometer, using the KBr disc method. In general this method gave unsatisfactory results due to the sample density in the disc. Fairly good infrared spectra were obtained by means of the Beckman IR-5A Spectrometer by the use of Fluorolube and Nujol mulls.

In order to identify the absorption bands shown in the spectra, the frequencies of a number of vibrational modes were compared with the frequencies assigned by Silverstein (12). According to his assignment the frequencies for the vibrational modes related to the structures in interest are given in Table II.

<table>
<thead>
<tr>
<th>Typical Vibrational Modes</th>
<th>Frequencies(cm(^{-1}))</th>
<th>Wave Length((\mu))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H stretching in Alkanes</td>
<td>3,000-2,840</td>
<td>3.3-3.5</td>
</tr>
<tr>
<td>C-H bending in Alkanes</td>
<td>1,375 (symm.)</td>
<td>7.28</td>
</tr>
<tr>
<td></td>
<td>1,450 (asymm.)</td>
<td>6.90</td>
</tr>
<tr>
<td>C=C stretching</td>
<td>1,200-3,500</td>
<td>8.3-12.5</td>
</tr>
<tr>
<td>O-H stretching (free)</td>
<td>3,700-3,500</td>
<td>2.72-2.86</td>
</tr>
<tr>
<td>C=O stretching</td>
<td>1,725-1,700</td>
<td>5.80-5.88</td>
</tr>
<tr>
<td>Carboxylate ion stretching</td>
<td>1,610-1,550 (Asymm.)</td>
<td>6.22-6.45</td>
</tr>
<tr>
<td></td>
<td>1,400-1,300 (symm.)</td>
<td>7.15-7.70</td>
</tr>
<tr>
<td>-O-O-H stretching</td>
<td>1,660-1,740</td>
<td>5.85-6.00</td>
</tr>
</tbody>
</table>
Infrared spectra for sample 1a, 1b, 2a, 2b, 3a, and 4a are shown in figures V to X. Specifically for the purpose of this study, the presence of the symmetrical and asymmetrical stretching frequencies appear in all the spectra. The presence of the \( \text{\text{\`C=O}} \) or \(-\text{\text{\`C-O\text{-}}\) stretching frequency at 5.9-6.0 \( \mu \) should be noted in most of the spectra but is conspicuously absent in sample 2a. The presence of the C-H stretching frequency can be noted in most of the spectra. And the presence of the O-H stretching frequency of solvated water molecules can be noted in some.
<table>
<thead>
<tr>
<th>Proposed Compounds</th>
<th>Composition (%)</th>
<th>B.M.</th>
<th>presence of IR Absorption band at 5.9μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot (\text{HOCOCH}_3)(\text{H}_2\text{O})]^+\text{NO}_3^-)</td>
<td>Calcd: 24.7 24.8 3.54 2.06</td>
<td>3.52</td>
<td>Yes</td>
</tr>
<tr>
<td>Found: 23.89 24.2 4.00 1.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot (\text{HOCOCH}_3)]^+\text{CH}_3\text{COO}^-)</td>
<td>Calcd: 25.5 29.2 3.81 0.0</td>
<td>3.68</td>
<td>Yes</td>
</tr>
<tr>
<td>Found: 25.6 29.2 3.66 0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Fe}_3\text{O}(\text{C}_2\text{H}_5\text{COO})_6 \cdot 2\text{H}_2\text{O}]^+\text{NO}_3^-)</td>
<td>Calcd: 23.2 30.0 4.73 1.90</td>
<td>3.52</td>
<td>No</td>
</tr>
<tr>
<td>Found: 23.0 27.0 4.76 1.89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Fe}_3\text{O}(\text{C}_2\text{H}_5\text{COO})_6 (\text{HOCOC}_2\text{H}_5)]^+\text{C}_2\text{H}_5\text{COO}^-)</td>
<td>Calcd: 21.8 37.5 5.34 0.0</td>
<td>3.61</td>
<td>Yes</td>
</tr>
<tr>
<td>Found: 22.3 39.3 5.18 0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Fe}_3\text{O}(\text{C}_3\text{H}_7\text{COO})_6 (\text{HOCOC}_3\text{H}_7)]^+\text{C}_3\text{H}_7\text{COO}^-)</td>
<td>Calcd: 19.3 44.1 6.56 0.0</td>
<td>3.63</td>
<td>Yes</td>
</tr>
<tr>
<td>Found: 19.4 ---- ---- 0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot 2(\text{HOCOCH}_3)]^+\text{FeCl}_4^-)</td>
<td>Calcd: 26.1 22.5 3.04 16.6</td>
<td>4.34</td>
<td>Yes</td>
</tr>
<tr>
<td>Found: 25.03 23.6 3.18 15.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
C. Discussion of Experimental Results.

**Basic iron (III) acetate complex** (1a) contains one nitrate ion equivalent per three iron (III) ions. An infrared band at 1690 cm\(^{-1}\) (5.9 \(\mu\)) indicates the presence of an unbridged carboxylic acid group. This must be interpreted as indicating a solvated acetic acid molecule as the anion present is undoubtedly the nitrate ion. A weak infrared band occurred at 2.8\(~\sim\)3.0 \(\mu\) where water would appear. A magnetic moment of 3.52 B.M. indicates the presence of three unpaired electrons per iron (III) ion. Chemical formula of compound indicates the composition \(\left[\text{Fe}_3\text{O(CH}_3\text{COO)}_6\cdot(\text{HOCOCH}_3)\text{H}_2\text{O}\right]^+\text{NO}_3^-\).

**Basic iron (III) acetate complex** (1b) contains no nitrate ion. This complex was made from 1a by high temperature equilibration with acetic acid. In the process the nitrate ion was replaced by an acetate anion. An infrared band at 1690 cm\(^{-1}\) (5.9 \(\mu\)) indicates the presence of a solvated acetic acid molecule and/or an acetate anion. A strong absorption band for C-H stretching at 2950 cm\(^{-1}\) (3.4 \(\mu\)) occurred as did for 1a, which might be due to the larger number of C-H linkage involved. A magnetic moment of 3.68 B.M. indicates the presence of three unpaired electrons per iron (III) ion. Chemical stoichiometric data along with the above data indicates \(\left[\text{Fe}_3\text{O(CH}_3\text{COO)}_6\cdot(\text{HOCOCH}_3)\right]^+\text{CH}_3\text{COO}^-\).

**Basic iron (III) propionate complex** (2a) contains one nitrate ion equivalent per three iron (III) ions. No infrared bands were observed in the region 1740-1660 cm\(^{-1}\) (5.85-6.00 \(\mu\)), indicating the absence of solvated propionic acid molecules. A distinguishable absorption band at 3500-3330 cm\(^{-1}\) (2.85-3.00 \(\mu\)) reveals what might
be an O-H stretching vibration which could be due to the presence of water molecules. A magnetic moment of 3.52 B.M. is similar to 1a and 1b and still points to the presence of three unpaired electrons. Chemical stoichiometry indicates the composition \([\text{Fe}_3\text{O(C}_2\text{H}_5\text{COO})_6 \cdot 2\text{H}_2\text{O}]^{+}\text{NO}_3^-\).

**Basic iron (III) propionate complex (2a)** contains no nitrate ion. This complex was prepared from 2a by high temperature equilibration with propionic acid and apparently resulted in the replacing of the nitrate group by the propionate anion. An infrared spectrum shows an absorption band at 1690 cm\(^{-1}\) (5.9 \(\mu\)) which indicates the presence of a solvated propionic acid molecule and/or propionate anion. No absorption band occurred for O-H stretching. The magnetic moment of 3.61 B.M. is similar in magnitude to that of 1a and 2a and still indicates the presence of three unpaired electrons per iron (III) ions. Chemical stoichiometric data give good agreement with the proposed formula \([\text{Fe}_3\text{O(C}_2\text{H}_5\text{COO})_6(\text{HOCOC}_2\text{H}_5)]^{+}\text{C}_2\text{H}_3\text{COO}^-\).

**Basic iron (III) butyrate complex (2a)** contains no nitrate ion. This complex was obtained by distilling the solution which apparently resulted in the replacing of the nitrate group by the butyrate anion. An infrared spectrum shows the absorption band at 1690 cm\(^{-1}\) (5.9 \(\mu\)) which indicates the presence of solvated butyric acid molecule and/or butyrate anion. No absorption band occurred for O-H stretching but a strong absorption band occurred at 2950 cm\(^{-1}\) (3.4 \(\mu\)) which is indicative of C-H stretching vibrations. A magnetic moment of 3.63 B.M. is similar in magnitude to that of the previously discussed complexes and indicates three unpaired electrons per iron (III) ion.
Although no microanalyses were made for carbon and hydrogen, on the basis of chemical stoichiometric data along with data on iron composition and the magnetic moment the following is proposed as the formula, \([\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot \text{HOCOCCH}_3]^+ \text{C}_3\text{H}_7\text{COO}^-].

Basic iron (III) acetate complex (4a) contains one chloride ion equivalent per one iron (III) ion or four chloride ions per four iron (III) ions. An infrared band at 1670 cm\(^{-1}\) (5.95 \(\mu\)) indicates the presence of solvated acetic acid. No absorption band at 2.8 \(\mu\) was found to indicate the presence of water.

The magnetic susceptibility \((\chi_3), 36.7 \times 10^{-6}\) cgs. and the average magnetic moment of
\[
\mu = 2.84 \sqrt{36.7 \times 10^{-6} \times 855.4/4 \times 297} = 4.34 \text{ B.M./Fe}
\]
probably indicates iron in a mixed magnetic orientation.

Taking the magnetic moment for \(\text{FeCl}_3\) as 5.68 B.M. as calculated from the susceptibility recorded in the Handbook of Chemistry and Physics, and assuming the \(\text{FeCl}_4^-\) ion has \(\text{Fe}^{+3}\) in the same magnetic orientation as in \(\text{FeCl}_3\), and further assuming that the \([\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot 2(\text{HOCOCCH}_3)]^+\) cation has a magnetic moment per iron (III) ion of 3.85 B.M., one can use a weighted averaging technique to estimate the average magnetic moment of all the iron (III) ions present. This gives
\[
\mu = (3 \times 3.85 + 1 \times 5.68)\text{B.M.}/4 = 4.30 \text{ B.M. which is in good agreement with the experimental value of 4.34 B.M.}
\]
Therefore, it is proposed that \(\text{FeCl}_4^-\) is associated as an anion with \([\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot 2(\text{HOCOCCH}_3)]^+\) as the cation. Chemical stoichiometric data along with the above data indicate, the composition
\([\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot 2(\text{HOCOCCH}_3)]^+\text{[FeCl}_4]^-\).
Figure V. IR Spectrum of $\text{Fe}_2\text{O}(\text{C}_{12}\text{H}_{22}\text{O}_{6})\cdot(\text{HOOCCH}_3)\cdot\text{H}_2\text{O}\cdot\text{NO}_3$.
Figure IX.
IR Spectrum of Fe₃O₄(C₃H₇O₇)₆·(HOCOC₂H₅) + C₃H₇COO⁻ (34)
Figure X.
IR Spectrum of \( [\text{Fe}_{3}(\text{OC})_{6}(\text{OH})_{2}] \cdot 2(\text{H}_{2}\text{O}_{2}) \), 9a

WAVELENGTH IN MICRONS
IV. Conclusions

Early in 1930 Treadwell and Fisch (2) prepared a ring structure for the iron (III) acetate complex, $[\text{Fe}_3(\text{CH}_3\text{COO})_6\text{(OH)}_2]^+$ indicating the iron with a coordination number of four or possibly six.

In 1959 Casey and Starke (4) (on the basis of some titration studies) proposed a non-ionizing iron (III) trinuclear complex, $[\text{Fe}_3(\text{X})_8]^+$ with either acetates or hydroxides attached to the trinuclear iron (III) structure. Starke (7) later proposed a structure for the iron (III) trinuclear complex, $[\text{Fe}_3(\text{CH}_3\text{COO})_7\text{OH} \cdot \text{nH}_2\text{O}]^+\text{NO}_3^-$ with $n$ varying from zero to four.

Recently Orgel (8) proposed on theoretical grounds a trinuclear basic acetate structure $[\text{Fe}_3\text{O}(\text{OOCR})]^+$ but made no attempt to substantiate that structure with experimental results.

This investigation was initiated in order to attempt to justify experimentally the structure suggested by Orgel (8). Initially six complexes were prepared all of which have different anions, alkanoate groups and/or solvated units. All six complexes appear to have three iron (III) ions per six bridged alkanoate units and an oxide ion. Magnetic moments range from 3.52-3.68 B.M. which indicates the presence of three unpaired electrons per iron (III) ion. If each iron (III) ion is thought to be $d^2sp^3$ hybridized, there will be three unpaired electrons in the unhybridized $d$ orbitals. The six pairs of electrons in the $d^2sp^3$ hybridized structure can be contributed by four bridged acetate groups, one by the $sp^2$ hybrid orbitals on the center oxide ion and a lone pair of electrons contributed by the iron (III) ion itself. This type of structure would require the oxide ion to possess $sp^2$ hybridization and be positioned at the center of an
equilateral triangle with the three iron (III) ions on the vertices. The anions and solvated units attached to the tri-nuclear complex $[\text{Fe}_3\text{O}(\text{OOCR})_6]^+$ can be changed under different experimental conditions. The number and type of solvated units present for each of the six compounds were judged on the basis of the elemental composition data for the compounds and the infrared spectra of the compounds. It is interesting to note however that the number of solvated units does not seem to exceed two and these are envisioned as being hydrogen bonded onto the central oxide ion.

On the basis of all the experimental data the structure for a basic iron (III) alkanoate complex can be proposed as shown in Figure XI on the following page.
Figure XI. Three dimensional bridged structure of basic iron(III) alkanoate complex.

In order not only to verify the original structure proposed by Orgel (8) but also to justify the present proposed structure, information from a complete X-ray or neutron diffraction study needs to be available. This study is being attempted presently by Oak Ridge National Laboratories.
V. Bibliography


3. Lars A. Welo, Phil. Mag. S. 7, 6, No. 36, 481 (1928).


VITA

Young Hee Kim was born on August 28, 1938 in Seoul, Korea. She received her primary and high school education in Seoul, Korea. She received her first two years of college education in Seoul National University and received a Bachelor of Arts degree from Cedar Crest College, Allentown, Pennsylvania in 1964. She did one year graduate work in Chemistry at the University of Michigan in 1964.

Since January, 1966 she has been enrolled as a graduate student in the Chemistry Department at the University of Missouri at Rolla.