Table IX. Some Distances and Angles in Comparable Iron Compounds

Atoms	Compound	Distance, A	Angle, deg	Ref
Fe–Fe	(1) $C_8H_8Fe_2(CO)_5$	2.742		18
	(2) $TMCOTFe_2(CO)_5$	2.724		*a*
	(3) $C_{10}H_8Fe_2(CO)_5$	2.782		10
Fe–C(allyl)	(1)	2.136, 2.113, 2.123		18
	(2)	2.115, 2.116, 2.109		*a*
		2.107, 2.065, 2.130		
	(3)	2.200, 2.050, 2.142		10
C–C(allyl)	(1)	1.398, 1.410		18
	(2)	1.399, 1.356		*a*
		1.372, 1.345		
	(3)	1.432, 1.391		10
Angle C–C–C(allyl)	(2)		126.2, 127.7	*a*
	(3)		122.8	10

[a] F. A. Cotton and M. D. LaPrade, *J. Am. Chem. Soc.*, **90**, 2026 (1968).

$Fe_2(CO)_6(C_6H_5C_2H)_3$. Although the differences, keeping in mind that the mean esd for an Fe–C distance is 0.007 Å, appear to be significant, it should be remembered that in $[\pi\text{-}C_3H_5PdCl]_2$ similar variations seemed to occur[20] but were not substantiated by a low-temperature crystallographic study.[16]

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Structure and Photodecomposition Studies of the Complex Acid, Hydrogen Aqueoethylenediaminetetraacetatoferrate(III), and Several of Its Metal(I) Salts

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Abstract: The alkali metal, ammonium, and tetramethylammonium salts of the aquoethylenediaminetetraacetatoferrate(III) anion, $Fe(OH_2)Y^-$, were prepared and characterized by elemental analyses, thermogravimetric analyses, and infrared spectroscopy. All were found to be less photosensitive to ultraviolet radiation in the 250 to 400 mμ region than the parent complex acid, $HFe(OH_2)Y$. Photosensitivity was measured as the rate of evolution of carbon dioxide and was found to increase generally with decrease in surface charge density (increase in ionic radius) of the companion cation. The influence of the companion cation is upon the Fe–O bonds between the iron and the ligand, and probably is due to its interaction with the oxygen atoms of the coordinated carboxylate groups.

Hoard, *et al.*,[2] have found from X-ray diffraction studies that the aquoethylenediaminetetraacetatoferrate(III) anion in both $LiFe(OH_2)Y \cdot 2H_2O$ and $RbFe(OH_2)Y \cdot H_2O$ is sexadentate and seven-coordinate, with an irregular pentagonal bipyramidal structure. Lambert, Godsey, and Seitz[3] found the diprotic complex acid, $HFe(OH_2)Y$, to be six-coordinate. A free carboxylic acid group of the ligand and the coordinated water molecule are the proton-donating groups. X-Ray studies by Hoard, Kennard, and Smith[4] substanti-

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(3) J. L. Lambert, C. E. Godsey, and L. M. Seitz, *ibid.*, **2**, 127 (1963).

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Table I. Experimental Analysis of $MFe(OH_2)Y \cdot nH_2O$ Complexes[a]

	%C		%H		%N		%Fe	
Compound	Found	Calcd	Found	Calcd	Found	Calcd	Found[b]	Calcd
$LiFe(OH_2)Y \cdot 2H_2O$	29.48	29.65	4.48	4.48	6.85	6.91		
$NaFe(OH_2)Y \cdot 2H_2O$	28.50	28.52	4.33	4.31	6.56	6.65		
$KFe(OH_2)Y \cdot H_2O$	28.67	28.65	3.90	3.85	6.70	6.68		
$RbFe(OH_2)Y \cdot H_2O$	25.57	25.80	3.70	3.46	5.79	6.02		
$CsFe(OH_2)Y \cdot 1.5H_2O$	22.43	23.00	3.08	3.28	6.00	5.37		
$NH_4Fe(OH_2)Y \cdot H_2O$	30.43	30.17	5.04	5.06	10.72	10.55	14.89	14.03
$N(CH_3)_4Fe(OH_2)Y \cdot 2H_2O$	35.18	35.61	6.26	6.40	8.83	8.90	11.79	11.83

[a] Determined by Galbraith Laboratories, Knoxville, Tenn. [b] Iron could not be determined in the presence of alkali metals by the methods used by the analyst.

ated this structure. The carboxylic acid group is the stronger proton-donating group, and upon neutralization it coordinates with the iron to form a seven-coordinate structure without displacing the coordinated water molecule.

This study of the complex acid and its alkali metal, ammonium, and tetramethylammonium salts was undertaken in order to obtain additional information regarding the structure of the complex anion and variations in its photosensitivity with change of companion cation. A subsequent study will report the results of Mössbauer spectroscopy studies of these complexes.

Experimental Section

Apparatus. The following instruments were used: a Leeds and Northrup pH meter and a National Appliance vacuum oven Model 5830 in the preparations; a Perkin-Elmer Model 337 spectrometer for obtaining the infrared spectra; an Aminco Thermo-Grav for obtaining the thermograms; and a Hanovia 100-W mercury arc lamp with Vycor and nickel oxide filters for irradiating the samples in the photodecomposition studies.

Preparation of the Complex Acid and Its Salts. All the salts were prepared by an acid + base reaction. The complex acid was prepared by the method of Lambert, Godsey, and Seitz,[3] with the following modifications: a smaller excess of ethylenediaminetetraacetatic acid was used and recrystallization of the product was improved by use of a temperature- and pressure-controlled vacuum oven. As the neutralization curve of the diprotic complex acid has a well-defined first inflection point at pH 4.7, the base used in each of the preparations was added until the pH of the solution was 4.7. The materials used were of reagent grade quality.

In the preparation of the lithium, rubidium, and cesium salts, the corresponding solid metal carbonate was added to approximately 1.5 to 2.0 g of the complex acid dissolved in a minimum quantity of deionized water. In the preparation of the sodium, potassium, ammonium, and tetramethylammonium salts, the corresponding hydroxide was added to the solution of the complex acid in the same manner as described for the carbonates.

Crystallization of the complex salts was best accomplished by slow evaporation of the aqueous solution in the vacuum oven at 30–35° and 200–250 mm pressure. The crystals were removed from the oven before complete dryness was reached and stored over anhydrous calcium sulfate for 2 to 4 days to remove adhering water. The composition of each of the salts is shown in Table I. The salts are extremely soluble in water.

Thermogravimetric Analyses. Samples containing 50.0 mg of material were heated from room temperature to 325° at a rate of 3°/min. Flowing dry nitrogen, at a flow rate of about 300 ml/min, was used as an inert atmosphere. Samples in a flowing dry air atmosphere gave thermograms that suggested chemical reaction to form iron(III) oxide.

Infrared Spectra of the Solid Salts. Spectra were obtained by several methods. Fluorolube was used to obtain mull spectra in the 4000–1200-cm^{-1} region, and Nujol was used in the 1333–400-cm^{-1} region. Pellet spectra were obtained from 500-mg potassium bromide pellets containing 1–3 mg of sample material. Comparison of the mull and pellet spectra indicated that no cation or bromide ion interchange occurred during fusion of the disk. Detailed examination was limited to the 1800–1500-cm^{-1} region where the antisymmetric COO stretching frequencies of the coordinated and protonated carboxylate groups appear.

Photodecomposition of the Complexes. Pellets containing 0.007 mmole of sample intimately mixed with 500 mg of potassium bromide were irradiated 20 min by the mercury arc lamp. A Vycor and nickel oxide filter combination was used to limit the effective radiation to between 250 and 400 mμ. Photodecomposition was followed by measuring the rate of evolution of carbon dioxide, expressed in terms of relative increase in the 2349-cm^{-1} vibration band of carbon dioxide, using the base-line technique. The carbon dioxide was shown in a previous study[3] to remain trapped quantitatively in the potassium bromide matrix until pellet ruputre occurred.

Results

Thermogravimetric Analyses. Descriptions of the thermograms are as follows.

$HFe(OH_2)Y$. From room temperature to 225° the compound was stable. At 225° decomposition began and there was a change in slope at 236° which terminated at 255° where the rate loss became constant for the remainder of the temperature region studied.

$LiFe(OH_2)Y \cdot 2H_2O$. From room temperature to 98° the compound was stable. At 98° decomposition started and a constant rate loss was reached at 125°. At 225° another thermal change began and reached a constant rate loss at 250°.

$NaFe(OH_2)Y \cdot 2H_2O$. From room temperature to 95° the compound was stable. At 95° thermal decomposition began and reached a plateau at 125°. A second decomposition started at 162° and leveled off at 195°. A third decomposition began at 245° and terminated at 270°.

$KFe(OH_2)Y \cdot H_2O$. From room temperature to 135° the compound was stable. Thermal decomposition began at 135°, but before this leveled off another thermal loss began at about 150°. The curve leveled off at 212°, but an additional thermal change began at 225° and leveled off at 263°.

$RbFe(OH_2)Y \cdot H_2O$. From room temperature to 140° the compound was stable. Thermal decomposition began at 140° and leveled off at 212°. At 220° an additional decomposition began and at 260° reached a constant rate loss.

$CsFe(OH_2)Y \cdot 1.5H_2O$. From room temperature to 135° the compound was stable. At 135° decomposition began and reached a plateau at 180°. Another thermal change began at 220° and leveled off at about 285°.

$NH_4Fe(OH_2)Y \cdot H_2O$. From room temperature to 142° the compound was stable. At 142° thermal decomposition began and reached a plateau at 180°. A rapid decomposition began at about 218° and continued throughout the temperature range studied without any plateau being attained in the curve.

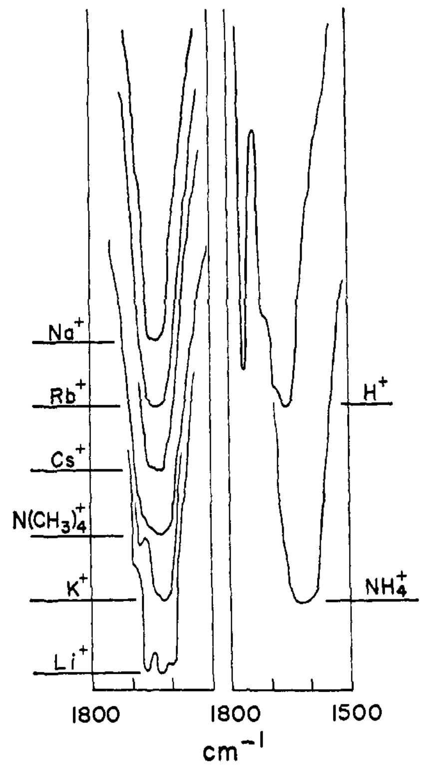

Figure 1. Antisymmetric stretching frequencies of the ligand carbonyl groups in the complex acid and its salts.

$N(CH_3)_4Fe(OH_2)Y \cdot 2H_2O$. Thermal decomposition started at 62° and reached a plateau at 140°. Decomposition began again at 210° but, before the curve reached a plateau, an additional decomposition started at about 270°.

Infrared Spectra. Figure 1 shows the absorption spectra of the parent complex acid and its salts in the 1800–1500-cm^{-1} region. Un-ionized carboxylic acid groups exhibit a sharp band at 1740 cm^{-1}, and this band appears only in the parent complex acid. The broader band between 1700 and 1575 cm^{-1} is typical of coordinated carboxylate groups and is present both in the complex acid and its salts. The three coordinated carboxylate groups of the parent complex acid are slightly differentiated in its spectra. In the spectra of the salts, the shape of the bands assigned to the coordinated carboxylate groups does not follow a regular pattern, even in the alkali metal series. The individual bands are practically indistinguishable in the spectra of the sodium, rubidium, and cesium salts but are differentiated to varying degrees in the lithium and potassium salts. The bands in the spectra of the ammonium and tetramethylammonium salts are undifferentiated, but the band is broader than those in the sodium, rubidium, and cesium salts. The broad band in the ammonium salt is shifted noticeably more than the others toward lower wave numbers.

Photodecomposition. Table II shows the relative amounts of carbon dioxide formed during a 20-min ultraviolet irradiation by the mercury arc lamp, compared to the increase under comparable irradiation for the parent complex acid.

Discussion

The empirical formula for this series of salts of the complex acid $HFe(OH_2)Y$, in which the companion cation is univalent, is $MFe(OH_2)Y \cdot nH_2O$, where $n \geq 1$.

Table II. Relative Photosensitivities of the Complex Acid, $HFe(OH_2)Y$, and Its Salts. Ionic Radii of Companion Cations

Compound	Relative photosensitivity	Ionic radius of companion cation, Å
$HFe(OH_2)Y$	1.00	...
$LiFe(OH_2)Y \cdot 2H_2O$	0.00	0.78
$NaFe(OH_2)Y \cdot 2H_2O$	0.14	0.98
$KFe(OH_2)Y \cdot H_2O$	0.30	1.33
$NH_4Fe(OH_2)Y \cdot H_2O$	0.67	1.43
$N(CH_3)_4Fe(OH_2)Y \cdot 2H_2O$	0.74	2.7[a]
$CsFe(OH_2)Y \cdot 1.5H_2O$	0.85	1.65
$RbFe(OH_2)Y \cdot H_2O$	0.87	1.49

[a] Measured from a Stuart–Briegleb model.

The thermal decomposition studies indicate that all apparently have one or more noncoordinated water molecules in their formulas that are lost between 60 and 150°. There apparently is one coordinated water molecule in the complex anion of each salt that is lost only at higher temperatures. Only for the sodium salt were the decomposition regions in the thermogram sufficiently well defined to permit a clear-cut differentiation between loss of coordinated water and loss of carbon dioxide.

The differentiation of the bands in the 1800–1500-cm^{-1} region of the infrared spectra for the lithium salt may be due to the fact that the carboxylate groups in that salt interact both with lithium ions and noncoordinated water molecules.[2] The shift of the broad band due to coordinated carboxylate groups in the ammonium salt toward lower wave numbers may be due to hydrogen bonding between the ammonium ion and the oxygen atoms of the carboxylate groups.

Electron transfer from the ligand to the iron in the photodecomposition of the complex most likely occurs at an Fe–O bond, as carbon dioxide is liberated. A correlation is seen between photosensitivity to ultraviolet radiation, as measured by the rate of carbon dioxide evolution, and the ionic radius of the companion cation. The surface charge density of the companion cation may therefore exert an influence on the Fe–O bonds through interaction with the oxygen atoms of the coordinated carboxylate groups. The relative photosensitivities decrease steadily from the salts of the larger rubidium, cesium, and tetramethylammonium ions, which have the lowest surface charge densities, to zero for the lithium salt, which has the highest surface charge density.

Complete structural studies of the lithium and rubidium salts have been reported,[2] which show that their crystal structures differ markedly. The water molecules in the lithium salt that are not coordinated to the iron enter into hydrogen bonding with oxygen atoms of coordinated carboxylate groups and also interact with the lithium ions. The noncoordinated water molecules in the rubidium salt play a less important role in its crystalline structure. In the lithium salt, the lithium ions are tetrahedrally coordinated to two noncoordinated water molecules and to two noncoordinated oxygen atoms of the carboxylate groups. The Li–O bond lengths for the latter are very slightly longer (1.920 and 2.006 Å) than the ideal, with the 1.920-Å bond associated with the carboxylate group that has the shortest Fe–O bond length in the complex anion of either salt. The rubidium ions in the rubidium salt are six-co-

Table III. Bond Lengths in the Lithium and Rubidium Salts

Companion cation–oxygen, Å	Associated iron–oxygen, Å
$LiFe(OH_2)Y \cdot 2H_2O$	
Li–O[a]	
1.920	1.938
2.006	2.110
$RbFe(OH_2)Y \cdot H_2O$	
Rb–O[a]	
2.91	2.078
3.01	2.078
Rb–O[b]	
2.95	1.993
3.09	2.078
Rb–OH_2[c]	
3.21	2.106
Rb–OH_2[d]	
3.15	

[a] Carboxylate oxygen not coordinated to the iron of the complex anion. [b] Carboxylate oxygen coordinated to the iron. [c] Water molecule coordinated to the iron. [d] Water molecule not coordinated to the iron.

ordinated to two noncoordinated oxygen atoms in carboxylate groups, to two coordinated oxygen atoms in carboxylate groups, to one water molecule that is coordinated to an iron in the complex anion, and to one noncoordinated water molecule. The Rb–O bond lengths to the oxygen atoms of the carboxylate groups (both coordinated and noncoordinated with the iron) are very slightly longer than ideal, while those to the water molecules are at least 0.25–0.30 Å longer than an ideal Rb–O bond length. Table III summarizes the bond-length data of Hoard, *et al.*,[2] for these salts.

Reasoning from the above data for these two salts, it appears that the companion cation affects the Fe–O bond lengths in the complex anion (and consequently the relative photosensitivities of the salts) by interaction with the oxygen atoms of the carboxylate groups. As the metal–oxygen bond lengths between the companion cations and the oxygen atoms of the carboxylate groups are nearly normal, the surface charge densities of the companion cations evidently have the anticipated influences upon the Fe–O bonds involved. The companion cation would be expected to have an electron-withdrawing effect on the oxygen atom of the Fe–O bond in generally direct proportion to the surface charge density of the companion cation. This would make the electron transfer from oxygen to iron more difficult upon ultraviolet irradiation as the surface charge density of the companion cation increased. The order of relative photosensitivities of the complex salts in Table II agrees with this conclusion. The parent complex acid is the most photosensitive, as the coordinated carboxylate groups have no companion cations (the noncoordinated carboxylate group with its proton is effectively insulated from interaction with the coordinated carboxylate groups). The relative photosensitivities of salts decrease roughly as the surface charge density of the companion cation increases, becoming nonphotosensitive in the case of the lithium salt.

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Coordination Studies by Mössbauer Spectroscopy of Some Metal(I) Salts of the Complex Acid, Hydrogen Aquoethylenediaminetetraacetatoferrate(III)

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Abstract: The coordination numbers of the central metal ion that exist when iron(III) is chelated with ethylenediaminetetraacetic acid, H_4EDTA, have been investigated by Mössbauer spectroscopy and magnetic susceptibility measurements. The complex acid, $HFe(OH_2)Y$, was found to be six-coordinate, and the anion in the M^+ salts, $MFe(OH_2)Y \cdot nH_2O$, was found to be seven-coordinate. The addition of the fourth negative carboxylate group to form the seven-coordinate anion of the salts produces a positive chemical shift in their Mössbauer spectra relative to the complex acid. The metal d orbitals of the iron are decreased, causing a decrease in the s-electron density at the iron nucleus. A small variation in the positive chemical shifts of the salts is ascribed to the influence of the companion cation on the iron–ligand Fe–O bonds through the carbonyl groups of the ligand.

Although the compounds of iron generally have coordination numbers of four and six, *i.e.*, tetrahedral and octahedral coordination environments, coordination numbers of five and seven have also been proposed. The Mössbauer spectra of many of the six-coordinate compounds of iron with both high- and low-spin configurations have been obtained,[2] and interpretation has aided in the characterization of their structures.[3–6]

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