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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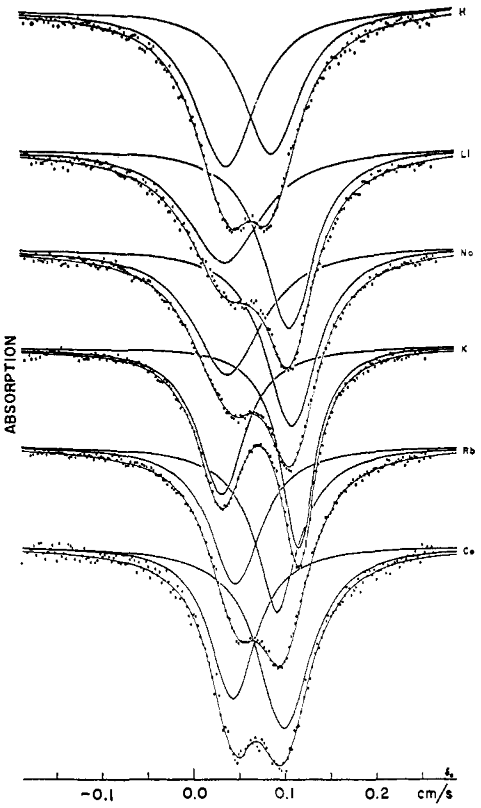

Figure 1. Mössbauer spectra of HFe(OH$_2$)Y and its salts at 298°K.

Hoard, *et al.*,[7-10] have investigated the stereochemistry of some ethylenediaminetetraacetato complexes of iron(III). They determined the crystalline structure of RbFe(OH$_2$)Y·H$_2$O and LiFe(OH$_2$)Y·2H$_2$O and presented evidence for the existence of seven-coordination in the Fe(OH$_2$)Y$^-$ anion. The X-ray data obtained from these salts were interpreted by them as being consistent with an irregular pentagonal bipyramidal structure for the anion. Hall and Lambert[11] studied the structures and photosensitivities of the alkali metal, ammonium, and tetramethylammonium salts of the Fe(OH$_2$)Y$^-$ anion.

Lambert, Godsey, and Seitz[12] presented evidence that the diprotic complex acid, HFe(OH$_2$)Y, is six-coordinate, with the one free carboxylic acid group of the ligand and the coordinated water molecule being the proton-donating groups. X-Ray studies by Hoard, Kennard, and Smith[9] substantiated this structure. Upon neutralization of the carboxylic acid group, it coordinates to the iron in a seven-coordinate structure without displacing the coordinated water molecule.

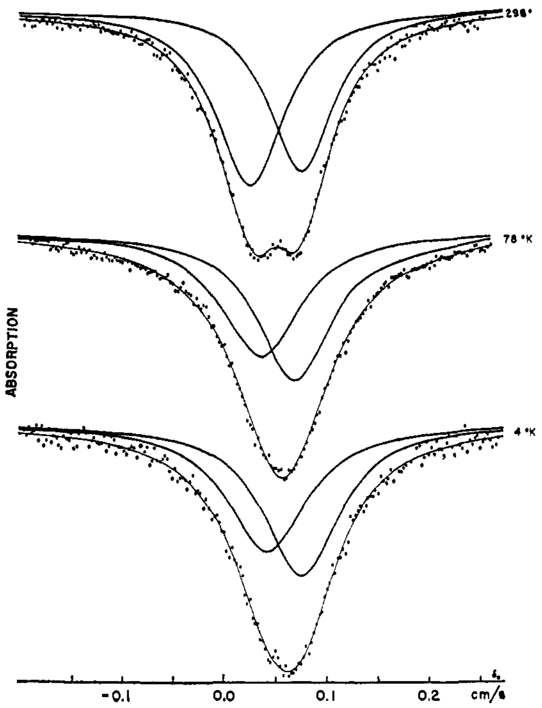

Figure 2. Temperature dependence of the Mössbauer spectra of HFe(OH$_2$)Y.

The character of the bonding of the iron(III) to the ligand can be obtained from Mössbauer spectroscopy data, as the s-electron density at the ^{57}Fe nucleus is directly related to the chemical shift. Furthermore, the electric field gradient (efg) at the nucleus, originating from the ligands, can be obtained from the quadrupole splitting.

The use of Mössbauer and magnetic susceptibility data provided additional information concerning the coordination in the complex acid and its salts as well as revealing a systematic effect on the iron(III)–ligand bonding due to the presence of different M$^+$ companion cation species. The data presented here support the idea of coordination number six for the complex acid and seven for its salts.

Experimental Section

Preparation of the Complex Acid and Its Salts. The complex acid and its salts were prepared by the methods described by Hall and Lambert.[11]

Mössbauer Spectra. The Mössbauer spectra were accumulated on the National Bureau of Standards Mössbauer spectrometer,[13] using a 5-mCi ^{57}Co(Pd) source and a 90% argon–10% methane proportional counter.

The spectra were obtained at 298°K on 0.2-g samples, which were finely powdered to avoid preferred crystal orientation, sealed between two 5-mil polyethylene disks. In order to study the temperature dependence of the Mössbauer parameters, the spectra of the complex acid and the potassium salt also were obtained at 78 and 4.2°K. The potassium salt was chosen for study because it had the best resolved doublet structure of the salts studied. The spectra are shown in Figures 1–3.

The spectrometer was calibrated against a single crystal of sodium nitroprusside.[14] A tandem arrangement was used in the low-temperature measurements, thus making it possible to measure the spectra of the sample and the calibration crystal simultaneously on the spectrometer. The storing of the data for the two spectra was done in the first and second 200-channel subgroups of a multi-

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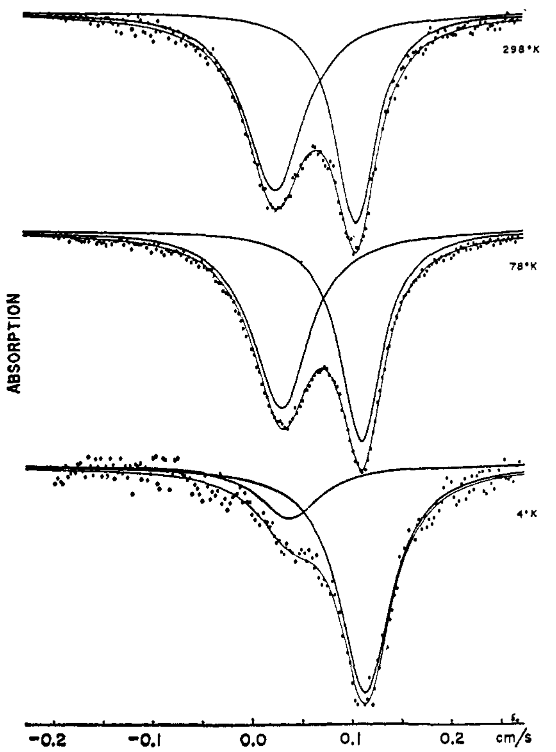

Figure 3. Temperature dependence of the Mössbauer spectra of $KFe(OH_2)Y \cdot H_2O$.

channel analyzer. This method eliminates the possibility of changes in the calibration of the spectrometer between measurements.

In order to obtain maximum resolution, a Doppler velocity spectrum covering the complete velocity range for iron compounds, *i.e.*, from -1 to $+1$ cm/sec, was measured, and the results were used to set the spectrometer to scan only the velocity range where resonance occurred. A computer program[15] using iterations to obtain the best least-squares fit was developed to fit experimental data points to a set of Lorentzian curves. An error analysis, based on the least-squares method, was made for each spectrum in order to obtain the standard deviation in the peak position, half-width, and amplitude of each peak.

Magnetic Susceptibility Measurements. The magnetic susceptibility measurements were obtained using a Gouy balance described by Duell and Lambert.[16] Sample tubes of 4-mm i.d. and 8 cm long were uniformly packed with finely powdered sample to a height of 7 cm. Only room-temperature data were obtained.

Results and Discussion

The Mössbauer ^{57}Fe spectra of these iron(III)-EDTA complexes show that the nuclear resonance occurs in the velocity range typical of high-spin iron(III) (d^5) complexes. The spectra at 298°K are doublets with a line width of four to five times the natural width and have asymmetrical intensities that are temperature dependent. The Mössbauer parameters for the complexes are given in Tables I and II. The most striking feature of the spectra are the large chemical shift (δo) difference between the six-coordinate complex acid and the seven-coordinate salts, and the asymmetry in the doublet intensity for the various salts.

The positive chemical shift for the M^+ salts with respect to the complex acid corresponds to a decrease in the s-electron density around the iron nucleus. Since the bonding in these iron(III) EDTA complexes is mostly ionic, the most direct explanation of this positive shift lies in the addition of a negative ligand to the coordination sphere of the iron. This would result in a decrease in the s-electron density at the iron nucleus. The small variation in the chemical shift for the salts is ascribed to the influence of the companion cation. The chemical shift values would correspond to a 4% 4s-electron density at the iron nucleus for the complex salts and a 1% 4s character for the parent complex acid using the Walker, Wertheim, and Jaccarino plot.[17] However, the use of this plot for high-spin iron(III) complexes presents serious difficulties.[18] The chemical shift increases considerably with decreasing temperature, which also indicates the ionic nature of the bond.

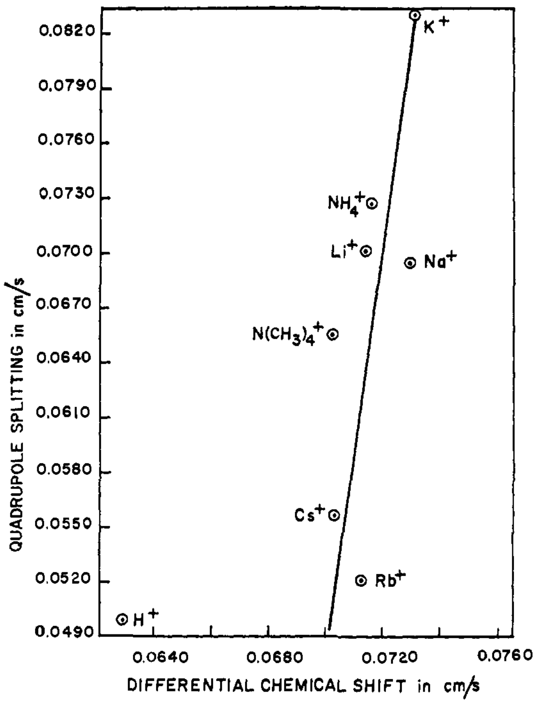

Figure 4. Quadrupole splitting *vs.* differential chemical shift for $HFe(OH_2)Y$ and its salts.

The electric field gradient (efg) at the iron nucleus for an octahedral crystal field is zero, and, since the iron(III) has a closed d^5 subshell, the quadrupole splitting for this configuration would be zero. The observed quadrupole splitting (ΔE_Q) for the parent complex acid, which has a distorted octahedral configuration, arises from the electric field gradient due to the nonidentical coordinating groups of the ligand. The large quadrupole splitting observed for the complex salts compared to the complex acid corresponds to a significant increase of the crystal-field splitting with respect to the complex acid. This arises in the transformation from the six-coordination of the complex acid to the seven-coordination of the complex salts. The pentagonal bipyramidal structure of the complex salts could remove the degeneracy of the d orbitals, which would account for the observed splitting.

The variation in the quadrupole splitting of the salts appears to be due partly to differences in the crystal structures of the salts. The quadrupole splitting is determined primarily by the ligand configuration of the complex anion, and the crystal structure will contribute to the quadrupole splitting only so far as it deforms the

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Table I. Mössbauer Parameters and Magnetic Moments at 25°[a]

Compound	Differential chemical shift, δ_0, cm/sec	Quadrupole splitting ΔE_Q, cm/sec	Line width, Γ_1 and Γ_2, cm/sec	Asymmetry ratio Peak S_P[b]	Asymmetry ratio Area S_A[c]	Magnetic moment, BM
$HFe(OH_2)Y$	0.0628	0.0498	0.0812 0.0762	0.92	0.86	6.16
$LiFe(OH_2)Y \cdot 2H_2O$	0.0713	0.0700	0.0996 0.0676	1.55	1.05	6.16
$NaFe(OH_2)Y \cdot 2H_2O$	0.0729	0.0695	0.0922 0.0692	1.40	1.05	6.22
$KFe(OH_2)Y \cdot H_2O$	0.0730	0.0831	0.0626 0.0454	1.36	0.98	6.06
$RbFe(OH_2)Y \cdot H_2O$	0.0712	0.0521	0.0800 0.0676	1.28	1.24	5.82
$CsFe(OH_2)Y \cdot 1.5H_2O$	0.0702	0.0557	0.0610 0.0706	1.19	1.38	5.99
$NH_4Fe(OH_2)Y \cdot H_2O$	0.0715	0.0726	0.0948 0.0762	1.40	1.12	5.96
$N(CH_3)_4Fe(OH_2)Y \cdot 2H_2O$	0.0702	0.0655	0.0976 0.1240	1.27	1.61	6.06

[a] The standard deviation for the differential chemical shift and quadrupole splitting is 0.005 cm/sec, and 0.001 cm/sec for the line width assuming a Lorentzian profile. [b] Peak asymmetry, S_P, is defined as the peak height of the more positive resonance peak as compared to the peak height of the less positive resonance peak. [c] Area asymmetry, S_A, is defined as the resonance effect of the more positive peak as compared to the resonance effect of the less positive resonance absorption.

Table II. Temperature Dependence of the Mössbauer Parameters of $HFe(OH_2)Y$ and $KFe(OH_2)Y \cdot H_2O$[a]

	Temp, °K	δ_0, cm/sec	ΔE_Q, cm/sec	Γ_1, cm/sec	Γ_2, cm/sec	S_P	S_A
$HFe(OH_2)Y$	298	0.0628	0.0498	0.081	0.076	0.92	0.86
	78	0.0714	0.0422	0.088	0.084	0.85	0.80
	4.2	0.0723	0.0358	0.092	0.091	0.78	0.77
$KFe(OH_2)Y \cdot H_2O$	298	0.0730	0.0830	0.063	0.045	1.36	0.98
	78	0.0825	0.0813	0.070	0.053	1.39	0.98
	4.2	0.0860	0.0760	0.076	0.063	4.26	3.54

[a] The standard deviation for the differential chemical shift and quadrupole splitting is 0.005 cm/sec, and 0.001 cm/sec for the line width assuming a Lorentzian profile.

ligand configuration. Figure 4 shows the empirical relation between the quadrupole splitting and the chemical shift. The quadrupole splitting increases with an increase in the differential chemical shift, but the effect of the companion cation does not appear to be directly related to either. The interaction of the cation with the iron(III) ion probably is due to a cationic effect on the carbonyl oxygen atoms of the coordinated carboxylate groups as previously suggested.[11] Less likely are a cationic effect upon the water molecules or a polarization of the d orbitals of the iron arising from a direct interaction of the companion cation and the d electrons. The cation effect on the chemical shift is a complicated one, because it reaches a maximum at potassium in the alkali metal series. Once the companion cation reaches a certain size, the cation effect appears to be proportional to the ionic radii. The temperature dependence of the quadrupole splitting is much smaller for the salt than for the parent acid, since for the salt this splitting is largely determined by the pentagonal bipyramidal configuration.

An additional characteristic of the Mössbauer spectra of these iron(III) EDTA complexes is the differences in the peak intensity of the doublet lines. This asymmetry has a marked temperature dependency and can be ascribed to either (1) crystal orientation,[19] (2) a Gol'danskii effect,[20] (3) relaxation phenomena,[21] or all three. Finely powdered samples were used so that any effect due to crystal orientation would be eliminated. The temperature studies indicated that there was no, or at most a small, Gol'danskii effect present. Several types of relaxation phenomena are possible and could be of importance. Electron spin relaxation effects, discussed by Blume[21] and by Bradford and Marshall,[22] give rise to asymmetric doublet intensities. The temperature dependence of the chemical shift and quadrupole splitting is very small so that only the population density of the ground state is affected. The line width of the positive peak of the doublet is also independent of temperature, but the second peak broadens considerably. From the theoretical analysis of Bradford and Marshall, the relaxation rate can be calculated, using the line-broadening and asymmetry parameter. A relaxation rate of 1.3×10^{-12} sec was obtained for the

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potassium salt at 298°K and 3×10^{-11} sec at 4.2°K. It is of considerable interest that the relaxation phenomena occur at room temperature, but this may not be so surprising when one considers the structure of the complex anion which is roughly pentagonal bipyramidal and that relaxation effects become more pronounced with lower symmetries. Also, the companion cation has a considerable effect on the relaxation time.

The fact that the observed line width is four to five times the natural width may also be ascribed as being due to electron spin relaxation effects. The $^6S_{5/2}$ state interaction with the nuclear spin produces a magnetic splitting of the energy levels of the excited and ground states. Therefore, instead of having two possible transitions to the ground state from the excited state, there are several. As the splitting is small and the transition energies very similar, the result is a broadening of the observed resonance line.

From the magnetic moments obtained for these compounds, shown in Table I, it is apparent that both the complex acid and the salts are high-spin iron(III) complexes. This is in agreement with the Mössbauer data. The fact that some of the observed magnetic moments are higher than that predicted by a spin-only value of five unpaired electrons may be due to the existence of a small internal magnetic field at the nucleus. This is also evidenced by the broadening in the resonance line.

Conclusions

The Mössbauer spectra of the M^+ iron(III) EDTA complex salts have several main features which indicate a seven-coordinate iron(III) species. This is in agreement with the work of Hoard, *et al.*, on iron(III) EDTA complex salts. The positive increase in the chemical shift for the salts with respect to the complex acid supports the idea of addition of a negative coordinating group to the coordination sphere of the iron. Also, the increased quadrupole splitting and the electron spin relaxation phenomena observed for the salts support the existence of a system with greatly lowered symmetry.

Further support of seven-coordination comes from a consideration of the Fe–O bond lengths in the iron–ligand bonding given by Hoard for the complex acid[9] and for the lithium and rubidium salts.[10] The Fe–O bond lengths expand upon salt formation. If the same coordination were to be assumed for both the complex acid and its salts, an increase in the Fe–O bond lengths should result in an expansion of the iron d orbitals with a resulting decrease in the shielding due to the d electrons and consequently an increase in s-electron density at the nucleus. However, this is not observed and instead a large decrease in the s-electron density is observed.

The magnetic susceptibilities of the complex acid and the M^+ salts showed them to be high spin. Also, Mössbauer spectra show that all the M^+ salts have identical bonding and from the Walker, Wertheim, and Jaccarino diagram there is only a 1% 4s character present in the complex acid and a 4% 4s character in the salts. This is approximately the same per cent 4s character which is observed in the hexafluoroferrate(III) anion. Thus the bonding in both the complex acid and the various M^+ salts can be assumed to be mostly ionic.

A comparison of the iron–ligand (oxygen) distances in the lithium and rubidium iron(III) EDTA salts from the X-ray data of Hoard, *et al.*,[10] with the expected Mössbauer effect may be of value. The shorter pair of Fe–O bonds in $LiFe(OH_2)Y \cdot 2H_2O$ average 1.969 Å (1.938 and 1.999 Å), and those in $RbFe(OH_2)Y \cdot H_2O$ average 1.993 Å. As the other pair of Fe–O bonds in each of the salts are significantly longer than these (2.119 and 2.078 Å, respectively), no comparison of them will be made. The chemical shift value is 0.0713 cm/sec for the lithium salt and 0.0712 cm/sec for the rubidium salt. Based on the shorter Fe–O bond lengths, one might expect a greater difference in their chemical shift values if there were any significant covalent bonding. Thus the magnetic susceptibility data and the Mössbauer chemical shift values support the idea of ionic bonding in the complexes. The larger quadrupole splitting observed for the lithium salt compared to the rubidium salt can also be explained from the X-ray data. The iron–ligand (Fe–O, Fe–N, and $Fe{-}OH_2$) bond lengths are similar in the complex anions of both salts except for one shortened Fe–O bond in the lithium salt that is not in the pentagonal girdle of two nitrogens, two carboxylate oxygens, and the coordinated water molecule. To this extent, the environment of the complex anion distorts its structure.

Photochemical studies reported in an earlier paper[11] indicated by differences in the rate of decarboxylation of the ligand upon ultraviolet irradiation that the iron–ligand (Fe–O) bonding was affected by the companion cation. In this paper, the Mössbauer spectra studies indicate that the companion cation has an effect upon the s-electron density around the nucleus of the iron as a result of its effect upon the d electrons of the iron(III) in the complex anion.

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