Preparation and Coordination Studies of the Complex Acid, Dihydrogen Diethylenetriaminepentaacetatoferrate(III) Dihydrate, and Several of Its Metal(I) Salts

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Abstract: The coordination numbers of the central metal ion in the iron(III) chelate of diethylenetriaminepentaacetic acid, H_5DTPA, and several of its salts have been studied by infrared spectroscopy, magnetic susceptibility measurements, Mössbauer spectroscopy, thermogravimetric analysis, and photodecomposition studies. The complex acid, its monoammonium salt, and its dialkali metal salts were found to be high-spin complexes. The results indicate the coordination number of the iron atom in the parent complex acid to be six; in the monoammonium salt, seven; and in the dialkali metal salts, eight. In coordination number six, three nitrogen atoms and three carboxylate groups of the ligand appear to be involved; and in coordination number seven, three nitrogen atoms and four carboxylate groups are involved. In coordination number eight, three nitrogen atoms and all five carboxylate groups are involved. The companion cations in the salts probably interact indirectly with the metal d orbitals of the iron through the carbonyl groups of the ligand *via* the Fe–O bonds to decrease their size, which in turn causes an increase in the shielding of the s electrons from the nucleus by the d electrons and consequently a decrease in s character.

In an earlier paper,[2] we presented evidence in support of seven-coordination in the M^+ salts of the iron(III) ethylenediaminetetraacetic acid system. As yet, there have been no reports of eight-coordination for the elements in the first transition series. Diethylenetriaminepentaacetic acid, H_5DTPA, has eight coordination sites (three nitrogen atoms and five carboxylate groups) when in the form of $DTPA^{5-}$ and consequently could act as an octadentate ligand. Sievers and Bailar[3] have reported evidence suggesting six-coordination for the solid complex acid, $H_2FeDTPA$. Vandegaer, Chaberek, and Frost[4] have studied the behavior of iron(II) and iron(III) ions in solution with diethylenetriaminepentaacetic acid by pH titration and redox titration measurements. However, no structural studies have been reported on the solid salts of this complex acid.

A study of the complex acid and its M^+ salts in the solid phase was undertaken in order to obtain information concerning the coordination of the DTPA ligand and some of its properties when functioning in a complex anion. It was also considered desirable to make a comparison between the iron(III) EDTA systems previously studied by us[2,5] and the corresponding iron(III) DTPA systems. The studies undertaken on these solid complexes were infrared absorption, magnetic susceptibility measurements, Mössbauer spectroscopy, thermogravimetric analysis, and photodecomposition.

The species studied were the complex acid, its monoammonium salt, and several of its dialkali metal salts. The nature of the companion cation was found to affect the structure and coordination number of the complex anion.

Experimental Section

Preparation of the Complex Acid. The method of preparation was similar to that of Lambert, *et al.*,[5,6] for the complex acid, hydrogen aquoethylenediaminetetraacetatoferrate(III). A heterogeneous mixture consisting of 40.5 g of diethylenetriaminepentaacetic acid (Baker reagent grade) and 0.1 mole of freshly prepared iron(III) hydroxide in 75 ml of deionized water was heated with stirring for approximately 1 hr at about 65° until no residue remained. To prepare the fresh iron(III) hydroxide, 40.4 g of reagent grade iron(III) nitrate, $Fe(NO_3)_3 \cdot 9H_2O$, was dissolved in 100 ml of water and the solution filtered. The iron(III) nitrate solution was then added dropwise with stirring to 100 ml of a solution containing 18.0 g of sodium hydroxide (1.5 times the stoichiometric amount necessary to form iron(III) hydroxide). Forty milliliters of concentrated ammonium hydroxide (28–30%) in 70 ml of water may be used in place of the sodium hydroxide solution. The freshly precipitated iron(III) hydroxide was washed five times by centrifugation.

After cooling overnight, the excess unreacted diethylenetriaminepentaacetic acid that precipitated from the reaction mixture was filtered off. The solution remaining was evaporated under vacuum at room temperature until about 30–35 ml remained. The solution was then filtered and the crystals of complex acid were dried in air. When stored over concentrated sulfuric acid for several days, or dried at 120°, both molecules of water in the formula were lost. The complex acid may be recrystallized by dissolving in a minimum amount of water and reprecipitating as above. The yield was approximately 80%.

The neutralization curve of the complex acid (Figure 1) shows one inflection at pH 7.0, indicating that both acid groups are equivalent. The equivalent weight determined by titration was 221 (theoretical for $H_2FeDTPA$ is 223).

Preparation of the Salts. In all the preparations, an acid + base reaction was employed. Either the anhydrous complex acid or its dihydrate may be used. The bases were solutions of the reagent grade hydroxides. Analyses of the complex acid and the salts are shown in Table I.

The lithium, sodium, and potassium salts were prepared by adding a solution of the corresponding hydroxide to a solution containing 2 to 2.5 g of the complex acid, dissolved in a minimum quantity of water until the pH of the resulting solution was 7.0. Two equivalents of base was added, thus giving salts of the general formula $M_2FeDTPA \cdot nH_2O$. In the preparation of the monoammonium salt, sufficient ammonium hydroxide was added to a solution con-

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[1] (a) Texas Instruments, Inc., Dallas, Texas; (b) National Bureau of Standards; (c) Kansas State University.

[2] J. J. Spijkerman, L. H. Hall, and J. L. Lambert, *J. Am. Chem. Soc.*, **90**, 2039 (1968).

[3] R. E. Sievers and J. C. Bailar, Jr., *Inorg. Chem.*, **1**, 174 (1962).

[4] J. Vandegaer, S. Chaberek, and A. E. Frost, *J. Inorg. Nucl. Chem.*, **11**, 210 (1959).

[5] L. H. Hall and J. L. Lambert, *J. Am. Chem. Soc.*, **90**, 2036 (1968).

[6] J. L. Lambert, C. E. Godsey, and L. M. Seitz, *Inorg. Chem.*, **2**, 127 (1963).

Table I. Experimental Analysis of Iron(III) DTPA Complexes[a]

Compound	%C Found	%C Calcd	%H Found	%H Calcd	%N Found	%N Calcd	%Fe Found	%Fe Calcd
$H_2FeDTPA \cdot 2H_2O$	34.96	34.88	4.96	5.02	8.46	8.71	11.52	11.58
$Li_2FeDTPA \cdot 3H_2O$	33.04	32.84	4.89	4.73	7.94	8.21		
$Na_2FeDTPA \cdot H_2O$	33.13	33.10	3.99	3.97	8.33	8.27	...[b]	
$K_2FeDTPA \cdot 2.5H_2O$	29.98	29.64	4.09	4.09	7.40	7.41		
$NH_4HFeDTPA \cdot H_2O$	34.40	34.94	5.27	5.24	11.35	11.64		

[a] Determined by Galbraith Laboratories, Knoxville, Tenn.; analysis for Fe could not be made in the presence of the alkali metals by their methods. [b] Flame photometry at the National Bureau of Standards gave a Na/Fe ratio of 2.04.

taining 2–2.5 g of the complex acid to neutralize only one of the proton-donating groups. Only the monoammonium salt could be obtained by the method of crystallization used.

To obtain the solid salts, the solutions were evaporated in a vacuum oven until they began to be syrupy. The solutions were then added dropwise with stirring to 500 ml of absolute ethanol. After cooling overnight at 0°, the yellowish brown solid salt was filtered off and dried over concentrated sulfuric acid for 2 days. If the salt did not precipitate on cooling, the ethanol solution was evaporated until crystals began to form. If the salt solution was too syrupy, a red material was obtained which had to be redissolved and the crystallization procedure repeated. The salts are extremely hygroscopic and the presence of water causes the formation of a gum. The DTPA salts are much more soluble in water than are the corresponding EDTA salts.

Infrared Spectra. Spectra were obtained using a Perkin-Elmer Model 337 infrared spectrometer with pellets containing 1–3 mg of sample in approximately 500 mg of potassium bromide. These were compared to mull spectra to make certain no decomposition or ion exchange occurred during fusion of the pellets. Fluorolube and Nujol were used as mulling agents in the 4000–1200-cm^{-1} and the 1300–400-cm^{-1} regions, respectively.

Magnetic Susceptibilities. The magnetic susceptibilities were obtained using a Gouy balance at room temperature with samples of the powdered solid complexes weighing 0.6–0.7 g.

Mössbauer Spectra. The Mössbauer spectra were obtained on a National Bureau of Standards spectrometer which employed a continuously variable velocity drive.[7] Measurements were obtained at 298°K on 0.2-g samples that were finely divided to avoid preferred orientation and sealed between two 5-mil polyethylene disks. Only room-temperature data were obtained. The spectrometer was calibrated against a single crystal of sodium nitroprusside before and after obtaining the spectra of the complexes.

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, using iterations to obtain the best least-squares fit, was used 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.

Thermogravimetric Analysis. Samples containing 50.0 mg of material were heated from room temperature to 325° in an Aminco Thermo-Grav at a rate of 3°/min in a nitrogen atmosphere flowing at a rate of about 300 ml/min.

Photodecomposition. Pellets containing 0.005 mmole of sample diluted with 500 mg of potassium bromide were irradiated with a Hanovia 100-W mercury arc lamp for 20 min. A Vycor and nickel oxide filter combination was used to limit the effective radiation to the region between 250 and 400 mμ. Changes in the bonding of the complex anion were followed by comparison of the infrared spectra before and after irradiation.

Results

Detailed examination of the infrared spectra was limited to the pellet spectra in the 1800–1500-cm^{-1} region where the antisymmetric stretching frequency of the COO groups occurs. Figure 2 shows the pellet spectra for the complex acid and its salts in this region. The medium intensity band at 1735 cm^{-1} in the group complex acid which is the antisymmetric COO stretching frequency for an un-ionized carboxylic acid is decreased and shifted to lower frequencies in the monoammonium salt, and disappears altogether in the alkali metal salts. The broad band due to ionized (and presumably coordinated) carboxylate groups between 1700 and 1600 cm^{-1} shows some differentiation of the individual bands in the lithium and sodium salts but none in the spectrum of the potassium salt. The approximate absorption maxima for the ionized carboxylate bands are shown in Table II. The magnetic moments, also listed in Table II, indicate that all the complexes are high spin.

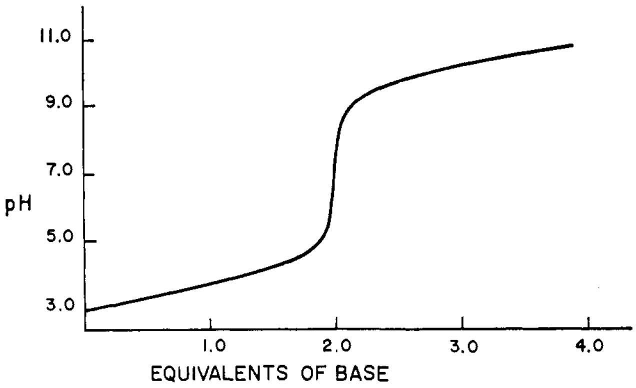

Figure 1. Neutralization curve for the complex acid, $H_2FeDTPA$

The Mössbauer spectra of the complex acid and its salts are shown in Figure 3, and the Mössbauer parameters are given in Table II. The spectra are very asymmetric doublets and have line widths of four to five times the natural width.

The parent complex acid lost over 90% of its water when heated for 2 days at 120°. The thermal decomposition curves of the complexes did not provide conclusive evidence concerning the nature of the water present, as there were no definite plateaus. For those complexes with more than one molecule of water in the empirical formula, thermal loss begins at about 60°. For the monohydrate salts, the thermal loss began at about 125°.

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(7) F. C. Ruegg, J. J. Spijkerman, and J. R. DeVoe, *Rev. Sci. Instr.*, **36**, 356 (1965).

Table II. Photodecomposition, Infrared, Magnetic Susceptibility, and Mössbauer Data on the Iron(III) DTPA Compounds

Compound	Photo-decompn[a]	Infrared absorption,[b] cm^{-1}	Magnetic moments, BM	Mössbauer spectra parameters[c]: Diff chem shift, cm/sec	Quad split, cm/sec	Line width, cm/sec 1	2	Asymmetry ratio Peak	Area
$H_2FeDTPA \cdot 2H_2O$	1.00	1650	6.16	0.0632	0.0844	0.081	0.121	3.55	2.40
$Li_2FeDTPA \cdot 3H_2O$	0.33	1640	5.96	0.0643	0.0829	0.056	0.069	0.68	0.52
$Na_2FeDTPA \cdot H_2O$	0.30	1630	5.99	0.0653	0.0953	0.082	0.074	0.27	0.30
$K_2FeDTPA \cdot 2.5H_2O$	0.28	1620	6.20	0.0662	0.0987	0.096	0.064	0.23	0.34
$NH_4HFeDTPA \cdot H_2O$	0.32	1650	6.21	0.0615	0.1095	0.103	0.078	0.24	0.32

[a] Relative absorption increase at 2349 cm^{-1} due to CO_2 formed during 20 min of ultraviolet irradiation. [b] Approximate absorption maximum for the ionized carboxylate band. [c] Differential chemical shift and quadrupole splitting obtained from computer curve fitting. Lorenztian line profiles were assumed. Standard deviation is 5×10^{-4} cm/sec.

The data in Table II also show the relative amounts of carbon dioxide formed after 20 min of ultraviolet irradiation, expressed in terms of an absorption increase at 2349 cm^{-1} using the base-line technique and compared to the corresponding increase noted for the parent complex acid. The absorption is due to carbon dioxide lost by a coordinated carboxylate group, which is trapped in the pellet.[6] The complex acid is seen to be considerably more photosensitive than any of its salts.

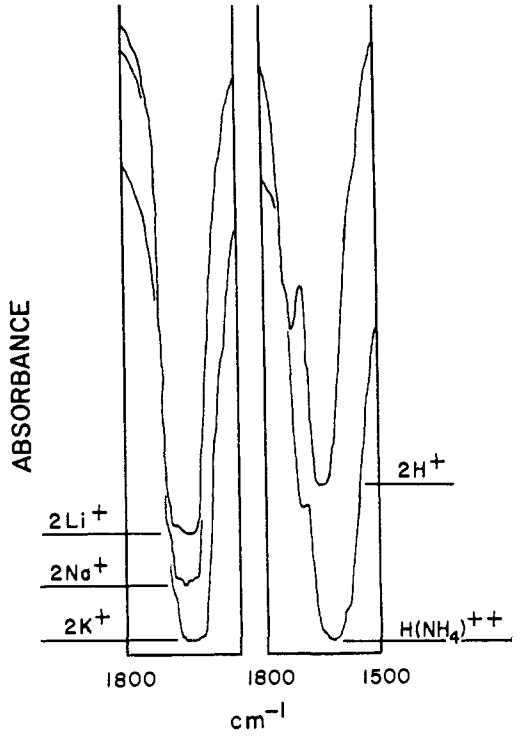

Figure 2. Pellet spectra for the complex acid, $H_2FeDTPA \cdot 2H_2O$, and its salts.

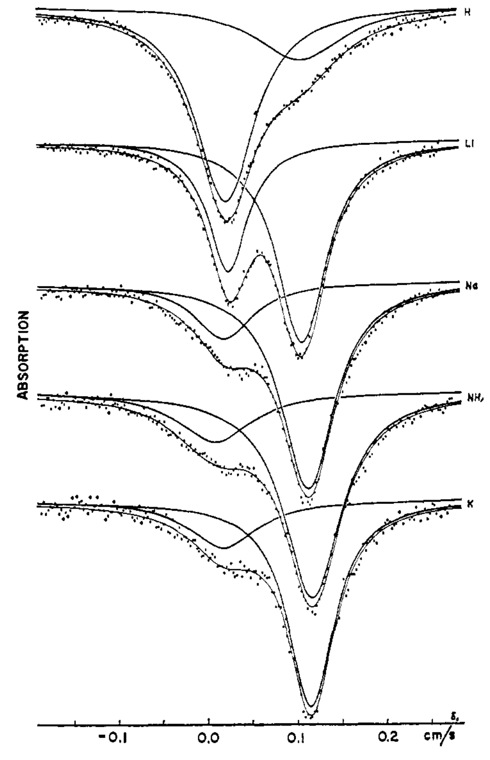

Figure 3. Mössbauer spectra of the complex acid, $H_2FeDTPA$, and its alkali metal salts at 25°.

Discussion

The elemental analyses indicate that water is present in all of the iron(III) DTPA complexes studied, and the low temperatures at which it is lost during thermal decomposition suggest that it is present as noncoordinated water.

The disappearance of the 1735-cm^{-1} band upon complete neutralization of the complex acid and its decrease upon formation of the monoammonium salt indicate that both protons in the diprotic complex acid come from un-ionized carboxylic acid groups. The equivalent acidity of the two groups is further demonstrated by the shape of the titration curve. The carboxylate group or groups formed upon neutralization then are available to complex with the central iron(III) ion and, as well be confirmed by Mössbauer data, increase the coordination number of the iron.

As in the case of the iron(III) EDTA complexes in an earlier study,[5] the parent complex acid proved to be the most photosensitive of the DTPA complexes studied to ultraviolet radiation. The monoammonium salt apparently is no more photosensitive than the dialkali metal salts, so the conclusion is that the presence of an un-ionized carboxylate group does not in itself confer greater photosensitivity on the complex.

The magnetic moments of the complex acid and its salts indicate that all are high-spin iron(III) complexes. The fact that some of observed magnetic moments are higher than those predicted for a spin-only value for five unpaired d electrons may be due to a small internal magnetic field at the nucleus. The Mössbauer Fe^{57} spectra of these complexes also show that nuclear resonance occurs in the velocity range typical of high-spin iron(III) complexes.[8]

The following features of the Mössbauer spectra are of primary interest: (a) the unusual chemical shifts observed for the complex acid, the monoammonium salt, and the dialkali metal salts; (b) the quadrupole splitting; (c) the complete inversion of peak intensity that occurs on salt formation; and (d) the very large asymmetry in the doublet intensity.

In a previous paper,[2] evidence was presented in support of the idea that coordination of a negative ligand, such as a carboxylate group, causes a decrease in s-electron density at the iron nucleus. Also, it is believed that coordination of a ligand such as a basic nitrogen atom which contains a lone pair of s electrons would cause an increase in the s electron density, but the magnitude of the effect of ligands on the chemical shift is not well established.

The negative chemical shift with respect to the complex acid for the monoammonium salt corresponds to an increase in the s-electron density around the iron nucleus. However, the positive chemical shift with respect to the complex acid (and also the monoammonium salt) for the dialkali metal salts corresponds to a decrease in the s-electron density. As the bonding in these iron(III) DPTA complexes is mostly ionic, the most direct explanation of these chemical shifts lies in the addition of ligand functional groups coordinated to the iron(III) ion. It is believed that the addition of a carboxylate group to the iron, which occurs in the transformation from the complex acid to the monosalt as well as in the transformation from the mono- to the disalts, will account for the observed chemical shift.

The chemical shift for the complex acid, $H_2FeDTPA \cdot 2H_2O$, is almost the same as that for the corresponding iron(III) EDTA complex acid, $HFe(OH_2)EDTA$.[2] This may be taken as evidence in support of six-coordination in the iron(III) DTPA complex acid. However, the DTPA ligand has three nitrogen atoms and three carboxylate groups which coordinate to the iron instead of two nitrogen atoms, three carboxylate groups, and one water molecule as in the case of the iron(III) EDTA complex acid. Of the various possible structures for the parent complex acid, as shown by Stuart–Briegleb models, the most likely is the six-coordinated structure that has three nitrogen atoms and three carboxylate groups coordinated to the iron. The driving force for the formation of the complex acid in its preparation is the neutralization of three carboxylic acid groups by the iron(III) hydroxide or hydrated oxide. The neutralization curve shows the two proton-donating groups of the diprotic complex acid to be equivalent and approximately equal in acid strength to carboxylic acid groups. The same acid strength was observed for the strongest of two proton-donating groups in hydrogen aquoethylenediaminetetraacetatoferrate(III), $HFe(OH_2)EDTA$.[5] The other proton-donating group in that case is the coordinated water molecule which is a weaker acid. For the two free carboxylic acid groups in $H_2FeDTPA \cdot 2H_2O$ to be equivalent, they must be located on different nitrogen atoms.

Models based on the above concept show that two octahedral structures are possible: one wherein the three nitrogens and the three carboxylate groups are arranged equatorially around the iron and another where both sets are arranged facially. As the bonding is ionic and presumably labile, charge distribution considerations in the ligand would favor the equatorial arrangement. In this structure, the middle nitrogen of the ligand is directly opposite a coordinated, negatively charged carboxylate group. The coordinating ability of the middle nitrogen atom thus may be weakened by a "*trans*" effect. As one carboxylic acid group is neutralized in forming the monosalt, the model of the resulting seven-coordinate structure shows that a carboxylate group no longer is directly across from the middle nitrogen atom, which then may coordinate more strongly to the iron and, although it is in competition with the tendency of the negative carboxylate group to cause a positive chemical shift, account for the negative relative chemical shift observed. When the fifth and last carboxylic acid group is neutralized and becomes coordinated to the iron in an eight-coordinate structure, the effect observed is the positive chemical shift, corresponding to a decrease in s-electron density around the iron nucleus, caused by a preponderate number of negative carboxylate groups.

The small variations in the chemical shifts for the dialkali metal salts result from the influence of the companion cation and may be explained as the effect of the surface charge density of the alkali metal cation on the iron–ligand (Fe–O) bonds through the carbonyl group as suggested in the previous study on the complex acid $HFe(OH_2)EDTA$ and its salts.[5] The result is a decrease in the d orbitals of the iron, which causes an increase in the shielding of the s electrons from the nucleus by the d electrons and consequently a decrease in s character.

The complete inversion of the peak intensity that occurs in the transformation from the complex acid to the salts is of considerable importance. The inversion is ascribed to the coordination of a carboxylate group to the iron. The coordination of additional carboxylate

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(8) J. J. Spijkerman, F. C. Ruegg, and J. R. DeVoe *in* "Mössbauer Effect Methodology," Vol. I, I. Gruverman, Ed., Plenum Press, New York, N. Y., 1965.

groups to the iron in positions opposite the middle nitrogen of the DTPA ligand will result in a change in the magnitude of the electric field gradient and especially in the direction of the electric field gradient vector.

The observed quadrupole splitting arises from a crystal field splitting and the asymmetry of the ligands. As the iron(III) ion, with d^5 configuration, has a half-filled d subshell and thus is spherically symmetric, it cannot contribute to the electric field gradient at the nucleus. The large quadrupole splitting observed for the iron(III) DTPA complexes, both in the acid and in the salts, indicates that the iron(III) DTPA complexes have lower symmetries than the corresponding iron(III) EDTA complexes.

An additional characteristic of the Mössbauer spectra of the iron(III) DTPA complexes is the differences in the peak intensity of the doublet lines, as well as the observed line broadening (four to five times). This asymmetry is due primarily to electron spin relaxation phenomena similar to that observed for the iron(III) EDTA complexes.[2] The very large asymmetry, much greater than for the iron(III) EDTA complexes, suggests complexes with extremely low symmetry.

It is believed that evidence presented in this paper supports the idea of six-coordination for the complex acid, seven-coordination for the monosalt, and eight-coordination for the disalts.

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