It is of interest to place these amides in the spectrochemical series with other ligands. Toward Ni(II) these results are obtained: NH_3 (1060) > H_2O (860) > DMF (850) > C_5H_5NO (840) ~ DEF (840) ~ NMF (838) > acetamide (824) > TMSO (775) ~ $(CH_3)_2SO$ (773) ~ DMA (769) > NMA (752) ~ DMBu (749).

Toward Cr(III) this series is found: NH_3 (2160) > H_2O (1740) > acetamide (1645) > urea (1600) > TMSO (1575) ~ $(CH_3)_2SO$ (1577) > C_5H_5NO (1539) > DMA (1517).

Except for the ligand pyridine N-oxide, the Dq value toward chromium is approximately twice that of the corresponding nickel complex. This fact, plus the low β values for the pyridine N-oxide complexes,[6] indicates that the interactions of metal ions with this ligand are less covalent than with the amides and sulfoxides.

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Preparation and Photodecomposition of the Complex Acid, Hydrogen Aquoethylenediaminetetraacetatoferrate(III)

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The diprotic complex acid, hydrogen aquoethylenediaminetetraacetatoferrate(III), was characterized and its photodecomposition by irradiation in the charge-transfer region studied. A first-order production of both iron(II) by electron transfer and carbon dioxide by decarboxylation of the ligand was observed. Infrared studies indicate the presence of one uncoördinated carboxylate group in the unirradiated chelate and that the decarboxylation occurs in a coördinated carboxylate group.

Jones and Long[2] commented briefly on the photosensitivity of the ethylenediamine tetraacetatoferrate(III) anion, FeY^-, in their study of the iron(III) and iron(II) chelates of that ligand, and proposed the mechanism

$$FeY^- + h\nu \longrightarrow FeY^{-2} + \text{decomp. prod. of } Y$$

$$FeY^{-2} + {}^1/{}_2H_2O + {}^1/{}_4H_2O \longrightarrow FeY^- + OH^-$$

$$\text{(repeated photoreduction–reoxidation)} \longrightarrow Fe(OH)_3\downarrow$$

Hill-Cottingham[3] has contended that this reaction sequence is not correct, as he found no decomposition of the ligand taking place.

In our study of the photochemical reduction of the complex acid, $HFeYH_2O$, by irradiation in the charge-transfer region, carbon dioxide was observed to be one of the end products. The ligand undergoes the loss of one chelating carboxylate group, presumably *via* a free radical mechanism.

Experimental

Preparation and Properties of the Complex Acid.—The method of preparation was similar to that of Brintzinger, *et al.*,[4] except that a slight excess of H_4Y over the stoichiometric amount was used. Forty 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. This solution then was added dropwise to a solution of 50 ml. of concentrated ammonium hydroxide (28–30%) and 50 ml. of water. The precipitated iron(III) hydroxide was washed five times by centrifugation and then added to a suspension of 35 g. of ethylenediaminetetraacetic acid (Fisher Certified grade, 99.2% purity by titration) in 100 ml. of water. The mixture was heated on a steam cone with stirring for approximately 1 hr. until no residue remained. Any uncomplexed free acid that precipitated when the solution cooled to room temperature was filtered from solution. Approximately 50 ml. of acetone was added and the solution heated on the steam bath until boiling ceased. This was repeated twice more with 50-ml. additions of acetone, by which time crystals of the complex acid began to form. Another 50 ml. of acetone was added and the solution set aside to cool to room temperature. The crystals of the complex acid then were collected, dissolved in a minimum quantity of water at room temperature, and reprecipitated by adding a large quantity of acetone. The yield was about 20 g. of bright yellow crystals.

Anal. Calcd. for $C_{10}H_{15}N_2O_9Fe$: C, 33.08; H, 4.16; N, 7.72; Fe, 15.38. Found: C, 33.02; H, 4.28; N, 7.66; Fe (as Fe_2O_3 from ash), 15.11.

The neutralization curve of the complex acid shows two inflections, one at pH 4.7 and the other at pH 9.7, indicating a diprotic acid whose pK_a values are approximately 2.2 and 7.6. The formula weight determined from the first inflection point was 363 (the theoretical for $HFeYH_2O$).

When excess iron(III) hydroxide was used to prepare the complex acid, a brown compound was obtained. Infrared spectra indicated the absence of a free carboxylic acid group by the absence of bands at 5.7 and 8.3 μ. Analysis showed 28.02% carbon, 4.28% hydrogen, 6.47% nitrogen, and 18.92% iron (from ignition to the ash), which indicated a ratio of Fe:Y:H_2O of 4:3:10.

If in the recrystallization of the complex acid only enough acetone was added to form a suspension of the solid, heating of the solution caused a dark red, oily liquid to form on the sides

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[1] Based upon a thesis submitted by Charles E. Godsey in partial fulfillment of the requirements for the degree of Master of Science, Kansas State University.

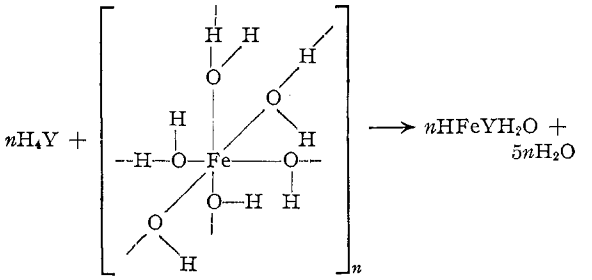
[2] S. S. Jones and F. A. Long, *J. Phys. Chem.*, **56**, 25 (1952).

[3] D. G. Hill-Cottingham, *Nature*, **175**, 347 (1955).

[4] V. H. Brintzinger, H. Thiele, and U. Müller, *Z. anorg. Chem.*, **251**, 289 (1943).

and bottom of the beaker. On air drying, the liquid formed a dark olive-green solid. The absence of the 5.7 and 8.3 μ bands indicated the absence of free carboxylic acid groups. Analysis showed 28.05% carbon, 4.25% hydrogen, 6.56% nitrogen, and 16.19% iron (from ignition to the ash), which indicated a ratio of F:Y:H_2O of 5:4:11.

Brintzinger, *et al.*, reported an anhydrous complex acid, HFeY, which was prepared by treating an excess of iron(III) hydroxide with H_4Y. Their product was reported to be anhydrous, but to gain a molecule of water on neutralization. Our method of preparation gave a complex acid containing one coördinated water molecule. This may be explained by the stoichiometry of the reaction



as the freshly prepared iron(III) hydroxide contains an average of three hydroxide ions per iron atom. Reference to Stuart–Breigleb models shows that some strain results in attempting to coördinate all six donor groups of Y to the iron. Unless the fourth carboxylic acid group is neutralized by a hydroxide ion (as it would be in Brintzinger's method of preparation), there would be little tendency for it to coördinate. The acid was found to be a high-spin complex by comparison of the magnetic susceptibility with several transition metal compounds of known susceptibilities. This also was found by Klemm,[5] who reported ionic bonding in the case of the ammonium salt, $NH_4FeY \cdot H_2O$, prepared by Brintzinger.

Ultraviolet Irradiation of the Complex Acid.—The KBr pellet technique was employed in the examination of reactants and reaction products. Each pellet contained 2.0 mg. of the compound being studied in 600 mg. of KBr, and was formed by thorough grinding of the components, drying under vacuum in the die for 15 min., and compressing under vacuum at 84,000 p.s.i. for 10 min.

The infrared spectra were obtained with a Perkin-Elmer Infracord equipped with a sodium chloride prism. The ultraviolet source was a General Electric mercury arc sun lamp. The output, according to the spectra distribution data supplied by the manufacturer, consists principally of the mercury line spectra between 300 and 600 mμ, with very little below 300 mμ. This was checked experimentally using a Bausch and Lomb grating monochromator and a Photovolt photometer with a 1P28 photomultiplier tube.

Ultraviolet absorption of the complex acid was determined in KBr and KCl pellets, and in aqueous solution. Each showed a single peak: 309 mμ in the KBr pellet, 230 mμ in the KCl pellet, and 257 mμ in aqueous solution. All three peaks tail out into the visible, giving the compound a yellow color.

Examination of the infrared absorption spectrum of the complex acid before irradiation indicated the presence of free carboxylic acid groups by bands at 8.3 and 10.8 μ, which decreased markedly after irradiation. A weak absorption band at 5.7 μ, characteristic of un-ionized α-amino carboxylic acids, also decreased after irradiation. A strong absorption band at 6.1 μ was attributed to ionized carboxylate groups, presumably chelated with the iron, and was seen to shift slightly in the direction of longer wave lengths when the iron(III) chelate was reduced to the iron(II) by ultraviolet irradiation. This shift was noted by Sievers and Bailar[6] when the charge to size ratio of the metal ion changes from more than 3.6 to less than 3.6, as it does with the change from iron(III) to iron(II). A significant increase was noted in a band at 7.1 μ after irradiation. This is characteristic of the deformation mode of a $-CH_3$ (or possibly a $=CH_2$) group attached to a nitrogen atom. This would be expected upon decarboxylation of one of the four acetato groups during irradiation.

Infrared spectra of irradiated and unirradiated complex acid free of a salt matrix environment were obtained by evaporating an acetone suspension of the finely ground solid on a sodium chloride plate. Except for the much broader bands attributable to absorbed water, the spectra closely resemble those obtained in KBr pellets, so interaction between the complex acid and KBr or KCl evidently does not take place. There was no increase in the 4.2 μ carbon dioxide band, as it was free to escape, while in the pellets it was mechanically contained.

In the KBr pellets, the carbon dioxide band at 4.2 μ increased after irradiation. The rate of formation of carbon dioxide from the complex acid was determined by irradiating a single pellet for intervals totaling 60 min. The pellet was removed periodically for infrared analysis. A steady increase in that absorption peak was measured by the baseline technique. A plot of the logarithm of absorbance *vs.* time gave a straight line for the first 25 min., indicating first-order production of carbon dioxide for that period. After 25 min., the 4.2 μ band became approximately constant, probably due to saturation of the pellet with carbon dioxide, although the reaction may have merely slowed down due to depletion of the iron(III) complex acid. The 4.2 μ absorption peak of a pellet irradiated for 60 min. was much reduced after being ground and reformed in the pellet press. Neither a disk of pure KBr nor one containing 2 mg. of Na_2H_2Y exhibited any increase in the 4.2 μ band upon 15 min. irradiation.

The rate of formation of the iron(II) chelate produced was determined by irradiating a series of disks for up to 60 min. Each disk was dissolved in 50 ml. of 5×10^{-4} *M* 2,2′-dipyridyl solution, and the absorbance of the solution measured at 522 mμ. The concentration of iron(II) was obtained by reference to a calibration curve. After 25 min., the rate of formation of iron(II) decreased, but until that time its rate of formation was essentially identical with that of carbon dioxide as determined above. The rate constant was calculated to be 2.08×10^{-3} sec.$^{-1}$. The decreased rate of formation of the iron(II) chelate after 25 min. may be attributed to rupture of the KBr lattice sufficient to cause scattering of the incident radiation although, as stated above, the reaction may have merely slowed down.

Specific qualitative tests of the irradiated complex acid were negative for H_2O_2, and the starch–iodide test for oxidizing agents such as Br_2 from bromide ion in the pellet and H_2O_2 also was negative. The photochemically produced iron(II) chelate is a strong reducing agent, capable of reducing Ag^+ to the metal even in neutral to slightly acid solution. The irradiated solid retains its reducing properties for many hours on standing in the dark. Qualitative observations have shown that the iron(II) chelate thus produced is a better reducing agent than the corresponding cobalt(II) and manganese(II) chelates formed in the same manner.

Discussion

The complex acid, $HFeYH_2O$, studied here is a monohydrate, and the water molecule is considered to be coördinated to the iron(III) ion. On the basis of infrared spectra, at least one carboxylic acid group of the ligand is not coördinated to the central metal ion. pK_{a1} (2.2) for the complex acid is approximately that of pK_{a1} for H_4Y (2.0). The second proton is believed to come from the coördinated water molecule. Assuming an octahedral structure for the chelate, the ligand is coördinated to the iron through its two amine nitrogens and three of its carboxylate groups. The brown compound prepared by Brintzinger's method with an

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[5] W. Klemm, *Z. anorg. Chem.*, **252**, 225 (1944).

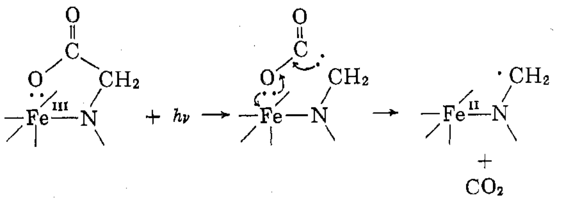
[6] R. E. Sievers and J. C. Bailar, Jr., *Inorg. Chem.*, **1**, 174 (1962).

excess of iron(III) hydroxide and the olive-green compound precipitated from hot acetone–water mixture do not contain undissociated carboxylic acid groups, and hence are different in structure from the complex acid described here.

EDTA has been observed to be a pentadentate ligand in chelates of Co(III)[7] and Pb(II).[8] Hoard, Smith, and Lind[9] concluded that the complex acid is sexadentate and seven-coördinate, with a trigonal prism structure having the water molecule bonded to the iron in the square face of the prisms opposite the nitrogen atoms. Hoard, Lind, and Silverton[10] found from X-ray data that $Fe(OH_2)Y^-$ in the salt $RbFe(OH_2)Y \cdot H_2O$ is sexadentate and seven-coördinate, with a configuration "loosely describable" as pentagonal bipyramidal.

The difference in structure apparently is due to the preparation of the complex acid $HFeYH_2O$ with excess H_4Y. The chelate ions of salts resulting from the neutralization of this complex acid probably would assume the configurations described by Hoard and coworkers.

Photolysis of the complex acid is considered to proceed in several steps, *viz.*, the transfer of one of the electrons from an oxygen on a chelated carboxylate group to the iron, followed by rearrangement of the carboxylate group to release carbon dioxide and produce a free radical.



The fate of the free radical is not clear. It probably undergoes one or more of several possible reactions to form stable products. These include reaction with the coördinated water molecule or, if in solution, a solvent water molecule to form hydroxyl free radicals and hydrogen atoms (and eventually oxygen and hydrogen). Reaction of two photochemically produced ligand free radicals to form a dimer also is possible in the solid state. The negative test for oxidizing agents such as Br_2 and H_2O_2 in the potassium bromide pellet after irradiation of the complex acid is understandable, as the strongly-reducing iron(II) complex persists for hours in the presence of the other products.

The coördinating groups of the Y and the H_2O produce a weak-field, high-spin complex, as the magnetic susceptibility measurements indicate. The strong reducing character of the iron(II) complex is due fundamentally to the sixth electron forced on the metal ion, which is not spin-stabilized at all. Whereas iron(III) and cobalt(III) chelates of weak-field ligands having carboxylate donor groups generally are stable but photosensitive, the corresponding manganese(III) chelates undergo spontaneous decomposition, apparently because of the added stability the fifth electron receives when added to the high-spin d^4 complex.

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(8) D. T. Sawyer and P. J. Paulsen, *ibid.*, **81**, 816 (1959).

(9) J. L. Hoard, G. S. Smith, and M. Lind, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 296.

(10) J. L. Hoard, M. Lind, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 2770 (1961).

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Reaction of Cobalt(II) Ethylenediaminetetraacetate with Ferricyanide

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The oxidation of $Co(EDTA)^{-2}$ by $Fe(CN)_6^{-3}$, while giving $Co(EDTA)^{-1}$ and $Fe(CN)_6^{-4}$ as final products, is found to differ from the usual electron transfer systems in that the reaction occurs in two distinct steps. The first of these is interpreted as a rapid, reversible association to give $[(EDTA_5)Co^{III}\text{–}NC\text{–}Fe^{II}(CN)_5]^{-5}$. The second, slower, process is then the dissociation of this binuclear species to give the final products.

Previous work in this Laboratory has been directed toward the kinetics of electron transfer systems, particularly those involving cobalt and other transition metal complexes of negative charge.[1–3] In particular, during the course of the investigation of the exchange between $Co(EDTA)^{-2}$ and $Co(EDTA)^{-1}$,[3] it was noticed that the former complex reacted with $Fe(CN)_6^{-3}$ at a measurable rate. In undertaking the present investigation of this reaction it was felt that we might have an interesting intermediary situation between the very slow $Co(EDTA)^{-1,-2}$ system and the rapid

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(1) A. W. Adamson, *J. Phys. Chem.*, **56**, 858 (1952).

(2) A. W. Adamson, *Rec. trav. chim.*, **75**, 809 (1956).

(3) A. W. Adamson and K. S. Vorres, *J. Inorg. Nucl. Chem.*, **3**, 205 (1960).