The electric field gradient (*efg*) can be completely specified in terms of $V_{zz} \equiv \partial^2 V/\partial z^2$, the z component of the *efg* tensor, and the asymmetry parameter η, defined by $\eta = (V_{xx} - V_{yy})/V_{zz}$. For ^{57}Fe, the nuclear spin of the first excited state is $I = ^3/_2$, and the Hamiltonian for the interaction between the nuclear electric quadrupole moment Q and the *efg* has eigenvalues

$$E_Q = \pm\frac{1}{4}eQV_{zz}(1 + \eta^2/3)^{1/2}$$

Let us consider first a molecule with either D_{3h} or C_{3v} symmetry and choose the threefold axis as the z direction of the *efg* tensor. Then η vanishes identically and the field gradient is axially symmetric. In this case the splitting of the $I = ^3/_2$ state is simply $\Delta = ^1/_2 eQV_{zz}$, and the magnitude of Δ depends entirely upon V_{zz}. For the triphenylphosphine derivatives studied by Collins and Pettit,[19] $[(C_6H_5)_3P]_2Fe(CO)_3$ with D_{3h} symmetry has $\Delta = 2.76$ mm sec^{-1}, while $(C_6H_5)_3PFe(CO)_4$ with C_{3v} symmetry has $\Delta = 2.54$ mm sec^{-1}. Thus, substitution at both apical positions *increases* V_{zz} rather than leading to a partial cancellation of effects. It is to be expected, of course, that the actual magnitude of this increase will depend upon the nature of the substituents.

Turning now to the complexes reported here, we can assume for the purpose of the present discussion that to first approximation the local symmetry about Fe in the $LFe(CO)_4$ and $LFe_2(CO)_8$ complexes is again C_{3v}. Note that the *efg* will depend principally on the atoms bonded directly to Fe and that, even if the ligand repels the equatorial carbonyl groups below the iron atom, this will not destroy the threefold axis. Thus, the quadrupole splitting will again be a function of only V_{zz}. If we now consider forming an $LFe(CO)_3$ complex, we must have either C_{2v} or C_s symmetry, as shown in Figures 1 and 2. In either case there will be a nonvanishing asymmetry parameter, which removes the axial symmetry, and the quadrupole splitting must be greater than for the C_{3v} case *unless* there is a decrease in V_{zz}. In view of the results for ffarsFe(CO)$_4$ and ffarsFe$_2$(CO)$_8$, which suggest that the splitting is essentially the same for apical substitution whether the ligand acts as a monodentate or bidentate group, we would anticipate that apical–equatorial substitution in the $LFe(CO)_3$ compounds (structures 1b and 2b) would not decrease V_{zz} by any appreciable extent. Such structures would therefore be expected to show an increase in splitting over that observed for the $LFe(CO)_4$ or $LFe_2(CO)_8$ complexes. Since both of the structures which are possible on the basis of the nmr measurements involve only equatorial substitution, we must conclude that this leads to a substantial reduction in V_{zz} as compared with the C_{3v} case.

These considerations suggest that in trigonal-bipyramidal complexes of the type $D_2Fe(CO)_3$ the Mössbauer quadrupole splittings can be used to distinguish between *cis*- and *trans*-disubstituted derivatives, since the latter appear to have significantly larger Δ values. On the other hand the quadrupole splitting is not likely to be sensitive to a change of structure such as between 1a and 2c. It is also doubtful that with $DFe(CO)_4$ complexes one could distinguish between C_{3v} and C_{2v} symmetry on the basis of the Mössbauer spectrum, since both V_{zz} and η will have different values for the two symmetry types.

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The Kinetics of Monomer–Dimer Interconversion of Iron(III)–Ethylenediaminetetraacetate and Related Chelates

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The kinetics of formation and decomposition of the Fe(III) dimers of EDTA, HEDTA, and CyDTA have been determined in aqueous solution by temperature-jump and stopped-flow methods. For the formation of the dimer, designated Fe_2L_2O, from the monomeric species, in labile equilibrium FeL(OH) and FeL(H$_2$O), $d[Fe_2L_2O]/dt = k_{12}[FeL(OH)]^2 + k_{12}'[FeL(H_2O)][FeL(OH)] - k_{21}[Fe_2L_2O] - k_{21}'[Fe_2L_2O][H^+]$. For the three systems the values of the rate constants at 25° and $I = 1.0$ M with NaNO$_3$ are, respectively: $k_{12} = 6.0 \times 10^2$, 9.0×10^2, and 90 M^{-1} sec^{-1}; $k_{12}' = 2.0 \times 10^4$, 6.0×10^4, and $\sim 10^2$ M^{-1} sec^{-1}; $k_{21} = 1.2$, 4.0, and 9.0 sec^{-1}; $k_{21}' = 5.0 \times 10^8$, 3.0×10^6, and $\sim 10^{10}$ M^{-1} sec^{-1}. The values are discussed.

There have been a large number of studies of the thermodynamics of polynuclear complex formation in aqueous solution, particularly by Sillén and his school.[1] The investigation of the kinetics of the formation and breakdown of these –O– and –OH– bridged complexes had lagged behind, mainly because of their rapidity and complexity. This situation however is beginning to change and the kinetics of reactions of bridged hydroxy or oxy species of iron(III),[2] uranium(VI) and vanadium-

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[1] L. G. Sillén, *Quart. Rev.* (London), **13**, 146 (1959).

[2] H. Wendt, *Z. Elektrochem.*, **66**, 235 (1962); T. J. Conocchioli, E. J. Hamilton, Jr., and N. Sutin, *J. Am. Chem. Soc.*, **87**, 926 (1965).

TABLE I

KINETIC DATA FOR FORMATION AND DECOMPOSITION OF IRON(III) DIMERS AT 25° ($I = 1.0$)

Ligand	k_{12}, M^{-1} sec^{-1}	k_{12}', M^{-1} sec^{-1}	k_{21}, sec^{-1}	k_{21}', M^{-1} sec^{-1}	Log (k_{12}/k_{21})	−Log ($K_a k_{12}'/k_{21}'$]
EDTA	6.0×10^2	2.0×10^4	1.2	5.0×10^8	2.7 (2.9)[a]	12.1 (12.2)[b]
HEDTA	9.0×10^2 [c]	6.0×10^4	4.0	3.0×10^6	2.4 (2.4)[a]	5.7 (5.8)[b]
CyDTA	90[d]	$\sim 10^2$	9[d]	$\sim 10^{10}$	1.0 (1.0)[a]	~17.0 (17.6)[b]
H_2O	~180[f]	~3[f]	0.35[e]	3.5[e]	2.7[e]	2.8[e]

[a] Value of log K_d.[7] [b] Value of pK_D.[7] [c] Value of 9.7×10^2 from stopped-flow experiments. [d] Stopped-flow experiments. [e] Reference 2. [f] Calculated from k_{21} and k_{21}'.

(V),[3] and chromium(VI),[4] as well as chromium(III) and vanadium(III),[5] have been investigated.

An interesting series of binuclear complexes involves the iron(III) chelates with EDTA, HEDTA, and CyDTA.[6] First detected by Gustafson and Martell[7] from potentiometric measurements of the hydrolysis of these chelates, the existence of the monomer–dimer equilibrium in aqueous solution has been further supported by spectral and magnetic susceptibility studies of the HEDTA chelate[8] and from the electrochemical behavior of the EDTA complex.[9] Equilibria 1–3 are postulated. Values for K_d and K_D are given in Table I.[7] In our formulation we use coordinated water in the mononuclear Fe(III) complex and an –O– (rather than a dihydroxy) bridge in the dimer, on the basis of the structure of isolated solids,[10,11] as well as from a consideration of their properties in solution.[8,10] These equilibria (where L = $EDTA^{4-}$, $n = 4$; L = $CyDTA^{4-}$, $n = 4$; or L = $HEDTA^{3-}$, $n = 3$), which are rapidly established, are very amenable to kinetic examination by relaxation methods.

$$FeL(H_2O)^{(3-n)+} \rightleftharpoons FeL(OH)^{(2-n)+} + H^+ \qquad K_a \qquad (1)$$

$$2FeL(H_2O)^{(3-n)+} \rightleftharpoons Fe_2L_2O^{(4-2n)+} + 2H^+ + H_2O \qquad K_D \qquad (2)$$

$$2FeL(OH)^{(2-n)+} \rightleftharpoons Fe_2L_2O^{((4-2n)+} + H_2O \qquad K_d \qquad (3)$$

The monomer–dimer changes have small ΔG and high ΔH values and there are sizable optical density changes in the visible region of the spectrum with small temperature variations,[8] all desirable features for the temperature-jump experiments described in this paper. The study of the formation of bridged species, *via* a redox or a dimerization reaction, is part of our interest in the kinetics of formation of transition metal complexes, in general.[12] In addition these type of dimerization reactions are important initial steps in polymerization processes, in general, and as such deserve attention.[13]

Experimental Section

Temperature-Jump Experiments.—The temperature-jump model used was purchased from Messanlagen Studiengesellschaft, Göttingen, West Germany. A jump of 3.5°, with the sample solution finishing at 25°, was used (0.1-μF capacitor charged to about 20 kV). The attendent change in equilibrium position was detected spectrally using a split-beam arrangement and registered on a Tektronix 564 storage oscilloscope using standard electronic arrangements. Fresh solutions were prepared using iron(III) solutions (standardized as the EDTA complex, $\epsilon_{258 m\mu}$ 9.4×10^3) containing weighed amounts of ligand, from commercial sources, their purity confirmed by base titration. Lutidine or acetate ion (0.05–0.5 M) and sodium nitrate were added to give the correct pH and ionic strength (1.0 M) for the experiments. About 10% excess ligand ensured complete complexation of the iron(III). Only one relaxation process was observed at several wavelengths; most runs were at 484 mμ, where only the dimer absorbs. A typical oscillogram is shown in Figure 1.

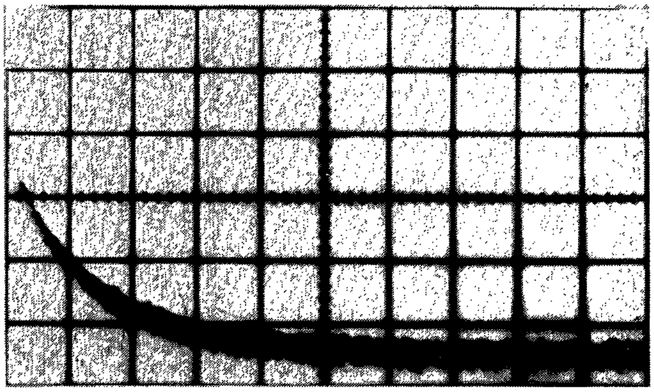

Figure 1.—Typical temperature-jump trace (λ 480 mμ)' Total [Fe(III)–HEDTA] = 5 mM; [Fe(HEDTA)OH^-] = 2.3 mM; pH 6.5; I = 1.0 M (with $NaNO_3$); T_0 = 21.5°; T_e = 25.0°; time scale, 50 msec/division. Increasing optical density upward.

The variation of τ with pH and with the concentration of FeL(OH), calculated from the total iron concentration and the K values and pH, is shown in Table II. The accuracy in τ was ±20% at the shorter times and ±10% at the longer times. Unless otherwise specified, the accuracy for the rate constants in Table I is ±25%.

Stopped-Flow Runs.—In a few experiments a glass–Lucite stopped-flow apparatus was used to measure the rate of formation of the iron(III)–HEDTA and –CyDTA dimers at pH ~6.7 and 480 mμ and pH ~11.4 and 484 mμ, respectively. Solutions of Fe(HEDTA)H_2O or Fe(CyDTA)H_2O^- at pH ~3.5 were mixed in the flow apparatus with a buffer at pH 6.7 or a basic solution (~10^{-2} M [OH^-]), respectively. The aquo species

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(3) M. P. Whittaker, J. Asay, and E. M. Eyring, *J. Phys. Chem.*, **70**, 1005 (1966).

(4) A. Lifshitz and B. Perlmutter-Hayman, *ibid.*, **65**, 2098 (1961); P. Moore, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 220 (1966).

(5) J. H. Espenson, *ibid.*, **4**, 1533 (1965), and references therein.

(6) EDTA = ethylenediamine-N,N,N′,N′-tetraacetate; HEDTA = N-(2-hydroxyethyl)ethylenediamine-N,N′,N′-triacetate; CyDTA = *trans*-1,2-cyclohexanediaminetetraacetate.

(7) R. L. Gustafson and A. E. Martell, *J. Phys. Chem.*, **67**, 576 (1963).

(8) H. Schugar, C. Walling, R. B. Jones, and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3712 (1967).

(9) H. J. Schugar, A. T. Hubbard, F. C. Anson, and H. B. Gray, *ibid.*, **91**, 71 (1969).

(10) N. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1964); G. H. Cohen and J. L. Hoard, *J. Am. Chem. Soc.*, **88**, 3228 (1966).

(11) S. J. Lippard, H. Schugar, and C. Walling, *Inorg. Chem.*, **6**, 1825 (1967).

(12) M. Eigen and R. G. Wilkins, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

(13) F. G. R. Gimblett, "Inorganic Polymer Chemistry," Butterworth and Co. Ltd., London, 1963, Chapter 3.

Table II

Temperature-Jump Relaxation Times at 25°

(I = 1.0 M, $NaNO_3$)

pH	10^4[Fe(III)]$_{total}$, M	10^4[Fe(HEDTA)-OH$^-$], M	τ, msec
4.0	25	9.2	2.5
4.0	50	16	1.8
4.3	25	11	3.8
4.3	50	19	3.2
4.3	100	32	2.6
4.5	10	5.9	7.6
4.5	25	13	5.9
4.5	50	21	4.8
4.5	100	33	2.9
4.7	10	6.4	13
4.7	25	13	9.1
4.7	50	22	7.0
5.0	25	14	11.5
5.0	50	23	8.6
5.0	100	35	5.6
6.5	10	7	137
6.5	25	15	117
6.5	50	23	80
		10^4[Fe(EDTA)-OH^{2-}], M	
6.0	80	2.0	2.0
6.5	40	3.0	5.1
6.5	80	5.7	4.8
6.5	160	11	3.8
7.0	40	6.7	12.0
7.0	80	12	9.0
7.0	160	19	6.4
7.5	40	10	24
7.5	80	16	21
7.5	160	24	16
8.0	160	26	40
8.5	20	8	300
8.5	40	12	200
9.0	20	8	285
9.0	40	12.5	240
9.0	80	18.5	186
9.0	160	27	134
9.3	160	72[a]	54

[a] CyDTA complex.

was very rapidly converted into the hydroxy species which then dimerized at a measurable rate. For the simple reaction $2FeL(OH) \rightleftharpoons Fe_2L_2O + H_2O$ (k_{12}, k_{21}), it can be easily shown that[14]

$$k_{12} = \frac{x_e}{(a^2 - x_e^2)t} \ln \left[\frac{x_e(a^2 - x_t x_e)}{(x_e - x_t)a^2} \right]$$

where a = [FeL(OH)]$_0$; *i.e.*, half the concentration of Fe(III) that is in one syringe, and x_t and x_e are the concentrations of dimer formed at time t and at equilibrium.

Results

The bulk of the measurements concerned the Fe(III)-EDTA and -HEDTA systems by the temperature-jump relaxation method. The pH ranges examined (Table II) were determined, at the lower end, by the concentration of the dimer becoming too small for a measurable temperature-jump effect or the rate of dimer decomposition then being too fast for stopped-flow experiments. Precipitation of iron(III) hydroxide or further base hydrolysis to dihydroxy mononuclear complexes occurred at the higher pH for the EDTA and HEDTA complexes.[7] The values of τ were independent of buffer concentration over a tenfold change.

For the mechanism outlined in (4), charges omitted,

$$\begin{tikzcd}
FeL(H_2O) + FeL(OH) \arrow[d, shift right, "OH^-"'] \arrow[dr, shift left, "k_{12}'(-H^+)"] & \\
FeL(OH) + FeL(OH) \arrow[u, shift right, "H^+"'] \arrow[r, shift left, "k_{12}"] & F_2L_2O + H_2O \arrow[ul, shift left, "k_{21}'(+H^+)"] \arrow[l, shift left, "k_{21}"]
\end{tikzcd} \tag{4}$$

it is easily shown by standard treatment that in buffered solutions ($\delta[H^+] \ll \delta C_i$) the one relaxation time observed (τ) is given by (5).[15,16] At a particular pH,

$$\begin{aligned} \tau^{-1} &= 4(k_{12} K_a + k_{12}'[H^+])(K_a + [H^+])^{-1}[FeL(OH)] + k_{21} + k_{21}'[H^+] \\ &= 4A[FeL(OH)] + B \end{aligned} \tag{5}$$

plots of τ^{-1} *vs.* 4[FeL(OH)] are linear, with slope A and intercept B. From a series of such plots at varying pH (Figure 2) further plots of $A(K_a + [H^+])$ *vs.* $[H^+]$ and B *vs.* $[H^+]$ can be drawn (Figure 3), from the intercept of which $k_{12}K_a$ and k_{21} and from the slopes of which k_{12}' and k_{21}', respectively, can be obtained. The figures show the results for the EDTA system. Similar plots can be made for the HEDTA complexes. The values for the various rate constants are collected in Table I. For the Fe(III)-EDTA and -HEDTA systems at pH 9.0 and 6.5, the predominant equilibrium is $2FeL(OH) \rightleftharpoons Fe_2L_2O + H_2O$ for which the simpler relaxation equation $\tau^{-1} = 4k_{12}[FeL(OH)] + k_{21}$ is applicable. There is only a small contribution from the H$^+$-catalyzed equilibria to the relaxation times ($\lesssim$10%), and it is from these experiments that the most accurate values of k_{12} and k_{21} are obtained. These were in good agreement with those obtained from the stopped-flow experiments for the HEDTA complex (Table I). At higher pH, further hydrolysis of precipitation occurred.[7] Only a couple of experiments were carried out on the Fe(III)-CyDTA system sufficient to establish reasonably accurate values for k_{12} and k_{21} by stopped-flow experiments and approximate ones for k_{12}' and k_{21}' by the temperature jump.

Discussion

The data are adequately explained in terms of scheme 4. This is shown by the linearity of the plots in Figures 2 and 3 and strongly supported by the good agreement (Table I) between the thermodynamic parameters determined potentiometrically[7] (1 M KCl) and those estimated from the kinetic results of this study (1 M $NaNO_3$). We shall briefly discuss first the decomposition and then the formation of the dimers.

The breakup of the dimer is described by a two-term rate law

$$-d(\text{dimer})/dt = \{k_{21} + k_{21}'[H^+]\}[Fe_2L_2O]$$

a behavior which is duplicated in the only other kinetic studies of depolymerization, namely, that of the ions

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[14] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 186.

[15] We have assumed, and our results bear out, that the equilibrium between the mononuclear acid and base forms, designated $FeL(H_2O)$ and FeL(OH), are rapidly established; see also ref 16.

[16] M. Orhanović and R. G. Wilkins, *Croat. Chem. Acta*, **39**, 149 (1967).

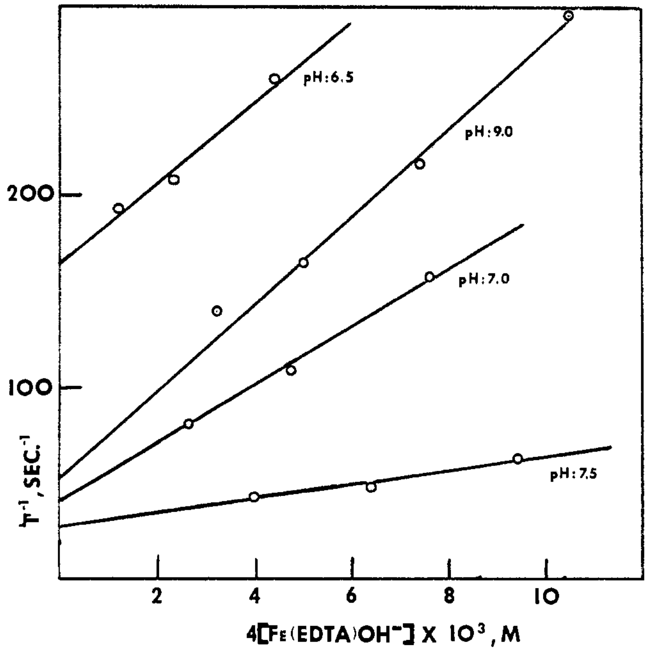

Figure 2.—Plot at 25° of τ^{-1} (sec^{-1}) against 4[Fe-EDTA)OH^{2-}] × 10^3 (*M*) at various pH. For pH 9.0, τ^{-1} × 40 sec^{-1} is plotted.

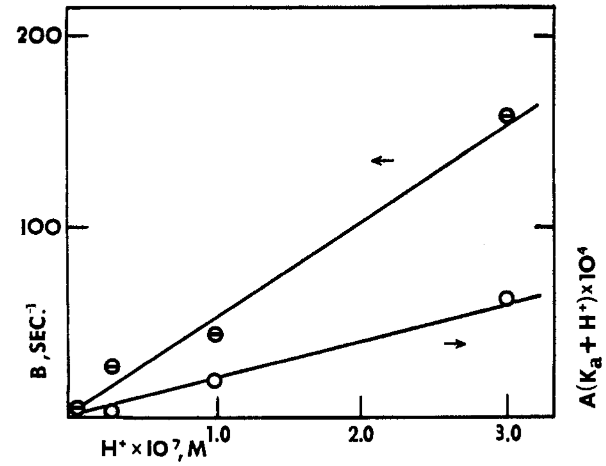

Figure 3.—Plots of *B* (sec^{-1}) and *A* (K_a + [H^+]) × 10^4 against [H^+] × 10^7 (*M*) for Fe(III)-EDTA systems at 25°.

$Fe_2(H_2O)_8(OH)_2^{4+}$,[2] $Co_2(en)_4(OH)_2^{4+}$,[17] $Cr_2O_7^{2-}$,[18] $Cr_2(phen)_4(OH)_2^{4+}$,[19] VOV^{4+}, and $VO(OH)_nCr^{(4-n)+}$.[5]

In all cases, in fact, except that of $Fe_2(OH)_2^{4+}$, the dimer breakup is *strongly* acid catalyzed with $k_{21}' \gg k_{21}$. An approximate value for k_{21} (0.5 sec^{-1} in 1 *M* $NaClO_4$ at 25°) for the EDTA system, obtained from chronocoulometric experiments,[9] is in satisfactory agreement with our own. All the iron(III) complexes have remarkably similar uncatalyzed decomposition (and formation) rate constants and it has been suggested[9] that an entering water forms with the chelates an unstable dihydroxy-bridged species similar to that believed present in the aquated dimer. The proton-assisted decomposition (not noted in the electrochemical study[9]) has rate constants for the chelated complexes some 10^6 or more times larger than for the simple iron(III)–aquo species. In the case of the EDTA and (particularly) CyDTA complexes, the second-order rate constants must be regarded as approximate since they approach diffusion-controlled values and this process might interact (kinetically) with the aquo–hydroxy equilibrium of the mononuclear species. The much larger values for k_{21}' may reflect a more easily protonated and disrupted single –O– bridge in the chelated dimers, compared with the less basic double bridge in the aquated dimer. A labile protonated $Cr_2O_7^{2-}$ ion has also been suggested for the cause of the strongly acid-catalyzed decomposition of dichromate ion.[18]

The dimer can form more easily from one molecule of the aquo species and one molecule of the hydroxy species than from two molecules of the hydroxy mononuclear iron(III) species. Part of the reason for this will reside in the increased electrostatic repulsion present with the latter but it is also likely in this case that it is more difficult to break an Fe–OH bond than an Fe–OH_2 bond in the formation of the dimer. We have indicated that the formation of dimers of this type may be controlled by the water-exchange rate and cited the dimerization of $Fe(H_2O)_5OH^{2+}$ as a possible example.[12] There are not definite data on the lability of the water or hydroxy group associated with the $FeL(H_2O)^{(3-n)+}$ or $FeL(OH)^{(2-n)+}$ ions, although the formation of a red-purple monoperoxide species from Fe(EDTA)-$(OH)_2^{3-}$ has a second-order rate constant,[16] 2.5 × 10^2 M^{-1} sec^{-1} at 25°. The water lability in the chelates would not be expected to differ markedly from that of $Fe(H_2O)_5OH^{2+}$ and the similarity of the k_{12} values for the four systems would thus be understandable on this basis.

Acknowledgment.—We are pleased to acknowledge the support of this work by the National Science Foundation (Grant GP-8099).

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[17] S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955).

[18] B. Perlmutter-Hayman, *J. Phys. Chem.*, **69**, 1736 (1965).

[19] D. Wolcott and J. B. Hunt, *Inorg. Chem.*, **7**, 755 (1968).