Mössbauer Investigation of Peroxo Species in the Iron(III)–EDTA–H_2O_2 System

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The reaction of a diiron(III)–EDTA complex with H_2O_2 in alkaline medium is studied by Mössbauer spectroscopy in conjunction with the rapid-freeze/quench technique in order to identify possible intermediate species during the formation and decomposition of the purple $(EDTA)Fe^{III}(\eta^2\text{-}O_2)^{3-}$ complex ion. Starting from the six-coordinate $[Fe^{III}EDTA]^-$ species at acidic pH, it is demonstrated that mononuclear complexes formed at a pH of about 1 are convert into the diiron(III)–EDTA complex $[(EDTA)Fe^{III}\text{-}O\text{-}Fe^{III}(EDTA)]^{4-}$ upon raising the pH to around 10.4. H_2O_2 reacts with the diiron(III) complex to give peroxide/hydroperoxide related adducts. Initially, the reaction tears apart the dimers to form a peroxo adduct, namely the seven-coordinate mononuclear $[(EDTA)Fe^{III}(\eta^2\text{-}O_2)]^{3-}$, which is stable only at very high pH. The decomposition of this peroxo adduct gives two new species, which are reported for the first time. The Mössbauer parameters of these species suggest a six-coordinate μ-peroxodiiron(III) complex $[(EDTA)Fe^{III}\text{-}(OO)\text{-}Fe^{III}(EDTA)]^{4-}$ and a seven-coordinate μ-hydroxo-μ-peroxodiiron(III) complex $[(EDTA)Fe^{III}\text{-}(OO)(OH)\text{-}Fe^{III}(EDTA)]^{5-}$. A badly resolved, extremely broad component is observed in the Mössbauer spectra during the conversion of the monomer to dimeric peroxo species, which may be attributed to the short-lived $[(EDTA)Fe^{III}\text{-}OO]^{3-}$ or $[(EDTA)Fe^{III}\text{-}OOH]^{2-}$ intermediate species.

Introduction

There has been increasing interest in the reactivity of the iron(III)–ethylenediaminetetraacetate (Fe^{III}-EDTA) system because of its importance in inorganic chemistry, biochemistry, and industrial chemistry.[1] One of the most important reactions is the formation of the purple peroxoiron complex $[Fe^{III}(EDTA)(\eta^2\text{-}O_2)]^{3-}$ in the reaction between $[Fe^{III}\text{-}(EDTA)]^-$ and hydrogen peroxide (H_2O_2)[1,2] as peroxoiron species play an important role in the oxygen activation and transfer reactions mediated by heme and nonheme iron proteins.[3,4] The characterization of a peroxoiron intermediate has been performed spectroscopically in methane monooxygenase and ribonucleotide reductase.[4,5] Peroxoiron complexes have also been shown to catalyze the polymerization of styrene and organic substrates.[6,7] The formation of a peroxoiron complex in the decomposition of hydrogen peroxide by Fe^{III} in aqueous solution is relevant in the chemistry of natural waters and atmospheric water droplets,[8–10] and the presence of a peroxo complex in Fenton-like ($Fe^{II} + H_2O_2$) and photo-Fenton ($Fe^{II} + H_2O_2 + UV$) reactions has been suggested.[11]

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Recently, we have studied the kinetics of the formation of the purple complex, $[Fe^{III}(EDTA)(\eta^2\text{-}O_2)]^{3-}$ by the reaction of $[Fe^{III}(EDTA)H_2O]^-$ with hydrogen peroxide by using a stopped-flow technique.[2] The rate law for the formation of the complex was found to be $d[\{Fe^{III}(EDTA)(\eta^2\text{-}O_2)\}^{3-}]/dt = k[\{Fe^{III}(EDTA)H_2O\}^-][H_2O_2]$, where the observed second-order rate constant, k, decreases with an increase in pH and appears to be related to the deprotonation of $[Fe^{III}(EDTA)H_2O]^-$ [Equation (1)].

$$[Fe^{III}(EDTA)H_2O]^- \overset{K_1}{\leftrightarrows} [Fe^{III}(EDTA)OH]^{2-} + H^+ \qquad pK_1 = 7.58^{[12]} \qquad (1)$$

Brausam and van Eldik[1] have performed a detailed study on the reaction between $[Fe^{III}(EDTA)(H_2O)]^-$ and hydrogen peroxide. The reaction consists of two steps, in which the second step is independent of the hydrogen peroxide concentration. The first involves the reversible end-on coordination of H_2O_2 to give an intermediate, $[Fe^{III}(EDTA)\text{-}OOH]^{2-}$, which undergoes an intramolecular rearrangement to give the high-spin Fe^{III} side-on bound peroxo complex $[Fe^{III}(EDTA)(\eta^2\text{-}O_2)]^{3-}$.

The kinetic measurements in the work of Brausam and van Eldik[1] and in our study were conducted using a total Fe^{III} concentration of $\leq 1 \times 10^{-3}$. Under these conditions,

the Fe^{III}–EDTA complex exists predominantly in the monomeric form (>90%). However, at concentrations higher than 1×10^{-3} M of the complex, the formation of a dimer occurs[12–15] [Equations (2) and (3)].

$$2\,[Fe^{III}(EDTA)OH]^{2-} \overset{K_2}{\leftrightarrows} [(EDTA)Fe^{III}\text{–}O\text{–}Fe^{III}(EDTA)]^{4-} + H_2O \qquad (2)$$

$$pK_2 = -2.95$$

$$2\,[Fe^{III}(EDTA)H_2O]^{-} \overset{K_3}{\leftrightarrows} [(EDTA)Fe^{III}\text{–}O\text{–}Fe^{III}(EDTA)]^{4-} + 2\,H^+ + H_2O \qquad (3)$$

$$pK_3 = 12.21$$

The overall equilibrium (3) represents the combination of Equations (1) and (2).

The spectral studies of the Fe^{III}–EDTA system at various pH's indicated that the concentration of the dimer species depends on the pH and the concentration of the complex.[12–17] The maximum concentration of the dimer is obtained at pH $\geq$ pK_1.

In recent years, there has been tremendous interest in diiron complexes due to their role in biological systems.[3,4,18] For example, several metalloproteins contain a carboxylate-bridged diiron center, which performs a variety of functions.[19,20] This has prompted many workers to develop small molecule synthetic model compounds for nonheme, dinuclear iron-based metalloproteins.[19–22] Studies of such compounds with hydrogen peroxide help us to understand the function of an enzyme that catalyzes an important chemical transformation. Moreover, characterizing the peroxodiiron(III) intermediates in the reactions will eventually enhance our understanding in the biological environment.[19,23]

In the present work, we have selected diiron(III)–EDTA {i.e., $[(EDTA)Fe^{III}\text{-}O\text{-}Fe^{III}(EDTA)]^{4-}$} as a simple compound to study the formation of peroxo-bridged complexes in the reaction with hydrogen peroxide at a pH of around 10.4. Mössbauer spectroscopy in conjunction with the rapid-freeze/quench technique was used to characterize the formation of the Fe^{III}–peroxo species formed during the reaction. The results demonstrate the conversion of the diiron(III)–EDTA complex into a purple Fe^{III}–peroxo species. In addition to the formation of the already characterized monomeric species $[Fe^{III}(EDTA)(\eta^2\text{-}O_2)]^{3-}$, another two peroxodiiron(III) species are reported for the first time.

Results and Discussion

Initially, the Mössbauer spectrum of 0.05 M $Fe(NO_3)_3$ at a pH of around 1.0 was measured as a simple reproduction of literature data[24] (Figure 1, a). The spectrum shows a slightly broadened, relaxational line shape, which is in agreement with the expected slow paramagnetic relaxation of monomeric Fe^{3+} ($3d^5$) species at this concentration. Addition of a stoichiometric excess of EDTA to the 0.05 M $Fe(NO_3)_3$ stock solution resulted in the formation of iron–EDTA species, as shown in Figure 1 (b). A well-developed sextet shows up, with some broadening, with a typical relaxation spectrum in the middle. Our spectrum is similar to those published by other authors who have studied the aqueous Fe^{III}–EDTA system in frozen solutions by Mössbauer spectroscopy.[25–27] The spectrum obviously indicates two different species, so it was evaluated as a superposition of a relaxational component for the central part (Species **A1**) using the Blume–Tjon two-state relaxation model implemented in MossWinn 3.0,[28] and a Lorentzian sextet (Species **A2**). The parameters are given in Table 1. Both components indicate that the relaxation rate of the Fe^{3+} spins decreases as an effect of the complexing agent. More importantly, it also shows that association of the Fe species does not take place, the significance of which at high pH will be seen later. Our observation, and the spectrum of the Fe–EDTA system (Figure 1, b) itself, are very similar to the spectrum found by Morup and Knudsen[29] for frozen aqueous solution of $FeCl_3$ containing $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5Cl]^{2+}$ species in about a 1:1 proportion.

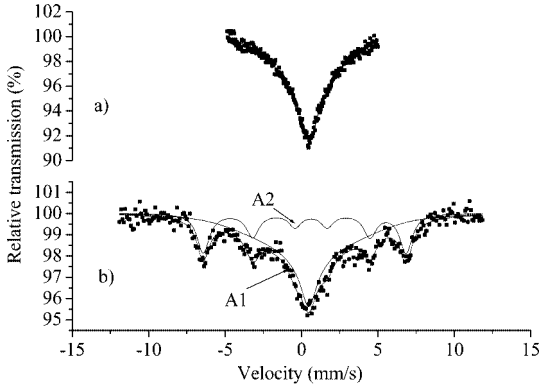


Figure 1. Mössbauer spectra of a frozen solution of 0.05 M $[Fe^{III}(EDTA)]^-$ at a pH of about 1 prepared with nitric acid (a) and after addition of EDTA in stoichiometric excess (b).

The structure of these monomeric species may be considered to be very close to that of $[Fe^{III}(EDTA)(H_2O)]^-$, which is present in solid $Na[Fe^{III}(EDTA)(H_2O)]\cdot 2H_2O$ (**S**). In this solid, the first water molecule is directly coordinated to the Fe^{3+} center, while the other two are crystal water molecules. We have measured the Mössbauer spectrum of solid $Na[Fe^{III}(EDTA)(H_2O)]\cdot 2H_2O$ at 80 K under the same conditions as the frozen solution samples so that direct comparison becomes possible. The well-known amplitude asymmetry of the doublet was observed, which is the result of the differing Larmor precession time of the m_I = 1/2 to 1/2 and m_I = 1/2 to 3/2 nuclear transitions (m_I is the magnetic quantum number) of the ^{57}Fe nucleus. Thus, the slight relaxational broadening of the doublet lines representing these two transitions is not the same under the same conditions. This phenomenon is often called the Blume effect.[30,31] The observed Mössbauer parameters (i.e., the

Table 1. Mössbauer parameters of various Fe^{III}–EDTA species observed at 80 K. δ: isomer shift; Δ: quadrupole splitting; 2ε: quadrupole shift (in case of magnetic splitting); B: internal magnetic field. The uncertainties of the parameters are estimated on the basis of the errors of individual fits of those spectra in which the abundance of that particular species was larger than 10%.

Species	Description	pH	Coord. number	δ [mm s^{-1}]	Δ or 2ε* [mm s^{-1}]	B [T]
S	$[Fe(EDTA)(H_2O)]^-$ in solid $Na[Fe(EDTA)(H_2O)]\cdot 2H_2O$		7	0.57(1)	0.66(1)	≈0
A1	$[Fe(EDTA–H)(H_2O)]$	≈1.0	6	0.48(11)	+0.16(45)*	30(6)
A2	$[Fe(EDTA)]^-$	≈1.0	6	0.43(2)	–0.44(5)*	41.2(2)
B	$[(EDTA)Fe\text{-}O\text{-}Fe(EDTA)]^{4-}$	≈10.4	6	0.455(5)	1.60(5)	0
F	$[(EDTA)Fe(\eta^2\text{-}O_2)]^{3-}$	≈10.4	7	0.62(4)	+0.53(5)*	51.1(5)
D	$[(EDTA)Fe\text{-}(OO)(OH)\text{-}Fe(EDTA)]^{5-}$	≈10.4	7	0.57(1)	0.40(3)	0
E	$[(EDTA)Fe\text{-}(OO)\text{-}Fe(EDTA)]^{4-}$	≈10.4	6	0.47(3)	0.85(4)	0

high isomer shift) given in Table 1 are consistent with sevenfold coordination of Fe^{3+} in the solid species **S**.[32] Note that the solubility limit of $Na[Fe^{III}(EDTA)(H_2O)]\cdot 2H_2O$ did not allow us to perform experiments in aqueous solution, in which magnetic relaxation would be absent, because, even in the solid, the average distance between Fe^{3+} ions is not small enough to speed up spin relaxation, so no magnetic field is observed.

There is an apparent contradiction between the isomer shifts observed for solid $Na[Fe^{III}(EDTA)(H_2O)]\cdot 2H_2O$ (**S**) and the aqueous Fe^{III}–EDTA complexes (**A1** and **A2**) at a pH of around 1.0 (Table 1). This is not surprising because one of the carboxylic groups is very likely to become protonated in highly acidic solution, which results in dechelation of this carboxylic group from the coordinative bond and results in sixfold coordination of the central Fe^{3+}. Such species have been observed by Spijkerman et al.[33] in the solid $Fe^{III}(EDTA\text{-}H)(H_2O)$ with Mössbauer parameters δ = 0.45(5) mm s^{-1} and Δ = 0.42(5) mm s^{-1} at 78 K. It is reasonable to assume that due to a protolytic equilibrium (which means acid-catalyzed exchange of a water molecule and a carboxylate group at one of the six coordination sites of the central Fe^{3+} ion), one of the two subspectra in our Mössbauer spectrum represents $[Fe^{III}(EDTA\text{-}H)(H_2O)]$, while the other can be assigned to $[Fe^{III}(EDTA)]^-$, both of which contain sixfold coordinated Fe^{3+}, in agreement with the observed isomer shifts. Since both the magnetic field and the relaxation time are expected to increase with increasing electron donation to the Fe 3*d* orbitals, we can tentatively assign the structure $[Fe^{III}(EDTA\text{-}H)(H_2O)]$ to species **A1** and $[Fe^{III}(EDTA)]^-$ to species **A2**, although the quadrupole splitting for species **A1** observed by us is smaller than that in ref.[33] Note that the quadrupole shift of **A2** may not be directly related to quadrupole splitting data obtained from Lorentzian fits of nonmagnetic species because the relative orientation of the electric field gradient and the magnetic field is not known. We note here that Kanamori et al.[34] have found hexacoordinate Fe^{III}–EDTA species in solution only at even lower pH (in 1–2 M HCl) using Raman spectroscopy, while at pH 1.2 they identified heptacoordinate species. The presence of chloride vs. nitrate anions (the latter in our case) may have some significance in this discrepancy.

As a next step, measurements on the Fe^{III}–EDTA system were conducted in alkaline medium. The pH of the 0.05 M Fe^{III}–EDTA solution was raised to about 10.4, which resulted in precipitation of some hydrous iron(III) oxide, as checked by a Mössbauer run. (This precipitation is most probably due to kinetic effects, and has also been observed by other authors.[35]) The solution was filtered and the filtrate was frozen to record the Mössbauer spectrum (Figure 2, a). The expected species present in alkaline solution is $[Fe^{III}(EDTA)OH]^{2-}$ [Equation (1)]. However, the Mössbauer spectrum of the frozen solution showed no sign of any magnetic splitting (in agreement with the observation of Kachanova et al.[26]) due to very fast spin-spin relaxation. The doublet of Figure 2 (a) can therefore be assigned to a dimer species. The Mössbauer parameters of the doublet were found to be δ = 0.44(2) mm s^{-1} and Δ = 1.6(1) mm s^{-1} (Table 1). Marton et al.[16] have assigned this doublet to an oxo-bridged species $[(EDTA)Fe^{III}\text{-}O\text{-}Fe^{III}\text{-}(EDTA)]^{4-}$ (**B**), which implies a coordination number of 7 for both Fe^{3+} centers. If this assignment is correct, the simple rule that an increasing coordination number results in increasing isomer shift, which seems to work for momoneric species,[32] would not work when going from monomer to dimer [Equation (2)]. This isomer shift implies sixfold coordination, which would be in agreement with the suggestion of Kanamori et al.,[34] who claim that one carboxylate on each Fe center is dechelated. On the other hand, the driving force for dechelation could be a tendency to gain a more symmetrical (closer to octahedral) and therefore energetically favorable structure for the ligand sphere of iron, which would certainly result in a low quadrupole splitting. In contrast, a large quadrupole splitting is observed, which is not characteristic for Fe^{3+} (although not uncommon for μ-oxo dimers[36]), and shows a highly distorted electronic structure. It has been proposed that the [Fe-O-Fe] moiety has a closely linear structure,[14,15] and now it is logical to assume that this linearity is, at least partially, enforced by the bulky and spatially highly restricted EDTA ligand, and that even after the dechelation of one carboxylate arm, it still remains severely distorted, causing a high quadrupole splitting in the Mössbauer spectrum. The stability of the Fe–O–Fe bridge seems to overcompensate the destabilization of the ligand sphere of iron caused by distortion. Thus, there seem to be more arguments in favor of the sixfold coordination of iron in the dimeric species **B**. Our reasoning is strongly supported by the single crystal XRD study of Ozarowski et al.[37] on $Na_4[(EDTA)Fe^{III}\text{-}O\text{-}Fe^{III}(EDTA)]\cdot 3H_2O$, who

found sixfold coordination with one dechelated carboxylate group for each EDTA ligand. Our results thus show that this coordination number is preserved in high pH aqueous solutions. On the other hand, it is interesting to note that Schugar et al.[35] have reported Mössbauer data on solid $Na_4[(EDTA)Fe^{III}\text{-}O\text{-}Fe^{III}(EDTA)]\cdot 12H_2O$, for which the isomer shift (0.44 mm s^{-1} at 77 K) matches our observation for dissolved $[(EDTA)Fe^{III}\text{-}O\text{-}Fe^{III}(EDTA)]^{4-}$ perfectly, although the quadrupole splitting is somewhat larger at 1.94 mm s^{-1}. This is an indication of different distortions of the ligand sphere of Fe^{3+} in the solid crystal and in the alkaline aqueous solution.

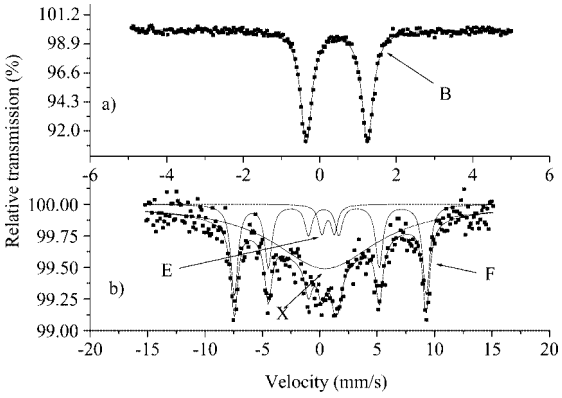


Figure 2. The Mössbauer spectrum of a frozen solution of the Fe^{III}–EDTA system at a pH of about 10.4 (a) and the spectrum after addition of excess H_2O_2 (b).

A very interesting example of the structure of the $[(EDTA)Fe^{III}\text{-}O\text{-}Fe^{III}(EDTA)]^{4-}$ moiety in solids has been presented by Gomez-Romero et al.,[38] who reported results on the heterobimetallic complex $[Cu^{II}(en)_2]_2[(EDTA)Fe^{III}\text{-}O\text{-}Fe^{III}(EDTA)]\cdot 2H_2O$ and also found six-coordinate iron, although the dechelated fourth carboxylate arm of EDTA is coordinated in this complex to the neighboring Cu center according to XRD analysis.

It should be pointed out that the Mössbauer parameters of monomeric $[Fe^{III}(EDTA)(OH)]^{2-}$ are not known because dissociation of the dimers at high pH would become significant in a low concentration range where recording a Mössbauer spectrum is not feasible even with ^{57}Fe-enriched material.

Finally, the Mössbauer study of the reaction of iron(III)–EDTA with H_2O_2 was conducted in alkaline medium. Addition of H_2O_2 to the Fe^{III}–EDTA system at a pH of around 10.4 gave a purple coloration of the solution, which has been attributed to the formation of an $[Fe^{III}(EDTA)(\eta^2\text{-}O_2)]^{3-}$ species (**F**) by several spectroscopic techniques.[39–41] The Mössbauer spectrum of the purple species shows a sextet (Figure 2, b), thus indicating that the dimer species (**B**) is converted into a monomer (**F**) by hydrogen peroxide. This is due to the side-on coordination of the peroxide ion, which saturates the coordination environment of the Fe center and steric hindrance does not allow the coordination of another Fe. The observed large isomer shift (Table 1) is consistent with an increased coordination number of the iron centers. Brausam and van Eldik[1] have suggested that iron is seven-coordinate in this complex, which means dechelation of one carboxylate arm (pentadentate EDTA), although they cited theoretical calculations in the literature that were in favor of sixfold coordination.[40] XAS measurements on peroxoiron(III) complexes with pentadentate N-donor ligands by Koehntop et al.[42] were not always conclusive either regarding the exact coordination number of iron (side-on or end-on bonding of O_2^{2-}). Our Mössbauer data support minimum sevenfold coordination on the basis of the large isomer shift. Horner et al.,[41] who prepared $[Fe^{III}(EDTA)(\eta^2\text{-}O_2)]^{3-}$ in a very pure form in solution, also found a large isomer shift but these authors did not discuss possible implications for the coordination number. A comparison with the six-coordinate $[Fe^{III}(EDTA\text{-}H)(H_2O)]$ (**A1**) and $[Fe^{III}(EDTA)]^-$ (**A2**) shows that the increase in the Fe 3*d* (spin-)density as a result of the "7th ligand" in the coordination sphere of Fe^{3+} appears to be enough to further raise the magnetic field to 50.4 T. It is also remarkable that the quadrupole shifts for the monomeric $[Fe^{III}(EDTA)]^-$ (**A2**) and monomeric $[Fe^{III}(EDTA)(\eta^2\text{-}O_2)]^{3-}$ (**F**) have opposite signs (Table 1). The exact interpretation of this observation would be difficult but the substantial difference in the symmetry of the two systems makes it quite reasonable.

In addition to species **F**, two other species, **E** and **X**, were also observed (Figure 2, b). A small doublet for species **E** co-exists with the sextet (species **F**), with an isomer shift of $\delta = 0.46$ mm s^{-1} (see Figure 2, b). This component was found to be formed from the sextet component. Doublet **E** has no magnetic splitting, therefore it was assigned to a dimer species (Table 1). It is worth mentioning that peroxodiiron(III) coordination compounds with other ligands have very similar Mössbauer parameters.[36] Species **X** shows-up with extreme line broadening, which is most probably due to relaxation.

The fate of the purple solution was studied in a separate experiment. In this experimental set-up, Fe^{III}–EDTA and H_2O_2 solutions were mixed in the dark and the Mössbauer spectrum of the frozen purple solution was recorded (Figure 3, a). We have observed many times in our experiments that light influences the rate of the reactions in the Fe–EDTA–H_2O_2 system. This effect is not unknown, but is rather unexplored in detail. We deliberately used this phenomenon to slow down or speed up reactions but we do not attempt in this work to give an explanation for this photochemical effect. The formation of species **F**, **E**, and **X** occurred similar to the observations made in the previous experiment (Figure 2, b). The frozen solution was then allowed to melt for 5 min at room temperature in the dark and a Mössbauer spectrum was recorded again after freezing of the solution (Figure 3, b). The fraction of doublet **E** increased slightly at the expense of **X**. Species **X** is thus an intermediate in the conversion of species **F** to **E**. After further aging at room temperature for 10 min under daylight conditions, an abrupt change in the Mössbauer spectra was observed. Species **F**, **E**, and **X** all disappeared, and a new species having a doublet with an isomer shift, δ, of 0.57 (**D**) formed in addition to the already known oxo-bridged species $[(EDTA)Fe^{III}\text{-}O\text{-}Fe^{III}(EDTA)]^{4-}$ (**B**; Figure 3, c).

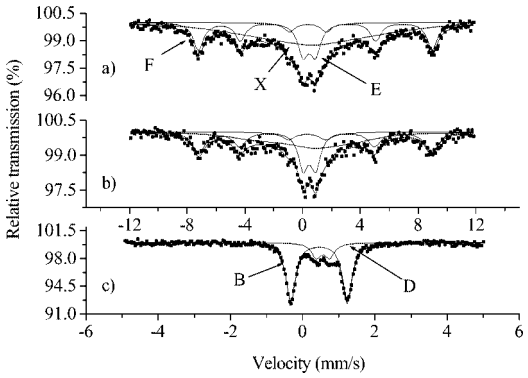


Figure 3.Mössbauer spectra of the Fe^{III}–EDTA–H_2O_2 system at a pH of about 10.4: a) initial state, b) after 5 min aging at room temperature (room temp.) in the dark, and c) after a further 10 min aging at room temp. in daylight.

The formation of species **B** from species **D** was confirmed by conducting the reaction between Fe^{III}–EDTA and H_2O_2 at room temperature in daylight, where formation and decay of the purple species is fast. The Mössbauer spectra of the reaction are given in Figure 4. Species **X** and **E** were not observed. This further suggests the intermediate nature of these species. The initial spectra show traces of the sextet of species **F** together with doublets of species **B** and **D** (Figure 4, a). Species **D** decays quickly to the original Fe^{III}–EDTA species **B** (Figure 4, b and c). It is noteworthy that the color of the solution belonging to the Mössbauer spectrum of Figure 4 (b) is still purple. Since **B** has a yellow color, species **D** should be responsible for the characteristic purple color of this solution. It is tentatively assumed (since it has been observed only together with the purple species **F**) that species **E** also has a purple color as a consequence of the presence of the peroxo moiety.

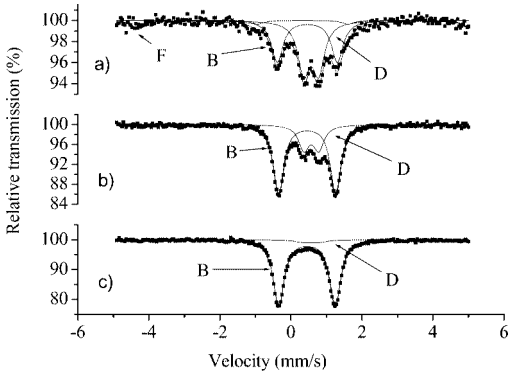


Figure 4. Evolution of Fe-bearing species in the Fe^{III}–EDTA–H_2O_2 system at a pH of about 10.4 in daylight: initial state (a), after 4 min aging at room temp. (b), and after 10 min aging at room temp. (c).

To further understand the conversions of species in the purple solution, another study was conducted at low temperature in darkness in order to slow down the reactions. The Fe^{III}–EDTA and H_2O_2 were mixed in an ice bath (ca. 0 °C) and the spectra were recorded after aging the mixture in consecutive three-minute steps (Figure 5). All agings were carried out at around 0 °C. A slow evolution of the various species from **B** to **F** (and **X**) to **E** at low temperature was observed. The formation and decomposition of species **X** is pronounced (Figure 5, c and d). Since species **X** shows up together with **F** and/or **E**, it is reconfirmed now that it should represent a very short-lived (to account for the extremely large line broadening) transitional state between **F** and **E**. We should note here that in the spectra c and d of Figure 5 and b of Figure 2, the assignment of the very small doublets (3–4%) to species E is rather tentative due to statistical insignificance; this doublet is fully developed only in the spectra in Figure 5 (e) and Figure 3 (a and b).

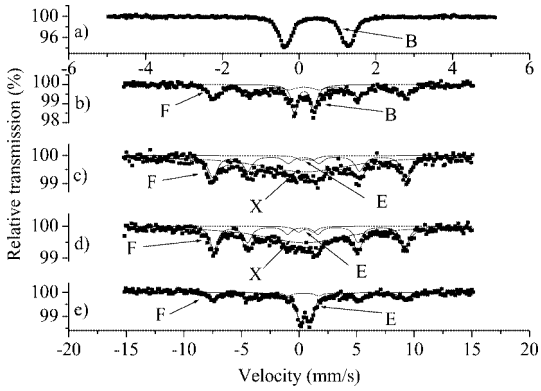
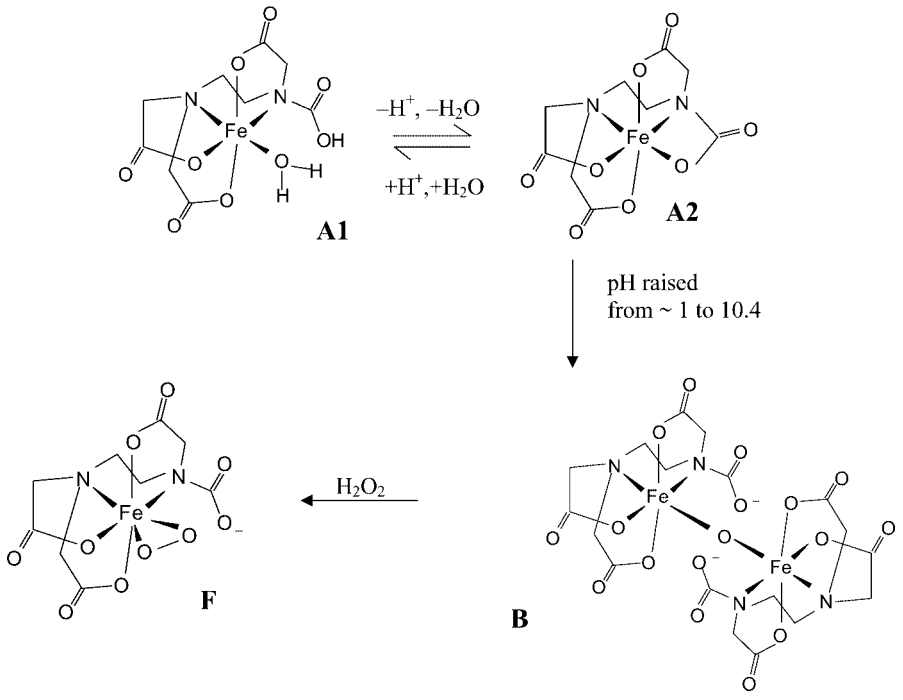


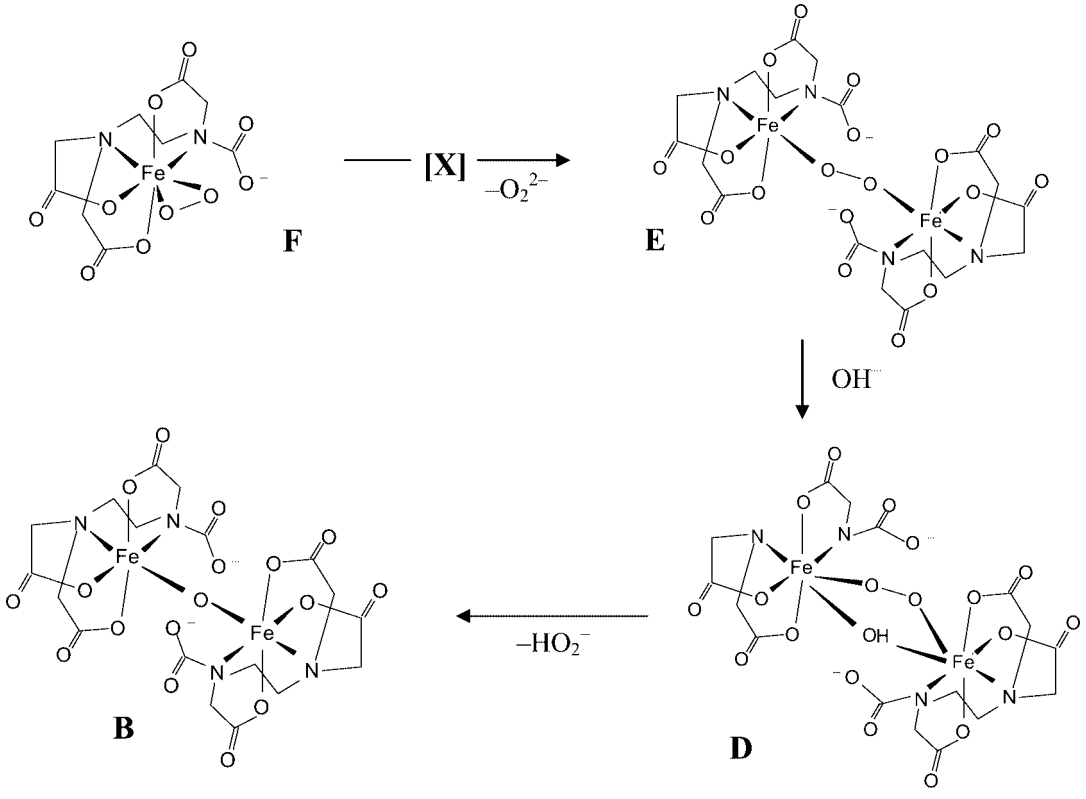
Figure 5. Evolution of Fe-bearing species in the Fe^{III}–EDTA–H_2O_2 system at a pH of about 10.4 (initial value before adding H_2O_2) at around 0 °C: a) before addition of H_2O_2, b) immediately after addition of H_2O_2, c) after 3 min aging at 0 °C, d) after an additional 3 min of aging at 0 °C, and e) after a second additional 3 min of aging at 0 °C.

The formation and the decomposition of species **F** may be summarized as shown in Schemes 1 and 2, respectively. In Scheme 1, the dimer species **B** is converted into the monomeric species **F** upon the addition of hydrogen peroxide. The decay of the monomer **F** to dimer **E** (Scheme 2) takes place through intermediate **X** (structure not shown).

The observation of species **X** is probably the consequence of an equilibrium giving a short-lived monomeric [(EDTA)-Fe^{III}-OO]$^{3-}$ species or its protonated form [(EDTA)Fe^{III}-OOH]$^{2-}$ (with end-on coordination of O_2^{2-} to iron). Only the much more stable dimer (**E**) clearly shows up in the Mössbauer spectra. The isomer shift of species **E** is practically the same as that of species **B** and formally corresponds to a sixfold coordinated monomeric species. This indicates that the dechelation of one carboxylate arm at each iron center occurs here, similar to the species **B**. At the same time, since the peroxo bridge allows larger separation of the Fe^{III}–EDTA moieties as compared to the case of a regular oxo bridge, the repulsion between the two pentadentate EDTAs and, inherently, their spatial distortion is smaller, which results in only half of the quadrupole splitting found for species **B**. It is noteworthy that in this picture, the isomer shift does not differ for a μ-oxo and a μ-peroxo species as the difference in the donicity of the oxo and peroxo oxygens (as a sixth ligand around the Fe^{3+} center) is probably not substantial.



Scheme 1.



Scheme 2.

The driving force for the transformation of monomeric species **F** to dimeric species **E** could be the loss of H_2O_2 due to its decomposition. The decomposition of H_2O_2 results in an increase in the pH since H_2O_2 is more acidic then H_2O. Therefore, further decomposition of species **E** may occur through the addition an OH^- ion to form a doubly bridged species **D**. Doubly and triply bridged binuclear complexes of Fe^{III} with nonequivalent bridging ligands are known, for example (μ-carboxylato)(μ-oxo)diiron(III)-type compounds.[43] We are not aware of any reports of (μ-hy-

droxo)(μ-peroxo)diiron(III) complexes, which may be due to their low stability, as found here. The isomer shift of species **D** is significantly higher than that of species **E**, which is in agreement with the increased coordination number (7). The decrease of the quadrupole splitting cannot be fully understood in this simple picture.

At this stage, decomposition (further loss) of H_2O_2 and the concomitant rise in pH logically drives us back to species **B**.

We have to mention here that the proposed structures for species **E** and **D**, which should be very logical, may not be the ultimate choice. For example, partial protonation of the peroxo bridge may occur, which would result in the species $[(EDTA)Fe^{III}\text{-}HOO\text{-}Fe^{III}(EDTA)]^{2-}$. However, such a species contains nonequivalent iron centers, and thus two doublets are always expected to be a pair in the Mössbauer spectrum. This is not observed. It is assumed that the position of the proton is not averaged out between the two oxygens on the Mössbauer timescale, and that the Mössbauer parameters of the two nonequivalent irons would be significantly different. Thus, since species **D** is a peroxo-type dimeric species, the increase of the isomer shift upon going from species **E** to **D** can be considered as a strong argument to support the formation of the double bridge.

Experimental Section

A stock solution of $Fe(NO_3)_3$ (0.05 M) was prepared by dissolving metallic iron (enriched in ^{57}Fe to ca. 90%) in nitric acid. The final pH of this stock solution was about 1.0. The Mössbauer measurements were performed by mixing the iron(III) solution (500 μL, 0.05 M) with solid EDTA. The amount of EDTA in the mixture was in excess and the final molar ratio of EDTA to Fe^{III} was 1.3:1. The pH of the solution, measured with a digital pH meter (Radelkis), was adjusted by adding KOH (0.5 M). At alkaline pH, some precipitate was observed in the Fe^{III}–EDTA solution. This precipitate were filtered off through a 5-μm filter. The filtrate was diluted with distilled water to achieve 1.0 mL total volume. No further precipitation of the solution was observed.

The reaction of Fe^{III}–EDTA with hydrogen peroxide was studied by adding H_2O_2 (50 μL, 30%) to the solution. The concentration of H_2O_2 in the final solution was in large excess. The resultant deep-purple solution was quenched immediately drop-by-drop on a pre-cooled metal slab almost completely immersed in liquid nitrogen. The freezing of the total volume (15–20 droplets) lasted for about half a minute. Vértes[24] has shown previously that this quenching technique (cooling speed ca. 30 °C s^{-1}) preserves the structure of the solution, and therefore the species existing in the liquid state can be studied. The frozen droplets were collected in a sample holder and placed into a bath-type cryostat filled with liquid nitrogen.

The frozen samples were measured by a conventional constant acceleration type Mössbauer spectrometer (Ranger). The spectrum evaluations were carried out with the assumption of a Lorentzian line-shape, unless otherwise stated, using MossWinn 3.0.[28] All isomer shifts are given relative to α-Fe at room temperature.

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