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Understanding of the Mode of Action of Fe^{III}–EDDHA as Iron Chlorosis Corrector Based on Its Photochemical and Redox Behavior**

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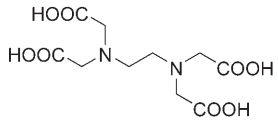
Abstract: The very low reduction potential of the chelate Fe^{III}–EDDHA (EDDHA = ethylenediamine *N,N′*-bis(2-hydroxy)phenylacetic acid) makes it unreactive in photochemically or chemically induced electron transfer processes. The lack of reactivity of this complex toward light invalidates photodegradation as an alternative mechanism for environmental elimination. However, in spite of its low reduction potential, the biological reduction of Fe^{III}–EDDHA is very effective. Based on electrochemical measurements, it is proposed that Fe^{III}–EDDHA itself is not the substrate of the enzyme ferric chelate reductase. Likely, at the more acidic pH in the vicinity of the roots, the ferric chelate in a closed form (FeL^-) could generate a vacant coordination site that leads to an open hexacoordinate species (FeHL) where the reduction of the metal by the enzyme takes place.

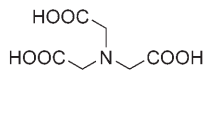
Keywords: chelate reductase · chlorosis · electrochemistry · electron transfer · iron · photochemistry

Introduction

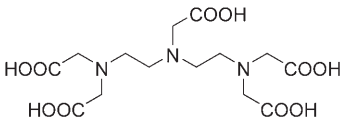
Polyaminecarboxylic acids have the ability to form stable water-soluble complexes with di- and trivalent metal ions. Accordingly, they are used to control the solubility and precipitation of metal ions in a broad range of areas, from domestic products to industrial and agronomic applications.[1,2] Owing to the increasing concern about their environmental impact, biotransformations and mineralization processes of the polyaminecarboxylic acids most widely used, nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) have been studied rather well. NTA is readily biodegradable,[3] but is under scrutiny due to possible adverse health effects.[4] On the other hand, the very effective chelating agent EDTA has the disadvantage of being quite persistent toward biological degradation, either as a free acid or as a metal complex.[1] This feature has directed some attention to other mechanisms of elimination based on abiotic processes, mainly photodegradation, oxidation by metal oxides or hydroxides and, to a smaller degree, sorption and sedimentation.



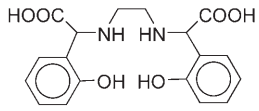
EDTA



NTA



DTPA



EDDHA

Studies about the photoreactivity of NTA,[5–7] EDTA[8–12] and diethylenetriaminepentaacetic acid (DTPA)[13] reveal that photochemical degradation can be a good abiotic alternative pathway in the removal of these chelating agents from water. These investigations have shown that Fe^{III}, Cu^{II}, and other divalent metal–NTA complexes are quite photo-

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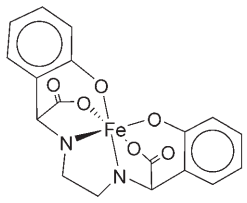
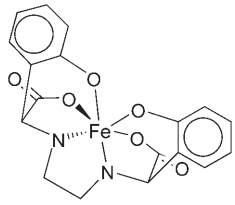
[**] EDDHA = ethylenediamine *N,N′*-bis(2-hydroxy)phenylacetic acid.

stable, whereas Fe^{III}–EDTA and Fe^{III}–DTPA are photolabile complexes, which when exposed to sunlight and in the presence of oxygen, lead to different photodegradation products that are found to be readily biodegradable.[13,14] Other metal complexes of EDTA (with Mg^{II}, Ca^{II}, Ni^{II}, Cu^{II}, Zn^{II}) are unreactive toward sunlight.[9,10] The photoreactivity of Fe^{III}–EDTA and Fe^{III}–DTPA has been explained in terms of a light-induced reduction of the Fe^{III} to a Fe^{II}, which is followed by the sequential fragmentation of the ligand.

Among polyaminecarboxylic acids, those bearing phenolate groups are well-known products massively used as micronutrient chelating fertilizers. In particular, ethylenediamine *N,N′*-bis(2-hydroxy)phenylacetic acid (EDDHA) is one of the most efficient iron-chelating agents employed to relieve iron chlorosis in plants. This nutritional disorder results in a decrease in the amount of chlorophyll in leaves and is caused by a low absorption of iron in alkaline soil conditions.[15] It has been estimated that in Mediterranean countries alone, more than 4000 metric tons of Fe^{III}–EDDHA and other structurally related phenolic ferric chelating agents are used every year. In spite of this fact, their biodegradation and photodegradation pathways are virtually unknown and the mechanism of iron release is subject of debate.[16]



Fe^{III}–*rac*-*o*,*o*-EDDHA



Fe^{III}–*meso*-*o*,*o*-EDDHA

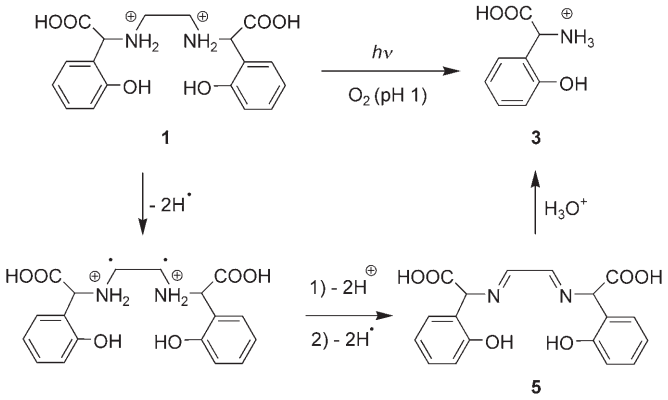
Abstract in Spanish: *El bajo valor del potencial de reducción del quelato Fe^{III}-EDDHA le convierte en un compuesto prácticamente inerte en procesos de transferencia electrónica, tanto inducida por vía química como por vía fotoquímica. Este hecho elimina la fotodegradación como una posible alternativa abiótica para la destrucción del Fe^{III}-EDDHA en el medio ambiente. Sin embargo, a pesar de su bajo potencial de reducción, el Fe^{III}-EDDHA es uno de los mejores correctores de clorosis férrica que se conocen, lo que implica que el proceso de reducción biológica de este complejo se produce de forma eficaz. En este trabajo, basándonos en medidas electroquímicas, proponemos que el complejo Fe^{III}-EDDHA en su forma (FeL^-) no es el sustrato de la enzima quelato reductasa férrica. Posiblemente, debido a la acidificación que se produce en la proximidad de las raíces, el complejo FeL^- podría generar una vacante de coordinación y adoptar una forma hexacoordinada abierta (FeHL) en la que se produce la reducción enzimática.*

Our current work is directed toward the synthesis of biologically active bioorganometallic compounds.[17] We are interested in the study of the mechanisms of reaction of metal–organic complexes,[18] to understand the effect of both ligand and metal in the biological action of these compounds.

Herein we report a study of the photochemical behavior of EDDHA, both as a free acid and as a Fe^{III} complex. Since it has been stated that the photodegradation of Fe^{III} polycarboxylate complexes requires the initial reduction of the Fe^{III} in a ligand-to-metal photoinduced electron transfer process,[19] in this work we will also study the behavior of the Fe^{III}–EDDHA in electron transfer reactions, which are either chemically or electrochemically induced. The ability of this complex toward reduction will help us to understand the mechanism of the iron-uptake in strategy-I plants, a process in which the enzyme ferric chelate reductase plays a major role.[16,20] The results of this study will allow us to evaluate the importance of the photochemical degradation in the removal of EDDHA and Fe^{III}–EDDHA from the environment.[21]

Results and Discussion

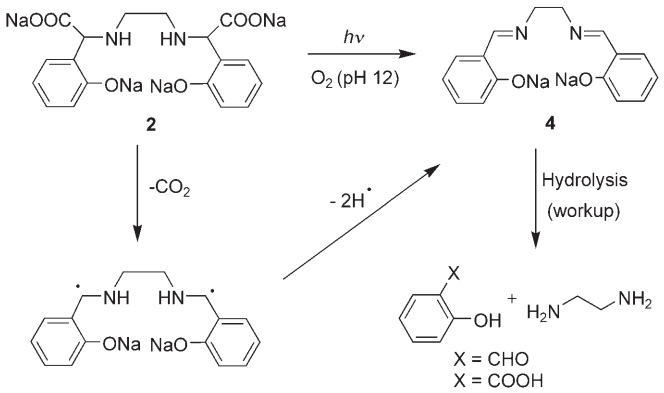
The photochemical behavior of EDDHA is unknown and for the purposes of this work is the first step towards understanding the photodegradation pathways and the photoproducts formed from the Fe^{III}–EDDHA complex. EDDHA as a free acid (isoelectric form) is insoluble in water in the pH range of 6–7 and hence the study of its photochemical behavior in solution should be done either in acidic medium (as hydrochloride **1** (see Scheme 1)) or in basic medium (as carboxylate and phenolate salt **2** (see Scheme 2)). Solutions of EDDHA in water at $pH < 2$ or $pH > 8$ are stable indefinitely when stored in the dark. The irradiations with UV/Vis light were done using a 400-W medium-pressure mercury lamp ($\lambda_{max} = 254$, 313, 365, 436 nm). For the visible-light experiments ($\lambda > 313$ nm) a Pyrex filter was used. The samples were irradiated for 24 h. The irradiation of solutions of EDDHA with UV/Vis light, in the presence of O_2 and



Scheme 1.

under acidic conditions (pH 1), leads to *o*-hydroxyphenyl glycine (**3**) as the main reaction product (44%), together with unaltered starting material (51%) (Scheme 1). The photodegradation is much slower in visible light ($\lambda >$ 313 nm) and only trace amounts of **3** were obtained after irradiation for 24 h (93% of EDDHA was recovered unaltered in the experiment). At basic pH values (pH 12), the main isolated photoproduct on both UV/Vis and visible irradiation is salicylaldehyde imine **4** (11%), accompanied by 73–75% of recovered unreacted starting material (Scheme 2). Additionally, hydrolysis of the imine **4** is observed, and salicylaldehyde together with its oxidation product (salicylic acid) were also identified in the crude reaction products. The same product distribution but in considerably lower yields was observed when the experiments were carried out in deaerated solutions. The irradiation of suspensions of EDDHA in water at pH 7 afforded the unaltered product after reaction times of 24 h under all conditions essayed.

These results indicate that the chelating agent EDDHA is rather stable to photodegradation. Only at extreme pH values, well above or below the typical environmental pH range (4 to 8), is some photoreactivity observed. The process is clearly pH-dependent and requires UV light. Under strong acidic conditions, **3** is formed, presumably by α-C–H fragmentation of the amino bonds followed by deprotonation and disproportionation, to finally form the unstable glyoxal imine **5**, which is hydrolyzed in the acidic medium (Scheme 1).[22] This type of reactivity is similar to that reported for DTPA, which after successive fragmentations leads to glycine as one of the main photodegradation products.[13] In a strong basic medium, EDDHA is less reactive. Salicylaldehyde imine **4** is formed in low yield by photoinduced decarboxylation of **2**, a well-known process for α-amino carboxylates (Scheme 2).[23]

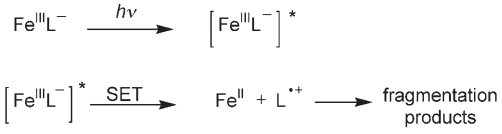


Scheme 2.

The chelate Fe^{III}–EDDHA is stable in the pH range 3–10.[24] The photochemical behavior of this compound has been studied at pH 2, 6.5, and 11, in the presence of O_2 and with UV or visible light. In acidic solution, the iron chelate was recovered practically unaltered after irradiation for 24 h. Trace amounts of **3** (< 2%) were detected in the reaction product. In basic medium, only small amounts (6%) of salicylic acid and salicylaldehyde were identified as degradation products. Finally, in neutral solution, the product was totally inert to photodegradation.

The results obtained in the different experiments show that Fe^{III}–EDDHA is very resistant to photochemical degradation. Solutions of the complex in water are almost totally inert to light irradiation, even when the experiment was carried out at pH values well above or below the pH range in which the iron chelate is stable. In those cases, the small amount of photoproducts detected should come from the photodegradation of the free ligand EDDHA, which is present in solution in equilibrium with the complex.[24]

The behavior of Fe^{III}–EDDHA toward light contrasts with that previously reported for the very photoreactive Fe^{III}–EDTA and Fe^{III}–DTPA.[7,12,13] In those cases, a mechanism analogous to that proposed for the photochemistry of Fe^{III}–oxalate[25] and Fe^{III}–citrate complexes[26] has been suggested (Scheme 3). After the excitation of the complex with



Scheme 3.

light, the Fe^{III} is reduced by electron transfer (SET) from one of the carboxylate groups of the ligand, leading to Fe^{II} and a carboxylate radical cation species from which the photofragmentation products could be formed. The irreversible oxidation of ferrous iron in the medium finally leads to the precipitation of iron hydroxide.

Our experimental results show that the photolytic ligand-to-metal electron transfer does not occur in Fe^{III}–EDDHA, at least not in a productive way. Maybe the ligand already transfers an electron to the metal (SET) and the radical cation is formed, but a fast back electron transfer reaction (BET) re-forms Fe^{III}, which impeding the progress of the reaction.[27] On the other hand, the formation of light-induced carboxylate radicals has been proposed for oxalates, malonates, and citrates, but even though this a very likely process for phenol-polyaminecarboxylic acids, there are no data reported about this reaction for such compounds.

It has been stated that there is a strong relationship between the photosensitivity of a metal chelate and the structure of the ligand.[28] Generally, transition-metal chelates have intense absorption bands assigned to transitions involving charge-transfer excitations. However, chelate ring chromophores such as iron phenanthroline and other related complexes are essentially insensitive to light despite their intense UV/Vis absorptions. This fact indicates that light absorption is not the only factor that determines the photoreactivity of a metal complex.

As we have discussed above, ligand-to-metal photoinduced electron transfer does not take place in the Fe^{III}–

EDDHA complex. However, the mechanism of iron release to plants from this type of chelate requires the reduction of Fe^{III} to Fe^{II}. Accordingly, we decided to explore the behavior of the Fe^{III}–EDDHA complex in the presence of chemical electron transfer reagents such as Na or Li naphthalenide,[29] samarium iodide (SmI_2),[30] or potassium graphite (C_8K).[31] The reactions were carried either in solution (naphthalenides, SmI_2) or in heterogeneous phase (C_8K). In all cases, the complex was recovered unaltered after the process. This fact was confirmed by ESI-MS of the reaction product, which showed a peak at *m/z* 412 $[M-H]^-$ (negative-ion mode) corresponding to unaltered Fe^{III}–EDDHA. If the reduction of the metal in the reaction medium had occurred, free Fe^{II} should have been released to the solution. Considering that the affinity of the EDDHA for Fe^{II} is very low ($\log K = 14.30$),[32] the free ligand should have been observed after the reaction, which was not the case. The reactivity of free EDDHA in the presence of the electron transfer reagents under the conditions essayed for the complex was also checked, but the product was recovered unaltered in all cases.

Redox behavior of Fe^{III}–EDDHA: The nature of the ligand in iron chelates is a key factor in the redox behavior of the complex. In fact, it is known that the extreme variability of the Fe^{III}/Fe^{II} redox potential can be finely tuned by well-chosen ligands.[33] The standard redox potential of the Fe^{III}/Fe^{II} couple in water is $+0.732$ V.[34] However, the range of redox potentials of the LFe^{III}/LFe^{II} couples can vary from -1.0 V to $+1.0$ V.[33] Thus, iron can encompass almost the entire biologically significant range of redox potentials, from -0.40 V for semiflavin/dihydroflavin to $+0.46$ V for the Fenton reagent or to $+0.94$ V for the O_2^-/H_2O_2 system. As far as we are aware, the redox properties of Fe^{III}–EDDHA have not been reported.

Redox properties of the free ligand EDDHA were studied first in order to evaluate its ability as electron donor in an electron transfer process. The cyclic voltammograms of 1 mM solutions of EDDHA at pH values ranging from 5.0 to 9.3 are displayed in Figure 1 and the corresponding E_{pa} values are summarized in Table 1. In all cases, they show a clear oxidation wave attributable to the oxidation of the phenol group. The higher E_{pa} values correspond to the more acid pH values, but as the pH of the medium increases, the phenol groups are deprotonated and the E_{pa} values consistently decrease.

Table 1. Electrochemical data obtained for *o,o*-EDDHA.

pH	E_{pa} [V]	pH	E_{pa} [V]
2.0	1.12	7.4	0.73
3.0	1.07	8.1	0.78
4.0	0.98	9.3	0.75
5.0	0.93	10.1	0.67
6.6	0.80	11.1	0.64

The reduction potential of the Fe^{III}–EDDHA/Fe^{II}–EDDHA couple can be estimated by applying the Nernst equation to the system [Eq. (1)], [33–35] where β^{III} and β^{II} are the stability constants of the Fe^{III}–EDDHA and Fe^{II}-EDDHA complexes, respectively, and $E°$ is 0.732 V.

$$E^o - E = 0.0591 \log (\beta^{III}/\beta^{II}) \quad (1)$$

Considering $\log\beta^{III}$ 35.09[23] and $\log\beta^{II}$ 14.30,[32] the calculated value of the reduction potential for the Fe^{III}–EDDHA/Fe^{II}–EDDHA couple is $E = -0.497$ V, which is significantly lower than those reported for the Fe^{III}/Fe^{II}–EDTA ($E = +0.120$ V) and Fe^{III}/Fe^{II}–DTPA ($E = +0.030$ V) couples.[33] Therefore, it is not surprising that Fe^{III}–EDDHA, Fe^{III}–EDTA, and Fe^{III}–DTPA showed very different behavior toward chemical and photochemical reduction. The consequences on the mode of action of those compounds should differ accordingly.

The cyclic voltammogram for Fe^{III}–EDDHA was registered and is depicted in Figure 2. It shows quasi-reversible electrochemistry with a half wave potential $E_{1/2} = -0.560$ V, [$E_{1/2} = (E_{pa} + E_{pc})/2$], even lower than the calculated value (-0.497 V). The very negative reduction potential reveals the greatly higher selectivity of EDDHA for Fe^{III} over Fe^{II},

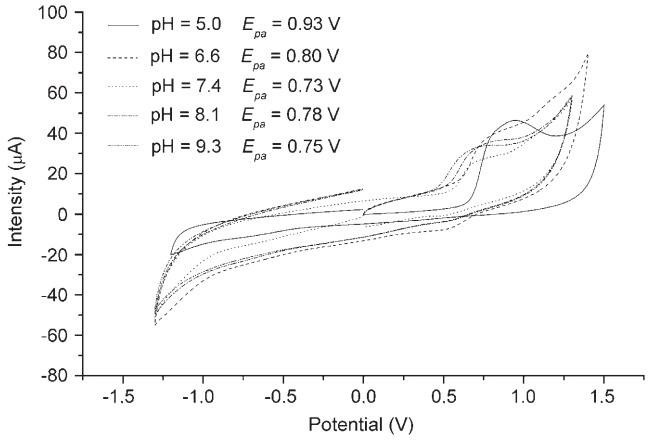


Figure 1. Cyclic voltammograms of the free ligand EDDHA (1 mM) in 0.1 M buffered phosphate solutions.

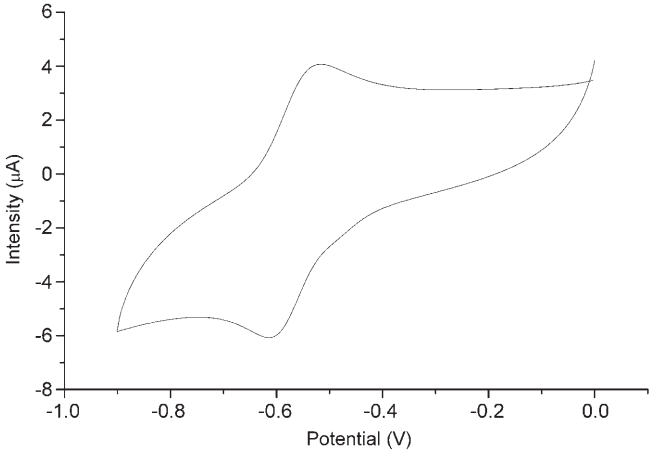


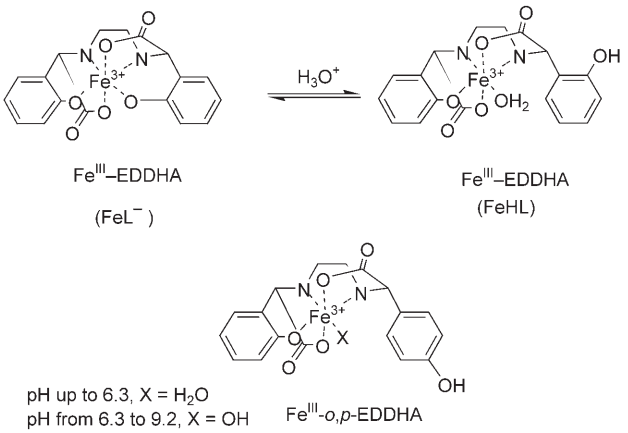
Figure 2. Cyclic voltammogram of Fe^{III}–EDDHA. Conditions: [$FeCl_3 \cdot 6H_2O$] 10^{-3} M, [*o,o*-EDDHA] 10^{-2} M, pH 7.4.

as reflected in the stability constants of the corresponding complexes. If reduction potentials are a good measurement of the electron-accepting ability of Fe^{III} complexes, the very low reduction potential of Fe^{III}–EDDHA explains its experimentally proved reluctance toward photoreduction and also to chemically induced reduction processes.

All these experimental data are of great importance to understand the mechanism of iron release from Fe^{III}–EDDHA in soils. Iron uptake by strategy-I plants involves the reduction of Fe^{III} to Fe^{II} by the NADPH-dependent enzyme ferric chelate reductase.[16,20] However, when considering the experimental value of the redox potential of this complex ($E = -0.560$ V), the reduction of Fe^{III}–EDDHA by a NADPH-enzyme ($E(\mathrm{NADPH/NADP^+}) = -0.324$ V) should not take place. This is very odd, as Fe^{III}–EDDHA is one of the most efficient correctors of iron chlorosis known.[23,36] It can be argued that the measured values of redox potentials should be considered cautiously, as they have been obtained in experimental conditions that are not fulfilled within cells. Although this is true, it is also reasonable to assume that the differences between calculated and real values should be small.[33]

A similar oddity in the reduction by biological reducing agents has been remarked for some ferrisiderophores, the chelating molecules released by bacteria and fungi growing under iron stress.[37] In these cases, it has been proposed that the *thermodynamically unfavorable* Fe^{III} to Fe^{II} biological reduction can be understood if a chelating agent Y, with strong affinity for Fe^{II}, was already present in the medium. Ferrisiderophores are released to bind Fe^{III} and the entire Fe^{III}–siderophore complexes are taken up back into the cell, where the reduction occurs. Then, complexing agent Y is able to take Fe^{II} from the resulting Fe^{II}–siderophore complex, since siderophores have little affinity for Fe^{II}. The biological reduction is driven to completion as now depends on the Fe^{III}–siderophore/Fe^{II} Y quotient (see [Eq. (1)]). This model cannot be applied to strategy I plants in which the iron is taken from extracellular ferric chelates and the reduction Fe^{III} to Fe^{II} by the enzyme takes place outside the cell.

Taking these points into consideration, the question is how the ferric chelate reductase is able to reduce Fe^{III} to Fe^{II} in Fe^{III}–EDDHA. It is known that strategy I plants increase their capacity for taking up iron by excreting protons from the root surface by activation of an ATPase.[16,20] Thus, it could be postulated that at the acid pH of the rhizosphere (pH 5), the enzymatic reduction does not take place at the Fe^{III}–EDDHA chelate itself, but at a different species were the reduction of the metal occurs more easily. A recent study has shown that in a wide pH range (4–10) the predominant form of Fe^{III}–EDDHA in solution is the closed octahedral species FeL^- (Scheme 4). However, at acid pH values it could be also in the form of the hexacoordinate open species (FeHL) (Scheme 4).[24] The formation of FeHL requires the generation of a vacant coordination site that is replaced by a water molecule, leaving one of the strong binding points of the chelate (the phenolic oxygen atom) free. All



Scheme 4.

this process could be induced by the lowering of the pH in the roots by the proton-pumping ATPase.

To support this hypothesis we have studied the redox behavior of the complex Fe^{III}–EDDHA at different acid pH values ranging from 3.1 to 6.0. The cyclic voltammograms are displayed in Figure 3. At the most acid pH values they

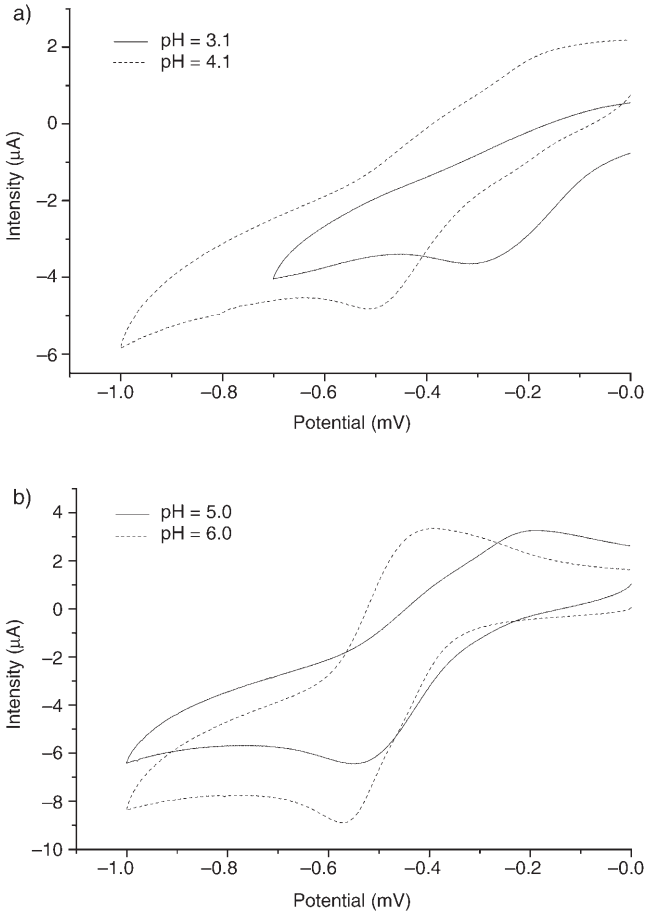


Figure 3. Cyclic voltammograms of Fe^{III}–EDDHA. Conditions: [$FeCl_3 \cdot 6H_2O$] 10^{-3} M, [*o*,*o*-EDDHA] 10^{-2} M in 0.1 M buffered phosphate solutions. a) pH 3.1 and 4.1; b) pH 5.0 and 6.0.

have a clear reduction wave at E_{pc} −0.30 V (pH 3.1) and E_{pc} −0.51 V (pH 4.1), whereas at higher pH values they show quasi-reversible reduction waves at $E_{1/2}$ −0.37 V (pH 5.0) and $E_{1/2}$ −0.48 V (pH 6.0). The electrochemical data are summarized in Table 2. The experimental results clearly

Table 2. Reduction potentials of Fe^{III}–EDDHA complexes at the different pH essayed.

Compound	pH	E_{pc} [V]	$E_{1/2}$ [V]
Fe^{III}–*o,o*-EDDHA	3.1	−0.30	
Fe^{III}–*o,o*-EDDHA	4.1	−0.51	
Fe^{III}–*o,o*-EDDHA	5.0	−0.54	−0.37
Fe^{III}–*o,o*-EDDHA	6.0	−0.57	−0.48
Fe^{III}–*o,o*-EDDHA	7.4	−0.61	−0.56
Fe^{III}–*o,p*-EDDHA	5.1	−0.30	−0.22

demonstrate that the ability of Fe^{III}–EDDHA toward reduction increases with the lowering of the pH in the medium. The higher concentration of the open species FeHL in the solution at lower pH values should be responsible for the systematic increase of the reduction potentials observed in Table 2.

The assumption that an open species such as FeHL could be the key to understanding the enzymatic reduction of the ferric chelate is also supported by a recent study about the structure and stability of the complex Fe–*o,p*-EDDHA, a positional isomer of Fe^{III}–EDDHA.[38] In this octahedral complex, the *p*-hydroxy phenolate group is unable to bind Fe^{III}, and depending on the pH, a water molecule (up to pH 6.3) or a hydroxy group (from pH 6.3 to 9.2) occupies the vacant coordination position (Scheme 4). In spite of this fact, it has been demonstrated that this complex is as efficient as Fe–*o,o*-EDDHA as iron chlorosis corrector. The structure of Fe–*o,p*-EDDHA (Scheme 4) is very similar to that of the open form FeHL and thence this complex is an excellent model to study the electrochemical behavior of the FeHL species. The cyclic voltammogram of Fe–*o,p*-EDDHA at pH 5.0 (X = H_2O in Scheme 4) is displayed in Figure 4 and the data are summarized in Table 2. It shows a quasi reversible reduction wave at $E_{1/2}$−0.22 V, a value considerably higher than that measured for the Fe^{III}–EDDHA in the FeL^- form ($E_{1/2}$ −0.56 V). The comparison between these two values provides an indication about the very different ability of the species FeHL (open) and FeL^- (closed octahedral) toward reduction.

Accordingly, we can propose a model that explains the reduction of Fe^{III}–EDDHA by the enzyme ferric chelate reductase. At the more acid pH in the vicinity of the roots, the complex Fe^{III}–EDDHA in the open form FeHL is reduced by the enzyme. Free Fe^{II} and EDDHA are released in the process and finally, the ferrous ion may be transported into the cell by a strong chelator Y (present in the cell membrane) in the form of a $Fe^{II}Y$ complex (Scheme 5). The complex Fe^{III}–*o,p*-EDDHA is already in the required FeHL open form and can be reduced directly by the enzyme.

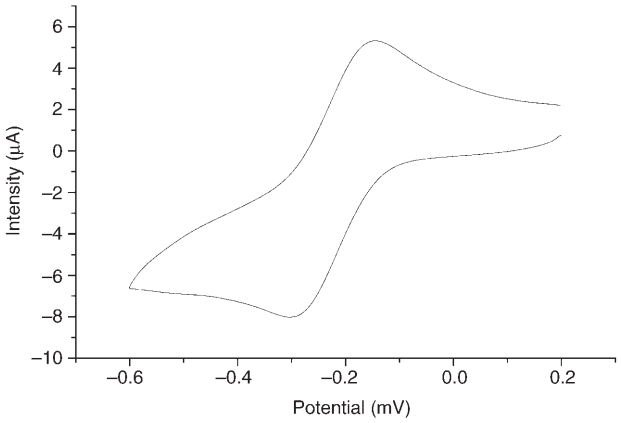
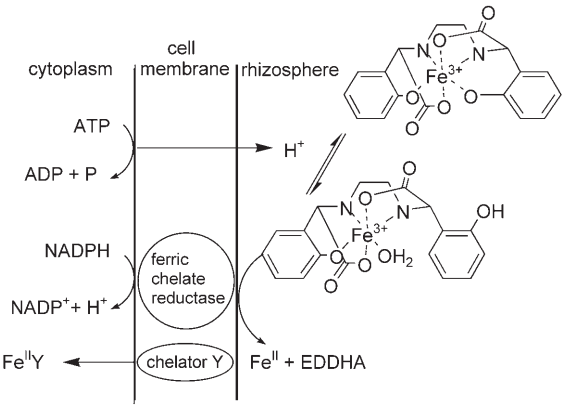


Figure 4. Cyclic voltammogram of Fe^{III}–*o,p*-EDDHA. Conditions: [$FeCl_3 \cdot 6H_2O$] 10^{-3} M, [*o,p*-EDDHA] 10^{-2} M in 0.1 M buffered phosphate solution, at pH 5.



Scheme 5.

Conclusion

In this work, we have demonstrated that Fe^{III}–EDDHA is very persistent toward photodegradation. This is due to the very low reduction potential of the complex, which makes it unreactive in photochemically or chemically induced electron transfer processes. In spite of these facts, the biological reduction of Fe^{III}–EDDHA by a ferric chelate reductase is very effective. The reduction does not take place on the complex in the FeL^- octahedral closed form, but on a hexacoordinate open species (FeHL) formed at the acid pH of the rizhosphere. The formation of this species requires the generation of a vacant coordination site in the FeL^- complex that is filled with a water molecule. Our electrochemical results demonstrate that the reduction of the complex in the open form FeHL should be easier than in the octahedral closed form FeL^-. Further investigation on the photochemistry and redox properties of other EDDHA-like iron complexes structurally related to Fe^{III}–*o,p*-EDDHA are currently in progress in our laboratories.

Experimental Section

General: Analytically pure *o,o*-EDDHA was prepared following our previously reported synthetic method.[24,39] The complex Fe^{III}–EDDHA was obtained as a sodium salt from the pure ligand *o,o*-EDDHA and ferric chloride in basic medium following the previously reported procedure.[40] Analytically pure *o,p*-EDDHA was prepared following our previously reported method.[38b] Reactions requiring an inert atmosphere were conducted under argon and the glassware was flame-dried under vacuum (<0.2 mm Hg). Tetrahydrofuran was distilled from sodium and benzophenone immediately prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded at 22 °C on Bruker Avance 300 (300.1 and 75.4 MHz) or Bruker 200-AC (200.1 and 50 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), $CDCl_3$ (^{13}C, 77.0 ppm), C_3D_6O (^{1}H, 2.0 ppm), C_3D_6O (^{13}C, 206.0 ppm), $D_2O/NaCO_3$ (^{1}H, 4.78 ppm), $D_2O/NaCO_3$ (^{13}C, 165.7 ppm). ESI-MS spectra were carried out in methanol using an ESQUIRE-LC (Bruker Daltonic, Bremen, Germany) ion trap spectrometer by using the negative-ion mode. The stainless-steel capillary was held at a potential of 5.0 kV. Nitrogen was used as nebulizer gas at a flow-rate of 3.98 L min^{-1} (nebulizer pressure 11 psi) at 150 °C.

Photochemical procedures: All photochemical reactions were carried out in distilled water at 22 °C in a magnetically stirred Pyrex vessel using a 400-W medium-pressure mercury lamp (λ_{max} 254, 313, 365, 436 nm) placed in a water-cooled quartz immersion well. For the visible-light experiments (λ_{max} 313 nm) a Pyrex filter was used. The pH of the different experiments was adjusted with HCl 2 M or NaOH 3 M solutions in distilled water. The samples were irradiated either in the presence or in the absence of O_2. In the experiments with O_2, air was bubbled through the solutions during the irradiation. In the deoxygenated experiments the samples were purged with argon for at least 20 min prior to the irradiation and then irradiated in sealed tubes.

UV/Vis irradiations of EDDHA in the presence of O_2

Irradiation at pH 1: A solution of **1** (100 mg, 0.27 mmol), in distilled water (45 mL) was irradiated for 24 h. The crude mixture was extracted at pH 5 with CH_2Cl_2, the extracts were dried ($MgSO_4$), filtered, and evaporated to dryness at reduced pressure, to yield *o*-hydroxyphenylglycine **3** (44 mg; 44 %): solid; ^{1}H NMR (200 MHz, C_3D_6O): δ = 7.34–7.31 (d, J = 7.5 Hz, 1H; ArH), 7.20–7.11 (t, J = 8.5 Hz, 1H; ArH), 6.88–6.81 (t, J = 7,5 Hz, 2H; ArH), 5.46 ppm (s, 1H); ^{13}C NMR (C_3D_6O): δ = 70.1, 116.5, 120.2, 129.1, 129.8, 155.8, 174 ppm. The aqueous layer was evaporated at reduced pressure to yield unreacted *o,o*-EDDHA (50 mg; 51 %): beige solid; ^{1}H NMR (300 MHz, $D_2O/NaCO_3$): δ = 7.26–7.13 (m, 4H; ArH), 6.88–6.78 (m, 4H; ArH), 4.44 (s, 1H), 4.37 (s, 1H), 2.94–2.75 ppm (m, 4H); ^{13}C NMR (300 MHz, $D_2O/NaCO_3$): δ = 44.4, 63.3, 116.9, 117.5, 123.5, 128.7, 128.8, 158.1, 177.3 ppm.

Irradiation at pH 12: A solution of **2** (100 mg, 0.27 mmol) in distilled water (45 mL) was irradiated for 24 h. After a workup analogous to that described above, imine **4** (11 mg; 11 %) and unreacted *o,o*-EDDHA (73 mg; 73 %) were obtained.

Imine 4: dark yellow solid; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.26 (s, 1H; CH=N), 7.27–7.14 (m, 2H; ArH), 6.90–6.75 (m, 2H; ArH), 3.86 ppm (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 59.6, 116.8, 118.5, 131.3, 132.2, 160.9, 166.4 ppm.

Irradiation at pH 7: A suspension of EDDHA (isoelectric form) (400 mg; 1.1 mmol) in distilled water (45 mL) was irradiated for 48 h. The suspension was filtered to yield unreacted EDDHA (250 mg; 62 %). The aqueous layer was extracted with CH_2Cl_2, the extracts were dried ($MgSO_4$), filtered, and evaporated to dryness at reduced pressure, to yield a 1:2 mixture of imine **4** and salicylaldehyde (10 mg; ratio determined by ^{1}H NMR spectroscopy). The aqueous layer was evaporated at reduced pressure to yield unreacted *o,o*-EDDHA (140 mg; 35 %) (overall yield 97 %).

UV/vis irradiations of EDDHA in absence of O_2

Irradiation at pH 1: A solution of **1** (100 mg; 0.27 mmol) in distilled water (45 mL) was irradiated for 24 h. After a workup analogous to that described above, *o,o*-EDDHA (80 mg, 80 %) was recovered from the aqueous fraction. The organic phase yielded *o*-hydroxyphenylglycine **3** (15 mg; 15 %).

Irradiation at pH 12: A degassed solution of **2** (100 mg; 0.27 mmol) in distilled water (45 mL) was irradiated for 24 h. After a workup analogous to that described above, imine **4** (10 mg; 13 %) was obtained from the organic phase. The aqueous phase yielded pure *o,o*-EDDHA (83 mg; 83 %).

Visible irradiations (λ > 313 nm) of EDDHA in the presence of O_2

Irradiation at pH 1: A solution of **1** (100 mg; 0.27 mmol) in distilled water (45 mL) was irradiated for 24 h. After a workup analogous to that described above, pure *o,o*-EDDHA (93 mg; 93 %) was recovered unaltered from the aqueous phase. Trace amounts of *o*-hydroxyphenylglycine **3** were detected by ^{1}H NMR spectroscopy in the residue obtained from the organic phase.

Irradiation at pH 12: A solution of **2** (400 mg; 1.1 mmol) in distilled water (45 mL) was irradiated for 24 h. After a workup analogous to that described above, imine **4** (45 mg; 11 %) was obtained from the organic phase and pure *o,o*-EDDHA (300 mg; 75 %) was recovered unaltered from the aqueous phase.

Irradiation at pH 7: A suspension of EDDHA (isoelectric form) (400 mg; 1.1 mmol) in distilled water (45 mL) was irradiated for 48 h. The suspension was filtered to yield unreacted EDDHA (280 mg; 70 %). The aqueous layer was extracted with CH_2Cl_2, the extracts were dried ($MgSO_4$), filtered, and evaporated to dryness at reduced pressure, to yield trace amounts (< 2 %) of salicylaldehyde (determined by ^{1}H NMR spectroscopy). The aqueous layer was evaporated at reduced pressure to yield unreacted *o,o*-EDDHA (106 mg; 26 %)) (overall yield 96 %).

Visible irradiations (λ > 313 nm) of EDDHA in the absence of O_2

Irradiation at pH 1: A degassed solution of **1** (100 mg; 0.27 mmol) in distilled water (45 mL) was irradiated for 2 h. After a workup analogous to that described above, *o,o*-EDDHA was quantitatively recovered from the aqueous fraction No products were obtained from the organic phase.

Irradiation at pH 12: A degassed solution of **2** (100 mg; 0.27 mmol) in distilled water (45 mL) was irradiated for 24 h. After a workup analogous to that described above, *o,o*-EDDHA was quantitatively recovered from the aqueous fraction No products were obtained from the organic phase.

UV/Vis irradiations of Fe^{III}-EDDHA in the presence of O_2

Irradiation at pH 2: A solution of the sodium salt of Fe^{III}–EDDHA (900 mg) in distilled water (200 mL) was irradiated for 24 h. The solution was filtered to remove any iron oxides formed and extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$), filtered, and evaporated to dryness at reduced pressure to yield *o*-hydroxyphenylglycine (**3**) (15 mg; 2 %) (identified by ^{1}H NMR spectroscopy). The aqueous layer was evaporated at reduced pressure and a purple solid [Na(Fe–EDDHA)] (702 mg; 78 %) was obtained. The analysis of the product was made by iron extraction following a reported procedure:[41] The chelate was dissolved in a deaerated 3 M KOH solution (15 mL) and was left to stand at room temperature for 20 min in the dark. The precipitated $Fe(OH)_3$ was removed by centrifugation, the clean solution was acidified at pH 6, and the solvent was evaporated under reduced pressure. The resulting beige solid was analyzed by NMR spectroscopy and identified as *o,o*-EDDHA by comparison of the signals of the NMR spectra with those of an authentic sample.

Irradiation at pH 11: A solution of the sodium salt of Fe^{III}–EDDHA (900 mg) in distilled water (200 mL) was irradiated for 24 h. A workup analogous to that described above yielded unaltered Na(Fe–EDDHA) (650 mg; 72 %) together with a 1:6 mixture of salicylaldehyde and salicylic acid (63 mg; 7 %) (analyzed by ^{1}H NMR spectroscopy).

Irradiation at pH 6.5: A solution of the sodium salt of Fe^{III}–EDDHA (1.0 g) in distilled water (200 mL) was irradiated for 72 h. A workup analogous to that described above yielded Na(Fe–EDDHA) in quantitative yield.

Visible irradiations (λ > 313 nm) of Fe^{III}–EDDHA in the presence of O_2

Irradiation at pH 2: A solution of the sodium salt of Fe^{III}–EDDHA (900 mg) in distilled water (200 mL) was irradiated for 24 h. A workup analogous to that described above yielded Na(Fe–EDDHA) unaltered

(823 mg; 91%) and a 1:2:2 mixture of *o*-hydroxyphenylglycine (**3**), salicylaldehyde, and salicylic acid (18 mg; 2%) (analyzed by ^{1}H NMR spectroscopy).

Irradiation at pH 11: A solution of the sodium salt of Fe^{III}–EDDHA (900 mg) in distilled water (200 mL) was irradiated for 24 h. A workup analogous to that described above yielded Na(Fe–EDDHA) unaltered (700 mg; 78%) together with a mixture of salicylaldehyde and salicylic acid (56 mg; 6%) (analyzed by ^{1}H NMR spectroscopy).

Irradiation at pH 6.5: A solution of the sodium salt of Fe^{III}–EDDHA (1.0 g) in distilled water (200 mL) was irradiated for 24 h. A workup analogous to that described above yielded quantitatively the starting Na(Fe–EDDHA) (trace amounts of imine **4** were detected).

Electron transfer reactions

General procedure for the reactions with Na/Li naphthalenide:[29] In a two-neck round-bottom flask equipped with reflux condenser and magnetic stirring bar, sodium and naphthalene in dry THF were stirred under argon for 4 h at room temperature (during which time the solution became dark green). The solution was transferred by using a cannula to a flask containing the chelate Na(Fe–EDDHA) or the free ligand (*o,o*-EDDHA) and stirred at room temperature overnight. The ratio chelate (or ligand)/sodium/naphthalene was 1:7.5:7.8. The reaction was quenched with water at 0°C and then filtered. The solid was dried and analyzed. In the experiments with the free ligand *o,o*-EDDHA, this product was recovered unaltered as shown by NMR spectroscopy. In the experiments with Na(Fe–EDDHA), the product was analyzed by ESI mass spectrometry, which revealed only the peak *m/z* 412 $[M-H]^-$ (negative-ion mode) for the unaltered product.

General procedure for the reactions of with SmI_2:[30] A solution of CH_2I_2 in anhydrous THF was added dropwise at room temperature to a stirred suspension of Sm in anhydrous THF under argon. The mixture was stirred until the color turned dark green (3 h) after which time most of the Sm^{III} had been consumed. The reaction mixture was stirred for an additional 30 min and transferred by using a cannula to a flask containing the chelate Na(Fe–EDDHA) or the free ligand (*o,o*-EDDHA). The ratio complex (or ligand)/Sm/CH_2I_2 was 1:2:1. The mixture was allowed to stir at room temperature overnight. The reaction was quenched and the filtrate was washed with CH_2Cl_2, dried, and analyzed.

Reactions of *o,o*-EDDHA with SmI_2: The formation of SmI_2 was accomplished as described above. The reaction was carried out either in THF, THF/MeOH (2:1), or THF/H_2O (1:1) mixtures using *o,o*-EDDHA/SmI_2 ratios of 1:2.2, 1:2.9, and 1:5. The reaction was quenched by addition of a few drops of 0.1 M HCl or phosphate buffer (pH 8). The analysis by NMR spectroscopy of the filtrate indicated that *o,o*-EDDHA was recovered unaltered in all cases.

Reactions of Na[Fe-EDDHA] with SmI_2: The formation of SmI_2 was accomplished as described above. The reaction was carried out either in THF, THF/MeOH (2:1), or THF/H_2O (1:1) mixtures using Na(Fe-EDDHA)/SmI_2 ratios of 1:2.2 and 1:5. The reaction was quenched by addition of a few drops of 0.1 M HCl or phosphate buffer (pH 8). Analysis of the product by ESI mass spectrometry revealed only the peak at *m/z* 412 $[M-H]^-$ (negative-ion mode) for the unaltered chelate.

General procedure for the reactions with potassium-graphite (C_8K) laminate:[31] In a two-neck round-bottom flask equipped with reflux condenser and magnetic stirring bar, graphite was heated (while stirred) under argon for 15 min at 150–160°C. Potassium was added under argon, and the mixture was kept at 160°C with careful stirring until the laminate had formed (10–15 min). **CAUTION**: The material was highly pyrophoric, necessitating cautious handling in thoroughly dried solvents. The distinctive *bronze* color of the mixture indicated that C_8K was formed and this was then suspended in anhydrous THF. A suspension of the chelate Na(Fe-EDDHA) or the free ligand (*o,o*-EDDHA) in THF at room temperature was added to this suspension. The ratio complex (or ligand)/graphite/potassium was 1:48:6. This suspension was allowed to stir overnight, quenched with water, and filtered through celite. The phases were separated with CH_2Cl_2 and dried under vacuum. The aqueous layer was analyzed. In the experiments with the free ligand (EDDHA), this product was recovered unaltered as shown by NMR spectroscopy. In the experiments with Na(Fe-EDDHA), analysis of the product by ESI mass spectrometry revealed only the peak *m/z* 412 $[M-H]^-$ (negative-ion mode) for the unaltered product.

The same results were obtained when lower excesses (3:1) of C_8K/Fe-EDDHA were employed.

Electrochemical measurements: Cyclic voltammetric experiments were performed at room temperature in 0.1 M phosphate buffer. A Metrohm 6.084.010 glassy carbon electrode (GCE) was used as working electrode. A BAS MF 2063 Ag/AgCl 3 M reference and a Pt wire counter electrode were employed. All voltammetric measurements were carried out using a PGSTAT 12 potentiostat from Autolab. The electrochemical software was the General Purpose Electrochemical System (GPES) (EcoChemie B.V.).

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