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Iron(III) Exchange Process between Hexadentate Tripodal Ligands: Models for the Ternary Complexes

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Using tripodal ligands as tools, the kinetics of iron removal from ferric complexes of the tripodal tris(hydroxyquinoline) ligands O-TRENSOX and of tris(catechol) TRENCAMS was investigated. Two hexadentate heterotripodal ligands were also examined (TRENSOX2CAMS with two hydroxyquinoline and one catechol subunits and TRENSOXCAMS2 with two catechol and one hydroxyquinoline subunits) as possible models of the ternary complexes involved in the iron exchange process. The main result of this kinetic study is the pertinence of the iron complexes of the mixed ligands as models for the transient and successive ternary complexes occurring in the iron exchange, which proceeds "arm-by-arm" between a homotopic ligand and the iron complex of another homotopic ligand.

Introduction

Microbial iron bioavailability is driven by the coordination chemistry of siderophores, which are iron-chelating agents that are excreted by microorganisms to render iron soluble in the environment and favor the uptake of this metal. Iron chelation by some natural or synthetic chelators can be applied to human diseases characterized by iron overload, and water-soluble iron complexes can be used to alleviate iron deficiency in plants, preventing and even reversing iron chlorosis. The coordination chemistry of a great number of water-soluble natural or synthetic iron chelators was recently reviewed, and it is usually considered that Fe^{III} removal from ferrisiderophore or from other biological complexes (transferrin carriers or storage complexes, receptor proteins, citrate, and low molecular-weight chelates) involves the formation of a ternary complex.[1] The dynamic of Fe removal from various Fe^{III} complexes was studied and the formation of the ternary complex is often consistent with the kinetic data.[2–4] Nevertheless, a molecular description of the "so-called ternary" complex was never discussed to the best of our knowledge. Recently, Crumbliss et al. described the formation of a ternary complex in a redox mechanism for iron release from a siderophore.[5]

Using tripodal ligands as tools and starting from the hypothesis of a step-by-step ("arm-by-arm") exchange, we investigated the kinetics of the iron removal from the ferric complexes of the tripodal tris(hydroxyquinoline) ligands O-TRENSOX ($\mathbf{L^0}$),[6] and $\mathbf{L'^0}$,[7] where $\mathbf{L^0}$ is anchored to a tertiary amine and $\mathbf{L'^0}$ to a tertiary carbon (Figure 1), and a tris(catechol) analogue built from a tertiary amine[8] TRENCAMS ($\mathbf{L^3}$). Two hexadentate heterotripodal ligands were also examined, TRENSOX2CAMS ($\mathbf{L^1}$) with two hydroxyquinoline units and one catechol[9] unit and TRENSOXCAMS2 ($\mathbf{L^2}$) with two catechol moieties and one hydroxyquinoline[9] building block (Figure 1). Our aim was to gain insight into the step-by-step ligand exchange processes via kinetic intermediates called "ternary complexes". In addition, kinetic experiments on the iron removal from EDTA by these tripodal ligands were carried out. All the collected results allow the analysis of the influence of the structure of the ligand and of the nature of the chelating groups on the kinetic parameters.

Results

We monitored the iron exchange reactions between two ligands using different competing ligand concentrations in pseudo first-order conditions. The global reaction of a ligand-exchange type is expressed by Equation (1) (charges omitted for clarity).

$$FeL + L' \rightarrow FeL' + L \quad (1)$$

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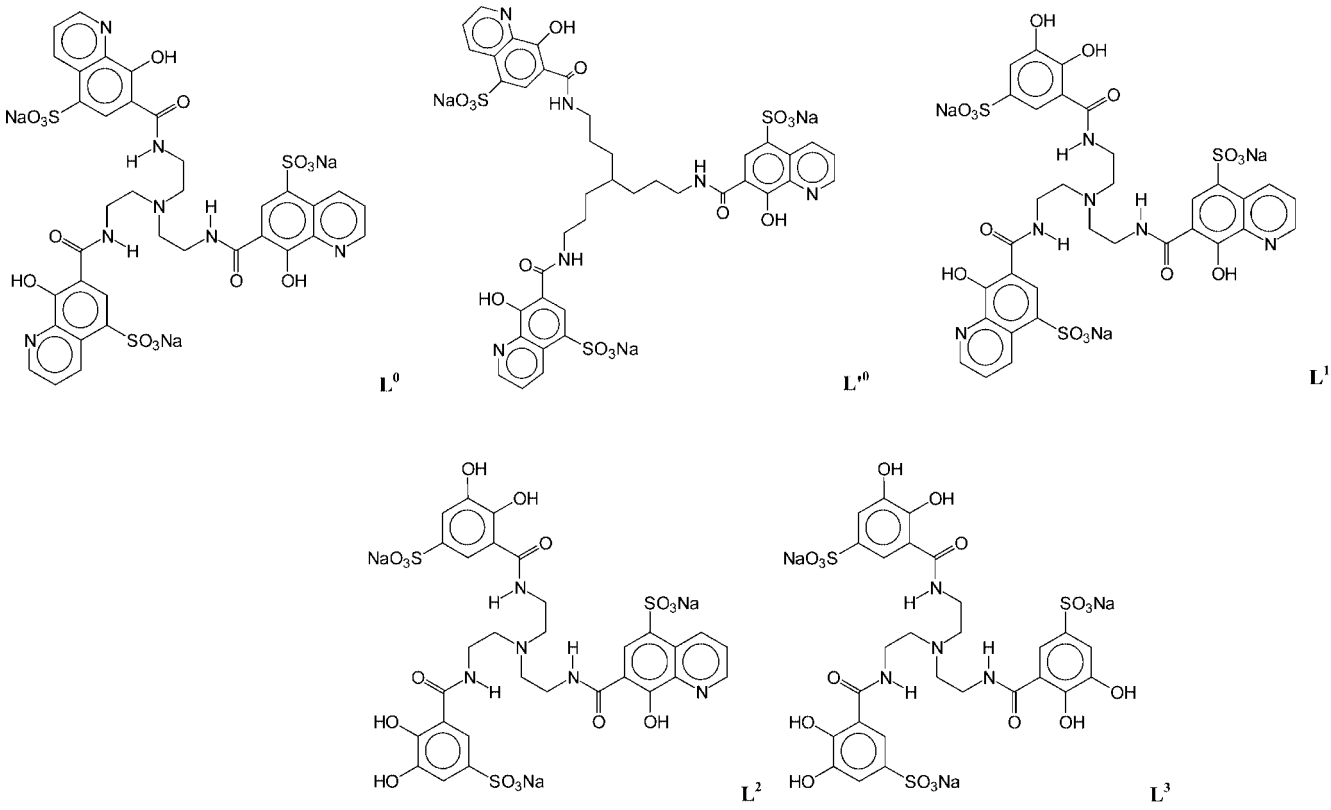

Figure 1. Chemical formulae of tripodal ligands $\mathbf{L}^n$ (n refers to the number of catechol groups in the tripodal ligand).

Three FeL complexes were studied: Fe-EDTA, Fe$\mathbf{L}^0$, and Fe$\mathbf{L}^3$; L′ was $\mathbf{L}^0$, $\mathbf{L}'^0$, $\mathbf{L}^1$, $\mathbf{L}^2$, and/or $\mathbf{L}^3$. In particular, this series of exchanges allows the study of the kinetics of adding a catechol or an 8-hydroxyquinoline arm into the iron coordination sphere and the effect of the structure of the tripodal ligand (i.e. homopodal or heteropodal, anchor group). During the exchange reaction, monoexponential growth of absorbance was observed in all cases at the selected wavelength of the FeL′ complex, indicating that the reaction proceeds via a single rate-limiting step. No variation in the amplitude of the absorbance was observed during the mixing time for all the studied systems, indicating that a fast step, involving a change in the coordination sphere around Fe^{III} does not occur before the first detectable step. The UV/Vis spectra were recorded as a function of the time and at the end of the kinetics. The structure of the final complex was supported by its absorption spectrum on the basis of our previous studies, particularly for the mixed coordination around Fe^{III}[9] related to one catechol and two 8-hydroxyquinoline groups as in Fe$\mathbf{L}^1$ or two catechol and one 8-hydroxyquinoline groups as in Fe$\mathbf{L}^2$ (see the λ_{max} and ε values in the Experimental Section).

Iron Exchange from Fe-EDTA

The reaction was monitored with $\mathbf{L}^0$, $\mathbf{L}'^0$, $\mathbf{L}^1$, $\mathbf{L}^2$, and $\mathbf{L}^3$. The reaction was found to be complete and to occur in one distinguishable step. A linear dependence of the observed pseudo first-order rate constant k^{obs} on [L′] with negligible intercept was observed [Equation (2)]. The values of k_1 are collected in Table 1.

$$k^{obs} = k_1 [L']_{tot} \quad (2)$$

Table 1. Kinetic data (k_1 values in $M^{-1}s^{-1}$) for the first step of the iron exchange reaction between FeL and L′.[a]

Competing	Ferric complex		
ligand	[Fe-EDTA]$^-$	[Fe$\mathbf{L}^0$]$^{3-}$	[Fe$\mathbf{L}^3$]$^{6-}$
$\mathbf{L}^0$	4.0 ± 0.5	–	1.9 ± 0.1
$\mathbf{L}^1$	14.2 ± 1.5	23 ± 1	5.5 ± 0.8
$\mathbf{L}^2$	97 ± 2	77 ± 4	1.1 ± 0.15
$\mathbf{L}^3$	145 ± 3	81 ± 4[b]	–
$\mathbf{L}'^0$	5.1 ± 0.4	–	–

[a] In aqueous 50 mM MOPS buffer, pH = 7.4, I = 0.1 M ($NaClO_4$) and at temperature T = 25.0 °C. [b] Intercept = $(6.6 \pm 0.6) \times 10^{-2}$ s^{-1}.

Iron Exchange from Fe-O-TRENSOX

The reaction was monitored with $\mathbf{L}^1$, $\mathbf{L}^2$, and $\mathbf{L}^3$ and was found to proceed in one distinguishable step. The UV/Vis spectra recorded as the reaction proceeded exhibited isosbestic points indicating that no intermediary species were formed during the reaction. For Fe$\mathbf{L}^0$ + $\mathbf{L}^3$, the reaction was complete (see Figure S1 in the Supporting Information). For Fe$\mathbf{L}^0$/$\mathbf{L}^1$, the spectrum recorded at the equilibrium was found to be similar to that of the Fe$\mathbf{L}^1$ complex,

indicating the substitution of an 8-hydroxyquinoline group by a catechol group. However, the substitution by the two 8-hydroxyquinoline groups of $\mathbf{L^1}$ does not change the spectrum and cannot be detected. For Fe$\mathbf{L^0/L^2}$ the spectrum recorded at the end of the first step is similar to the spectrum of the Fe$\mathbf{L^2}$ complex, indicating the substitution of two 8-hydroxyquinoline groups by two catechol groups. Figure 2 shows the UV/Vis spectra recorded as the reaction proceeds.

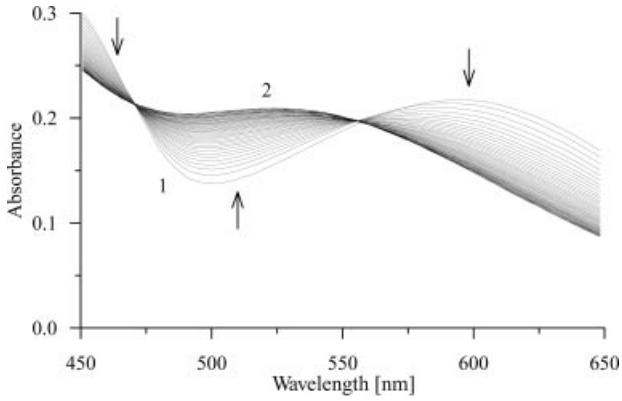

Figure 2. UV/Vis spectra recorded as a function of time for the exchange Fe$\mathbf{L^0/L^2}$; experimental conditions: [Fe$\mathbf{L^0}$] = 0.04 mM, [$\mathbf{L^2}$] = 0.4 mM, pH = 7.4 (50 mM MOPS buffer), I = 0.1 M ($NaClO_4$), T = 25 °C. (1) t = 0 s, (2) 260 s; the arrows indicate the direction of change as the reaction proceeds.

The plots of k^{obs} versus the ligand concentration show a linear dependence with a negligible intercept except for Fe$\mathbf{L^0/L^2}$. The values of k_1 are reported in Table 1.

Iron Exchange from TRENCAMS

The spectrum recorded at the end of the reaction of Fe$\mathbf{L^3}$ with $\mathbf{L^1}$ or $\mathbf{L^2}$ is similar to the spectrum of the $\mathbf{FeL^2}$ complex, indicating the substitution of a catechol group by an 8-hydroxyquinoline group (see Figure S1 in the Supporting Information). The reaction was found to proceed in one detectable step. The plot of k^{obs} versus the ligand concentration shows a linear dependence with negligible intercept. The values of k_1 are reported in Table 1.

For the reaction of Fe$\mathbf{L^3}$ with $\mathbf{L^0}$, two steps were observed as deduced from the two-exponential growth of absorbance measured at 600 nm. The spectrum recorded at the end of the first step is similar to the spectrum of the Fe$\mathbf{L^2}$ complex, indicating the substitution of a catechol group by an 8-hydroxyquinoline group (species noted $\mathbf{L^0}$Fe$\mathbf{L^3}$), and the spectrum recorded at the equilibrium after the second step is similar to the spectrum of the Fe$\mathbf{L^1}$ complex, which indicates that the substitution of a second catechol group by an 8-hydroxyquinoline group (species noted $\mathbf{L^0}$Fe$\mathbf{L^3}$*). The plot of k_1^{obs} (first step) versus the ligand concentration shows a linear dependence with a nonzero intercept while k_2^{obs} was found to be independent of the ligand concentration. This is consistent with the reactions according to Equations (3) and (4) and the rate law according to Equation (5) by considering the two reactions occur independently since $k_1^{obs} >> k_2^{obs}$.

$$\mathrm{Fe}\mathbf{L^3} + \mathbf{L^0} \rightleftharpoons \mathbf{L^0}\mathrm{Fe}\mathbf{L^3}\ k_1, k_{-1} \quad (3)$$

$$\mathbf{L^0}\mathrm{Fe}\mathbf{L^3} \rightarrow \mathbf{L^0}\mathrm{Fe}\mathbf{L^3}^*\ k_2 \quad (4)$$

$$k_1^{obs} = k_1[L^0] + k_{-1} \quad (5)$$

Thus, the values $k_1 = 1.9 \pm 0.1\ M^{-1}s^{-1}$, $k_{-1} = (2.1 \pm 0.2) \times 10^{-4}\ s^{-1}$, and $k_2 = (2.3 \pm 0.3) \times 10^{-5}\ s^{-1}$ were obtained.

Discussion

The general feature resulting from the kinetic studies is that the iron exchange reactions proceed in one detectable step except for the exchange Fe$\mathbf{L^3/L^0}$ (two detectable steps). Hence, the formation of an intermediate ternary complex was only shown for this last case. In a previous investigation on the acid dissociation kinetics of the Fe^{III} complexes with these tripodal ligands, we observed a very fast dissociation of one arm of the ligand which is maintained in proximity to the first coordination sphere of Fe^{III}.[10] This indicates that the complex has one labile arm thus favoring the formation of the precursor complex and then the substitution by one arm of the competing ligand. So, it is reasonable to propose that the kinetic rate constant k_1 represents the substitution rate of one arm of the initial complex by one arm of the competing ligand. In addition, this study clearly reveals the effect of the nature of the entering group, catechol or an 8-hydroxyquinoline group, on the ligand substitution rate constants.

Iron Exchange with Homotopic Ligands $\mathbf{L^0}$, $\mathbf{L'^0}$, and $\mathbf{L^3}$

For the iron exchange from the EDTA complex, the final spectrum indicates that the reaction is complete. The same result is obtained with the heterotopic ligands. It is proposed that when the first arm of the incoming ligand is attached, EDTA dissociates rapidly and next two arms quickly coordinate to Fe^{III} via catechol or the 8-hydroxyquinoline groups. The values of k_1 shows that the substitution rate of the catechol group ($145\ M^{-1}s^{-1}$) is about one order of magnitude faster than that of the 8-hydroxyquinoline (4.0 and $5.1\ M^{-1}s^{-1}$). Similar values for k_1 were obtained for the iron exchanges between Fe$\mathbf{L^0}$ and $\mathbf{L^3}$ ($81\ M^{-1}s^{-1}$) or between Fe$\mathbf{L^3}$ and $\mathbf{L^0}$ ($1.9\ M^{-1}s^{-1}$ for the first step).

Iron Exchange with Heterotopic Ligands $\mathbf{L^1}$ and $\mathbf{L^2}$

For the exchanges Fe$\mathbf{L^0/L^1}$ and Fe$\mathbf{L^0/L^2}$, the nature of the entering group was clearly identified as a catechol group on the basis of the spectrum change. In a previous paper,[9] we determined the UV/Vis parameters for the ferric complexes with a mixed catechol/8-hydroxyquinoline coordina-

tion sphere. In addition, the values of k_1 (23 and 77 $M^{-1}s^{-1}$ for Fe**L**^{0}/**L**^{1} and Fe**L**^{0}/**L**^{2}, respectively) are of the same order of magnitude as those for the exchanges Fe**L**^{0}/**L**^{3} (81 $M^{-1}s^{-1}$) and Fe-EDTA/**L**^{3} (145 $M^{-1}s^{-1}$), which correspond to the substitution by a catechol arm. For the exchanges Fe**L**^{3}/**L**^{1} and Fe**L**^{3}/**L**^{2}, the entering group was identified as an 8-hydroxyquinoline unit according to the spectral change. The values of k_1 (5.5 and 1.1 $M^{-1}s^{-1}$ for Fe**L**^{3}/**L**^{1} and Fe**L**^{3}/**L**^{2}, respectively) are of the same order of magnitude as those for the exchanges Fe**L**^{3}/**L**^{0} (1.9 $M^{-1}s^{-1}$), Fe-EDTA/**L**^{0} (4.0 $M^{-1}s^{-1}$), or Fe-EDTA/**L**$'^0$ (5.1 $M^{-1}s^{-1}$), which correspond to the substitution by an 8-hydroxyquinoline arm. All these results indicate that the substitution rate is mainly controlled by the nature of the entering group. Accordingly, the iron exchange rates from Fe-EDTA with **L**^{1} and **L**^{2}, 14.2 and 97 $M^{-1}s^{-1}$, respectively, can be attributed to the substitution by the catechol arm. Table 2 summarizes the values of k_1 for the three series of iron exchange collected according to the nature of the chelating group that enters in the iron coordination sphere.

The fact that close k_1 values are obtained for one type of entering group (catechol or 8-hydroxyquinoline) in the different exchange systems suggests that the step is the substitution of one arm of the initial complex by one arm of the competing ligand, leading to the formation of an intermediate ternary complex before the substitution of the two other arms. The higher substitution rate measured for the catechol group can be attributed to its greater electron donor ability and to its lower bulkiness relative to the 8-hydroxyquinoline group. This might be also attributed to the charge of the incoming chelating group that depends on the protonation state of the ortho hydroxy groups. Indeed, a negative deprotonated hydroxy is assumed to be more reactive than the protonated one. For the catechol groups in **L**^{1}, **L**^{2}, and **L**^{3} the lower pK_a is 5.62,[9] 5.55,[9] and 5.57,[8] respectively, indicating that the hydroxy group of one arm is deprotonated at pH 7.4, whereas for the 8-hydroxyquinoline groups the lower pK_a is 7.44[6] for **L**^{0} and 6.68[7] for **L**$'^0$. For the sake of comparison, the numbers of deprotonated OH groups in the catechol and 8-hydroxyquinoline moieties are reported in Table 2. Analysis of the data shows that k_1 cannot be directly related to the protonation state of the OH group. It is thus suggested that the negative charge of the incoming group is not a decisive factor for the rate constant.

It should be pointed out that the substitution rate by the catechol group is decreasing as the number of 8-hydroxyquinoline groups increases (or inversely as the number of catechol groups decreases) in the competing ligand: 81, 77, or 23 $M^{-1}s^{-1}$ for Fe**L**^{0}/**L**^{3}, **L**^{2}, or **L**^{1}, respectively, and 145, 97, or 14.2 $M^{-1}s^{-1}$ for Fe-EDTA/**L**^{3}, **L**^{2}, or **L**^{1}, respectively. In contrast, the same trend is not observed for the substitution rate by the 8-hydroxyquinoline group (substitution of Fe**L**^{3} by **L**^{0}, **L**^{1}, or **L**^{2}; 1.9, 5.5, or 1.1 $M^{-1}s^{-1}$, respectively). This indicates that steric factors rather than statistical factors occur: the 8-hydroxyquinoline group is assumed to slow down the entering of the tripodal ligand in the iron coordination sphere.

Our results suggest that iron exchange occurs step-by-step, each arm of the incoming tripodal ligand substitutes successively the leaving ligand as the coordination bonds are broken. This is clearly evidenced for the iron exchange between Fe**L**^{3} and **L**^{0} since the formation of an intermediate ternary complex having a mixed coordination 8-hydroxyquinolinate/catecholate could be identified from the UV/Vis spectra as previously published.[9] A probable mechanism is depicted in Figure 3. The same process is assumed to occur for the exchange between Fe**L**^{0} and **L**^{3}, but the coordination of the second and the third catechol groups is fast relative to the first one. This can be inferred by the labilizing effect of strong electron pair donors as catechol ligands, which increases the electron density of the metal, weakening the bonds with the coordinated donor atoms. Replacement of a coordinated group by a catechol group in the first coordination shell enhances the ligand exchange of the remaining arms. In contrast, in the case of the reaction between Fe**L**^{3} and **L**^{0}, the substitution of the second arm of the tripodal ligand is very slow (k_2 = 2.3 10^{-5} s^{-1}). It is suggested that the substitution of catechol groups by poorer electron pair donors as 8-hydroxyquinoline groups diminishes the electron density at the iron center, slowing down the exchange of the remaining coordinating arms. In addition, this effect is enhanced by the steric effect of the incoming 8-hydroxyquinoline group. The sensitivity of the rate constant to the nature of the bidentate group of the incoming ligand indicates a rather associative character of the mechanism for

Table 2. Kinetic data (k_1 values in $M^{-1}s^{-1}$) for the first step of the iron exchange reaction between FeL and L′[a]collected according to the entering group.

Competing ligand	Catechol as an entering group			8-Hydroxyquinoline as an entering group		
	[Fe**L**^{0}]$^{6-}$	[Fe-EDTA]$^-$	Number of OH deprotonated[b]	[Fe**L**^{3}]$^{6-}$	[Fe-EDTA]$^-$	Number of OH deprotonated[b]
L^0				1.9	4.0	0.5
L^1	23	14.2	1	5.5		0
L^2	77	97	1.5	1.1		0
L^3	81	145	3			
L$'^0$					5.1	1.5

[a] In aqueous 50 mM MOPS buffer, pH = 7.4, I = 0.1 M ($NaClO_4$) and at temperature T = 25.0 °C. [b] at pH = 7.4; half value indicates a partially deprotonated group (pH ≈ pK_a).

these series of iron exchange. In summary, the exchange rate constants of the first step depend on the nature of the entering arm (catechol or 8-hydroxyquinoline) and on the nature of second and third arm of the incoming tripodal ligand (homotripodal or heterotripodal; Figure 3).

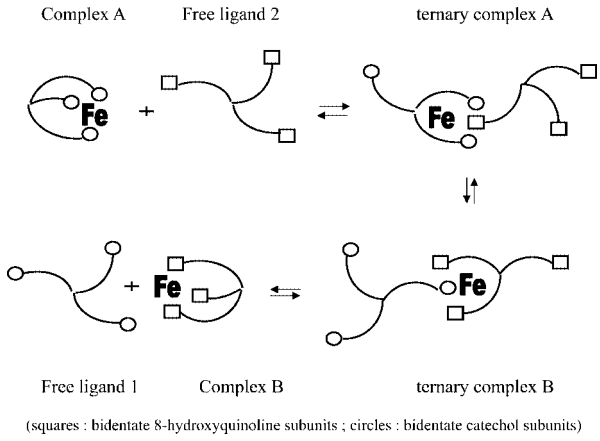

Figure 3. Successive steps for the ligand exchange at the iron center via ternary complexes.

Conclusions

The main result of this study is the pertinence of the Fe**L**^{1} and Fe**L**^{2} complexes as models for the transient and successive ternary complexes occurring in the iron exchange processes between Fe**L**^{0} and **L**^{3} and between Fe**L**^{3} and **L**^{0}. The results allow the first molecular description of the ternary complex formed during the iron exchange between two abiotic siderophores. Generally, ligand exchanges are slow, but they are facilitated by the formation of the so-called ternary ferric complexes with the two ligands bound to Fe^{III}. Our study supports this concept.

Experimental Section

Materials: All commercial reagents were of the highest purity grade and used without further purification. Iron(III) stock solutions were prepared by dissolving the appropriate amount of ferric perchlorate hydrate (Aldrich) in standardized $HClO_4$ solution. The solutions were standardized for ferric ion concentration spectrophotomerically by using a molar extinction coefficient of 4160 $M^{-1}\,cm^{-1}$ at 240 nm.[11] The ligands were synthesized according to procedures previously described (**L**^{0},[6] **L′**^{0},[12] **L**^{1},[9] **L**^{2},[9] and **L**^{3}[8]).

Kinetics Studies: Iron(III) exchange kinetics between Fe**L**^{0} and **L**^{1}, **L**^{2}, or **L**^{3}, between Fe**L**^{3} and **L**^{0}, **L**^{1}, or **L**^{2}, and between Fe-EDTA and **L**^{0}, **L**^{1}, **L**^{2}, **L**^{3}, or **L**^{4} were studied in aqueous 50 mM MOPS buffer, pH = 7.4, I = 0.1 M ($NaClO_4$), and at temperature T = (25.0 ± 0.2) °C. The kinetics were studied under pseudo first order conditions by using a large excess of the entering ligand over the complex. Initial concentration of the FeL complex was 2.0×10^{-5} mol L^{-1}, initial concentration of ligand L′ was varied in a range from 2×10^{-4} to 1.2×10^{-3} mol L^{-1}. Fast kinetic measurements were performed with a KINSPEC UV (BIO-LOGIC Company, Claix, France) stopped-flow spectrophotometer equipped with a diode array detector (J & M) and connected to a microcomputer; slow kinetic measurements were performed with a Perkin–Elmer Lambda2 or Varian Cary 50 UV/Vis spectrophotometer. The kinetic data were treated on line with the commercial BIO-KINE program (BIO-LOGIC Company, Claix, France). In each run, equal volumes of solutions of the complex and of the ligand were mixed. The absorbance changes with time were recorded at the maximum of the charge-transfer band of the complex that is formed, specifically, λ_{max} = 490, 525, and 550 nm for Fe**L**^{3},[8] Fe**L**^{2},[9] and Fe**L**^{1},[9] respectively, and 595 nm for Fe**L**^{0}[6] and Fe**L′**^{0}.[7] Some visible spectra from 400 to 650 nm were recorded in time by using a diode array detector.

Supporting Information (see footnote on the first page of this article)**:** Figures S1 and S2: UV/Vis spectra recorded as a function of time for the exchanges Fe**L**^{0}/**L**^{3} and Fe**L**^{3}/**L**^{2}. Tables S1 to S8: rate constants values for the different exchanges FeL/L′.

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[1] A.-M. Albrecht-Gary, A. L. Crumbliss in *Metals Ions in Biological Systems* (Eds.: A.Sigel, H. Sigel), Marcel Dekker, New-York, **1998**, vol. 35, pp. 239–327.
[2] Y. Hara, M. Akiyama, *J. Am. Chem. Soc.* **2001**, *123*, 7247–7256.
[3] A. Stinzi, C. Barnes, K. N. Raymond, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 10691–10696.
[4] B. Faller, H. Nick, *J. Am. Chem. Soc.* **1994**, *116*, 3860–3865.
[5] K. A. Mies, J. I. Wirgau, A. L. Crumbliss, *Biometals* **2006**, *19*, 115–126.
[6] G. Serratrice, H. Boukhalfa, C. Béguin, P. Baret, C. Caris, J.-L. Pierre, *Inorg. Chem.* **1997**, *36*, 3898–3910.
[7] F. Biaso, Thesis, Université Joseph Fourier Grenoble, France, **2002**.
[8] F. Thomas, C. Béguin, J. L. Pierre, G. Serratrice, *Inorg. Chim. Acta* **1999**, *291*, 148–157.
[9] A.-M. Albrecht-Gary, S. Blanc, F. Biaso, F. Thomas, P. Baret, G. Gellon, J.-L. Pierre, G. Serratrice, *Eur. J. Inorg. Chem.* **2003**, 2596–2605.
[10] G. Serratrice, F. Biaso, F. Thomas, C. Béguin, *Eur. J. Inorg. Chem.* **2004**, 1552–1565.
[11] R. Bastian, R. Weberling, F. Palilla, *Anal. Chem.* **1956**, *28*, 459–462.
[12] D. Imbert, Thesis, Université Joseph Fourier, Grenoble, France, **2000**.

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