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Mechanistic Information on the Reversible Binding of NO to Selected Iron(II) Chelates from Activation Parameters[§]

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Mechanistic insight on the reversible binding of NO to Fe^{II} chelate complexes as potential catalysts for the removal of NO from effluent gas streams has been obtained from the temperature and pressure parameters for the "on" and "off" reactions determined using a combination of flash photolysis and stopped-flow techniques. These parameters are correlated with those for water exchange reactions on the corresponding Fe^{II} and Fe^{III} chelate complexes, from which mechanistic conclusions are drawn. Small and positive $\Delta V^{\ddagger}$ values are found for NO binding to and release from all the selected complexes, consistent with a dissociative interchange (I_d) mechanism. The only exception in the series of studied complexes is the binding of NO to $[Fe^{II}(nta)(H_2O)_2]^-$. The negative volume of activation observed for this reaction supports the operation of an I_a ligand substitution mechanism. The apparent mechanistic differences can be accounted for in terms of the electronic and structural features of the studied complexes. The results indicate that the aminocarboxylate chelates affect the rate and overall equilibrium constants, as well as the nature of the substitution mechanism by which NO coordinates to the selected complexes. There is, however, no simple correlation between the rate and activation parameters and the selected donor groups or overall charge on the iron(II) complexes.

Introduction

It has been our interest in recent years to find metal chelates for the selective and efficient binding of NO in aqueous solution, to be employed in alternative denitrification processes.[1] The fundamental coordination chemistry involves the reversible or partially reversible binding of NO to inexpensive and highly soluble chelate complexes of iron(II).[2,3] Aminocarboxylate complexes of iron(II) are known for their ability to bind NO rapidly[4−7] and are therefore used to enhance the solubility of NO in aqueous solution in industrial applications in order to remove NO from exhaust gases.

On the other hand, the iron(II) polyaminocarboxylate complexes have recently become of interest as potential agents for the control of nitric oxide levels during NO-mediated pathological events in the human body. Septic shock is the most dramatic manifestation of systematic acute inflammatory reactions which can lead to tissue damage, a severe drop in blood pressure, and vascular collapse.[8−10] In this context, the finding of new drugs that can reduce the nitric oxide level in this and other diseases has become a current clinical goal. This proposition has stimulated Shepherd et al. to synthesize and characterize several $Fe^{II}(L)(NO)$ complexes of aminocarboxylate and pyridyl-based ligand systems.[11] They have found that although the studied complexes bind nitric oxide very rapidly, forming relatively

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[§] Dedicated to Prof. Dr. Karl Wieghardt on the occasion of his 60th birthday.

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stable NO adducts, the parent $Fe^{II}(L)$ complexes are inherently oxygen sensitive, which will limit their utilization as NO scavengers in the bloodstream. However, independent studies revealed that iron(III) complexes such as Fe^{III}(dtpa) bind to NO upon reduction to Fe^{II} at physiologically relevant potentials and are able to protect mice against death caused by septic shock.[12] In this respect, little mechanistic information is presently available on the nitrosylation reactions of aminocarboxylate complexes of iron(II), although some scattered rate constants for these reactions and stability constants are reported in the literature.[13−25]

In a recent paper[1] we reported the extent to which the reversible binding of NO to polyaminecarboxylate complexes of iron(II), shown in reaction 1, can be tuned by the selected chelate. In general, a good correlation between the oxygen sensitivity of the chelated iron(II) complex and the formation constant for the Fe−NO complex, i.e., the ability of chelated iron(II) to bind NO, was found. This trend correlated with a decrease in the reversibility of the reaction, i.e., the ability of the formed Fe−NO complex to release NO, and an increasing tendency of the Fe−NO complex to exist as $Fe^{III}-NO^-$ in solution. The latter complex undergoes subsequent decomposition during which chelated iron(III) and N_2O are formed.

$$Fe^{II}(L)H_2O + NO \rightleftharpoons Fe^{II}(L)NO + H_2O \quad k_{on}, k_{off}$$
$$K_{NO} = k_{on}/k_{off} \quad (1)$$

In a subsequent paper we reported systematic kinetic studies on the reaction of NO with selected Fe^{II} complexes, based on their rather unique behavior as observed in our more general and qualitative investigation referred to above.[26] Four different kinetic techniques were employed to study the binding reaction of NO to a series of aminocarboxylate complexes of Fe^{II}. The fastest rate constant for the binding of NO was found in the case of $edta^{4-}$, which is ca. 4 times faster than for the reaction of $Fe^{II}(hedtra)H_2O$ with NO. All other complexes have significantly lower stability constants due to their lower binding rate constants. In general, a good agreement between the values of the formation constant K_{NO} calculated from the kinetic data and those determined directly with the aid of a combined spectrophotometric and potentiometric (NO sensitive electrode) technique was observed. Unfortunately, detailed mechanistic insight into such processes cannot be obtained from the rate law and corresponding rate constants only.[26]

For that reason we have now performed a more detailed study of the effect of temperature and pressure on the kinetics of the binding and release of NO on a series of selected complexes, and we report in this paper the activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$) for the studied reactions. These include the reaction of NO with Fe^{II} complexes of $mida^{2-}$ and $edta^{4-}$ as typical representatives of complexes which behave rather differently with respect to the binding of NO. The mida complex shows almost no oxygen sensitivity, exhibits a low binding affinity for NO, and releases NO almost completely reversibly on passing an inert gas through the solution. In contrast, the edta complex of Fe^{II} is extremely oxygen sensitive, shows a very high binding affinity for NO, and releases NO only slowly when treated with an inert gas. Kinetic studies on the "on" and "off" reactions were performed using stopped-flow and flash photolysis techniques. A detailed comparison in terms of oxygen sensitivity, binding constant for NO, and kinetic data for the "on" and "off" reactions was made for the closely related edta and hedtra systems. In addition, the nta complex was investigated since it shows an intermediate behavior in terms of its reversibility, oxygen sensitivity, and rate constants as compared to the edta and mida systems. In order to throw more light on the nature of the intimate mechanism involved in the binding of NO, water exchange reactions on selected Fe^{II} chelate complexes were performed using ^{17}O NMR techniques. These results provide a quantitative basis for the assignment of reaction mechanisms that can account for the earlier observed trends.

Experimental Section

Materials. Chemicals of analytical reagent grade and deionized water were used throughout this study. The complexes were prepared in solution from $Fe^{II}SO_4 \cdot 7H_2O$ and $Na_2(H_2edta)$, hedtra, nta (Aldrich), and mida (Akzo Nobel). The complex $K[Ru(Hedta)Cl] \cdot 2H_2O$ was prepared from $K_2[RuCl_5(H_2O)]$ according to literature methods.[27] Acetic acid/sodium acetate buffers were used to control the pH of the solutions, and $NaClO_4$ was used to adjust the ionic strength of the medium. NO gas, purchased from Messer Griesheim or Riessner Gase in a purity of at least 99.5 vol %, was cleaned from trace amounts of higher nitrogen oxides such as N_2O_3 and NO_2 by passing it through an Ascarite II column (NaOH on silica gel, Sigma-Aldrich). NO from a gas tank should not be used after 6 months following the date of its industrial preparation, since decomposition causes a drastic decrease in the purity of the gas. The decomposition is pressure dependent, which led us to only use bottles filled with a maximum pressure of 20 bar, and resulted in a longer lifetime of the NO gas.

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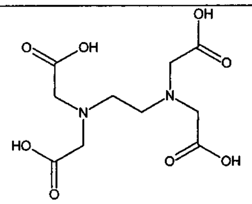
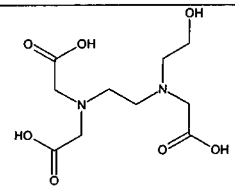
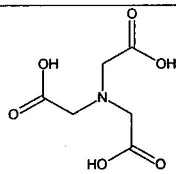
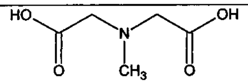
Table 1. Summary of the Chelate Ligands Used within This Study

Structure	Abbreviation	Name
	edta	Ethylenediaminetetraacetic acid
	Hedtra	Hydroxyethylenediaminetriacetic acid
	nta	Nitrilotriacetic acid
	mida	Methyliminodiacetic acid

Preparation of Solutions. Preliminary studies demonstrated that Fe^{II}(edta) and Fe^{II}(hedtra) are extremely oxygen sensitive and are rapidly oxidized to Fe^{III}(edta)/(hedtra). In order to avoid this complication and possible side reactions with NO, all Fe^{II} solutions were prepared in the absence of O_2. A stock solution of the ligand containing $NaClO_4$ (to adjust the ionic strength) was degassed on a vacuum line and washed a few times with inert gas (1 min/mL), before the Fe^{II} salt was added. The $K[Ru(Hedta)Cl]\cdot 2H_2O$ complex was dissolved in aqueous solution in the absence of a buffer, under which conditions it rapidly aquates to the corresponding aqua complex.[28,29] The pH was adjusted with NaOH and $HClO_4$. The nitrosyl complexes of Fe^{II}(edta), Fe^{II}(hedtra), Fe^{II}(nta), Fe^{II}(mida), and $Fe^{II}(mida)_2$ (see Table 1 for selected abbreviations) were prepared by passing NO through the ferrous solutions for some minutes. In order to remove noncoordinated NO, the solutions were bubbled for a short time with inert gas, before they were transferred with the aid of gastight syringes to the stopped flow unit or spectrophotometer cells. Blank experiments indicated that no O_2 entered the test solutions during the chosen handling procedure.

Kinetic Measurements. Stopped-Flow. The kinetics of nitric oxide release from nitrosylated Fe^{II}(L) complexes was studied on a thermostated (±0.1 °C) stopped-flow spectrometer (SX-18 MV, Applied Photophysics) coupled to an online data acquisition system. High-pressure stopped-flow experiments were performed on a custom-built instrument described previously[30] at pressures up to 130 MPa. At least five kinetic runs were recorded under all conditions, and the reported rate constants represent the mean values. The kinetic data were analyzed with the OLIS KINFIT program.

Laser Flash Photolysis. Laser flash photolysis kinetic studies were carried out with the use of the LKS.60 spectrometer from Applied Photophysics for detection and a Nd:YAG laser (SURLITE I−10 Continuum) pump source operating in the second ($\lambda_{exc} = 532$ nm) harmonic (245 mJ pulses with ~7 ns pulse widths). Spectral changes at appropriate wavelength were monitored using a 100 W xenon arc lamp, monochromator, and photomultiplier tube PMT−1P22. The absorbance reading was balanced to zero before the flash, and data were recorded on a digital storage oscilloscope DSO HP 54522A and then transferred to a computer for subsequent analysis. Gastight quartz cuvettes and a pill-box cell combined with high-pressure equipment[31] were used at ambient and under high pressure (up to 170 MPa), respectively. At least 30 kinetic runs were recorded under all conditions, and the reported rate constants represent the mean values of these.

The rate constant for the NO uptake reaction is detected around 435 nm, where a maximum in the UV/vis spectrum for Fe(L)NO is present. A stock solution of NO is prepared in a gastight syringe by degassing a 0.2 M acetate buffer solution (pH = 5.0), followed by saturation with NO. Dilutions of known concentration were prepared from this saturated solution by use of a syringe technique. Oxygen free solutions of iron(II) complexes were prepared and diluted to appropriate concentrations on the vacuum line.

Water Exchange Reactions. Variable-temperature/pressure Fourier transform ^{17}O NMR spectra were recorded at a frequency of 54.24 MHz on a Bruker Advance DRX 400WB spectrometer equipped with a superconducting BC-94/89 magnet system. The temperature dependence of the ^{17}O line broadening was studied over as wide a temperature range as experimentally necessary (268−353 K). A homemade high-pressure probe described in the literature[32] was used for the variable-pressure experiments which were conducted at the selected temperature (see Table 3) and at ambient, 30, 60, 90, 120, and 150 MPa pressure. A standard 5 mm NMR tube cut to a length of 45 mm was used for the sample

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Table 2. Summary of Kinetic and Thermodynamic Parameters at 25 °C for the Reversible Binding of NO to a Series of Fe^{II} Chelate Complexes

complex	k_{on}, $M^{-1}\,s^{-1}$	k_{off}, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	K (k_{on}/k_{off}), M^{-1}	K, M^{-1}	method
Fe^{II}(edta) **1**	$(2.4 \pm 0.1) \times 10^8$		24 ± 1	-4 ± 3	$+4.1 \pm 0.2$			fp[a]
		91.0 ± 0.4	61 ± 2	-5 ± 7	$+7.6 \pm 0.6$ (10.4 °C)			sf[b]
						$(2.1 \pm 0.5) \times 10^6$	$(2.1 \pm 0.2) \times 10^6$	
Fe^{II}(hedtra) **2**	$(6.1 \pm 0.1) \times 10^7$		26 ± 1	-12 ± 3	$+2.8 \pm 0.1$			fp
		4.2 ± 0.1	73 ± 1	11 ± 4	$+4.4 \pm 0.8$ (25.0 °C)			sf
						$(1.1 \pm 0.4) \times 10^7$	$(1.5 \pm 0.2) \times 10^7$	
Fe^{II}(nta) **3**	$(2.1 \pm 0.1) \times 10^7$		24 ± 1	-22 ± 3	-1.5 ± 0.1			fp
		9.3 ± 0.6	66 ± 1	-5 ± 4	-3.5 ± 0.7 (25.0 °C)			sf
						$(1.8 \pm 0.3) \times 10^6$	$(1.8 \pm 0.2) \times 10^6$	
Fe^{II}(mida) **4**	$(1.9 \pm 0.1) \times 10^6$		40 ± 1	8 ± 3	$+7.6 \pm 0.4$			fp
		57.3 ± 0.4	47 ± 2	-55 ± 5	$+6.8 \pm 0.4$ (10.3 °C)			sf
						$(2.1 \pm 0.6) \times 10^4$	$(9.5 \pm 0.7) \times 10^3$	
$Fe^{II}(mida)_2$ **5**	$(1.8 \pm 0.1) \times 10^6$		34 ± 1	-13 ± 3	$+8.1 \pm 0.2$			fp
		62.2 ± 0.6	64 ± 1	5 ± 5	$+5.1 \pm 0.5$ (10.0 °C)			sf
						$(3.0 \pm 0.4) \times 10^4$	$(2.2 \pm 0.6) \times 10^4$	

[a] Flash photolysis. [b] Stopped flow.

Table 3. Kinetic Parameters for Water Exchange Reactions on Mida Complexes of Iron(II)

	k_{ex} at 25 °C, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	k (1 bar),[a] s^{-1}	k (temp),[b] s^{-1}
Fe^{II}(mida) **4**	1.8×10^7	27 ± 3	-16 ± 11	$+1.2 \pm 0.2$ (10.0 °C)	1.3×10^7	1.2×10^7
$Fe^{II}(mida)_2$ **5**	2.4×10^7	39 ± 3	27 ± 10	$+3.2 \pm 0.2$ (9.0 °C)	1.5×10^7	1.5×10^7

[a] Rate constant at atmospheric pressure extrapolated from the pressure dependence data. [b] Rate constant from the temperature dependence data extrapolated to the temperature at which the pressure dependence was studied.

solutions. The pressure was transmitted by a movable macor piston, and the temperature was controlled as described elsewhere.[32]

Other Measurements. UV/vis spectra were recorded on a Cary 1G UV/vis spectrophotometer from Varian using a 1 cm quartz cuvette directly attached to a round flask with a sideways gas connection. pH measurements were performed with the aid of a Mettler Delta 340 pH-meter. The reference electrode was filled with NaCl instead of KCl to prevent precipitation of $KClO_4$. The determination of the stability constants K_{NO} was performed as described elsewhere.[1] The concentration of free nitric oxide in solution was determined with an ISO-NOP electrode connected to an ISO-NO Mark II nitric oxide sensor from World Precision Instruments. The NO electrode consists of a membrane-covered anode which selectively oxidizes NO to NO_3^- ions. The resulting current is proportional to the concentration of NO in solution. The NO electrode was calibrated daily with fresh solutions of sodium nitrite and potassium iodide according to the method suggested by the manufacturers. The calibration factor nA/μM was determined with a linear fit program.

Results and Discussion

We first focus on the nature of the selected complexes in solution. The net charge on the complex is given when the composition of the complex in solution can be specified, e.g., $[Fe^{II}(edta)]^{2-}$. A coordinated water molecule was detected in the crystal structure of the seven-coordinate edta complex,[33] which can therefore be represented by the formula $[Fe^{II}(edta)(H_2O)]^{2-}$. So far no crystal structure is known for the Fe^{II} complex of hedtra, but based on our earlier studies[1,26] and the results from this study, the complex is expected to be present as a seven-coordinate species in solution with one water molecule bound to the iron center. The species distribution for the Fe^{II} complexes of mida[1] indicates that at pH 5, where most of the experiments were performed, mainly the 1:1 complex will exist in solution when a 10% excess of the ligand was used. The 1:2 complex will only be present as the major species when a large excess (ca. 20-fold) of $mida^{2-}$ is used. It is presently not known whether these complexes are six- or seven-coordinate species in solution. Surprisingly little has been reported on the speciation of the Fe^{II}(nta) system. The $[Fe^{II}(nta)(H_2O)_2]^-$ complex has a moderate log K_1 value of 8.83 at 20 °C.[34] The 2:1 complex, $[Fe^{II}(nta)_2]^{4-}$, was reported to have a small log K_2 of 4.3 at 20 °C; these workers also report a small tendency to form the pendant protonated $[Fe^{II}(ntaH)(H_2O)_3]$ species.[35] Therefore, for a 1:1 ratio of Fe^{II} and nta^{3-}, it is reasonable to assume that the major species in solution is the six-coordinate $[Fe^{II}(nta)(H_2O)_2]^-$ complex.

In the presence of L, the reaction product is $[Fe^{II}(L)NO]^{x-}$, i.e., $\{Fe{-}NO\}^7$, which can formally be stabilized as either $[Fe^{I}(L)(NO^+)]^{x-}$ or $[Fe^{III}(L)(NO^-)]^{x-}$. The tendency of Fe^{II}(L) to reversibly bind NO correlated directly with the oxygen sensitivity of the Fe^{II} complexes, suggesting that Fe(L)NO is stabilized in the form of $Fe^{III}(L)(NO^-)$ similar to that found for the binding of dioxygen, viz., $Fe^{III}(L)(O_2^-)$.[1] Information on the nature of the Fe(L)NO product was obtained from FT-IR spectroscopy and analyses of the decomposition products. In the case of Fe^{II}(L)NO (L = $edta^{4-}$), a characteristic NO band is observed around 1777 cm^{-1}, which is assigned to the binding of NO as $Fe^{III}{-}NO^-$.[1] This assignment is in good agreement with the description of the electronic structure of the $\{FeNO\}^7$ unit reported for the two

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nitrosyl ($S = {}^3/_2$) complexes [Fe^{II}(edta)NO] and [Fe^{II}(Me_3-TACN)(NO)(N_3)$_2$] by Solomon and co-workers.[36] A combination of experimental (X-ray absorption, EPR, SQUID magnetic susceptibility, resonance Raman spectroscopy, near-IR/UV−vis absorption, and MCD) and theoretical (SCF-Xα-SW) methods indicated that in such complexes iron is best described as high spin Fe^{3+} ($S = {}^5/_2$) and NO as NO^- ($S = 1$), which are antiferromagnetically coupled to produce the total spin state of $S = {}^3/_2$.[36] The slightly shifted bands for the other [Fe^{II}(L)NO]$^{x-}$ complexes also correspond to species formally written as [Fe^{III}(L)(NO^-)], indicating a pronounced electron donation from the metal to the ligand. Furthermore, spectroscopic studies on non-heme iron nitrosyl centers in proteins[36−43] and inorganic complexes,[44−49] in combination with sophisticated theoretical calculations, provide compelling evidence that the $\{FeNO\}^7$ unit with spin quartet ground state ($S_t = {}^3/_2$) in the structurally well characterized iron nitrosyl complexes is best described by a bonding model based on high-spin Fe^{III} antiferromagnetically coupled to NO^- ($S = 1$). Recently, the same binding mode was found for the nitrosyl complex formed in the classical “brown-ring” reaction of $[Fe(H_2O)_6]^{2+}$ with NO. From the spectral (EPR, Mössbauer, and UV−vis) data reported for this nitrosyl product, it is clear that the complex can be formulated as $[Fe^{III}(H_2O)_5(NO^-)]^{2+}$ and not as $[Fe^{I}(H_2O)_5(NO^+)]^{2+}$ as claimed before.[50]

Kinetics of the “On” Reaction. The binding of NO to complexes of the type Fe^{II}(L) can be expressed by the overall reaction given in eq 1. Based on a literature report[51] in which k_{on} was measured directly at low temperature for the binding of NO to [Ru^{III}(edta)H_2O]$^-$ using stopped-flow techniques, similar experiments were performed for the reaction of [Fe^{II}(edta)H_2O]$^{2-}$ with NO. In the case of [Ru^{III}(edta)H_2O]$^-$, the authors reported a value for k_{on} of 1×10^7 M^{-1} s^{-1} in phosphate buffer at pH 7.4 and 7.3 °C. In order to measure such high rate constants on the stopped-flow instrument, second-order reaction conditions and low concentrations of both reaction partners were selected to obtain conditions where the reaction is slower than the dead time (2−4 ms) of the stopped-flow instrument. Similar experiments with the edta and hedtra complexes of Fe^{II} at low temperature and low reactant concentrations revealed that k_{on} for these complexes is on the limit or faster than 5×10^7 M^{-1} s^{-1} at pH 5 and 25 °C, i.e., very similar to that reported for [Ru^{III}(edta)H_2O]$^-$. The high k_{on} values make these complexes ideal candidates to study the reverse release of NO from complexes that bind NO less efficiently. Alternatively, an excess of such a complex can be used to study the release of NO from a complex that exhibits a similar reactivity toward NO, since the concentration ratio then determines the nature of the final product and the extent to which the rate-determining release of NO will be observed.

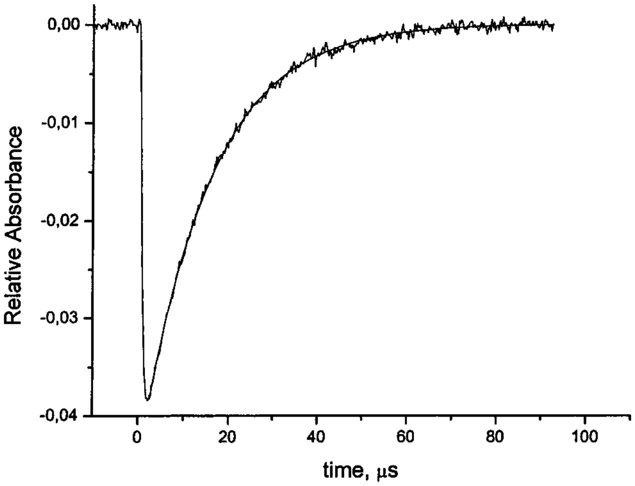

Figure 1. Typical absorbance−time plot for the reaction of [Fe^{II}(nta)(H_2O)$_2$]$^-$ with NO at pH 5.0 (0.2 M NaAc), I = 0.5 M ($NaClO_4$), and 25 °C: photolysis wavelength = 532 nm, detection wavelength = 439 nm, [Fe^{II}] = 4×10^{-3} M, [NO] = 0.38×10^{-3} M.

Relaxation techniques (viz., flash photolysis) can be employed to study rapid, reversible complex-formation reactions. On application of relaxation kinetics to reaction 1, the observed first-order rate constant is given by eq 2 under the experimental conditions selected in this study,

$$\begin{aligned} k_{obs} &= k_{on}\{[Fe^{II}(L)H_2O]_e + [NO]_e\} + k_{off} \\ &= k_{on}[Fe^{II}(L)H_2O] + k_{off} \end{aligned} \qquad (2)$$

where $[Fe^{II}(L)H_2O]_e$ and $[NO]_e$ represent the equilibrium concentrations of the Fe^{II}(L) complex and the free NO in solution, respectively. According to eq 2, measurements of k_{obs} as a function of the sum of the equilibrium concentrations should enable the determination of k_{on} and k_{off}.

A typical flash-photolysis trace is shown in Figure 1. The Fe^{II}(edta) **1** complex is the species with the highest complex-formation rate constant for NO. The concentration depen-

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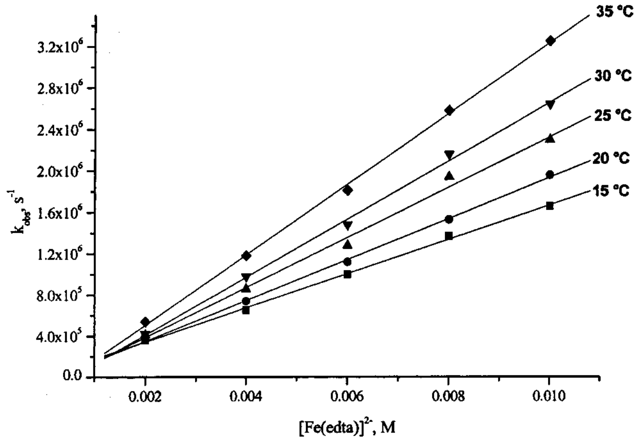

Figure 2. k_{obs} measured at different temperatures at pH = 5.0 (0.2 M NaAc) as a function of $[Fe^{II}(edta)]^{2-}$ concentration: photolysis wavelength = 532 nm, detection wavelength = 432 nm, [NO] = 2.0×10^{-4} M.

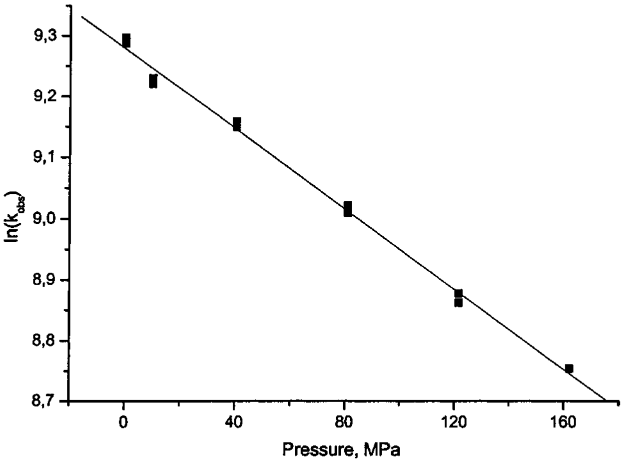

Figure 3. k_{obs} as a function of pressure for the reaction of Fe^{II}(mida) with NO measured at pH = 5.0 (0.2 M NaAc) and 25 °C: $[Fe^{II}]$ = 0.005 M, [mida] = 0.0055 M, photolysis wavelength = 532 nm, detection wavelength = 443 nm, [NO] = 4.0×10^{-4} M.

dence of k_{obs} resulted in a linear plot as predicted by eq 2 from which $k_{on} = (2.4 \pm 0.1) \times 10^8$ M^{-1} s^{-1} at 25 °C (pH = 5). This result agrees well with literature data,[2,13,15,17,18,26] where rate constants around 1.3×10^8 M^{-1} s^{-1} at different pHs and temperatures were found. Similar measurements were performed for Fe^{II}(hedtra) **2**, Fe^{II}(nta) **3**, Fe^{II}(mida) **4**, and $Fe^{II}(mida)_2$ **5**, and a typical concentration dependence for **3** is shown in Figure S1 (see Supporting Information). The intercepts of such plots do not allow an accurate determination of k_{off}, and for that reason k_{off} was measured directly in a different way (see further discussion). The reactions were all studied as a function of temperature and pressure for which typical examples are shown in Figures 2 and 3, respectively. The temperature dependence of k_{on} was used to construct Eyring plots from which the activation parameters $\Delta H^{\ddagger}_{on}$ and $\Delta S^{\ddagger}_{on}$ were determined, whereas the activation volume for the "on" reaction, $\Delta V^{\ddagger} = -RT(\mathrm{d}\ln(k_{on})/\mathrm{d}P)_T$, was determined from the slope of the plot of $\ln(k_{on})$ versus pressure. The values of k_{on} at 25 °C and its activation parameters are summarized in Table 2.

Kinetics of the "Off" Reaction. In principle it is possible to measure k_{off} directly, and not via the determination of an intercept according to eq 2, by treatment of the Fe^{II}(L)NO complex with another complex that binds NO more efficiently than the system under investigation. Under such conditions, release of NO can become the rate-limiting step, which means that k_{off} can be determined directly from the observed kinetic trace. Two suitable complexes to determine k_{off} for the release of NO from $Fe^{II}(mida)_2NO^{2-}$ are $Fe^{II}(edta)(H_2O)^{2-}$ and $Ru^{III}(edta)H_2O^{-}$, which both react very rapidly (k_{on} is ca. 1×10^8 M^{-1} s^{-1} at pH 5 and 25 °C) with NO to form the corresponding nitrosyl complexes. When an excess of either of these complexes is employed such that the release of NO, i.e., k_{off}, becomes the rate-limiting step, then the observed rate constant should be independent of the excess concentration employed.

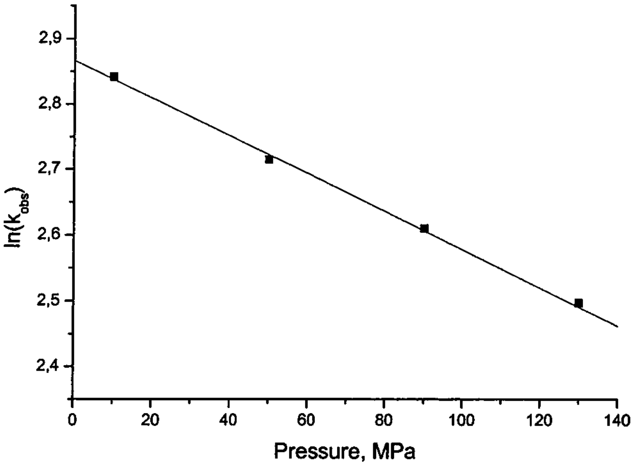

Figure 4. k_{obs} for the release of NO from $[Fe^{II}(mida)NO]$ recorded on the stopped-flow instrument as a function of pressure measured at pH = 5.0 (0.1 M NaAc), λ_{det} = 386 nm, and 10.3 °C: $[Fe^{II}(mida)NO] = 1.5 \times 10^{-3}$ M, $[Fe^{II}(edta)] = 2.5 \times 10^{-3}$ M, I = 0.5 M ($NaClO_4$).

The release of NO from $Fe^{II}(edta)NO^{2-}$ with $Ru^{III}(edta)H_2O^{-}$ as a scavenger was complete within 100 ms, and k_{off} was calculated to be 91 ± 0.4 s^{-1} (a typical stopped-flow trace for this reaction is shown in Figure S2, Supporting Information). The lowest values were found for $Fe^{II}(hedtra)NO^{-}$ and $Fe^{II}(nta)NO^{-}$ with k_{off} = 4.2 ± 0.1 and 9.3 ± 0.6 s^{-1} at 25 °C, respectively. Significantly higher rate constants were obtained for Fe^{II}(mida)NO (k_{off} = 57.3 ± 0.4 s^{-1}) and $Fe^{II}(mida)_2NO$ (k_{off} = 62.2 ± 0.6 s^{-1}). From the temperature and pressure dependence of k_{off} [see typical examples in Figure S3 (Supporting Information) and Figure 4], the activation parameters were determined, and they are summarized in Table 2.

Kinetic data for the release of NO in the case of edta and nta are available from the literature.[2,22] In the case of Fe^{II}(edta) the predicted literature value of $k_{off} > 60$ s^{-1} could be confirmed, whereas a significantly lower rate was measured in the case of the nta complex in the present study. The trapping technique employed enables a direct measurement of the dissociation rate constant and in principle must result in more accurate values than those obtained using indirect methods.

Water Exchange Reactions. The exchange rate of solvent molecules between the bulk and the coordination site of the different paramagnetic $[Fe^{II}(L)(H_2O)_x]^{y-}$ complexes was determined by ^{17}O NMR from measurements of the transverse relaxation rates of the bulk solvent nuclei. From the observed experimental values, where $\Delta\nu_{\mathrm{obs}}$ and $\Delta\nu_{\mathrm{solvent}}$ are the half-widths of the ^{17}O NMR lines for solvent in the bulk in the presence and absence of the $\mathrm{Fe^{II}}$ complex, respectively, together with the mole fraction of the bound water, P_{m}, the reduced transverse relaxation rates ($1/T_{2\mathrm{r}}$) can be calculated for each temperature and pressure. According to the Swift and Connick equation,[52,53] $T_{2\mathrm{r}}$ is related to τ_{m} and $T_{2\mathrm{m}}$, the mean lifetime and the transverse relaxation time of coordinated water in the inner sphere of $\mathrm{Fe^{II}}$ in the absence of chemical exchange, respectively. The exchange rate k_{ex} ($=1/\tau_{\mathrm{m}}$) between coordinated and bulk water is given by eq 3.

$$\frac{1}{T_{2\mathrm{r}}} = \frac{1}{P_{\mathrm{m}}}\left\{\frac{1}{T_2} - \frac{1}{{T_2}^0}\right\} = \pi\frac{1}{P_{\mathrm{m}}}\{\Delta\nu_{\mathrm{obs}} - \Delta\nu_{\mathrm{solvent}}) = \frac{1}{\tau_{\mathrm{m}}}\left\{\frac{{T_{2\mathrm{m}}}^{-2} + (T_{2\mathrm{m}}\tau_{\mathrm{m}})^{-1} + {\Delta\omega_{\mathrm{m}}}^2}{({T_{2\mathrm{m}}}^{-1} + {\tau_{\mathrm{m}}}^{-1})^2 + {\Delta\omega_{\mathrm{m}}}^2}\right\} + \frac{1}{T_{2\mathrm{os}}} \tag{3}$$

$\Delta\omega_{\mathrm{m}}$ is the difference in resonance frequency between the O-17 nuclei of the solvent in the first coordination sphere and in the bulk. The total outer-sphere contributions to $T_{2\mathrm{r}}$, arising from long-range interactions of the paramagnetic unpaired electron of the iron complex with the water outside the first coordination sphere, are represented by $T_{2\mathrm{os}}$.

The temperature dependence of $\Delta\omega_{\mathrm{m}}$ is given by $\Delta\omega_{\mathrm{m}} = A/T$, where Bloembergen[54] suggests $A = [\omega g_{\mathrm{eff}}\beta\vec{B}S(S+1)]/(g_{\mathrm{N}}\beta_{\mathrm{N}}3k_{\mathrm{B}})$, but the constant A is determined as a parameter in the treatment of the line broadening data. $T_{2\mathrm{m}}$ is assumed to have a simple temperature dependence given by $1/T_{2\mathrm{m}} = \mathrm{A_m}\exp(E_{\mathrm{m}}/RT)$, and the solvent-exchange rate constant k_{ex} is equal to $1/\tau_{\mathrm{m}} = k_{\mathrm{ex}} = (k_{\mathrm{b}}T/h)\exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT)$. The contributions of $1/T_{2\mathrm{m}}$ and $1/T_{2\mathrm{os}}$ to $1/T_{2\mathrm{r}}$ were found to be negligible in the systems studied, so that eq 3 reduces to eq 4. The exchange rate constant is assumed to have a simple pressure dependence given by $1/\tau_m = k_{ex} = {k_{ex}}^0 \exp\{(-\Delta V^{\ddagger}/RT)\cdot P\}$. In the systems described here, our approach was to carry out pressure dependent measurements at a temperature corresponding to the slow exchange region.

$$\frac{1}{T_{2\mathrm{r}}} = \frac{1}{\tau_{\mathrm{m}}}\left\{\frac{{\Delta\omega_{\mathrm{m}}}^2}{{\tau_{\mathrm{m}}}^{-2} + {\Delta\omega_{\mathrm{m}}}^2}\right\} \tag{4}$$

The results of these measurements are summarized in Table 3. A typical plot of the temperature dependent measurements is shown in Figure S4, and the results for the pressure dependent study of the $\mathrm{Fe^{II}}$(mida) complex are presented in Figure S5 (Supporting Information). The values obtained for ${k_{\mathrm{ex}}}^0$ from the pressure dependence measurements (at ambient pressure) are all in good agreement with the corresponding values for ${k_{\mathrm{ex}}}^0$ extrapolated from the temperature dependence study at ambient pressure to the particular temperature as shown in Table 3.

The iron(II) complexes of mida were successfully measured with this technique, which led to the rate and activation parameters for the water exchange process summarized in Table 3. Although a satisfactory line broadening was observed for the $\mathrm{Fe^{II}}$(nta) complex at room temperature, no data could be calculated from the spectra recorded at higher temperature. The complex seemed to be oxidized (or destroyed) during these measurements at temperatures higher than 40 °C, which led to a dramatic decrease in the line width. Unfortunately, no noteworthy line broadening was found in the cases of $\mathrm{Fe^{II}}$(hedtra) and $\mathrm{Fe^{II}}$(edta). The water exchange process is presumably too fast to be measured using this technique.

Mechanistic Interpretation. The fastest rate constant for the binding of NO was found in the case of $\mathrm{Fe^{II}(edta)H_2O}$, which is ca. 4 times faster than the reaction of $\mathrm{Fe^{II}(hedtra)H_2O}$ with NO. Taking into account the 22 times faster NO release from the edta complex, the nitrosyl adduct of the hedtra complex is around 5 times more stable than the edta complex at 25 °C. On this basis we can account for the reported difference in the stability constants for these two complexes. The $\mathrm{Fe^{II}}$(nta)NO complex has approximately the same stability constant as the edta complex, where in this case both k_{on} and k_{off} are smaller. The iron(II) complexes of mida have significantly lower stability constants due to their lower k_{on} values and relatively high k_{off} values.

The thermal activation parameters for the "on" reaction of NO with complexes **1**, **2**, and **3** show rather similar activation enthalpies around 25 ± 2 kJ mol^{-1}, whereas the entropy of activation decreases from -4 ± 3 to -12 ± 3 and -22 ± 3 J K^{-1} mol^{-1} along the series, respectively. The reactions of the 1:1 and 1:2 complexes of mida exhibit significantly higher enthalpies of activation, viz., 40 ± 1 and 34 ± 1 kJ mol^{-1}, respectively, but rather similar (close to zero) activation entropies, viz., $+8 \pm 3$ and -13 ± 3 J K^{-1} mol^{-1}, respectively.

From the pressure dependence of the forward rate constant (k_{on}), the volumes of activation for complexes **1**, **2**, **4**, and **5** were determined to be $+4.1 \pm 0.2$, $+2.8 \pm 0.1$, $+7.6 \pm 0.4$, and $+8.1 \pm 0.2$ cm^3 mol^{-1}, respectively. These complex-formation reactions can be best described by a dissociative interchange ($\mathrm{I_d}$) mechanism based on these values.[55] The exception is the reaction of $\mathrm{Fe^{II}}$(nta) with NO, which exhibits a definite negative volume of activation, viz., -1.5 ± 0.1 cm^3 mol^{-1}, suggesting that the reaction most probably occurs via an associative interchange ($\mathrm{I_a}$) mechanism.

The water exchange measurements for the complexes **4** and **5** led to exchange rates of 1.8×10^7 and 2.4×10^7 s^{-1} at 25 °C, respectively, which far exceed the rates of the "on" reaction measured for these complexes under the selected experimental conditions. This suggests that the water exchange reaction controls the substitution process with NO. The activation entropies determined for these reactions differ quite considerably, which is not unusual for such measurements and can be interpreted as close to zero. The experi-

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mental activation volumes are lower limits of the expected values as a result of the selected temperature. The values are rather similar for both the 1:1 and 1:2 complexes and suggest the operation of a dissociative interchange (I_d) mechanism.[56] Thus the available rate parameters for these water exchange reactions support the same mechanism as concluded for the binding of NO, which should be the case if water dissociation controls the substitution behavior of such complexes.

The decrease in the values of k_{off} from 91 s^{-1} (**1**) to 4.2 s^{-1} (**2**) is accompanied by an increase in the activation enthalpy from 61 ± 2 kJ mol^{-1} (**1**) to 73 ± 1 kJ mol^{-1} (**2**), whereas the entropy of activation is found to be around zero. Remarkably low $\Delta H^\ddagger$ and very negative $\Delta S^\ddagger$ values, viz., 47 ± 2 kJ mol^{-1} and −55 ± 5 J K^{-1} mol^{-1}, respectively, were found for the Fe(mida) **4** complex. The volumes of activation for the NO release reaction of the complexes **1**, **2**, **4**, and **5** were all found to be around 5 ± 2 cm^3 mol^{-1}, viz., +7.6 ± 0.6, +4.4 ± 0.8, +6.8 ± 0.4, and +5.1 ± 0.5 cm^3 mol^{-1}, respectively. These values clearly indicate that the "off" reaction also follows a dissociative interchange (I_d) in agreement with the principle of microscopic reversibility. Alternatively, the release of NO from $Fe^{III}-NO^-$ in the "off" reaction can be visualized as a homolysis reaction that results in the formation of Fe^{II} and NO, in which bond cleavage is accompanied by formal reduction of Fe^{III} to Fe^{II}, and involves the simultaneous entry of a water molecule, i.e., a water "assisted" homolysis reaction. This process is suggested to have an overall dissociative character balanced by the volume decrease as a result of the participating water molecule. Again the Fe^{II}(nta)NO system is an exception with $\Delta V^\ddagger = -3.5 \pm 0.7$ cm^3 mol^{-1}, suggesting that this "off" reaction involves partial bond formation prior to the release of NO, i.e., an associative interchange (I_a) mechanism.

From the above discussion we can conclude that for complexes **1**, **2**, **4**, and **5**, the reversible binding of NO can be best described by an I_d mechanism, which is also in agreement with that found for water exchange on complexes **4** and **5**. The only exception in the selected series of complexes seems to be the Fe^{II}(nta) system, and the reported data suggest the operation of an I_a mechanism.

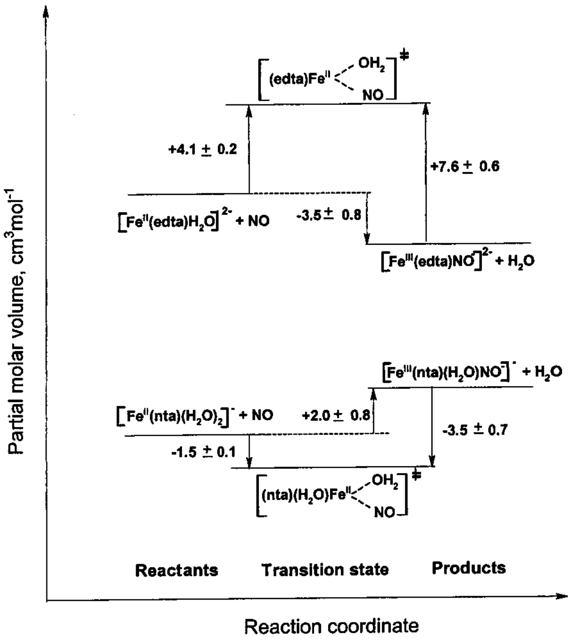

Figure 5. Volume profiles for the reversible binding of NO to $[Fe^{II}(edta)H_2O]^{2-}$ and $[Fe^{II}(nta)(H_2O)_2]^-$.

The apparent difference in the complex-formation mechanism of the nta complex as compared to the other complexes studied must be due to the fact that the nta complex is six-coordinate in solution, whereas it is for instance known that the edta complex is seven-coordinate.[33] This would mean that complexes **1**, **2**, **4**, and **5** all react with NO according to an I_d mechanism as a result of their seven-coordinate, 20 valence electron character. The six-coordinate nta complex will then tend to react according to an I_a mechanism due to its six-coordinate, 18 valence electron character. The difference in mechanism for these complexes becomes very apparent from the volume profiles for the edta and nta systems presented in Figure 5. The smaller partial molar volume of the transition state for the reaction of Fe^{II}(nta) with NO as compared to the larger partial molar volume of the transition state for the reaction of Fe^{II}(edta) with NO clearly supports the operation of an I_a ligand substitution mechanism. Volume compression versus volume expansion typically characterizes I_a versus I_d ligand substitution mechanisms, respectively.[55] In addition, the overall reaction volumes for these two systems also differ significantly, viz., the edta complex undergoes an overall volume collapse on the binding of NO, whereas the nta complex undergoes a volume increase on the binding of NO. This difference must be related to volume changes associated with the displacement of water by NO in the seven- and six-coordinate complexes, respectively, and the formal oxidation of Fe(II) to Fe(III).

On comparing the iron(II) complexes of $mida^{2-}$ and $edta^{4-}$ in terms of their application as catalysts for the exhaust gas denitrification process, the reaction of Fe^{II}(mida) with NO is approximately 100 times slower than the corresponding reaction with $Fe^{II}(edta)H_2O$, which accounts for almost the same difference in the value of K_{NO}. This apparent disadvantage of the mida complex could for example be partially canceled by longer contact time between the exhaust gas and the catalyst. In addition, the mida complex is almost oxygen insensitive, which prevents unwanted oxidation of the chelate and allows the effective regeneration of the catalyst.

Conclusions

The results of this study illustrate the important influence of the aminocarboxylate chelates on the values of the rate constants and overall equilibrium constant, as well as on the nature of the mechanism for the binding and release of NO. There seems to be no simple correlation between these constants and the selected donor groups or overall charge on the iron(II) complexes. Electronic/structural features must control the coordination number of the studied complexes and as a result their mechanistic behavior. Such mechanistic

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information can only be revealed by the activation parameters, where $\Delta V^{\ddagger}$ has once again shown to be a crucial parameter in distinguishing between different possible mechanisms. In addition, the correlation with similar parameters for solvent exchange reactions on the metal complexes enables the elucidation of the chemical process that actually controls the reactivity of the system, and thus provides further mechanistic insight.

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Supporting Information Available: A total of five figures in which plots of $\ln(1/T_{2r})$ as a function of temperature and pressure for water exchange on Fe^{II}(mida), a plot of k_{obs} as a function of Fe^{II}(nta) concentration for the reaction with NO, and a kinetic trace and temperature dependence for the release of NO from Fe(edta)-NO are reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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