

Articles

Influence of Chelate Effects on the Water-Exchange Mechanism of Polyamminecarboxylate Complexes of Iron(III)

Thorsten Schnepfenseper, Sabine Seibig, Achim Zahl, Peter Tregloan,[†] and Rudi van Eldik*

Institute for Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany

Received November 17, 2000

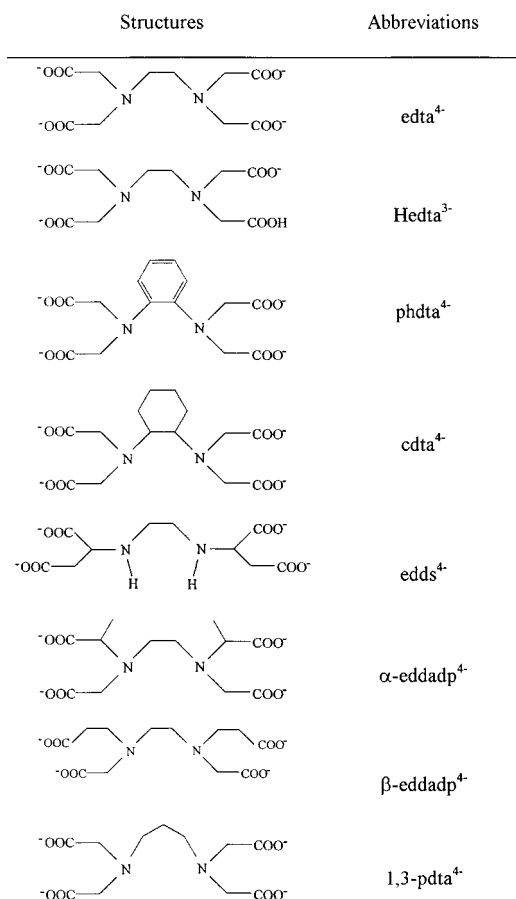
The effect of temperature and pressure on the water-exchange reactions of complexes of the type $[\text{Fe}^{\text{III}}(\text{L})(\text{H}_2\text{O})_x]^{n-}$, where L = edta⁴⁻ (ethylenediaminetetraacetate), Heda³⁻ (monoprotonated form of edta), cdta⁴⁻ (*trans*-1,2-diaminocyclohexanetetraacetate), edds⁴⁻ (*s,s*-ethylenediaminedisuccinate), 1,3-pdta⁴⁻ (1,3-propylenediaminetetraacetate), and α,β -eddap⁴⁻ (α,β -ethylenediaminediacetatedipropionate), was studied by employing ¹⁷O NMR techniques. The effect of potentially hexadentate ligands, covering a systematic variation of the size, substituents, and overall coordination geometry, on iron(III) complexes was investigated in terms of the lability of the coordinated water and the underlying exchange mechanism. For most of the systems studied, the results are in agreement with a dissociatively activated water-exchange mechanism for the seven-coordinate complexes. The absolute magnitudes of the volumes of activation are small and fit an I_d mechanism. The results contribute to a better understanding of the nature, reactivity, and substitution mechanism of the selected complexes in solution.

Introduction

Polyamminecarboxylate chelates have a very wide application in coordination chemistry. Their use in analytical chemistry is well-known. We have an ongoing interest in their use as scavengers for species such as NO in environmental applications.¹ There is a complex interplay between factors such as the overall coordination geometry and the number and lability of coordinated solvent (usually water) which controls the substitution behavior and other properties of such metal chelates. Recent reports have demonstrated how polyamminecarboxylate chelates can introduce a changeover from six- to seven-coordinate on an iron(III) center resulting in complex speciation depending on the concentration and pH.^{2,3}

A fundamental aspect of the mechanistic behavior of such $[\text{Fe}^{\text{III}}(\text{L})(\text{H}_2\text{O})_x]^{n-}$ complexes concerns the lability and mechanism of the exchange and substitution of coordinated solvent, as well as the ways in which this can be tuned by the selected chelate. We have now studied the water-exchange reactions of a series of complexes of the type $[\text{Fe}^{\text{III}}(\text{L})(\text{H}_2\text{O})_x]^{n-}$ using ¹⁷O NMR line broadening techniques. The chelates chosen, summarized in Scheme 1, are potentially hexadentate ligands and cover a systematic variation of the diamine function in terms of the nature of the bridging groups (edta⁴⁻, cdta⁴⁻, and phdta⁴⁻) and the chelate size (edta⁴⁻ and 1,3-pdta⁴⁻), the introduction

Scheme 1



[†] On leave from the School of Chemistry, The University of Melbourne, 3052 Parkville, Australia.

- (1) Schnepfenseper, T.; Finkler, S.; Czap, A.; van Eldik, R.; Heus, M.; Nieuwenhuizen, P.; Wreesmann, C.; Abma, W. *Eur. J. Inorg. Chem.* **2001**, 491.
- (2) Mizuta, T.; Wang, J.; Miyoshi, K. *Inorg. Chim. Acta* **1990**, *175*, 121.
- (3) Solans, X.; Font-Altaba, M.; Garcia-Orcaín, J. *Acta Crystallogr.* **1984**, *Sect. C*, 635.
- (4) Seibig, S.; van Eldik, R. *Inorg. Chim. Acta* **1998**, *279*, 37.

of substituents on the carboxylate groups (α -eddadp⁴⁻), and the lengthening of the carboxylate arm (edds⁴⁻ and β -eddadp⁴⁻). These ligands should affect the nature of the coordination geometry around the iron center and as a result allow us to probe their effects on the lability of the coordinated water.

The structures of Fe^{III} complexes of polyaminocarboxylates are of particular interest because they can adopt six- and seven-coordination as a result of the critical radius of the Fe^{III} cation (0.79 Å) and the spherically symmetrical d⁵ electronic configuration of the metal ion. Several structures of Fe^{III} and Fe^{II} complexes are known where the hexadentate ligand is bound to a single iron center forming an octahedral coordination sphere, or, in other cases, an additional labile water molecule is coordinated at the seventh position.^{3–11} Such seven-coordinate complexes can adopt two geometrical configurations: pentagonal bipyramidal and monocapped trigonal prismatic. Since these geometries are energetically very similar, it often happens that the molecule adopts an intermediate geometry. Except for Fe^{III}(α -eddadp), crystal structures of all the Fe^{III} complexes investigated in this study are known and discussed in more detail below.

The most widely studied complex is the Fe^{III}(edta) system.^{2,3,6–8,12} Depending on the counterions, it has been isolated in the solid state as either a six- or seven-coordinate species, with edta always acting as a hexadentate ligand with or without an additional water molecule as the seventh ligand. The possibility of an eight-coordinate structure has been discussed.⁸ In acidic medium, an octahedral Fe^{III} complex has been crystallized with protonated edta acting as a pentadentate ligand with one nonbonding protonated carboxylate arm and a water molecule in the sixth coordination position.^{2,7} There is also an iron(II) structure known where two of the carboxylate arms are protonated, but both are coordinated to the Fe^{II} center, and an additional water molecule completes the seven-coordinate geometry.⁹

In the cases of Fe^{III}(cdta),^{4,5} Fe^{III}(phdta),¹⁰ Fe^{III}(4-Cl-phdta),¹³ and Fe^{III}(4-methyl-phdta),¹⁴ exclusively seven-coordination has been observed. For the Fe^{III} complexes of 1,3-pdta,^{4–11,15} α -eddadp^{4–11} and (S,S-edds),^{4–16} only octahedral geometries have been reported, i.e., without a coordinated water molecule in the solid state. It seems that in the case of Fe^{III}(edta), when the chelate is only capable of forming five-membered chelate rings, the central metal is slightly too large to be enclosed in an octahedral environment. The enlargement of the chelate rings in pdta⁴⁻ and α -eddadp⁴⁻ allows the formation of the octahedral six-coordinate complex. The exact coordination geometry of these complexes in solution remains a more open question.

On the basis of the available structural information, significantly different reactivities as well as mechanistic behavior for the water-exchange reactions of these complexes might be expected. A tuning of the chelate and the coordination sphere, along with particular experimental conditions, could lead to a variety of reactivities and water-exchange mechanisms.

In this work, we have studied the water-exchange reactions of the series of [Fe^{III}(L)(H₂O)_x]ⁿ⁻ complexes as a function of both temperature and pressure to obtain a complete set of activation parameters. Mizuno et al. reported such measurements for the [Fe^{III}(phdta)H₂O]⁻ system and, based on a volume of activation of +4.6 cm³ mol⁻¹, assigned an I_d mechanism for the water-exchange reaction.¹⁰ ΔV^\ddagger has been demonstrated to be a sensitive mechanistic indicator, especially when dealing with symmetrical solvent exchange reactions, where there are no major contributions from changes in electrostriction.^{17–19} In this context, it is relevant to note the very different activation volumes reported for water exchange on aquated Fe^{III} in the absence of a chelating ligand.^{20,21} The values of –5.4 and +7.0 cm³ mol⁻¹ for water exchange on [Fe(H₂O)₆]³⁺ and [Fe(H₂O)₅-OH]²⁺ were interpreted in terms of I_a and I_d exchange mechanisms, respectively. In this case the changeover in mechanism accompanying the deprotonation of a coordinated water molecule is ascribed to the trans effect of coordinated hydroxide on the departing ligand. This deprotonation also causes an acceleration of the water-exchange rate constant by ca. 10³. The objective of the present study was to allow a more systematic analysis of the influence of chelate effects on the water-exchange mechanism of chelated Fe^{III} complex ions.

Experimental Section

Synthesis. H₄edta, α -eddadp (Aldrich), *trans*-cdta, Fe(ClO₄)₃ × 9H₂O, NaClO₄ (Fluka), α -/ β -eddadp (Sigma), edds, 1,3-pdta (Akzo Nobel) and H₂O¹⁷ 10-at. % (Deutero GmbH) were used as supplied without further purification. For the syntheses of [Fe^{III}(L)(H₂O)_x]ⁿ⁻, Fe(ClO₄)₃ × 9H₂O (113.6 mg, 0.22 mmol) was added to a solution of H₄L (10% more than the stoichiometric ratio) in deionized H₂O (10 mL, I = 0.55 M (NaClO₄), pH = 5 (NaAc)). The bright yellow solution was stirred for some minutes. The final pH of the solutions was close to 4.0 (see Table 1). The solutions for the variable temperature and pressure measurements were deoxygenated on a vacuum line by freeze–thaw technique or by bubbling Ar through the solution for 10 min. After addition (of 0.08 mL) of 10-at. % H₂¹⁷O enriched water to (0.72 mL) complex solution, transfer to the NMR tube or high-pressure NMR tube was performed under Ar atmosphere using Schlenk techniques.

Measurements. Variable-temperature/pressure Fourier transform ¹⁷O NMR spectra were recorded at a frequency of 54.24 MHz on a Bruker Avance DRX 400WB spectrometer equipped with a superconducting BC-94/89 magnet system. The temperature dependence of the ¹⁷O line broadening was obtained over as wide a temperature range as possible for each system (273 to 388 K). A homemade high-pressure probe described in the literature²² was used for the variable-pressure experiments which were conducted at the selected temperature (see Table 1) 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 solutions. The pressure was transmitted by a movable macor piston, and the temperature was controlled as described elsewhere.²²

- (5) Cohen, G. H.; Hoard, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 3228.
 (6) Solans, X.; Font-Altaba, M.; Garcia-Oricain, J. *Acta Crystallogr.* **1985**, *Sect. C*, 525.
 (7) Kennard, C. H. L. *Inorg. Chim. Acta* **1967**, *1*, 2, 347.
 (8) Lind, M. D.; Hamor, M. J.; Hamor, T. A.; Hoard, J. L. *Inorg. Chem.* **1964**, *3*, 34.
 (9) Mizuta, T.; Wang, J.; Miyoshi, K. *Inorg. Chim. Acta* **1995**, *230*, 119.
 (10) Mizuno, M.; Funahashi, S.; Nakasuka, N.; Tanaka, M. *Inorg. Chem.* **1991**, *30*, 1550.
 (11) Yamamoto, T.; Mikata, K.; Miyoshi, K.; Yoneda, H. *Inorg. Chim. Acta* **1988**, *150*, 237.
 (12) Lopez-Alcala, J. M.; Puerta-Vizcaino, M. C.; Gonzales-Vilchez, F. *Acta Crystallogr.* **1984**, *Sect. C*, 939.
 (13) Sanchiz, J.; Dominguez, S.; Mederos, A.; Brito, F.; Arrieta, J. M. *Inorg. Chem.* **1997**, *36*, 4108.
 (14) Hernandez-Padilla, M.; Sanchiz, J.; Dominguez, S.; Mederos, A.; Arrieta, J. M.; Zuniga, F. J. *Acta Crystallogr.* **1996**, *Sect. C*, 1618.
 (15) Okamoto, K.; Kanamori, K.; Hidaka, J. *Acta Crystallogr.* **1990**, *Sect. C*, 1640.
 (16) Pavelcik, F.; Kettmann, V. *Collect. Czech. Chem. Commun.* **1983**, *48*, 1376.

- (17) Frey, U.; Helm, L.; Merbach, A. E. *Dynamics of Solution and Fluid Mixtures by NMR*; Delpuech J.-J., Ed.; Wiley: Chichester, 1995; p 263.
 (18) van Eldik, R.; Dücker-Benfer, C.; Thaler, F. *Adv. Inorg. Chem.* **2000**, *49*, 1.
 (19) Drljaca, A.; Hubbard, C. D.; van Eldik, R.; Asano, T.; Basilevsky, M. V.; le Noble, W. J. *Chem. Rev.* **1998**, *98*, 2167.
 (20) Swaddle, T. W.; Merbach, A. E. *Inorg. Chem.* **1981**, *20*, 4212.
 (21) Grant, M.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 55.
 (22) Zahl, A.; Neubrand, A.; Aygen, S.; van Eldik, R. *Rev. Sci. Instrum.* **1994**, *65*, 882.

Table 1. Summary of All Kinetic and Activation Parameters for Water Exchange on Complexes of the Type $[\text{Fe}^{\text{III}}(\text{L})(\text{H}_2\text{O})_x]^{n-}$

system	experimental conditions	k_{ex} at 298 K, d s $^{-1}$	ΔH^\ddagger , kJ mol $^{-1}$	ΔS^\ddagger , J K $^{-1}$ mol $^{-1}$	A	ΔV^\ddagger , cm 3 mol $^{-1}$	k (1 bar), a s $^{-1}$	k (temp), b,d s $^{-1}$	ref
$[\text{Fe}^{\text{III}}(\text{cdta})(\text{H}_2\text{O})]^-$	21 mM, pH 4.08, $I = 0.5$ M	1.4×10^7	28 ± 1	-14 ± 4	7.3×10^9				<i>c</i>
$[\text{Fe}^{\text{III}}(\text{cdta})(\text{H}_2\text{O})]^-$	29 mM, pH 4.07, $I = 0.5$ M	1.3×10^7	25 ± 1	-25 ± 4	7.1×10^9				
$[\text{Fe}^{\text{III}}(\text{cdta})(\text{H}_2\text{O})]^-$	combined data	1.3×10^7	27 ± 1	-18 ± 4	7.1×10^9				
$[\text{Fe}^{\text{III}}(\text{cdta})(\text{H}_2\text{O})]^-$	21 mM, 283 K, pH 4.1, $I = 0.5$ M					$+4.0 \pm 0.2$	$(6.5 \pm 0.1) \times 10^6$	7.0×10^6	
$[\text{Fe}^{\text{III}}(\text{cdta})(\text{H}_2\text{O})]^-$	29 mM, 283 K, pH 4.1, $I = 0.5$ M					$+4.0 \pm 0.1$	$(6.8 \pm 0.1) \times 10^6$	7.0×10^6	
$[\text{Fe}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$	45 mM, pH 3.9, $I = 0.5$ M	6.8×10^7	24.4 ± 0.3	-13.0 ± 0.8	6.5×10^9				<i>c</i>
$[\text{Fe}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$	30 mM, pH 3.9, $I = 0.5$ M	7.6×10^7	23.1 ± 0.2	-16.5 ± 0.5	7.3×10^9				
$[\text{Fe}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$	29 mM, pH 3.9, $I = 0.5$ M	7.7×10^7	24.7 ± 0.2	-11.0 ± 0.6	6.8×10^9				
$[\text{Fe}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$	combined data	7.2×10^7	24.3 ± 0.7	-13 ± 2	6.9×10^9				
$[\text{Fe}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$	45 mM, 298 K, pH 4, $I = 0.5$ M					$+1.6 \pm 0.3$	$(6.3 \pm 0.1) \times 10^7$	7.3×10^7	
$[\text{Fe}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$	30 mM, 298 K, pH 4, $I = 0.5$ M					$+2.2 \pm 0.3$	$(6.2 \pm 0.1) \times 10^7$	7.3×10^7	
$[\text{Fe}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]^-$	combined data					$+1.9 \pm 0.3$			
$[\text{Fe}^{\text{III}}(\text{Hedta})(\text{H}_2\text{O})]$	30 mM, pH 1.0, $I = 0.5$ M	7.8×10^7	22 ± 1	-20 ± 3	6.4×10^9				<i>c</i>
$[\text{Fe}^{\text{III}}(\text{Hedta})(\text{H}_2\text{O})_2]$	30 mM, pH 1.0, $I = 0.5$ M	3.8×10^7	22 ± 1	-26 ± 3	3.2×10^9				
$[\text{Fe}^{\text{III}}(\text{Hedta})(\text{H}_2\text{O})]$	30 mM, 294 K, pH 1.0, $I = 0.5$ M					$+2.1 \pm 0.2$	$(5.5 \pm 0.1) \times 10^7$	6.8×10^7	
$[\text{Fe}^{\text{III}}(\text{phdta})(\text{H}_2\text{O})]^-$	see ref 10	1.2×10^7	26 ± 3	-22 ± 9	8.2×10^9	$+4.6 \pm 0.2$	—	—	10
$[\text{Fe}^{\text{III}}(\alpha\text{-eddap})(\text{H}_2\text{O})]^-$	20 mM, pH 4.3, $I = 0.5$ M, $T < 303$ K, (1)	9.4×10^7	26 ± 2	-5 ± 6	6.7×10^9				<i>c</i>
$[\text{Fe}^{\text{III}}(\alpha\text{-eddap})(\text{H}_2\text{O})]^-$	20 mM, pH 4.3, $I = 0.5$ M, $T > 303$ K, (2)	3.1×10^5	33 ± 3	-29 ± 7	6.8×10^8				
$[\text{Fe}^{\text{III}}(\alpha\text{-eddap})(\text{H}_2\text{O})]^-$	20 mM, pH 4.3, $I = 0.5$ M, all param floated (1),(2)	(1) 2.3×10^8 (2) 2.5×10^6	36 ± 4 24 ± 2	$+36 \pm 14$ -42 ± 4	1.3×10^{10} 2.2×10^9				
$[\text{Fe}^{\text{III}}(\alpha\text{-eddap})(\text{H}_2\text{O})]^-$	20 mM, pH 4.3, $I = 1.0$ M, all param floated (1),(2)	(1) 2.6×10^8 (2) 2.8×10^6	33 ± 2 32 ± 2	$+27 \pm 8$ -14 ± 6	1.2×10^{10} 2.7×10^9				
$[\text{Fe}^{\text{III}}(\alpha\text{-eddap})(\text{H}_2\text{O})]^-$	20 mM, 294 K, pH 4.3, $I = 0.5$ M					$+3.0 \pm 0.4$	$(1.7 \pm 0.1) \times 10^8$	2.2×10^8	<i>c</i>
$[\text{Fe}^{\text{III}}(\text{edds})(\text{H}_2\text{O})]^-$	20 mM, pH 4.4, $I = 0.5$ M	4.3×10^5	48 ± 2	$+24 \pm 9$	1.9×10^8				<i>c</i>
$[\text{Fe}^{\text{III}}(\text{edds})(\text{H}_2\text{O})]^-$	20 mM, 293 K, pH 4.4, $I = 0.5$ M					-14.4 ± 0.4	$(1.2 \pm 0.1) \times 10^5$	3.0×10^5	
$[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$	see ref 20,21	1.6×10^2	64 ± 2	$+12 \pm 7$	—	-5.4 ± 0.4	—	—	20, 21
$[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$	see ref 20,21	1.4×10^5	42 ± 1	$+5 \pm 4$	—	$+7.0 \pm 0.3$	—	—	20, 21

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. c This work. d k_{ex} quoted at 298 K and at the temperature of the pressure measurements is calculated from the relevant activation parameters and is subject to the errors in those quantities.

Data Treatment. The rates of exchange of solvent molecules between the bulk and a coordination site on the paramagnetic $[\text{Fe}^{\text{III}}(\text{L})(\text{H}_2\text{O})]^{n-}$ complexes were determined by ^{17}O NMR. From the observed line widths, where $\Delta\nu_{\text{obs}}$ and $\Delta\nu_{\text{solvent}}$ are the half widths of the ^{17}O NMR signal of solvent in the presence and absence of the Fe^{III} complex, the reduced transverse relaxation rates ($1/T_{2r}$) can be calculated for each temperature and pressure. According to the Swift and Connick equation,^{23,24} T_{2r} is related to τ_m , the mean coordinated solvent lifetime, and T_{2m} , the transverse relaxation time of coordinated water in the inner sphere of $\text{Fe}(\text{III})$ in the absence of chemical exchange. The exchange rate constant between coordinated and bulk water, $k_{\text{ex}} = 1/\tau_m$. The relationships between these is summarized in eq 1.

$$\frac{1}{T_{2r}} = \frac{1}{P_m} \left\{ \frac{1}{T_2} - \frac{1}{T_2^0} \right\} = \pi \frac{1}{P_m} (\Delta\nu_{\text{obs}} - \Delta\nu_{\text{solvent}}) = \frac{1}{\tau_m} \left\{ \frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2} \right\} + \frac{1}{T_{2os}} \quad (1)$$

P_m is the mole fraction of solvent in the exchanging site compared to the bulk solvent; $\Delta\omega_m$ is the difference between the resonance frequency of oxygen-17 nuclei of solvent in the metal ion first coordination sphere and in the bulk. The outer-sphere contributions to T_{2r} , 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_{2os} .

The temperature dependence of $\Delta\omega_m$ was assumed to be simple reciprocal function A/T , where A ,²⁵ was determined as a parameter in the treatment of the line broadening data. T_{2m} , where it was included in the data treatment, was assumed to have a temperature dependence given by $1/T_{2m} = A_m \exp(E_m/RT)$.

The solvent-exchange rate constant $k_{\text{ex}} = 1/\tau_m = (k_B T/h) \exp\{(\Delta S^\ddagger/R) - (\Delta H^\ddagger/RT)\}$. The contribution of $1/T_{2m}$ and $1/T_{2os}$ to $1/T_{2r}$ was found to be negligible in most of the systems studied, so that eq 1 reduces to eq 2.

$$\frac{1}{T_{2r}} = \frac{1}{\tau_m} \left\{ \frac{\Delta\omega_m^2}{\tau_m^{-2} + \Delta\omega_m^2} \right\} \quad (2)$$

The exchange rate constant is assumed to have a simple pressure dependence given by

$$1/\tau_m = k_{\text{ex}} = k_{\text{ex}}^0 \exp\{(-\Delta V^\ddagger/RT)P\} \quad (3)$$

where k_{ex}^0 is the rate constant for solvent exchange at 1 bar. In the systems described here, our approach was to carry out pressure-dependent measurements at a temperature as close as practicable to the optimal exchange region (generally around the maximum in $\ln(1/T_{2r})$ vs $1/T$). The reduced relaxation time, T_{2r} and the value of $\Delta\omega_m$ (calculated using the value of A determined from the temperature dependence and assumed to be pressure independent²⁶) were substituted into eq 2 to determine $1/\tau_m$ at each pressure. In all cases, plots of $\ln(k_{\text{ex}})$ vs P were linear within experimental error and the volumes of activation could be calculated directly from the slope $(-\Delta V^\ddagger/RT)$. The extrapolated values for k_{ex}^0 from the pressure dependence measurements, were in good agreement with the corresponding values for k_{ex}^0 from the temperature-dependent measurements at ambient pressure, calculated at that particular temperature as shown in Table 1.

As will be shown below, the line-broadening experiments for the $[\text{Fe}(\alpha\text{-eddap})(\text{H}_2\text{O})]^-$ system show a complex temperature dependence which we have interpreted as arising from the presence of two isomers each of which can undergo solvent exchange in solution. In that case, the excess broadening will have contributions from both exchange processes as summarized in eq 4, where P'_m and P''_m refer to the mole fractions of solvent in each isomeric water site and the T_{2r} are the respective reduced relaxation times. The measured reduced relaxation

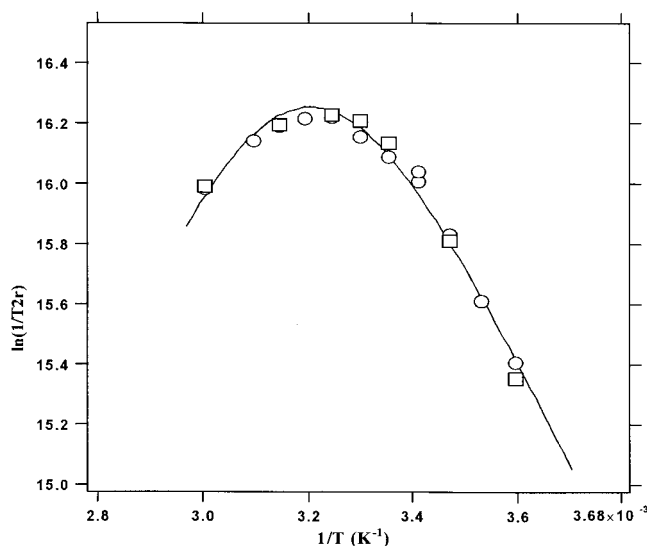


Figure 1. Plot of $\ln(1/T_{2r})$ versus $1/T$ for water exchange on $[\text{Fe}^{\text{III}}(\text{cdda})\text{H}_2\text{O}]^-$ at ambient pressure. Exp. conditions: circles: $[\text{Fe}^{\text{III}}(\text{cdda})\text{H}_2\text{O}] = 20.6 \text{ mM}$; $I = 0.5 \text{ M}$ (NaClO_4); $\text{pH} = 4.1$, squares: $[\text{Fe}^{\text{III}}(\text{cdda})\text{H}_2\text{O}] = 28.7 \text{ mM}$; $I = 0.5 \text{ M}$ (NaClO_4); $\text{pH} = 4.1$, curve fit: $\Delta H^\ddagger = 27.1 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -18.2 \text{ J K}^{-1} \text{ mol}^{-1}$, $A = 7.1 \times 10^9$, $k_{\text{ex}} = 1.2 \times 10^7 \text{ s}^{-1}$.

time will be given by eq 5, where P_m is the conventional total mole fraction of exchanging sites and F' is the fraction of the first isomer. If there is only one isomer, eq 5 reduces to eq 1.

$$\left(\frac{1}{T_2} - \frac{1}{T_2^0} \right) = \frac{P'_m}{T_{2r}'} + \frac{P''_m}{T_{2r}''} \quad (4)$$

$$\frac{1}{T_{2r}} = \pi \frac{1}{P_m} \{ \Delta\nu_{\text{observed}} - \Delta\nu_{\text{solvent}} \} = \frac{F}{T_{2r}'} + \frac{(1-F)}{T_{2r}''} \quad (5)$$

Results and Discussion

Experiments on the water exchange on $[\text{Fe}^{\text{III}}(\text{cdda})\text{H}_2\text{O}]^-$ were carried out with 21 mM and 29 mM Fe^{III} complex at $I = 0.5 \text{ M}$ (NaClO_4) and $\text{pH} = 4.0$; the data were analyzed separately and simultaneously. Preliminary experiments indicated that the measured exchange rate constants did not depend on the excess chelating ligand and buffer concentration employed. An example of the temperature dependence of the reduced transverse relaxation rate for the system is shown in Figure 1, and the pressure dependence of the exchange rate constant is included in Figure 4. A fit of the data to eqs 1, 2, and 3 as described above leads to the activation parameters in Table 1. The form of the plot and the kinetic and activation parameters are very similar to those reported by Mizuno et al. for water exchange on the structurally almost equivalent $[\text{Fe}^{\text{III}}(\text{phdta})\text{H}_2\text{O}]^-$ complex.¹⁰ Based in particular on the activation volume values, the mechanism is concluded to be I_d in character (see further Discussion).

The $[\text{Fe}^{\text{III}}(\text{edta})\text{H}_2\text{O}]^-$ complex at $\text{pH} = 4$ showed a similar behavior to the cdda complex except that the curvature was less pronounced and no maximum in $\ln(1/T_{2r})$ was observed up to $1/T = 3.7 \times 10^{-3} \text{ (0 }^\circ\text{C)}$, the lowest temperature studied). At $\text{pH} = 1$, the monoprotonated edta complex produced a very similar set of data to the nonprotonated complex. The similarity in the rate constants at 298 K and in the activation parameters for the edta, cdda, and phdta systems, including the activation

(23) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307.

(24) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1964**, *41*, 2553.

(25) Bloembergen, N. *J. Chem. Phys.* **1957**, *27*, 595.

(26) Newman, K. E.; Meyer, F. K.; Merbach, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 1470–1476.

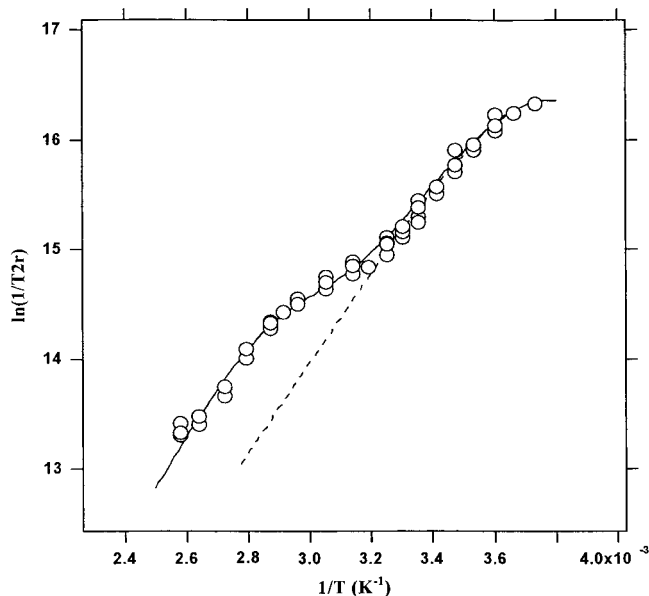


Figure 2. Plot of $\ln(1/T_{2r})$ versus $1/T$ for water exchange on $[\text{Fe}^{\text{III}}(\alpha\text{-eddap})\text{H}_2\text{O}]^-$ at ambient pressure. Exp. conditions: $[\text{Fe}^{\text{III}}(\alpha\text{-eddap})\text{H}_2\text{O}]^- = 20 \text{ mM}$; $I = 0.5 \text{ M}$ (NaClO_4); $\text{pH} = 4.3$. Dashed curve is fit for data at $T < 303 \text{ K}$ assuming single exchange process giving $\Delta H^\ddagger = 25.9 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -5 \text{ J K}^{-1} \text{ mol}^{-1}$, $A = 6.7 \times 10^9$, $k_{\text{ex}} = 1.1 \times 10^8 \text{ s}^{-1}$. Solid curve is fit for all temperatures assuming two exchange processes with $\Delta H^\ddagger = 25.9 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -5 \text{ J K}^{-1} \text{ mol}^{-1}$, $A = 6.7 \times 10^9$, $k_{\text{ex}} = 1.0 \times 10^8 \text{ s}^{-1}$ (parameters fixed) and $\Delta H^\ddagger = 33.0 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -29 \text{ J K}^{-1} \text{ mol}^{-1}$, $A = 6.8 \times 10^8$, $k_{\text{ex}} = 2.9 \times 10^5 \text{ s}^{-1}$. The results for the simultaneous fit are included in Table 1.

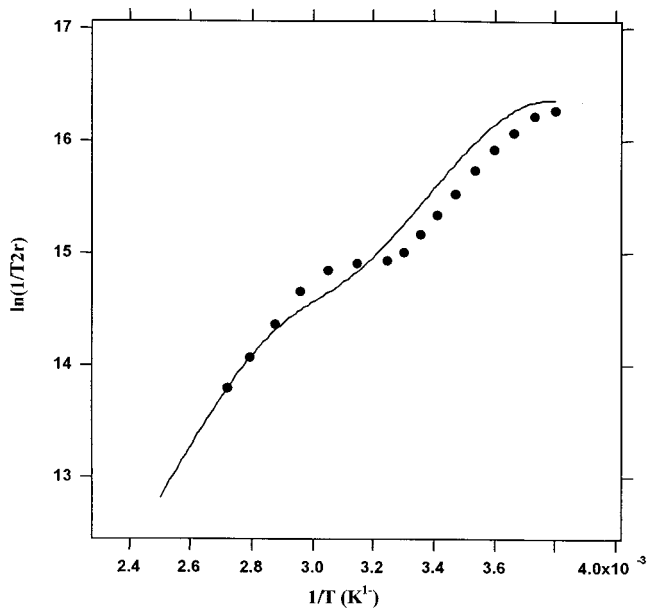


Figure 3. Plot of $\ln(1/T_{2r})$ versus $1/T$ for water exchange on $[\text{Fe}^{\text{III}}(\alpha\text{-eddap})\text{H}_2\text{O}]^-$ at ambient pressure in comparison to the data fit for $I = 0.5 \text{ M}$ (solid line). Experimental conditions: circles $[\text{Fe}^{\text{III}}(\alpha\text{-eddap})\text{H}_2\text{O}]^- = 20 \text{ mM}$; $I = 1.0 \text{ M}$ (NaClO_4); $\text{pH} = 4.3$. First exchange process: $\Delta H^\ddagger = 25.1 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -6.6 \text{ J K}^{-1} \text{ mol}^{-1}$, $A = 6.2 \times 10^9$, $k_{\text{ex}} = 1.1 \times 10^8 \text{ s}^{-1}$. Second exchange process: $\Delta H^\ddagger = 42.5 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 5.2 \text{ J K}^{-1} \text{ mol}^{-1}$, $A = 1.1 \times 10^9$, $k_{\text{ex}} = 4.1 \times 10^5 \text{ s}^{-1}$.

volumes, all of which are small positive values, strongly suggests the maintenance of the seven-coordinate geometry of the edtaH complex in solution and an I_d mechanism for the water-exchange process. There are two models which would meet this criterion. First, at low pH the protonated carboxylate group remains coordinated to retain a seven-coordinate complex

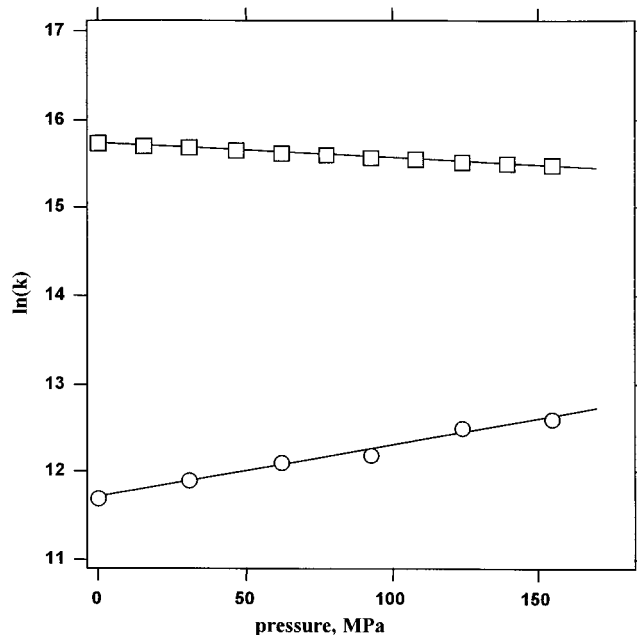


Figure 4. Plots of $\ln(k)$ versus pressure for water exchange on $[\text{Fe}^{\text{III}}(\text{cdta})\text{H}_2\text{O}]^-$ ($T = 283 \text{ K}$) and $[\text{Fe}^{\text{III}}(\text{edds})]^-$ ($T = 293 \text{ K}$). Experimental conditions: squares are for $[\text{Fe}^{\text{III}}(\text{cdta})\text{H}_2\text{O}]^- = 28.7 \text{ mM}$; $I = 0.5 \text{ M}$ (NaClO_4); $\text{pH} = 4.1$; giving $\Delta V^\ddagger = +4.0 \text{ cm}^3 \text{ mol}^{-1}$. Circles are for $[\text{Fe}^{\text{III}}(\text{edds})]^- = 20 \text{ mM}$; $I = 0.5 \text{ M}$ (NaClO_4); $\text{pH} = 4.4$ giving, $\Delta V^\ddagger = -14.4 \text{ cm}^3 \text{ mol}^{-1}$.

of the type $[\text{Fe}^{\text{III}}(\text{Hedta})\text{H}_2\text{O}]$. This contrasts with observations in the solid state where only an octahedral complex, in which the protonated carboxylate group is not coordinated, was isolated from acidic medium,^{2,7} though as noted above, Fe^{II} complexes are known where protonated carboxylate arms remain coordinated to the metal center. The second model is that the protonated arm becomes pendant, and the site is taken up by another solvent molecule in a species $[\text{Fe}^{\text{III}}(\text{Hedta})(\text{H}_2\text{O})_2]$; in this situation there are twice as many exchanging sites per metal center, and this doubling of P_m has been accounted for in the data in Table 1. The mechanistic conclusions, however, are the same, and an I_d process is indicated for this complex also. The very close similarity of the rate and activation parameters to those of $[\text{Fe}^{\text{III}}(\text{edta})\text{H}_2\text{O}]^-$ complex we believe indicates that the carboxylate remains coordinated.

The $[\text{Fe}^{\text{III}}(\text{eddap})\text{H}_2\text{O}]^-$ complexes form a very interesting group. The ^{17}O NMR measurements for the β -eddap complex, where two carboxylate arms are coordinated via six-membered rings, showed no significant line broadening. The structures adopted by all of the Fe^{III} -diaminetetracarboxylate systems seem finely balanced; the range of structures identified for the edta complex and referred to above, depending on the counterions and crystallization conditions such as pH, are testament to this. In contrast to the previous systems described, we propose that the elongated carboxylate arms can now fully encapsulate the Fe^{III} center to form an octahedral complex and exclude the coordination of a water molecule as a seventh ligand. The system possesses no exchangeable solvent moiety.

In contrast, solutions of $[\text{Fe}^{\text{III}}(\alpha\text{-eddap})\text{H}_2\text{O}]^-$ shows substantial line broadening. The temperature dependence of the reduced relaxation rate is complex and is shown in Figure 2 for $I = 0.5 \text{ M}$. While sections of the data could be analyzed separately, the dependence was also fully fitted on the assumption that two independent water-exchange reactions contribute to T_{2r} . Treatment of the data above 303 K ($1/T = 3.3 \times 10^{-3}$) as a single process, below 303 K as a single process and the

Table 2. Variation in Two-site Fitted Parameters for $[\text{Fe}^{\text{III}}(\alpha\text{-eddadp})\text{H}_2\text{O}]^-$ ^{17}O Line Broadening ($I = 1.0 \text{ M}$) as a Function of Proposed Isomeric Site Occupancy

occupancy of site 1, F	0.10	0.50	0.90
ΔH^\ddagger_1 (kJ mol $^{-1}$)	32.8	32.8	32.8
ΔS^\ddagger_1 (J K $^{-1}$ mol $^{-1}$)	40	27	22
A_1	6.0×10^{10}	1.2×10^{10}	6.7×10^9
k_{298} (s $^{-1}$)	1.5×10^{10}	2.7×10^8	1.6×10^9
ΔH^\ddagger_2 (kJ mol $^{-1}$)	32.5	32.5	32.5
ΔS^\ddagger_2 (J K $^{-1}$ mol $^{-1}$)	−20	−14	−1
A_2	1.5×10^9	2.7×10^9	1.4×10^{10}
k_{298} (s $^{-1}$)	1.4×10^9	2.1×10^6	1.0×10^7

full data set, which is the result of five replicate experiments, as two simultaneous kinetic processes, where the activation parameters and A terms for each process are simultaneously fitted, are all included in Table 1. The results are consistent, suggesting two processes with similar activation energies which differ in rate by around a factor of 100 throughout the temperature range. At an ionic strength of 1.0 M, the balance of the processes changes marginally (Figure 3), with the slower process enhanced compared with behavior at 0.5 M ionic strength.

The $[\text{Fe}^{\text{III}}(\alpha\text{-eddadp})\text{H}_2\text{O}]^-$ ^{17}O line broadening data were analyzed assuming a fixed value of fractional site occupancy, F , though it is quite possible that this balance changes throughout the temperature range; data in Figures 2, 3 and Table 1 all assume $F = 0.5$. Comparison of the results at $I = 0.5 \text{ M}$ and $I = 1.0 \text{ M}$ indicate that the individual rate constants and activation parameters are not significantly affected by ionic strength, although the balance of processes, driven presumably by a slight shift in relative concentration, is modified. Furthermore, the results in Table 2 show that the kinetic parameters are not qualitatively altered by the assumed value of F . Although the kinetic parameters are necessarily affected by the value assumed for F , the general observation is that over a wide range of F , process 1 is faster, the activation enthalpies for both processes are essentially identical and process 1 has a more positive activation entropy. Analysis of high-pressure measurements at 294 K assumed, based on the relative values of k_1 and k_2 , that path 1 is the dominant kinetic route for exchange, so that ΔV^\ddagger is associated with that reaction. The activation volume of $+3.0 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$ matches those in the other complexes, suggesting that an I_d mechanism is maintained for exchange in the $\alpha\text{-eddadp}$ system.

We can speculate about the possible forms of the $[\text{Fe}^{\text{III}}(\alpha\text{-eddadp})\text{H}_2\text{O}]^-$ complex that give rise to this line broadening behavior. For this ligand, two of the carboxylate sidearms have methyl substituents, and there exists the possibility of a range of geometric isomers. In a pentagonal bipyramidal geometry, both the methylated sidearms of the $\alpha\text{-eddadp}^{4-}$ could occupy “equatorial” positions in the seven coordinate complex, both occupy axial positions, or one links to an axial and one to an equatorial coordination site. In a capped trigonal prismatic structure, two isomeric possibilities occur, with the methylated sidearms sharing one plane of the trigonal prism or coordinated in a “trans” arrangement to opposite corners of the structure. Our observation of two simultaneously exchanging sites and our report⁴ that the *cdta* complex, like many others, is closest to a trigonal prismatic structure, might support this as the best description of the solution geometry for the $\alpha\text{-eddadp}$ complex.

When the nitrogen–nitrogen backbone of the chelate is elongated to give a six-membered ring as in the case of $[\text{Fe}^{\text{III}}(1,3\text{-pdta})\text{H}_2\text{O}]^-$, only a slight line broadening compared to the pure solvent is observed (3 to 35 Hz). Errors on the

relaxation parameters were large and a satisfactory fit could not be achieved. Nevertheless, the observations suggest that a mechanism for solvent exchange is available. It is possible that a small proportion of the complex in solution exists as a seven-coordinate species with one exchangeable water molecule.

The line width measurements on the $[\text{Fe}^{\text{III}}(\text{edds})\text{H}_2\text{O}]^-$ complex showed a temperature dependence in which at temperatures above 310 K the data were not reproducible. Restricting the analysis to points below 310 K leads to the data reported in Table 1. A number of features are notable. While still labile for an iron(III) complex, the rate of exchange is significantly slower at 298 K than the other complexes in the series. The activation enthalpy and entropy are more positive; the activation volume is significantly negative ($-14.4 \text{ cm}^3 \text{ mol}^{-1}$; data are plotted in Figure 4). As outlined below, we are of the opinion that the ligand may allow the formation of an octahedral monoqua complex and that the nature of the ligand creates an option for an associative exchange mechanism.

The rate constants reported for water exchange on the Fe^{III} chelates in Table 1 are all between 3 and 6 orders of magnitude higher than for water exchange on $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$. This acceleration can partially be ascribed to the labilizing influence of the polyaminecarboxylate chelate, and partially to the change in coordination number from 6 to 7. This acceleration is in most of the studied cases accompanied by small positive volumes of activation, which in comparison to the data for the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ system, suggests a changeover to a dissociatively activated reaction mode for the enhanced water exchange on the chelated complexes. By way of comparison, the deprotonation of a coordinated water molecule on $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ results in an acceleration of the water-exchange rate constant of ca. 10^3 , which is also accompanied by a changeover to a more dissociative mechanism (Table 1). A changeover to a seven-coordinate complex will in a similar way to the introduction of a hydroxo ligand induce a changeover to a more dissociative mechanism since we are then dealing with a 19 electron species. The lowest acceleration on introducing a chelate was observed for the *edds* system, and here the volume of activation suggests the operation of a limiting associative mechanism, since the value is very close to that predicted for such a mechanism.²⁷

The diamine backbone of the chelate (*edta*,⁴⁻ *cdta*⁴⁻, and *phdta*⁴⁻) seems to have little influence on the water-exchange rate constant and mechanism, though if the encapsulating ligand is expanded slightly by extending the NN link, as in the *pdta* system, the labile seven-coordinate exchange seems to be “turned down” as observed by the marginal line broadening, perhaps as a result of substantial changeover to a six-coordinate complex, leading to a reduction in P_m and minimal excess broadening. If two of the carboxylate arms are extended as in the *edds* system, exchange is “turned off” completely; we have speculated that this is due to adoption of octahedral geometry around the Fe(III) ion.

Now we turn to the influence of substituents on and extension of the carboxylate arms. The data for the $\alpha\text{-eddadp}$ complex in the lower temperature range, is once again in very close agreement with the data for the *edta*, *cdta*, and *phdta* complexes, from which it follows that the methyl substituent on the carboxylate arm has no significant effect on the water-exchange mechanism.

In the case of the *edds* system, the water-exchange reaction is much slower than for the other complexes and the activation volume supports the operation of an associative mechanism.

(27) Kowall, T.; Caravan, P.; Bourgeois, H.; Helm, L.; Rotzinger, F. P.; Merbach, A. E. *J. Am. Chem. Soc.* **1998**, *120*, 6569.

We propose that this must be due to the formation of a six-coordinate complex in which edds⁴⁻ is a pentadentate ligand and water occupies the sixth coordination site. It then seems reasonable that such a six-coordinate complex follows an associative mode of water exchange as observed for instance for [Fe(H₂O)₆]³⁺. The volume of activation is more negative than the data for the hexaaqua complex, pointing to a limiting A mechanism.²⁷ This may result from the ability of the six-coordinate ground state to form a true seven-coordinate intermediate due to the particular structure of the edds chelate. In comparison to edta,⁴⁻ this chelate is expected to be less sterically stressed due to the presence of two succinic groups.

For most of the systems studied, the results are in agreement with a dissociatively activated water-exchange mechanism for the seven-coordinate complexes. The absolute magnitudes of the volumes of activation are small and would fit most closely with an I_d mechanism. However, little is known about ground-state labilization in such seven-coordinate complexes, with the result that observed volumes of activation, although small, could also be in line with a limiting D mechanism. Ground-state labilization involving the lengthening of the Fe–OH₂ bond, could lead to a significant increase in the partial molar volume. In this situation, the extension of the Fe–O bond length to reach a limiting D transition state might be accompanied by a volume increase of only a few cm³ mol⁻¹.

Conclusions

The results of this study have demonstrated the sensitivity of the water-exchange process for complexes of the type [Fe^{III}(L)(H₂O)_x]ⁿ⁻ on the nature of the spectator chelate. Not only does this control the rate of the water-exchange process, but also the nature of the underlying mechanism. The work has also demonstrated the ability of ¹⁷O NMR measurements, especially as a function of high pressure, to add to our understanding of fundamental processes related to the substitution behavior of polyaminecarboxylate complexes in solution. Although many structures of such complexes have been resolved in the solid state, little is known about their nature, reactivity, and substitution mechanisms in solution. This study demonstrates the way in which such systems can be studied and their behavior can be resolved.

Acknowledgment. The authors gratefully acknowledge financial support from the Fonds der Chemischen Industrie, the Max-Buchner-Forschungstiftung, and DAAD (visiting fellowship to PAT).

Supporting Information Available: Tables with water-exchange rate constants as a function of temperature and pressure for the investigated complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC001304P