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Water Exchange of the (*o*-Phenylenediamine-*N,N,N',N'*-tetraacetato)ferrate(III) Complex in Aqueous Solution As Studied by Variable-Temperature, -Pressure, and -Frequency Oxygen-17 NMR Techniques

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The crystal structure of potassium aqua(*o*-phenylenediamine-*N,N,N',N'*-tetraacetato)ferrate(III) dihydrate, $(K[Fe(OH_2)(phdta)] \cdot 2H_2O)$, has been determined by X-ray crystallography. The central iron(III) ion is seven-coordinate, with one water molecule being hydrated. Water-exchange rates of the iron(III) complex with $phdta^{4-}$ in aqueous solution have been studied as a function of temperature and pressure by the oxygen-17 NMR line-broadening method. Activation parameters for water exchange have been determined as follows: $k(25^\circ C) = (1.2 \pm 0.2) \times 10^7 s^{-1}$, $\Delta H^\ddagger = 26 \pm 3 kJ mol^{-1}$, $\Delta S^\ddagger = -22 \pm 9 J K^{-1} mol^{-1}$, and $\Delta V^\ddagger = 4.6 \pm 0.2 cm^3 mol^{-1}$. The positive activation volume indicates that the water exchange proceeds via a dissociative interchange mechanism.

Introduction

Valuable results have been accumulated from a number of studies on the solvent exchange at solvated metal ions by the high-pressure NMR method. For example, the study of water exchange on divalent metal ions across the first-row transition-metal series has demonstrated the changeover from associative interchange I_a to dissociative interchange I_d mechanisms along the series.^{1,2} This changeover has been rationalized in terms of changes in ionic radius and of filling of d orbitals. The solvent exchange of the d^5 manganese(II) ion is known to proceed via an associative interchange mechanism in water,¹ methanol,³ and acetonitrile.⁴ Recently, however, positive volumes of activation have been reported for solvent exchange on the manganese(II) ion in *N,N*-dimethylformamide (DMF)⁵ and acetic acid.⁶ Such a positive activation volume has been interpreted in terms of the bulkiness of coordinated solvent molecules. Furthermore, the activation volume for the solvent exchange of manganese(II) acetate in acetic acid has been determined to be $+6.7 \pm 0.6 cm^3 mol^{-1}$,⁶ which is more positive than that ($+0.4 \pm 0.7 cm^3 mol^{-1}$) for the hexakis(solvent)manganese(II) ion in acetic acid. It has been claimed that the coordinated solvent molecules are labilized by electron donation from bound ligands such as CH_3COO^- to the metal ion and that the activation mode of the reaction becomes less associative.

On the other hand, the effect of the bulkiness of coordinated solvent molecules and the labilization effect due to the bound ligand have already been confirmed to be operative in the complexation of the d^5 iron(III) ion in several solvents.⁷⁻⁹ One of the purposes of this work is to demonstrate the bound multidentate ligand effect on solvent exchange of iron(III) complexes on the basis of activation volumes. We selected PhDTA (*o*-phenylenediamine-*N,N,N',N'*-tetraacetic acid, H_4phdta)¹⁰ as a multidentate ligand. We have studied the species of Fe(III)-PhDTA in aqueous solution and the crystal structure of the Fe(III)-PhDTA complex prior to kinetic investigations.

Experimental Section

Sample Preparation. Sodium and potassium salts of the Fe(III)-PhDTA complex were prepared by mixing the aqueous solutions of iron(III) trichloride and PhDTA and by adjusting the pH¹¹ to 4.5 with

Table I. Crystallographic Data for $K[Fe(OH_2)(phdta)] \cdot 2H_2O$

formula	$C_{14}H_{18}N_2O_{11}KFe$	Z	2
color	yellowish brown	cryst dimens/	$0.20 \times 0.20 \times$
fw	485.26	mm	0.15
space group	monoclinic, <i>P2/c</i>	radiation	Mo $K\alpha$ (graphite-monochrom, $\lambda = 0.71073 \text{ \AA}$)
a/ \AA	8.6379 (15)	abs coeff/ cm^{-1}	10.291
b/ \AA	13.0992 (15)	$\Delta\rho_{max}/e \text{ \AA}^{-3}$	0.77
c/ \AA	8.1842 (8)	R	0.0611
β/deg	96.428 (9)	R_w	0.0567
cell vol/ \AA^3	920.21 (19)	temp/ $^\circ C$	20
$d_{obs}/g \text{ cm}^{-3}$	1.728		
$d_{cal}/g \text{ cm}^{-3}$	1.743		
R_{int}	0.086		

*Uncertainties in the last significant digit are shown in parentheses.

sodium or potassium hydroxide. Anal. Found (calcd) for $Na[Fe(OH_2)(phdta)] \cdot 2H_2O$: N, 5.97 (6.03); C, 35.84 (35.83); H, 3.87 (3.91). Calcd (found) for $K[Fe(OH_2)(phdta)] \cdot 2H_2O$: N, 5.77 (5.83); C, 34.65 (34.65); H, 3.74 (3.66); Fe, 11.54 (11.51). The sodium salt was a very thin crystal, while the potassium salt was suitable in size for an X-ray structural measurement.

Solutions for the potentiometric determination of the pK_a 's of the Fe(III)-PhDTA complex were prepared by mixing solutions of PhDTA and iron(III) perchlorate under nitrogen atmosphere. Sodium perchlorate used for adjusting the ionic strength was recrystallized twice for purification.

Aqueous solutions of the Fe(III)-PhDTA complex for the NMR samples were prepared in the presence of excess PhDTA at $I = 1.0 mol kg^{-1}$ ($NaClO_4$) at a pH of ca. 4.2. The solvent water was enriched by addition of 20% ^{17}O -enriched water (Merck). The solution containing the same components as the NMR sample solution except for the iron(III) ion served as an NMR reference solution. The solution for variable-temperature NMR measurement was degassed on the vacuum line by the freeze-thaw technique and then sealed under vacuum. Transfer of the sample solution into a high-pressure NMR tube (o.d. 7 mm) was performed under nitrogen gas in a drybox.^{6,12} The compositions of the sample solutions used for the NMR experiments are summarized in Table SI (supplementary material).

Measurements. The structure of $K[Fe(OH_2)(phdta)] \cdot 2H_2O$ was solved by the Monte Carlo direct method¹³ with the aid of MULTAN78¹⁴ on a Rigaku AFC-5R diffractometer, utilizing 1959 unique reflections ($I > 3\sigma(I)$) according to a procedure similar to that described elsewhere.¹⁵ The cell dimensions only were refined with Cu $K\alpha$ radiation ($\lambda = 1.5417 \text{ \AA}$, monochromated from graphite, 20 reflections for $29.25^\circ < 2\theta < 35.62^\circ$). In the full-matrix least-squares refinements, all non-H atoms were refined independently with anisotropic thermal parameters. Hydrogen atoms were refined with isotropic temperature factors equivalent to those for bonded atoms, but attempts to locate all H atoms were unsuccessful. Details of the crystal data, experimental conditions, and a summary of refinement details are given in Table I.

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- pH = $-\log [H^+]$, where $[H^+]/mol \text{ dm}^{-3}$ is the hydrogen ion concentration.

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Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters ($B_{eq}/\text{\AA}^2$) for $K[\text{Fe}(\text{OH}_2)(\text{phdta})]\cdot 2\text{H}_2\text{O}^a$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Fe1	0.50000 (0)	0.12574 (6)	0.25000 (0)	1.52 (3)
K2	1.00000 (0)	0.05157 (10)	0.75000 (0)	2.30 (4)
N3	0.33930 (34)	0.26954 (23)	0.25716 (37)	1.49 (7)
O4	0.50000 (0)	-0.03129 (32)	0.25000 (0)	3.86 (14)
O5	0.28948 (32)	0.08082 (22)	0.33035 (37)	2.38 (7)
O6	0.08535 (32)	0.11707 (25)	0.46256 (35)	2.58 (8)
O7	0.42004 (32)	0.14756 (20)	0.01504 (32)	2.09 (7)
O8	0.24058 (37)	0.21088 (25)	-0.17322 (37)	2.95 (8)
O9	1.00000 (0)	0.35556 (53)	0.75000 (0)	5.50 (21)
C10	0.42233 (40)	0.36582 (29)	0.25919 (44)	1.66 (8)
C11	0.34312 (53)	0.45872 (37)	0.27105 (62)	2.77 (11)
C12	0.42204 (59)	0.54985 (35)	0.26162 (65)	3.18 (12)
C13	0.25490 (47)	0.25395 (31)	0.40330 (53)	2.00 (9)
C14	0.20460 (41)	0.14291 (29)	0.40132 (44)	1.78 (9)
C15	0.22867 (44)	0.26170 (32)	0.10411 (50)	1.92 (9)
C16	0.29964 (44)	0.20389 (31)	-0.03102 (49)	1.91 (9)
O17	1.01433 (175)	0.46574 (75)	0.46008 (194)	9.14 (51)

^a $B_{eq} = \frac{8}{3}\pi^2 \sum_i U_{ij} a_i^* a_j^* a_i^* a_j^*$. Uncertainties in the last significant digit are shown in parentheses.

The acid dissociation constants of Fe(III)-PhDTA were determined by potentiometry using a pH meter (Metrohm 605) with a glass electrode (Metrohm EA 109T) and a calomel electrode filled with a saturated NaCl solution (Metrohm AG 9100). The ionic strength was maintained at $I = 1.00 \text{ mol dm}^{-3}$ (NaClO_4), and the temperature was kept at $25.0 \pm 0.1 \text{ }^\circ\text{C}$ during titration. The liquid-junction potential was corrected for.

Variable-temperature Fourier-transform ^{17}O NMR spectra were obtained with JEOL JNM-FX100, JNM-GX270, and JNM-GX400 instruments operating at 13.50, 36.63, and 54.21 MHz, respectively, with an external deuterium lock. A 5- or 8-mm-o.d. NMR sample tube was immersed in a 10-mm-o.d. NMR tube containing deuterated DMF ($\text{DMF-}d_7$) as a lock solvent. Sample temperature was measured by using a thermistor (SPD-02-10A, Takara Thermistor Co.) placed in a 5-mm-o.d. NMR tube containing the solvent alone instead of a sample. The uncertainty in temperature was estimated to be $0.5 \text{ }^\circ\text{C}$.

Variable-pressure FT oxygen-17 NMR spectra were recorded on JEOL-GX270 and JEOL-FX100 spectrometers equipped with high-pressure NMR probes that were constructed in our laboratory.^{6,12}

Analysis of NMR Line-Broadening Data. The exchange rate of solvent molecules between the bulk and the coordination site of a paramagnetic metal ion is estimated from the transverse relaxation rate of the bulk solvent nuclei. The solvent ^{17}O NMR line broadening, $(T_{2p}P_M)^{-1}$, due to a paramagnetic metal ion is expressed as $(T_{2p}P_M)^{-1} = \pi(\Delta\nu_{\text{obsd}} - \Delta\nu_{\text{solv}})P_M^{-1}$, where $\Delta\nu_{\text{obsd}}$ and $\Delta\nu_{\text{solv}}$ are the half-height widths of the ^{17}O NMR spectra of solvent in the bulk in the presence and absence, respectively, of the iron(III) ion. P_M is the ratio of the number of solvent molecules bound to iron(III) to that of solvent molecules in the bulk. Since $P_M \ll 1$ under the present experimental conditions, $(T_{2p}P_M)^{-1}$ is given by the modified Swift-Connick equation¹⁶⁻¹⁸

$$(T_{2p}P_M)^{-1} = \frac{1}{\tau_M} \frac{T_{2M}^{-2} + (T_{2M}\tau_M)^{-1} + (\Delta\omega_M)^2}{(T_{2M}^{-1} + \tau_M^{-1})^2 + (\Delta\omega_M)^2} + T_{2os}^{-1} \quad (1)$$

where τ_M and T_{2M} are the mean lifetime and the transverse relaxation time of the oxygen-17 nucleus of the solvent molecule in the inner sphere of iron(III), $\Delta\omega_M$ is the difference in resonance frequency between oxygen-17 nuclei of the solvent in the inner sphere and in the bulk, and T_{2os}^{-1} is the relaxation term due to the interaction in the outer sphere of the Fe(III) complex. The temperature dependence of $\Delta\omega_M$ is given by $\Delta\omega_M = -C_{\omega}/T$.^{19,20} T_{2M} is assumed to have a simple temperature dependence given by $T_{2M}^{-1} = (C_M/T) \exp(E_M/RT)$. The solvent-exchange rate constant k is equal to $\tau_M^{-1} = (k_B T/h) \exp(-\Delta H^*/RT + \Delta S^*/R)$.

Results and Discussion

Crystal Structure of $K[\text{Fe}(\text{OH}_2)(\text{phdta})]\cdot 2\text{H}_2\text{O}$. The atomic coordinates and isotropic thermal parameters are given in Table II, selected bond lengths and angles are found in Table III, and an ORTEP²¹ view of the $[\text{Fe}(\text{OH}_2)(\text{phdta})]^-$ moiety is shown in

Table III. Bond Lengths (\AA) and Angles (deg) for $K[\text{Fe}(\text{OH}_2)(\text{phdta})]\cdot 2\text{H}_2\text{O}^a$

(i) Bond Lengths			
Fe1-N3	2.344 (3)	Fe1-O7	1.990 (3)
Fe1-O4	2.057 (4)	Fe1-O5	2.087 (3)
(ii) Bond Angles			
N3-Fe1-N3'	73.08 (15)	N3-Fe1-O5	71.30 (11)
N3-Fe1-O5'	140.70 (11)	N3-Fe1-O7	76.49 (11)
N3-Fe1-O7'	90.16 (11)	N3-Fe1-O4'	143.46 (7)
O5-Fe1-O5'	147.24 (16)	O5-Fe1-O7	97.17 (11)
O5-Fe1-O7'	87.49 (11)	O4-Fe1-O5'	73.62 (8)
O7-Fe1-O7'	163.48 (16)	O7-Fe1-O4	98.26 (8)
C10-N3-C13	113.44 (30)	C10-N3-C15	109.82 (29)
C13-N3-C15	109.95 (29)	C10-N3-Fe1	113.93 (21)

^a The prime indicates the symmetry code $1-x, y, 1/2-z$. Uncertainties in the last significant digit are shown in parentheses.

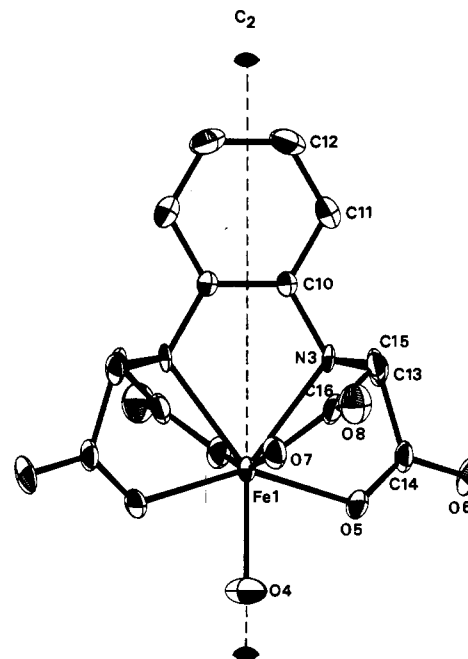


Figure 1. ORTEP view of the $[\text{Fe}(\text{OH}_2)(\text{phdta})]^-$ anion (H atom excluded).

Figure 1. Other crystallographic data are summarized in Tables SII-SIV.

The $[\text{Fe}(\text{OH}_2)(\text{phdta})]^-$ ion is hexadentate, seven-coordinate, and monohydrated and is stereochemically akin to the anionic iron(III) chelates of EDTA (ethylenediamine- N,N,N',N' -tetraacetic acid, H_4edta)²²⁻²⁵ and of CyDTA (cyclohexanediamine- N,N,N',N' -tetraacetic acid, H_4cydta)²⁶ and also to the hepta-coordination moiety of the Mn(II)-PhDTA complex.²⁷ Though a pseudo- C_2 axis has usually been observed in the aforementioned chelates, the present complex alone has a 2-fold axis passing through Fe and O of the hydrated water molecule. The high symmetry of the Fe(III)-PhDTA complex should reflect the structure of PhDTA, wherein the two nitrogen atoms and the phenylene group are on the same plane.

The present PhDTA complex has a roughly pentagonal-bipyramidal shape, as has been observed in most Fe(III)-EDTA

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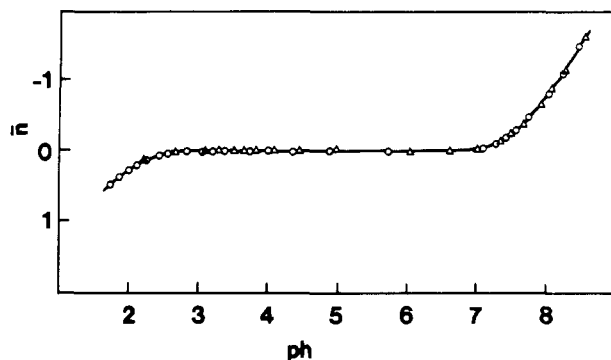


Figure 2. pH dependence of the averaged protonation number (\bar{n}) of Fe(III)-PhDTA. $C_{\text{Fe(III)-PhDTA}}$: $5.41 \times 10^{-3} \text{ mol dm}^{-3}$ (O); $2.71 \times 10^{-3} \text{ mol dm}^{-3}$ (Δ).

complexes. The carboxylate O5, O5' and the water O4 constitute a pentagonal equatorial plane together with the two nitrogen atoms N3 and N3', and then O7 and O7' occupy the apical positions (see Figure 1). The former five atoms are approximately in the plane, because calculation results in 362.92° as the sum of the five angles that are formed around the central metal ion Fe1 in the pentagon. O7-Fe1 is not so perpendicular to the plane, but leans slightly toward N3. The sum of the five angles of the chelate ring Fe1-N3-C10-C10'-N3'-Fe1 is 539.5° , which is nearly equal to 540° valid for a planar pentagon.

We shall compare seven-coordinated and monohydrated Fe(III) complexes with related amino polycarboxylates L (L = PhDTA, EDTA, CyDTA). Comparison of Fe-N bond lengths reveals that the PhDTA chelate has the longest distance (2.344 Å) among the Fe(III)-L complexes (2.325 Å for EDTA²² and 2.290 Å for CyDTA²⁶). This fact can be interpreted in terms of the basicity of the nitrogen atoms in L. The phenylene group in PhDTA is electron-withdrawing, while the ethylene group in EDTA and the cyclohexane group in CyDTA are electron-donating. Logarithmic values of the protonation constant for the tetravalent anions of PhDTA, EDTA, and CyDTA, $\log(K_{\text{H}}/M^{-1})$, are 6.41,¹⁰ 8.85,²⁸ and 9.30,²⁸ respectively. Thus, the stronger the basicity of the nitrogen atoms, the shorter the Fe-N bond length. On the other hand, such a simple relation is not found in bond lengths between the central metal ion and the water oxygen atom, Fe-O_w.²⁹ However, the mean bond length of the five Fe-O bonds changes monotonically with $\log K_{\text{H}}$ values (Fe-O_{av}/Å = 2.042 for the K salt of Fe(III)-PhDTA, 2.056 for the Li salt of Fe(III)-EDTA,²² and 2.062 for the Ca salt of Fe(III)-CyDTA²⁶). Interestingly, calculation of the average bond length Fe-X_{av} for the seven Fe-X (X = both O and N) bonds leads to a finding that it is almost constant, i.e. ca. 2.13 Å, irrespective of different ligands and counterions.³⁰ This constancy may correspond to the second bond length variation rule proposed by Gutmann.³¹ All the Fe-O_w bonds in the Fe(III)-L complexes are longer than that (1.990 Å) in the hexaquaairon(III) ion in aqueous solution as determined by an EXAFS method.³²

Another interesting feature is obtained by comparing the bond lengths of the two types of carboxylate groups which are defined by the 2-fold axis.²² The out-of-plane Fe-O7 bond is shorter by

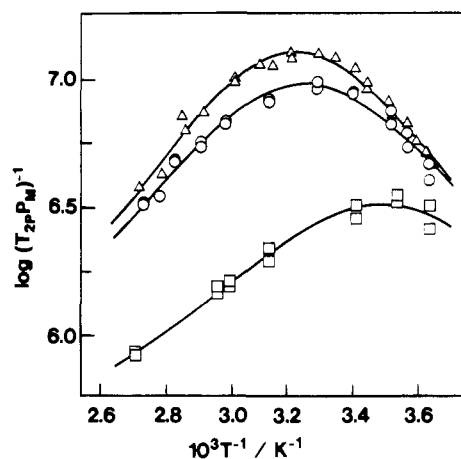


Figure 3. Variation of the solvent water oxygen-17 relaxation rates (T_{2pP_M})⁻¹ with temperature for Fe(III)-PhDTA in aqueous solution: Δ , 54.21 MHz ¹⁷O; O, 36.63 MHz ¹⁷O; \square , 13.50 MHz ¹⁷O. $C_{\text{Fe(III)-PhDTA}}$ = 7.88×10^{-3} and $9.67 \times 10^{-3} \text{ mol kg}^{-1}$; pH = 4.5.

0.097 Å than the in-plane Fe-O5 bond, but the O7-C16 bond is longer by 0.09 Å than O5-C14 (see Figure 1). The nonchelating O8-C16 bond is again shorter by 0.021 Å than the corresponding O6-C14 bond.

Proton Dissociation Constants of the Fe(III)-PhDTA Complex. pH dependence of the average protonation number (\bar{n}) of Fe(III)-PhDTA at two different concentrations is shown in Figure 2. The coincidence of \bar{n} plots at the two concentrations indicates the absence of a polymerization reaction under the present conditions. Proton dissociation constants were determined to be $pK_1 = 1.05 \pm 0.05$ and $pK_2 = 8.17 \pm 0.02$ at 25.0 °C and $I = 1.00 \text{ mol dm}^{-3}$ (NaClO₄).

Judging from the K_1 value, the Fe(III)-PhDTA complex should have no free acetate group dissociated from the central metal ion in the neutral pH range, because the proton dissociation constant of the nonchelating acetic acid group is usually of the order of magnitude of $10^{-3} \text{ dm}^3 \text{ mol}^{-1}$.¹⁰ Therefore, PhDTA should coordinate to the iron(III) ion as a hexadentate ligand, as shown by the crystal structure in Figure 1. The second proton dissociation is attributable to the hydrolysis of a coordinated water. Therefore, K_1 and K_2 are defined as follows: $K_1 = [\text{Fe}(\text{OH}_2)(\text{phdta})^-][\text{H}^+]/[\text{Fe}(\text{OH}_2)(\text{Hphdta})]$ and $K_2 = [\text{Fe}(\text{OH})(\text{phdta})^{2-}][\text{H}^+]/[\text{Fe}(\text{OH}_2)(\text{phdta})^-]$. The Fe(III)-PhDTA complex exists exclusively as the $[\text{Fe}(\text{OH}_2)(\text{phdta})]^-$ anion over the pH range from 3.5 to 5.5.

Water Exchange on the Fe(III)-PhDTA Complex. We recorded NMR spectra of sample solutions with three different concentrations of the Fe(III)-PhDTA complex ($C_{\text{Fe(III)-PhDTA}}$), and T_{2P}^{-1} was proportional to $C_{\text{Fe(III)-PhDTA}}$. All data for line widths ($\Delta\nu_{\text{obsd}} - \Delta\nu_{\text{soln}}$) are given in Table SV (supplementary material). The temperature dependence of the line width (T_{2pP_M})⁻¹ normalized by P_M for Fe(III)-PhDTA is shown in Figure 3. The results clearly show the relation $\tau_M^{-1} \gg T_{2os}^{-1}$, which is confirmed by the T_{2os}^{-1} term for Fe(H₂O)₆³⁺.³³ Thus, the NMR and kinetic parameters were estimated by use of the nonlinear least-squares method applied to eq 1 without the T_{2os}^{-1} term. At the first step, the parameters were computed from all data for three different frequencies, ω , by keeping the linear relation in frequency: $C_\omega = C'_\omega \omega$. Then by fixing the values of ΔH^\ddagger and ΔS^\ddagger (24.1 kJ mol⁻¹ and -27.5 J K⁻¹ mol⁻¹, respectively) obtained above, we determined the values of C_M and E_M to be $2.6 \times 10^7 \text{ K s}^{-1}$ and 6.6 kJ mol⁻¹, respectively, from the fitting of the data at 13.50 MHz, because T_{2M}^{-1} contributes significantly to T_{2P}^{-1} at 13.50 MHz. Finally, ΔH^\ddagger , ΔS^\ddagger , and C_ω for each frequency were evaluated by fixing the obtained values of C_M and E_M .³⁴ Values of $\Delta H^\ddagger/\text{kJ mol}^{-1}$,

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(29) Fe-O_w bond lengths/Å: 2.057 for the K salt of Fe(III)-PhDTA; 2.090 for the Ca salt of Fe(III)-CyDTA;²⁶ 2.107 for the Li salt,²⁴ 2.122 for the Na salt,²⁵ 2.111 for the K salt,^{24b} 2.106 for the Rb salt,²² 2.109 for the Ag and Tl salts,^{24a} 2.09 for the guanidinium salt,²³ 2.132 for the ethylenediammonium (EDA) salt,^{24b} and 2.107 for the tetraethylammonium (TEA) salt^{24b} of Fe(III)-EDTA complexes.

(30) Average Fe-X_{av} bond lengths/Å: 2.128 for the K salt of Fe(III)-PhDTA; 2.127 for the Ca salt of Fe(III)-CyDTA;²⁶ 2.133 for the Li salt,²² 2.199 for the Na salt,²⁵ 2.137 for the K salt,^{24a} 2.126 for the Rb salt,²² 2.133 for the Ag salt,^{24a} 2.127 for the Tl salt,^{24a} 2.14 for the guanidinium salt,²³ 2.136 for the EDA salt,^{24b} and 2.127 for the TEA salt^{24b} of Fe(III)-EDTA complexes.

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(34) In the case of the present system, in the high-temperature range, T_{2P}^{-1} at the higher frequencies 36.63 and 54.21 MHz is predominated by the term $(\Delta\omega_M)^2\tau_M$ and the T_{2M}^{-1} term contributes to T_{2P}^{-1} only at the lower frequency 13.50 MHz.

Table IV. Kinetic Parameters for Water Exchange on Fe(III) Complexes

	$k(25\text{ }^\circ\text{C})/$ s^{-1}	$\Delta H^\ddagger/$ kJ mol^{-1}	$\Delta S^\ddagger/$ J K^{-1} mol^{-1}	$\Delta V^\ddagger/$ $\text{cm}^3 \text{mol}^{-1}$	ref
[Fe(OH ₂)- (phdta)] ⁻	1.2×10^7	26 ± 3	-22 ± 9	4.6 ± 0.2	this work
[Fe(OH ₂) ₆] ³⁺	1.6×10^2	64.0 ± 2.5	12.1 ± 6.7	-5.4 ± 0.4	33, 36
[Fe(OH ₂) ₅ - (OH)] ²⁺	1.4×10^5	42.4 ± 1.5	5.3 ± 4.0	7.0 ± 0.3	33, 36

$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$, and $C_w/K \text{rad s}^{-1}$ were determined to be 25 ± 3 , -30 ± 8 , and $(1.8 \pm 0.1) \times 10^9$ for 13.50 MHz, 24 ± 1 , -29 ± 4 , and $(5.9 \pm 0.2) \times 10^9$ for 36.63 MHz, and 27 ± 1 , -16 ± 3 , and $(8.2 \pm 0.2) \times 10^9$ for 54.21 MHz, respectively. Thus, the C_w values obtained are nearly proportional to the observed NMR frequency: the C_w values are 22, 25, and 24 at 13.50, 36.63, and 54.21 MHz, respectively. The solid curves in Figure 3 were depicted by use of the NMR and kinetic parameters obtained above.³⁵ Taking into account experimental conditions and errors, we think it reasonable to accept $\Delta H^\ddagger = 26 \pm 3 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -22 \pm 9 \text{ J K}^{-1} \text{mol}^{-1}$ for the water exchange of the Fe(III)-PhDTA complex (Table IV).

As apparent from Figure 3, the chemical exchange region is observed below 5 °C by both 54.21- and 36.63-MHz ¹⁷O NMR spectroscopy: $(T_{2P}P_M)^{-1} = \tau_M^{-1}$. Then we recorded the NMR spectra of reference and sample solutions at 1.2 °C at various pressures up to 250 MPa. $\log(\pi\Delta\nu_{\text{solv}})$ for water and $\log k_p$ for the water-exchange rate are plotted against pressure P in Figure 4. The volume of activation is given by $\Delta V^\ddagger = -RT(\partial \ln k_p/\partial P)_T$. The plot of $\log k_p$ vs P is linear, and thus we obtained the activation volume of $4.6 \pm 0.2 \text{ cm}^3 \text{mol}^{-1}$ from the slope.

Water exchange of the Fe(III)-PhDTA complex is much faster than that on the hexaaquairon(III) ion (see Table IV). This fact comes mainly from the difference in activation enthalpy. The value of ΔV^\ddagger for water exchange on the hexaaquairon(III) ion is negative, while that for the Fe(III)-PhDTA complex is positive: solvent exchange proceeds via an associative interchange mechanism for the former, while a dissociative interchange mechanism is operative for the latter. The same effect is seen in solvent exchange on the pentaquahydroxoiron(III) ion compared with the hexaaquairon(III) ion.³⁶ By the electron donation from ligands such as phdta⁴⁻ or OH⁻, the electron density of the iron(III) atom should increase and the bond of a coordinated water molecules may be weakened (the bound ligand effect). In fact, as shown above, the Fe-O_w bond length of the Fe(III)-PhDTA crystal is longer than that of the hexaaquairon(III) ion. As a result, the water exchange of the Fe(III) complex with an electron-donating ligand proceeds much faster and more dissociatively than that of the hexaaquairon(III) ion.^{37,38} On the other hand,

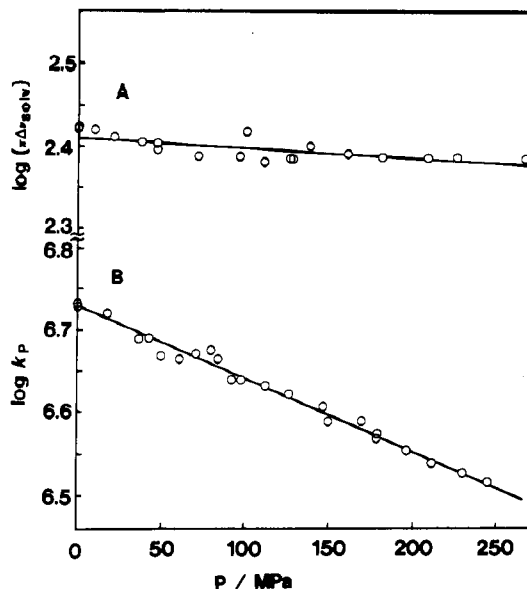


Figure 4. Pressure dependence of the solvent water oxygen-17 relaxation rates at 1.2 °C and $I = 1.0 \text{ mol kg}^{-1}$ (NaClO_4): (A) pressure dependence of $\log(\pi\Delta\nu_{\text{solv}})$ for water; (B) pressure dependence of $\log k_p$ for water exchange of the Fe(III)-PhDTA complex ($C_{\text{Fe(III)-PhDTA}} = 1.14 \times 10^{-2} \text{ mol kg}^{-1}$).

negative entropy of activation indicates that, during the activation process with a dissociative interchange mode, two interchanging water molecules may interact with the oxygen atoms of the carboxylate groups of the coordinated PhDTA via hydrogen bonding. Similar hydrogen-bonding effects have been demonstrated in the enhancement of rates for the anation of the $\text{Ru}^{\text{III}}(\text{OH}_2)(\text{edta})^-$ and $\text{Cr}^{\text{III}}(\text{OH}_2)(\text{edta})^-$ complexes.³⁹⁻⁴¹ The interaction in the second sphere such as hydrogen bonding as well as dipole interaction seems to be not so much reflected in the volume but is sensitive to the entropy.¹²

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Supplementary Material Available: Composition of sample solutions for NMR measurements (Table SI), structure determination summary, atomic coordinates, and anisotropic thermal parameters for all atoms including H atoms together with estimated standard deviations for K-[Fe(OH₂)(phdta)]·2H₂O (Tables SII and SIV), and relaxation data as a function of temperature and pressure (Table SV) (11 pages); observed and calculated structure factors (Table SIII) (6 pages). Ordering information is given on any current masthead page.

(35) Deuterated DMF was used as the external standard for the chemical shift. Although available values of the chemical shift were comparable to the $\Delta\omega_M$ values estimated from the line-broadening data, we did not cite here the chemical shift obtained from the external standard, which was not accurate generally.

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(37) A preliminary experiment has been carried out to estimate rates of the water exchange on related iron(III) complexes with EDTA and CyDTA. Over the temperature range from 1 to 95 °C, the chemical exchange region was not observed. Thus water-exchange rates for Fe(III)-EDTA and Fe(III)-CyDTA should be faster than that for Fe(III)-PhDTA. This finding is consistent with the bound ligand effect, as described above.

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