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Article

Rates of Ligand Exchange between $>\mathrm{Fe^{III}{-}OH_2}$ Functional Groups on a Nanometer-Sized Aqueous Cluster and Bulk Solution

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Variable-temperature ^{17}O NMR experiments were conducted on the nanometer-sized Keplerate $\mathbf{Mo_{72}Fe_{30}}$ cluster, with the stoichiometry $[\mathrm{Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}[Mo_2O_7(H_2O)]_2[H_2Mo_2O_8(H_2O)](H_2O)_{91}]}\cdot{\sim}150\mathrm{H_2O}$. This molecule contains on its surface 30 $\mathrm{Fe(H_2O)}$ groups forming a well-defined icosidodecahedron, and we estimated the rates of exchange of the isolated $>\mathrm{Fe^{III}{-}OH_2}$ waters with bulk aqueous solution. Both longitudinal and transverse ^{17}O-relaxation times were measured, as well as chemical shifts, and these parameters were then fit to the Swift–Connick equations in order to obtain the rate parameters. Correspondingly, we estimate: $k_{ex}^{298} = 6.7(\pm 0.8) \times 10^{6}$ s^{-1}, which is about a factor of $\sim 4 \times 10^{4}$ times larger than the corresponding rate coefficient for the $\mathrm{Fe(OH_2)_6}^{3+}$ ion of $k_{ex}^{298} = 1.6 \times 10^{2}$ s^{-1} (Grant and Jordan, 1981; *Inorg. Chem. 20*, 55–60) and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 26.3 ± 0.6 kJ mol^{-1} and –26 ± 0.9 J mol^{-1} K^{-1}, respectively. High-pressure ^{17}O NMR experiments were also conducted, but the cluster decomposed slightly under pressure, which precluded confident quantitative estimation of the $\Delta V^{\ddagger}$. However, the increase in the reduced transverse-relaxation time with pressure suggests a dissociative character, such as a *D* or I_d mechanism. The enhanced reactivity of waters on the $\mathbf{Mo_{72}Fe_{30}}$ cluster is associated with an increase in the $\mathrm{Fe^{III}{-}OH_2}$ bond length in the solid state of ~0.1 Å relative to the $\mathrm{Fe(OH_2)_6}^{3+}$ ion, suggesting that a correlation exists between the $\mathrm{Fe^{III}{-}OH_2}$ bond length and k_{ex}^{298}. Although there are only few high-spin Fe(III) complexes where both exchange rates and structural data are available, these few seem to support a general correlation.

Introduction

Most inorganic chemists do not appreciate the extent to which their work can help Earth scientists. Many of the most pressing questions in low-temperature geochemistry concern the reactivities of individual functional groups at oxide mineral surfaces, meaning their Brønsted acid−base properties, the rates of ligand substitution, and the rates of electron exchange. As one can imagine, the field relies heavily on computer simulation because so few minerals exist that have well-constrained surface structures in water.

We have been taking a different approach by using nanometer-sized aqueous clusters to provide experimental models that isolate the key functional groups for spectroscopic characterization.[2] In contrast to a colloidal suspension of minerals where the surface structures are unknown, these inorganic clusters are structurally well constrained. Here we begin a study of $>\mathrm{Fe^{III}{-}OH_2}$ functional groups on a nanometer-sized aqueous cluster with the stoichiometry $[\mathrm{Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}[Mo_2O_7(H_2O)]_2[H_2Mo_2O_8(H_2O)]}$ $\mathrm{(H_2O)_{91}]}\cdot{\sim}150\mathrm{H_2O}$. [$\mathbf{Mo_{72}Fe_{30}}$, Figure 1], which is part of a class of spherical systems with the general formula $[(\mathrm{pentagon})_{12}(\mathrm{linker})_{30}]$ or $[\mathrm{Mo(Mo)_5}]_{12}(\mathrm{Linker})_{30}]$, also called Keplerates.[3−7] With this molecule, one can illuminate some pressing questions about ligand-exchange rates in subcolloidal Fe(III) oxyhydroxide materials, such as whether the rates scale with bond lengths and if deprotonation of some

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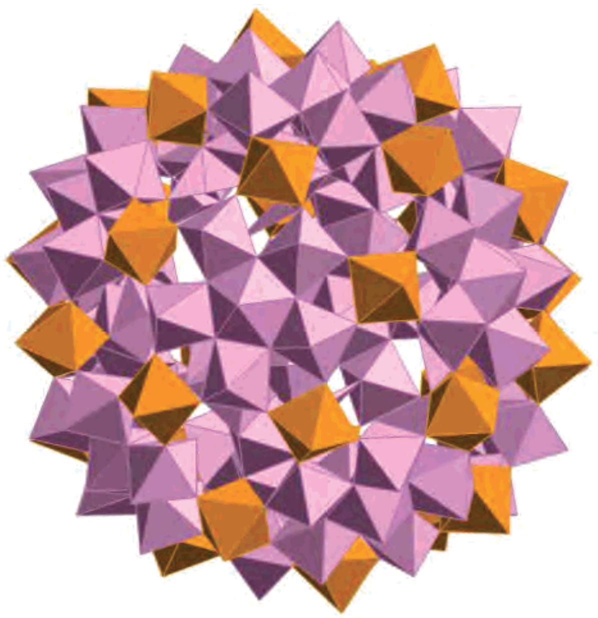

Figure 1. Near-spherical aqueous cluster, containing 72 Mo(VI)−oxide polyhedra (purple) and 30 Fe(III) as $Fe(O)_6$ octahedra (brown).

of the isolated waters affects the reactivities of those that remain.

The $Mo_{72}Fe_{30}$ Keplerate Molecule. The **$Mo_{72}Fe_{30}$** molecule is nearly spherical [Figure 1] and has 72 molybdenum polyhedra that are organized into sets of 12 pentagonal Mo-(Mo)$_5$-type units (comprising a central MoO_7 pentagonal bipyramid linked via edges to five MoO_6 octahedra) and separated from one another by 30 Fe(III)(O)$_6$ linkages. Each of these linkages exposes a single terminal $>Fe^{III}-OH_2$ functional group to the aqueous solution. Inside the near-spherical capsule there are 12 additional water molecules bound to the Fe(III) centers. The remaining 18 octahedral coordination sites on the Fe(III) linkages are bridges to molybdate (two of $[Mo_2O_7(H_2O)]$ type and one of $[H_2Mo_2O_8(H_2O)]$ type) or to acetate ligands.[8] The details of internal coordination are unimportant to the present study since these internal moieties cannot interact with bulk solution; the metal skeleton of the cluster remains intact and prevents access of the internal sites to the bulk solution (see below). The interested reader is referred to Müller et al.[5] for discussion of the structural details.

The only acidic functional groups on the surface of the nanometer-sized molecule are the $>Fe^{III}-OH_2$, which are moderately weak and become fully protonated at low pH (<2.9[9]). As the **$Mo_{72}Fe_{30}$** molecule dissolves into solution, some of these $>Fe^{III}-OH_2$ sites deprotonate to make the molecule slightly anionic. That these molecules remain intact in the aqueous phase is well established through characteristic Raman spectrum (due to their high symmetry, the free clusters exhibit only a few well-defined lines) and light-scattering investigations.[9] The latter method also shows that at higher pH values the intact clusters show a very slow assembly to giant vesicles.[9] Related results were also obtained by mass spectroscopy.[10] The Fe^{III} are weakly antiferromagnetically coupled and linkage of the triangular Fe^{III}_3 units leads to an unprecedented type of spin frustration, which is important to materials science.[11]

Experimental Methods

Preparation of the $Mo_{72}Fe_{30}$. The material was prepared according to the method of Müller et al.[5] The self-buffered pH of the solution of this material is typically ~3.5 because of partial deprotonation of some of the $>Fe^{III}-OH_2$ sites. The pH of the solutions were decreased to <3 by adding 0.1 M HCl in order to suppress the very slow aggregation of individual clusters.[9] The solid was added into the mixture of 1 M HCl, isotopically normal, and ^{17}O-enriched (40%) water in such a way that the final acid concentration was 4 mM and it contained 1% ^{17}O. After preparation, the solutions were heated at 328 K during 6−8 h in sealed NMR tubes to ensure that any aggregates were completely dissociated. In variable-pH measurements, the acid concentration varied between 1.6 and 6.7 mM. The pH range of these experiments was limited to $2 < pH < 3$ because of the cluster stability; it decomposes slowly at pH < 2 and forms larger aggregates containing the intact clusters at pH > 3.[9,12−14] In all cases, the final volume was 0.6 mL and the total iron concentration was 30 mM.

^{17}O NMR Measurements. The water-exchange rates were obtained by measuring the longitudinal- and transverse-relaxation times (T_1 and T_2) and the chemical shift as a function of temperature for the **$Mo_{72}Fe_{30}$** molecule in water. Variable-temperature ^{17}O NMR longitudinal- and transverse-relaxation time measurements on aqueous solution of the **$Mo_{72}Fe_{30}$** were carried out using a 5 mm probe on an 11.7 T magnet ($\nu_o = 67.8$ MHz for ^{17}O) Bruker Avance spectrometer located at the UCD NMR facility. They were referenced to an acidified water solution (aqueous $HClO_4$, pH 3.3) that was enriched to 1% in $H_2{}^{17}O$.

Longitudinal ^{17}O relaxation times were measured by the inversion−recovery pulse sequence, and the transverse-relaxation times were obtained by the Carr−Purcell−Meiboom−Gill spin−echo technique.[15] The temperature was measured by a substitution technique using a copper−constantan thermocouple fitted into the NMR tube. The accuracy of the measured temperature was about ±0.1 K. To improve sensitivity in ^{17}O NMR, ^{17}O-enriched water (40% $H_2{}^{17}O$, Isotec) was added to the solutions to yield ~1% ^{17}O enrichment. The temperature varied between 280.3 and 376 K, $[Fe^{3+}]$ was 32 mmol/kg of solvent, and the pH was 2.7. Variable-pressure ^{17}O relaxation rates were measured at 311.7 K and $[Fe^{3+}] = 29.2$ mmol/kg of solvent up to a pressure of 250 MPa on a Bruker ARX-500 spectrometer equipped with a homemade high-pressure probehead.

Data Analysis. The analysis of the ^{17}O NMR data was performed using Micromath Scientist (version 2.0, Salt Lake City, UT). The

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reported errors correspond to one standard deviation obtained by the statistical analysis unless otherwise indicated.

Results and Discussion

Calculation of k_{ex}^{298}. The reduced ^{17}O NMR T_1 and T_2 relaxation rates, as well as chemical shifts, are shown in Figure 2 as a function of temperature. Although the reduced T_2 values contain information about chemical exchange, a large number of parameters must be calculated to reduce the raw data. Moreover, in the fast-exchange regime, T_1 has some minor influence over the τ_m value. To better constrain the rate parameters, we simultaneously fit the T_1 values and the chemical shifts, as well as the T_2 values, to the Swift and Connick equations:[16]

$$\frac{1}{T_{1r}} = \frac{1}{P_m}\left[\frac{1}{T_1} - \frac{1}{T_{1A}}\right] = \frac{1}{T_{1m} + \tau_m} \tag{1}$$

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left[\frac{1}{T_2} - \frac{1}{T_{2A}}\right] = \frac{1}{\tau_m}\,\frac{T_{2m}^{-2} + \tau_m^{-1}T_{2m}^{-1} + \Delta\omega_m^{\ 2}}{(\tau_m^{-1} + T_{2m}^{-1})^2 + \Delta\omega_m^2} \tag{2}$$

$$\Delta\omega_r = \frac{1}{P_m}(\omega - \omega_A) = \frac{\Delta\omega_m}{(1 + \tau_m T_{2m}^{-1})^2 + \tau_m^2\Delta\omega_m^2} \tag{3}$$

where $1/T_1$, $1/T_2$, and ω are $1/T_{1A}$, $1/T_{2A}$, and ω_A the measured ^{17}O NMR relaxation rates and angular frequencies of the $\mathbf{Mo_{72}Fe_{30}}$ solutions, and the acidified reference solution, respectively. The parameter τ_m is the mean residence time of a bound water molecule and is equal to $1/k_{ex}$, where k_{ex} is the water exchange rate.

From these values one can calculate the reduced relaxation rates and chemical shift, $1/T_{1r}$, $1/T_{2r}$, and ω_r according to eqs 1−3, where P_m is the molar fraction of bound water, $1/T_{1m}$ and $1/T_{2m}$ are the relaxation rates of the bound water, and $\Delta\omega_m$ is the chemical shift difference between bound and bulk water. We used the full eqs 2 and 3 and the simplified eqs 4 and 5 model where the $\Delta\omega_m$ contribution is considered to be negligible.

$$\frac{1}{T_{1r}} = \frac{1}{\tau_m + T_{1m}} \tag{4}$$

$$\frac{1}{T_{2r}} = \frac{1}{\tau_m + T_{2m}} \tag{5}$$

Although the calculated values do not differ much depending upon whether we use the full or the simplified models, the corresponding errors vary considerably.

The $\Delta\omega_m$ parameter is determined by the hyperfine or scalar coupling constant, $A/\hbar$ (eq 6), where g_L is the isotropic Landé g factor, μ_B is the Bohr magneton (9.274×10^{-24} J T^{-1}), B represents the magnetic field (11.7 T), S is the electron spin, and k_B is the Boltzmann constant:

$$\Delta\omega_m = \frac{g_L\mu_B S(S+1)B}{3k_B T}\,\frac{A}{\hbar} \tag{6}$$

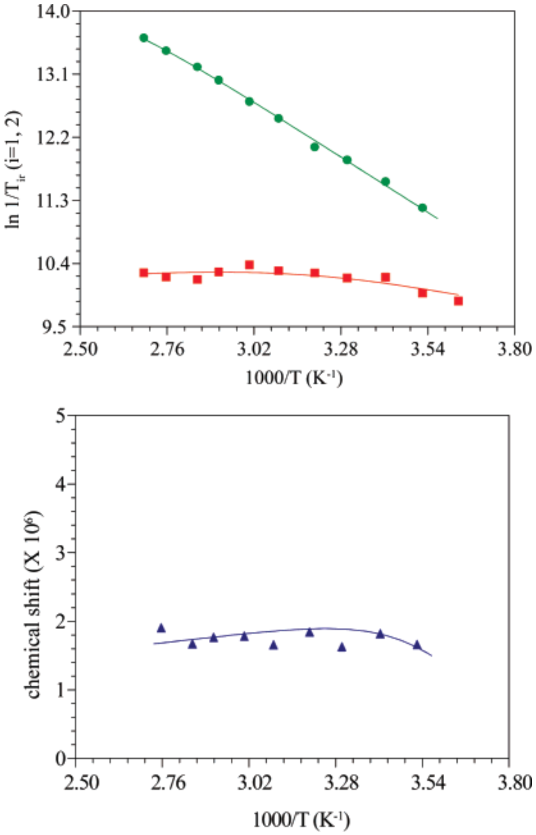

Figure 2. (top) Reduced values of T_1 (red squares) and T_2 (green circles) ^{17}O relaxation rates. (bottom) Reduced chemical shift at 11.7 T. The solid lines correspond to the simultaneous fit of all measured data, as described in the text, to the Swift−Connick equations for relaxation.

The outer-sphere contribution to the chemical shift is typically small and neglected,[17] and we neglect it here. In our analysis, we considered that there is only one exchangeable water molecule coordinated to each $>Fe^{III}$ on the $\mathbf{Mo_{72}Fe_{30}}$ ion in estimating P_m. Although some $>Fe^{III}$ sites have an additional bound water pointing to the interior of the molecule, these probably do not exchange with bulk solution. This assumption, that only the surface waters can exchange, is reasonable as the Fe^{III} are strongly bonded to the negatively charged $Mo(Mo)_5$ framework and do not dissociate. The slow aggregation of the clusters, proceeding over months in aqueous solution,[9] is via hydrolysis of some $>Fe^{III}-OH_2$ and linkage of clusters via hydroxyl bridges.

The ^{17}O longitudinal-relaxation rates are mainly influenced by the rotation of the molecule and the quadrupolar coupling constant. The full relation is given by eq 7, where γ_S is the electron and γ_I is the nuclear gyromagnetic ratio ($\gamma_S = 1.76 \times 10^{11}$ rad s^{-1} T^{-1}, $\gamma_I = -3.626 \times 10^7$ rad s^{-1} T^{-1}), μ_0 is the permeability constant ($\mu_0/4\pi = 1 \times 10^{-7}$), $\hbar$ is Planck's constant divided by 2π, r_{FeO} is the Fe−O distance (we used both 2.075 and 2.088 Å from X-ray crystallography,[23] see below), I is the nuclear spin ($I = 5/2$ for ^{17}O), χ is the quadrupolar coupling constant, and η is an asymmetry

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parameter, where $\chi(1 + \eta^2/3)^{1/2} = 7.58$ MHz using the quadrupolar coupling constant for acidified water:[18]

$$\frac{1}{T_{1\mathrm{m}}} = \left[\frac{1}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2\gamma_\mathrm{I}^2\gamma_\mathrm{S}^2}{r_\mathrm{FeO}^6} S(S+1)\right] \times \left[6\tau_{\mathrm{d}1} + 14\frac{\tau_{\mathrm{d}2}}{1+\omega_\mathrm{S}^2\tau_{\mathrm{d}2}^2}\right] + \frac{3\pi^2}{10}\frac{2I+3}{I^2(2I-1)}\chi^2(1+\eta^2/3)\tau_\mathrm{RO} \quad (7)$$

where

$$\frac{1}{\tau_{\mathrm{d}i}} = \frac{1}{\tau_\mathrm{m}} + \frac{1}{\tau_\mathrm{RO}} + \frac{1}{T_{i\mathrm{e}}} \quad i = 1, 2 \quad (8)$$

τ_RO, the rotational correlation time follows exponential temperature dependence:

$$\tau_\mathrm{RO} = \tau_\mathrm{RO}^{298} \exp\left\{\frac{E_\mathrm{R}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \quad (9)$$

In transverse-relaxation, the scalar relaxation mechanism, $1/T_{2\mathrm{sc}}$, dominates

$$\frac{1}{T_{2\mathrm{m}}} \cong \frac{1}{T_{2\mathrm{sc}}} = \frac{S(S+1)}{3}\left(\frac{A}{\hbar}\right)^2\left(\tau_{\mathrm{s}1} + \frac{\tau_{\mathrm{s}2}}{1+\tau_{\mathrm{s}2}^2\omega_\mathrm{s}^2}\right)\frac{1}{\tau_{\mathrm{s}i}} = \frac{1}{\tau_\mathrm{m}} + \frac{1}{T_{i\mathrm{e}}} \quad (10)$$

and, within eq 10, the longitudinal electronic relaxation term dominates and is the determining parameter of the transverse-relaxation rate. Previous work has found that the dipole−dipole interaction is ineffective in the longitudinal electronic relaxation;[17] therefore, the zero-field splitting and the spin-rotation contribute.

For the electron-spin relaxation rates, $1/T_{1\mathrm{e}}$ and $1/T_{2\mathrm{e}}$, we used the equations developed by McLachlan:[19]

$$\left(\frac{1}{T_{1\mathrm{e}}}\right) = \frac{32}{25}\Delta^2\left(\frac{\tau_\mathrm{v}}{1+\omega_\mathrm{S}^2\tau_\mathrm{v}^2} + \frac{4\tau_\mathrm{v}}{1+4\omega_\mathrm{S}^2\tau_\mathrm{v}^2}\right) \quad (11)$$

$$\left(\frac{1}{T_{2\mathrm{e}}}\right) = \frac{32}{50}\Delta^2\left[3\tau_\mathrm{v} + \frac{5\tau_\mathrm{v}}{1+\omega_\mathrm{S}^2\tau_\mathrm{v}^2} + \frac{2\tau_\mathrm{v}}{1+4\omega_\mathrm{S}^2\tau_\mathrm{v}^2}\right] \quad (12)$$

$$\tau_\mathrm{v} = \tau_\mathrm{v}^{298} \exp\left\{\frac{E_\mathrm{V}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \quad (13)$$

where Δ^2 is the trace of the square of the transient zero-field-splitting (ZFS) tensor, τ_v is the correlation time for the modulation of the ZFS with the activation energy E_v, and ω_s is the Larmor frequency of the electron spin. In addition, the inverse binding time (or exchange rate, k_ex) of the water molecules in the inner sphere is also assumed to obey the Eyring equation (eq 14), where $\Delta S^\ddagger$ and $\Delta H^\ddagger$ are the entropy and enthalpy of activation for the exchange, and k_ex^{298} is the exchange rate at 298.15 K. In order to better constrain the activation parameters, we use a modified form of the Eyring equation (eq 15) that includes estimated values of k_ex^{298}. This expression of the Eyring equation is typically used[17] because the value k_ex^{298} is constrained from earlier equations (e.g., eqs 1−13) leaving $\Delta H^\ddagger$ as the primary parameter produced in this fit, which is then reinserted into eq 14 to yield an estimate of $\Delta S^\ddagger$:

$$\frac{1}{\tau_\mathrm{m}} = k_\mathrm{ex} = \frac{k_\mathrm{B}T}{h}\exp\left\{\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}\right\} \quad (14)$$

$$\frac{1}{\tau_\mathrm{m}} = k_\mathrm{ex} = \frac{k_\mathrm{ex}^{298}T}{298.15}\exp\left\{\frac{\Delta H^\ddagger}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right\} \quad (15)$$

Both the experimental data and the fitted curves are shown in Figure 2. All of the best-fit parameters are given in Table 1 where we compare our results to other high-spin Fe$^\mathrm{III}$ compounds. As one can see, the surface >Fe$^\mathrm{III}$−OH$_2$ sites on the **Mo$_{72}$Fe$_{30}$** molecule are considerably more reactive ($k_\mathrm{ex}^{298} = 6.7 \times 10^6$ s^{-1}) than on the Fe(H$_2$O)$_6^{3+}$(aq) ion ($k_\mathrm{ex}^{298} = 1.6 \times 10^2$ s^{-1}) but slightly less reactive than the various aminocarboxylate complexes, such as Fe$^\mathrm{III}$EDTA and its derivatives, where one coordinative position is occupied by a water molecule.[20] The differences in reactivity correlate with lengthened Fe$^\mathrm{III}$−OH$_2$ bond lengths. The Fe$^\mathrm{III}$−OH$_2$ bond length for the Fe(H$_2$O)$_6^{3+}$ ion in a crystal structure with 1,3,5tris(sulfomethyl)benzene counterions, for example, is 1.996 ± 0.002 Å[21] and in alums it is 1.994 and 2.002 Å.[22] In the **Mo$_{72}$Fe$_{30}$** molecule the average distance is 2.075−2.088 Å.[23] There are several crystal structures available for high-spin Fe$^\mathrm{III}$ aminocarboxylate complexes[24−32] with different counterions, and in these studies the Fe$^\mathrm{III}$−OH$_2$ bond length varies between 2.12 and 2.08 Å. These lengths are averaged and plotted in Figure 3 along with the values of k_ex^{298}.[20] The differences in reactivity correlate with lengthened Fe$^\mathrm{III}$−OH$_2$ bonds, although the coordination number of Fe(III) differs in the series. The Fe(III) is heptacoordinated in the EDTA (and in its derivatives) with a single water

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Table 1. Best-Fit ^{17}O NMR Parameters That Were Obtained from the Simultaneous Analysis of Longitudinal- and Transverse-Relaxation Rates and the Chemical Shifts[a]

parameter	$\mathbf{Mo_{72}Fe_{30}}$	$Fe(H_2O)_6^{3+}$ [b]	$(FeEdta)^-$ [c]	FeEdtaH[c]	$(FeCDTA)^-$ [c]
k_{ex}^{298}/s^{-1}	$(6.7 \pm 0.8) \times 10^6$	1.6×10^2	6.8×10^7	7.8×10^7	1.3×10^7
$\Delta H^{\ddagger}$/kJ mol^{-1}	26.3 ± 0.6	64	24.4	22	25
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	-26 ± 0.9	12.1	−13	−20	−25
r_{Fe-O}/Å	2.088[d]	1.996[e]	2.105[f]	2.104[g]	2.105[h]
$A/\hbar/10^6$ rad s^{-1}	13.6 ± 3.9				
τ_R^{298}/ps	175 ± 12				
E_R/kJ mol^{-1}	4.2 ± 1				
τ_v^{298}/ps	9210 ± 520				
E_v/kJ mol^{-1}	25 ± 1.2				
$\Delta^2/10^{17}$ s^{-2}	2.4 ± 0.1				

[a] For comparison, the values of $Fe(H_2O)_6^{3+}$ and various aminocarboxylate complexes are shown. FeEdta = Fe(III)−ethylenediaminetetraacetic acid; FeEdtaH = FeEdta with one acetate group protonated; FeCDTA = Fe(III) cyclohexanediaminetetraacetic acid. [b] Reference 1. [c] Reference 20. [d] Reference 8. [e] References 21 and 22. [f] References 24−31. [g] Reference 31. [h] Reference 32.

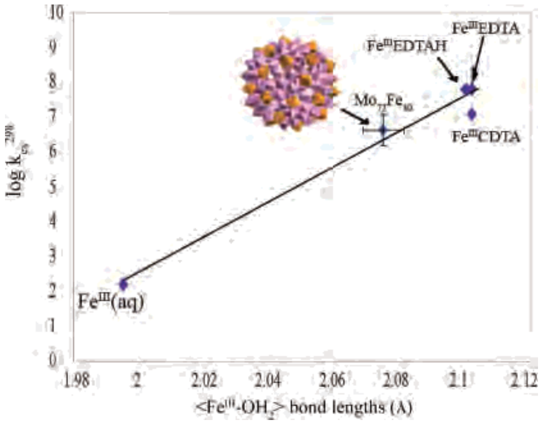

Figure 3. Correlation between $Fe^{III}-OH_2$ bond lengths and values of $\log(k_{ex}^{298})$, the rates of water exchange, for a series of high-spin Fe^{III} complexes. The uncertainties correspond to the range in values calculated for the bond length: $2.075 \text{ Å} \leq r_{FeO} \leq 2.088$ Å.

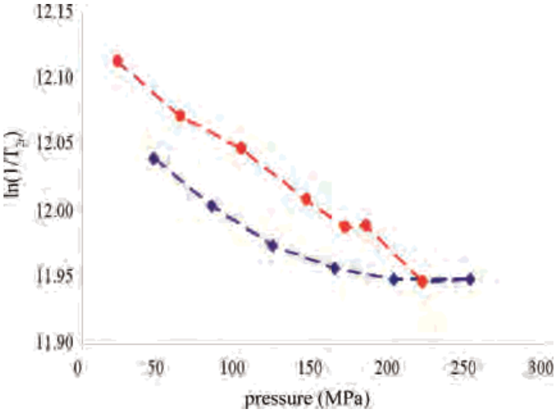

Figure 4. Reduced transverse relaxation rate ($1/T_{2r}$) as a function of pressure (MPa). Blue squares indicate rates while pressure was increasing, and red circles indicate measurements with decreasing pressure. The dashed lines are drawn to guide the eyes and are not a fit to the equations.

occupying the seventh position. The Fe(III) is hexacoordinated in Fe^{3+}(aq) and in the $\mathbf{Mo_{72}Fe_{30}}$ molecule. A better correlation might be established by using only hexacoordinated Fe(III) complexes, but such data do not yet exist. Nevertheless, the general trend suggests a useful correlation between bond length and water exchange rate.

Such a correlation would be enormously useful to geochemists who are attempting to assign reactivities to the functional groups on extended structures for which experiments are impossible (see Wang et al.[33]). So far, crystal-truncation-rod studies have not been able to assign bond lengths to bound waters at surfaces with great accuracy, which means that data on aqueous clusters, such as the Al(III) Keggin clusters[34] and these Keplerates, are probably the only reliable guides. Although the number of studies of large molecules are few, there is a strong correlation between bond lengths and rates of exchange.

Additionally, it is important to geochemists that the rates of transverse relaxation, and thus the values of k_{ex}^{298}, do not vary with solution pH, albeit over a narrow range ($2 < \text{pH} < 3$). Over this pH range, the $\mathbf{Mo_{72}Fe_{30}}$ molecule varied in the extent of protonation ($pK_a \approx 2.9$[9]) and all of the protonation sites correspond to waters bound to the Fe(III) atoms. The relaxation times do not change above experimental error over this variation in pH, indicating that the rates of solvent exchanges are nearly constant as the molecule develops charge. Deprotonation of an aquo monomer complex is usually associated with considerable labilization of the remaining waters.[22] One question that arises in geochemistry is the extent to which this labilization is a local effect or is general across an extended structure with many bound waters and hydroxyls that can interconvert. The results for the $\mathbf{Mo_{72}Fe_{30}}$ molecule, where the >Fe−OH is isolated from other >$Fe-OH_2$ sites, indicate that there is little general labilization due to deprotonation. A different result would have been achieved if the sites were not so isolated from one another, as might be found on the edges of minerals with close sets of acidic bound waters.

High-Pressure ^{17}O NMR Experiments. In order to assess the mechanism of water exchange on the $\mathbf{Mo_{72}Fe_{30}}$ complex, we have intended to carry out variable-pressure ^{17}O transverse-relaxation rate measurements at 311.7 K. First, we measured T_2 with increasing pressure up to 250 MPa and then reversed the pressure to check for hysteresis, which we found [Figure 3]. Although the hysteresis is conspicuous, it can be explained by very small amounts of decomposition of the $\mathbf{Mo_{72}Fe_{30}}$ complex to release $Fe(H_2O)_6^{3+}$(aq) monomers. Decomposition of 1% or less of the $\mathbf{Mo_{72}Fe_{30}}$ complex dramatically increases the molar fraction of bound waters

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(33) Wang, J.; Rustad, J. R.; Casey, W. H. *Inorg. Chem.* **2007**, *46* (8), 2962−2964.

(34) Casey, W. H. *Chem. Rev.* **2006**, *106* (1), 1−16.

(P_m) and affects the ^{17}O NMR signal. Another explanation is that increased pressure induced aggregation of the **$Mo_{72}Fe_{30}$** complexes into larger ‘blackberry’ structures[12,13] that are slow to dissociate on our experimental time scales. For these reasons, we did not attempt to assign a value of $\Delta V^{\ddagger}$ to the exchange of waters from the **$Mo_{72}Fe_{30}$** complex. The decreasing tendency of $\ln(1/T_{2r})$ with pressure suggests an I_d pathway, and we can estimate an activation volume not more than $+2$ cm^3 mol^{-1}; however, we recognize that it is difficult to defend this assignment confidently with irreversible data.

Conclusions

Large aqueous oligomers, such as the **$Mo_{72}Fe_{30}$** complex, have the potential to considerably advance our understanding of ligand-exchange processes in geochemical materials. Here we show that the rates of exchange of waters bound to the $>Fe^{III}-OH_2$ functional groups on this 2.5 nm molecule can be measured using standard ^{17}O NMR methods.

The results establish a link between the nanoclusters and smaller aqueous molecules. The rates of solvent exchange from $>Fe^{III}-OH_2$ sites on the **$Mo_{72}Fe_{30}$** complex are $\sim 10^4$ more rapid than for the simple aquo ion, $Fe(H_2O)_6^{3+}$, but slightly slower than $Fe^{III}-EDTA$ and its derivatives [Table 1]. We observe that small changes in pH near the pK_a of the sites have almost no effect on the rates of exchange of bound waters. Thus, the effect of deprotonation is muted across the 30 bound waters, and perhaps acid−base chemistry will have little effect of rates of solvent exchange in larger molecules with isolated waters and on colloids. Recently, geochemists established a correlation between calculated $Al-OH_2$ bond lengths and rates of solvent exchange that extends across many orders of magnitude.[33] The motivation for establishing this correlation was a desire to assign reactivities to the functional groups on colloidal mineral surfaces. A similar correlation will ultimately be possible for high-spin Fe^{III} solid surfaces if more aqueous complexes can be added to the correlation.

Finally, whereas the bound waters in this **$Mo_{72}Fe_{30}$** cluster are all labile, in another cluster with inert trivalent metals, such as the **$Mo_{72}Cr_{30}$**,[35] the waters could be replaced stepwise. Such a cluster would allow fine control of the surface chemistry and lead to new compounds by directed substitution.

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