Solvent ^{1}H NMRD Study of Hexaaquochromium(III): Inferences on Hydration and Electron Relaxation

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The water proton nuclear magnetic relaxation dispersions (NMRD) of hexaaquochromium(III) in water and in water−glycerol solutions were obtained at several temperatures and viscosities. The data were analyzed in terms of the available theories by taking into account the contributions from first sphere, second sphere, and outer sphere water molecules. A meaningful analysis was possible by taking advantage of the structural model obtained from ^{17}O relaxation data, which was recently made available in the literature (Bleuzen, A.; Foglia, F.; Furet, E.; Helm, L.; Merbach, A.; Weber, J. *J. Am. Chem. Soc.* **1996**, *118*, 12 777). Dynamic parameters, like the molecular rotational time, the exchange time of the water protons of the first coordination sphere, the correlation time for electron relaxation, and the magnetic field dependence of electron relaxation were obtained. The possible contribution to water proton relaxivity of second sphere water molecules for some other hexaaqua complexes is also discussed.

Introduction

Hydration of chemical substances in water solutions is an important piece of knowledge in fully understanding their reactivity and dynamic behavior.[1] Typically, the chemical properties of metal ions in water solutions are determined by water molecules interacting with the ions, giving rise to the so-called "first coordination sphere".[2−4] Weaker interactions are also present between the first coordination sphere and further water molecules. In some cases, these interactions may be strong enough to give rise to a "second coordination sphere", and the water molecules involved are thereby still distinguishable from bulk water molecules. The distinction between second sphere and bulk solvent is based on the water exchange rate, which is longer than the diffusional correlation time.[5,6] Direct information on the second coordination sphere has been obtained in some cases.[7−11]

One way of revealing the presence of interactions between the central metal ion and the surrounding water molecules is monitoring magnetic effects on water nuclei caused by the metal ion when the ion is paramagnetic. These effects can be detected through Nuclear Magnetic Relaxation Dispersion (NMRD) measurements. Water proton NMRD is a technique based on the measurements of the nuclear longitudinal relaxation time of solvent water protons as a function of the magnetic field, and it provides information on the dynamics of the ion−solvent interactions (like the proton-exchange rate, the electron relaxation time, and the mechanisms which give rise to electron relaxation) and the structure of the system (like the proton−unpaired electrons distance and the hyperfine coupling constants).[12−22] However, the information is of bulk type, and only the match between NMRD profiles and theoretical models

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allows inferences on the contributions of first, second, and outer sphere water molecules.[5,6,23−25] The presence of second sphere waters may in fact provide a non-negligible contribution to proton relaxation, and thus it can be important to increase relaxivity of complexes synthesized as MRI contrast agents.[5,6,25]

The water proton relaxation times in the presence of paramagnetic solutes include contributions from dipolar and contact coupling with the unpaired electrons. The total effect of dipolar coupling depends on the number of coordinated water protons, their distance from the unpaired electrons, and the correlation time that modulates the interaction, which is governed by the smaller of electron relaxation time, rotational correlation time, and chemical exchange time. Contact coupling depends on the magnitude of the hyperfine coupling and on the smaller of the electron relaxation time and the chemical exchange time. Thus, the field dependence of nuclear relaxation may also provide information on the field dependence of electron relaxation.

The NMRD profiles of several metal aqua ions have been analyzed and theoretically understood, in particular in our laboratory, including copper(II),[26,27] manganese(II),[28,29] cobalt(II),[27] nickel(II),[27,30,31] iron(III),[32] oxovanadium(IV),[33] titanium(III),[34] gadolinium(III),[35,36] and other lanthanides.[37] Some ions showed no field dependence for electron relaxation in a range up to 50 MHz (like Cu^{2+}, Ti^{3+}, Co^{2+}, Ln^{3+} systems but Gd^{3+}) whereas some others (VO^{2+}, Mn^{2+}, Fe^{3+}, Ni^{2+}, Gd^{3+} systems) exhibit a field dependence; the different behaviors are attributed to the different mechanisms of electron relaxation. For all of these ions, the analysis provided estimates of the number/distance of water molecules in the first coordination sphere and, when applicable, of the rotational correlation time. Outer sphere effects are also accounted for.[38,39] The issue of the presence of a well defined second coordination sphere has not been specifically addressed.

Recently, ^{17}O NMR data on hexaaquochromium(III) have been analyzed and interpreted in terms of two coordination spheres.[11] The number of second sphere water molecules and their distance from the metal ion, obtained in ref 11, were imposed in the interpretation of the NMRD data. The present analysis allows us to obtain a complete picture of the chromium(III) water system including first, second, and outer sphere molecules, the dynamics of the system, and the electronic properties. With this in mind, we have here recorded an extensive set of NMRD data on hexaaquochromium(III), from 0.01 to 800 MHz, as a function of temperature and viscosity, and at controlled pH values, to obtain the best possible estimates of all of the relevant parameters influencing the measured profiles.

This allowed us to further characterize this system which had been extensively studied in the past.[26,40−44] The difficulty in understanding the proton NMRD profiles is, in fact, caused by the slow exchange of first coordination sphere water protons and by the fact that the longitudinal relaxation rates are insensitive to the field dependence of the electron relaxation time. The fact that the first coordination sphere water protons exchange slowly causes a smaller contribution to bulk water proton relaxation, and any contribution of second and outer sphere waters should be more easily detectable.

Experimental Section

$Cr(ClO_4)_3$ and glycerol-d_5 were purchased from Aldrich and used without further purification. To avoid partial hydrolysis of the hexaaquachromium(III), 1 M perchloric acid, nitric acid, or hydrochloric acid was used as a medium. The stock solutions contained 1 mM $Cr(H_2O)_6^{3+}$. The different media were used in order to determine if the presence of different anions with different stability constants could influence the relaxivity of a 1 mM chromium(III) solution. Preliminary experiments showed that the relaxivity was the same when 1M of perchloric acid, nitric acid, or hydrochloric acid was used as a medium. Therefore, all samples were prepared by using 1 M perchloric acid solution. The viscosity of the solvent was increased by a factor 10 by adding 60% glycerol-d_5 w/w to the stock solution. The relaxivity of the latter sample was calculated by taking into account the change in the molar fraction.

The longitudinal water proton relaxation rates in the 0.01−50 MHz range were measured at different temperatures (in the range 278−333 K) using a Koenig−Brown field cycling relaxometer[12,15] and at 500 and 800 MHz using the inversion recovery (for R_1 measurements) and the CPMG (for R_2 measurements) pulse sequences on Bruker DRX Avance 500 and DRX Avance 800 instruments, respectively. The errors on the individual data points are estimated to be lower than 5%. The net paramagnetic relaxation rates, R_{1p} and R_{2p}, were obtained by direct subtraction of the solvent (pure water or water/glycerol mixture) relaxation rates from the total relaxation rates of the solutions containing the hexaaqua chromium(III) ions.

Theoretical Background

The nuclear relaxation theory for paramagnetic systems was originally developed by Solomon[45] under a dipole−dipole approximation and extended by Bloembergen[46] to include contact contribution

$$R_{1M} = R_{1M(dip)} + R_{1M(con)} \qquad (1)$$

$$R_{2M} = R_{2M(dip)} + R_{2M(con)}$$

where R_{1M} and R_{2M} indicate the longitudinal and transverse relaxation rates of coordinated water protons (first and second coordination spheres), respectively. All protons in the first coordination sphere will have the same distance, as will all

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protons in the second coordination sphere. The correlation times for dipolar relaxation are provided by the fastest of electron relaxation, rotation and water proton residence time

$$\tau_{c(i)}{}^{-1} = \tau_{s(i)}{}^{-1} + \tau_r{}^{-1} + \tau_M{}^{-1} \tag{2}$$

as all of them can modulate the dipolar coupling energy and, therefore, can cause nuclear relaxation. The correlation time for contact relaxation is given by

$$\tau_{e(i)}{}^{-1} = \tau_{s(i)}{}^{-1} + \tau_M{}^{-1} \tag{3}$$

since only electron relaxation and chemical exchange can modulate the coupling. In fact, rotation does not influence the reciprocal orientations of the nuclear magnetic moment and of the fractional electron magnetic moment located at the nucleus site.

According to the modified Solomon−Bloembergen−Morgan equations, if the electron relaxation is field dependent, the relaxation mechanisms for the electron spin system mainly arise from the modulation of the transient zero field splitting as a result of collision with solvent molecules in solution.[43,44] Equations were derived for $S = 3/2$ systems[43] and are reported in the Supporting Information, together with equations for the field dependence of outer-sphere relaxation[38,39] and equations relating R_{1M} and R_{2M} to the observable solvent proton relaxation rate enhancements R_{1p} and R_{2p}.

Results

The ^{1}H NRMD profiles expressed as R_{1p} (s^{-1} mM^{-1}) of a water solution of $Cr(H_2O)_6{}^{3+}$ at 278, 298, 313, and 333 K are shown in Figure 1. The data span from 0.01 to 50 MHz. Data at 500 and 800 MHz for both R_{1p} and R_{2p} at 278, 298, and 313 K are also shown. A dramatic increase in R_{1p} values at low and intermediate fields is observed with increasing temperature. The profiles also change with increasing temperature; one dispersion only is present at the lowest temperature, at a frequency somewhat lower than 10 MHz, whereas two dispersions are clearly visible in the profiles at higher temperature, one at about 10 MHz and one at about 0.5 MHz. The profile at 333 K is reminiscent of the profile for an Mn(II) aqua ion in water solution.[29] The former dispersion corresponds to a correlation time in the range from 10^{-10} to 10^{-11} s, which is on the order of the expected rotational time for an aqua ion, and the latter dispersion to a correlation time of about 5×10^{-10} s, which is of the order expected for the electron relaxation time.[19] As it happens, for the Mn(II) aqua ion, the high field dispersion is then ascribed to the presence of dipolar contribution, and the low field dispersion is ascribed to the presence of contact contribution. These assignments can be easily checked from the functional forms of contact and dipolar contributions. According to Stokes−Einstein law[47,48]

$$\tau_r = \frac{4\pi\eta r^3}{3kT} \tag{4}$$

(η indicates the viscosity of water solution) τ_r increases with decreasing temperature, and correspondingly the position of the high field dispersion moves toward lower fields, the correlation time for dipolar relaxation corresponding to the rotational time, as the electron relaxation time is longer.

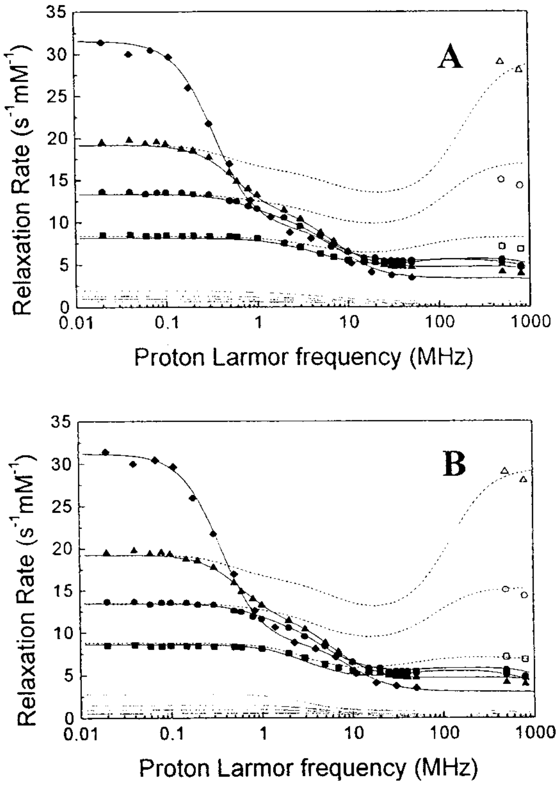

Figure 1. Water proton NMRD profiles of hexaaqua chromium(III) solutions at pH 0 and 278 (■), 298 (●), 313 (▲), and 333 (◆) K. Solid symbols indicate R_1 measurements and open symbols R_2 measurements. (A) The solid lines represent the best fit profiles of R_1 according to Model 1; dashed lines indicate the best fit profiles of R_2; dotted lines indicate the outer-sphere contribution to R_1 (the highest curve is related to the profile at 278 K, the lowest to the profile at 333 K). (B) The solid lines represent the best fit profiles of R_1 according to Model 2; dashed lines indicate the best fit profiles of R_2; dotted lines indicate the contribution to R_1 from second sphere waters (the highest curve is related to the profile at 278 K, the lowest to the profile at 333 K).

As immediately noted, the relaxation rates at low and intermediate fields increase with increasing temperature. This behavior is characteristic of a slow exchange regime, since τ_M decreases with increasing temperature. The occurrence of slow exchange can also explain the fact that the dispersion related to the contact contribution is not present in the low temperature profile. In fact, below 300 K, R_{1p} is strongly affected by τ_M, which hinders any increase in relaxivity, thus causing the contact dispersion to disappear.

Two separate fits of the data in Figure 1 were performed and compared. In the first fit (Model 1), it was assumed that the chromium(III) ion was surrounded by six waters in the first coordination sphere, and that bulk water molecules (outer sphere water) were allowed a distance between d, the distance of closest approach, and infinity. Two cases were considered, $d = 3.5$ Å, as typically assumed,[13,16,17,20,21] and $d = 4.5$ Å, as expected for water molecules approaching the first coordination sphere waters from their oxygen side.[6,22] In the second model, the proposed[11] second sphere of water molecules was also added, and the outer sphere waters were given longer distances of closest approach (5.5 Å (case a) and 6.5 Å (case b)) (see Figure 2). The number of free parameters was the same in the two models.

Model 1: First Coordination Sphere + Outer Sphere. The experimental R_{1p} curves at the four temperatures can be fitted by using the equations reported in ref 43 with the assumption that only six first coordination sphere waters plus outer sphere molecules contribute to the observed NMRD. In principle, each

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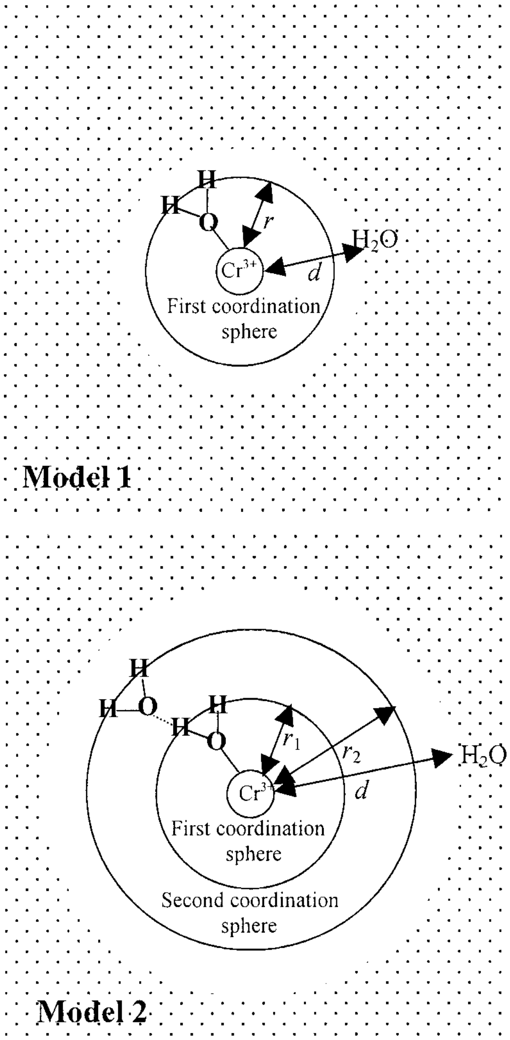

Figure 2. Sketch of the two hydration models: model 1 ($r = 2.71$ Å, $d \leq r_{\text{outer-sphere}} < \infty$; case a: $d = 3.5$, case b: $d = 4.5$ Å) and model 2 ($r_1 = 2.71$, $r_2 = 4.5$ Å, $d \leq r_{\text{outer-sphere}} < \infty$; case a: $d = 5.5$, case b: $d = 6.5$ Å).

curve should be fitted with at least five parameters, since τ_r, τ_{M1}, τ_s, the water protons' paramagnetic ion distance r, and the contact coupling constant $A/\hbar$ have to be taken into account. If τ_s were field dependent, the two parameters Δ_t, the transient ZFS, and τ_v, the correlation time which describes the spin-lattice time dependent interactions, instead of a single τ_s, should be used as adjustable parameters. The situation can be improved if $A/\hbar$, Δ_t, and r are considered invariant with temperature in the present small temperature range. Thus, all the curves can be fitted together with a total of 15 parameters (4 τ_r, 4 τ_{M1}, 4 τ_v, $A/\hbar$, Δ_t, and r) instead of 24. Furthermore, we expect an Arrhenius relationship with temperature for rotational and electron correlation times[11,49]

$$\tau_{s,r} = A\, e^{B/T}$$

and a Eyring relationship for the exchange time,[11,19,49]

$$\tau_{M1} = \frac{A}{T} e^{B/T}$$

and therefore, we end up with a total of nine parameters. By doing this, we can reduce the number of independent parameters and effectively improve the confidence in the derived parameters.

It turns out that it is possible to fit the profiles with many sets of the nine parameters. In particular, Δ_t ranging from 0.08 to 0.5 cm^{-1} and $A/\hbar$ between 1.5 and 2.5 MHz are consistent with the profiles. Furthermore, it is not possible to establish from the fit whether the electron relaxation is constant or field dependent. Therefore, we tried to obtain this information from independent measurements. The R_{2p} data acquired at high fields prove that τ_s is indeed field dependent. In fact, a hump in the values of R_{2p} at high fields is expected only in the presence of an increasing correlation time, due to the nondispersive terms present in the equation for the contact contribution to transverse relaxation.

A simultaneous fit of R_{1p} and R_{2p} data was thus performed. By inclusion of R_{2p} data, a stable set of the nine best fit parameters can be obtained. The fit provided a value for r of 2.71 Å, in excellent agreement with X-ray and EXAFS measurements.[10,11] The best fit profiles are reported in Figure 1A as solid and dashed lines for R_{1p} and R_{2p} data, respectively, and the best fit parameters are collected in Table 1A. The fit might be considered to be acceptable, although clearly the transverse relaxation rates at high field are not perfectly reproduced. As far as the best fit parameters are concerned, it appears that the rotational correlation time τ_r is 2−3 times larger than expected for an hexaaquo ion,[41] and the diffusional correlation time τ_D is of the same order of magnitude as τ_r.[15]

Model 2: First Coordination Sphere + Second Coordination Sphere + Outer Sphere. In this model, we adopt the recent description[11] of hexaquochromium(III) as having a well-defined second coordination sphere made by 13 water molecules, whose protons are at a distance of 4.5 Å from the metal ion. The contribution of such second sphere water molecules was taken into account by imposing an exchange time provided by the relationship $\tau_{M2} = 7.057 \times 10^{-12}/T \exp(2563/T)$ s.[11] The value of r was fixed to 2.71 Å, and the distance of closest approach was fixed to 5.5 or 6.5 Å (see Figure 2). The best fit profiles are reported in Figure 1B, again as solid and dashed lines for R_{1p} and R_{2p} data, respectively, and the resulting best fit parameters are reported in Table 1B. The goodness of the fit of R_{2p} data improves considerably, as judged by visual inspection of the best fit curves in Figure 1 and by the quadratic error (equal to 16 and 9 for Models 1 and 2, respectively).

Outer Sphere and Second Sphere Effects. The fits for both Models 1 and 2 were performed by assuming for the outer-sphere relaxation a distance of closest approach of 3.5 or 4.5 Å (Model 1) or of 5.5 or 6.5 Å (Model 2) and a diffusion coefficient, D, calculated equal to 1.3, 2.4, 3.4, 5.2 × 10^{-5} cm^2 s^{-1} for T = 278, 298, 313, 333 K, respectively. It must be pointed out that in the case of hexaaquochromium(III), differently from what happens for other aqua ions, it is important to take into account the outer-sphere relaxation in the fit procedure. In fact, outer-sphere contributes about 2 s^{-1} at low fields in case $d = 3.5$ Å (dotted lines in Figure 1A). This value is less than 10% for the high temperature profiles, but it is about 25% for the lowest temperature profile. Therefore, it affects differently the profiles acquired at different temperature, thus influencing the best-fit values of all parameters and not only of r. The same reasoning holds for second sphere water molecules, whose effect ranges from 2.8 s^{-1} at 278 K to 0.6 s^{-1} at 333 K at low fields (dotted lines in Figure 1B).

Electronic Relaxation Times and Ancillary Experiments. To further investigate the field dependence of the electron relaxation rates, we measured the proton relaxation rates of a

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Table 1. Best Fit Parameters of the NMRD Profiles of Hexaaqua Chromium(III) Solutions. The Fit Was Performed as Indicated in the Text

A. Cr(III) pH0 − Model 1

		278 K	298 K	313 K	333 K
r (Å)	2.71				
D (cm^2/s)	(fixed)	1.3×10^{-5}	2.4×10^{-5}	3.4×10^{-5}	5.2×10^{-5}
d (Å)	3.5−4.5 (fixed)				
Δ_t (cm^{-1})[a]	0.10−0.12				
τ_v (s)	6.66×10^{-15} exp(1764/T) 5.16×10^{-15} exp(1705/T)	3.8−2.4 × 10^{-12}	2.5−1.6 × 10^{-12}	1.9−1.2 × 10^{-12}	1.3−0.9 × 10^{-12}
τ_r (s)	$1.07 \cdot 10^{-14}$ exp(2626/T) 9.71×10^{-15} exp(2680/T)	135−149 × 10^{-12}	72−78 × 10^{-12}	47−51 × 10^{-12}	28−30 × 10^{-12}
τ_{M1} (s)	$2.30 \times 10^{-8}/T$ exp(3398/T) $2.07 \times 10^{-8}/T$ exp(3416/T)	17−16 × 10^{-6}	6.9−6.6 × 10^{-6}	3.8−3.6 × 10^{-6}	1.8−1.7 × 10^{-6}
A/h (MHz)	2.35−2.27				

B. Cr(III) pH0 − Model 2

		278 K	298 K	313 K	333 K
r (Å)	2.71 (fixed)				
D (cm^2/s)	(fixed)	1.3×10^{-5}	2.4×10^{-5}	3.4×10^{-5}	5.2×10^{-5}
d (Å)	5.5−6.5 (fixed)				
Δ_t (cm^{-1})[b]	0.11				
τ_v (s)	1.16×10^{-15} exp(2255/T) 1.56×10^{-15} exp(2177/T)	3.9×10^{-12}	2.2−2.3 × 10^{-12}	1.6×10^{-12}	1.0−1.1 × 10^{-12}
τ_r (s)	5.43×10^{-15} exp(2818/T) 4.41×10^{-15} exp(2885/T)	137−142 × 10^{-12}	69−71 × 10^{-12}	44×10^{-12}	25×10^{-12}
τ_{M1} (s)	$1.61 \times 10^{-9}/T$ exp(4221/T) $2.05 \times 10^{-9}/T$ exp(4148/T)	23−22 × 10^{-6}	7.6×10^{-6}	3.7×10^{-6}	1.5×10^{-6}
A/h (MHz)	2.12−2.19				

[a] $\tau_{s0(1)} = 3.1 \times 10^{-10}$, 4.7×10^{-10}, 6.3×10^{-10}, and 8.9×10^{-10} s at 278, 298, 313, and 333 K, respectively. [b] $\tau_{s0(1)} = 2.3 \times 10^{-10}$, 3.8×10^{-10}, 5.4×10^{-10}, and 8.4×10^{-10} s at 278, 298, 313, and 333 K, respectively.

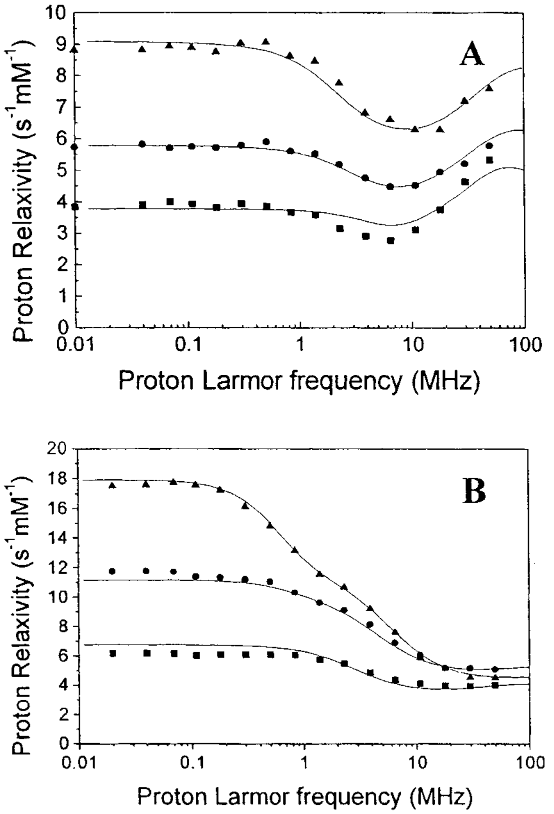

Figure 3. (A) Water proton NMRD profiles of hexaaqua chromium(III) solutions with 60% glycerol and 278 (■), 298 (●), and 313 (▲) K. The lines represent the best fit profiles. (B) Water proton NMRD profiles of hexaaqua chromium(III) solutions at pH 1 and 278 (■), 298 (●), and 313 (▲) K. The lines represent the best fit profiles.

hexaaqua chromium(III) solution in a water/glycerol mixture, 60% w/w, at 278, 298, and 313 K. The profiles are reported in Figure 3A. Again, with increasing viscosity, the increase of relaxivity at high field becomes pronounced, indicating the occurrence of a field-dependent electron relaxation time. In fact, when the viscosity of the solvent is increased by a factor of 10, the molecular motion is slowed about 1 order of magnitude, so that the correlation time τ_c is more sensitive to the electron relaxation time. On the other hand, the latter can increase due to the $\omega_s\tau_v$ dispersion present in the equations for the field dependence of electron relaxation. The fit performed on the R_{1p} data of Cr(III) in the water/glycerol solution at 278, 298, and 313 K provides values of the fitting parameters in reasonable agreement with those obtained from data acquired in water solution. In particular, Δ_t best-fit values were in the range 0.09−0.12 cm^{-1}. To improve the quality of the fits, three values for τ_{M1} at the three temperatures were used as fitting parameters. The values of Δ_t and $A/\hbar$ were imposed to be the same in the two solutions, and the rotational time in the water/glycerol solution was imposed to be 10 times longer than in the water solution, according to the Stokes−Einstein relationship (eq 4). The resulting best fit profiles are reported in Figure 3A as solid lines. From the fit, r is equal to 2.8 Å, and the distance of closest approach d is around 8 Å.

The values of τ_v, which are typically of the order expected for the mean lifetime between collisions of molecules, are consistent with the values theoretically expected and experimentally found for other aqua ions. As for Gd(III), Mn(II), and Fe(III) aqua ions, τ_v increases with viscosity.[27,29,32,50] In fact, since τ_v is related to collisions of solvent molecules with solvated ions, it is expected to be slowed by viscous solvents. From the fit of the profiles acquired in a water−glycerol solution, τ_v is found to be 14, 7.3, and 4.8 × 10^{-12} s at 278, 298, and 313 K, respectively. The value of Δ_t, 0.11 cm^{-1}, is in fair agreement with the reported value of 0.087 cm^{-1} obtained by EPR measurements.[43,51] The low field value obtained for the electron relaxation time is also in good agreement with the value estimated in previous works, equal to 5 × 10^{-10} s at 300

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(50) Melton, B. F.; Pollak, V. L. *J. Phys. Chem.* **1969**, *73*, 3669.
(51) Levanon, H.; Charbinsky, S.; Luz, Z. *J. Chem. Phys.* **1970**, *53*, 3056.

K,[52] as isthe contact coupling constant A/h, previously estimated to be equal to 2 MHz.[52]

The fit shows that r changes somewhat with solution viscosity, thus indicating that glycerol may partly replace water in the coordination sphere. Likewise, the fit indicates that the distance of closest approach for outer-sphere relaxation increases up to 8 Å. The chemical exchange rate was found to be lower than for all other aqua ions, except VO(II); the rate increases with viscosity, the system remaining in a slow exchanging regime as far as the first coordination sphere waters are concerned.

Since the pH could have changed by the dilution with glycerol, profiles for water solution of hexaaquochromium(III) at pH 1 were acquired at 278, 298, and 313 K (Figure 3B). The profiles are very similar to those for pH 0. This ensures that at pH 1, Cr(III) remains hexaaqua coordinated, with substantial hydrolysis beginning only at higher values of pH. The fit, performed by taking for τ_r, τ_v, Δ_t, and $A/\hbar$ the values obtained for the solution at pH 0, provides again a value of 2.72 Å for r and longer values for τ_{M1} (41, 10, and 4 $\times$ 10^{-6} s at 278, 298, and 313 K, respectively) with respect to the pH 0 solution.

Therefore, even if water exchange in the first hydration sphere of Cr^{3+} is very slow,[1] water proton exchange determines a τ_{M1} value of about 6 (pH 0) or 10 (pH 1) $\times$ 10^{-6} s at 298 K. An upper limit for τ_{M2} was instead fixed to the value measured for water exchange in the second hydration sphere, that is about 130 $\times$ 10^{-12} s at 298 K.[11]

Discussion

Critical Analysis of the Relevant Best Fit Parameters. In both models, the calculations were performed by using the equations for nuclear relaxation derived to take into account the different longitudinal and transverse electron relaxation rates characteristic of all electron levels and transitions.[43] No appreciable difference was found by using the simplified approach proposed in ref 44. From the fit, according to Model 2, the electron relaxation rate at room temperature is provided by

$$\tau_{s(1)}^{-1} = 2.3 \times 10^{20}\ \mathrm{s}^{-2}\left[\frac{\tau_v}{1+\omega_S^2\,\tau_v^2} + \frac{4\tau_v}{1+4\omega_S^2\,\tau_v^2}\right]$$

and thus, at low fields $\tau_{s0(1)}^{-1} = (1.1 \times 10^{21}\ \mathrm{s}^{-2})\tau_v$, and at high fields $\tau_{sHF(1)}^{-1} = (4.6 \times 10^{20}\ \mathrm{s}^{-2})/(\omega_S^2\tau_v)$. This demonstrates that indeed $\tau_r < \tau_s$ (see the values reported in Table 1) at low fields, and therefore at all fields, since τ_s increases with increasing field. At 500 MHz and room temperature, for instance, $\tau_s = 2 \times 10^{-8}$ s is obtained. The analysis of the NMRD profiles actually does not provide the value of r, the distance of the water protons from the paramagnetic center, but rather the ratio n/r,[6] where n is the number of coordinated water molecules. However, the value of $n = 6$ for hexaaquachromium(III) is well established from a variety of experimental evidences.

Relevance of the $\boldsymbol{\tau_r}$ Parameter to Assess the Validity of Models 1 and 2. Theoretical considerations predict τ_r to be around 3 $\times$ 10^{-11} s[15,41] and r to be about 2.7 Å[10,11] for the chromium(III) hexaquo complex. The value of r is confirmed by high-resolution X-ray and EXAFS data.[10,11] In our fit using both Models 1 and 2, τ_r results are too large by a factor of 2−3. This value is actually in much better agreement with Model 2. Indeed, the second sphere water molecules are roughly twice as many as the first coordination sphere waters, and thus, the apparent molecular weight of the hydrated ion should be about three times the molecular weight of the hexaaquachromium(III) ion considered in the absence of second sphere water molecules. Moreover, the fact that the rotational time of the hydrated ion is sensitive to the presence of the second sphere waters is an important independent verification that the lifetime of these water molecules, albeit much shorter than that of the first coordination sphere waters, is still longer than τ_r. In other words, a hydrated chromium ion will be able to rotationally reorient several times in solution before a second sphere water molecule leaves the complex, and therefore, the actual tumbling object is the ion with both coordination spheres of water.

Second Coordination Sphere and Existing NMRD Data for Other Hydrated Metal Ions. These observations prompted us to repeat the fits of the NMRD data for Fe^{3+} and VO^{2+} aqua ions by imposing the presence of second coordination sphere waters. The NMRD profiles of these ions show rotational times somewhat larger than was expected for an aquaion ($\tau_{r(Fe)} = 5.3 \times 10^{-11}$, $\tau_{r(VO)} = 4.1 \times 10^{-11}$ s, at 298 K), whereas the value of r is somewhat smaller ($r_{Fe} = 2.62$, $r_{VO} = 2.58$ Å).[32,33] We found that equally good or slightly better fits can be obtained by including the contribution of second sphere water molecules, with distances for the first sphere waters of 2.65−2.7 Å. Therefore, introduction of second sphere waters may also be needed for these other ions. However, the fact that the rotational time increases much less than 3 times the value expected for an hexaaqua ion may suggest that second sphere waters are more labile, i.e., their exchange time is of the order of the rotational time.

Concluding Remarks

We have shown that the ^{1}H NMRD profiles water solutions of the chromium(III) aquaion complex are sensitive to the rotational correlation time of the complex, which is 2−3 times the value expected for an aquaion, and in order to i) obtain a good fit and ii) reconcile τ_r with a structural model, it is necessary to consider the contribution to relaxivity of second-sphere water molecules. The exchange time of the latter is confirmed to be longer than both the diffusional correlation time and the rotational time of the complex, both being around 70 $\times$ 10^{-12} s at room temperature. The resulting model is that of a hydrated chromium(III) ion that reorients as a rigid object carrying both first and second sphere water molecules.

The field dependence of electron relaxation and the exchange rate of first sphere water protons were also obtained.

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Supporting Information Available: Equations useful in the calculation of the paramagnetic relaxation enhancements due to dipolar and contact interactions (eqs S1−S2), in the presence of field dependent electron relaxation rates in the $S = 3/2$ case (eqs S3−S7), and equations for the average electron relaxation rates (eqs S8−S9); equations are also given to relate the paramagnetic relaxation enhancement of coordinated water protons to the experimentally observable solvent proton relaxation enhancements (eqs S10−S12) and to calculate the outer-sphere contribution to relaxation (eqs S13−S19) (5 pages).

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