Electronic Relaxation of the Titanium(III) Hexaaqua Complex Detected by Solvent Water ^{1}H NMRD Spectroscopy

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Introduction

NMRD (nuclear magnetic relaxation dispersion) is a technique that allows the measurement of the nuclear longitudinal relaxation time as a function of the magnetic field.[1-3] In paramagnetic systems the nuclear relaxation time includes contributions from dipolar and contact coupling with the unpaired electrons. The dipolar term depends on a geometric factor, which is defined as $G = \sum_i(n_i/r_i^6)$, where n_i is the number of protons at distance r_i, and on a correlation time that can be the electronic longitudinal or transverse relaxation time or the rotational correlation time. The contact term depends on the magnitude of the hyperfine coupling and on the electronic transverse relaxation time. In favorable cases information on both mechanisms is obtained. We have studied the solvent water ^{1}H NMRD of titanium(III) hexaaqua ions with the aim of obtaining dynamic information through the dipolar contribution to nuclear T_{1M}^{-1} and information on electronic relaxation through the contact contribution to T_{1M}^{-1}. The latter information provides an independent measurement of the electronic relaxation time.

Our attention has been recently focused on the electronic relaxation mechanisms of hexaaqua complexes. The general strategy is to increase the rotational correlation time by increasing the viscosities of the solvent or to measure the contact contribution to relaxation when possible.

We report here that in the case of hexaaquatitanium(III) the contact contribution is measurable from the NMRD profiles. Such a term has been reported to be observed in manganese(II),[4-7] chromium(III),[2,4-6] and oxovanadium(IV)[8] aqua ions, cases in which the electronic relaxation time has been found to depend on the magnetic field. In the case of $Ti(H_2O)_6^{3+}$ we observe that the electronic relaxation time is magnetic field independent between 0.01- and 600-MHz proton Larmor frequency. We discuss these new findings with the focus of electronic relaxation in solution and of available EPR data. The obtained proton unpaired electron hyperfine coupling constant is in excellent agreement with literature data. The water proton exchange rate is estimated from high-field T_2 data.

Experimental Section

$TiCl_3$ was purchased from Merck and used without further purification. HCl (0.5 M) was used to minimize the hydrolysis of the titanium(III) aqua complex. It was reported that the 0.01-1.0 M acid concentration can keep ≥98% titanium(III) aqua complex in the form of $Ti(H_2O)_6^{3+}$.[9] Ti^{3+} concentrations were evaluated from the absorption spectrum using a molar absorbance at 20 100 cm^{-1} of 4.9 M^{-1} cm^{-1}.[10] All the manipulation was done under a N_2 atmosphere to avoid oxidation of titanium(III) to the diamagnetic titanium(IV).

The NMRD profiles were obtained with a Koenig-Brown relaxometer, installed at the University of Florence thanks to an agreement between the latter and the IBM Watson Research Center of Yorktown Heights, NY. Descriptions of the apparatus and the methods of data collection were given elsewhere.[2] The temperature was controlled by surrounding the sample with circulating liquid freon, a perfluorinated hydrocarbon. Its temperature can be stabilized to ±0.2 °C in the range -10 to +35 °C.

The water proton relaxivity measurements at high field were performed using the following spectrometers: at 90 MHz, Bruker CXP 90; at 200 MHz, Bruker MSL 200; at 600 MHz, Bruker AMX 600. The proton spin-lattice relaxation times were measured using the inversion-recovery method, and the proton transverse relaxation times from the relation $T_2 = (\pi\Delta\nu)^{-1}$, where $\Delta\nu$ is the half-height line width. The temperature was controlled using standard variable-temperature equipment provided by spectrometer manufacturers.

Blank solutions containing appropriate amounts of zinc aqua ions usually show negligible difference in T_1^{-1} values with those of pure water,[11] so the net paramagnetic relaxivity rates, T_{1p}^{-1}, were obtained by direct subtraction of the relaxation rates from the solvent, which, in turn, are small and almost constant in the NMRD frequency range. T_{1M}^{-1}, the full paramagnetic relaxation enhancement, was obtained using the following equation:

$$T_{1p}^{-1} = f_M(T_{1M} + \tau_M)^{-1} \qquad (1)$$

where f_M is the molar fraction of the protons sensing the paramagnetic center and τ_M is the residence time.

Results and Discussion

The ^{1}H NMRD profiles expressed as T_{1p}^{-1} (s^{-1} mM^{-1}) of water solutions of $Ti(H_2O)_6^{3+}$ at 5, 20, and 35 °C are shown in Figure 1A. We found that, with increasing temperature, the proton relaxivity decreases. So, the hydrogens of $Ti(H_2O)_6^{3+}$ exchange fast with those of the solvent, and we can reasonably drop the term τ_M in eq 1.[12] Another striking feature of the NMRD profiles of $Ti(H_2O)_6^{3+}$ is that, at all three temperatures, there is only one dispersion for each curve in the NMRD frequency scales, and that the ratio of the relaxation rate at high fields to that at low fields is smaller than 3/10, which is not expected when the through-space interactions between the nuclear and the electronic magnetic moments dominate the relaxivity.[13,14] The dispersion must be an ω_S dispersion (see below); otherwise, if it were an ω_I dispersion, it would give a correlation time of around 2×10^{-8} s, which is unreasonable because of the onset of the rotational correlation time, the value of which has already been well established to be around 3×10^{-11} s at room temperature.[3] This assumed correlation time could not be the electronic relaxation time either.[15] The high relaxivity at low fields indicates that another contribution is present; this can be reasonably ascribed to the scalar interaction

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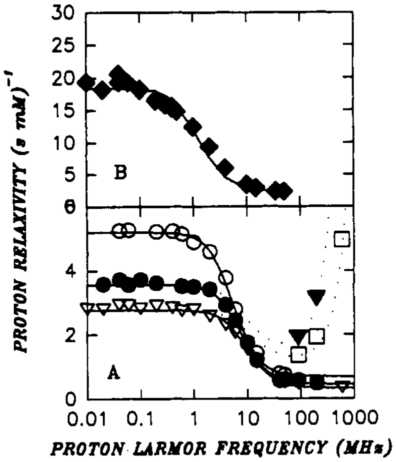

Figure 1. Solvent water ^{1}H NMRD profiles for $Ti(H_2O)_6^{3+}$ in water solution (A) of T_{1p}^{-1} at 5 °C (○), 20 °C (●), and 35 °C (▽) and of T_{2p}^{-1} at 20 °C (▼) and 35 °C (□) and in water solution containing 65% glycerol-d_8 (B) of T_{1p}^{-1} at 20 °C (◆). The curves represent the simultaneous best fit of all data (T_{1p}^{-1}, —; T_{2p}^{-1}, ···) using the Solomon–Bloembergen equations (eqs 2 and 7) including the effect of exchange on T_{2p}^{-1} (eq 8) (see text).

of nuclear magnetic moments with unpaired spin density delocalized at the nuclei themselves.[16,17] Since the electronic relaxation time of $Ti(H_2O)_6^{3+}$ is fast,[15] it is quite possible that both the contact dispersion and the dipolar dispersion superimpose one to the other.

The measured paramagnetic relaxivity always includes the inner-sphere contribution, which comes from the dipolar and the scalar interactions, and the outer-sphere contribution, which arises from the diffusional motion of the solvent near the paramagnetic species.[18-23] This latter contribution can be estimated to be around 10% of the total relaxation rates measured here and thus neglected.[3] The inner-sphere contribution is described by the well-known Solomon–Bloembergen equation:[14,16]

$$T_{1M}^{-1} = \frac{2}{15}\left(\frac{\mu_o}{4\pi}\right)^2\frac{\gamma_N^{\,2}g_e^{\,2}\mu_B^{\,2}S(S+1)}{r^6}[3J(\omega_I) + 7J(\omega_S)] + \frac{2}{3}S(S+1)(A_c/\hbar)^2\frac{\tau_S}{1+\omega_S^{\,2}\tau_s^{\,2}} \quad (2)$$

where the first term represents the dipolar contribution and the second the contact contribution. $J(\omega)$ is the spectral density.

$$J(\omega) = \frac{\tau_c}{1 + \omega^2\tau_c^{\,2}} \quad (3)$$

ω_I and ω_S are the nuclear and the electronic Larmor precession frequencies, respectively. τ_c is the correlation time and is expressed as follows:

$$\tau_c^{\,-1} = \tau_s^{\,-1} + \tau_r^{\,-1} + \tau_M^{\,-1} \quad (4)$$

where τ_s is the electronic relaxation time and τ_r is the rotational correlation time. The other symbols have the usual physical meanings.

Table I. Best Fit Parameters Obtained by Fitting the Data in Figure 1A to the Solomon–Bloembergen Equations

temp (°C)	τ_r (s)	τ_s (s)	σ^2 [a]
5	5.4×10^{-11}	5.7×10^{-11}	0.18
20	3.3×10^{-11}	4.0×10^{-11}	
35	2.3×10^{-11}	3.2×10^{-11}	

$G = 3.7 \times 10^{-14}$ pm^{-6}

$A_c/h = 4.5$ MHz

[a] σ^2 is the sum of the square residues of the minimization of all the points of the three curves with the Solomon–Bloembergen equations.

We turn to fit the data with eq 2 assuming six equivalent inner-sphere water molecules. (This assumption is justified by D_{3d} symmetry of this molecule.[15] Trigonal Jahn–Teller distortions, if present, are assumed to be fast on the NMR time scale.) The fit was performed by multidimensional minimization of the merit function by Powell's method.[24] In principle, we should fit the three curves separately. However, it is taken into consideration that the geometric factor and the hyperfine coupling constant should not vary with temperature. So, we fit all three curves together, in order to reduce the number of independent parameters and to obtain the three τ_r, three τ_s, the geometric factor, and the hyperfine coupling constant. The fit is satisfactory (Figure 1A), and the best fit values are reported in Table I.

The accuracy on the derived parameters is quite good, despite the simultaneous use of the dipolar and the contact terms and the similarity of the obtained τ_r and τ_s values. Although two separate dispersions are not observed, the presence of the contact term is beyond any doubt because the low field/high field relaxivity ratio is much higher than 10/3 at low temperature. The best fit value of the A_c/h parameter is in good agreement with that obtained from isotropic shift measurements of the water proton.[25] The geometric factor, G, when six equivalently coordinated water molecules are assumed, gives an average metal–proton distance of 2.62 Å. The proton–metal distance is in the lower end of the range of expected values.[2,3,8,17,26,30,31] If a 10% outer-sphere contribution is subtracted from the data, the estimated distance increases to 2.67 Å.

We see from Table I that τ_r decreases with temperature as expected from the Stokes–Einstein law,[27,28] which is valid for spherical Brownian particles isotropically rotating in the medium

$$\tau_r = 4\pi\eta a^3/3kT \quad (5)$$

For hexaaqua complexes, τ_r at 25 °C is usually around 3.0×10^{-11} s, and our data are in good agreement with it. These considerations further support the reliability of the fitting procedure. We can now turn to the analysis of the best fit τ_s values with some confidence.

Unlike the hexaaqua systems of some other metal ions, VO^{2+},[8] Mn^{2+},[4-6,29] Cr^{3+},[4-6] and Fe^{3+},[30] the electronic relaxation time *decreases* with increasing temperature. A decrease of the electronic relaxation time with increasing temperature has also been observed in the case of a manganese(III) porphyrin complex.[31] The decrease is very strong at high field. Indeed, in the manganese(III) case, it has been demonstrated that the

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electronic relaxation process is characterized by a modulation of the electron–lattice interaction with a correlation time τ_v of the order of 10^{-11} s. Therefore, τ_s is field dependent starting from about 2 MHz, and the temperature dependence is given by the direct relationship between τ_s and τ_v expected beyond the $\omega_S{}^2\tau_v{}^2$ dispersion. This is not the case for the present system, where the decrease of the electronic relaxation time with increasing temperature is observed at low field. In the case of the manganese(III) porphyrin complex, a small decrease in τ_s at low field could also occur.[31] In that case, it should be due to a strong temperature dependence of the quadratic zero-field splitting.

The present behavior and the τ_s values obtained here are in reasonable agreement with the earlier report from EPR.[15] The relaxation time from line shape analysis of X-band EPR spectra is around 4.4×10^{-11} s at 5 °C.[15] We also learn that the electronic relaxation time is not field dependent up to 600 MHz, since τ_s is comparatively equal to τ_r in this system and thus contributes significantly to the total correlation time: there is no indication that the total correlation time changes in our frequency range.

It has been proposed that the electron in $Ti(H_2O)_6{}^{3+}$ relaxes through an Orbach mechanism,[15] in both the frozen and liquid solutions. Should this be true, then electron relaxation time in solution should obey an equation of the type

$$\tau_s{}^{-1} = \frac{C}{\delta_{0n}{}^2\tau_c}[\exp(\hbar\delta_{0n}/kT) - 1]^{-1} \qquad (6)$$

where $\hbar\delta_{0n}$ is the excitation energy to the first excited states and τ_c here is a mean correlation time for intermolecular fluctuations.[32] C is a constant. Such an equation predicts correctly the present temperature dependence and a field independence of τ_s. Our data confirm, for the first time, this field independence extending over about 5 orders of magnitude in magnetic field up to 14 T.

The Orbach mechanism described by eq 6 implies that τ_c increases with viscosity as τ_r does.[32] The Orbach mechanism[33] in the solid state implies a dependence of $\tau_s{}^{-1}$ on $(v^5\rho)^{-1}$, where v is the velocity of sound and ρ is the density. We have performed a measurement on a solution containing 65% glycerol-d_8 (ρ = 1.17, $v \approx 1800$ m/s[37]) (Figure 1B). Both ρ and v are somewhat larger than those of pure water, suggesting that τ_s should increase about 3 times. The fitting provides a τ_s of 2.6×10^{-10} s, which is about 6 times longer than in water. This finding is thus qualitatively consistent with what is expected from an Orbach mechanism both in solution and in the solid state.

The water proton transverse relaxation rate, $T_{2M}{}^{-1}$, where T_{2M} is defined analogously to T_{1M}, is given by

$$T_{2M}{}^{-1} = \frac{1}{15}\left(\frac{\mu_o}{4\pi}\right)^2\frac{\gamma_N{}^2g_e{}^2\mu_B{}^2S(S+1)}{r^6}[3J(\omega_I) + 13J(\omega_S) + 4\tau_c] + \frac{1}{3}S(S+1)(A_c/\hbar)^2\left[\frac{\tau_s}{1+\omega_S{}^2\tau_s{}^2} + \tau_s\right] \qquad (7)$$

where all the terms have already been defined. The general-formula to relate $T_{2p}{}^{-1}$ to $T_{2M}{}^{-1}$ is

$$T_{2p}{}^{-1} = \frac{f_M}{\tau_M}\,\frac{T_{2M}{}^{-2} + T_{2M}{}^{-1}\tau_M{}^{-1} + (\Delta\omega_M)^2}{(T_{2M}{}^{-1} + \tau_M{}^{-1})^2 + (\Delta\omega_M)^2} \qquad (8)$$

where $\Delta\omega_M$ is the chemical shift difference between the paramagnetic and diamagnetic species and $T_{2p}{}^{-1}$ is also defined in a way similar to $T_{1p}{}^{-1}$.[1] The experimental $T_{2p}{}^{-1}$ between 90 and 600 MHz show a sharp increase with the magnetic field. Since T_1 measurements indicate the field independence of τ_s, this sharp increase can only be due to the chemical exchange contribution to $T_{2p}{}^{-1}$. From eqs 7 and 8 and the estimate of $\Delta\omega_M$ from the hyperfine coupling constant through eq 9,[35] we can calculate the

$$\Delta\omega_M = \frac{A_c}{\hbar}\,\frac{g_e\mu_BS(S+1)}{3\gamma_NkT}\omega_I \qquad (9)$$

τ_M values, which are 4.2×10^{-7} and 1.2×10^{-7} s at 20 and 35 °C, respectively, and then the whole $T_{2p}{}^{-1}$ profiles (see dotted curves in Figure 1A). We noted that the hydrogen exchange rate is substantially faster than the oxygen exchange rate (τ_M = 1.0 × 10^{-5} s[25]). As already noticed in other metal aqua complex systems,[8,36] τ_M of hydrogen may be faster due to the independent exchange with the bulk solution.

With the chemical exchange rates at hand, we examine our assumption for analyzing the ^1H NMRD profiles. Indeed, the chemical exchange rate is much larger than the $T_{1M}{}^{-1}$. It does not substantially affect the proton longitudinal relaxivity.

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