Structures of Dysprosium(III) Triflates in Water, Methanol, and 2-Propanol As Studied by ^{17}O and ^{19}F NMR Spectroscopy

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The structures of $Dy(CF_3SO_3)_3$ in water, methanol, and 2-propanol have been investigated with the use of multinuclear NMR techniques. Dy(III)-induced ^{17}O NMR shifts of the solvent afforded estimates of the average number of inner-sphere solvent molecules. Information on the location of the triflate anion was obtained by longitudinal ^{19}F relaxation rates. The data suggest that the predominant species in the various solvents are $[Dy(H_2O)_8][CF_3SO_3]_3$, $[Dy(CF_3SO_3)_{1-2}(CH_3OH)_6][CF_3SO_3]$, and $Dy(CF_3SO_3)_3$(*i*-PrOH)$_3$. Upon addition of water to solutions of $Dy(CF_3SO_3)_3$ in anhydrous organic solutions the solvent molecules and the triflate anions are expelled from the first coordination sphere of Dy(III) simultaneously.

Introduction

Scandium(III) and lanthanide(III) trifluoromethanesulfonates (triflates) are efficient Lewis acid catalysts in many organic reactions, such as additions of amines to nitriles,[1] Diels−Alder reactions,[2] Friedel−Crafts acylations,[3] Michael additions,[4] nitrations,[5] acetylations of alcohols,[6] and O- and S-glycosylation of sugars.[7] These catalysts are water-tolerant and, consequently, can be applied both in organic and in aqueous solutions. For reactions in organic solution, reuse is possible after recovery of the rare earth triflate by treatment of the reaction mixture with water followed by concentration of the aqueous layer. It has been reported that the choice of the solvent can influence the selectivity of reactions.[8] Solvation of the Ln(III) cation and coordination of counterions may be important factors in this respect.

We are engaged in an investigation on Meerwein−Ponndorf−Verley reductions of ketones,[9,10] and therefore, we are particularly interested in the structure of lanthanide complexes in 2-propanol, which is the commonly used solvent (and hydrogen donor) in this reaction. As a first step to get more insight into the structures of the complexes involved in these reactions, we have investigated the solvation of Dy(III) triflates in 2-propanol using multinuclear magnetic resonance techniques. In these studies, we exploited paramagnetic properties of the Dy(III) ion, which gives rise to induced chemical shifts and relaxation rates of resonances of ligand nuclei in its proximity.[11,12] For comparison studies with methanol and water as the solvents were included in this investigation. Solution structural investigations of lanthanide triflates in the latter solvents using other techniques have been reported.[13] To get an impression of the strength of the interaction between the metal ion and the solvate and counterion, we also included competition experiments with mixtures of an organic solvent and water.

Experimental Section

Materials. Lanthanide triflates were prepared from the corresponding oxides and trifluoromethanesulfonic acid.[14] They were dried at 150 °C under vacuum for one night prior to use. All solvents used in the NMR experiments were analytical grade. The organic solvents were stored over zeolite KA.

NMR Measurements. NMR analyses were carried out on a Varian Inova-300 spectrometer.

The measurements with D_2O as solvent were carried out with frequency locking of the spectrometer on Deuterium. All other solvents used were not deuterated. No frequency locking of the spectrometer was applied during measurements with these solvents. ^{17}O NMR spectra were measured using 10 mm sample tubes. Before and after each shift measurement on a sample containing $Dy(CF_3SO_3)_3$, the sample was replaced by a sample containing only the concerning solvent or mixture of solvents in the same composition. Then, with this sample, the diamagnetic positions of the concerning resonances were determined. The shift of the resonance(s) due to drift of the magnetic field appeared to be negligible. ^{17}O parameters were determined by fitting of the observed resonances with Lorenzian line functions using the standard Varian software. Downfield shifts are denoted as positive. The chemical shifts measured were corrected for bulk magnetic susceptibility effects

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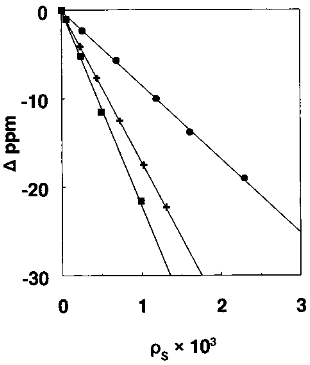

Figure 1. Plots of the Dy(III)-induced ^{17}O shift versus the molar ratio Dy(III)/solvent (ρ_S) for Dy(CF_3SO_3)$_3$ in methanol (+), 2-propanol (●), and D_2O (■) at 50 °C. The shifts for the former two solvents are corrected for bulk magnetic susceptibility effects (see text).

due to the presence of a paramagnetic ion using eq 1 (see Results and Discussion). ^{19}F NMR measurements were carried out using 5 mm sample tubes. Longitudinal relaxation rates, $1/T_1$, were obtained by the inversion recovery method.[15]

Molecular modeling was performed with the use of the HyperChem program (version 3, MM+ force field, HyperCube Inc., Gainsville, FL).

Results and Discussion

Solvation of Dy(CF_3SO)$_3$. Upon stepwise addition of Dy(CF_3SO_3)$_3$ to 2-propanol or methanol at 50 °C, the ^{17}O resonance of the solvent shifted toward lower frequencies. The induced shift showed a linear relationship with the molar ratio Dy(III)/solvent (ρ_S, correlation coefficients $>$0.999), which shows that the exchange of the solvent between the Dy(III) complex and the bulk is rapid on the ^{17}O NMR time scale. Since the measurements were carried out without frequency locking of the spectrometer, the induced shifts (Δ) contain a contribution due to the change of the bulk magnetic susceptibility upon addition of Dy(CF_3SO_3)$_3$ (Δ_χ). This contribution was calculated with eq 1.[16]

$$\Delta_\chi = \frac{4\pi c}{3T}\left(\frac{\mu_{\text{eff}}}{2.84}\right)^2 \times 10^3 \tag{1}$$

Here c is the concentration of Dy(III) in mol L^{-1}, T is the temperature, and μ_{eff} is the effective magnetic moment of Dy(III) (10.6 μ_B). Figure 1 displays the Dy(III) induced shifts as a function of ρ_S, after correction for Δ_χ. For comparison, the Dy(III)-induced shifts for D_2O are included in this figure.

The induced shift of a nucleus of a ligand upon coordination to a paramagnetic lanthanide(III) ion arises via three mechanisms: the diamagnetic (Δ_d), the contact (Δ_c), and the pseudocontact mechanisms (Δ_p).[11]

$$\Delta = \Delta_d + \Delta_c + \Delta_p \tag{2}$$

Induced ^{17}O NMR shift measurements with the diamagnetic La(III) triflate showed that the diamagnetic shifts for these systems are negligible. Previously, it has been shown that the Dy(III)-induced ^{17}O NMR shift of a Dy(III)-coordinated oxygen atom (Δ_O) is almost completely of contact origin ($\geq$85%) and that this shift is almost independent of the nature and the stoichiometry of the concerning complex.[11] This can be ascribed to the low sensitivity of the hyperfine coupling constant to structural changes. For example, the induced ^{17}O NMR shifts of Dy(III)-bound carboxylate and hydroxyl oxygens of glycolate differ by only 7%.[17]

In the present case, the Dy(III)-induced ^{17}O NMR shift measurements were performed at $\rho_S < 2.5 \times 10^{-3}$. At those low concentrations, the induced shift of a solvent ^{17}O nucleus is given by eq 3.[18]

$$\Delta = n\rho_s\Delta_O \tag{3}$$

The slopes of the straight lines in Figure 1 are, consequently, determined by n and Δ_O. It is known that the hydration number of Dy(III) in solutions of $DyCl_3$ or Dy(ClO_4)$_3$ in water is eight.[19,20] The slopes of the lines for the Dy(III)-induced water shifts for $DyCl_3$ and Dy(CF_3SO_3)$_3$ were identical within the experimental error, which indicates that the hydration number of Dy(III) in aqueous solutions of Dy(CF_3SO_3)$_3$ is eight as well. From the latter slopes and using eq 3 with $n = 8$, the value of Δ_O was calculated to be -2725 ppm. Then, with this value and the slopes of the lines for 2-propanol and methanol, average Dy(III) solvation numbers of 3.1 ± 0.2 and 6.2 ± 0.4 were calculated for these solvents, respectively.

Previously, we have found, in an analogous way, that the solvation number of Dy(III) for $DyCl_3$ in CD_3OD is 5.[21] Three Cl^- ligands complete the first coordination sphere, which is in good agreement with conclusions in the literature based on other techniques.[22,23] The higher solvation number obtained for Dy(CF_3SO_3)$_3$ suggests that not all triflate anions are in the first coordination sphere of Dy(III). The low solvation number of Dy(CF_3SO_3)$_3$ in 2-propanol can be ascribed to the steric bulk of the 2-propanol ligand.

Location of the Triflate Counterion. With the aim to get more information on the Dy(III)-coordination of the triflate anions in the various solvents, longitudinal ^{19}F relaxation rate measurements were carried out on 0.04 M solutions of Dy(CF_3SO_3)$_3$. We chose for this approach, since ^{17}O NMR measurements on the triflate anion would require ^{17}O labeling and Dy(III)-induced ^{13}C and ^{19}F shifts are rather small. The contact contribution is decreasing rapidly with the number of bonds separating the paramagnetic center and the nucleus under study, whereas the pseudocontact contribution is reduced due to exchange of the triflate anion between several locations with respect to the magnetic axes of the system.[11]

The longitudinal ^{19}F relaxation rates obtained are compiled in Table 1. The large differences in magnitude of these rates indicate that large differences in triflate coordination exist between solutions in water and those in organic solvents. Comparison of the relaxation rates of Dy(CF_3SO_3)$_3$ with those of the diamagnetic La(CF_3SO_3)$_3$ complexes shows that the diamagnetic contribution to the total relaxation rate is negligible.

Two paramagnetic contributions should be envisaged: (i) a dipolar one ($1/T_{1,\text{dip}}$) caused by through space interactions due to the random fluctuations of the electronic field of Dy(III)[24,25]

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Table 1. Longitudinal ^{19}F relaxation rates (s^{-1})[a] of 0.04 M solutions of $Ln(CF_3SO_3)_3$ (Ln = Dy, La) at 50 °C and 282.4 MHz; Comparison with Calculated Values for Inner-Sphere Coordinated Triflate

	experimental		calcd for Dy-bound	
solvent	$Dy(CF_3SO_3)_3$	$La(CF_3SO_3)_3$	$CF_3SO_3^-$	n_{triflate}[c]
water	7.36	0.15	124−184	0
methanol	76	0.3	143−186	1.2−1.8
2-propanol	245	*b*	222−329	2.2−3

[a] Accuracy ±3%. [b] Measurement impossible due to low solubility. [c] Number of Dy(III) bound $CF_3SO_3^-$ ligands. For calculation, see text.

and (ii) the Curie contribution ($1/T_{1,\mathrm{Curie}}$), which arises from the interaction of the nuclear spin with the thermal average of the electronic spins (eq 4).[26,27]

$$\frac{1}{T_{1,\mathrm{p}}} = \frac{1}{T_{1,\mathrm{dip}}} + \frac{1}{T_{1,\mathrm{Curie}}} \tag{4}$$

Dy(III) has a very short electronic relaxation time ($T_{1e} \approx 10^{-13}$ s). If zero-field splitting effects are neglected,[28] $1/T_{1,\mathrm{p}}$ can be given by the simplified Solomon−Bloembergen equation, eq 5.[24,25]

$$\frac{1}{T_{1,\mathrm{dip}}} = \frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_I^2 \mu_{\mathrm{eff}}^2 \beta^2}{r^6} T_{1e} \tag{5}$$

Here, $\mu_0/4\pi$ is the magnetic permeability of a vacuum, γ_I is the magnetogyric ratio of the nucleus under study, μ_{eff} is the effective magnetic moment of Dy(III), β is the Bohr magneton, and r is the distance between the nucleus under study and Dy(III). The Curie spin contribution can be expressed as[26,27]

$$\frac{1}{T_{1,\mathrm{Curie}}} = \frac{6}{5}\left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{\gamma_I^2 H_0^2 \mu_{\mathrm{eff}}^4 \beta^4}{(3kT)^2 r^6}\right)\left(\frac{\tau_R}{1 + \omega_I^2 \tau_R^2}\right) \tag{6}$$

where H_0 is the magnetic field strength, k is the Boltzmann constant, T is the temperature, τ_R is the rotational tumbling time of the complex, and ω_I is the Larmor frequency of the nucleus under study. The Curie contribution can often be neglected for small molecules, but not for Dy(III), because this lanthanide has a relatively large effective magnetic moment. From eqs 5 and 6 it can be calculated that $T_{1,\mathrm{Curie}}^{-1}/T_{1,\mathrm{dip}}^{-1} = 0.9 \times 10^{10}\tau_R$ for the conditions applied in this study. Since τ_R is usually between 10 and 100 ps for small molecules, it can be concluded that the contribution due to the Curie mechanism is substantial for Dy(III).

With the use of eqs 5 and 6, ^{19}F relaxation rates were calculated for models representing the triflate anion in the first and in the second coordination sphere of the Dy(III) ion. Values of T_{1e} of lanthanides other than Gd(III) are usually not very dependent on the structure of bound ligands.[29,30] Therefore, we have used here the value reported for the Dy(III) aquo ion ($T_{1e} = 2.99 \times 10^{-13}$ s).[30] Good estimations for τ_R can be obtained with the Debye−Stokes−Einstein equation (eq 7).

$$\tau_R = \frac{4\pi a^3 \eta}{3kT} \tag{7}$$

Here, a is the effective radius of the complex and η is the viscosity of the solvent. The values of a were evaluated with molecular models in which the Dy(III) ion was coordinated to three triflate ions and to an essentially arbitrarily chosen number of solvent molecules (6 for water, methanol, and 3 for 2-propanol). For η, the viscosities of the pure solvents were taken. In this way, τ_R values of 27.1, 29.4, and 146.1 ps were estimated for water, methanol, 2-propanol, and acetonitrile, respectively.

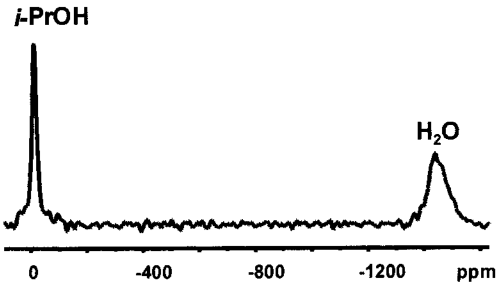

Figure 2. ^{17}O NMR spectrum of a solution of 80 mg of $Dy(CF_3SO_3)_3$ in 3.7 mL of 2-propanol, after addition of 2 μL of 10% ^{17}O-labeled water at 50 °C and 40.7 MHz.

A search in the Cambridge Crystallographic Database afforded structures of 13 Ln(III) complexes with triflate anions in the first coordination sphere of the Ln(III) ion. The total number of triflate anions was 27 (see Supporting Information). The orientations of these triflate ligands with respect to the Ln(III) ions were very similar. All triflates were bound in a monodentate fashion through sulfonate oxygens with averaged positions given by ∠Ln−O−S = 150 ± 10° and ∠Ln−O−S−C = 183 ± 31°. All triflate anions were in a staggered conformation. Ln−F distances were corrected for the differences between the ionic radius of Dy(III) and the other Ln(III) ions, using the data for 9-coordinated Ln(III) ions reported by Shannon,[31] to give the following average distances: Dy−F(1) = 4.82 ± 0.18 Å, Dy−F(2) = 5.00 ± 0.18 Å, and Dy−F(3) = 5.99 ± 0.07 Å. With these distances and eqs 5−6, Dy(III)-induced relaxation rates were calculated. The calculated relaxation rates are very sensitive for small variations in distances, the ranges of calculated values for the distances mentioned above are included in Table 1.

Ln(III)−F distances of triflates in the second coordination sphere are much larger. For example, the $[Ln(H_2O)_9](CF_3SO_3)_3$ complexes have Ln(III)−F distances of 6.3−7.5 Å in the crystal structures.[32,33] Equations 5 and 6 also apply for a triflate in the second coordination sphere, assuming that the residence time of a triflate in the second coordination sphere is long compared with the time required for a triflate ion and the Dy(III) complex to diffuse past each other. With the use of these equations, it can then be calculated that Dy(III) induced relaxation rate enhancements are about 15 s^{-1} for a ^{19}F nucleus of triflate in the second coordination sphere. For the organic solvents, these distances will be larger and then the relaxation rate enhancements become negligible. Assuming that the exchange between triflates in the first and second sphere is fast on the ^{19}F NMR time-scale, the experimental relaxation rate ($1/T_{1,\mathrm{exp}}$) is the

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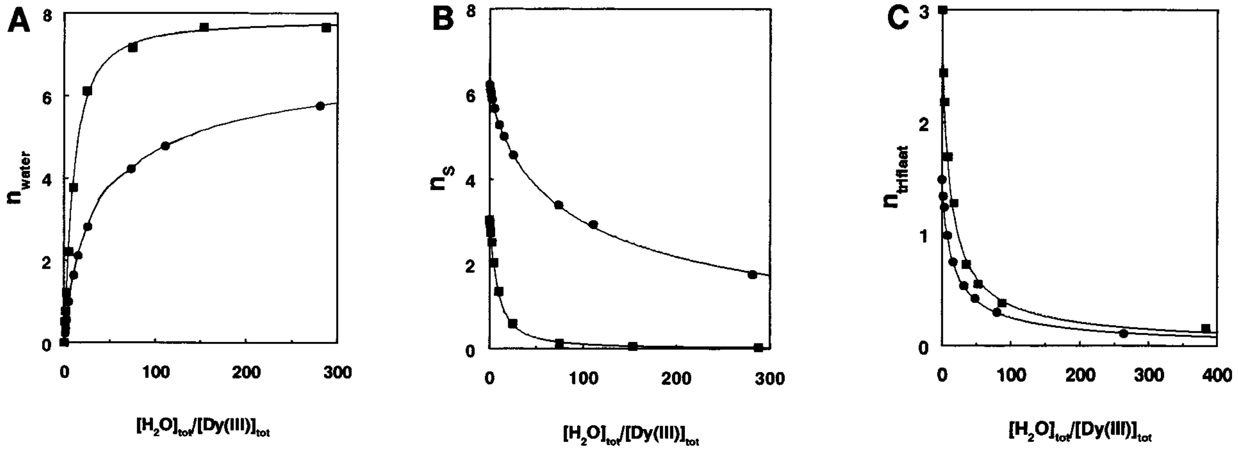

Figure 3. Number of Dy(III)-coordinated water molecules (A), organic solvent (B), and triflate anions (C) as a function of the molar ratioH_2O/Dy(III) for solutions in 2-propanol (■) and methanol (●).

weighted average of the relaxation rates in the first and the second coordination sphere (see eq 8).

$$\frac{1}{T_{1,\mathrm{exp}}} = \frac{f_1}{T_{1,1}} + \frac{f_2}{T_{1,2}} \tag{8}$$

Here $1/T_{1,1}$ and $1/T_{1,2}$ are the relaxation rates of a triflate nucleus in the first and second coordination sphere, respectively, and f_1 and f_2 are the molar fractions of the corresponding triflate ligands. The total number of triflate ions per Dy(III) cation is three, thus $f_1 = n_{\mathrm{triflate}}/3$, where n_{triflate} is the number of triflate molecules in the first coordination sphere of Dy(III). Since $1/T_{1,2}$ is negligible, it follows that

$$n_{\mathrm{triflate}} = \frac{1/T_{1,\mathrm{exp}}}{1/T_{1,1}} \times 3 \tag{9}$$

The obtained data are compiled in Table 1. These numbers have to be considered with some caution, because of the uncertainties in τ_R and T_{1e}. It is clear, however, that the triflate ligands are predominantly in the first coordination sphere in 2-propanol solution. According to the results of the ^{17}O NMR studies, the first coordination sphere of this complex is completed by 3 2-propanol ligands. A similar stoichiometry, Ln(O-*i*-Pr)$_3$(X)$_3$, has been found in the solid state for Ln = Sm and X = Br,[34] and for Ln = La, Ce and X = I.[35] Dinuclear structures with two μ-Cl bridges have been reported for complexes of $LnCl_3$ in 2-propanol in the solid state.[36−38] However, structures with triflate as bridging anions do not play a role in the solutions of $Dy(CF_3SO_3)_3$ investigated in this study, because dimerization would have been reflected in much larger longitudinal^{19}F relaxation rate enhancements than have been observed. In methanol solution, the triflate ligands compete with methanol for coordination in the first coordination sphere of Dy(III). Under the conditions applied, on the average one triflate anion enters the first coordination sphere. As was already shown by ^{17}O NMR (see above), triflate is not coordinated to Dy(III) in aqueous solution. The Dy(III)-induced ^{19}F relaxation rate enhancement is smaller than should be expected for coordination in the second coordination sphere analogous to the crystal structure. Apparently, the triflate anion is, on the average, at a larger distance from Dy(III).

Influence of Added Water on the Solution Structure of $Dy(CF_3SO_3)_3$ in Organic Solvents. To study the effect of added water on the coordination of Dy(III) in solutions of $Dy(CF_3SO_3)_3$ in methanol and 2-propanol, water was added stepwise to 0.04 M samples (3 mL) at 50 °C. For the first portions (up to 10 μL) 10% ^{17}O labeled water was applied. After addition of 2 μL of water the ^{17} O NMR water signal became observable at an extremely large negative shift, for example at −2780 ppm with respect to the diamagnetic position for 2-propanol (see Figure 2). Upon a further increase of the amount of water the negative induced shifts of both the water and the solvent resonance decreased. After each addition, the ^{17}O chemical shifts of water and of the solvent (methanol or 2-propanol) were determined. From the Dy(III)-induced shifts the number of Dy(III)-bound water and solvent molecules were calculated using the procedures outlined above. In another experiment, the effect of stepwise addition of water on the longitudinal ^{19}F relaxation rates was measured (for data see Supporting Information). From these data, the number of inner-sphere triflate anions was calculated. The resulting stoichiometric data are depicted as a function of the molar ratio H_2O/Dy(III) in Figure 3.

It can be seen that water expels the organic solvent molecules and simultaneously triflate anions from the first coordination sphere of Dy(III). The preference of Ln(III) ions for coordination of water rather than of triflate has been concluded previously from conductivity studies.[39] From the shape of the curves in Figure 3, it can be concluded that the affinity of Dy(III) for water is larger in 2-propanol than in methanol. The present data do not allow an accurate thermodynamic description of the many equilibria involved in these competition experiments. A crude measure of the affinity of Dy(III) for water in the solvents could be obtained, by assuming that the affinity of Dy(III) for water is independent of the presence of other ligands, which is not very unreasonable in view of the almost pure electrostatic interactions between lanthanide ions and ligands.[13] In other words, it is assumed that the stepwise formation constants of the consecutive water additions are equal. Then Dy(III) can be considered to have eight equivalent coordination sites for water

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and an apparent equilibrium constant K can be defined:

$$K = \frac{[S(H_2O)]}{[S][H_2O]} \tag{10}$$

Here [S] is the "concentration" of free water donor sites and $[S(H_2O)]$ is the "concentration" of occupied sites. Fitting of the data with eq 9 and the appropriate mass balances afforded K values of 5.1 ± 0.3 and 0.59 ± 0.07 mol L^{-1} for 2-propanol and methanol, respectively.

Conclusions

NMR Spectroscopy is a useful tool to study the solvation of salts of paramagnetic ions. The induced shifts give information on the number of lanthanide-bound solvent molecules. In the present case combination of these techniques and ^{19}F NMR spectroscopy afforded a picture of the solution structures of $Dy(CF_3SO_3)_3$. In water Dy(III) is coordinated by 8 water molecules and all triflate anions are in the outer sphere. However, in less polar solvents including 2-propanol and methanol, the triflate anions enter the inner-coordination sphere. The data suggest that the predominant species in 2-propanol is $Dy(i\text{-}PrOH)_3(CF_3SO_3)_3$. In methanol triflate is partly in the inner-sphere and partly in the outer-sphere. Addition of water to a solution of $Dy(CF_3SO_3)_3$ in one of these organic solvents results in the replacement of both the Dy(III)-coordinated solvent molecules and triflate anions by water molecules. The coordination of anions and of solvent molecules may play an important role in catalysis with lanthanide complexes, where the substrate molecules have to compete with both the solvent and the counterions for coordination to the Ln(III) cation.

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Supporting Information Available: Listings of crystal structure data on Ln(III)-bound triflates retrieved from the Cambridge Crystallographic Data Base, and ^{17}O NMR shifts and ^{19}F longitudinal relaxation rates of samples of $Dy(CF_3SO_3)_3$ in 2-propanol, methanol, and with added water. This material is available free of charge via the Internet at http://pubs.acs.org.

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