# 57. Variable Temperature Multinuclear NMR. Investigation of Dimethylformamide Exchange on the Octakis (*N, N*-dimethylformamide)-thulium (III) Ion

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## *Summary*

The rate of DMF exchange on $[Tm(DMF)_8]^{3+}$ has been determined by $^1H$- and $^{13}C$-NMR. linebroadening techniques. $^1H$-NMR. yields the following solvent exchange parameters; $\Delta H^* = 33.2$ ($\pm 0.5$) kJ mol$^{-1}$, $\Delta S^* = 9.9$ ($\pm 2.4$) J K$^{-1}$ mol$^{-1}$ and $k$ (200 K) $= 2.94$ ($\pm 0.09$) $\times 10^4$ s$^{-1}$, whilst results from $^{13}C$-NMR. are similar. No evidence, by $^{35}Cl$-NMR., was found of contact ion-pair formation when the perchlorate salts were used.

**Introduction.** - The rate of water exchange on the lanthanide aquo-ions has only been established in the case of $Gd^{3+}$ ($k$ (298 K) $= 10.6 \times 10^8$ s$^{-1}$) [1] [2] and lower limits for the other heavy ions were set forth in early $^{17}O$-NMR. studies [3]. A large body of indirect evidence [4] suggests that there is a change in coordination number (nine to eight) across the series with the early lanthanides exhibiting nine-coordination in aqueous solution and probably methanol [5] as well. $^1H$-NMR. solvation studies [6] and $^{17}O$-shift studies [3], however, have been unable to provide support for the suggestions and controversy still exists.

Due to a lack of direct experimental data in the area of solvent exchange on the tripositive lanthanide ions, our knowledge of the kinetics of ligand-substitution processes on these ions has consequently remained rather nebulous. This work seeks to extend the scope of the solvent-exchange studies to non-aqueous solvents, and in particular, to *N,N*-dimethylformamide (DMF). The solvent nuclei under NMR. observation are the formyl H- and the carbonyl C-atom, these atoms being selected because of their proximity to the paramagnetic ion when the solvent is coordinated (giving thus larger shifts [7]) and because of their favourable NMR. characteristics (their resonances being, *e.g.* far from other ones and their spin having both value ½).

**Theory.** - The *Swift & Connick* approach [8] was utilized to determine kinetic parameters. The transverse NMR.-relaxation time $T_2$, and the chemical shift (relative to that of pure solvent), $\Delta\omega_s$ (rad s$^{-1}$) for the free or coalesced signal are dependent on various parameters as follows [9]:

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$$\frac{1}{T_{2r}}=\frac{1}{P_m}\left(\frac{1}{T_2}-\frac{1}{T^0_{2A}}\right)=\frac{1}{\tau_m}\left[\frac{T_{2m}^{-2}+(T_{2m}\tau_m)^{-1}+\Delta\omega_m^{2}}{(T_{2m}^{-1}+\tau_m^{-1})^2+\Delta\omega_m^{2}}\right]+\frac{1}{T_{2os}} \tag{1}$$

$$\Delta\omega_r=\frac{\Delta\omega_s}{P_m}=\frac{\Delta\omega_m}{(\tau_m/T_{2m}+1)^2+\tau_m^{2}\Delta\omega_m^{2}}+\Delta\omega_{os} \tag{2}$$

where $T^0_{2A}$ is the relaxation time of the pure solvent, $T_{2m}$ is the relaxation time of the coordinated solvent in the absence of exchange, $P_m$ is the mole fraction of coordinated solvent, $\tau_m$ is the residence time of a coordinated solvent molecule and $\Delta\omega_m$ is the chemical shift between free and coordinated solvent in the absence of exchange. In order to take into account outer-sphere relaxation and shift effects experienced by the free solvent even in the absence of exchange due to long range dipolar interaction with the paramagnetic centre, the outer-sphere shift ($\Delta\omega_{os}$) and relaxation-time ($T_{2os}$) terms are incorporated. The inner- and outer-sphere relaxation times are assumed to have a simple temperature dependence given by [9]:

$$\frac{1}{T_{2m}}=A_m\exp\left(\frac{E_m}{RT}\right) \tag{3}$$

$$\frac{1}{T_{2os}}=A_{os}\exp\left(\frac{E_{os}}{RT}\right) \tag{4}$$

From transition-state theory, $\tau_m$ may be related to the pseudo-first-order reaction rate constant, $k$ and temperature by the *Eyring* equation:

$$k=\frac{1}{\tau_m}=\frac{k_BT}{h}\exp\left(\frac{\Delta S^*}{R}-\frac{\Delta H^*}{RT}\right) \tag{5}$$

Finally, the temperature dependence of $\Delta\omega_m$ can be formulated as a power series [9-11] in $1/T$ but only the first three terms will be considered.

$$\Delta\omega_m=\frac{B_1}{T}+\frac{B_2}{T^2}+\frac{B_3}{T^3} \tag{6}$$

**Experimental Part.** - *Materials.* DMF *(Fluka, puriss.)* was purified by fractional distillation at reduced pressure. Benzene and acetonitrile were purified by conventional methods [12]. $^{13}$C-enriched benzene (90%, *Stohler*) was used as received. All liquid reagents were stored in dark bottles over previously activated 4A molecular sieves. A sample of anhydrous lanthanum perchlorate was donated by Professor *J.-C. G. Bünzli* of this institute.

*Preparation of* $[Ln(DMF)_8](ClO_4)_3$ (Ln = La [13], Tm, Lu). The hydrate lanthanide perchlorates were initially prepared from the reaction of the oxide (99.9%, *Research Chemicals*) with 70% perchloric acid *(Merck)*. 2.0 g of the hydrated salt was stirred with triethylorthoformate (*Fluka*, 10 g) at 60° for about one hour according to the method of *Van Leewen & Groeneveld* [14]. When DMF (2.4 g) was added to the dehydration mixture, an oil was produced which was subsequently cooled to induce crystallization. The crystals were filtered under vacuum in a glove-box (water < 6 ppm), washed with sodium-dried ether and pumped down on a vacuum line to remove volatile impurities. Yields of the hygroscopic products were essentially quantitative. The metal content of the complexes was checked by EDTA titration and/or by an ion-exchange technique [15].

*NMR. measurements.* Solutions for NMR. study were prepared by weight in the glove-box. In the case of $^{1}$H-NMR. samples the internal reference was 1% *w/w* benzene unless otherwise specified whereas for $^{13}$C-NMR. samples it was *ca.* 0.4% *w/w* $^{13}$C-enriched benzene.

$^{1}$H-NMR. spectra were obtained on *Bruker CXP-200* and *WP-60* instruments operating at 200 MHz and 60 MHz respectively with an internal deuterium lock. Precision-bore coaxial NMR. tubes *(Wilmad)* were employed. The 2 mm o.d. inner tube contained the sample whilst the outer tube incorporated the lock substance ($CD_2Cl_2$ or $C_2D_2Cl_4$). $^{13}$C-NMR. spectra (10 mm tubes) were recorded on the *CXP-200* at 50.3 MHz with $^{1}$H-broad-band decoupling but without lock. For both $^{1}$H- and $^{13}$C-NMR. experiments, shimming of the spectrometer was executed using the free induction decay of the sample. Inhomogeneity was estimated from the width of the benzene resonance. $^{35}$Cl-NMR. spectra were run at 19.6 MHz on the *CXP-200* with 10 mm sample tubes without lock.

Sample temperatures were measured before and after spectral accumulation by substituting the sample with a calibrated platinum resistance [16] immersed in a solution of identical composition, or by substitution with methanol or ethylene glycol samples. The temperature was found to be independent of the rate of sample rotation within experimental error (± 0.5 K).

$T_2$ measurements were made from the full width at half height of the NMR. absorption resonance, or, alternatively (for narrow $^{13}$C-signals) by using a *Carr-Purcell-Meiboom-Gill* pulse sequence in cases where the linewidth of the benzene resonance was greater than 10% of that of the carbonyl C-atom. Chemical shifts were measured relative to the internal reference but ultimately relative to pure DMF. The temperature dependence of the pure DMF linewidths and the internal reference-DMF shifts were established from the appropriate 'blank' samples and taken into account for subsequent calculations.

Tables of $^{1}$H- and $^{13}$C-NMR. shifts and $1/T_{2r}$ (measured in the presence and absence of $Tm^{3+}$) as a function of temperature are available from the authors.

**Results and treatment of data.** - As a first part of this study, the tendency of $ClO_4^-$ to form contact ion-pairs with the lanthanide ions in various solutions was assessed using variable temperature $^{35}$Cl-NMR. The measured $^{35}$Cl-NMR. linewidths and solution compositions are presented in *Table 1*. It is clear from the data that, in the case of acetonitrile solutions, significant ion-pairing exists [17-20]. By contrast, there appears to be no detectable ion-pairing in DMF solution once some allowance is made for inhomogeneity and/or viscosity effects. *Stengle et al.* [17] [18] have made similar conclusions for alkali metal and alkaline earth cations in these solvents. In DMF the lanthanide perchlorates dissociate as 1:3 electrolytes [21] and hence for the $Tm^{3+}$ concentration range covered here *(vide infra)* no

Table 1. *Variation of the $^{35}$Cl-NMR. linewidth* (Hz) *of some perchlorates in DMF and acetonitrile with concentration and temperature*

| Solution composition | Linewidth (Hz) | | | Reference |
|---|---|---|---|---|
| | 305 K | 273 K | 243 K | |
| 0.193 m $La^{3+}$ in DMF[a] | 2.0 | - | 3.9 | e |
| 0.0568 m $La^{3+}$ in DMF[a] | 1.6 | - | 2.4 | e |
| 0.0797 m $Lu^{3+}$ in DMF[b] | 1.7 | - | 3.4 | e |
| 0.201 m $La^{3+}$ in $CH_3CN$[a] | 261 | 315 | 428 | e |
| 0.0546 m $La^{3+}$ in $CH_3CN$[a] | 206 | - | - | e |
| 0.5 M $Li^{+}$ in $CH_3CN$ | 20[c] | - | - | [17] |
| 0.5 M $Na^{+}$ in $CH_3CN$ | 6[c] | - | - | [17] |
| 0.1 M $Mg^{2+}$ in $CH_3CN$ | 51[c] | - | - | [17] |
| 0.5 M $Mg^{2+}$ in DMF | $<5$[c,d] | - | - | [17] |

[a]) The solute was anhydrous $La(ClO_4)_3$. [b]) The solute was $[Lu(DMF)_8](ClO_4)_3$. [c]) Temperature of probe *ca.* 30°. [d]) Magnetic field inhomogeneity was 5 Hz. [e]) This work.

significant contact ion-pair formation is expected. Indeed, the marked increase in the dielectric constant of DMF with decrease in temperature [22] should prevent association even at very low temperatures (*ca.* 200 K).

The calculation of kinetic parameters by NMR. line-broadening analysis requires a knowledge of $P_m$ and, therefore, of the coordination number of the metal ion in solution. For highly paramagnetic ions (such as $Tm^{3+}$) it is rarely directly measurable with sufficient precision so that resort must be made to indirect methods [23]. One of these involves the addition of a non-coordinating diluent which would enable accurate integration of free and coordinated solvent resonances by reducing signal size disparities under slow exchange conditions. *Figure 1* shows the $^1$H-NMR. spectrum of a $[Tm(DMF)_8](ClO_4)_3/DMF/CD_2Cl_2$ solution mixture at 185 K. At this temperature the coordinated formyl $^1$H-resonance is too broad to be detected but integration may be conveneniently carried out utilizing the other resonances. Such an integration yielded a solution coordination number of 7.7±0.2 which is close to that in the solid state. Thus, eight would seem to represent the minimum and most likely coordination number in the absence of diluent.

*Figures 2* and *3* show the inverse temperature dependence of $\ln(1/T_{2r})$ and $\Delta\omega_r$ if eight-coordination is assumed. It is evident from the experimental data that

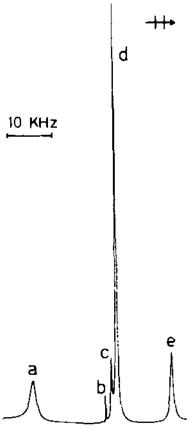

Fig. 1. *360-MHz-$^1$H-NMR. spectrum of a $[Tm(DMF)_8](ClO_4)_3/DMF/CD_2Cl_2$ solution* ($P_m$ = 0.478) *at 185 K.* The resonances a-e are assigned as follows[a]): *a*) $N-CH_3$ *trans* to formyl proton of coordinated DMF; *b*) residual proton resonance of incompletely deuteriated $CD_2Cl_2$; *c*) formyl proton of free DMF; *d*) both $N-CH_3$ resonances of free DMF, and *e*) $N-CH_3$ *cis* to formyl proton of coordinated DMF. The spectrum was run on a *Bruker WH-360* spectrometer with an internal deuterium lock.

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[a]) The resonances due to the $N-CH_3$ groups of coordinated DMF (a and e) were assigned on the basis of two criteria. Firstly, a crossover of exchange-averaged $N-CH_3$ resonances, which occurs at about room temperature, means that at even higher temperature, the coalesced $N-CH_3$ signal involving a is in fact the upfield $N-CH_3$ signal and this, presumably, corresponds to the upfield (*trans* to formyl) $N-CH_3$ signal of very dilute paramagnetic or diamagnetic DMF solutions [26]. Secondly, under very slow exchange conditions the broadest coordinated $N-CH_3$ resonance would be expected (for dipolar relaxation) to belong to the group closest to the paramagnetic centre (*trans* to the formyl proton), which from *Figure 1*, is evidently a.

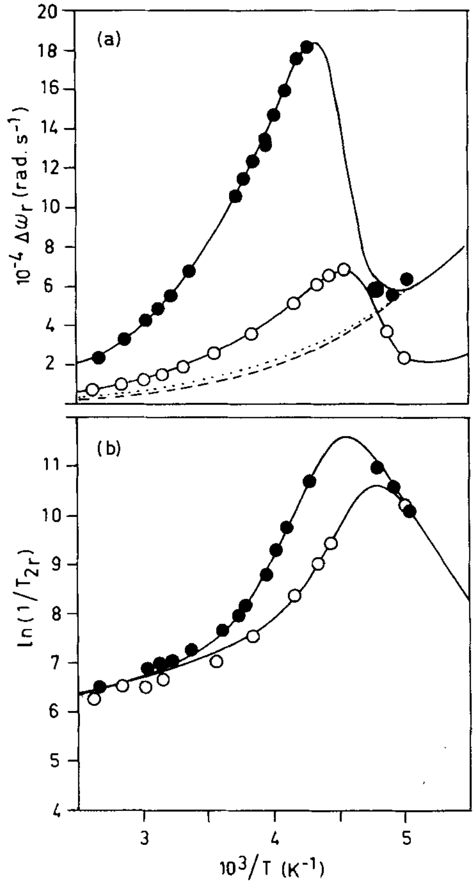

Fig. 2. *Variable temperature $^1$H-NMR. data for [Tm(DMF)$_8$](ClO$_4$)$_3$ in DMF.* a) Chemical shifts as a function of inverse temperature: ● = 200-MHz-normalized shifts $\Delta\omega_r$ (2 solutions; $P_m = 0.0250$ and 0.0125); ○ = 60-MHz-normalized shifts $\Delta\omega_r$ ($P_m = 0.0126$); ———, calculated-$\Delta\omega_r$ curves; .........., calculated-200-MHz-$\Delta\omega_{os}$ curve from *Equation 7;* ------, calculated-200-MHz-$\Delta\omega_{os}$ curve from *equation 9. b)* $T_2$ values as a function of inverse temperature: ● = 200-MHz-normalized $T_{2r}$ ($P_m = 0.0250$ and 0.0125); ○ = 60-MHz-normalized $T_{2r}$ ($P_m = 0.0126$); ———, calculated-ln(1/$T_{2r}$) curves. The internal shift reference was 1% *w/w* benzene.

the very slow exchange condition is not satisfied even at the lowest temperature accessible. A proper evaluation of the outer-sphere broadening is therefore impossible but since the dipolar effect falls off sharply with distance ($r^6$) [24] it is probably negligible in relation to the total broadening. Supporting evidence for this conclusion comes from the inherently narrow linewidth of the internal reference which shows only a small predictable variation with temperature. Therefore, in the treatment of data, the $T_{2os}$ term was neglected. In the case of the outer-sphere shift term, $\Delta\omega_{os}$, which manifests itself under slow exchange conditions, it is clearly neither negligible (the dipolar shift [24] is expected to depend on $r^{-3}$) nor extensively

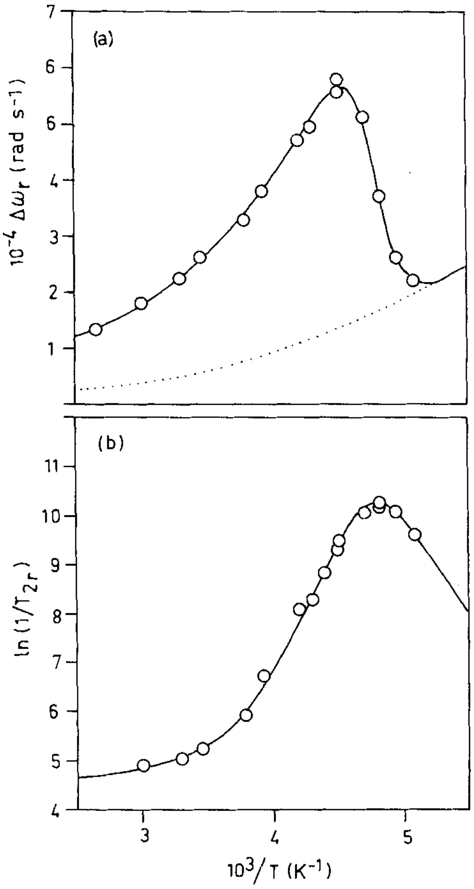

Fig. 3. *Variable temperature $^{13}C$-NMR. data for $[Tm(DMF)_8](ClO_4)_3$ in DMF. a)* Chemical shifts as a function of inverse temperature: ○ = 50.3-MHz-normalized shifts $\Delta\omega_r$ ($P_m = 0.0486$); ———, calculated-$\Delta\omega_r$ curve; .........., calculated-$\Delta\omega_{os}$ curve from *Equation 7. b)* $T_2$-values as a function of inverse temperature: ○ = 50.3-MHz-normalized $T_{2r}$ ($P_m = 0.0486$). The internal shift reference was 0.4% *w/w* $^{13}C$-enriched benzene.

well defined (*Fig. 2a* and *3a*). However, if it is assumed that the temperature dependence of $\Delta\omega_{os}$ is directly proportional to that of $\Delta\omega_m$, then a 'compensatory' proportionality constant, $C_1$, may be introduced in the least-squares fit to allow for the long range effect. Thus,

$$\Delta\omega_{os} = C_1\Delta\omega_m = C_1\left(\frac{B_1}{T} + \frac{B_2}{T^2} + \frac{B_3}{T^3}\right) \tag{7}$$

In general,

$$\Delta\omega_{os} = \Delta\omega'_{os}(\mathrm{DMF}) - \Delta\omega'_{os}(\mathrm{Ref.}) \tag{8}$$

where $\Delta\omega'_{os}$(DMF) is the shift of free DMF (induced by the paramagnetic ion) relative to that of pure DMF and $\Delta\omega'_{os}$(Ref.) is the corresponding shift of the reference. Unfortunately, it is not possible to directly measure the temperature dependence of any of these three quantities in *Equation 8* over the whole temperature range in the absence of bulk susceptibility data. In order to assist in the clarification of the situation, two internal references, viz. benzene and nitromethane were used in a $^1$H-NMR. study. The fast exchange $\Delta\omega_r$ values calculated with nitromethane as reference were slightly lower (approximately 4%) than the corresponding $\Delta\omega_r$ values using benzene. In the slow exchange region, $\Delta\omega_r (=\Delta\omega_{os})$ was clearly smaller for nitromethane. Using *Equations 1, 2, 3, 5, 6* and *7* and optimizing the eight parameters ($A_m$, $E_m$, $\Delta H^*$, $\Delta S^*$, $B_1$, $B_2$, $B_3$ and $C_1$) in a simultaneously weighted¹) non-linear least-squares fit of 200 and 60 MHz²). $^1$H-NMR. data, it was found that all parameters except $C_1$ were independent of the choice of reference. For benzene, $C_1 = 0.17$ whilst for nitromethane, $C_1 = 0.12$. Intuitively, it might be predicted that the temperature dependence of $\Delta\omega_{os}$ would follow that of $\Delta\omega_m$ (as above) or else that of $\Delta\omega'_{os}$ (Benzene) $-$ $\Delta\omega'_{os}$ (Nitromethane)³), a quantity which can be readily measured. Allowing for the latter possibility with

$$\begin{aligned}\Delta\omega_{os} &= C_2\,(\Delta\omega'_{os}(\text{Benzene}) - \Delta\omega'_{os}(\text{Nitromethane}))\\ &= C_2\left(\frac{B'_1}{T} + \frac{B'_2}{T^2} + \frac{B'_3}{T^3}\right)\end{aligned} \tag{9}$$

where $B'_1$, $B'_2$ and $B'_3$ are previously determined constants and $C_2$ now replaces $C_1$ in the eight-parameter least-squares fit, it was found that the derived $\Delta H^*$ and $\Delta S^*$ values were very close to the ones derived using *Equation 7*. This can be seen from *Table 2*. Similar arguments may be proposed for the $^{13}$C-NMR. study. Consequently, the $^1$H- and $^{13}$C-$\Delta\omega_r$ data in *Figures 2a* and *3a* pertain only to benzene reference and the final results in *Table 2* computed using *Equation 7*. The calculated $\Delta\omega_r$ and $\ln(1/T_{2r})$ curves are represented in *Figures 2* and *3*. The temperature dependencies of $\Delta\omega_{os}$ as determined from *Equations 7* and *9* are also shown in *Figures 2a* and *3a*.

**Discussion.** - As this paper represents one of the few reported studies of solvent exchange on a lanthanide ion, comparisons with other lanthanide systems are very

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¹) In principle, the weight of each observation should be given by $w_i = 1/\sigma_i^2$ where $\sigma_i$ is the usually unknown standard deviation of the i-th observation. Since the $1/T_{2r}$ values are expected to have similar relative errors, they were treated in logarithmic form with equal weights. The $\Delta\omega_r$ values should have similar absolute errors and were, therefore, equally weighted [9]. For the combined 200 MHz/60 MHz $^1$H-NMR. fit there are two data sets for each frequency, giving a total of four representative standard deviations which need to be determined. In practice, the following procedure was employed. Approximate weights for each data set were initially introduced, and, after a preliminary fit, a root-mean-square deviation of the experimental and calculated points for each set was calculated. This value was set equal to the standard deviation of the data set whereby new weights could be assigned. The fit was then repeated using the revised weights.

²) The value of $1/T_{2m}$ was assumed to be field-independent. This should be the case for dipole-dipole induced broadening in the extreme narrowing condition provided the electron spin relaxation time is short and field-independent [24]. No detectable field effec on $T_{2m}$ was observed at high temperatures.

³) The temperature dependence of $\Delta\omega'_{os}$(Benzene) and that of $\Delta\omega'_{os}$(Nitromethane) should be directly proportional and hence directly proportional to their difference.

Table 2. *Derived NMR. and kinetic parameters*

| | H-Atom[a,b]) From *Eqn. 7* | H-Atom[a]) From *Eqn. 9* | C-Atom[b]) From *Eqn. 7* |
|---|---|---|---|
| $\Delta H^*$ [kJ mol$^{-1}$] | 33.18 (±0.5) | 33.56 | 32.32 (±1.0) |
| $\Delta S^*$ [J K$^{-1}$ mol$^{-1}$] | 9.85 (±2.4) | 11.70 | 3.3 (±4.5) |
| $k$ (298 K) [s$^{-1}$] | $3.1 (\pm 0.3) \times 10^7$ | 3.3 | $2.0 (\pm 0.3) \times 10^7$ |
| $k$ (200 K) [s$^{-1}$] | $2.94 (\pm 0.09) \times 10^4$ | 2.93 | $2.2 (\pm 0.1) \times 10^4$ |
| $A_m$ [s$^{-1}$] | 68 (±17) | 69 | 27 (±29) |
| $E_m$ [kJ mol$^{-1}$] | 7.0 (±0.7) | 7.0 | 4.2 (±2.7) |
| $B_1$ [rad s$^{-1}$ K] | $3.8 (\pm 0.5) \times 10^7$ | 3.3 | $8.3 (\pm 2.8) \times 10^6$ |
| $B_2$ [rad s$^{-1}$ K$^2$] | $-3.0 (\pm 0.3) \times 10^{10}$ | −2.7 | $-4.6 (\pm 1.6) \times 10^9$ |
| $B_3$ [rad s$^{-1}$ K$^3$] | $7.1 (\pm 0.4) \times 10^{12}$ | 6.7 | $1.1 (\pm 0.2) \times 10^{12}$ |
| $C_1$ | 0.171 (±0.004) | | 0.26 (±0.02) |

[a]) Combined 200 MHz/60 MHz fit. [b]) The errors represent one standard deviation.

limited. The calculated DMF exchange rate constant at 298 K *(Table 2)* is significantly less than the water exchange rate constant at 298 K for the Tm(III) aquo-ion [25] ($k$(298 K) = $1.4 \times 10^8$ s$^{-1}$), the Gd(III) aquo-ion [1] [2] ($k$(298 K) = $10.6 \times 10^8$ s$^{-1}$), and the remaining waters in the Gd-PDTA$^-$ complex ($k$(298 K) = $3.3 \times 10^8$ s$^{-1}$) [1]. This result is in accord with a general trend, namely, that for the vast majority of metal ions the overall rate of non-aqueous solvent exchange, and in particular, DMF exchange, is lower than that of water exchange. The sign and magnitude of $\Delta S^*$ has, in the past, given useful mechanistic information for closely related solvent exchange systems [9], but in the present case the small positive $\Delta S^*$ cannot be considered diagnostic of mechanism. However, for the exchange of small solvent molecules on the relatively large tripositive lanthanide ions a moderately facile interchange process could be anticipated to be operative.

To obtain further insight into the DMF exchange process further variable temperature NMR. work and variable pressure experiments are in progress with other members of the lanthanide series.

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