Multinuclear Magnetic Resonance Study of the Complexation of Lanthanide(III) Cations with Tetrahydropyran-2-methanol *

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The complexation of lanthanide(III) ions in tetrahydropyran-2-methanol (thpm) and in thpm–water mixtures has been investigated using ^{139}La, ^{35}Cl, ^{17}O and ^{13}C shift and relaxation measurements. The ligand thpm binds in a didentate manner, forming a 2:1 complex containing inner-sphere chlorides, when used as the sole solvent. The location of the gadolinium(III) ion with respect to the thpm ligand in the $[Gd(thpm)_2]^{3+}$ complex, as determined from ^{13}C longitudinal relaxation-rate measurements, confirmed the didentate binding of thpm. Lanthanide(III) ions bind D_2O preferentially in thpm–D_2O mixtures.

An interesting synthetic route to ether carboxylates is an O-alkylation of α,β-unsaturated dicarboxylates with compounds containing hydroxyl group(s) mediated by multivalent metal ions. The metal ions act as templates and contribute to the reaction by activation of the hydroxyl group(s) upon co-ordination. Thus new ligands have been synthesised by the addition to maleate of *e.g.* glycolate, glyoxylate, malate, tartrate, glycerol, *etc.* in aqueous alkaline slurry (pH >11) in the presence of larger than stoichiometric quantities of Ca^{II}.[1–4] Part of our research interest in recent years has been focused on the improved synthesis, the kinetic and mechanistic study of this reaction and of the complexes present in solution using lanthanide, aluminium and titanium ions as catalysts or promoters.[5–9]

The O-alkylation addition of polyols to maleate in aqueous media occurs in competition with the addition of water, the extent of which will depend on the ability of the hydroxyl group(s) of the polyol to form a complex by displacement of water molecules from the inner co-ordination sphere of the metal ions.

As a preliminary to the study of O-alkylation with cyclic sugars we have investigated tetrahydropyran-2-methanol (thpm) and tetrahydrofurfuryl alcohol (thfa) as simple models for the pyranose and furanose forms, respectively. The results of O-alkylation of maleate with thpm, thfa and some related compounds, mediated by La^{III}, will be reported separately. This paper deals with a multinuclear NMR spectroscopic study, in combination with molecular mechanics calculations, of the complexation of multivalent metal ions in thpm (Fig. 1) and in thpm–water mixtures.

The tripositive lanthanides constitute the longest series of chemically similar metal ions. The steric requirements of the ligands determine the geometry of their complexes because lanthanide–ligand bonds are predominantly electrostatic in nature. In addition, La^{III} and Lu^{III} are diamagnetic while the other lanthanide(III) ions are paramagnetic. Hence the effects of lanthanide(III) ions on both the chemical shifts and the relaxation times of the different nuclei of organic ligands can be translated into information on the chelation of the ligand, and the type, stoichiometry and geometry of the complexes in solution.

Results and Discussion

Solvation of $LnCl_3$ *in thpm.*—Results from previous research show that whereas lanthanide(III) ions are completely solvated in aqueous solutions of $LnCl_3$ (<2 mol dm^{-3}),[10–15] there is inner-sphere Ln–Cl bonding in organic solvents like methanol, acetonitrile, acetone, nitromethane, tetrahydrofuran and dimethylformamide, which display lower nucleophilicity than does water towards metal ions.[10,11,15–17] However, the didentate ethylene glycol was found to be a stronger ligand than water for lanthanide(III) ions and no inner-sphere Ln–Cl bonding was observed in its $LnCl_3$ solutions.[9] The solvation of $LnCl_3{\cdot}xH_2O$ by thpm in thpm–D_2O mixtures was therefore investigated, using ^{139}La, ^{35}Cl and ^{17}O NMR spectroscopy.

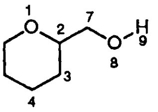

Fig. 1 Numbering of nuclei in thpm used in this study

Plots of ^{139}La and ^{35}Cl chemical shifts (δ) as a function of % (v/v) thpm are shown in Fig. 2(*a*). All the signals measured were Lorentzian. The increase in ^{139}La chemical shifts as water is replaced by thpm is small up to 60% thpm (6.8 ppm) and thereafter rises rapidly to a value of δ 70.5 in 90% thpm. The linewidth of the signal increased concomitantly and there is no detectable signal above 90% thpm. The ^{35}Cl chemical shifts increased likewise to δ 7.2 in 60% thpm and δ 95 in 100% thpm. This downfield trend in chemical shifts is evidence of a change in the average lanthanum(III) and Cl^- co-ordinating species.[18] Small ^{139}La and ^{35}Cl shifts (*ca.* 10 ppm) are expected when inner-sphere co-ordination is absent as reported for $LaCl_3$ solutions in water[11,13] and ethylene glycol (*e.g.* δ −19 and 7 for ^{139}La and ^{35}Cl, respectively at 350 K),[9] while large shifts are true for inner-sphere complexes in methanol (*e.g.* δ 293 and 167 for ^{139}La and ^{35}Cl, respectively at 305 K).[18] We conclude that there are La–Cl inner-sphere complexes present at higher thpm concentrations.

The predominant relaxation mechanism of ^{139}La and ^{35}Cl (spin quantum number $I > \frac{1}{2}$) in solution involves the interaction of their nuclear quadrupole moment (Q) with the electric field gradient (q) at the nucleus. Usually the extreme-narrowing conditions apply (rapid tumbling, $\omega_0\tau_c \ll 1$, where ω_0 is the resonance frequency) and the resonance signals are Lorentzian, thus the relaxation rates are given by[19] equation (1)

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{10}\pi^2\frac{(2I+3)}{I^2(2I-1)}\left(\frac{e^2qQ}{h}\right)^2\left(1+\frac{\eta^2}{3}\right)\tau_c = \pi\Delta\nu_{\frac{1}{2}} \quad (1)$$

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* *Non-SI unit employed:* St = 10^{-4} m^2 s^{-1}.

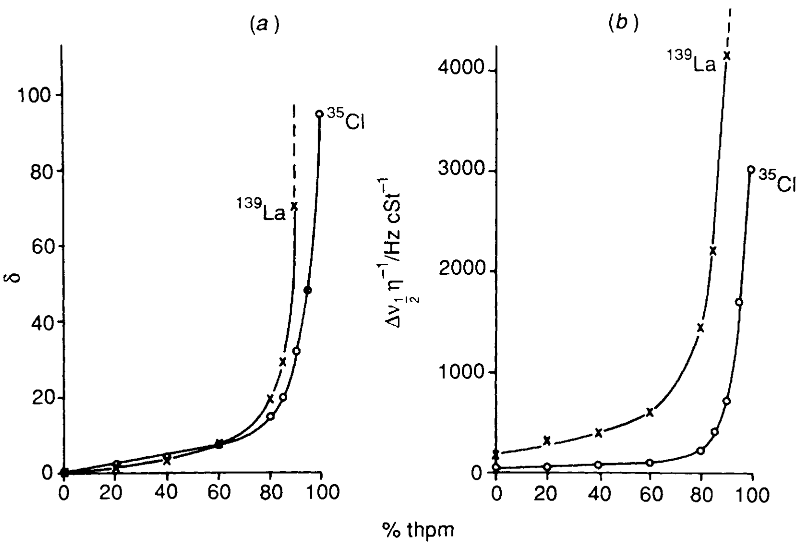

Fig. 2 Plots of ^{139}La and ^{35}Cl chemical shifts (*a*) and viscosity-corrected linewidths (*b*) *versus* % (v/v) thpm in D_2O–thpm solutions containing 0.1 mol dm^{-3} $LaCl_3 \cdot 7H_2O$ at 353 K. The viscosities were 0.450, 0.714, 1.152, 1.791, 2.604, 2.706, 2.816, 2.937 and 3.040 cSt for 0, 20, 40, 60, 80, 85, 90, 95 and 100% thpm, respectively

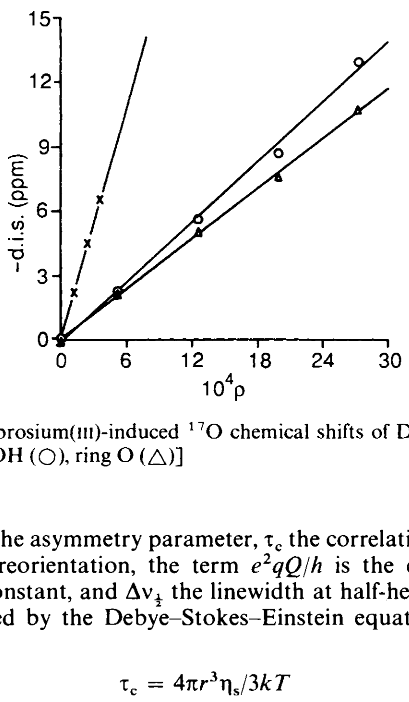

Fig. 3 Dysprosium(III)-induced ^{17}O chemical shifts of D_2O (×) and thpm [CH_2OH (○), ring O (△)]

where η is the asymmetry parameter, τ_c the correlation time for molecular reorientation, the term e^2qQ/h is the quadrupole coupling constant, and $\Delta\nu_{\frac{1}{2}}$ the linewidth at half-height; τ_c can be estimated by the Debye–Stokes–Einstein equation (2), by

$$\tau_c = 4\pi r^3 \eta_s / 3kT \qquad (2)$$

assuming that the species are rigid spheres in motion,[12,20] where η_s is the solution viscosity, *r* the radius and *k* the Boltzmann constant.

The magnitude of the field gradient due to the counter ion is strongly dependent on the interionic distance; therefore solvent-separated ion pairs give rise to line broadening which is negligible when compared with the effect of ions in contact. However, changes in τ_c also affect the linewidth and obscure the effect of a change in *q*. For the case of simple systems in dilute solutions, if we assume that τ_c is governed by the same factors which influence a mobile sphere in a viscous medium, then it will be proportional to the viscosity of the solution. Therefore, the linewidths ($\Delta\nu_{\frac{1}{2}}$) of ^{139}La and ^{35}Cl were corrected for the viscosity. Hence the formation of an inner-sphere La–Cl complex (contact ion pairs) should be observable as a strong increase in $\Delta\nu_{\frac{1}{2}}/\eta_s$. The $\Delta\nu_{\frac{1}{2}}/\eta_s$ values of ^{35}Cl [Fig. 2(*b*)] increase slowly up to 60% thpm and thereafter rise steeply to a value of 3023 Hz cSt^{-1} in 100% thpm. The $\Delta\nu_{\frac{1}{2}}/\eta_s$ values of ^{139}La follow the same trend, increasing to a value of 4176 Hz cSt^{-1} in 90% thpm. The inference is that while La–Cl and La–thpm inner-sphere co-ordination are insignificant below 60% thpm, there are increasing interactions above 60% thpm. In addition, the large $\Delta\nu_{\frac{1}{2}}/\eta_s$ values indicate the presence of very asymmetric species in solution. A similar trend was observed in methanol though smaller in magnitude.[18] In ethylene glycol, where no inner-sphere La–Cl complexes exist, the $\Delta\nu_{\frac{1}{2}}/\eta_s$ values were found to be 875 and 380 Hz cSt^{-1} for ^{139}La and ^{35}Cl, respectively.[9]

The absence of a detectable ^{139}La signal above 90% thpm is attributed to the formation of highly asymmetric inner-sphere La–Cl complexes, co-ordinated to the larger thpm molecules, with larger radii. The asymmetric charge distribution around the ^{139}La and ^{35}Cl nuclei in solution results in enhanced electric field gradients which cause increased quadrupolar relaxation rates. The point of rapid increase in the values of δ and $\Delta\nu_{\frac{1}{2}}/\eta_s$ for ^{35}Cl seems to lag behind those for ^{139}La. This is probably due to the $\Delta\nu_{\frac{1}{2}}$ of the ^{139}La NMR signals being dependent on co-ordination with both thpm and Cl^- while the $\Delta\nu_{\frac{1}{2}}$ of the ^{35}Cl NMR signals are predominantly dependent on co-ordination with La^{III}.

Dysprosium(III)-induced shifts (d.i.s.) of the ^{17}O resonances of oxygen-containing ligands provide valuable information on the oxygen complexation sites of ligands as well as on the stoichiometry of the complex. The d.i.s. mechanism is predominantly of contact origin, hence significant induced shifts are only observed for oxygens directly co-ordinated to the paramagnetic dysprosium(III) nucleus. The d.i.s. of each bound ^{17}O nucleus is constant, almost independent of the nature of the ligand in question and also of other ligands present co-ordinated to the Dy^{III}.[21] The ^{17}O nuclei showed fast ligand exchange on the NMR time-scale and linear plots (Fig. 3) of the upfield d.i.s. *versus* the dysprosium(III)/ligand molar ratios (ρ) for D_2O and thpm (correlation coefficients >0.999) were obtained. The slopes correspond to *n*Δ, where *n* is the number of bound oxygens and Δ is the shift of a bound ^{17}O. Since very low concentrations ($\rho < 3 \times 10^{-3}:1$) of Dy^{III} were used the assumption made was that the average dysprosium(III) species present in D_2O are solvated by nine D_2O molecules.* Extrapolation of

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* The hydration of lanthanide(III) ions is a subject of controversy. Merbach and co-workers[22] concluded from neutron diffraction difference studies that the co-ordination number of Dy^{III} is eight for 0.3 and 1 mol dm^{-3} acidified solutions of $DyCl_3$ and $Dy(ClO_4)_3$ in D_2O.

Table 1 Solvation of Dy^{III} as deduced from Dy^{III}-induced ^{17}O NMR shifts at 353 K

	Dy^{III}-induced shifts[a] (ppm)			Bound O atoms[b]		
		thpm			thpm	
System	D$_2$O	OH	O	D$_2$O	OH	O
D$_2$O	−17 631			9		
thpm	−86[c]	−4670	−3862	0.3	2.4	2.0
D$_2$O–thpm[d] (1:1 v/v)	−17 435	−125	−60	8.9	0.06	0.03

[a] Extrapolated to ρ = 1:1, where ρ is the molar ratio of Dy^{III} added as DyCl$_3$·6H$_2$O to the relevant ligand. The relative errors are less than 1%. [b] Average number per Dy^{III}. See text for calculations. [c] Observed after addition of 1 μl of 10% ^{17}O-enriched water (see text). [d] 87:13 molar ratio.

Table 2 Experimental[a] and calculated relaxation rates for the system Gd–thpm

Carbon nucleus	thpm ($\times 10^{-5}$ s^{-1}) exptl.[c]	thpm ($\times 10^{-5}$ s^{-1}) calc.[d]	thpm–D$_2$O[b] ($\times 10^{-3}$ s^{-1}) exptl.[e]	thpm–D$_2$O[b] ($\times 10^{-3}$ s^{-1}) calc.[f]
2	0.152	0.149	0.622	0.623
6	0.118	0.120	0.568	0.566
7	0.221	0.219	0.902	0.892
3	0.040	0.036	0.408	0.404
5	0.035	0.033	0.407	0.395
4	0.026	0.025	0.377	0.379

[a] Extrapolated to ρ = 1:1. [b] 1:1 v/v. [c] ρ = (0–1.15) × 10^{-4}:1. [d] Calculated for Gd^{III}–O^8 distance of 0.242 nm, Gd^{III}–O^8–C^7 108.7° and Gd^{III}–O^8–C^7–C^2 −64.2°. [e] ρ = (0–8.24) × 10^{-4}:1. [f] Calculated assuming 68% didentate and 32% monodentate species for Gd^{III}–O^8 0.2508 nm, $T_{1\text{inter}}$ = 0.36 s, Gd^{III}–O^8–C^7 60°, Gd^{III}–O^8–C^7–C^2 60 and 180° and $k = 0.9 \times 10^{-53}$.

the d.i.s. of D$_2$O to ρ = 1:1 and dividing by 9 gives the bound shift of −1959 ppm for each oxygen donor site (see Table 1). The value at ρ = 1:1 for the ring oxygen in thpm is −3862 ppm, which when divided by −1959 ppm gives an average of two ring-oxygen atoms of thpm per Dy^{III}. Likewise the average number of hydroxyl oxygens of thpm per Dy^{III} is 2.4 (Table 1). Thus thpm binds in a didentate manner and forms a 2:1 complex with Dy^{III}. The results also suggest that the hydroxyl group of thpm is more strongly co-ordinated to Dy^{III} than its ring oxygen. The amount of water in the samples was too low to be observable by ^{17}O NMR spectroscopy in natural abundance. However, after addition of 1 μl of 10% ^{17}O-enriched water to a sample of 40.4 mg DyCl$_3$·6H$_2$O in 4 cm^3 thpm a water ^{17}O signal could be observed at δ −86. The average number of bound waters per Dy^{III} in this sample is estimated to be only 0.3, using the procedure described above. The combined results from the ^{139}La, ^{35}Cl and ^{17}O NMR data indicate that [Ln(thpm)$_2$Cl$_3$] is the predominant complex species present in dilute solutions of LnCl$_3$ in thpm.

The order of affinity of Ln^{III} is D$_2$O > Cl$^-$ > thpm, which is confirmed by the competition experiment with a mixture of thpm and D$_2$O (1:1 v/v) shown in Table 1. The results show that Dy^{III} binds D$_2$O preferentially. Since, in this case, the bound shift for the hydroxyl group of thpm is twice that of the ring oxygen, probably thpm is partly present bound in a monodentate fashion to Dy^{III} in the mixture.

Lanthanide(III)*-induced* ^{13}C *Relaxation Measurements and Determination of Complex Geometry*.—Gadolinium(III)-induced relaxation-rate enhancement data are particularly suitable for elucidation of the geometry of ligands in the proximity of Ln^{III}. Since Gd^{III} has the longest electronic relaxation times among Ln^{III}, the relaxation rates of ligand nuclei in its complexes are very large (> 10^3 s^{-1}).[23] Hence ^{13}C relaxation-time measurements are carried out at low Gd^{III}/L molar ratios (ρ ≤ 10^{-3}:1), whereby Gd^{III} will be mainly present in its highest liganded state GdL$_m$ (m = 2 for thpm). Assuming that the mean residence time of thpm in the gadolinium(III) complex is short with respect to the longitudinal relaxation time [T_1(GdL$_m$)], then the measured relaxation rate ($1/T_{1\text{obs}}$) can be expressed as[24–26] in equation (3) where $1/T_{10}$ is the relaxation rate at ρ = 0. So a

$$1/T_{1\text{obs}} = [m\rho/T_1(\text{GdL}_m)] + (1/T_{10}) \qquad (3)$$

plot $1/T_{1\text{obs}}$ *versus* ρ should be linear with slope m/T_1(GdL$_m$), which can be related to the molecular structure as[24–26] in equation (4) where r is the distance between Gd^{III} and the ^{13}C

$$1/T_1(\text{GdL}_m) = (k/r^6) + (1/T_{1\text{inter}}) \qquad (4)$$

nucleus, k a constant, and $1/T_{1\text{inter}}$ the contribution of intermolecular interactions to the relaxation (proportional to the amount of Gd^{III} added).

The relaxation rates of the ^{13}C nuclei in thpm were measured at six different gadolinium(III) concentrations [ρ = (0–1.152 × 10^{-4}:1)] and a linear relationship between $1/T_{1\text{obs}}$ and ρ was observed. The slope values [$2/T_1$(GdL$_m$)] obtained, displayed in Table 2, indicate that co-ordination of Gd^{III} to thpm occurs predominantly near O^1 and O^8. This was confirmed by fitting the $2/T_1$(GdL$_m$) values to those calculated using equation (4). The geometry of thpm in the complex used in the fitting procedure was generated by Allinger MM2 force-field calculations[27] assuming a $^5C_2$ conformation with an equatorial hydroxymethyl group. Of the nine possible rotamers that with O^1–C^2–C^7–O^8 56.12° and C^2–C^7–O^8–H^9 −50.69° was selected as the most likely conformation of thpm in the complex. The location of Gd^{III} with respect to the ligand was varied and the ^{13}C longitudinal relaxation rates for different locations then calculated using equation (4) until an optimum fit was obtained; k was used as a scaling factor between the observed and calculated values. The goodness of the fit between calculated and observed relaxation enhancements, expressed in equation (5) as the agreement factor (*RF*),[28,29,*] was 0.0235, which is excellent.

$$RF = \left(\frac{\sum_{i=1}^{n} w^i\{[1/T_1(\text{GdL}_m)] - (1/T_1)_{\text{calc}}\}^2}{\sum_{i=1}^{n} w^i[1/T_1(\text{GdL}_m)]^2}\right)^{\frac{1}{2}} \qquad (5)$$

The calculated and the experimental longitudinal relaxation rates (Table 2) are identical within limits of experimental error. The optimised values for this minimum were $T_{1\text{inter}}$ = 0.016 s, Gd^{III}–O^8 0.242 nm, Gd^{III}–O^8–C^7 108.7° and Gd^{III}–O^8–C^7–C^2 −64.2°, whereas $k = 2.10 \times 10^{-53}$. The coordinates were then utilised to calculate a Gd^{III}–O^1 distance of 0.254 nm, confirming that didentate complexation occurs as depicted in Fig. 4.

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[*] w^i was taken as $(\sigma_{n-1})^{-2}$ from $1/T_{1\text{obs}}$ values.

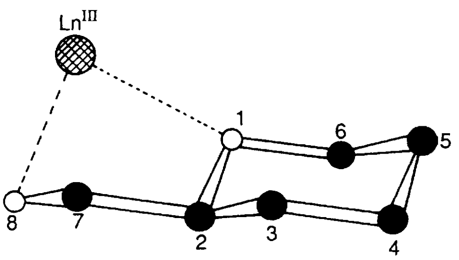

Fig. 4 Geometry of the Ln^{III}–thpm complex

Table 3 Carbon-13 relaxation data for degassed samples of thpm at 50.3 MHz and 353 K

Carbon nucleus	T_{10}^{a}/s	T_1^{b}/s	$(T_{1\,compl})^{-1}$/ s^{-1}	N^{c}	$10^{10}\tau_c$/s
2	5.848	3.266	5.985	1	1.68
6	3.355	1.822	11.09	2	1.56
7	3.272	1.785	11.27	2	1.58
3	3.021	1.681	11.68	2	1.64
5	2.582	1.507	12.23	2	1.72
4	2.980	1.652	11.90	2	1.68

[a] In the absence of $LaCl_3·7H_2O$. [b] In the presence of $LaCl_3·7H_2O$ ($\rho = 1.13 \times 10^{-2}:1$). [c] N = number of bound protons.

The constant k can be represented by equation (6) where m is

$$k = \frac{2}{5}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma^2\beta^2\mu^2{}_{eff}\tau_c m \qquad (6)$$

the number of bound ligands in the complex. Substituting the values for the other terms in the reduced Solomon–Bloembergen equation for Gd^{III} [equation (4)][24–26] gives a value for $m\tau_c = 2.1 \times 10^{-10}$ s. Thus $\tau_c = 1.05 \times 10^{-10}$ s when $m = 2$.

Alternatively, the correlation time (τ_c) can be estimated from the longitudinal relaxation rates of the diamagnetic complex $[La(thpm)_2]^{3+}$. The magnetic dipole–dipole relaxation of ^{13}C due to N protons bound to the carbon for $\omega_0\tau_c \ll 1$ can be expressed as in equation (7), where $K = 3.56 \times 10^{10}$ s^{-2}.

$$\left(\frac{1}{T_{1,2}}\right)_{DD}[^{13}C_{intra}] = N\frac{\hbar^2\gamma^2[^{13}C]\gamma^2[^1H]}{r^6_{CH}}\tau_c = NK\tau_c \qquad (7)$$

Combining equations (3) and (7) gives (8) where $1/T_1$ is the

$$\frac{1}{T_{1\,compl}} = \left(\frac{1}{T_1} - \frac{1}{T_{10}}\right) \times \frac{1}{2\rho} = NK\tau_c \qquad (8)$$

observed relaxation rate, $1/T_{10}$ is the relaxation rate of free thpm, and $1/T_{1\,compl}$ is the relaxation rate of the $[La(thpm)_2]^{3+}$ complex. The ^{13}C longitudinal relaxation rates were measured on degassed and vacuum-sealed samples at two different lanthanum(III) concentrations ($\rho = 0$ and $1.13 \times 10^{-2}:1$) and τ_c calculated for each ^{13}C nucleus as shown in Table 3. The average value $\tau_c = (1.64 \pm 0.06) \times 10^{-10}$ s which is in good agreement with that calculated for the $[Gd(thpm)_2]^{3+}$ complex. Substitution into equation (2), values of $r = 0.67$ nm for $\tau_c = 1.05 \times 10^{-10}$ s and $r = 0.78$ nm for $\tau_c = (1.64 \pm 0.06) \times 10^{-10}$ s are obtained consistent with the diameter of the complex as estimated from Dreiding models.

The experimental Gd^{III}-induced relaxation-rate enhancements of thpm in thpm–D_2O (1:1 v/v) (Table 2) were substantially lower than in pure thpm confirming that D_2O is bound by Ln^{III} in preference to thpm. The greatest decrease was observed for C^2, C^6 and C^7. A good fit between experimental and calculated relaxation rates could only be obtained when a contribution for monodentate species was included in the calculations. An optimum fit ($RF = 0.006$) was calculated for 68% didentate and 32% monodentate species with $T_{1\,inter} = 0.36$ s, Gd^{III}–O^8 0.2508 nm, Gd^{III}–O^8–C^7 60° and Gd^{III}–O^8–C^7–C^2 60 and 180°, whereas $k = 0.9 \times 10^{-53}$.

In conclusion, multinuclear NMR spectroscopy proves to be a suitable technique for determination of the type of complex species present in $LnCl_3$-catalysed O-alkylation with thpm. In thpm, the asymmetric $[Ln(thpm)_2Cl_3]$ is the predominant species present, thpm binding in a didentate manner through its α-hydroxyether structural unit. The thpm ligand is weaker than D_2O and Cl^- and therefore it is weakly bonded, probably also partly in a monodentate manner, to Ln^{III} in aqueous mixtures. Since complexation of Ln^{III} by displacement of inner-sphere water molecules is essential for Michael-type O-alkylation of maleate with the exocyclic hydroxymethyl group of thpm, this reaction is likely to occur in the absence or near absence of water, whilst it may probably be inhibited in aqueous solution. The same trend may occur with addition of maleate to the exocyclic hydroxymethyl group of pyranose sugars and a solvent other than water may be required.

Experimental

Materials.—The $LaCl_3·7H_2O$ and thpm (98%) were purchased from Janssen Chimica, $DyCl_3·6H_2O$ (>99.99%) and D_2O (99.9 atom% D) from Aldrich, $Gd(NO_3)_3·6H_2O$ from Ventron, and ^{17}O-enriched water (10%) from Icon Services, Summit, NJ, USA.

Viscosity Measurements.—The viscosities of solutions of $LaCl_3·7H_2O$ in thpm–water mixtures were determined with an Ubbelohde viscometer.

NMR Measurements.—All NMR measurements were performed at 353 K unless otherwise stated. The ^{139}La and ^{35}Cl NMR spectra were recorded with a Varian VXR-400 S spectrometer at 56.5 and 39.2 MHz respectively on samples of 0.1 mol dm^{-3} $LaCl_3·7H_2O$ in D_2O–thpm mixtures. The chemical shifts were measured with respect to a 0.1 mol dm^{-3} solution of $LaCl_3·7H_2O$ in D_2O as external standard. The chemical shifts and linewidths were determined by fitting the experimental peaks with Lorentzian curves.

The ^{17}O NMR spectra were recorded with a Varian VXR-400 S spectrometer at 54.2 MHz. Weighed portions (4 cm^3) of thpm or D_2O contained in 10 mm NMR tubes were used and $DyCl_3·6H_2O$ was added in portions of *ca.* 10 mg. The deuterium signal of D_2O was used as internal lock where possible, while the measurements in thpm were corrected for bulk magnetic susceptibility effects.[30] The Dy^{III}-induced shifts *versus* the molar ratios Dy^{III}/solvent (ρ) were fitted with a linear function to give the induced shift of water per added Dy^{III}.

Unambiguous assignment of the ^{13}C NMR resonances of thpm was achieved by using the two-dimensional INADEQUATE[31] pulse sequence on a Varian VXR-400 S spectrometer at 100.58 MHz. The longitudinal relaxation times T_1 were recorded with a Nicolet NT-200 WB spectrometer at 50.31 MHz in 12 mm tubes using a [(90°$_x$ 180°$_y$ 90°$_x$)–τ–90°–acquire] inversion-recovery pulse sequence. The relaxation times were then calculated by fitting with a three-parameter equation to correct for inhomogeneous radio-frequency fields which produce incomplete inversion by the 180° pulse.[32] The relaxation-rate enhancements as a function of ρ were fitted with a linear function to obtain the induced relaxation rates ($1/T_1$) at ρ = 1:1. The different gadolinium(III) concentrations were obtained by successive addition of small volumes (10–30 μl) of a stock solution of $Gd(NO_3)_3·6H_2O$ in thpm (0.052 mol dm^{-3}) or in water (0.114 mol dm^{-3}) for thpm–D_2O (1:1 v/v).

The Delphi computer program[33] was used for the empirical force-field calculations.

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