Analysis of Multinuclear Lanthanide Induced Shifts. Part 6.[1] Structures of Lanthanide(III) Tris(oxydiacetate) Complexes in Aqueous Solution

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The structure of the series of lanthanide(III) tris(oxydiacetate) complexes in aqueous solution has been investigated with the use of ^1H, ^{13}C, and ^{17}O n.m.r. The data show that these complexes are not isostructural. In the first half of the series a nine-co-ordinate structure, with three oxydiacetates bound in a tridentate fashion, predominates. Upon going to the heavier lanthanides a carboxylate of one of the oxydiacetate ligands is expelled from the first co-ordination sphere. As a result of slow exchange between the two enantiomeric forms of the complexes, a separation of the geminal methylene protons is observed at 6 °C and 200 MHz.

Lanthanide(III) cations can co-ordinate with a variety of organic ligands. The interactions are largely electrostatic resulting in non-directional bonds, similar to ligand–alkali metal and ligand–alkaline earth metal bonds. The chemical and paramagnetic properties of the Ln^{III} cations make them useful in many facets of chemistry, such as catalysis,[2,3] organic synthesis,[4,5] biochemistry,[6,7] and of course as a tool in structural analysis with the use of n.m.r. spectroscopy.[8] Moreover, Ln^{III} chelates are becoming increasingly important in medical diagnostic techniques using Magnetic Resonance Imaging.[9]

Oxydiacetate (oda) is known to form relatively stable 1:1, 1:2, and 1:3 complexes with Ln^{III} cations,[10,11] It has been shown that in single crystals of $Na_3[Ln(oda)_3]\cdot2NaClO_4\cdot6H_2O$ (Ln = Ce, Nd, Gd, or Yb), oda acts as a tridentate ligand.[12,13] The Ln^{III} cation is nine-co-ordinated in a twisted tricapped trigonal prism of D_3 symmetry. A distortion of this symmetry to C_1 in single crystals of $Na_3[Eu(oda)_3]\cdot6H_2O$ has been ascribed to packing forces.[14] ^{139}La N.m.r. studies have shown that in aqueous solution oda also co-ordinates in a tridentate fashion.[15] With the use of Gd^{III}-induced ^{13}C relaxation rate enhancements, it has been demonstrated that in $[Gd(oda)_3]^{3-}$ the predominant co-ordination mode is similar.[16] Furthermore, the results of Gd^{III}-induced ^1H relaxation measurements[16] and Dy^{III}-induced ^{17}O chemical shift measurements[17] indicated that the Gd^{III} and Dy^{III} complexes have no water in the first co-ordination sphere of the cation. Foster and Richardson[18] and Horrocks and co-workers[14] have shown with the use of luminescence spectral techniques that $[Eu(oda)_3]^{3-}$ is tris(tridentate) and has D_3 symmetry in aqueous solution.

The present paper describes a study of the structures of the various $[Ln(oda)_3]^{3-}$ ions in aqueous solution, using the Ln^{III}-induced ^1H, ^{13}C, and ^{17}O chemical shifts. It is shown that structural changes occur among these complexes.

Results

The 200-MHz ^1H n.m.r. spectra of a D_2O solution containing $Na_2(oda)$ (0.2 mol dm^{-3}) and a paramagnetic lanthanide salt with a metal to ligand ratio (ρ) of 0.1 showed, at 6 °C, slow exchange between the protons of free oda (*i.e.* oda^{2-}) and those co-ordinated to Ln^{III} in $[Ln(oda)_3]^{3-}$. For the lighter lanthanides (Ln = Ce—Dy) a single methylene ^1H signal was observed for $[Ln(oda)_3]^{3-}$. Surprisingly, *two methylene signals* were present in the ^1H spectra of $[Ln(oda)_3]^{3-}$ with Ln^{III} = Ho—Yb. It may be noted that, under the same conditions, the ^{13}C n.m.r. spectra of all the $[Ln(oda)_3]^{3-}$ anions showed only a single methylene signal.

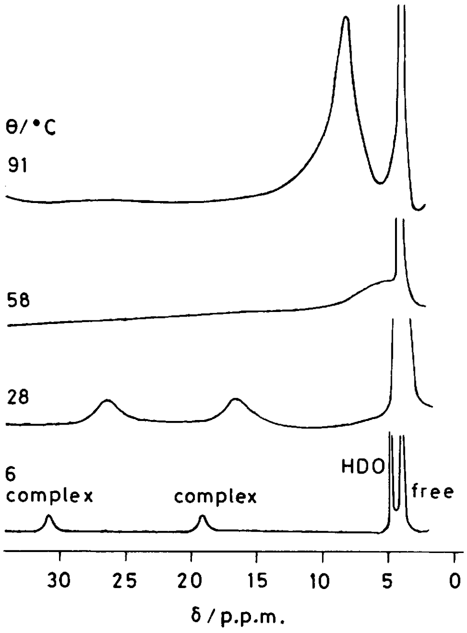

Figure 1. ^1H N.m.r. spectra of a 0.2 mol dm^{-3} solution of $Na_2(oda)$ in D_2O in the presence of Tm^{III}; molar ratio Tm^{III}:oda = 0.1, pH 6.5

Upon increasing the temperature, coalescence of the two methylene ^1H signals occurred, followed by coalescence of the resulting signal with that of free oda (Figure 1). The linewidths were rather large in several of the n.m.r. spectra at 6 °C. Therefore, the bound shifts for the nuclei of the various $[Ln(oda)_3]^{3-}$ were determined from fast-exchange spectra obtained upon successive additions of small portions of a Ln^{III} chloride to a 0.2 mol dm^{-3} oda solution at 73 °C. The bound shifts were derived from plots of Ln^{III}-induced shifts *versus* ρ by extrapolation to ρ = 1:3. Unfortunately, most of the ^{17}O-bound shifts of oda could not be determined, due to slow exchange and excessive line broadening in the signals of $[Ln(oda)_3]^{3-}$. The values obtained are compiled in Table 1, together with some of the slow-exchange data.

The agreement between the slow and the fast exchange data is in general quite good, taking into account the influence of the temperature on Ln^{III} induced shifts.[19–22] Exceptions are found in the data for Ln = Tb^{III} and Dy^{III}, where the sign of the induced shift reverses upon increasing the temperature from 6 to 73 °C.

Table 1. Ln^{III}-induced shifts of $[Ln(oda)_3]^{3-}$ and $[Ln(oda)]^+$ (p.p.m.)[a]

	$[Ln(oda)_3]^{3-}$ at 73 °C[b]					$[Ln(oda)_3]^{3-}$ at 6 °C[c]		$[Ln(oda)]^{+}$[d]
Ln	H_2O	COO	COO	CH_2	CH_2	CH_2		CH_2
La	0.5	14.2	−0.13	1.35	0.35			0
Ce	0.4	91.9	−1.67	5.85	3.38	*e*		
Pr	0.2	185.5	−1.15	9.59	5.25	5.48		14.9[f]
Nd	0.5	*e*	−3.83	5.08	2.04	1.98		5.6
Sm	0.5	*e*	2.08	0.93	0.30	0.66		0.7
Eu	−0.2	*e*	0.11	−8.35	−3.60	−3.71		−13.4
Tb	−0.7	*e*	−8.90	−27.29	−4.08	6.12		92
Dy	−0.0	*e*	−1.60	−24.76	−3.43	5.93		100
Ho	−0.1	*e*	−16.14	−38.57	*e*	−11.44	−13.28	30
Er	0.0	*e*	−23.95	−24.24	−6.03	−8.06	−10.48	−38
Tm	0.2	*e*	−22.00	15.97	*e*	15.19	26.96	−61
Yb	0.3	*e*	−13.19	2.04	4.61	3.66	6.76	−26[g]
Lu	0.2	5.8	−0.00	−0.27	0.24	0.24		

[a] Downfield shifts are positive. [b] This work, 0.2 mol dm^{-3} $Na_2(oda)$ in D_2O, pH 6.9; fast-exchange data, bound shifts were obtained by extrapolation to $\rho = 1:3$. [c] This work, slow-exchange data. [d] Data from ref. 23. [e] Not observed, due to exchange broadening. [f] Absolute induced shifts, room temperature $[Pr(oda)_2]^-$, 8.1; $[Pr(oda)]^+$, 7.2 (this work). [g] Absolute induced shifts: $[Yb(oda)_2]^-$, −4.37; $[Yb(oda)]^+$, −11.58 (this work).

Table 2. Values of F and G for $[Ln(oda)_3]^{3-}$ (Ln = La—Eu) in D_2O at 73 °C*

Nucleus	F	$G_{exp.}$	$G_{calc.}$
COO	−36.8	−0.432	0.061
COO	−0.04	0.008	0.007
CH_2	−0.68	−0.042	−0.044
CH_2	−0.19	−0.029	−0.029

* The G values are relative, the corresponding optimised relative k values[33] are: Ce −100.0 (by definition), Pr −150.9, Nd −29.6, Sm 0.9, and Eu 83.9.

The ^1H n.m.r. spectra of all the Yb^{III} complexes at 6 °C appeared to be in the slow-exchange region. The induced shifts of the 1:2 and 1:1 complexes were −4.37 and −11.58 p.p.m., respectively. No separation of methylene ^1H signals was observed in these cases. The exchange between the 1:1, 1:2, and 1:3 Pr–oda complexes was fast with respect to the ^1H n.m.r. time-scale at 6 °C. The induced ^1H shifts of these complexes were estimated to be 7.2, 8.1, and 5.48 p.p.m., respectively. For comparison, the ^1H shifts for $[Ln(oda)]^+$, reported by Williams and co-workers[23] are also included in Table 1.

Discussion

Magnitudes of the Ln^{III}*-induced Shifts.*—The shift (Δ) induced at a nucleus of a ligand upon binding to a Ln^{III} cation can be expressed as the sum of the diamagnetic shift (Δ_d), the contact shift (Δ_c), and the pseudo-contact shift (Δ_p), equation (1).

$$\Delta = \Delta_d + \Delta_c + \Delta_p \qquad (1)$$

The diamagnetic shifts were estimated from an interpolation of the bound shifts for the diamagnetic ions La^{III} and Lu^{III}. Both the contact and the pseudo-contact shifts can be expressed as the product of a term that is characteristic of the Ln^{III} cation (k) but independent of the ligand [$\langle S_z \rangle$ and k, respectively] and a second term that is characteristic of the ligand nucleus under study but independent of the Ln^{III} cation (F and G, respectively), equation (2). Values of $\langle S_z \rangle$ and k have been calculated by

$$\Delta' = \Delta - \Delta_d = \langle S_z \rangle F + kG \qquad (2)$$

Bleaney,[19] Golding and Halton,[24] and Pinkerton *et al.*[25] The parameter F describes the relative contact interaction value for each ligand nucleus, and G is related to the geometry of the complex according to equation (3).[19] Here, r, θ, and φ are the

$$G = C\frac{3\cos^2\theta - 1}{r^3} + C'\frac{\sin^2\theta\cos 2\varphi}{r^3} \qquad (3)$$

spherical co-ordinates of the observed nucleus with respect to Ln^{III} at the origin and with the principal magnetic axis as the z axis. For axially symmetric complexes $C' = 0$. Internal reorientations in the complexes may result in effective axial symmetry.[26,27]

Equation (2) can be rearranged into two linear forms, equations (4) and (5). Previously, it was shown that plotting

$$\frac{\Delta'}{\langle S_z \rangle} = F + \frac{k}{\langle S_z \rangle}G \qquad (4)$$

$$\frac{\Delta'}{k} = \frac{\langle S_z \rangle}{k}F + G \qquad (5)$$

bound shift data according to equations (4) and (5) may be useful for checking whether a series of Ln^{III} complexes is 'isostructural' or not.[28,29] The ionic radius of the Ln^{III} ions decreases regularly through the series. The consequent gradual (minor) variations in complex structures may evidence as an abrupt break in plots according to equation (4), whereas plots according to equation (5) remain almost linear.[29] When both plots of $\Delta'/\langle S_z \rangle$ *versus* $k/\langle S_z \rangle$ and plots of Δ'/k *versus* $\langle S_z \rangle/k$ show irregularities, it is likely that major structural changes occur among the lanthanide complexes, such as a change in co-ordination number or in the way of binding of the ligand.[29] Figure 2 shows that the latter is the case for $[Ln(oda)_3]^{3-}$: both plots show large deviations from linearity, particularly for the heavier Ln^{III} cations. The plots of $\Delta'/\langle S_z \rangle$ *versus* $k/\langle S_z \rangle$ indicate a change in the sign of G on going from Ce^{III} to Yb^{III}. This behaviour contrasts with that of $[Ln(oda)]^+$. For $[Ln(oda)]^+$ Williams and co-workers[23] found excellent agreement of the Ln^{III}-induced shifts of the methylene protons, which are almost completely of pseudo-contact origin, and the k values (see Table 1). Analogous results were obtained for $[Ln(pydca)_3]^{3-}$ (pydca = pyridine-2,6-dicarboxylate),[30–32] the solid-state and solution structures of which are very similar to the solid-state structure of the oda complexes.

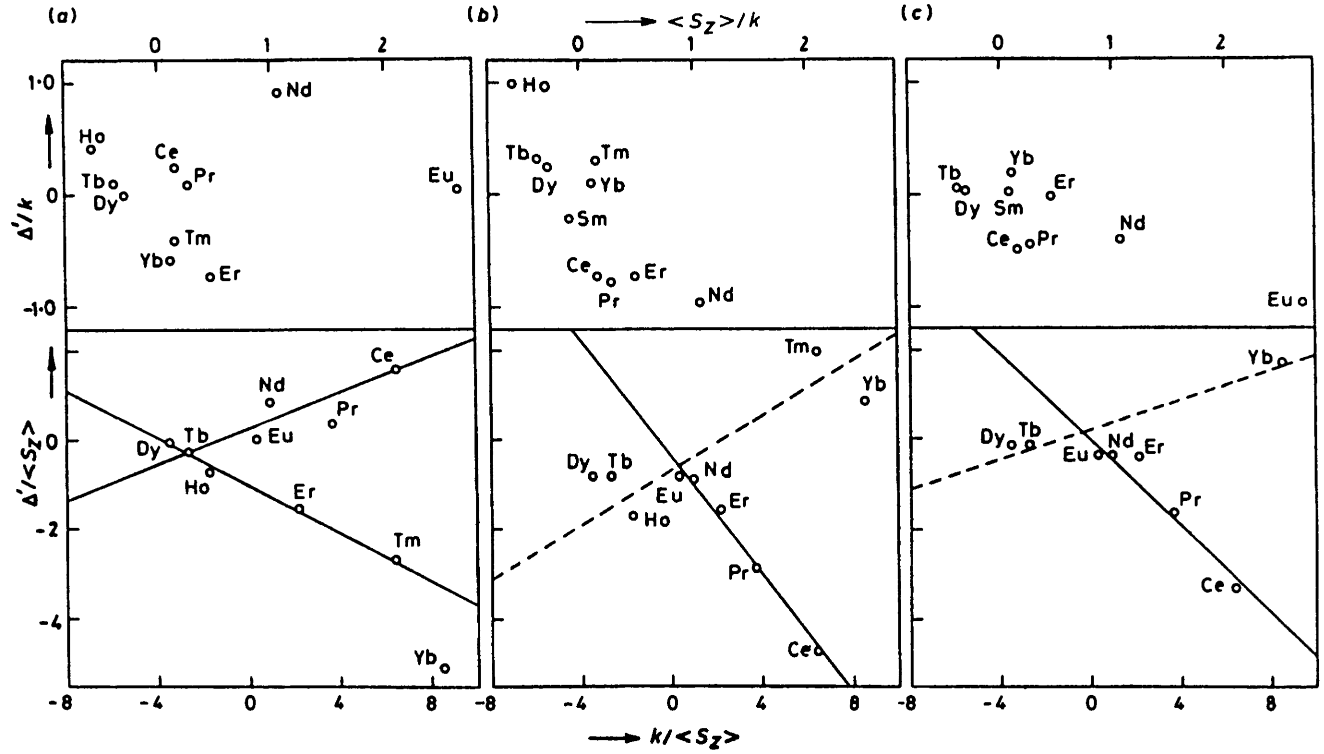

Figure 2. Plots of $\Delta'/\langle S_z\rangle$ *versus* $k/\langle S_z\rangle$ and Δ'/k *versus* $\langle S_z\rangle/k$ for the various oda nuclei at 73 °C: (*a*) COO, (*b*) CH_2, and (*c*) CH_2; dashed lines indicate doubt about physical relevance of a line through the relevant data points

For the lighter members of the lanthanide series (Ln = Ce—Eu), the plots of $\Delta'/\langle S_z\rangle$ *versus* $k/\langle S_z\rangle$ for $[Ln(oda)_3]^{3-}$ show rather good linearity. Moreover, the trends in the induced ^1H shifts are analogous to those of $[Ln(oda)]^+$ and $[Ln(pydca)_3]^{3-}$. Therefore, separation of the experimental shift into contact and pseudo-contact shifts was performed for $[Ln(oda)_3]^{3-}$ (Ln = Ce—Eu) using the procedure described previously.[33] The *F* and *G* values obtained are given in Table 2. The experimental *G* values were compared with *G* values calculated with the use of equation (3) ($C' = 0$) for structures with D_3 symmetry generated from the single-crystal structure of $Na_3[Ce(oda)_3]\cdot 2NaClO_4\cdot 6H_2O$ [13] by stepwise rotations of the oda ligands around the bonds between Ln^{III} and the ether oxygens. An optimal fit was obtained for a structure, in which the rotation of the oda ligands was only 3° with respect to the single-crystal structure. From Table 2, it can be seen that the agreement between the experimental and calculated *G*-values is excellent for the C and H nuclei. The agreement is not good for the carboxylate ^{17}O nuclei, but that experimental *G* value is not very accurate, since only data for Ce^{III} and Pr^{III} were available, and moreover, the linewidths in the relevant spectra were very large. On the basis of the present results, together with those of our previous n.m.r. investigations [8] and of the luminescence studies of Foster and Richardson [18] and Horrocks and co-workers,[14] it is concluded that the structures of $[Ln(oda)_3]^{3-}$ for the first half of the lanthanide series are closely similar to the solid-state structure of the Ce^{III} complex.

The reversal of the sign of *G* upon going to the heavier Ln^{III} cations cannot be explained by a distortion of such a structure. It may be supposed that in any solution structure of a nine-co-ordinate $[Ln(oda)_3]^{3-}$ complex, with the oda ligands bound in a tridentate fashion, a three-fold axis of symmetry is present. A reversal of the sign of *G* of the methylene protons, for example, would require then that the angle θ of these nuclei changes from 70—80° to less than 54°, which is impossible for such structures. Furthermore, the irregularities in the plots of Δ'/k *versus* $\langle S_z\rangle/k$ suggest that the magnitude of *F* changes among the various $[Ln(oda)_3]^{3-}$ complexes. This in turn indicates that the co-ordination of the ligands changes.[29] The Ln^{III}-induced water ^{17}O shifts are very small for all the Ln^{III} cations, which shows that in none of the complexes is water present in the first co-ordination sphere. Therefore, it is most likely that for the heavier Ln^{III} cations (which have smaller ionic radii), an eight-co-ordinate $[Ln(oda)_3]^{3-}$ complex becomes the predominant species in solution. In this structure one of the oda ligands is probably co-ordinated in a bidentate manner *via* one of the carboxylate oxygens and the ether oxygen (see Figure 3). Co-ordination of one of the oda ligands in an acetate-like fashion (bidentate, *via* both carboxylate oxygens) seems unlikely, since this co-ordination mode would give rise to a relatively low association constant K_3, which is not in agreement with the rather small decrease of K_3 near the end of the Ln^{III} series [10] (see Table 3). The proposed eight-co-ordinate structures have low symmetry. Consequently, large differences in chemical shifts of the nuclei of the individual oda ligands should be expected. However, no separation of the oda signals was observed. This can be rationalized by a high fluxionality in these complexes, possibly as a result of rapid internal substitution of a Ln^{III} bound by a free carboxylate group.

The temperature dependence of the Ln^{III}-induced ^1H shifts for Tb^{III} and Dy^{III} is very large (see Table 1), indicating that for these systems the value of the equilibrium constant for the eight- and the nine-co-ordinate structures is near unity. The relative insensitivity of the Yb^{III}-induced ^1H shifts suggests that for that cation, the eight-ordinate complex predominates.

The thermodynamic properties of Ln^{III}-oda systems have been studied extensively by Grenthe and co-workers.[10,11,34—38] These authors have shown that in systems, where changes in co-ordination number or in geometry occur across the lanthanide series, a minimum or maximum can be expected in the curve of

Table 3. Values of log K_3 for $[Ln(oda)_3]^{3-}$ *

Ln^{III}	La	Ce	Pr	Nd	Sm	Eu	Gd
log K_3	1.84	2.31	2.40	2.66	2.90	3.16	3.11
Ln^{III}	Tb	Dy	Ho	Er	Tm	Yb	Lu
log K_3	3.27	3.38	3.36	3.21	3.07	2.81	2.61

* Data from ref. 9; $K_3 = [Ln(oda)_3{}^{3-}]/[oda^{2-}][Ln(oda)_2{}^{-}]$.

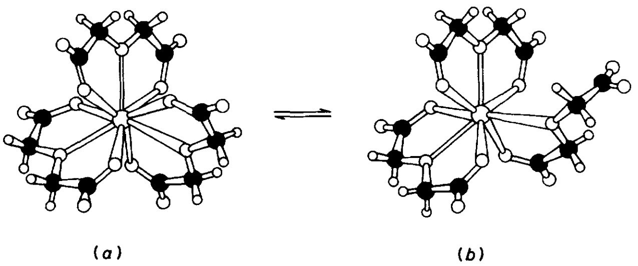

Figure 3. Schematic representation of the (*a*) nine- and (*b*) eight-co-ordinate structures of $[Ln(oda)_3]^{3-}$ in aqueous solution

the heat capacity C_p (or ΔC_p) as a function of the atomic number.[11] The $[Ln(oda)_3]^{3-}$ systems show a shallow minimum in the partial molar heat capacity curve around Tb^{III} (ref. 37, Figure 3). This is in good agreement with the large temperature influence on the Ln-induced ^1H shifts in the same region of the lanthanide series that was observed in the present n.m.r. investigation.

Grenthe and co-workers observed a pronounced maximum in the heat capacity curves of the $[Ln(oda)_2]^-$ systems around Dy^{III}.[11] This could be explained by a shift of the hydration equilibrium of these complexes [equation (6)] as a function of

$$[Ln(oda)_2(H_2O)_x]^- \rightleftharpoons [Ln(oda)_2(H_2O)_y]^- + (x - y)H_2O \quad (6)$$

the atomic number across the lanthanide series.[11] Most likely $x = 3$ and $y = 2$. A comparison of our ^1H n.m.r. data on the Pr^{III}- and Yb^{III}-oda systems at 6 °C also suggests a change of co-ordination number or complex geometry for the $[Ln(oda)_2]^-$ complexes between the lighter and the heavier lanthanides. The Ln^{III}-induced ^1H shifts of the 1:1, 1:2, and 1:3 Ln^{III}-oda complexes for Ln = Pr (7.2, 8.1, and 5.5 p.p.m., respectively) show relatively small differences, but those for Ln = Yb (−11.6, −4.4, and 5.2 p.p.m., respectively) differ significantly. The Ln^{III}-induced ^1H shifts of the $[Ln(oda)]^+$ systems[23] do not show any anomalies, and, therefore, these complexes are probably nine-co-ordinate with a co-ordination polyhedron analogous to that of $[Ln(oda)_3]^{3-}$ for Ln = Ce—Eu.

Several other examples of a change of co-ordination number from nine to eight among a series of Ln^{III} complexes have been reported in the literature. For instance, the Ln^{III}–L complexes (L = 1,4,7-triazacyclononane-*N,N′,N″*-triacetate) have been shown to be nine-co-ordinate for Ln = Pr, Nd, and Eu and eight-co-ordinate for the heavy lanthanides (Ln = Tb, Dy, Ho, Er, Tm or Yb). The decrease in co-ordination number is a consequence of the decrease in the number of bound waters from 3 to 2.[39,40]

Exchange Phenomena.—From the fact that at 6 °C a separation was observed for the methylene ^1H signals of $[Ln(oda)_3]^{3-}$ (Ln = Ho—Yb), whereas at the same time only a single methylene ^{13}C signal was observed, it may be concluded that this separation is caused by anisochronism of geminal methylene protons. Unfortunately, the large linewidths precluded the observation of couplings in the ^1H n.m.r. spectra. The methylene protons of oda are diastereotopic in the proposed structure of $[Ln(oda)_3]^{3-}$. In the ^1H spectrum at 6 °C of the diamagnetic $[Lu(oda)_3]^{3-}$ no separation of these protons was observed. Apparently the chemical shift difference between these protons is only large enough to attain the slow-exchange region in the paramagnetic complexes. Usually, the ligand exchange in a series of Ln^{III} complexes decreases upon going from La^{III} to Lu^{III}. In addition the induced shifts in the first half of the series are usually smaller than in the second half. Probably therefore, no separation between the methylene protons could be observed for Ln = La—Dy.

No attempt was made fully to analyze the variable-temperature n.m.r. spectra, but a rough estimate, using coalescence temperatures, showed that $\Delta G^\ddagger$ for the exchange of the methylene protons in the complex, and the exchange of these protons with those of free oda^{2-} is *ca.* 13 kcal mol^{-1} (*ca.* 54 kJ mol^{-1}) both for $[Tm(oda)_3]^{3-}$ and for $[Yb(oda)_3]^{3-}$. This suggests that the same mechanism is involved in these processes, namely a dissociation–association mechanism between the two enantiomeric complexes.

Conclusions

The $[Ln(oda)_3]^{3-}$ complexes are not isostructural in aqueous solution. For the lighter Ln^{III} cations a nine-co-ordinate geometry similar to that in the solid state predominates, with oda acting as a tridentate ligand. Upon going to the heavier Ln^{III} cations a carboxylate group of one of the oda ligands is expelled from the first co-ordination sphere. For the heavier Ln^{III} cations the exchange between the methylene protons is slow with respect to the n.m.r. time-scale as a consequence of slow exchange between the two enantiomeric complexes.

Experimental

The n.m.r. experiments were performed on a Nicolet 200 WB spectrometer using a 12-mm sample tube with a 0.2 mol dm^{-3} solution of 5% ^{17}O-enriched disodium oxydiacetate in D_2O at 73 °C and at pH 6.9 unless stated otherwise. Chemical shifts were measured with respect to the ^1H Bu^t signal of 0.25% t-butyl alcohol at 1.20 p.p.m. as an internal standard. The Ln^{III}-induced shift measurements were performed at at least six different Ln^{III}–oda molar ratios (ρ = 0—0.25). The $LnCl_3{\cdot}6H_2O$ salts used were obtained from Alfa Products. The Ln^{III} contents were determined by an ethylenediaminetetra-acetate titration with arsenazo I as the indicator. Water (20% ^{17}O-enriched) was obtained from Rohstoff-Einfuhr Düsseldorf, and ethyl diazoacetate from Aldrich.

^{17}O-Enriched oxydiacetate was synthesized by reaction of ethyl diazoacetate with ^{17}O-enriched water, followed by hydrolysis of the resulting diethyl ester of oxydiacetate acid.

Acknowledgements

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