# Studies of Lanthanide(III) Dipicolinate † Complexes in Aqueous Solution. Part 2.[1] Hydration

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A method for obtaining the hydration numbers of some lanthanide(III) complexes has been developed. Proton relaxation rates of the hydrogen atoms which are a constituent part of the ligands, $A_n$, bound to $Ln^{III}$ ions in the complex $[MA_n(OH_2)_{x_n}]$ are compared with those of bound water, which is in fast exchange with bulk water (A = dipicolinate). The method is applied to the lanthanide(III) mono- and bis-dipicolinate complexes and shows that they are bound to six and three water molecules respectively, resulting in nine-co-ordinate complexes. The tris complexes have no inner-sphere water.

In the previous paper[1] we have discussed the internal mobility within the lanthanide(III) mono-, bis-, and tris-dipicolinate complexes in solution and the disposition of the dipicolinate anions in each of these complexes. It was found that the dispositions of dipicolinate anions relative to the central $Ln^{III}$ ion (Ln = a lanthanide) were similar to that of a nine-co-ordinate, tricapped trigonal pyramid. The vacant positions were assumed to be occupied by water molecules in fast exchange with that of bulk water. In this paper we shall describe the outer- and inner-sphere water molecules of these complexes.

For the lanthanide(III) complexes in solution at room temperature the rate of exchange between the bound water and bulk water is very fast[2] compared with the time scale of n.m.r. experiments. Consequently any measured property of the bulk water obtained by an n.m.r. experiment will, in fact, be a weighted average including the bound water. To overcome this problem, Fratiello *et al.*[3] tried to determine the hydration numbers of the $Ln^{III}$ aquo-ions at low temperature in mixed solvents, where the rate of exchange of water molecules is slow. Direct and indirect measurements of the areas of the separate n.m.r. signals of the bound and free water molecules were made. Unfortunately, the concentrations of the metal ions, anions, and water used make it difficult to obtain precise hydration numbers at known degrees of complexation. Proton relaxation *enhancements* of solvent water by $Gd^{III}$, which is a special case because of the long electron relaxation time of $Gd^{III}$ ions, have been used[4,5] at higher temperatures and gave a hydration number of eight to ten, but this method could not be used for other members of the lanthanide(III) series. In this paper we have used perturbations of the relaxation times of the n.m.r. signals, arising both for protons within ligands and water, of lanthanide(III) complexes caused by the presence of the different paramagnetic $Ln^{III}$ ions to determine hydration numbers all along the series.

## EXPERIMENTAL

Stock lanthanide(III) perchlorate and disodium dipicolinate solutions were prepared as described earlier.[1]

TABLE 1

Relaxation rates($s^{-1}$), $1/T_p$ and $1/T_m$, of *para* and *meta* protons respectively in dipicolinate bound to lanthanide(III) ions

| Metal ion | Complex | | | | | |
|---|---|---|---|---|---|---|
| | Mono | | Bis | | Tris | |
| | $1/T_p$ | $1/T_m$ | $1/T_p$ | $1/T_m$ | $1/T_p$ | $1/T_m$ |
| Ce | 0.4 ± 0.1 | 0.9 ± 0.1 | | | | |
| Pr | 0.8 ± 0.1 | 2.0 ± 0.2 | 2.3 ± 0.2 | 4.3 ± 0.3 | | |
| Nd | 2.7 ± 0.2 | 5.8 ± 0.4 | 3.4 ± 0.3 | 6.7 ± 0.5 | | |
| Tb | | | | | 32.5 ± 2.0 | 65.0 ± 5.0 |
| Dy | | | | | 82.0 ± 6.0 | 145.0 ± 10.0 |
| Ho | | | | | 27.1 ± 2.4 | 54.6 ± 4.0 |
| Er | | | | | 31.0 ± 2.5 | 62.0 ± 5.0 |
| Tm | 18.5 ± 1.3 | 39.0 ± 2.3 | 16.9 ± 1.0 | | 10.0 ± 0.7 | 21.5 ± 1.7 |
| Yb | 3.1 ± 0.2 | 7.1 ± 0.5 | 3.1 ± 0.3 | | 1.7 ± 0.1 | 3.4 ± 0.2 |

Solutions of lanthanide(III) mono-, bis-, and tris-dipicolinate were prepared by mixing the required ratios of the corresponding metal : ligand at a pD of 5.7 ± 0.3 except for the tris complexes where the pD was raised to *ca.* 7.0. Measurements of the longitudinal relaxation times, $T_{p,m}$, of *para* and *meta* protons of these complexes at 24 ± 1 °C were obtained from the signal height observed after a 180–$\tau$–90° pulse sequence using different time intervals, $\tau$. A Bruker HX90 spectrometer operated in the Fourier-transform mode was used throughout. Results were corrected for the diamagnetic contribution using data for the lanthanum(III) complexes.

Duplicate solutions containing 1 : 0.5, 1 : 1, 1 : 1.5, 1 : 2, 1 : 2.5, and 1 : 4 mol ratios of $Ln^{III}$ : dipicolinate were prepared in $H_2O$ at pH 5.2 ± 0.3. Measurements of $T_1$ for water were made at 24 ± 1 °C using a Bruker Minispec 20 spectrometer. Values of $T_1$ were obtained from the passage of the signal intensity through zero ($1/T_1 = 0.693/\tau_0$) in 180—90° pulse sequences. Values obtained by this method for more than 50 samples differed by less than 2% from those obtained from logarithmic plots using measurements of the recovery of magnetisation.

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† Pyridine-2,6-dicarboxylate.

## RESULTS AND DISCUSSION

Results of the longitudinal relaxation-rate measurements for the *meta*, $1/T_m$, and *para*, $1/T_p$, protons of the mono, bis, and tris complexes of lanthanide(III) dipicolinate are listed in Table 1. Not all the lanthanide(III) dipicolinate complexes have been studied, since the *para* and *meta* protons of the bound ligands are not resolved in the tris complexes of $Ce^{III}$, $Pr^{III}$, $Nd^{III}$, and $Sm^{III}$ and in the case of the europium(III) complexes the relaxation rates are too near to that of the diamagnetic lanthanum(III) complexes for precise calculation of the paramagnetic contributions. Figure 1 shows the spectra of the ytterbium(III) tris-dipicolinate complex during a series of 180°–τ–90° pulse sequence measurements.

In the case of the bis complexes no measurements were possible for *meta* protons of the complexes of the metal ions in the second half of the $Ln^{III}$ series, since their resonances were not observed at room temperature.[1] Inhomogeneity of the radio-frequency magnetic field over the sample due to the huge shift that the protons experience made it difficult to measure the relaxation rates of *para* and *meta* protons of some of the lanthanide(III) mono and bis complexes.

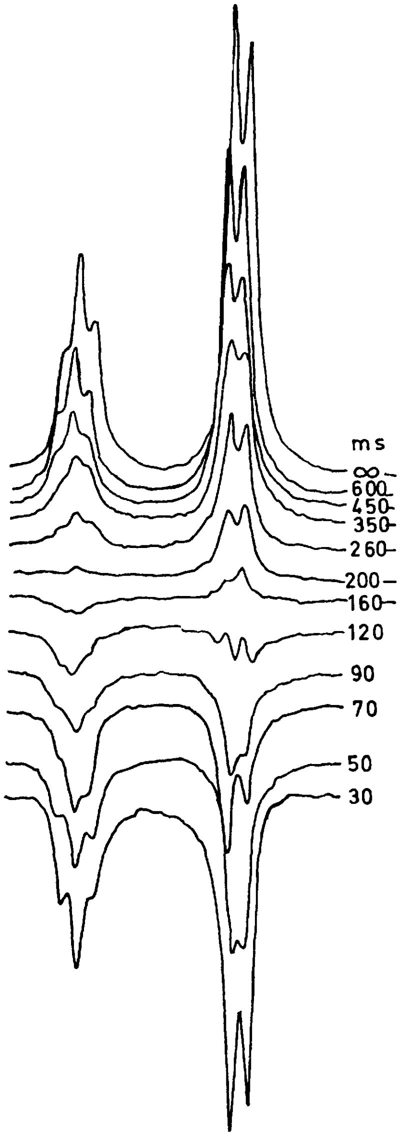

FIGURE 1 90 MHz N.m.r. spectra of *meta* and *para* protons of the ytterbium(III) tris-dipicolinate complex at various time intervals, τ, of the 180°–τ–90° sequence

The relaxation rate of a diamagnetic nucleus near a paramagnetic $Ln^{III}$ centre, except for $Gd^{III}$, is given by the reduced Solomon–Bloembergen equation [5] (1) where

$$\frac{1}{T_{1,2}} = \frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_I{}^2\mu^2\beta^2\tau_e}{r^6} \qquad (1)$$

$1/T_{1,2}$ is either the longitudinal or the transverse relaxation rate of the nucleus, $\gamma_I$ is the magneto-gyric ratio, $\mu$ is the magnetic moment, $\beta$ is the Bohr magneton, $r$ is the distance from the nucleus to the paramagnetic centre, and $\tau_e$ is the correlation time, here the electron-spin relaxation time, which governs the interaction. The longitudinal relaxation rate of a diamagnetic nucleus near to a $Ln^{III}$ ion is independent of frequency in the range studied.[6] The relaxation rates $1/T_m$ of the *meta* protons of different lanthanide(III) complexes are greater than those of the corresponding *para* protons, $1/T_p$, see Table 1, because the former are nearer to the paramagnetic centre than the latter. It is also to be noticed that the relaxation rates of these protons are different for the three complexes of the same metal ion. The electron-spin relaxation time of a given $Ln^{III}$ ion is dependent on the binding ligands. The average relaxation ratio for the tris complexes, *i.e.* $1/T_m : 1/T_p$, is $2.0 \pm 0.3 : 1$ and that for the mono complexes is $2.3 \pm 0.4 : 1$. These relaxation ratios are the same, within experimental error, irrespective of the nature of the central ion. This constancy of the relaxation ratio along the $Ln^{III}$ series shows that the interaction between the electron and nuclear spins is isotopic. The observation of isotropic interaction between protons and lanthanide ions is in agreement with studies on cytidine 5′-monophosphate,[7] and the average ratio of $2.2 \pm 0.3 : 1$ for all the complexes studied, see Table 1, agrees well with the calculated ratio of $(r_p/r_m)^6$ using a La–N bond length of 2.4—2.7 Å. The reported [8] bond length for the solid ytterbium(III) complex is 2.5 Å.

For the $Ln^{III}$ aquo-ions in solution, the rate of exchange of water is very fast [2] so that the relaxation rate of water protons, $1/T_{obs.}$, is the weighted mean of contributions from water in the inner sphere, $1/T_n$, in the outer sphere, $1/T_{os}$, and in bulk water $1/T_w$. Hence, equation (2) holds

$$\frac{1}{T_{obs.}} = \frac{x_nB}{WT_n} + \frac{zB}{WT_{os}} + \left(\frac{W - x_nB - zB}{W}\right)\frac{1}{T_w} \qquad (2)$$

for $[MA_n(OH_2)_{x_n}]$ and $z$ outer-sphere water molecules where $W$ is the molarity of water in the solution and $B$ is the concentration of the complex-ion species in the solution. Rearranging gives equation (3). Under con-

$$\frac{1}{T_{obs.}} = \frac{B}{W}\left[\frac{x_n}{T_n} + \frac{z}{T_{os}} - \frac{(x_n + z)}{T_w}\right] + \frac{1}{T_w} \qquad (3)$$

ditions where $T_w \gg T_{os} > T_n$, the third term in the brackets is negligible and the molar relaxation enhancement (m.r.e.) is given by equation (4). For the tris-

$$\frac{1}{B}\left(\frac{1}{T_{\text{obs.}}} - \frac{1}{T_w}\right) = \frac{1}{W}\left(\frac{x_n}{T_n} + \frac{z}{T_{os}}\right) \qquad (4)$$

dipicolinate complexes $x_3 = 0$, and m.r.e. is $z/WT_{os}$, which can then be used as the outer-sphere contribution and can be subtracted from the m.r.e. for the mono and bis complexes to give the inner-sphere contributions. Analogous equations[9] apply to the three dipicolinate complexes $[MA_n(OH_2)_{x_n}]$ under conditions where the $Ln^{III}$ ion exists essentially in the form of one complex only.

The molal longitudinal relaxation enhancement (m.l.r.e.), $1/T_n$, of water protons at 24 ± 1 °C of the lanthanide(III) mono-, bis-, and tris-dipicolinate complexes is given in Table 2. These results are averaged values from measurements on duplicated solutions containing different ratios of metal : ligand. The results in Table 2 show that the values of $1/T_n$ of solutions containing the tris-dipicolinate complexes are still relatively high, in spite of the fact that no inner-sphere water molecules remain, due to the influence of the paramagnetic centre on outer-sphere water molecules. We can prove that there is no contribution of inner-sphere water molecules as follows.

TABLE 2

Values ($s^{-1}$) of the molal relaxation rates of solvent water, in the presence of different lanthanide(III)–dipicolinate complexes measured at 20 MHz, 24 ± 1 °C

| Metal ion | Complex | | |
|---|---|---|---|
| | Mono | Bis | Tris |
| Ce | 4.8 ± 0.3 | 4.3 ± 0.4 | 2.3 ± 0.3 |
| Pr | 6.6 ± 0.3 | 6.5 ± 0.3 | 2.6 ± 0.1 |
| Nd | 18.5 ± 0.8 | 12.7 ± 0.5 | 3.2 ± 0.1 |
| Sm | 1.4 ± 0.2 | 1.0 ± 0.3 | 0.1 ± 0.1 |
| Eu | 1.3 ± 0.2 | 0.9 ± 0.3 | 0.1 ± 0.1 |
| Tb | 241.0 ± 10.0 | 149.0 ± 6.0 | 58.0 ± 2.0 |
| Dy | 378.0 ± 10.0 | 235.0 ± 7.0 | 108.0 ± 4.0 |
| Ho | 268.0 ± 8.0 | 141.0 ± 5.0 | 37.4 ± 1.0 |
| Er | 224.0 ± 5.0 | 110.0 ± 3.0 | 62.4 ± 2.0 |
| Tm | 152.0 ± 5.0 | 56.7 ± 2.5 | 19.6 ± 1.0 |
| Yb | 36.0 ± 2.0 | 15.7 ± 1.2 | 4.3 ± 0.2 |

Luz and Meiboom[10] derived an equation for the estimation of the outer-sphere contribution to the relaxation rate $1/T_{os}$ by averaging the dipolar contribution over the volume between the sphere of closest approach, $d$, and infinity. For the $Ln^{III}$ ions equation (5) holds

$$\frac{1}{T_{os}} = \frac{N\gamma_I^2\mu_0^2\mu^2\beta^2\tau_c}{9\pi d^3} \qquad (5)$$

where $N$ is the number of ions per $m^3$. Combining equations (1) and (5) for the case of *para* protons in the ligand gives equation (6) where $K = \frac{4}{3}\pi N$. Thus a plot of log $1/T_{os}$ for the tris complexes against log $1/T_p$ should

$$\log\frac{1}{T_{os}} = \log\frac{1}{T_p} + \log K\left(\frac{r_p^6}{d^3}\right) \qquad (6)$$

give a straight line of unit slope and intercept log $K(r_p^6/d^3)$. The same treatment applies for the *meta* protons. Figure 2 shows plots of log $1/T_p$ and log $1/T_m$. The continuous lines are drawn with unit slopes. The results clearly show that there is a linear dependence between the relaxation times of protons in ligands directly bound to $Ln^{III}$ ions and that of the outer-sphere water molecules. Using the values of the intercepts, −0.05 and 0.25, for the *meta* and *para* plots respectively and a value of 2.52 Å for the Ln–N bond length in the ytterbium(III) tris-dipicolinate complex,[8] a value of 4.5 ± 0.1 Å was obtained for the distance of the closest approach, $d$, of water molecules in the ytterbium(III) tris complex. This value is in good agreement with a value of 5.0 Å for the distance of closest approach of water molecules in the second sphere of the aquo-ion, calculated assuming that the radius of a water molecule is 1.43 Å. There is no evidence for inner-sphere water in these complexes.

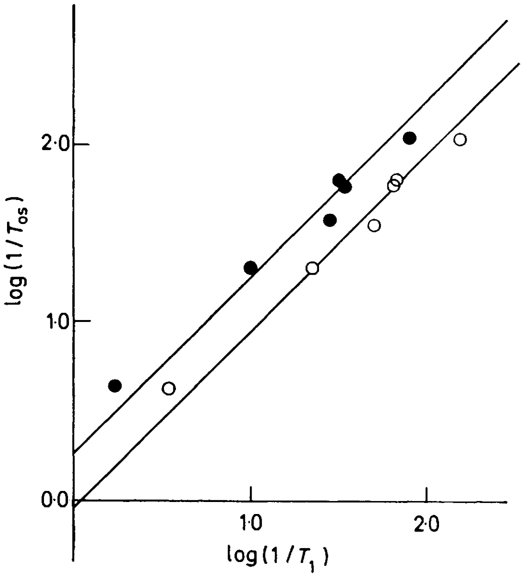

FIGURE 2 Plot of the logarithms of the molal longitudinal relaxation enhancement of different lanthanide(III) tris-dipicolinate complexes against the logarithms of the corresponding rates for *para* (●) and *meta* (○) protons in the ligands

The relaxation enhancement of water molecules in the presence of the mono- and bis-dipicolinate lanthanide(III) complexes is a result of the contribution on inner- and outer-sphere water molecules. The contribution of the inner sphere is given by equation (7) (neglecting $1/T_W$,

$$\frac{1}{T_n} = \frac{x_n}{W}\frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\gamma_I^2\mu^2\beta^2}{r_H^6}\tau_c \qquad (7)$$

which is very small in comparison). Here $r_H$ is the distance of water protons from the paramagnetic centre. Combination of equations (1) and (7) gives (for the *para* proton) equation (8). Thus a plot of log $1/T_n$ (after sub-

$$\log\frac{1}{T_n} = \log\frac{1}{T_p} + \log\frac{x_n}{W}\left(\frac{r_p}{r_H}\right)^6 \qquad (8)$$

tracting the outer-sphere contributions to the total relaxation obtained for the tris complexes, see Table 2) against log $1/T_p$ should give a straight line of unit slope and intercept of log $(x_n/55.5)(r_p/r_H)^6$. The same treatment applies to *meta* protons.

Figure 3 shows a plot of log $1/T_n$ for the mono complexes and log $1/T_n$ for the bis complexes against the corresponding values of log $1/T_p$ and Figure 4 shows the analogous plot for that of the *meta* protons. In both Figures, spin-lattice relaxation rates are used for the mono complexes and spin–spin relaxation rates for the bis complexes. The solid lines are drawn with unit slope.

The intercepts are 0.50 and 0.85 for the *meta* and *para* protons respectively. Using bond-distance values[8] of 2.60 Å for Ln–N and 2.58 Å for Ln–O,[11] 5.7 ± 0.2 and 2.8 ± 0.1 were obtained for the hydration numbers of the lanthanide(III) mono- and bis-dipicolinate complexes respectively. The results strengthen the previous suggestion[1] that the structures are nine-co-ordinate and approximately tricapped trigonal pyramidal. They require six and three water molecules, for the mono and bis complexes respectively, to complete the nine-co-ordinate structure. The results indicate that no change in the hydration number or in the denticity of the dipicolinate complexes is taking place along the lanthanide series.

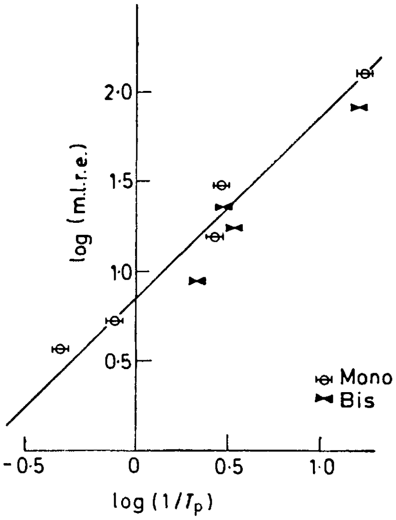

FIGURE 3 Plot of the logarithms of the molal longitudinal relaxation enhancements (m.l.r.e.) of the lanthanide(III) mono- and bis-dipicolinate complexes against the logarithms of the corresponding rates for *para* protons

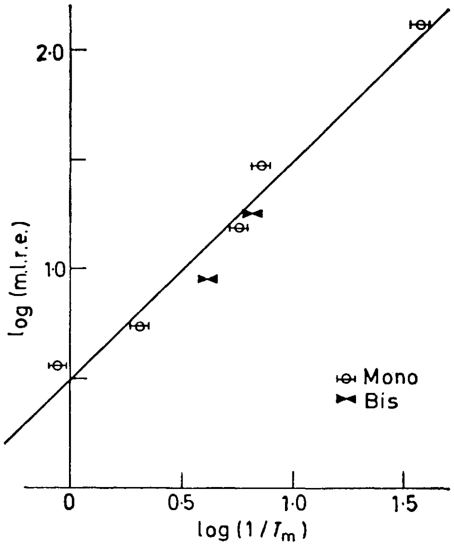

FIGURE 4 Plot of the logarithms of the molal longitudinal relaxation enhancements (m.l.r.e.) of the lanthanide(III) mono- and bis-dipicolinate complexes against the logarithms of the corresponding rates for *meta* protons

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