Studies of Lanthanide(III) Pyridine-2,6-dicarboxylate Complexes in Aqueous Solution. Part 1. Structures and ^1H Nuclear Magnetic Resonance Spectra

By **Basim M. Alsaadi, Francis J. C. Rossotti,** and **Robert J. P. Williams,*** Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

Conformations of lanthanide(III) pyridine-2,6-dicarboxylate (dipicolinate) complexes have been studied in solution by analysis of their ^1H n.m.r. spectra. The structure of the tris complexes (Ln = any lanthanide) could be described as a tricapped-trigonal prism for cations in the second half of the series. The bis complexes are shown to exist in states of fast exchange between different conformations. The ligands are mobile on the surface of the complexes and the carboxylate groups move into different positions within the complexes. A decrease in the rate of exchange occurs with decreasing radius of the central ion, reaching a shallow minimum at the thulium(III) complex. Using the paramagnetic perturbation of the n.m.r. signals of different protons in these bis complexes, a structure for the dispositions of the dipicolinate anions similar to that expected for a tricapped-trigonal prism is obtained for all the different lanthanide(III) complexes. Investigation of the n.m.r. spectra of the mono complexes has indicated that the mobility of the ligand is higher than in the bis complexes, but that the disposition of the dipicolinate ligands is similar.

THE relationship between the metal co-ordination number of lanthanide complexes in solution and their properties has received considerable attention.[1-5] There is ample evidence that the co-ordination number is greater than six in aqueous solution. Recent *X*-ray diffraction studies on lanthanide(III) aquo-ions show that the co-ordination number is either eight or nine [2,6-8] throughout the series. Despite this apparent similarity in structure, no simple variation of measured physicochemical properties of the complexes with the crystallographic ionic radius has been found, but rather the variation takes on an S-shape, the so-called tetrad effect. This has led many workers [2,3] to assume that a change in the co-ordination number of the central ion or in the structure of the complexes occurs along the series. In this paper we shall be concerned with the study of the structure of lanthanide(III) mono, bis, and tris complexes (Ln = any lanthanide) of 2,6-dipicolinate in aqueous solution. The study uses the perturbation of the shifts of the n.m.r. spectra of the above complexes caused by the presence of paramagnetic lanthanide(III) ions. The general method and its applications have been summarised recently.[9]

EXPERIMENTAL

Materials.—2,6-Dipicolinic acid (B.D.H.) was used without further purification. The purity ($\geqslant 99.5\%$) was checked potentiometrically. A stock solution of the disodium salt was prepared by dissolving an accurately weighed amount of the acid in a solution containing 99% equivalence of sodium hydroxide. The solution was filtered through a Millipore filter paper and stored in a polyethylene bottle.

Lanthanide (Ln) perchlorate solutions (0.2 mol dm^{-3}, 25 cm^3) were prepared from the corresponding oxides, except for the cerium solution which was made from the carbonate ($\geqslant 99.9\%$ purity, Rare Earth Products Ltd.). A weighed amount of lanthanide oxide (or cerium carbonate) was suspended in hot water (20 cm^3). The mixture was added slowly with stirring to a dilute solution (30 cm^3) containing slightly less than the equivalent amount of perchloric acid to dissolve *ca.* 98% of the oxide and kept near the boiling point. The mixture was left boiling until the reaction was complete (pH >6). The solution was then filtered, to remove unchanged oxide, and evaporated to 25 cm^3. The solution was acidified with dilute perchloric acid to pH 2.8 ± 0.1, filtered through a Millipore filter paper, and boiled for 20 min. If the pH showed any increase, more acid was added and the procedure repeated. The final solution, 25 cm^3, was filtered through a Millipore filter paper and transferred directly to a volumetric flask. Stock solutions showed no hydroxo-precipitate for a period of more than 3 years.

All the lanthanide perchlorate solutions were readily prepared using the above method except for those of cerium and terbium. The former needed a 20% excess of cerium carbonate and a longer boiling time of 3 h. The latter needed concentrated perchloric acid to dissolve the oxide and complete solution was only achieved by successively concentrating and diluting the solution. The cerium(III) solution was tested for the absence of cerium(IV).

Solutions of lanthanide(III) perchlorate were standardised, prior to use, by titrating against 0.01 mol dm^{-3} edta solution (edta = ethylenediaminetetra-acetate) using xylenol orange as indicator [10] with the reaction buffered (by acetate) at pH 5.8.

Procedure.—A series of solutions of lanthanide(III) and dipicolinate ions containing different metal-to-ligand ratios of 1 : 0.5, 1 : 2, 1 : 2.5, and 1 : 4 was prepared by mixing the appropriate metal perchlorate and sodium dipicolinate solutions, adjusting the pH carefully by using dilute Na[OH] and then gently evaporating to dryness. Solution and evaporation were then repeated twice from D_2O. Solutions for measurement (1 cm^3) were made up in D_2O and the pD was checked again to ensure that it was within the range 5.7 ± 0.3.

The concentration of the solutions used for ^1H n.m.r. studies depended on the metal and the type of the complex. Solutions (0.025 mol dm^{-3}) of Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, and Eu^{III} were easily prepared at the lower metal : ligand ratios above, although solutions of concentration >0.01 mol dm^{-3} were not obtainable for Tb^{III}, Dy^{III}, Ho^{III}, and Er^{III}, and only 0.02 mol dm^{-3} solutions could be prepared for Tm^{III} and Yb^{III}. A concentration of 0.15 mol dm^{-3} could be obtained for all the tris complexes at the 1 : 4 metal : ligand ratio, but in the present study 0.05 mol dm^{-3} solutions were used. The pD was raised to 7.0 to prevent their dissociation.

The n.m.r. spectra were recorded using either a Bruker 270 MHz spectrometer with a superconducting magnet (Oxford Instrument Company) or a Bruker HX90 spectrometer operating in the Fourier-transform mode. Transformation of the stored free induction decays, phase correction, and plotting of the spectra were carried out with a Nicolet 1085 computer. Probe temperatures in the 90 MHz spectrometer were measured using a precalibrated thermocouple and that of the samples in the 270 MHz spectrometer were calibrated using the shifts of the praseodymium(III) mono(dipicolinate) complex, which had previously been studied at 90 MHz. t-Butyl alcohol was used as an internal standard for shift measurement. The paramagnetic contributions to the shifts of the n.m.r. lines were obtained by correcting for the diamagnetic contribution by using the spectra of the corresponding lanthanum(III) complexes.

The spectra of the bis complexes were obtained in 50% v/v CD_3OD-D_2O over the temperature range −56 to 90 °C.

RESULTS

A typical series of n.m.r. spectra of the lanthanide(III) dipicolinate complexes at 27 °C was given by the holmium(III) complexes, see Figure 1. Solutions containing 1 : 4, 1 : 2.5, 1 : 2, and 1 : 0.5 metal : ligand mol ratios were examined. The aim of using some of these solutions was to obtain spectra which relate effectively to a single complex, *e.g.* those of 1 : 0.5 mol ratio. No change was observed in the magnitude of the shifts or the ratio of the shifts of different protons in the mono complexes when the spectrum for the 1 : 0.5 ratio was compared with that at a 1 : 1 mol ratio. There is no contribution to the spectrum of the 1 : 2 complexes from those of the 1 : 1 or 1 : 3 complexes at a 1 : 2.5 ratio. Only one set of sharp signals was seen for the 1 : 2 complexes, which are undergoing slow exchange. Other ratios were chosen to see if any exchange occurred between the bound and the free ligand in a mixture of complexes, and, in the case of the 1 : 4 mol ratio in order to avoid incomplete formation of the tris complex.

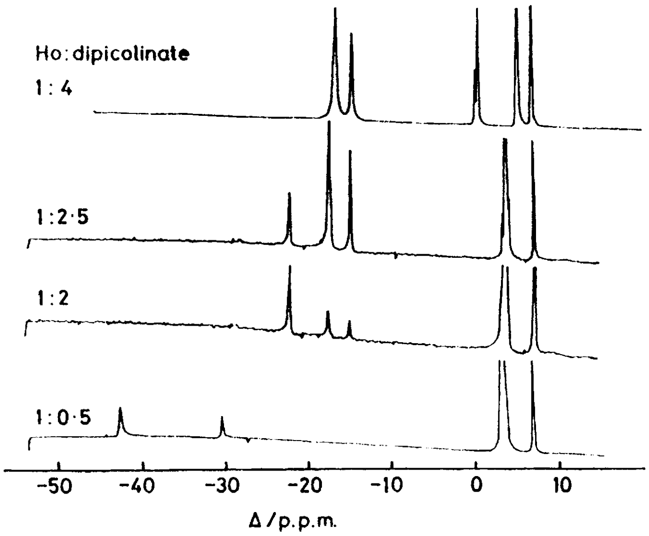

FIGURE 1 The 90-MHz ^1H n.m.r. spectra of dipicolinate ligands in the presence of various mol ratios of holmium(III) ions in D_2O as solvent at 25 °C

The spectrum of the solutions of 1 : 4 mol ratio at 27 °C showed two separate signals of relative area 2 : 1 for the holmium(III) and other heavy lanthanide complexes. They correspond to the *meta*- and *para*-protons of the bound ligands. This was confirmed in the case of ytterbium(III) solutions where signals of the bound ligand were seen to be a doublet (six protons per complex) and a triplet (three protons per complex) respectively. In addition to these two signals, two others appeared with a very small shift, if any, from those of the diamagnetic position of the ligand. These observations confirm earlier reports.[11,12] The spectrum of the praseodymium(III) solution showed only one signal corresponding to both the *meta*- and *para*-protons plus another very broad signal located near the diamagnetic position. The neodymium(III) solution at 1 : 4 mol ratio gave a spectrum of nearly separate signals for the *meta*- and *para*-protons, but somewhat broadened, and the free-ligand signal was also broad. The samarium(III) solution, which has the smallest isotropic shift, see Table 1, gave one signal corresponding to both the *meta*- and *para*-protons and another signal for the free ligand. Europium(III) solutions showed separate signals for the *meta*- and *para*-protons and also for the free ligand. In the case of all the early lanthanides the broadening of the lines indicated that the complexes are undergoing some exchange process.

TABLE 1

Shifts of the *para*, Δ_p, and *meta*, Δ_m, protons of the ligands in lanthanide mono- and tris-(dipicolinates), measured relative to the diamagnetic lanthanum(III) complexes in D_2O at 270 MHz and 300 K

Metal ion	Δ_p/p.p.m.			Δ_m/p.p.m.		
	mono	bis	tris	mono	bis	tris
Ce	−2.08			−2.36		
Pr	−5.25	−5.16	−4.01	−6.70	−6.50	−4.01
Nd	−2.39	−2.51	−2.21	−3.25	−3.16	−2.32
Sm	−0.39	−0.34	−0.46	−0.47	−0.42	−0.46
Eu	+3.74	+3.57	+3.22	+5.60	+5.00	+4.13
Tb	−36.87	−35.12	−25.80	−49.00	very broad	−29.59
Dy	−55.56	−58.91	−28.23	−76.21		−32.71
Ho	−30.37	−22.79	−15.29	−42.57		−17.87
Er	+17.05	+17.21	+8.74	+21.33		+10.37
Tm	+33.70	+26.30	+17.97	+44.24		+21.20
Yb	+14.53	+10.30	+6.59	+19.90		+7.62

The spectra of the solutions of 1 : 2.5 mol ratio at 27 °C, again using holmium(III) as an example, see Figure 1, showed no signals located near the diamagnetic position and due to the free ligand. In addition to the signals of the tris(dipicolinate) the spectrum showed another signal, which was shifted to lower field. This signal has an area corresponding to two protons per complex, *i.e.* it must be due to the two *para*-protons of the bis complex. The same result was found with solutions of cations of the second half of the series. In the case of the ytterbium(III) solution this signal was a triplet, *i.e.* that of the *para*-protons in the bis complexes. Solutions of Pr^{III}, Nd^{III}, and Eu^{III} showed, in addition to the signals of the tris(dipicolinate) complexes, two signals which were a doublet and a triplet, of relative area 2 : 1. The new signals must belong to the bis complexes. The samarium(III) solution did not show any separation of the *meta*- and *para*-signals due to its very small shift. The appearance of separate signals for the free dipicolinate in the second half of the series and for the bound ligand in each of the lanthanide(III) complexes indicated that only slow or very slow exchange was taking place between the free ligand and the bis and tris complexes. In some cases the magnitudes of the shifts of the 1 : 3 complexes obtained in the absence of an excess of ligand, *i.e.* at 1 : 2.5 mol ratio, were slightly greater than those obtained in the presence of an excess of dipicolinate. This was especially true in the second half of the series and indicates some exchange with the free ligand. The peak of the free ligand was also slightly shifted.

In solutions of 1 : 2 mol ratio at 27 °C all the signals corresponding to free dipicolinate or tris complexes were effectively absent from the spectra. There was only one signal from the solutions of the second half of the series corresponding to the bis complexes. Further investigation of the behaviour of the spectra of the bis complexes,[13] in the case of ytterbium(III) bis(dipicolinate) was carried out using solutions of 50% v/v CD_3OD-D_2O. Increasing the temperature caused another signal to appear and further increase in the temperature sharpened this new signal, which had an area corresponding to four protons per complex. This signal was due to the *meta*-protons. The complexes of Tm^{III}, Er^{III}, Ho^{III}, Dy^{III}, and Tb^{III}, see Figure 2, showed very similar behaviour but over different ranges of temperature. In the case of Dy^{III} and Tm^{III} no sharpening of the signal was observed (see Figure 2) before the solution started to boil. Below room temperature two new signals of equal area, each equal to that of the *para*-proton, appeared. These signals must arise from differently disposed *meta*-protons; one shifted upfield, m_1, in the cases of Yb^{III}, Tm^{III}, and Er^{III}, *i.e.* in the same direction as that of the *para*-proton signal, and the other shifted downfield, m_2, see Figure 2.

As mentioned before, the spectra of the bis complexes of Pr^{III}, Nd^{III}, and Eu^{III} showed, at room temperature, two signals corresponding to the *meta*- and *para*-protons, *i.e.* four and two protons respectively per complex. Decreasing the temperature causes the doublet of the *meta* signals to broaden, see Figure 3. As the temperature was dropped further the signal disappeared leaving that of the *para*-proton only. Further decrease in the temperature did not result in any change in the spectra until −56 °C where the solutions freeze. In the case of the praseodymium(III) complex, the temperature was taken to −63 °C in 70% CD_3OD-D_2O. At or around this temperature the expected two *meta* signals appear clearly, one shifted downfield, m_1, and the other shifted upfield, m_2.

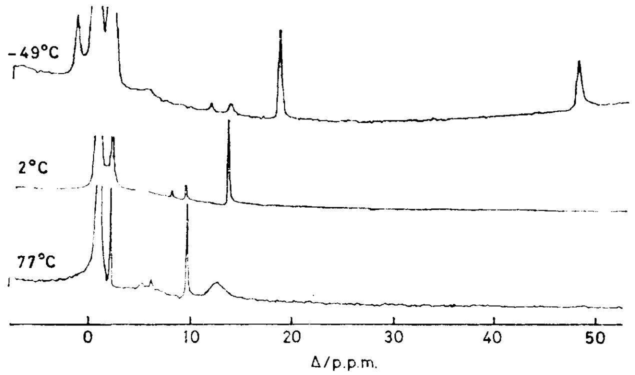

FIGURE 2 Effect of temperature on the 90-MHz ^1H n.m.r. spectrum of dipicolinate ligands in the thulium bis complex with 50% v/v CD_3OD-D_2O as solvent. Note the two *meta*-proton peaks at *ca.* 50 and −5 p.p.m. at −49 °C and their coalescence to a single peak at 13 p.p.m. at 77 °C. The sharp peak in the centre of the spectrum at −49 °C is that of the *para*-proton

The spectrum of a solution of holmium(III) dipicolinate of 1 : 0.5 mol ratio, and those of the rest of the second half of the series, shows only two separate signals of area 2 : 1 and corresponding to all the *meta*- and *para*-protons in the complex. The spectra of the complexes of the first half of the lanthanide(III) series showed the fine structure of the *meta*-(doublet), and *para*-(triplet), protons. The lanthanum(III) solution at 27 °C, like that of the bis complex, showed nearly completely resolved fine structure with the *para*-proton signal shifted further downfield.

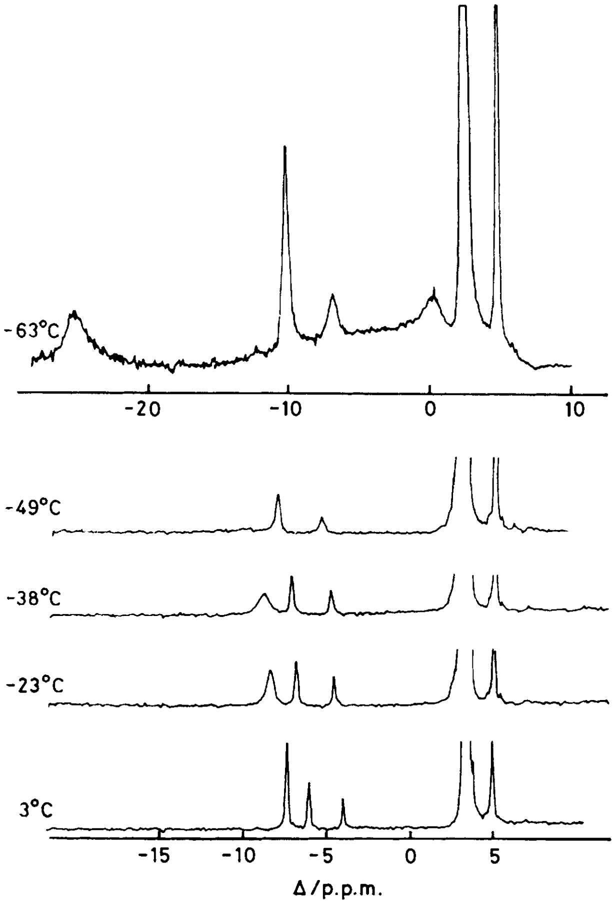

FIGURE 3 Proton n.m.r. spectra of the praseodymium bis(dipicolinate) at various temperatures. Top spectrum taken at 270 MHz and using 70% v/v CD_3OD-D_2O as solvent; lower spectra at 90 MHz and using 50% v/v CD_3OD-D_2O as solvent

DISCUSSION

The tris(dipicolinate) complexes in the second half of the series show an average paramagnetic shift ratio between *meta*- and *para*-protons (taken in the absence of an excess of ligand, *i.e.* at the 1 : 2.5 mol ratio), which is constant and equal to 1.17 ± 0.01, see Table 1. The shift ratios in the first half of the series are somewhat different and these differences are outside experimental error. Although a moderate rate of exchange between the free and bound ligand would affect the shift ratio at a 1 : 4 mol ratio, the effect is clearly extremely small at the 1 : 2.5 mol ratio. The reason for the small difference in behaviour between the early and late members of the lanthanide series might be due to a variety of internal motions within the complexes. Contact shifts were shown to be absent using the procedures described previously.[9]

Where there is constancy of the shift ratio along a series of lanthanide(III) complexes, it may be assumed that the shifts are purely dipolar and that the complexes possess axial symmetry. The equation describing the ratio of the dipolar shifts of *meta*- and *para*-protons is then given by [14] (1) where $\Delta_{m,p}$ are the shifts of the *meta*-

$$\frac{\Delta_m}{\Delta_p} = R_{m,p} = \left(\frac{3\cos^2\theta_p - 1}{3\cos^2\theta_m - 1}\right)\left(\frac{r_p}{r_m}\right)^3 \qquad (1)$$

and *para*-protons in the dipicolinate ligands, $r_{m,p}$ their distances from the metal ion, and $\theta_{m,p}$ are the angles between the vectors joining each nucleus to the probe atoms and the symmetry axis.

Intraligand distances derived from accurate bond lengths and angles reported [15] for pyridine were used to calculate the following distances: [11] N–H_p 3.89 Å; from H_m perpendicular to the line joining N–H_p, 2.15 Å; and from N to the previous right-angle intersection, 2.60 Å.

An *X*-ray crystallographic determination [16] of the structure of the solid tris complex showed that the three tridentate dipicolinate ligands are disposed to give a nine-co-ordinate species with D_3 symmetry. The three nitrogen atoms lie in a plane normal to the C_3 axis and the angle θ_p between the C_3 rotational axis and the Ln–H_p vector is 90°. Using this geometry a value of 73.8 ± 0.02 is obtained for θ_m. Essentially the same value, 73°, has been obtained by Donato and Martin.[11] Consequently a value of 46 ± 1° is obtained for the angle α between the planes of the aromatic rings and the planes bisecting them and containing the three nitrogen atoms.

The n.m.r. spectral behaviour of the bis complexes is quite different from those of the tris and mono complexes. It is obvious that, at low temperature, where two signals appear for *meta*-protons in the ligands, these signals must arise from differently disposed *meta*-protons relative to the metal ion.[13] As the temperature is increased these two differently disposed *meta*-protons start to exchange. This exchange causes the two signals, m_1 and m_2, to broaden until they disappear. At higher temperatures, where the rate of exchange is greater than the separation in Hz, the signals collapse and coalesce with each other giving one signal. Further increase in the temperature increases the rate of exchange and consequently sharpens the new signals. The average shift ratios of m_1 : p and m_2 : p, at low temperatures, are 2.60 ± 0.10 and −0.12 ± 0.08. The mean shift ratio is therefore 1.24 ± 0.08 which is the same as that found at high temperatures, *i.e.* 1.29 ± 0.03 for the combined *meta*-protons. A plot of the shifts of m_1 and m_2 of the bis complexes of Yb^{III} and Tm^{III} against the reciprocal of the absolute temperature is shown in Figure 4. Extrapolation of these two plots to high temperature shows that the average of these expected hypothetical shifts is very much the same as that found for the *meta*-protons at high temperatures. This clearly indicates that, on changing the temperature, no change in the average structure or in the symmetry axis takes place. Similar behaviour for complexes of several different metal ions again indicates that these complexes are isostructural with axial symmetry [13] and that the shifts arise from dipolar interactions.

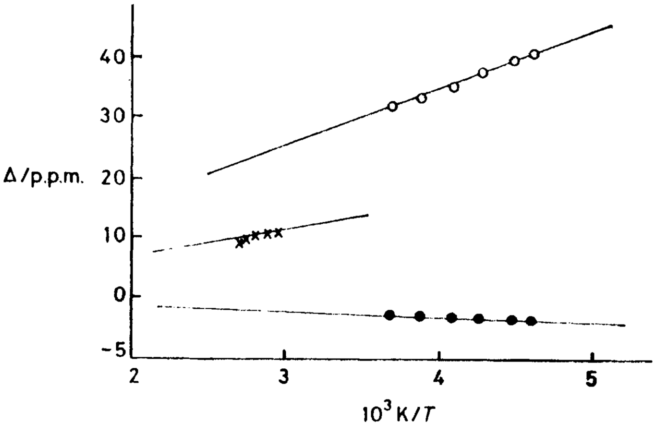

FIGURE 4 A plot of the shifts of the *meta*-proton peaks of ytterbium bis(dipicolinate) against the reciprocal of the absolute temperature. At low temperatures, there are two peaks (● and ○) but at high temperatures, there is only one, averaged peak (×)

Using the values of the ratios of the shifts of the m_1 and m_2 protons to that of the *para*-proton for the bis complexes, at low temperatures, the values of θ_{m_1}, θ_{m_2}, and θ_p were found, by computer-search analysis,[9] to be 84 ± 2, 53.6 ± 0.5, and 67.5 ± 0.5° respectively, using an M–N bond length of 2.4—2.7 Å. The angle α between the planes of the aromatic rings and the plane bisecting them and containing the two nitrogen atoms was found to be 47 ± 1°. The angle θ_p of 67.5 ± 0.5° corresponds to an N^1–M–N^2 angle 135 ± 1° and indicates that the disposition of dipicolinate rings is similar to that expected for a nine-co-ordinate tricapped-trigonal prism completed by three water molecules.[17] An N^1–M–N^2 angle of 135° is slightly greater than that of 120° for a perfect trigonal prism. This may result from a reduction in the interaction between the two pyridine rings. Elsewhere [18] we show that three water molecules are in fact present in these complexes.

Since increase in the temperature only affected the shift and broadening of the *para*-proton in an expected manner, the exchange between the two *meta*-protons must be occurring while the M–H_p axis acts as a rotational axis. This can be achieved by rotation through an angle of 96° around the M–H_p axis. There is no reason why rotation to the other side by 84° could not take place, except for steric hindrance when the two carboxylate groups cross each other, but this leaves the two *meta*-

protons unaffected. It is very likely that the high-temperature motion involves full rotation about the M–H_p axis, which makes the two *meta*-protons equivalent while not affecting the *para*-proton.

At low temperatures the rate of exchange of the *meta*-protons is less than the separation (in Hz) between the two signals. At high temperatures the rate of exchange is greater than the separation between the two signals (one signal is observed which sharpens on increasing the rate of exchange). The rate of exchange at the coalescence temperature is given by[19] $k = \pi(\nu_{m_1} - \nu_{m_2})/2$ where k is the rate of exchange and ν is the shift in Hz. Clearly this expression indicates that the coalescence temperature is dependent on the frequency at which the n.m.r. signals are measured. The coalescence temperatures of the bis complexes were measured at two different frequencies, 90 and 270 MHz, see Table 2.

TABLE 2

The coalescence temperatures, $^*T$, of the two *meta* signals for the lanthanide(III) bis(dipicolinate) complexes at 90 and 270 MHz, together with the values of the shift for the *para*-protons, Δ_p, at these temperatures in 50% v/v CD_3OD–D_2O

	270 MHz		90 MHz	
Ln^{III}	$^*T$/°C	Δ_p/p.p.m.	$^*T$/°C	Δ_p/p.p.m.
Pr	-31.0 ± 0.5	-7.30	-36.0 ± 0.5	-7.61
Nd	-40.0 ± 0.5	-3.46	-45.0 ± 0.5	-3.52
Eu	-13.5 ± 0.5	4.02	-19.5 ± 0.5	4.12
Tb	33.0 ± 1.0	-33.79	26.0 ± 1.0	-34.90
Dy	63.5 ± 1.0	-48.25	55.5 ± 1.0	-50.00
Ho	47.5 ± 1.0	-20.01	39.5 ± 1.0	-21.65
Er	62.0 ± 1.0	14.95	54.0 ± 1.0	16.01
Tm	74.0 ± 1.0	20.20	65.0 ± 1.0	21.52
Yb	54.0 ± 1.0	9.16	44.0 ± 1.0	9.45

Using the magnitude of the shift of the *para* signal, ν_p, as a measure of the expected separation between the two *meta* signals in the absence of exchange, *i.e.* $(\nu_{m_1} - \nu_{m_2}) = 2.8\ \nu_p$, rates of exchange, k, were calculated from the observed separation of these two signals. Rates of exchange were obtained at two temperatures for each lanthanide(III) bis complex and were estimated at 25 °C by using the equation $k = k_0\,e^{-E/RT}$ where E, the activation energy for the exchange process, was found to be 100 ± 20 kJ mol^{-1} for all the lanthanides studied.

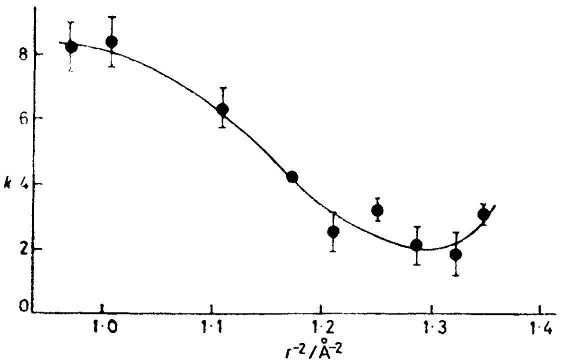

FIGURE 5 A plot of the logarithms of the rate constants, k, for the internal motion of the dipicolinate ligands at 25 °C for the series of lanthanide(III) bis(dipicolinate) complexes against the reciprocals of the squares of the lanthanide(III) cationic radii. From left to right, the ions are Pr^{III}, Nd^{III}, Eu^{III}, Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}, Tm^{III}, and Yb^{III}

Figure 5 shows the variation of the exchange rates, at room temperature, with the reciprocal of the squares of the cationic radii. At the beginning of the series with Pr^{III} and Nd^{III}, the rate of spinning of the ligand is very fast and comparable to that of the rate of exchange of water molecules.[20] A drop in the exchange rate is seen on moving towards Tm^{III}, where it reaches a shallow minimum. A similar trend was found for the rates of exchange of water molecules in lanthanide(III) aquo-complexes,[20] but the magnitude of the drop was very much less than that found in the present study.

For lanthanide(III) ions an electrostatic interaction with water molecules and ligands might have been expected to increase regularly along the series. The rigidity of the lanthanide(III) bis(dipicolinate) complexes in solution would accordingly increase with decreasing cationic radius. Indeed, the results show a general decrease in the rate of spinning with decreasing radius, but the decrease is not regular near the end of the series and there appears to be a shallow minimum at Tm^{III}. This indicates that there may be an extra rigidity at Tm^{III}, associated with the $4f$ core rather than with cationic size. The exact nature of any such ligand-field term is unknown, but it is known that the ligand-field splittings of the thulium(III) aquo-ion complexes are greater than in any other lanthanide complex.[21]

In all the lanthanide(III) mono(dipicolinate) complexes studied, except samarium(III), the shift of the pair of *meta*-protons is always larger in magnitude than that of the *para*-proton and has the same sign. The constancy of the *meta* to *para* shift ratio within the lanthanide series (1.32 ± 0.07) indicates that the shifts are purely dipolar and that these complexes possess axial symmetry. The shift ratio was used to calculate θ_m and α (see tris and bis complexes above) on the assumption that the symmetry axis was perpendicular to the M–H_p direction. Values of $\theta_m = 78 \pm 1°$ and $\alpha = 33 \pm 5°$ were obtained (α is the angle which the plane of the aromatic ring forms with the plane bisecting it and perpendicular to the symmetry axis). The value of $\alpha = 33 \pm 5°$ obtained is very far from those found for the tris and bis complexes (46 and 47° respectively). Another possibility was therefore tested where the symmetry axis was allowed to lie along the M–N–H_p vector, *i.e.* $\theta_p = 0$, and all three *meta*- and *para*-protons fall inside the shift cone. A shift ratio of 1.19, for an M–N bond length of 2.5 Å, is found on this assumption. This ratio is not sensitive to change in the M–N bond length and thus this solution is unlikely. A third possibility is that the two *meta*-protons are equivalent due to averaging through exchange processes similar to those found in the bis complexes. In fact the shift ratio and the magnitude and sign of the shifts are very similar to that found in the bis complexes at high temperatures and this could well imply that the symmetry axis is at *ca.* 60° to the plane of the ligand, giving $\alpha = 46°$. In the case of the thulium(III) mono complex, the probe temperature was taken down to −65 °C using 70% v/v CD_3OD-D_2O as solvent in a search for a rigid form, but no change in the spectrum was detected, suggesting that motion, if any, must be very fast.

The results show that no change in structure occurs along the lanthanide series for any of the three dipicolinate complexes. The co-ordination number is probably nine and the structure a tricapped-trigonal prism in each case. This implies that the mono- and bis-(dipicolinate) complexes retain six and three water molecules respectively in their inner co-ordination sphere. An experimental investigation of the hydration of the complexes is reported elsewhere.[18]

[9/850 *Received*, 1*st June*, 1979]

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