Structure of Lanthanide(III) Mono- and Bis-dipicolinates in Solution

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Summary The ^{1}H n.m.r. spectra of lanthanide(III) mono- and bis-dipicolinate complexes show that, in aqueous solutions and at room temperature, each ligand is spinning about its metal–nitrogen bond axis; the instantaneous structure of the bis-complex is probably a tricapped trigonal prism, in which three water molecules complete a nine-co-ordinate complex.

The use of lanthanide aquo-cations, Ln^{III}, as structural shift probes has been reviewed recently.[1] The ratios of the pseudocontact shifts, $R_{i,j}$ of n.m.r. lines of different protons of a substrate binding to a lanthanide ion, which has a fast electron relaxation time, are given by equation (1), where

$$\frac{\Delta_i}{\Delta_j} = R_{i,j} = \frac{r_j^3\,(3\cos^2\theta_i - 1)}{r_i^3\,(3\cos^2\theta_j - 1)} \qquad (1)$$

$\Delta_{i,j}$ are the shifts of the nuclei i and j, $r_{i,j}$ their distances from the metal ion and $\theta_{i,j}$ are the angles between the vectors joining each nucleus to the probe atom and the symmetry axis. The equation assumes axial symmetry, which is taken to be the case if the different Ln^{III} ions give identical ratios, $R_{i,j}$. Clearly effective axial symmetry for many complexes can only be achieved by thermal averaging.[2,3] The deduced distances, $r_{i,j}$, can be confirmed using proton spin relaxation induced by lanthanide ions. If the proton spin relaxation is isotropic for each lanthanide complex,[1] the ratios of the relaxation rates ($1/T_1$ and $1/T_2$) would be independent of the lanthanide ion used and proportional to the inverse ratios of the sixth power of $r_{i,j}$.[1] An interesting test of the assumptions behind the use of both shift and relaxation probes has arisen in the following study of the 1 : 1 and 1 : 2 Ln^{III} dipicolinate complexes. The 1 : 3 dipicolinate complexes have been studied earlier and the above approach to conformational analysis was shown to be successful.[4,5]

Solutions containing Ln^{III} mono- and bis-dipicolinate complexes were prepared, in D_2O, pD = 5·7 ± 0·3, at a concentration of 0·01M metal ion. The 0·5 : 1 and 2 : 1 ligand to metal molar ratios give solutions containing almost entirely 1 : 1 and 2 : 1 complexes respectively. The ^1H n.m.r. spectra of the bis complex solutions were examined in 50% v/v D_2O–CD_3OD, over a temperature range of −56 to +96 °C. The ^1H n.m.r. spectra were recorded on Brüker 90 and 270 MHz n.m.r. spectrometers operating in the Fourier transform mode. The conformations of the complexes were found by computer techniques described earlier.[1]

The ^1H n.m.r. spectra, at room temperature, of Ln^{III} mono-dipicolinates (Ln = Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, and Yb, with La as a diamagnetic blank) showed two signals, corresponding to *meta* (2) and *para* (1) hydrogens. The ratio of the two shifts was found to be 1·32 ±0·05 in all cases. The complexes thus appear to have effective axial symmetry. Longitudinal relaxation rates ($1/T_1$) of the above signals are given in the Table. The ratios of the relaxation rates are reasonably constant within the experimental errors for the different lanthanides. This indicates that the relaxation mechanism for these nuclei in the presence of different lanthanide ions is isotropic. The relaxation ratio, 2·3 ± 0·4, agrees well with the ratio of $(r_p/r_m)^6$ assuming an Ln–N bond length in the range 2·4—2·7 Å.[4]

TABLE. Values of the relaxation rates of H_p and H_m of different lanthanide mono-dipicolinate complexes, measured using 180°–τ–90° sequence at 90 MHz.

Metal ion	$(1/T_{1p})$ /s^{-1a}	$(1/T_{1m})$ /s^{-1a}	$(1/T_{1m})$ /$(1/T_{1p})$
Pr	0·8 ± 0·1	2·0 ± 0·2	2·5 ± 0·5
Nd	2·7 ± 0·2	5·8 ± 0·4	2·2 ± 0·3
Tm	18·5 ± 1·3	39·0 ± 2·3	2·1 ± 0·3
Yb	3·1 ± 0·2	7·1 ± 0·5	2·3 ± 0·3

[a] After substracting the diamagnetic contribution.

In order to describe the observations on the bis-dipicolinate complexes, we refer first to a specific example. The ^1H n.m.r. spectra, at room temperature, of Yb bis-dipicolinate (Figure) showed only one signal (a triplet) corresponding to two *para* protons per complex. Its shift is nearly identical to that in the 1 : 1 complexes. Increasing the temperature causes another signal to appear which is very broad at 55 °C but has narrowed considerably by 90 °C. The signal has twice the area of the *para* triplet and a shift ratio to it of 1·26 ± 0·02. Decreasing the temperature, below room temperature, causes two broad signals of equal area to appear in addition to that of the *para* proton signal. These signals must arise from two differently disposed *meta* protons: one shifted upfield and the other downfield relative to the diamagnetic position. The ^1H n.m.r. spectra of all other lanthanide ions showed very similar behaviour but over different ranges of temperature. The ratios of the two new signals, m_1, m_2, to that of the *para* proton were found to be 2·77 ± 0·02 and −0·245 ± 0·005 respectively. The mean shift ratio of these two *meta* protons to that of the *para* is 1·26 ± 0·02, which is the same shift ratio as that found at high temperatures for the average *meta* protons relative to the *para*. This indicates that there is no change in the average structure or the symmetry axis on changing the temperature. The results for the mono- and bis-dipicolinate complexes indicate that, at all temperatures, the molecules have effective axial symmetry.

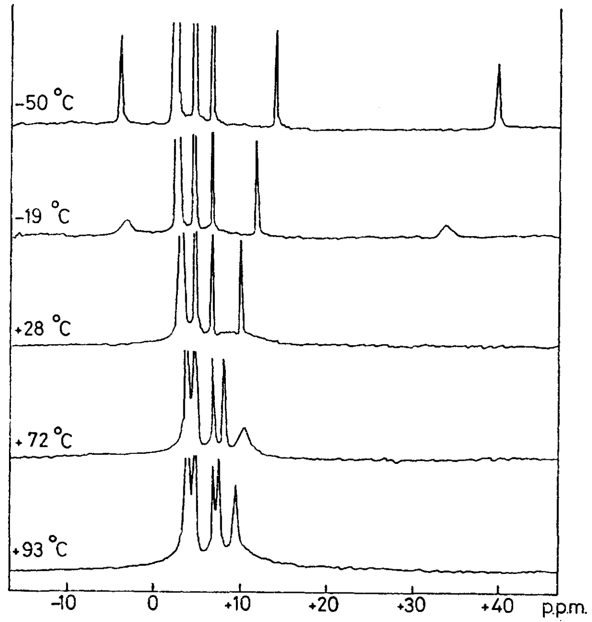

FIGURE. 90 MHz ^1H n.m.r. spectra of Yb bis-dipicolinate at various temperatures, sweep width 6000 Hz.

Using the ratios of H_{m_1} and H_{m_2} to that of the *para* proton for the bis-dipicolinate complexes, the values of θ_{m_1}, θ_{m_2}, and θ_p were found by computer search analysis to be 82, 53, and 67° respectively. The angle, α, which the plane of the dipicolinate anion forms with the plane bisecting the two rings and containing the two nitrogen atoms was found to be 47°. The finding that θ_p is 67°, *i.e.* the angle N^1–M–N^2 is 134°, suggests that the complex is a tricapped trigonal prism presumably with three water molecules completing a nine-co-ordinate complex. The symmetry axis is at 67° to the M–N direction which obviously differs from that of the tris-complex.

However, this complex in a static form has no higher symmetry element than a two-fold rotation axis. Axial symmetry can be generated by fast rotational motion about the symmetry axis. A fast flipping oscillation about the M–N bond of 86° between the two possible ways of setting up the above orientation of each of the dipicolinate ligands in the 2 : 1 complex is permitted also in which the distinction between the two *meta* protons is preserved. The high temperature motion must then involve full rotation about the M–N axis which makes the *meta* protons equivalent. As required by the shift data the mean shift ratio of the *meta* to the *para* protons is not altered by the motion and the position of the *para* proton relative to the metal symmetry axis is unaltered at all temperatures. Full rotation of the ligand may well occur in the mono-complexes. No rotation is required in the tris-complex to generate its axial symmetry.

Different Ln^{III} bis-dipicolinate complexes have different coalescence temperatures for the signals of the two *meta* protons. Coalescence temperatures were measured at two different frequencies, 90 and 270 MHz, and, together with the knowledge of the differences in the magnitude of the shift produced by each Ln^{III}, the rate of spinning of the ligand was found to decrease the smaller the size of the lanthanide cations, *i.e.* the rate of spinning is Pr>Nd>Tb>Ho>Er>Yb.

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