Hydration of Complexone † Complexes of Lanthanide Cations

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The ^1H n.m.r. spectra of some lanthanide(III) complexone complexes have been studied. The investigation showed that these complexes exist in states of fast exchange between different conformations on the surface of the metal ion. Measurements of the relaxation enhancements of water in the presence of these complexes showed a general decrease in the enhancements with increasing denticity of the ligands. This decrease was generally directly related to the hydration number of the complexes, but was also dependent on changes in electron-spin relaxation rates in different complexes.

In previous papers [1-3] we have discussed the variation of the chemical shifts and the relaxation times of the ^1H n.m.r. spectra of lanthanide, Ln^{III}, aquo-ions and their dipicolinate (pyridine-2,6-dicarboxylate) complexes. Initially it was found [1] that in the mono- and bis-dipicolinate complexes the ligands are in a state of fast exchange on the surface of the complexes. The ligands oscillate rapidly about the M–N bond axis. We then developed [2] a method by which we could determine the hydration numbers of these lanthanide(III) dipicolinate complexes. In this paper we shall apply the same methods to the study of the structure and co-ordination number of some of the complexes of Ln^{III} involving the ligands (complexones): dtpa, diethylenetriamine-*NNN'N''N''*-penta-acetate; edta, ethylenediamine-*NNN'N'*-tetra-acetate; hedta, *N*-(2-hydroxyethyl)ethylenediamine-*NNN'*-triacetate; nta, nitrilotriacetate; dpa, dipicolinate.

EXPERIMENTAL

Lanthanide(III) perchlorate solutions were prepared as described earlier.[1] The acid H_5dtpa (B.D.H.) was recrystallised twice from water and dried in vacuum at *ca.* 100 °C. Its purity, $\geqslant 99\%$, was checked potentiometrically. The salt $Na_2[H_2edta]$ (B.D.H.) of 99.5% purity was used without further purification. It was dried at 80 °C for 3 h. The salt $Na_3[hedta]$ (Aldrich), purity $\geqslant 99\%$, was standardised against standard $Cu[SO_4]$ solution and used without further purification. The acid H_3nta (B.D.H.) was recrystallised twice from water, and dried at 120 °C under vacuum. Its purity, $98.5 \pm 0.3\%$, was checked using standardised $Cu[SO_4]$ as titrant. The acid H_2dpa (B.D.H. pure) was used without further purification.

Preparation of Metal Complexes.—In a typical preparation of a metal–ligand complex, *e.g.* $[Ln(edta)]^-$, a known volume of metal solution was delivered into a specimen tube and a weighed amount of water added to it. To this solution a volume of the ligand solution corresponding to a 1 : 1.02 mole ratio, *i.e.* an excess of 2%, was added. The solutions were adjusted to the optimum calculated pH for the complete formation of a single complex, *e.g.* $[Ln(edta)]^-$, only. The pH, 7.5—8.0, was adjusted using dilute Na[OH] solution, 0.03 mol dm^{-3}. The pH was tested with a narrow-range pH paper and any solution which did not fall into the required range of pH was rejected. The final volume ranged from 1 to 2 cm^3.

Five solutions of concentration range 0.01—0.1 mol kg^{-1} of each of the complexes, $[Ln(nta)]$, $[Ln(hedta)]$, $[Ln(edta)]^-$, $[Ln(dtpa)]^{2-}$, and $[Ln(nta)_2]^{3-}$ (Ln = Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, or Yb), and duplicate solutions of Ln and dpa solutions of different mole ratio [2] were prepared. Solutions for the n.m.r. measurements were made in D_2O under the same conditions.

Measurements of the longitudinal relaxation enhancements and the recording of the n.m.r. spectra were carried out as described earlier.[2,3]

RESULTS

The proton n.m.r. spectra of $[Ln(edta)]^-$, $[Ln(hedta)]$, and $[Ln(dtpa)]^{2-}$ showed very broad signals at room temperature. Increasing the temperature narrowed these signals considerably, for the complexes in the first half of the lanthanide series. Lowering the temperature below room temperature, even to a very low temperature, in CD_3OD–D_2O (50% v/v), did not result in any re-emergence of sharp signals. The observations at high temperature are similar to those observed for the dipicolinate complexes implying fast exchange amongst different conformers of the ligands in their complexes.[2] At low temperature, where we had hoped that any motion would be frozen out in a similar way to that observed in the study of the dipicolinate complexes, the observation of a single average spectrum suggests that, even at these temperatures, one motion or another is taking place at a moderate rate. Thus, it is not possible to obtain structural information from the perturbation of the shifts of different n.m.r. signals of the ligands. In the rest of this report we shall be concentrating on the water signals to obtain information regarding changes in hydration numbers along the series of lanthanide(III) complexone complexes.

The results of the measurements of the molal longitudinal relaxation enhancement, m.l.r.e., at the probe temperature, 39.5 ± 0.5 °C, using a Bruker Minispec P. 20 for $[Ln(dpa)]^+$, $[Ln(nta)]$, $[Ln(hedta)]$, $[Ln(edta)]^-$, $[Ln(dpa)_2]^-$, $[Ln(dtpa)]^{2-}$, and $[Ln(nta)_2]^{3-}$ are given in Table 1. The individual values are results of measurements on five solutions of each lanthanide(III) complexone complex of different concentrations. The results were subjected to a least-squares analysis. In the case of the [Ho(hedta)] complex a series of solutions in the concentration range 0.002—0.01 mol kg^{-1} were prepared within the pH range 5—7. Measurements of m.l.r.e. on these solutions gave constant molal relaxation enhancement indicating that no hydroxo- or polynuclear species exist within these ranges of pH and molal ion concentrations.

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† In this paper a complexone denotes an aminopolycarboxylate chelating agent.

Table 2 gives the results of measurements of the longitudinal and transverse relaxation enhancement, m.t.r.e., of some of the [Ln(edta)]$^-$ complexes at 20 and 2.7 MHz. The results show clearly that there is no appreciable change in the enhancements with frequency change. The results, *i.e.* m.l.r.e. = m.t.r.e. and that m.l.r.e. is frequency independent, are the same as those obtained for the aquo-ions.[3] We conclude that the enhancements in the presence of these complexes are therefore determined by the very short electron-spin relaxation times of the lanthanide(III) central ions.[3]

TABLE 1

Molal relaxation enhancements (kg mol^{-1} s^{-1}) of water protons in the presence of various lanthanide(III) complexes at 39 °C and 20 MHz

Metal ion	Ligand							
	H_2O	mono-dpa	nta	hedta	edta	bis-dpa	bis-nta	dtpa
Ce	8.1 ± 0.2	4.8 ± 0.3	5.6 ± 0.2	5.3 ± 0.1	4.2 ± 0.1	4.2 ± 0.3	2.8 ± 0.1	2.7 ± 0.1
Pr	10.2 ± 0.2	6.6 ± 0.3	6.0 ± 0.2	4.7 ± 0.1	3.9 ± 0.1	6.5 ± 0.3	2.9 ± 0.1	2.2 ± 0.1
Nd	21.4 ± 0.5	18.1 ± 0.5	14.6 ± 0.3	14.5 ± 0.3	11.6 ± 0.1	13.5 ± 0.5	6.3 ± 0.1	8.6 ± 0.1
Sm	1.7 ± 0.1	1.4 ± 0.2	1.1 ± 0.1	1.2 ± 0.1	1.0 ± 0.3	0.9 ± 0.3	0.4 ± 0.2	0.6 ± 0.1
Eu	1.6 ± 0.1	1.3 ± 0.2	1.1 ± 0.1	1.2 ± 0.1		0.9 ± 0.3	0.4 ± 0.2	0.6 ± 0.1
Tb	315.0 ± 6.3	254.0 ± 8.0	218.0 ± 5.0	198.0 ± 4.0	137.5 ± 3.0	160.0 ± 7.0	110.0 ± 3.0	82.5 ± 2.0
Dy	560.0 ± 11.2	382.0 ± 10.0	277.0 ± 5.0	222.5 ± 5.0	170.6 ± 3.0	235.0 ± 7.0	142.0 ± 3.0	96.0 ± 2.0
Ho	368.0 ± 7.4	267.0 ± 10.0	219.0 ± 5.0	153.0 ± 3.0	163.0 ± 3.0	149.0 ± 8.0	79.3 ± 2.0	83.0 ± 2.0
Er	380.0 ± 7.6	229.0 ± 8.0	194.0 ± 4.0	131.0 ± 3.0	123.0 ± 2.5	110.0 ± 3.5	72.0 ± 1.5	62.0 ± 1.7
Tm	379.0 ± 7.6	148.0 ± 5.0	133.0 ± 3.0	67.5 ± 1.5	42.0 ± 0.7	60.0 ± 2.0	41.6 ± 2.5	57.0 ± 1.2
Yb	49.5 ± 1.0	35.6 ± 2.0	25.3 ± 0.7	14.9 ± 0.3	12.3 ± 0.3	15.0 ± 1.0	6.6 ± 0.2	11.6 ± 0.3

Table 3 gives the molal relaxation enhancements of the solvent protons in the presence of [Ln(edta)]$^-$ complexes (Ln = Tb, Dy, Ho, Er, Tm, or Yb) at various temperatures. In general, the results are similar to those for the aquo-ion solutions, *i.e.* a small decrease in the enhancements with increasing temperature. Table 3 also includes the calculated activation energy, $\Delta E^{\ddagger}$, of the rate enhancements.[3] The values of $\Delta E^{\ddagger}$ are of the same magnitude as for lanthanide(III) aquo-ions but their order is different.

TABLE 2

Molal relaxation enhancements (kg mol^{-1} s^{-1}) of water protons in the presence of some lanthanide(III) edta complexes at 39 °C and at different frequencies

Metal ion	m.l.r.e. (20 MHz)	m.l.r.e. (2.7 MHz)	m.t r.e. (2.7 MHz)
Nd	11.6 ± 0.3	11.0 ± 0.5	11.6 ± 0.5
Tb	135.0 ± 4.2	140.0 ± 5.6	142.3 ± 6.0
Dy	170.0 ± 5.2	180.0 ± 7.2	175.0 ± 7.0
Ho	157.3 ± 6.0	152.0 ± 5.0	160.5 ± 6.0

TABLE 3

Effect of temperature on m.l.r.e. (kg mol^{-1} s^{-1}) of different lanthanide(III) edta complexes at 20 MHz

Metal ion	θ_c/°C (±0.5)						$\Delta E^{\ddagger}$/ kJ mol^{-1}
	8.9	14.9	25.1	34.9	45.6	57.2	
Tb	148.6	144.6	140.0	135.4	134.7	132.1	1.95
Dy	194.8	189.5	183.5	180.0	174.7	172.5	2.00
Ho	168.6	165.9	162.7	161.7	158.5	157.0	1.15
Er	139.0	135.0	129.2	124.6	120.2	115.8	2.93
Tm	43.6	43.4	42.2	41.7	41.0	39.8	1.48
Yb	12.6	12.4	11.8	11.5	11.1	10.6	2.77

DISCUSSION

In a previous paper [2] we have shown that the molal relaxation rate enhancement is the sum of the contribution from the outer and inner aquo-spheres of the lanthanide(III) complexes. The contribution of the inner sphere, bound water, is given by equation (1) [3] where X_0 is the number of water molecules bound to the

$$\text{m.l.r.e.} = \frac{X_0}{W}\left(\frac{1}{T_{\mathrm{M}}} - \frac{1}{T_{\mathrm{W}}}\right) \qquad (1)$$

central lanthanide ion and where, using conventional symbols, $1/T_{\mathrm{M}}$ is given by equation (2).

$$1/T_{\mathrm{M}} = \frac{20}{15}\left(\frac{\gamma_{\mathrm{I}}^2\mu^2\beta^2}{r^6}\right)\tau_{\mathrm{s}} \qquad (2)$$

The molal relaxation enhancements should show a regular decrease with decreasing number of water molecules in the first hydration sphere of the complex, assuming that the electron-spin relaxation time of the central lanthanide(III) ion is independent of the change of the environment in different complexes.

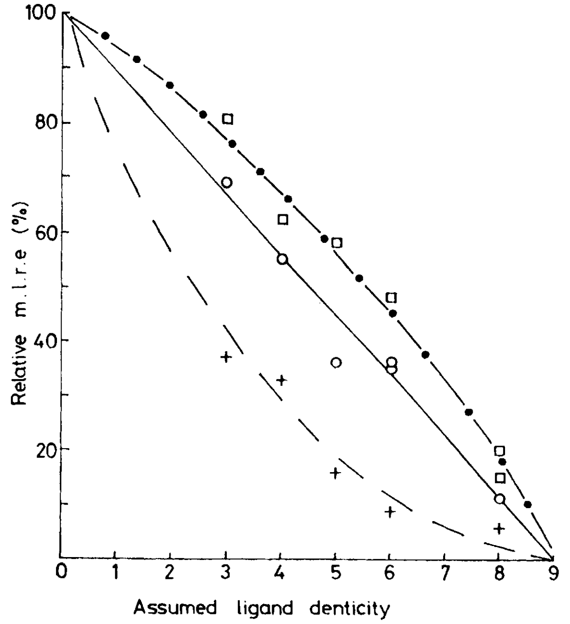
Using a value of 4.8 Å for the averaged outer-sphere closest approach of water molecules for all of these complexes,[4] the percent contribution of the outer-sphere to the total relaxation enhancements in each of the above complexes has been calculated.[4] The value is some 12% of the m.l.r.e. for the aquated ions. Table 4 gives the molal relaxation enhancements of solvent protons of different lanthanide(III) complexes, after subtracting this calculated outer-sphere contribution. The values for each complex are given relative to that of its aquo-ion, scaled to 100. Table 4 clearly shows that, in general, m.l.r.e. decreases with an increase in the number of carboxylate and amino-donor groups of each ligand, *i.e.* with the expected decrease of the number of water molecules around the central ion. In general the enhancements in the presence of different ligands falls in the order mono-dpa complex > nta > hedta > edta = bis-dpa > dtpa = bis-nta. The denticity increases in the reverse direction. However a plot of the m.l.r.e. percentages, from Table 4, against the total numbers of amino- and carboxylate donor groups of each complexone, *i.e.* the denticity, gives three somewhat different results for different groups of lanthanide(III) ions. (*i*) A linear dependence between m.l.r.e. and the denticity, passing through 100% (aquo-ion) and zero (the outer-sphere value) at an extrapolated denticity of nine was found for the complexes of

$\mathrm{Pr}^{\mathrm{III}}$ and $\mathrm{Ho}^{\mathrm{III}}$, Figure. This result strongly suggests that all the available carboxylate and amino-groups of each ligand are taking part in the binding to the central lanthanide(III) ion, that the total co-ordination number is nine in all the complexes, and that there is no change in the electron-spin relaxation time, τ_s, of these ions in different complexes. Of course a fortuitous compensation in the effect of different factors could have occurred. (*ii*) A smooth variation of m.l.r.e. with denticity, with values of m.l.r.e. at intermediate ligand denticity falling somewhat above the straight line but passing through 100 (aquo-ion) and zero at a denticity close to nine for each of the complexes of $\mathrm{Ce}^{\mathrm{III}}$, $\mathrm{Nd}^{\mathrm{III}}$, $\mathrm{Sm}^{\mathrm{III}}$, $\mathrm{Eu}^{\mathrm{III}}$, and $\mathrm{Tb}^{\mathrm{III}}$. The deviation is greatest at $\mathrm{Nd}^{\mathrm{III}}$. (*iii*) A smooth curve lying below the first line was found for the complexes of $\mathrm{Dy}^{\mathrm{III}}$, $\mathrm{Er}^{\mathrm{III}}$, $\mathrm{Tm}^{\mathrm{III}}$, and $\mathrm{Yb}^{\mathrm{III}}$ with the largest deviation at $\mathrm{Tm}^{\mathrm{III}}$, Figure. The curve passes through the points 100% (aquo-ion) and has an intercept at 0% at a denticity close to nine.

TABLE 4

Relative (%) m.l.r.e. values for various complexone complexes at 39 °C after correction for outer sphere effects

	Ligand							
Metal ion	H_2O	dpa	nta	hedta	edta	bis-dpa	bis-nta	dtpa
Ce	100	56	62	55	41	41	17	16
Pr	100	66	54	40	30	50	17	16
Nd	100	80	62	58	43	48	15	20
Sm	100	80	55	59	45	48	13	18
Eu	100	79	64	65		47	14	16
Tb	100	76	63	55	36	41	18	14
Dy	100	66	45	35	25	34	14	9
Ho	100	69	55	36	36	35	11	12
Er	100	58	47	30	26	24	10	11
Tm	100	37	33	16	9	13	6	8
Yb	100	67	47	27	21	25	7	13



Dependence of the relative value of m.l.r.e. (%) on ligand denticity for various lanthanide(III) complexes. The denticities are dpa (3), nta (4), hedta (5), edta (6), 2·dpa (6), dtpa (8). Results are given for holmium (○)(—), neodymium (□)(—·—), and thulium (+)(— — —)

In order to explain these observations we refer again to the results obtained with the dipicolinate series of complexes. It was shown [1,2] that all the lanthanide ions have the same conformation in each of the complexes $[\mathrm{Ln(dpa)}]^+$, $[\mathrm{Ln(dpa)_2}]^-$, and $[\mathrm{Ln(dpa)_3}]^{3-}$. It was reasonable to conclude that the co-ordination number in the complexes was the same, nine, in all cases. When we plot m.l.r.e. against denticity for ligands including the different complexes of dipicolinate we observe that in the large majority of cases all the data fall on a single smooth curve. The ligands give complexes of very different conformation (symmetry) so that symmetry does not appear to effect m.l.r.e. generally. In fact the simplest conclusion from equation (1) is that, while the co-crdination number remains fixed at nine in all complexes, τ_s varies differently for different cations. Examination of the case for which there is the greatest deviation from linearity in the plot of denticity against m.l.r.e. supports this conclusion, *i.e.* the series of thulium(III) complexes.

We have found [3-5] that, in particular, thulium(III) complexes of unidentate ligands are anomalous in their chemical shift ratio, that the thulium(III) aquo-ion has the longest electron-spin relaxation time, τ_s, and that τ_s of this aquo-ion has the largest temperature dependence. We attributed the anomalies of $\mathrm{Tm}^{\mathrm{III}}$ to relatively larger ligand-field splittings.[3] The anomalies disappeared in chelated complexes of $\mathrm{Tm}^{\mathrm{III}}$, *i.e.* complexes of higher denticity.[3] The τ_s value is itself dependent upon fluctuations of electrons amongst the electronic states generated by random thermal motions. A larger ligand-field splitting means that there is a Boltzman type restriction upon the number of electronic states which enter into these fluctuations. Changes in ligand-field strength will then produce changes in the availability of states and hence alter τ_s. In the case of $\mathrm{Tm}^{\mathrm{III}}$ the anomalies in the chemical shift ratio again disappear with multidentate ligands and at higher temperatures, and it is noticeable that τ_s is decreased by these changes more markedly than for any other lanthanide(III) ions,

TABLE 5

Calculated values of the spin relaxation times ($10^{13}\tau_s$/s) in lanthanide(III) complexes

	Metal ion										
Ligand	Ce	Pr	Nd	Sm	Eu	Tb	Dy	Ho	Er	Tm	Yb
H_2O	0.90	0.57	1.15	0.45	0.09	2.03	2.99	1.94	2.38	3.69	1.37
dpa	0.75	0.52	1.37	0.53	0.10	2.35	2.91	2.01	2.06	2.05	1.39
nta	1.00	0.54	1.25	0.48	0.08	2.35	2.56	1.94	1.98	2.00	1.19
hedta	1.14	0.50	1.53	0.63	0.13	2.52	2.34	1.59	1.63	1.30	0.81
edta	1.10	0.52	1.50	0.60		2.18	2.24	2.13	1.90	1.01	0.84
Bis-dpa	1.14	0.86	1.75	0.58	0.12	2.54	3.09	1.95	1.70	1.44	1.02
Bis-nta	1.36	0.72	1.58	0.50	0.10	3.34	3.55	1.98	2.15	1.95	0.89
dtpa	1.33	0.54	2.10	0.74	0.15	2.51	2.40	2.09	1.89	2.68	1.57
Tris-dpa	2.10	1.00	1.10	0.20	0.09	2.90	4.50	1.65	3.20	1.60	1.00

Table 5. A simple explanation of the variation of m.l.r.e. with denticity then is that it follows both the changes in τ_s and in the hydration numbers. The most reasonable explanation for the variety of observations in Table 5 is that all the complexes studied are nine-co-ordinate but that τ_s varies systematically, but differently for different metal ions, as the number of water molecules decreases.

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