Determination of the Number of Inner-sphere Water Molecules in Lanthanide(III) Polyaminocarboxylate Complexes

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The hydration numbers of various dysprosium(III) polyaminocarboxylates have been determined from the $\mathrm{Dy^{III}}$-induced ^{17}O NMR water shifts. The results are in good agreement with those obtained by other techniques. The data indicate that formation of polynuclear species occurs in the iminodiacetate and nitrilotriacetate systems.

The chemical properties of lanthanide(III) cations and the effects they induce in NMR parameters of nuclei in their proximity make them valuable for a variety of purposes. These cations and their chelates are employed as a tool in structural analysis with the use of NMR spectroscopy.[1–4] Chelates of the paramagnetic lanthanide $\mathrm{Gd^{III}}$ are being used in medical diagnostics with the magnetic resonance imaging technique.[5–9] Stable water-soluble chelates, especially $[\mathrm{Gd(dtpa)}]^{2-}$ (dtpa = diethylenetriamine-*N,N,N′,N″,N″*-pentaacetate) and $[\mathrm{Gd(tadta)}]^{-}$ (tadta = 1,4,7,10-tetraazacyclododecane-*N,N′,N″,N‴*-tetraacetate), are the most popular because of their low *in vivo* toxicity and rapid excretion properties.[10–13] These chelates remain in circulation long enough to affect the relaxation rates of water in body fluids and tissues, altering the contrast in tissue with high water content. One of the factors contributing to increase the water ^{1}H relaxation rates of the gadolinium(III) chelates is the number of water molecules that can co-ordinate directly to the metal ion. Therefore, techniques are needed to measure the number of inner-sphere water molecules of lanthanide(III) complexes allowing judicious choices to be made in developing paramagnetic contrast agents for specific applications.

Previously, it has been observed that, for paramagnetic lanthanide(III) ions, the contact contribution to the $\mathrm{Ln^{III}}$-induced shift of a $\mathrm{Ln^{III}}$-bound ^{17}O nucleus is almost independent of the nature of the ligand in question and also of the other ligands co-ordinated to the $\mathrm{Ln^{III}}$.[14–16] Therefore, the $\mathrm{Ln^{III}}$-induced ^{17}O shifts can be utilized to establish the co-ordination sites of the ligand and to determine the stoichiometry of the complex. For $\mathrm{Dy^{III}}$ as the lanthanide, the induced ^{17}O shift (d.i.s.) is dominated by the contact shift (usually >85%) and a laborious dissection of the observed induced shift into the contact and pseudo-contact contributions is not needed. The procedure applied in previous work[14–16] usually consisted of titration of an aqueous solution of the organic ligand with $\mathrm{Dy^{III}}$. In this way information is obtained on the complex in which the $\mathrm{Dy^{III}}$ is surrounded by the maximum number of organic ligands.

Here we report on a study of the determination of the number of co-ordinated waters in a series of dysprosium(III) polyaminocarboxylates, using a modified procedure. Since most of the complexes concerned have rather high stability constants, it was possible to determine the bound-water ^{17}O shifts of a complex with a chosen stoichiometry by monitoring the d.i.s. of ^{17}O of water as a function of the concentration of that complex. The general applicability of this method of determination of water co-ordination numbers of dysprosium(III) complexes is discussed and the results are compared with other methods which use NMR relaxation and luminescence spectroscopy.

Experimental

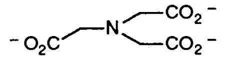
Ligand Abbreviations.—tadta = 1,4,7,10-Tetraazacyclododecane-*N,N′,N″,N‴*-tetraacetate; dtpa = diethylenetriamine-*N,N,N′,N″,N″*-pentaacetate; pdtta = *N″*-(propylcarbamoylmethyl)diethylenetriamine-*N,N,N′,N″*-tetraacetate; dpdtta = *N,N″*-di(propylcarbamoylmethyl)diethylenetriamine-*N,N′,N″*-triacetate; edda = ethylenediamine-*N,N′*-diacetate; edta = ethylenediaminetetraacetate; hedta = *N′*-2-hydroxyethylethylenediamine-*N,N,N′*-triacetate; ida = iminodiacetate; tanta = 1,4,7-triazacyclononane-*N,N′,N″*-triacetate; nta = nitrilotriacetate; ttha = triethylenetetraamine-*N,N,N′,N″,N‴,N‴*-hexaacetate.

Materials.—The ligands utilized were obtained from Aldrich as the free acids, except for pdtta and dpdtta, which were synthesised by published procedures.[17] The lanthanide(III) chlorides, in the form of hexahydrates, were obtained from Aldrich.

NMR Measurements.—The solutions of the lanthanide complexes were prepared in deionized water containing 20% D_2O, from measured amounts of stock solutions of the lanthanide chlorides and appropriate ligands. The pH of the final solutions was adjusted with HCl or tetramethylammonium hydroxide pentahydrate. The pH values quoted are direct readings as measured on a Crison micropH 2002 pH meter equipped with a glass electrode at 21 ± 0.5 °C. The glass electrode was calibrated by measuring the electromotive force of standard buffers at pH 4.000 and 7.020.

The d.i.s. measurements were performed at a $\mathrm{Dy^{III}}$/ligand molar ratio (ρ) corresponding to the desired complex stoichiometry, by variation of the concentration of the complex over the range from 15 to at least 100 mmol dm^{-3}. The natural-abundance ^{17}O NMR experiments were run at 27.122 MHz on a Varian XL-200 spectrometer, using 10 mm sample tubes. Probe temperatures were 21 ± 0.5 °C. The ^{17}O shifts, measured using the ^{17}O shift of water as external reference, were obtained with a precision of ±0.15 ppm. The spectra were measured using a pulse width (90° pulse) of 50 μs and acquisition times of 0.2 s, with a digital resolution of 0.18 Hz.

edta



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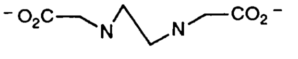

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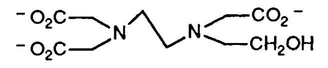
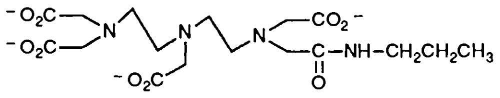
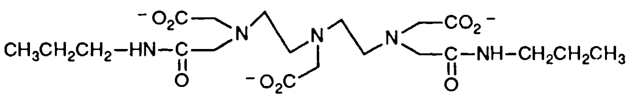


hedta



pdtta



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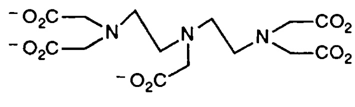
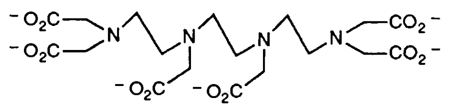


dtpa



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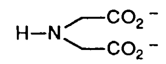

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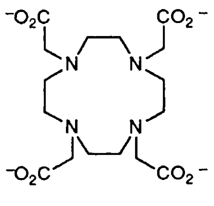
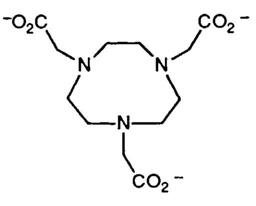


tadta



tanta

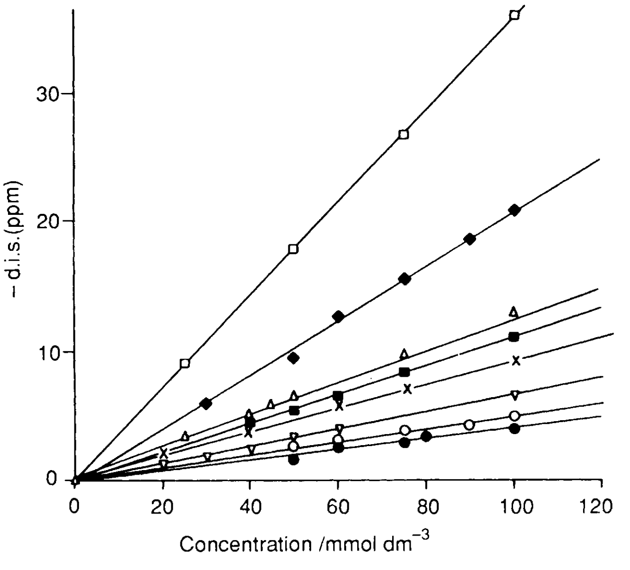


Fig. 1 Oxygen-17 NMR shifts of water *versus* dysprosium(III) chelate concentration for solutions of $DyCl_3$ (□), Dy(edda) (◆), Dy(hedta), pH 7.0 (△), $Dy(edda)_2$ (■), Dy(edta) (×), Dy(dpdtta) (▽), Dy(dtpa) (○), Dy(hedta), pH 10.0 (●)

The ^{139}La NMR spectra were measured at 56.499 MHz on a Varian VXR-400 S spectrometer using a pulse width (90° pulse) of 35 μs and acquisition times of 0.04 s, with a digital resolution of 6 Hz.

Results and Discussion

Addition of the dysprosium(III) complexes to water resulted in a shift of the water ^{17}O NMR signal to lower frequencies. The exchange of water was fast on the ^{17}O NMR time-scale. Assuming that the d.i.s. of a water ^{17}O nucleus is independent of the nature and of the stoichiometry of the complex, the experimental induced shift of a complex $Dy(ligand)_n(H_2O)_q$ can be given by equation (1). Here Δ is the shift of a water ^{17}O

$$\text{d.i.s.} = q\Delta[Dy(ligand)_n(H_2O)_q]/[H_2O] \qquad (1)$$

nucleus bound in the complex. The complex concentrations used were relatively low (usually < 150 mmol dm^{-3}). Therefore $[H_2O]$ is approximately constant and a plot of the d.i.s. *versus* $[Dy(ligand)_n(H_2O)_q]$ should give a straight line with slope $q\Delta/[H_2O]$, if q is independent of the concentration of the complex. For $\rho = 1$ and concentrations ranging from 15 to 100 mmol dm^{-3} the dysprosium(III) polyaminocarboxylate systems studied usually showed this linear relationship. However, for the Dy^{III}–ida and –nta systems deviations from linearity were observed. Some typical examples are depicted in Fig. 1, and the slopes of the lines, in the cases where linear relationships were observed, are compiled in Table 1.

The hydration of the lanthanide(III) ions is a subject of some controversy; hydration numbers of eight and nine have been proposed.[24] Recently, Merbach and co-workers[25] have concluded from neutron-scattering difference studies that the co-ordination number of Dy^{III} is eight for 0.3 and 1 mol dm^{-3} solutions of $DyCl_3$ and $Dy(ClO_4)_3$ in D_2O. On the other hand, Brücher *et al.*[26] have shown that the hydration number of Lu^{III} increases upon dilution up to values ≥ nine. Therefore, we assume that, for the low dysprosium concentrations that we

Table 1 Values of q for dysprosium(III) polyaminocarboxylate complexes at 21 °C derived from ^{17}O chemical shifts; comparison with literature values of corresponding complexes of Eu^{III}, Gd^{III} and Tb^{III}

				q		
Ligand	ρ	pH	$q\Delta[H_2O]^{-1}$ [a]/ ppm dm^3 mol^{-1}	NMR[b]	Fluorescence[c,d]	NMRD[e]
H_2O		3.5	−357	9.0	9.0[c]	9
edta	1.00	7.0	−90	2.3	2.5,[c] 2.6[d]	2.6–3
dtpa	1.00	7.0	−52	1.3	1.2,[c] 1.1[d]	1
pdtta	1.00	6.8	−69	1.7	1.1[c]	1
dpdtta	1.00	6.5	−67	1.7	1.0[c]	1
ttha	1.00	7.0	−6	0.2	0.2[d]	0
hedta	1.00	7.0	−126	3.2	2.9,[c] 3.2[d]	3.2
	1.00	10.0	−39	1.0	1.2[d]	1
edda	1.00	6.2	−207	5.2		
	1.00	5.3	−237	6.0		
	0.50	5.7	−105	2.6		
	0.25	6.2	−25	0.6		
tanta	1.00	7–8	−102[f]	2.5[f]	3.3[c]	2
tadta	1.00	7–8	−74[f]	1.9[f]	1.2[c]	1

[a] Slope of the plot of d.i.s. *versus* the concentration of the complex. [b] This work. [c] Values for the corresponding europium(III) complexes, see refs. 18 and 19. [d] Values for the corresponding terbium(III) complexes, see refs. 20 and 21. [e] Values for the corresponding gadolinium(III) complexes, see refs. 19–22. [f] Calculated from values for the dysprosium(III) complexes, see ref. 23.

Table 2 Values of q for Dy^{III}–ida and –nta complexes at 21 °C, derived from ^{17}O chemical shifts; comparison with literature values of the corresponding europium(III) complexes

				q	
Ligand	ρ	pH	$q\Delta[H_2O]^{-1}$ [a]/ ppm dm^3 mol^{-1}	NMR[b]	Fluorescence[c]
ida[d]	1.00	6.2	−157	4.0	
ida[d]	1.00	5.7	−216	5.4	
ida[e]	1.00	6.2	−157	4.0	
ida[f]	1.00	5.7	−50	1.3	
ida[e]	0.50	6.2	−55	1.4	
ida[e]	0.30	6.2	−4	0.1	
nta[d]	1.00	7.0	−114	2.9	5.0
nta[e]	1.00	7.0	−103	2.6	
nta[f]	1.00	7.0	−47	1.2	
nta[g]	1.00	7.0	−39	1.0	
nta[e]	0.50	7.0	−36	0.9	1.3

[a] Slope of the plot of d.i.s. *versus* the concentration of the complex. [b] This work. [c] Values for the corresponding europium(III) complexes (7 mmol dm^{-3}, pH 7.0), see ref. 18. [d] Samples obtained by successive dilutions of a 50 mmol dm^{-3} solution. [e] As *d* but starting from a 100 mmol dm^{-3} solution. [f] As *d* but starting from a 200 mmol dm^{-3} solution. [g] As *d* but starting from a 350 mmol dm^{-3} solution.

have used in the aqueous system, Dy^{III} is hydrated by nine water molecules. From the slope of the line concerned (−357 ppm dm^3 mol^{-1}) it can be calculated that, under the conditions applied, the value of $\Delta/[H_2O]$ for a co-ordinated water molecule is $-357/9 = -40$ ppm dm^3 mol^{-1}. Then, using this value and equation (1), from the slopes of the plots of d.i.s. *versus* the concentration of the complex the water co-ordination numbers (q) were calculated (see Table 1). For comparison, q values of Eu^{III}, Gd^{III} and Tb^{III} as obtained by luminescence spectroscopy[18,20,21] and nuclear magnetic relaxation dispersion (NMRD) measurements[19–22] are also included in Table 1. The agreement appears to be quite good.

Assuming a constant co-ordination number for Dy^{III} of nine, there are obviously $(9 - q)$ co-ordination positions left for the organic ligand. The data in Table 1 show that the polyaminocarboxylates are co-ordinated to the Dy^{III} ion *via* the maximum possible number of nitrogen and carboxylate donor sites. The q values for Dy^{III}(pdtta) and Dy^{III}(dpdtta) are both one, which suggests co-ordination of the amide function to the lanthanide ion. This is in agreement with previous predictions based on Gd^{III} NMRD studies,[19] a recent X-ray crystal structure study of Raymond and co-workers[27] on the related di(ethylamide), and with some recent ^{13}C NMR studies.[28]

The results for the Dy^{III}(hedta) system (see Table 1) show a pH dependence of q. At pH 7 $q = 3$, whereas increasing the pH to 10.0 lowers q to 1. This may be ascribed in part to an increase of the ligand denticity as a result of the deprotonation of the CH_2OH group around pH 10.[29] The decrease of q by a factor of three suggests that some oligomerization might occur, similarly to more extensive effects of this nature which were observed for the ida and nta systems (see below). These q values are in agreement with the results of luminescence and NMRD studies on some other Ln(hedta) complexes (Ln = Eu, Tb or Gd), which leads to the conclusion that monomers exist below pH 9 and oligomers at higher pH values.[20,21]

For the Dy^{III}–edda system the stability constants of the 1 : 1 and 1 : 2 complexes are relatively low and protonation of the 1 : 1 complex cannot be neglected.[30] Consequently the experimental q may have contributions from more than one species. Therefore, we compared these q values with those calculated from reported stability constants[30] and using water co-ordination numbers of five and one for the 1 : 1 and 1 : 2 species, respectively. For ρ = 1 the experimental q at pH 6.2 agrees very well with the value of 5.0 calculated for a mixture of 73% of Dy^{III}(edda), 14% of Dy^{III}(aq) and 13% of Dy^{III}(edda)$_2$. Lowering the pH to 5.3 leads to an increase of q by one unit. The calculated speciation shows that this could be attributed mostly to an increase of Dy^{III}(aq) rather than to protonation of Dy^{III}(edda). Using the calculated concentrations a q value of 5.5 was obtained, which agrees with the experiment.

For ρ = 0.25, the q value of 0.6 at pH 6.2 reflects full formation of the 1 : 2 complex, in accordance with the calculated speciation.

In the Dy^{III}–edda system at ρ = 0.5, the experimental q value of 2.6 at pH 5.7 was different from that expected for a complex stoichiometry of 1 : 2. This is explained by the presence of 33% of 1 : 1 and 67% of 1 : 2 complexes in solution, as calculated from published stability constants.

In the case of the Dy^{III}–ida and –nta systems, besides the problem of relatively low stability constants for the ida complexes, the results were found to depend on the method of preparation of the solutions. Table 2 shows data obtained from measurements on samples prepared by successive dilutions of stock solutions of given ρ and pH values. The d.i.s. of Dy^{III}(ida)$_3$ was negligible, indicating that $q = 0$ for this complex. If we assume a co-ordination number of nine for Dy^{III}, this implies that ida has three donor sites per ligand, as expected. The q

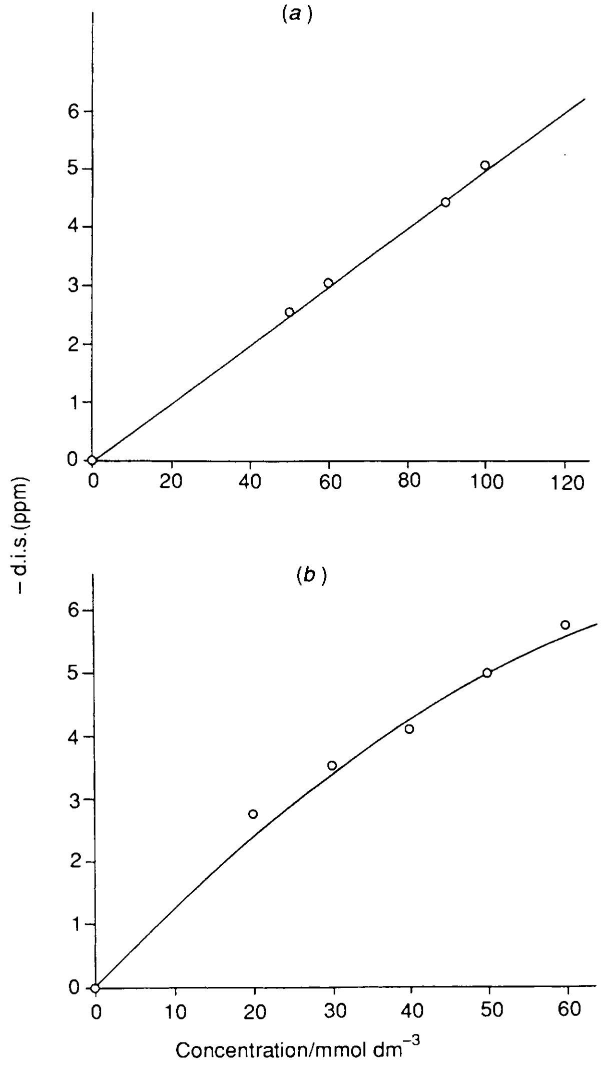


Fig. 2 Oxygen-17 NMR shifts of water *versus* concentration for the Dy^{III}–nta system (ρ = 1.00, pH 7.0): (*a*) prepared by successive dilutions of a 200 mmol dm^{-3} stock solution; (*b*) solutions prepared independently

Table 3 Contact contributions to the ^{17}O NMR shifts of water for various dysprosium(III) complexes with different water co-ordination number *q*

System	q^a	% Contact shift	Ref.
$Dy^{III}(aq)$	9	94	35
$Dy^{III}L^1{}_3{}^b$	2.8	85	36
$Dy^{III}(edta)$	2.1	99	23
$Dy^{III}(tanta)$	1.9	78	23
$Dy^{III}(tadta)$	0.6	35	23
$Dy^{III}(dtpa)$	0.8	91	37
$Dy^{III}L^2{}_2{}^c$	1.1	70	16

[a] As determined after separation of contact and pseudo-contact contributions. [b] L^1 = Glycolate (1 −). [c] L^2 = Triphosphate (5 −).

values obtained at ρ = 0.5 and 1 are lower than expected for complexes of stoichiometry $Dy^{III}(ida)_2$ and $Dy^{III}(ida)$, respectively. In the case of $Dy^{III}(ida)$ the *q* value was shown to be pH and concentration dependent. An increase in concentration of the stock solution causes a decrease of the measured *q* value. Increase of the pH at a fixed concentration of the complex had the same effect. Both increase of the concentration and the pH resulted in a marked increase of the viscosity of the sample. At concentrations ⩾150 mmol dm^{-3} or pH ⩾7 the samples appeared not to be stable with time, the pH was dropping gradually and gels were obtained after occasional adjustment of the pH. These phenomena indicate that for these systems polymeric species are formed, probably through hydroxo and acetate bridges.

A similar behaviour was observed for $Dy^{III}(nta)$ (see Table 2). Fig. 2 compares plots of d.i.s. values as a function of the concentration of the complex, obtained when a 200 mmol dm^{-3} solution of $Dy^{III}(nta)$ was diluted and where individual solutions were prepared separately at concentrations below 100 mmol dm^{-3}. In the second case the initial slope corresponds to *q* = 3.4, indicating that in highly diluted solutions a dimeric structure with on average three co-ordinated water molecules per Dy^{III} predominates.[14] For more concentrated solutions the hydration of the complex apparently decreases (*q* = 2.8), so the degree of oligomerization increases. Probably acetate bridges such as those found in the crystal structure of $[Dy(nta)]\cdot 2H_2O$ play an important role.[31] When successive dilutions from a stock solution were made, a linear plot with a slope corresponding to *q* = 1.2 was obtained, indicating that the depolymerization process upon dilution is quite slow.

Formation of polymeric species for solutions of lanthanide complexes at high concentration and/or pH has been observed before.[32,33] The formation of gels is enhanced if the lanthanide chloride and the ligand are mixed as solids and then dissolved.

The process of gel formation was studied using ^{139}La NMR spectroscopy. A 100 mmol dm^{-3} aqueous solution of La^{III}–ida at ρ = 1.00 and pH 7.0 yielded, sometime after its preparation by dissolving a mixture of the solids, a ^{139} La NMR signal with a chemical shift of 90 ppm relative to $La^{III}(aq)$, which corresponds to a 1 : 1 mixture of $La^{III}(ida)$ and $La^{III}(ida)_2$ in rapid exchange.[29] This signal was also much broader (linewidth 4100 Hz) than that obtained by mixing stock solutions to a final concentration of 100 mmol dm^{-3} (linewidth 1800 Hz).[29] This indicates that some disproportionation of La(ida) is occurring, yielding $La^{III}(ida)_2$ and large aggregates that escape observation by ^{139}La NMR spectroscopy. A similar phenomenon has been observed for the La^{III}–nta system at ρ = 1.00, where formation of $La(nta)_2$ was observed by ^{139}La NMR spectroscopy upon increase of the pH.[34]

Conclusion

The present results demonstrate the applicability of ^{17}O NMR spectroscopy to the study of dysprosium(III) complexes of polyaminocarboxylates. The d.i.s. of the water, measured in natural abundance, provides valuable information on the stoichiometry and the hydration of the complexes. This measurement requires not more than 1 min of spectrometer time. By monitoring the d.i.s. as a function of the complex concentration, the occurrence of self-association can be detected.

A separation of contact and pseudo-contact contributions to the experimental ^{17}O shifts is not needed to obtain reliable water co-ordination numbers. From comparison of cases where such separations have been performed it is concluded that for *q* ⩾2 the contact contribution is larger than 78% of the total shift (see Table 3). The pseudo-contact contributions can be quite large only when *q* = 1, because the water molecule may be located near the main magnetic axis [for instance Dy(tadta)] and an averaging of its geometric term *via* rapid exchange processes is impossible. Therefore the maximum absolute error of *q* by this method is one.

Acknowledgements

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