Analysis of Multinuclear Lanthanide Induced Shifts. Part 5.[1] The Co-ordination Polyhedron of 1 : 3 Lanthanide(III)–Glycolate Complexes in Aqueous Solution

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Experimental ^{17}O, ^{13}C, and ^{1}H bound shifts have been determined for the complexes of lanthanide(III) cations with glycolate (L) in D_2O at pD 4.5. These shifts were separated into diamagnetic, contact, and pseudocontact contributions. The contact shifts show that the stoicheiometry of these complexes is $LnL_3(D_2O)_3$. Glycolate is co-ordinated in a bidentate fashion *via* one of the carboxylate oxygens and the hydroxylic oxygen. From the pseudocontact shifts it is concluded that lanthanide(III) cations are surrounded by nine oxygens constituting a distorted tricapped trigonal prism, in which the three capping positions are occupied by carboxylate oxygens.

The chemical properties of lanthanide(III) cations (Ln^{III}) and the effects they induce in n.m.r. parameters of nuclei in their proximity make them valuable for a variety of purposes. Lanthanide(III) cations and their chelates are employed as a tool in structural analysis with the use of n.m.r. spectroscopy.[2–4] The physical and chemical properties of the Ln^{III} cations are closely related to those of Ca^{II} and, therefore, the paramagnetic Ln^{III} cations are useful probes for the 'n.m.r.-silent' Ca^{II} ions in structural analysis of Ca^{II} complexes in solution.[5] Moreover, Ln^{III} cations are of importance in many other facets of chemistry, such as catalysis,[6,7] organic synthesis,[8] and biochemistry.[9,10] Finally, Ln^{III} chelates are becoming increasingly important in medical diagnostic techniques using n.m.r. spin imaging.[11] For these reasons it is important to develop a more complete understanding of the structures of lanthanide complexes in solution.

The most easily accessible n.m.r. parameters, the ^{1}H lanthanide(III) induced shifts (l.i.s.) are used frequently in structural analysis of monofunctional organic compounds in organic solution.[2,3] In those cases the chelates $[Ln(fod)_3]$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate) and $[Ln(tmhd)_3]$ (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate) are used as shift reagents, and structural information can be obtained by fitting the pseudocontact shift to the McConnell–Robertson equation.[12] The structural analysis of Ln^{III} complexes of polyfunctional organic ligands in aqueous solution, in particular of relatively small ligands, is much less straightforward and has been investigated less extensively. First, it is usually difficult to determine the orientation of the magnetic axis in the analysis of the pseudocontact shifts of polyfunctional compounds. Secondly, the Ln^{III} cation is in close proximity to more ligand nuclei, so greater contributions to the induced shifts result from diamagnetic and contact shifts. Therefore, a proper analysis requires separation of the various shift contributions.

Using Gd^{III} induced relaxation rate enhancements[4,13] and Dy^{III} induced ^{17}O shifts[4] it has been possible to determine the donor sites in polyfunctional ligands and to gain some information on the geometry of the ligands with respect to the Ln^{III} cation. However, this affords only limited information on the spatial relationships of the various ligands around the Ln^{III} cations. The co-ordination polyhedron of Ln^{III} in aqueous systems requires determination of the pseudocontact shifts of as many ligand nuclei as possible.

The present paper describes an analysis of the shifts induced by a series of Ln^{III} cations upon the ^{17}O, ^{13}C, and ^{1}H resonances of the Ln–glycolate–D_2O system. The Ln^{III} induced shifts are separated into diamagnetic, contact, and pseudocontact shifts. The donor sites and the stoicheiometry are derived from the contact shifts, and the pseudocontact shifts are used to obtain a description of the co-ordination polyhedron around the Ln^{III} cation. Glycolate (L) was employed because it is the simplest representative of the polyhydroxycarboxylates, an important class of chelating ligands with high affinity for Ca^{II} and Ln^{III} cations.[4,14]

Results and Discussion

Determination of Induced Shifts.—Lanthanide induced line-broadening often makes the observation of ^{17}O nuclei in natural abundance spectra very difficult. Therefore, we prepared glycolate that was 5% ^{17}O-enriched at both hydroxylic and carboxylate oxygen nuclei. The labelled compound was synthesized by hydrolysis of ethyl diazoacetate with ^{17}O-enriched water, followed by saponification of the resulting ethyl glycolate with NaOH in ^{17}O-enriched water (Scheme).[15]

$$N_2CHCOOEt \xrightarrow{H_2{}^{17}O} H^{17}O\text{–}CH_2COOEt \xrightarrow{H_2{}^{17}O\text{–}NaOH} H^{17}O\text{–}CH_2\text{–}C^{17}OONa$$

Scheme.

In order to avoid dissociation of the OH function of glycolate (L) in the Ln–L complexes,[16,17] the induced shifts were measured between pD 4.6 and 4.8. The Ln^{III} complexes formed are relatively stable and, therefore, these small pH variations resulted in no observable changes in the chemical shifts. The n.m.r. spectra obtained upon addition of Ln^{III} chloride to a glycolate solution in D_2O at 73 °C were in the fast-exchange region for all nuclei studied: time-averaged spectra of the free and the bound ligands were observed. The spectra were measured at elevated temperature (73 °C) to reduce the quadrupolar relaxation rate of the ^{17}O nuclei. Upon plotting the Ln^{III} induced shifts *versus* the Ln^{III}:ligand ratio (ρ), for $\rho \leqslant 0.1$ straight lines were obtained with correlation coefficients typically better than 0.999. The induced shifts extrapolated to $\rho = 1$ are summarised in Table 1. Provided that the association constants are high and that the Ln^{III} complex with *n* co-ordinated ligands is the predominant one,[18–20] extrapolation to a lanthanide:ligand ratio of 1:*n* would yield the bound shift (Δ) of a ligand nucleus. Consequently, extrapolation of the

Table 1. Lanthanide induced shifts[a] (p.p.m.) for $Ln^{III}L_y(D_2O)_x$ complexes in D_2O at pD 4.5 and 73 °C

	^{17}O			^{13}C		^{1}H
Ln	COO	OH	D_2O	COO	CH_2	CH_2
La	44	0	388	3.96	4.94	0.95
Ce	253	198		20.67	19.12	7.73
Pr	490	417	1 003	41.33	36.95	16.86
Nd	630	694	1 498	13.17	27.85	10.52
Sm	−46	−1	303	16.79	8.00	1.72
Eu	−1 240	−1 560	−2 497	−2.40	−27.32	−14.25
Gd	*b*	*b*	*b*	73.02	−56.58	*b*
Tb	−3 101	−5 375	−7 386	528.60	111.11	54.85
Dy	−2 121	−4 623	−6 692	694.66	190.61	89.19
Ho	−2 143	−3 746	−4 501	302.58	75.19	27.90
Er	−1 780	−1 992	−1 550	−136.63	−56.31	−26.36
Tm	−1 600	−1 247	−692	−332.01	−118.77	−49.01
Yb	−575	−262	742	−158.87	−40.73	−15.21
Lu	23	1	211	1.86	4.39	1.00

[a] Shifts extrapolated to $\rho = 1$ [ρ is defined with respect to the ligand concerned, *viz.* glycolate (L) or D_2O]. Values are equal to $n\Delta$, where $n = x$ or y; downfield shifts are positive; estimated relative errors 2—5%; total glycolate concentration 0.2 mol dm^{-3}. [b] Not observable due to excessive line broadening.

Table 2. Calculated distribution (%) of glycolate ligand (L) over Ln^{III} complexes at $\rho = 0.05$*

Ln	$[LnL]^{2+}$	$[LnL_2]^+$	$[LnL_3]$
La	2	39	59
Ce	2	39	59
Pr	1	20	79
Nd	1	17	82
Sm	0	10	90
Eu	0	12	88
Tb	1	23	77
Dy	0	9	91
Ho	0	10	89
Er	0	8	92
Tm	0	8	92
Yb	0	7	93
Lu	0	6	94

* Using β values from ref. 14 ($I = 0.1$ mol dm^{-3}, 25 °C); total glycolate concentration 0.2 mol dm^{-3}. The variation of the calculated values between $\rho = 0.02$ and $\rho = 0.1$ is less than 3%; percentage of LnL_n is defined as $100n[LnL_n]/([LnL] + 2[LnL_2] + 3[LnL_3])$.

induced shifts to a lanthanide:ligand ratio of unity affords a value of $n\Delta$, the stoicheiometrically uncorrected bound shift.

In order to get an impression of the composition of the solutions measured, calculations were performed using the stability constants compiled in ref. 14. Under these conditions applied, the Ln^{III} cation added is almost completely complexed to glycolate. The relative amounts of the 1:1, 1:2, and 1:3 complexes (see Table 2) are almost independent of ρ.* The calculations show that for La^{III} and Ce^{III} a considerable amount of 1:2 complex should be expected, whereas for the heavier Ln^{III} cations the 1:3 complex is predominant.

Separation of the observed Shifts into Diamagnetic, Contact, and Pseudocontact Shifts.[26]—The shift (Δ) induced at a nucleus of a ligand upon binding to a Ln^{III} cation can be expressed as the sum of the diamagnetic shift (Δ_d), the contact shift (Δ_c), and the pseudocontact shift (Δ_p): equation (1).

$$\Delta = \Delta_d + \Delta_c + \Delta_p \qquad (1)$$

The diamagnetic shift is usually relatively small, and it arises from effects such as conformational changes, inductive effects and direct field effects. We will use the average of the shifts at $\rho = 1$ of the diamagnetic La^{III} and Lu^{III} complexes as an estimate for the diamagnetic shift.

The contact and the pseudocontact shifts can each be written as the product of two terms, one that is characteristic of the Ln^{III} cation but independent of the ligand, and a second term that is characteristic of the ligand nucleus under study but independent of the Ln^{III} cation. The independence of these terms makes it possible to determine their values from the experimental l.i.s. obtained using a series of lanthanides with a single substrate. The lanthanide-dependent, ligand-independent terms are $\langle S_z \rangle$ (contact) and k (pseudocontact), while the lanthanide-independent, ligand-dependent terms are F (contact) and G (pseudocontact). The bound shift for a particular ligand nucleus can be written as in equation (2). Values of $\langle S_z \rangle$ and k have

$$\Delta' = \Delta - \Delta_d = \langle S_z \rangle F + kG \qquad (2)$$

been calculated by Bleaney *et al.*,[27,28] Golding and Halton,[29] and Pinkerton *et al.*[30]

Equation (2) can be rearranged into two linear forms: equations (3) and (4). Previously it was shown that plotting bound shift data according to equations (3) and (4) may be

$$\frac{\Delta'}{\langle S_z \rangle} = F + \left(\frac{k}{\langle S_z \rangle}\right) G \qquad (3)$$

$$\frac{\Delta'}{k} = \left(\frac{\langle S_z \rangle}{k}\right) F + G \qquad (4)$$

useful to check whether a series of Ln^{III} complexes is isostructural or not.[12,31] The ionic radii of the Ln^{III} ions decrease regularly through the series, producing gradual (minor) variations in complex structures and corresponding variations in G. This sometimes shows up as an abrupt break in plots according to equation (3), whereas plots according to

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* From several studies it has been concluded that a 1:4 Ln–L complex can be formed.[21–25] Because of random computational errors the reported stability constants, β_4, are, however, not very reliable, but we assume that under the conditions applied, the concentration of the 1:4 complex is negligible.

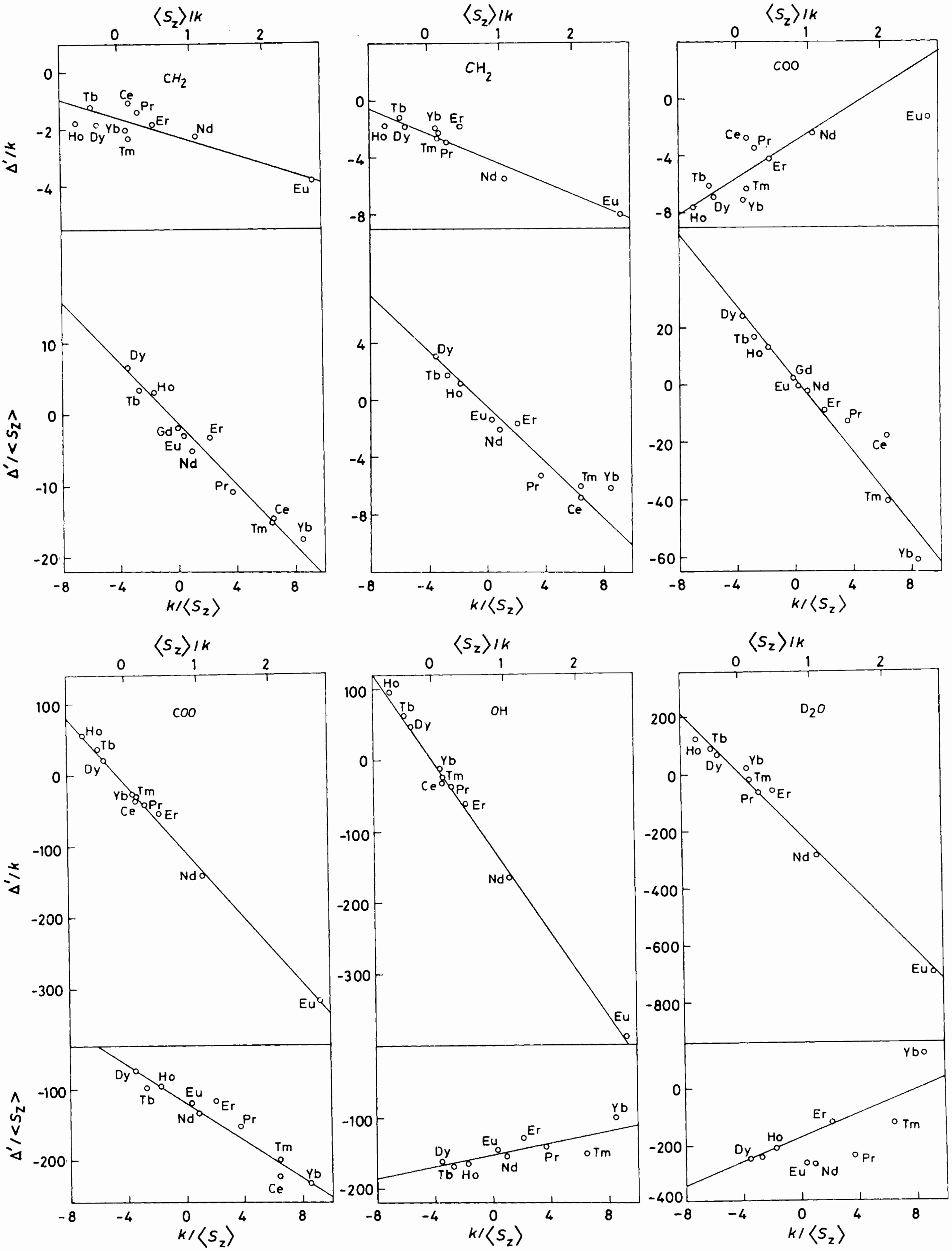

Figure 1. Plots of $\Delta'/\langle S_z\rangle$ *versus* $k/\langle S_z\rangle$ and of Δ'/k *versus* $\langle S_z\rangle/k$ for the various nuclei in the Ln–glycolate complex at 73 °C, pD 4.5

equation (4) remain almost linear.[1a] When both plots of $\Delta'/\langle S_z\rangle$ *versus* $k/\langle S_z\rangle$ and plots of Δ'/k *versus* $\langle S_z\rangle/k$ show irregularities, it is likely that somewhere along the lanthanide series there has been a major structural change, such as a change in co-ordination number or in the ligand binding geometry.[1a]

The same procedure may also have diagnostic value in cases like the present one, where it is not clear whether the experimental shifts extrapolated to $\rho = 1$ (Table 1) represent $n\Delta$ for a single Ln^{III} complex or are contaminated with contributions for other species. If no single complex (*i.e.*, no specific value of n) predominates in solution, differing contributions from $n = 2$ or 3 along the lanthanide series should result in plots according to equations (3) and (4) that show irregularities. Plotting the data of Table 1 according to equations (3) and (4) (see Figure 1) gives straight lines in both cases.

The preceding analysis suggests that the Ln^{III} induced shifts (Table 1) are the stoicheiometrically uncorrected bound shifts ($n\Delta$) of discrete Ln^{III}–L complexes (rather than average shifts for some undefined mixture of complexes). In addition, it can be concluded that these complexes are almost isostructural along the lanthanide series.

Once data for the various ligand nuclei have been used to calculate the values of $n\Delta$ for several Ln^{III} cations, the values of nF and nG can be obtained by regression analysis.[26] This was performed according to the procedure described previously.[32] The stoicheiometrically uncorrected relative values of F and G (*i.e.* nF and nG) are given in Table 3. Application of only a part of the data set (for instance only the data for Ln = Dy to Yb) gave almost identical results, as should be expected from the plots presented in Figure 1. This further supports our argument that a single, isostructural complex predominates throughout the entire lanthanide series.

The sign of the F values of all nuclei in the glycolate ligand, with exception of the carboxyl carbon, are negative. This suggests the relative importance of the spin delocalization mechanism of the electron spin transmission compared with the spin polarization mechanism.

Stoicheiometry of the Ln–L *Complexes as derived from the* F *Values.*—Previously we have observed that the values of the F parameter for lanthanide bound oxygens were all in a rather small range of -70 ± 11 at 73 °C.[18,33] Apparently the F value of a particular co-ordinated oxygen nucleus is almost independent of other structural effects. The stoicheiometrically uncorrected F values given in Table 3 correspond to a Ln^{III}–ligand ratio of 1 (in which the ligand is glycolate or D_2O). Division of the F values of the ^{17}O nuclei by -70 gives an estimate of the number of the various Ln^{III} co-ordinated oxygens. The F value for ^{17}O nuclei of the carboxylate group is an average of two oxygens, and the contribution of the non-co-ordinating oxygen to the contact shift can be neglected. Therefore, the number of bound carboxylate oxygens is $2 \times 120/70 \approx 3.4$. Analogously the estimated numbers of co-ordinated OH oxygens and D_2O ligands are found to be 2.2 and 2.8 respectively. Usually, in aqueous lanthanide systems with relatively small ligands the co-ordination number is nine.[4] On the basis of the present results in combination with those of our previous Gd^{III} induced relaxation rate enhancement studies,[13] which demonstrated that glycolate is co-ordinated almost exclusively (>94%) in a bidentate fashion *via* one of the carboxylate oxygens and the hydroxyl oxygen, it is concluded that for the experimental conditions used here the predominant complex in solution is $[LnL_3(D_2O)_3]$. It may be noted that the procedure used here gives a rather low value for the number of co-ordinated OH oxygens. Further investigation will be needed to obtain refined F values for various types of oxygen atoms. For the time being we believe that it is advisable to use the method presented here in combination with other techniques, such as Gd^{III} induced relaxation rate enhancements.[4]

Table 3. F And G values of $LnL_y(D_2O)_x$ calculated from the lanthanide induced shifts extrapolated to $\rho = 1$ at pD 4.5 and 73 °C

Nucleus	C*OO*	*O*H	D_2*O*	*C*OO	*C*H$_2$	C*H*$_2$
*nF**	−121.9	−154.3	−195.6	1.97	−2.15	−0.95
*nG**	−11.01	3.16	13.13	−6.34	−2.64	−1.17

* n = Number of co-ordinated ligands concerned ($n = x$ or y).

Geometry of the Complexes from the Pseudocontact Shifts.—The G values are related to the geometry of the complex according to equation (5).[27] Here r, θ, and ψ are the spherical

$$G = C\frac{3\cos^2\theta - 1}{r^3} + C'\frac{\sin^2\theta\cos2\psi}{r^3} \qquad (5)$$

co-ordinates of the observed nucleus, where the lanthanide nucleus lies at the origin and the principal magnetic axis of the system defines the z axis, and C and C' are the crystal field coefficients, which are assumed to be constant along the lanthanide series.

The large number of geometrical parameters in the $[LnL_3(D_2O)_3]$ complex precludes optimization of each of them by a fitting procedure of the experimental data to equation (3). Therefore, we have employed some constraints that were obtained by extrapolation from crystal structure data for related compounds. A direct comparison between molecular structures of lanthanide complexes of carboxylates in crystals and in solution is often difficult because of the occurrence of bridging water and carboxylate groups in the solid state.[34] This 'self-association' is present in Ln–glycolate crystal structures,[35–37] but our n.m.r. measurements were performed under conditions where self-association is negligible.[38] On the other hand, the donor atoms usually are the same in the solid state and in solution, and the Ln–donor atom distances lie in narrow ranges for both crystal and solution structures.[4] For example, all of the reported Ln^{III}–O distances in Ln–glycolate complexes fall in the range 2.3—2.5 Å.[35–37]

In the solid state, the majority of nine-co-ordinated Ln^{III} complexes have a lanthanide co-ordination polyhedron that can be described as a tricapped trigonal prism. The nona-aqua Ln^{III} complexes appear to have a perfect tricapped trigonal prism structure with D_{3h} symmetry (Figure 2).[39] Favas and Kepert[40] have explained the geometries of these complexes using a computational model in which the repulsions between the Ln–O bonds are minimized. Similar logic has been applied successfully to molecular mechanics calculations of seven-co-ordinate lanthanide complexes.[41] In tris(bidentate ligand)tris-

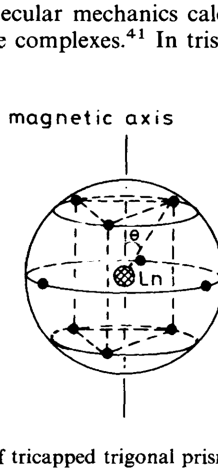

Figure 2. Geometry of tricapped trigonal prism

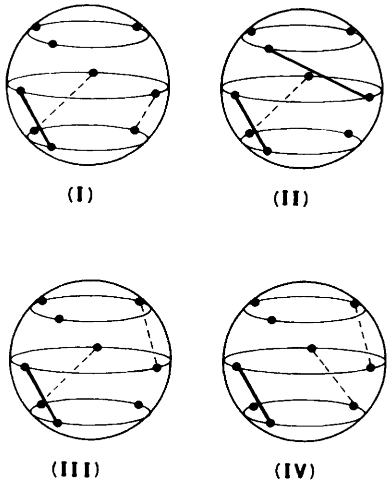

Figure 3. Four groups of isomers of the tricapped trigonal prism of tris(bidentate ligand)tris(unidentate ligand)lanthanide complexes

Table 4. Comparison of experimental and calculated G and θ values for the $[LnL_3(D_2O)_3]$ complex

Nucleus	$G_{exp.}$	$G_{calc.}$[a]	θ_{calc}[b]	θ[c]
COO[d]	−3.67	−3.62	91.1[e] 81.2[f]	90
OH	1.05	1.00	51.6	47—50
COO	−2.11	−2.35	77.7	
CH$_2$	−0.88	−0.76	60.9	
CH$_2$[d]	−0.39	−0.27	49.1 70.3	
D_2O[g]	4.38	4.38	138.1	132—135

[a] Calculated for minimal agreement factor, using the optimum θ values and equation (3): a.f. = 0.04 (ref. 37). [b] Optimum θ value. [c] θ In crystal structures of tris(bidentate ligand)tris(monodentate ligand)lanthanide complexes, see Table 4 of ref. 33. [d] When two geometrically non-equivalent nuclei are magnetically equivalent as a result of fast exchange, the average G value is given. [e] The co-ordinated carboxylate oxygen. [f] The non-co-ordinated carboxylate oxygen. [g] This nucleus was not included in the optimisation procedure (see text).

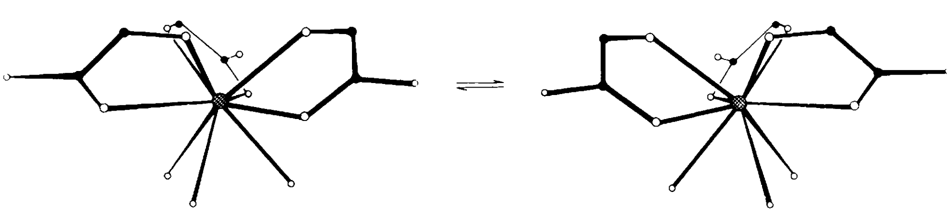

Figure 4. Structure of $[LnL_3(D_2O)_3]$

(unidentate ligand)lanthanide complexes with a tricapped trigonal prismatic co-ordination of the Ln^{III} cation, four groups of isomers are possible (Figure 3).[40] A bidentate ligand with non-equivalent donor sites can be attached to a face of the trigonal prism in two ways, and the number of members in each isomer group is further increased by chirality. Favas and Kepert[40] have examined the stereochemistry of isomer (**I**) using their model. When replacing six unidentate ligands by three bidentate ligands, the most important distortion is a twist of the triangular faces of the prism with respect to each other. The magnitude of the twist is dependent upon the bite of the ligand. The other angular parameters, particularly θ, the deflection from the C_3 axis, are relatively independent of the bite of the bidentate ligand. These results are in excellent agreement with experimentally determined crystal structures such as that for $[Gd(O_2CMe)_3]\cdot 4H_2O$.[42]

For determination of the solution structure of $[LnL_3(D_2O)_3]$ (L = glycolate), the oxygen donor atoms were assumed to form a sphere around the Ln^{III} cation with a radius of 2.47 Å in a distorted tricapped trigonal prismatic fashion. We employed the structure corresponding to isomer (**I**) in Figure 3, and C_3 symmetry was imposed with the water oxygens lying equidistant from each pair of adjacent glycolate oxygens. For this model the second term in equation (3) is zero and the magnetic axis is collinear with the C_3 axis. The approximation that all the lanthanides are isostructural does not introduce substantial errors in the prediction of l.i.s. values.[1a] In the crystal structures of various Ln–glycolate complexes[35–37] the OOC–C–O– array of each glycolate ligand chelated to the Ln^{III} forms a nearly planar five-membered ring; moreover, *ab initio* calculations have shown that the planar configuration of glycolate is highly favourable.[43] Therefore a similar configuration was assumed for the structure in solution. The position of the glycolate ligands was then varied with respect to the magnetic axis, taking into account the constraints imposed by the tricapped trigonal prismatic model. After each variation the G values were calculated with equation (5) and compared with the experimental values in Table 3. The agreement between these values was expressed in the form of an agreement factor (a.f.).[44,*] An optimum fit was obtained for a geometry in which all co-ordinated carboxylate oxygens are near the equator (θ = 92°) and the OH oxygens are at θ = 52°. This procedure yielded a value of 99.9 for the constant C in equation (5). Using this value of C together with the experimental G value of the water ^{17}O, we calculated the position of the water oxygens to be θ = 138°. The experimental and calculated G and θ values are compared in Table 4 and the structure obtained is depicted in Figure 4.

The magnitude of the shift of the OH oxygen is very sensitive to changes of θ, because of the reversal of the sign of G at θ = 54.7°. Interchange of the donor atoms for one of the glycolate ligands in such a way that the OH oxygen is at the equator produces a large change in the predicted l.i.s., and the agreement factor increases from 0.04 to 0.30. Therefore the data unambiguously show that structures with OH groups at capping positions can be rejected. The preferred positions of the carboxylates can be explained by the electrostatic repulsion between these negatively charged groups, which is minimized at the equator. On the basis of the present data, it is not possible to exclude geometries in which all three glycolate ligands do not lie

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[*] a.f. = $[\Sigma W_i(G_{obs.} - G_{calc.})^2/\Sigma W_i G_{obs.}^2]^{\frac{1}{2}}$, where W_i is a weighting factor.

in the same hemisphere [*viz.* isomers (**II**)—(**IV**) in Figure 2]. We assume, however that structures (**II**)—(**IV**) are less favourable, since symmetry distortions would be required to accommodate the glycolate ligands.

The solution structure thus derived closely resembles the structures of crystalline tris(bidentate ligand)tris(unidentate ligand)lanthanide complexes (see Table 4). Crystalline nine-co-ordinated LnL_3 complexes[35] have geometries corresponding to structure (**II**) in Figure 2, but the OH groups are found on the capping positions and the co-ordinated carboxylate oxygens at the corners of the prism. This appears to result from the self-association which occurs in the crystal: there are no water molecules in the first co-ordination sphere of Ln^{III}, but instead oxygens of bridging glycolates occupy the remaining prismatic corners. The self-association may also be responsible for the fact that for crystalline LnL_3 complexes with Ln = Gd to Lu,[36,37] the co-ordination number of Ln^{III} is only eight. In solution a change of the co-ordination number from nine to eight between the lighter and the heavier lanthanides would have resulted in a change of F values, so such a structural change can be rejected on the basis of the present data.

It should be noted that the proposed nine-co-ordinate complex has a chiral configuration around the Ln^{III} cation. Therefore, a racemic mixture must be present in solution (see Figure 4). The enantiotopic methylene protons of glycolate will become diastereotopic upon complexation. In the paramagnetic Ln^{III} complexes the induced shift for the two diastereotopic methylene protons of each enantiomer must be different, but fast isomerisation of the Λ and Δ enantiomers (*via* dissociation–association) results in interchange of the magnetic as well as the chemical environment of these two nuclei, and only one (averaged) signal for these hydrogens is observed. Reuben[45] observed that in the related glycolatobis[(*S*)-lactato(2−)]praseodymium(III) complex the methylene protons of glycolate are anisochronous. In that case two diastereoisomers occur because of the chirality of the lactate ligand. Molecular models show that the steric strains in these diastereoisomers are different, and, therefore, their concentrations are not equal. Thus the ligand-exchange processes cannot result in equal (averaged) lanthanide induced shifts for the geminal methylene protons of the glycolate ligand in this mixed-ligand system, and two signals must be expected. Recently a separation of the diastereotopic geminal methylene protons in $[Ln(oda)_3]^{3-}$ complexes (oda = oxydiacetate) was observed under conditions of slow exchange on the n.m.r. time-scale.[46]

The proposed structure for the $[LnL_3(D_2O)_3]$ complexes in solution is very similar to those of the $[Ln(pydca)_3]^{3-}$ complexes (pydca = pyridine-2,6-dicarboxylate) both in solution and in the solid state.[47—49] The structure of the corresponding bis-pydca complex is shown to be analogous:[49] the disposition of the two pydca ligands is similar to that in the tris-pydca complex and the tricapped trigonal prism is completed by three water molecules.

In order to obtain further support for the structure of the Ln–glycolate complex, we have investigated the ^1H lanthanide induced shifts of the mixed-ligand system Eu–pydca–glycolate (1:2:1). The large association constant of Eu^{III} with pydca (log $\beta_2 = 15.86$)[50] ensures that the pydca ligand is completely bound to Eu in a 2:1 ratio under these conditions. Three additional co-ordination sites remain available, so only a $Eu(pydca)_2L(D_2O)_x$ stoicheiometry needs to be considered.

The ^1H lanthanide induced shifts were determined from n.m.r. spectra obtained upon addition of $Na[Eu(pydca)_2]$ to a glycolate solution in D_2O at 25 °C. A straight line was obtained upon plotting the induced shifts *versus* ρ (for $\rho < 0.2$). The bound shift for glycolate in the $Eu(pydca)_2L$ complex, determined from the slope of this line, is −5.69 p.p.m. The bound shift for the $EuL_3(D_2O)_3$ complex under the same conditions was −5.73 p.p.m. (a value of −4.75 p.p.m. was observed at 73 °C). The excellent agreement between these values supports our conclusions with regard to the stoicheiometry and the structure of the Ln–glycolate complexes investigated.

Conclusions

Lanthanide induced shifts provide information on a variety of structural parameters of Ln^{III} complexes in solution. Usually the large degree of freedom in complexes with small ligands hampers a complete structural analysis on the basis of induced shifts alone.[33] An extrapolation of *X*-ray data, however, affords some reasonable constraints that can facilitate such an analysis. The donor sites of the ligands and the stoicheiometry of the complex can be determined from the contact shifts, whereas the pseudocontact shifts yield important information on both the geometry of the ligands itself and the co-ordination polyhedron of the Ln^{III} cation.

Experimental

N.M.R. Measurements.—N.m.r. spectra were recorded with a Nicolet NT-200WB spectrometer using a 12-mm sample tube with a 0.2 mol dm^{-3} solution of 5% ^{17}O-enriched sodium glycolate in D_2O at 73 °C and pH 4.6—4.8. Chemical shifts were measured with respect to the butyl ^1H signal of t-butyl alcohol as internal standard. The measurements were performed for at least seven different Ln^{III}–glycolate ratios (ρ = 0.0—0.12); usually at $\rho \geqslant 0.15$ precipitation occurred.

Materials.—Water (20% ^{17}O-enriched) was obtained from Rohstoff Einfuhr, Düsseldorf, and ethyl diazoacetate from Aldrich. The $LnCl_3 \cdot 6H_2O$ salts were obtained from Alfa Products. The Ln^{III} content was determined by ethylenediamine-*NNN′N′*-tetra-acetate titration using arsenazo I as the indicator.

Preparation of ^{17}O-enriched sodium glycolate.[14] Ethyl diazoacetate (1 cm^3, 9.6 mmol) was added dropwise to 10% ^{17}O-enriched H_2O (5 cm^3) at 0 °C. After the evolution of nitrogen ceased, the solution was extracted with CH_2Cl_2 (2 × 2 cm^3). To the water layer was added an additional 1 cm^3 of ethyl diazoacetate at 0 °C. This procedure was repeated six times. The combined CH_2Cl_2 extracts were washed with aqueous NaCl (15 cm^3) and dried over $MgSO_4$. Distillation yielded 3.86 g of $H^{17}OCH_2COOEt$, b.p. 53—54 °C (1.9 kPa). This ester was added to a solution of NaOH (1.6 g) in 5% ^{17}O-enriched H_2O (15 cm^3), and after stirring at room temperature for 5 min, the solution was poured into ethanol (200 cm^3). Filtration of the precipitate and subsequent drying *in vacuo* over zeolite KA gave 3.22 g of ^{17}O-enriched sodium glycolate.

Calculations.—The stoicheiometrically uncorrected bound shifts were obtained from the slopes of the straight lines obtained upon plotting the induced shifts *versus* the ρ values. The separation of contact and pseudocontact shifts was performed by weighted least-squares regression, using the procedure described previously.[32] The inverse of the squared standard deviation in the bound shifts was taken as the weighting factor in each case. Optimization of structural parameters of the complex by fitting calculated and experimental G values was carried out both *via* a non-linear regression procedure, and by scanning the agreement factor as a function of systematic variation in the structural parameters.

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