Inorganica Chimica Acta, 160 (1989) 7–9

A Note on the Solution Structure of Bistriphosphato–Lanthanide(III) Complexes in Water

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(Received June 16, 1988)

Abstract

Some comments on the analysis of lanthanide induced shifts are given with particular reference to the recent paper of S. M. Anson, R. B. Homer and P. S. Belton, *Inorg. Chim. Acta, 138* (1987) 241. It is shown that in the lanthanide bistriphosphate complexes $[Ln(PPP)_2(H_2O)]^{7-}$, the pseudocontact shifts of the ^{31}P and ^{17}O nuclei in the triphosphate ligands and those of the water ^{17}O nuclei have opposite signs. This suggests that the triphosphate ligands prefer the equatorial region ($55 < \theta < 125°$), whereas the Ln^{III} coordinated water prefers the axial region ($0 < \theta < 55°$, $125 < \theta < 180°$). Several monovalent counterions are present in the second coordination sphere.

Introduction

Some years ago we reported on the complexation of lanthanide(III) cations with triphosphate $(PPP)^{5-}$ with the use of multinuclear NMR [1]. The Ln^{III} induced shift and relaxation data indicated that in the 1:2 lanthanide(III)–triphosphate complex each triphosphate is coordinated through two oxygens of one PO_3 group, one oxygen of the other PO_3 group, and one oxygen of the PO_2 moiety (see Fig. 1), with rapid interconversion of the two PO_3 groups as to their coordination. The Ln^{III} coordination polyhedron is completed by one water whilst seven alkali metal counterions are present in the second coordination sphere.

Recently Anson *et al.* have reinvestigated these complexes with the use of ^{31}P and ^{23}Na NMR spectroscopy and terbium(III) luminescence [2]. These authors state that we have used C^D values of the wrong sign in the separation of the lanthanide induced shifts into contact and pseudocontact shifts, resulting in supposedly incorrect F and G values. Furthermore these authors have interpreted our lanthanide induced water ^{17}O shifts in a way, which in our opinion, needs to be revised. The papers [1, 2] differ also about the number of coordinated waters, the coordination of the triphosphate, and the position of the counterions. Here we give some comments on the paper of Anson *et al.* [2].

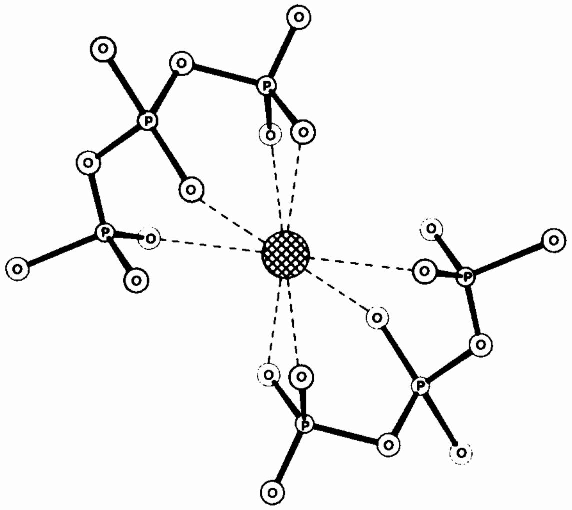

Fig. 1. Schematic representation of the coordination of triphosphate in the $[Ln(PPP)_2(H_2O)]^{7-}$ complex.

Discussion

The Separation of Lanthanide Induced Shifts

The paramagnetic shift (Δ) induced at a nucleus of a ligand upon binding to a Ln^{III} cation is the sum of the contact shift (Δ_c) and the pseudocontact shift (Δ_p) (eqn. (1)). Both the contact and the pseudocontact shifts can be expressed as the product of a term that is characteristic of the Ln^{III} cation but independent of the ligand ($\langle S_z \rangle$ and C^D, respectively), and a second term that is characteristic of the ligand nucleus under study but independent of the Ln^{III} cation (F and G, respectively) (see eqn. (2)). Values of $\langle S_z \rangle$ and C^D for the various lanthanides have been tabulated in the literature [3–7]. According to

$$\Delta = \Delta_c + \Delta_p \tag{1}$$

$$\Delta = \langle S_z \rangle F + C^D G \tag{2}$$

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$$C^{\mathrm{D}} = g^2 J(J+1)(2J-1)(2J+3)\langle J\|\alpha\|J\rangle \qquad (3)$$

$$G = -\beta^2/[60(kT)^2] \times [(3\cos^2\theta - 1)/r^3] \times 2A_2^0\langle r^2\rangle \qquad (4)$$

Bleaney *et al.* [3,4] for an axially symmetric complex, the values of C^{D} and G are given by eqns. (3) and (4), where θ and r are polar coordinates of the nucleus under study, A_2^0 is a crystal field coefficient and the other symbols have their usual meaning.

It should be noted that the C^{D} values are independent of the convention used for the definition of the sign of the lanthanide induced shifts. The pre-sign of the right-hand side of eqn. (4), however, reverses for the opposite sign convention. Here downfield induced shifts are defined as positive. Usually, the C^{D} values tabulated in the literature are scaled to either −100 [3,4] or +100 [6] for $\mathrm{Dy^{III}}$. We have chosen a scaling to −100 [1], whereas Anson *et al.* have used a scaling to +100 [2]. It is assumed that for a series of isostructural lanthanide complexes the crystal field coefficients remain constant. Usually, the magnitude and the sign of these constants are not known. Thus the theory provides relative rather than absolute signs of the term $C^{\mathrm{D}}G$ in eqn. (2) [4]. Analogous equations can be derived for an effective axially symmetric model [8,9], which is more likely in the present case.

When the paramagnetic lanthanide induced shifts of a series of isostructural complexes are known, the F and the *relative* G values can be calculated by methods evaluated by Reilley *et al.* [10]. The preferred method is a multiple regression (A_0), less favorite alternatives are plotting the data according to the two linear forms of eqn. (2) (methods A_1 and A_2, respectively).

$$\Delta/C^{\mathrm{D}} = (\langle S_z\rangle/C^{\mathrm{D}})F + G \qquad (5)$$

$$\Delta/\langle S_z\rangle = F + (C^{\mathrm{D}}/\langle S_z\rangle)G \qquad (6)$$

If the Δ values are defined in the same way, e.g. downfield induced shifts defined as positive, then the two methods of scaling of C^{D} (namely to −100 or +100 for $\mathrm{Dy^{III}}$) result in *relative* G values with the same magnitude but with opposite signs. This is confirmed by a comparison of the G values obtained (see Table 1).

In the structural analysis the G values obtained for the various nuclei can be compared with values calculated with eqn. (7).

$$G = k(3\cos^2\theta - 1)/r^3 \qquad (7)$$

Here k is a factor to scale the experimental values to the calculated ones. Therefore, a reversal of the sign of C^{D} in eqn. (2) will finally result in a reversal of the sign of k, which parameter is not of any use in the structural analysis.

TABLE 1. G values for $^{31}\mathrm{P}$ in $[\mathrm{Ln(PPP)_2}]^{7-}$ complexes

Source	$\mathrm{P}_{\alpha,\gamma}$	P_β
ref. 1[a]	−2.6	−3.1
ref. 2[b]	2.3	2.7
ref. 2[c]	2.6	3.3

[a] Calculated with multiple regression (method A_0), excluding data of P_β for $\mathrm{Tb^{III}}$. [b] Calculated with method A_2, excluding data for $\mathrm{Sm^{III}}$. [c] Recalculated by the present authors with multiple regression (method A_0), excluding data for $\mathrm{Sm^{III}}$.

The $\mathrm{Ln^{III}}$-coordinated Waters

Anson *et al.* have determined the number of $\mathrm{Ln^{III}}$-coordinated waters from $\mathrm{Tb^{III}}$ luminescence lifetimes to be 1.9 at pH 7, whereas the NMR measurements were performed at pH 8 [2]. From Fig. 5 in their paper [2], it can be calculated that the number of coordinated waters is only 1.5 at pH 8, which is in good agreement with the value that we have determined with the use of $\mathrm{Ln^{III}}$ induced $^{17}\mathrm{O}$ contact shifts (1.1 ± 0.2) [1]. It may be expected that upon decreasing the pH, one of the terminal phosphate groups protonates, and consequently it may be expelled from the first coordination sphere of $\mathrm{Ln^{III}}$ by water.

Anson *et al.* have calculated G values for water $^{17}\mathrm{O}$ nuclei [2] from our lanthanide induced shift data [1] and obtained a positive G value [2]. As outlined above, this corresponds to a negative G value with our sign convention for C^{D}. We have obtained, however, a positive G value too, using separation method A_0. In Fig. 2, the $^{17}\mathrm{O}$ data are plotted according to eqns. (5) and (6). When separation method A_1 is used G is the intercept in Fig. 2a. The uncertainty of G obtained in this way is large, due to the scatter of the points; no definitive conclusions about its sign are possible. Figure 2b (corresponding to separation method A_2), however, leaves no doubt that G, which is given by the slope in that Figure, is positive. It should be noted, however, that a multiple regression (method A_0) always has to be preferred for the determination of F and G values [10].

It may be concluded that all G values of the triphosphate $^{31}\mathrm{P}$ and $^{17}\mathrm{O}$ nuclei are negative [1], whereas the G value of the water $^{17}\mathrm{O}$ nucleus is positive. If it is assumed that the effective axially symmetric model applies, the comparable G values for the $^{31}\mathrm{P}$ nuclei suggest an orientation of the (pseudo) magnetic axis, which is about perpendicular to the plane through the $\mathrm{Ln^{III}}$ ion and the P atoms (see Fig. 3). Consequently the opposite sign of the G value of the water $^{17}\mathrm{O}$ nucleus indicates that the coordinated waters have preference for positions in the positive shift cone ($0 < \theta < 55°$, $125 < \theta < 180°$) (see Fig. 3). This is in contrast to the conclusion of

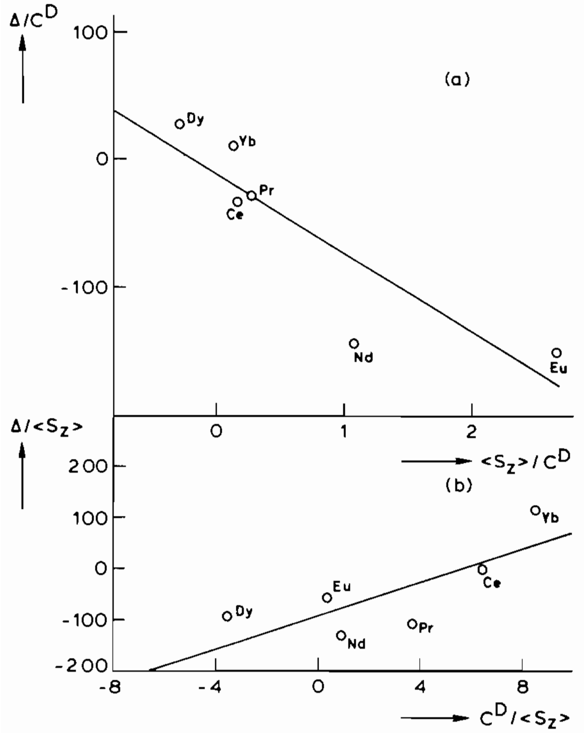

Fig. 2. Plots of Δ/C^{D} *vs.* $\langle S_z\rangle/C^{\mathrm{D}}$ and $\Delta/\langle S_z\rangle$ *vs.* $C^{\mathrm{D}}/\langle S_z\rangle$ for the ^{17}O water nuclei in $[\mathrm{Ln(PPP)_2(H_2O)}]^{7-}$ complexes. Shifts to higher frequencies are denoted as positive, C^{D} values are scaled to −100 for $\mathrm{Dy^{III}}$.

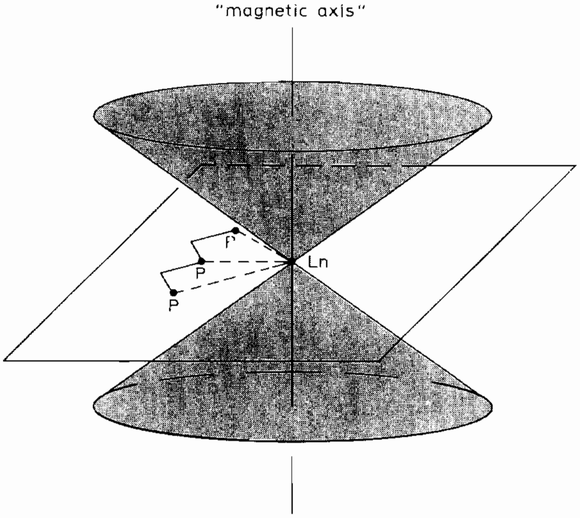

Fig. 3. The positive and negative shift cones in the $[\mathrm{Ln(PPP)_2(H_2O)}]^{7-}$ complex (see text). The positive shift cone is shaded.

Anson *et al.* [2] based on an incorrect *G* value, that the waters are in the 'equatorial' region, a result that also seems unlikely for steric reasons.

The Counterions in the Second Coordination Sphere

Assuming a 1:1 complex between $[\mathrm{Ln(PPP)}]^{7-}$ and $\mathrm{Na^+}$ Anson *et al.* [2] have correlated ^{23}Na shifts of the $\mathrm{Dy^{III}}$ complex with the use of eqn. (8), where K_{Na} is the association constant for the binding of $\mathrm{Na^+}$ to $[\mathrm{Dy(PPP)_2}]^{7-}$ and $[c_x]$ is the total concentration of $[\mathrm{Dy(PPP)_2}]^{7-}$. The linearity observed, however, has been incorrectly used as an argument in favour of a 1:1 stoichiometry [2]; it is known that other stoichiometries also may result in linear plots [11].

$$1/\delta_0 = (1/\delta_1 K_{\mathrm{Na}}[c_x]) + (\mathrm{Na^+}/\delta_1[c_x]) \qquad (8)$$

Recently Mota de Freitas *et al.* have studied the coordination of $\mathrm{Li^+}$ counterions to $[\mathrm{Dy(PPP)_2}]^{7-}$ complexes [12]. They found by ^{7}Li NMR spectroscopy that five $\mathrm{Li^+}$ ions saturate all binding sites on $[\mathrm{Dy(PPP)_2}]^{7-}$ at pH 5.5, while seven are required at pH 7.5, with one $\mathrm{Li^+}$ ion binding to a high affinity site at both pH values. These results are in good agreement with our previous conclusions based on $\mathrm{Tm^{III}}$ induced ^{6}Li longitudinal relaxation rate enhancements [1], and strongly indicate that also for $\mathrm{Na^+}$ several cations will be bound to the $[\mathrm{Ln(PPP)_2}]^{7-}$ complexes, though one of the sites may be preferable.

Acknowledgements

Thanks are due to Profs. D. Mota de Freitas and C. F. G. C. Geraldes for sending a preprint of their paper.

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