



**Table I.** Observed  $^{17}\text{O}$ -Bound Shifts (ppm) in  $\text{Ln}(\text{TP})_2(\text{D}_2\text{O})_x$  at 73 °C

Ln	$\Delta(\text{PO}_3)^a$	$\Delta(\text{PO}_2)^b$	$\Delta(\text{D}_2\text{O})^c$
La	9	8 - 38	-110
Ce	69	67 - 100	95
Pr	160	159 - 219	205
Nd	201	193 - 264	490
Sm	-15	-16 - 5	20
Eu	<i>d</i>	<i>d</i>	-710
Dy	<i>d</i>	<i>d</i>	-2870
Yb	<i>d</i>	<i>d</i>	190

<sup>a</sup>PO<sub>3</sub>: nonbridging oxygens at P<sub>α</sub> and P<sub>γ</sub>. <sup>b</sup>PO<sub>2</sub>: nonbridging oxygens at P<sub>β</sub>. Upper and lower limits are given as the PO<sub>2</sub> signal is hidden under the large PO<sub>3</sub> signal. <sup>c</sup>Calculated as (55.3/0.35) × slope of  $\text{LnIS}(\text{D}_2\text{O})$  vs.  $\rho$ . <sup>d</sup>Not observed owing to slow exchange.

$\text{Na}_3\text{P}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$  in  $\text{D}_2\text{O}$  as external standard, respectively, and  $^6\text{Li}$  chemical shifts with respect to 5 M LiCl in  $\text{D}_2\text{O}$  as external standard. Downfield induced shifts are denoted as positive.

Relaxation rates were measured after bubbling nitrogen gas through the sample for 10 min. The longitudinal relaxation rates were determined using a [(90°<sub>x</sub>180°<sub>y</sub>90°<sub>x</sub>)-τ-(12°)-acq] inversion recovery pulse sequence. The  $1/T_1$  values were calculated using a three-parameter fit of the experimental data.<sup>17</sup> The  $1/T_2$  values were calculated from the linewidths at half-height by way of the relation  $1/T_2 = \pi\Delta\nu_{1/2}$ .

**Materials.** Water (20%  $^{17}\text{O}$ -enriched) was obtained from Rohstoff-Einfuhr Düsseldorf, and the  $\text{LnCl}_3\cdot 6\text{H}_2\text{O}$  salts were from Alfa Products. STP (purity >99%) was obtained by repetitive precipitation from 33% aqueous ethanol<sup>18</sup> of commercial STP (Alfa Products), which contained about 15% diphosphate.

**$^{17}\text{O}$ -Enriched Pentasodium Triphosphate.**<sup>18,19</sup> Water (5%  $^{17}\text{O}$ -enriched, 13.9 mL, 0.772 mol) was added cautiously to  $\text{PCl}_5$  (22.8 g, 0.110 mol) at 0 °C in the course of 30 min. The mixture was then kept under vacuo at 40 °C to remove HCl, yielding 16.4 g of a mixture of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{O}$ . This mixture was brought to pH 5.3 with a concentrated NaOH solution and heated at 550 °C for 5 h in a porcelain dish. After the reaction mixture was cooled, an equal amount of pure nonlabeled STP was added and the resulting mixture was purified as described above to give 11.3 g 2.2%  $^{17}\text{O}$ -enriched pentasodium triphosphate (as the hexahydrate) (23.7 mmol, yield 11%):  $^{31}\text{P}$  NMR (80.99 MHz,  $\text{D}_2\text{O}$ , 25 °C)  $\delta$  0.0 (d,  $J = 18.8$  Hz), -14.44 (t,  $J = 18.8$  Hz);  $^{17}\text{O}$  NMR (27.13 MHz,  $\text{D}_2\text{O}$ , 94 °C)  $\delta$  124 (broad m), 107.8 (d,  $J = 80$  Hz), 100.2 (partially overlapping with the signal at  $\delta$  107.8).

## Results and Discussion

**Ln(III)-Induced  $^{17}\text{O}$  Shifts.** Previously, we have observed that Dy(III) gives rise to an induced shift per bound oxygen, which is rather independent of the nature of the oxygen.<sup>14</sup> Therefore Dy(III)-induced  $^{17}\text{O}$  shifts are useful to determine the coordinating oxygens of a ligand. Unfortunately, upon addition of  $\text{DyCl}_3$  to a solution of STP in  $\text{D}_2\text{O}$  at 73 °C, no shift of the TP  $^{17}\text{O}$  signals was observed. The intensities of the  $^{17}\text{O}$  signals, however, were reduced proportionally to the amount of Dy(III) added. Apparently, the TP ligand exchange is slow on the NMR time scale. The signals of the Dy(III) complex could not be observed, probably as the result of extensive line broadening. The decrease of the intensity of the  $^{17}\text{O}$  signals of the free ligand as a function of the molar ratio of added Dy(III)/total TP ( $\rho$ ) confirmed the formation of a 1:2 Dy(III)-TP complex.<sup>16</sup> The behavior of the water- $^{17}\text{O}$  signal showed that the  $\text{D}_2\text{O}$  ligand exchange is fast with respect to the NMR time scale.

In order to obtain information on the coordination of TP, we attempted to use another Dy(III) shift reagent,  $\text{NaDy}(\text{edta})$ . This should give rise to a mixed ligand complex,  $[\text{Dy}(\text{edta})(\text{TP})]^{6-}$ , with a lower stability constant than  $\text{Dy}(\text{TP})_2$ .<sup>7-20</sup> This might result in a shorter residence time of the TP ligand in the complex. Although a faster exchange of the TP ligand was indeed observed, line broadening still did not allow any conclusions on the TP coordination. Therefore, we screened some of the other Ln(III) cations as shift reagent for  $^{17}\text{O}$ . It appeared that the lighter

**Table II.** *F* and *G* Values of  $\text{Ln}(\text{TP})_2(\text{D}_2\text{O})_x$  Calculated<sup>a</sup> from  $^{17}\text{O}$ -Bound Shifts at 73 °C

signal	PO <sub>3</sub>	PO <sub>2</sub>	D <sub>2</sub> O
<i>F</i>	-39.7 ± 0.3	-43 ± 12	-74 ± 7
<i>G</i>	-3.1 ± 0.1	-5 ± 4	+8 ± 2
no. of Ln(III)	4 <sup>b</sup>	4 <sup>b</sup>	8

<sup>a</sup>Using the data of Table I. <sup>b</sup>La, Ce, Pr, and Nd.

Ln(III) cations (La(III), Ce(III), Pr(III), Nd(III), and Sm(III)) gave rise to fast TP ligand exchange with respect to the NMR time scale. This may be ascribed to both the generally observed higher ligand exchange rate in complexes of the lighter Ln(III) cations,<sup>21,22</sup> and the smaller shifts induced by these cations (vide infra). The bound shifts of the  $\text{Ln}(\text{TP})_2(\text{D}_2\text{O})_x$  complexes, derived from the slopes of the straight lines in plots of the  $\text{LnIS}$  vs.  $\rho$ , are summarized in Table I.

The experimental bound shifts can be corrected for any contributions caused by conformational changes, inductive effects, and direct field effects by subtracting the bound shifts of the corresponding diamagnetic La(III) or Lu(III) complexes. The resulting paramagnetic shift ( $\Delta$ ) is a combination of contact (through-bonds) shift and pseudocontact (through-space) shift, and can be expressed by the equation:

$$\Delta = \Delta_c + \Delta_p = F\langle S_z \rangle + GC^D \quad (1)$$

Here the first term of the right-hand side represents the contact shift as the product of a ligand-dependent parameter *F* and a Ln(III)-dependent parameter  $\langle S_z \rangle$ , and the second term represents the pseudocontact shift as the product of a Ln(III)-dependent parameter *C*<sup>D</sup> and a term *G* dependent upon the geometry of the ligand:

$$G = K_1 \frac{(3 \cos^2 \theta - 1)}{r^3} + K_2 \frac{(\sin^2 \theta \cos 2\phi)}{r^3} \quad (2)$$

Here *r*,  $\theta$ , and  $\phi$  are the spherical coordinates of the observed nucleus with respect to Ln(III) at the origin and with the principal magnetic axis of the system as *z* axis. *K*<sub>1</sub> and *K*<sub>2</sub> are dependent upon crystal-field parameters and temperature.<sup>23-26</sup> Rapid random reorientations of the ligand may cause vanishing of the pseudocontact shift.

Previously we observed that Dy(III)-induced  $^{17}\text{O}$  shifts of various relative weakly complexing ligands are predominantly of contact origin.<sup>14</sup> The induced shifts per bound oxygen were all in a rather small range. For TP, because of the required fast exchange, we had to rely on Ln(III) ions other than Dy(III). Since the assumptions made in the studies with Dy(III) might not be valid here, a separation of contact and pseudocontact shift was performed. The data of Table I were fit to eq 1 with Reilley's nonlinear regression procedure,<sup>27</sup> using literature values of  $\langle S_z \rangle$ <sup>28</sup> and *C*<sup>D</sup>.<sup>29</sup> The resulting *F* and *G* values are given in Table II.

From the *F* values in  $\text{Ln}(\text{H}_2\text{O})_9^{3+}$ , given by Reilley,<sup>27</sup> it can be calculated that the contribution to *F* per bound oxygen is -70 ± 11.<sup>30</sup> The *F* value of the PO<sub>3</sub> group is an average of six oxygens, of which the contributions of the noncoordinating oxygens to the contact shift presumably can be neglected.<sup>31</sup> Therefore, the

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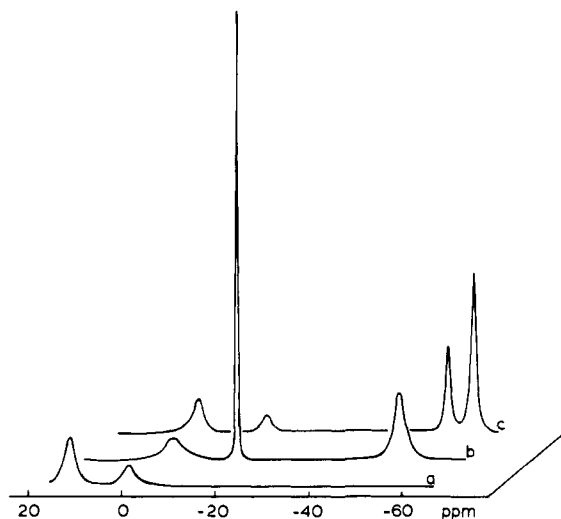
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**Figure 1.** Examples of  $^{31}\text{P}$  NMR spectra of  $\text{Ln}(\text{TP})_2$  complexes, illustrating fast and slow exchange on the  $^{31}\text{P}$  NMR time scale (25 °C;  $\rho = 0.25$ ): (a) Ce(III) fast exchange:  $\delta$  9.7 ( $\text{P}_{\alpha,\gamma}$ ),  $-3.7$  ( $\text{P}_\beta$ ). (b) Eu(III) fast exchange for  $\text{P}_\beta$ ,  $\delta$   $-13.9$ ; slow exchange for  $\text{P}_{\alpha,\gamma}$ ,  $\delta$  0.0 (free ligand),  $-48.3$  (complex). (c) Yb(III) slow exchange:  $\delta$  0.0 ( $\text{P}_{\alpha,\gamma}$ , free ligand),  $-14.4$  ( $\text{P}_\beta$ , free ligand),  $-52.6$  ( $\text{P}_\beta$ , complex),  $-58.6$  ( $\text{P}_{\alpha,\gamma}$ , complex).

**Table III.** Observed  $^{31}\text{P}$ -Bound Shifts (ppm) in  $\text{Ln}(\text{TP})_2(\text{D}_2\text{O})$  at 25 °C

Ln	$\Delta\text{P}(\alpha,\gamma)$	exchange <sup>a</sup>	$\Delta\text{P}(\beta)$	exchange <sup>a</sup>
La	-0.7	fast	+1.9	fast
Ce	+19.5	fast	+21.4	fast
Pr	+26.1	slow	+12.8	fast
Nd	+21.0	slow	+1.9	fast
Sm <sup>b</sup>	+3.2	intermediate	+9.1	intermediate
Eu	-48.3	slow	+0.9	fast
Gd <sup>c</sup>			-52.2	intermediate
Tb	+125.8	slow	+394.2	slow
Dy	+142.6	slow	+252.6	slow
Ho	+40.9	slow	+122.7	slow
Er	-134.8	slow	-118.2	slow
Tm	-194.1	slow	-213.2	slow
Yb	-58.6	slow	-38.2	slow
Lu	-0.6	fast	+2.6	slow

<sup>a</sup>Slow: separate signals for free and complexed TP observed; fast: averaged signals observed. <sup>b</sup>Calculated from experiments at 80 °C (fast exchange). <sup>c</sup>Calculated from experiments at 90 °C (fast exchange).

number of bound oxygens of the two  $\text{PO}_3$  groups in TP is  $(6 \times -39.7/-70) = 3.4 \pm 0.5$ .

Analogously, the number of coordinated  $\text{PO}_2$  oxygens and  $\text{D}_2\text{O}$  ligands can be calculated to be  $1.2 \pm 0.5$  and  $1.1 \pm 0.2$ , respectively. Assuming a coordination number of 9 for the Ln(III) ion, it can be concluded that the stoichiometry of the Ln(III)-TP complex is  $\text{Ln}(\text{TP})_2(\text{D}_2\text{O})$ , with one of the  $\text{PO}_2$  oxygens and three of the  $\text{PO}_3$  oxygens of each TP ligand coordinated.

As the signal of the P-O-P oxygens was very broad, accurate LnIS values for these nuclei could not be determined. It was clear, however, that the LnIS did not exceed 10 ppm. This supports the assumption that the contact shift in noncoordinated oxygens can be neglected.

**Ln(III)-Induced  $^{31}\text{P}$  Shifts.** The shape of the observed  $^{31}\text{P}$  NMR spectra of the Ln(III)-doped samples appeared to be dependent upon the Ln(III) ion (as a consequence of the ionic radius and the induced shift), the concentration, and the temperature; both fast and slow exchange with respect to the  $^{31}\text{P}$  NMR time scale were observed (see Figure 1).

In contrast to  $^{17}\text{O}$  NMR, here in the cases with slow ligand exchange the signals for the complexed ligand could be observed. Once more, integrals in the slow exchange spectra confirmed the

**Table IV.**  $F$  and  $G$  Values of  $\text{Ln}(\text{TP})_2(\text{D}_2\text{O})$  Calculated<sup>a</sup> from  $^{31}\text{P}$  Bound Shifts at 25 °C.

signal	$\text{P}_{\alpha,\gamma}$	$\text{P}_\beta$
$F$	$-3.7 \pm 0.3$	$-1.4 \pm 0.5$
$G$	$-2.6 \pm 0.1$	$-3.1 \pm 0.2$
no. of Ln(III)	13	13

<sup>a</sup>Using the data of Table III, excluding Tb for  $\text{P}_\beta$ , because of its negative influence on the goodness of fit.

**Table V.** Values of  $1/T_{1,\text{exp}}$ ,  $1/T_{2,\text{exp}}$ , and Residence Times at 25 °C.

Ln(III)	$\rho$	$1/T_{1,\text{exp}}$ ( $\text{s}^{-1}$ )		$1/T_{2,\text{exp}}$		$\tau_{\text{compl}}^a$ ( $10^{-3}$ s)
		$\text{P}_{\alpha,\gamma}$	$\text{P}_\beta$	$\text{P}_{\alpha,\gamma}$	$\text{P}_\beta$	
La	0	0.150	0.217			
Nd	0.309	0.37	0.56			
Eu	0.373	12.20	10.83			
Gd	0.108	0.71	0.75	1525		0.66
Tm	0.0009	7.81	7.94			>0.23
Yb	0.131	43.67	56.82	824	838	1.2
Yb	0.119	5.38	7.46	550	518	1.9

<sup>a</sup>Calculated from  $1/T_{2,\text{exp}} = 1/T_{2,\text{compl}} + 1/\tau_{\text{compl}}$  with  $1/T_{2,\text{compl}} = 1/T_{1,\text{compl}}$ .

1:2 stoichiometry of the Ln-TP complex, as should be expected considering the high association constants<sup>16</sup> and low  $\rho$  values used ( $\rho < 0.3$ ). The bound shifts were evaluated from plots of the LnIS vs.  $\rho$  in the case of fast exchange or directly from the shift difference between free and complexed species in the case of slow exchange (Table III).

A separation between contact and pseudocontact shifts as described above afforded the  $F$  and  $G$  values given in Table IV. It may be noted that no break in  $F$  and  $G$  values was observed between the lighter (La-Gd) and heavier (Tb-Lu) lanthanides.

The contact shifts appear to be very small in comparison with those observed for  $^{17}\text{O}$  (see Table II). Since the sign of these shifts is the same, a spin delocalization pathway, possibly in combination with a spin polarization pathway, is involved in the electron spin transmission through the TP ligand.

The Ln(III) coordination derived from  $^{17}\text{O}$  NMR implies equal Ln(III)-P distances. The magnitudes of the  $G$  values of the two different P nuclei are about the same. Inspection of molecular models shows that this can be explained by a position of the (pseudo) magnetic axis which is about perpendicular to the plane through the Ln(III) ion and the P atoms, when it is assumed that in eq 2 the second term on the right-hand side can be neglected as a result of axial symmetry or averaging due to ligand reorientations.<sup>32,33</sup>

**Ln(III)-Induced Relaxation Rate Enhancements.** Ln(III)-induced longitudinal ( $1/T_1$ ) and transversal ( $1/T_2$ ) relaxation rate enhancements may afford information on both the residence time of the entities involved in the complexation and the distances between the nuclei under consideration and the Ln(III) ion.

$^{31}\text{P}$  LnIRE values were determined for a selection of Ln(III) ions (see Table V). In those cases where separate signals were observed for free and complexed ligand (see Table III), the LnIRE values for both signals appeared to be identical. The magnetization recovery curve after the inverting nonselective  $180^\circ$  pulse was always single exponential within the experimental accuracy. Application of a selective (soft)  $180^\circ$  pulse<sup>34-37</sup> on either the signals for the free ligand or those for the complex gave analogous results: the magnetization transfer between free and complexed nuclei is fast on the experimental time scale. It can be concluded that the relaxation is in the fast exchange region as defined by

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Table VI. Ln(III)-P Distances (Å) as Calculated from  $1/T'_{1, \text{compl}}$ 

Ln	Ln-P <sub>α,γ</sub>	Ln-P <sub>β</sub>
Nd	3.44 ± 0.05	3.52 ± 0.05
Eu	3.06 ± 0.08	3.13 ± 0.08
Tm	3.59 ± 0.08	3.43 ± 0.05
Yb	3.57 ± 0.05	3.38 ± 0.05

McLaughlin and Leigh.<sup>38,39</sup> This phenomenon does not often occur when separate signals are observed for the exchanging entities. According to McLaughlin and Leigh, and taking into account the high association constants of the 1:2 complexes, in the fast exchange region the following approximation is valid<sup>39</sup> for both the free ligand and the complex:

$$1/T_{1, \text{exp}} = 2\rho/T_{1, \text{compl}} + (1 - 2\rho)/T_{1, \text{fl}} \quad (3)$$

Here  $1/T_{1, \text{exp}}$  is the experimental longitudinal relaxation rate,  $1/T_{1, \text{compl}}$  is the relaxation rate of the Ln(TP)<sub>2</sub> complex, and  $1/T_{1, \text{fl}}$  is the relaxation rate of the free ligand.<sup>40</sup>

In the fast exchange region (with separate signals for complex and free ligand), the transversal relaxation rates of TP in the free and the complexed state can be evaluated with eq 4 and 5, respectively:<sup>39</sup>

$$\text{free ligand: } 1/T_{2, \text{exp}} = 1/T_{2, \text{fl}} + 1/\tau_{\text{fl}} \quad (4)$$

$$\text{complex: } 1/T_{2, \text{exp}} = 1/T_{2, \text{compl}} + 1/\tau_{\text{compl}} \quad (5)$$

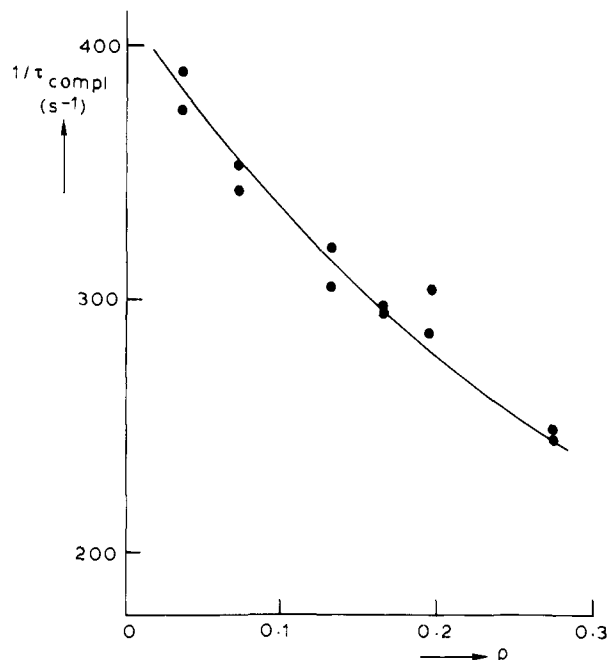
Here  $\tau_{\text{fl}}$  and  $\tau_{\text{compl}}$  are the residence times of the TP ligand in the free and the complexed state, respectively. From eq 3 and 5, and assuming that  $1/T_{2, \text{compl}} = 1/T_{1, \text{compl}}$ ,<sup>42</sup> the values of  $\tau_{\text{compl}}$  for the Eu(III), Tm(III), and Yb(III) complexes were calculated (see Table V). The magnitudes of  $\tau_{\text{compl}}$  obtained were in good agreement with the rough estimate of  $\tau_{\text{compl}}$  for Lu(TP)<sub>2</sub> from coalescence ( $\tau_{\text{compl}} = 3 \times 10^{-3}$  s). The magnitudes of  $\tau_{\text{compl}}$  also agree with the generally observed trend of increasing lifetimes upon decreasing Ln(III) ionic radius.<sup>21,22</sup> Therefore, the  $\tau_{\text{compl}}$  values show that the condition for the use of the fast exchange approximation for  $1/T_1$  (eq 3) is fulfilled.<sup>39</sup>

Gd(III) is often the Ln(III) ion of choice in relaxation rate enhancement studies because of its isotropic *g* tensor. Moreover, the enhancements induced by Gd(III) are much larger than those by the other Ln(III) ions, because of its much larger electron relaxation time.<sup>43</sup> Therefore, the measurements with Gd(III) were performed at low  $\rho$  values ( $\rho < 10^{-3}$ ). Under this condition eq 6 can be used to obtain  $1/T_{1, \text{compl}}$ .<sup>38</sup>

$$1/T_{1, \text{exp}} = 2\rho/(T_{1, \text{compl}} + \tau_{\text{compl}}) + 1/T_{1, \text{fl}} \quad (6)$$

The values of  $1/T_{1, \text{exp}}$  for the Gd(III) system are of the same order of magnitude as the  $1/\tau_{\text{compl}}$  values obtained so far. Although in this case an accurate value of  $T_{1, \text{compl}}$  cannot be evaluated from these relaxation rates from  $1/T_{1, \text{exp}}$  and eq 6, it can be concluded that  $\tau_{\text{compl}} > 0.23 \times 10^{-3}$  s.

The  $1/T_{1, \text{compl}}$  values for the other paramagnetic Ln(III) ions were corrected for any diamagnetic contributions by using the  $1/T_{1, \text{compl}}$  value of La(TP)<sub>2</sub> to give  $1/T'_{1, \text{compl}}$ . The ratio of  $1/T'_{1, \text{compl}}$  for P<sub>α,γ</sub> and P<sub>β</sub> appears to be rather independent of the Ln(III) ion used, showing that the interaction with the Ln(III) ion gives rise to isotropic relaxation behavior.<sup>42</sup> Assuming that the contact contribution to the LnIRE is negligible,<sup>42</sup>  $1/T'_{1, \text{compl}}$  can be related to the distances between the Ln(III) ion and the

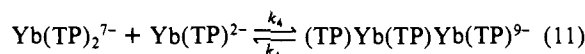
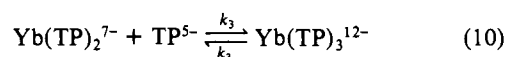
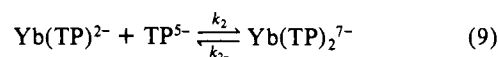
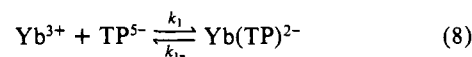
Figure 2. Relation between  $1/\tau_{\text{compl}}$  and  $\rho$  in the Yb(III)-TP system.

P nucleus under consideration with the reduced Solomon-Bloembergen equation:<sup>42,43</sup>

$$1/T'_{1, \text{compl}} = 4/3(\mu_0/4\pi)^2(\mu^2\gamma^2\beta^2T_{1e}/r^6) \quad (7)$$

Here  $\mu_0/4\pi$  is the magnetic permeability under vacuum,  $\mu$  is the magnetic moment,  $\gamma$  is the magnetogyric ratio,  $\beta$  is the Bohr magneton, and  $T_{1e}$  is the electron spin relaxation time. The latter parameter is shown to be rather independent of the ligation of the Ln(III) cation.<sup>44-46</sup> Using the  $T_{1e}$  values for the Ln(III)-aquo cations given by Alsaadi et al.,<sup>44</sup> from  $1/T'_{1, \text{compl}}$  and eq 7, the Ln(III)-P distances were calculated (Table VI). The distances obtained point to a structure of Ln(TP)<sub>2</sub>(D<sub>2</sub>O) in which the two PO<sub>3</sub> groups and the PO<sub>2</sub> moiety are coordinated with the Ln(III) cation. Any substantial contribution of structures in which only two of the phosphate moieties of TP are coordinated can be excluded. The structural picture thus obtained is analogous to that proposed for the Ln-ATP complex by Williams et al.<sup>9</sup>

**Triphosphate Ligand Exchange Mechanism.** The TP exchange mechanism has been studied in some detail for the Yb(III)-TP system. Several equilibria (eq 8-11) have been considered. In these equilibria D<sub>2</sub>O and the monovalent counterions are not taken into account.



In eq 10 a 1:3 Yb-TP complex is involved. Since the coordination number of Yb(III) usually does not exceed 9 or 10, the coordination of TP in this complex will differ from that in Yb(TP)<sub>2</sub><sup>7-</sup>.

Equilibrium 11 is a self-association mechanism, in which a binuclear complex is involved. Self-association is a commonly observed phenomenon in Ln complexation.<sup>13</sup> Equations 12 and

(38) J. S. Leigh, Jr., *J. Magn. Reson.*, **4**, 308 (1971).

(39) A. C. McLaughlin and J. S. Leigh, Jr., *J. Magn. Reson.*, **9**, 296 (1973).

(40) From measurements of  $1/T_1$  of the <sup>1</sup>H nuclei in the internal standard *tert*-butyl alcohol, the contribution to the relaxation of intermolecular interactions was shown to be negligible.<sup>41</sup>

(41) J. A. Peters, H. van Bekkum, and W. M. M. J. Bovée, *Tetrahedron*, **38**, 331 (1982).

(42) J. Reuben and D. Fiat, *J. Chem. Phys.*, **51**, 4918 (1969).

(43) R. A. Dwek, "Nuclear Magnetic Resonance in Biochemistry", Clarendon Press, Oxford, 1973, Section 9.4.

(44) B. M. Alsaadi, F. J. C. Rossotti, and R. J. P. Williams, *J. Chem. Soc., Dalton Trans.*, 2147 (1980).

(45) B. M. Alsaadi, F. J. C. Rossotti, and R. J. P. Williams, *J. Chem. Soc., Dalton Trans.*, 2151 (1980).

(46) P. D. Burns and G. N. LaMar, *J. Magn. Reson.*, **46**, 61 (1982).

13 for the residence times  $\tau_{\text{fl}}$  and  $\tau_{\text{compl}}$  can be derived from eq 8 - 11.

$$1/\tau_{\text{fl}} = k_1[\text{Yb}^{3+}] + k_2[\text{Yb}(\text{TP})_2^{2-}] + k_3[\text{Yb}(\text{TP})_2^{7-}] \quad (12)$$

$$1/\tau_{\text{compl}} = k_2 + k_3[\text{TP}^{5-}] + k_4[\text{Yb}(\text{TP})_2^{2-}] \quad (13)$$

From eq 12 it follows that  $1/\tau_{\text{fl}}$ , and concurrently the line width of the free ligand signals, should increase upon increase of  $\rho$ . This was indeed observed. The line width of the complex signals, on the other hand, appeared to decrease upon increase of  $\rho$  (see Figure 2). Since  $k_3[\text{TP}^{5-}]$  is the only term in eq 13 that decreases at higher  $\rho$  values, equilibrium 10 will play an important role in the exchange mechanism.

Fitting of the experimental  $1/\tau_{\text{compl}}$  values to eq 13 with neglect of  $k_4[\text{Yb}(\text{TP})_2^{2-}]$  gives  $k_2 = 120 \text{ s}^{-1}$  and  $k_3 = 780 \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ . Inclusion of  $k_4[\text{Yb}(\text{TP})_2^{2-}]$  into the fitting procedure gives only a slight improvement of the fit, which was rather insensitive for the value of  $k_4$ . Anyhow, it is clear that both associative (eq 10 and/or 11) and dissociative (eq 9) mechanisms are operative in the TP ligand exchange.

**Monovalent Counterions.** As stated before, the highly charged Ln-TP complexes have a strong affinity for cations. This has led to the application of these systems as shift reagents for monovalent cations.<sup>2</sup> Up to the maximum  $\rho$  values used in the present study ( $\rho \leq 0.25$ ), a linear relation between the LnIS and  $\rho$  was observed for <sup>23</sup>Na. A bound <sup>23</sup>Na shift of 61.3 ppm in the Na<sub>7</sub>Tm(TP)<sub>2</sub>(D<sub>2</sub>O) complex, which is expected to be almost completely dipolar in origin, was calculated from extrapolation of the TmIS to  $\rho = 0.5$ . This rather high value compared with the bound <sup>31</sup>P shifts (see Table III) suggests that the Na(I) counterions in the Na<sub>7</sub>Tm(TP)<sub>2</sub>(D<sub>2</sub>O) complex prefer distinct positions. If this would not be the case, Na(I) would experience all possible pseudocontact shifts equally, resulting in an average shift of about zero.<sup>47</sup> Using our previous assumptions about the position of the magnetic axis and the applicability of the (pseudo)axial form of eq 2, the sign of the induced shift implies that the Na(I) cations have a preference for sites with  $-54.7^\circ < \theta < +54.7^\circ$ , in the proximity of the negatively charged oxygens coordinated to the Ln(III) ion.

In order to obtain an estimate of the distance between Na(I) and Tm(III), an attempt was made to measure the TmIRE of <sup>23</sup>Na. Unfortunately, the relaxation rate in a 0.35 M aqueous solution of STP was already too high to allow any TmIRE measurement. Therefore, an equivalent amount of LiCl (up to 1.75 M) was added and <sup>6</sup>Li NMR was applied for the relaxation rate measurements. The <sup>6</sup>Li nucleus has a quadrupolar moment which is smaller by a factor of  $\sim 100$  than that for <sup>23</sup>Na. Consequently, smaller relaxation rates for the undoped samples are to be expected. The addition of LiCl resulted in 37% reduction of the TmIS for <sup>23</sup>Na. The TmIS for <sup>6</sup>Li was about equal to the reduction of the TmIS for <sup>23</sup>Na, and, therefore, it may be concluded that 37% of Na(I) coordinated to Tm(TP)<sub>2</sub><sup>7-</sup> is replaced by Li(I). From the observed TmIRE for <sup>6</sup>Li at  $\rho = 0.25$ ,<sup>48</sup> the longitudinal relaxation rate in the complex M<sub>7</sub>Tm(TP)<sub>2</sub> (M = Li and Na) was calculated to be  $1.25 \text{ s}^{-1}$ . From this, with the use of eq 3 and 7, a mean Tm-Li distance of 5.8 Å was calculated. This suggests that the seven monovalent cations are in the second coordination sphere of the Tm(III)-(TP) system. If the number of monovalent cations in the second coordination sphere were lower, the calculation would result in a smaller Tm-Li distance, which seems less likely.

(47) Cf. C. C. Bryden, C. N. Reilley, and J. F. Desreux, *Anal. Chem.*, **53**, 1418 (1981).

(48) The  $1/T_1$  values for <sup>6</sup>Li measured were: 5 M LiCl, 0.0011 s<sup>-1</sup>; 0.35 M STP, 1.75 M LiCl + Tm(III) at  $\rho = 0.25$ , 0.83 s<sup>-1</sup>; 0.35 M STP, 1.75 M LiCl + La(III) at  $\rho = 0.15$ , 0.019 s<sup>-1</sup>.

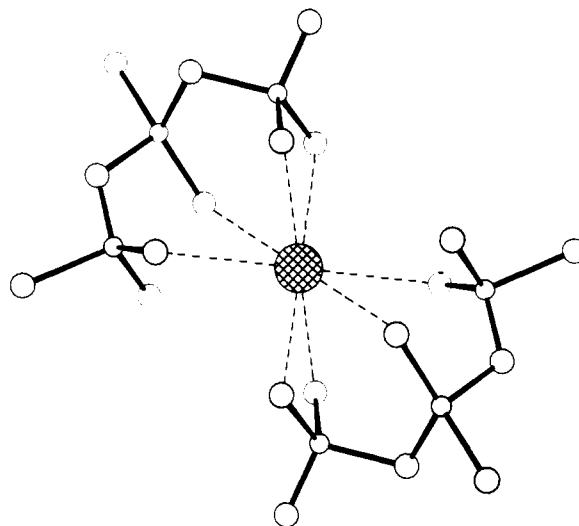


Figure 3. Structure of the Ln(TP)<sub>2</sub><sup>7-</sup> system.

It may be noted that a structure analogous to the binuclear complex NaLn(TP)<sub>2</sub><sup>6-</sup> suggested by Chu et al.,<sup>2</sup> in which the monovalent cation is very close to Ln(III), would give rise to a much larger TmIRE than was observed.

### Conclusions

The <sup>31</sup>P NMR data reveal that the 1:2 Ln-TP complexes are isostructural. Both <sup>31</sup>P and <sup>17</sup>O NMR shows that the two PO<sub>3</sub> groups and the PO<sub>2</sub> moiety of TP are all coordinated to the Ln(III) cation. The Ln(III)-induced <sup>17</sup>O shifts indicate that the PO<sub>2</sub> and one of the PO<sub>3</sub> groups are coordinated in a monodentate fashion, while the other PO<sub>3</sub> group is coordinated in a bidentate fashion. The experimental data demonstrate that the two PO<sub>3</sub> groups show a rapid interconversion as to their coordination. One D<sub>2</sub>O ligand is also present in the first coordination sphere leading to a coordination number of 9 for Ln(III). The <sup>23</sup>Na and <sup>6</sup>Li NMR data indicate that the negative charge of the Ln(TP)<sub>2</sub><sup>7-</sup> complex is neutralized by seven monovalent cations in the second coordination sphere of the Ln(III) cation. These cations show some preference for positions in the proximity of Ln-coordinated oxygen atoms that carry the negative charge. The resulting structure of the Ln(TP)<sub>2</sub><sup>7-</sup> system is depicted in Figure 3.

The present study demonstrates that slow exchange phenomena sometimes may hamper the use of LnIS measurements on <sup>17</sup>O and of LnIRE measurements. Since the exchange rate usually is dependent upon the Ln(III) cation, these problems can be overcome by a proper choice of the shift reagent and/or by the study of mixed ligand systems.

Further work on triphosphate monoesters of organic hydroxy compounds is in progress.

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**Registry No.** La(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-51-1; Ce(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-52-2; Pr(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-53-3; Nd(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-54-4; Sm(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-55-5; Eu(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-56-6; Gd(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-57-7; Tb(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-58-8; Dy(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-59-9; Ho(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-60-2; Er(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-61-3; Tm(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-62-4; Yb(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-63-5; Lu(TP)<sub>2</sub>(H<sub>2</sub>O), 93453-64-6; <sup>17</sup>O, 13968-48-4.