Inorg. Chem. **1995**, *34*, 4336−4342

^{13}C and ^{31}P NMR Study of Paramagnetic Lanthanide(III) Texaphyrins[1]

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Received January 12, 1995[⊗]

A ^{13}C NMR study of representative trivalent lanthanide texaphyrins **LnTx(NO$_3$)$_2$** (Ln = La, Ce, Pr, Nd, Eu, and Y) is presented. The carbon-13 resonances were assigned on the basis of 2D proton−carbon correlation spectroscopy. The metal-centered dipolar contributions to the observed isotropic shifts of paramagnetic complexes have been calculated on the basis of previously determined magnetic anisotropy parameters and X-ray crystal structures. The origin of carbon-13 contact shift contribution is discussed. ^{31}P NMR results for the diphenyl phosphonate derivatives of Ce(III), Pr(III), Nd(III), Eu(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), and Yb(III) texaphyrins are also presented.

Introduction

The texaphyrins (Figure 1) are unique porphyrin-like macrocyclic ligands that can coordinate large metal ions.[2] So far they are the only known five-coordinate, fully aromatic macrocycles that can coordinate lanthanide(III) cations. In fact, with the exception of the radioactive cation Pm(III), the whole series of lanthanide(III) complexes La → Lu has been synthesized, with many of these being characterized by X-ray crystallography.[2k,l] As a general rule, these lanthanide(III) complexes are exceptionally stable. Because of this stability and other properties that arise as a consequence of the aromatic ligand framework, the lanthanide(III) texaphyrins appear to be attractive candidates for use in such timely biomedical applications as magnetic resonance imaging (MRI) contrast enhancement and photodynamic therapy (PDT).[2b,d,j] On a more purely chemical level, the lanthanide(III) texaphyrins also define a near-unique series of compounds within which to explore issues associated with paramagnetic NMR spectroscopy.

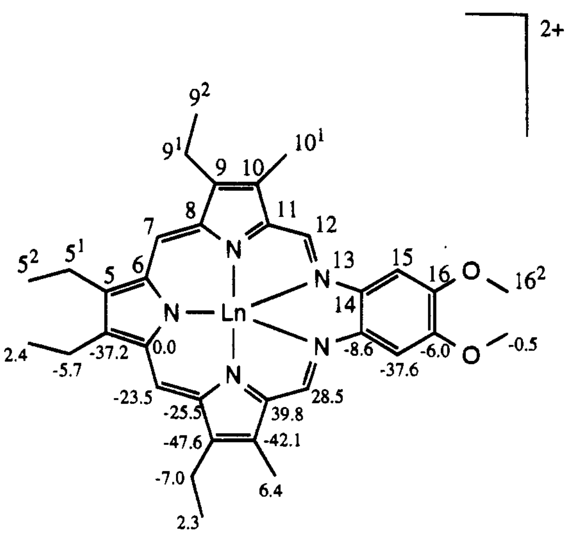

Figure 1. Atom-labeling scheme for the lanthanide(III) texaphyrin complexes considered in this study (upper part) and values of the $\delta_{lc} + \delta_{con}$ terms for the indicated carbon positions in the **EuTx(NO$_3$)$_2$** complex (lower part).

In the previous paper we presented the results of a thorough ^{1}H NMR study of paramagnetic lanthanide(III) texaphyrins and showed the profound effect that changes in axial ligation can have on the ^{1}H NMR spectra of these compounds.[3] Here, we present the results of a ^{13}C NMR investigation made using several representative parent bis(nitrate) derivatives, **LnTx(NO$_3$)$_2$**.[1] In contrast to what was observed in the proton case, where the isotropic shifts are dominated by dipolar contributions in all but the imino proton position, the carbon-13 isotropic shifts are found to be affected to a large extent by contact contributions as the result of through-bond spin delocalizations. Also presented in this paper are the results of a ^{31}P NMR analysis of the bis(diphenyl phosphate) adducts, **LnTx(P)$_2$**, that may be obtained from the addition of sodium diphenyl phosphate (**NaP**) to **LnTx(NO$_3$)$_2$**. This analysis serves to confirm the facility of the sequential axial ligand exchange processes previously monitored using paramagnetic ^{1}H NMR spectroscopy.

Experimental Section

The lanthanide texaphyrins, as their bis(nitrate) adducts, **LnTx(NO$_3$)$_2$**, were synthesized as previously described.[2k] The diphenyl phosphate derivatives **LnTx(P)$_2$** were generated in solution by adding a known amount of diphenyl phosphate sodium salt (**NaP**) to starting solutions of **LnTx(NO$_3$)$_2$**. Phosphorus-31 spectra were acquired on NT-360 and Bruker AM-500 spectrometers, and carbon-13, on Bruker AM-500 spectrometer. ^{13}C chemical shifts were referenced to TMS using solvent signals, and ^{31}P shifts were referenced to external H$_3$PO$_4$. The spectra were measured at 296 K using a 2:1 (v/v) mixture of chloroform-*d* and methanol-*d*$_4$ as the solvent. HMQC spectra were acquired using 256 data points in F1 and 2048 data points in F2. The

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1995.

(1) Abbreviations: used in paper: **H·Tx**, 4,5,9,24-tetraethyl-16,17-dimethoxy-10,23-dimethyl-13,20,25,26,27-pentaazapentacyclo-[20.2.1.1^{3,6}.1^{8,11}.0^{14,19}]heptacosa-1,3,5,7,9,11(27),12,14,16,18,20,22,-(25),23-tridecaene; **P$^-$**, diphenyl phosphate monoanion,

(2) (a) Sessler, J. L.; Hemmi, G.; Mody, T. D.; Murai, T.; Burrel, A.; Young, S. W. *Acc. Chem. Res.* **1994**, *27*, 43. (b) Sessler, J. L.; Murai, T.; Lynch, V.; Cyr, M. *J. Am. Chem. Soc.* **1988**, *110*, 5586. (c) Sessler, J. L.; Murai, T.; Hemmi, G. *Inorg. Chem.* **1989**, *28*, 3390. (d) Harriman, A.; Maiya, B. G.; Murai, T.; Hemmi, G.; Sessler, J. L.; Mallouk, T. E. *J. Chem. Soc., Chem. Commun.* **1989**, 314. (e) Magda, D.; Miller, R. A.; Sessler, J. L.; Iverson, B. L. *J. Am. Chem. Soc.* **1994**, *116*, 7439. (f) Maiya, B. G.; Mallouk, T. E.; Hemmi, G.; Sessler, J. L. *Inorg. Chem.* **1990**, *29*, 3738. (g) Sessler, J. L.; Murai, T.; Lynch, V. *Inorg. Chem.* **1989**, 28, 1333. (h) Kenedy, M. A.; Sessler, J. L.; Murai, T.; Ellis, P. D. *Inorg. Chem.* **1990**, *29*, 1050. (i) Sessler, J. L.; Mody, T. D.; Ramasamy, R.; Sherry A. D. *New. J. Chem.* **1992**, *16*, 541. (j) Sessler, J. L.; Mody, T. D.; Hemmi, G. W.; Lynch, V.; Young, S. W.; Miller, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 10368. (k) Sessler, J. L.; Mody, T. D.; Hemmi, G. W.; Lynch, V. *Inorg. Chem.* **1993**, *32*, 3175. (l) Sessler; J. L.; Burrell, A. K. *Top. Curr. Chem.* **1991**, *161*, 177.

(3) Lisowski, J.; Sessler, J. L.; Lynch, V.; Mody, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 2273−2285.

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data were zero filled to 2K × 2K and filtered in both dimensions using a square sine bell function. HMBC spectra were obtained using a 512 × 2048 data matrix, zero-filled to 2K × 2K. A sine function and a square sine function were used for apodization in F2 and F1, respectively. For both techniques, the TPPI phase cycling method was applied in F1.

As explained in the Results and Discussion section, the La(III) texaphyrin complexes **LaTx(NO$_3$)$_2$** and **LaTx(P)$_2$** were used as diamagnetic standards for the calculation of isotropic shifts. For the carbon-13 NMR analyses, the geometric factors used in the calculation of the metal-centered dipolar shifts were derived from the X-ray crystal structure of **GdTx(NO$_3$)$_2$**,[2k] whereas, for the phosphorus-31 study, the relevant data were derived from the corresponding **DyTx(P)$_2$** structure.[3]

Results and Discussion

General Considerations. Most lanthanide trivalent ions are paramagnetic and thus induce substantial chemical shifts in the ^{1}H NMR signals of protons located in the vicinity of the metal center.[4] This, for instance, has led to the widespread use of paramagnetic lanthanide-containing species as NMR shift reagents.[5,6] Also, certain paramagnetic lanthanide complexes are used as and/or show promise for use in contrast-enhanced MRI applications. As a result, considerable interest continues to be devoted to the study of various paramagnetic lanthanide complexes.

In paramagnetic complexes, including those derived from the lanthanide series, interaction between unpaired spin on the central metal ion with the nuclear spins of ligand atoms leads to shifts in the resonance positions of a given nucleus in the monitored NMR spectrum. This is the so-called isotropic shift, δ_{iso}, and is equal to the difference between the chemical shift of a given nucleus and position in the paramagnetic species in question and the chemical shift of the same locus in an appropriate diamagnetic reference compound.[4] In general, this interaction can be considered as being derived from two kinds of limiting mechanisms. The first of these involves through-space interactions between electron and nuclear magnetic dipoles; it leads to what are known as dipolar or pseudocontact shifts. In terms of origin, these pseudocontact shifts can be further divided into metal-centered (δ_{mc}) and ligand-centered (δ_{lc}) dipolar contributions.[4] Metal-centered dipolar shifts are related to the gross unpaired spin density residing on the central paramagnetic metal cation and are dependent on the magnetic anisotropy of the complex as well as on the position in space of a given nucleus. For nuclei other then proton, the dipole–dipole interactions, including unpaired spin delocalized into ligand orbitals, can lead to substantial ligand-centered dipolar shifts (δ_{lc}).

The second mechanism accounting for interaction between electron and nuclear spins involves mediated, through-bond Fermi contact interactions (contact shift δ_{con}); these depend on the nature of the bonding network connecting a given nucleus with the central paramagnetic species. The magnitude of these contact shifts generally reflects the covalency of the metal-to-ligand bonds and the extent of spin delocalization within the ligand framework. This, in turn, makes NMR analyses of paramagnetic species a method from which insight into the electronic structure of the subject complexes may be obtained.

Under conditions where both of the above mechanisms can be operative, the isotropic shift is thus equal to

$$\delta_{\mathrm{iso}} = \delta_{\mathrm{mc}} + \delta_{\mathrm{lc}} + \delta_{\mathrm{con}} \qquad (1)$$

Spectral Assignments of Carbon-13 NMR Spectra. The ^{13}C NMR spectra of lanthanide texaphyrins consist of 17 signals as expected on the basis of their structure and symmetry (Figure 2, Table 1). Due to the solubility and relaxation limitations in acquisition of the spectra of lanthanide texaphyrins, we have limited the ^{13}C NMR portion of the present study to the La(III), Ce(III), Pr(III), Nd(III), and Eu(III) bis(nitrate) texaphyrins, **LnTx(NO$_3$)$_2$**, and the Yb(III) diphenyl phosphate adduct, **YbTx(P)$_2$**. For the diamagnetic La(III) complex, a full assignment of the resonances is not possible from the simple 1D spectra, although it is possible to assign the type of carbon giving rise to a given signal (i.e., quartenary vs secondary, etc.) on the basis of the observed chemical shift range and editing techniques such as APT or DEPT.

The problem of assignment difficulty is enhanced in the case of the paramagnetic texaphyrin complexes. Here additional paramagnetic contributions to the chemical shifts serve to "shuffle" the signals. These contributions are impossible to predict reliably since both dipolar and contact terms need to be considered. Further complicating the problem of assignment is that another standard method,[4,5] involving analysis of relaxation times, fails to give unequivocal assignments for systems as complex as these.[7] Thus, an alternative method of making these critical assignments was sought.

We thought it might be possible to assign the resonances by taking advantage of the sensitivity inherent in two modern, inverse detection-based 2D proton–carbon correlation methods, namely HMQC (heteronuclear multiple-quantum correlation)[8] and HMBC (heteronuclear multiple-bond correlation).[9] In the

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(4) For NMR of paramagnetic complex, see e.g.: (a) La Mar, G. N.; Horrocks, W. DeW., Jr.; Holm, R. H., Eds. *NMR of Paramagnetic Molecules*; Academic Press; New York, 1973. (b) Bertini, I.; Luchinat, C. *NMR of Paramgentic Molecules in Biological Systems*; Benjamin/Cummings: Menlo Park, CA, 1986. (c) Bertini, I.; Turano, P.; Vila, A. J. *Chem. Rev.* **1993**, *93*, 2833.

(5) For reviews of shift reagents and paramagnetic NMR of lanthanide complexes see: (a) Horrocks, W. DeW., Jr. Chapter 12 in ref 4a. (b) Fisher, R. D. Chapter 13 in ref 4a. (c) Sivers, R. E., Ed. *Nuclear Magnetic Resonance Shift Reagents*; Academic Press Inc.: New York, 1973. (d) Reuben, J.; Elgavish, G. A. in *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, Jr., K. A.; Erying, L., Eds.; North-Holland Publishing Co.; Amsterdam, 1979; Chapter 38. (e) Ascenso, J. R.; Xavier, A. V. in *Systematics and the Properties of the Lanthanides*; Shina, S. P., Ed.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1983; Chapter 11. (f) Sherry, A. D.; Geraldes, C. F. G. C. In *Lanthanide Probes in Life, Chemical, and Earth Sciences Theory and Practice*; Bunzli, J.-C. G., Ed.; Elsvier: Amsterdam, 1989; Chapter 4.

(6) There is a vast literature on the NMR study of paramagnetic lanthanide(III) complexes. For example see: (a) Barry C. D.; North, A. C. T.; Glasel, J. A.; Williams, R. J. P.; Xavier, A. V. *Nature* **1971**, *232*, 236. (b) Willcot, M. R., III; Lenkinski, R. E.; Davis, E. D. *J. Am. Chem. Soc.* **1972**, *94*, 1744. (c) Cramer, R. E.; Dubois, R.; Seff, K. *J. Am. Chem. Soc.* **1974**, *96*, 4125. (d) Marinetti, T. D.; Snyder, G. H.; Sykes, B. D. *J. Am. Chem. Soc.* **1975**, *97*, 6562. (e) Horrocks, W. DeW., Jr.; Sipe, J. P., III. *Science*, **1972**, *177*, 994. (f) Agresti, D. G.; Lenkinski, R. E.; Glickson, J. D. *Biochem. Biophys. Res. Commun.* **1977**, *76*, 711. (g) Dobson, C. M.; Geraldes, C. F. G. C.; Ratcliffe, G.; Williams, R. J. P. *Eur. J. Biochem.* **1978**, *88*, 259. (h) Geraldes, C. F. G. C.; Williams, R. J. P. *Eur. J. Biochem.* **1978**, *85*, 463. (i) Bassfield, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 4168. (j) Singh, M.; Reynolds, J. J.; Sherry, A. D. *J. Am. Chem. Soc.* **1983**, *105*, 4172. (k) Lee, L.; Sykes, B. D. *Biochemistry* **1983**, *22*, 4266. (l) Babushkina, T. A.; Zolin, V. F.; Koreneva, L. G. *J. Magn. Reson.* **1983**, *52*, 169. (m) Jenkins, B. G.; Lauffer, R. B. *J. Magn. Reson.* **1988**, *80*, 328. (n) Peters, J. A.; Nieuwenhuizen, M. S. *J. Magn. Reson.* **1985**, *65*, 417. (o) Kemple, M. D.; Ray, B. D.; Lipkowitz, K. B.; Prendergast, F. G.; Rao, B. D. N. *J. Am. Chem. Soc.* **1988**, *110*, 8275. (p) Konami, H.; Hatano, M. *Chem. Phys. Lett.* **1989**, *160*, 163. (q) Sink, R. M.; Buster, D. C.; Sherry A. D. *Inorg. Chem.* **1990**, *29*, 3645. (r) Geraldes, C. F. G. C.; Sherry, D. A.; Kiefer, G. E. *J. Magn. Reson.* **1992**, *97*, 290. (s) Aime, S.; Botta, M.; Ermondi, G. *Inorg. Chem.* **1992**, *31*, 4291. (t) Capozzi, F.; Cremonini, M. A.; Luchinat, C.; Sola, M. *Magn. Reson.* **1993**, *31*, S118.

(7) In principle, the paramagnetic contributions to T_1^{-1} and T_2^{-1} are proportional to the inverse sixth power of the metal ion-to-monitored nucleus distance (ref 4). In the case of texaphyrins, however, there are too many positions that lie at more or less the same radial distance away from the paramagnetic metal center.

(8) Bax, A.; Subramanian, S. *J. Magn. Reson.* **1986**, *67*, 565.

Table 1. Values of Chemical Shift (δ), Isotropic Shift (δ_{iso}), and Calculated Dipolar Shift (δ_{dip}) or Sum of Contact Shift and Ligand-Centered Dipolar Shift ($\delta_c + \delta_{lc}$) for Lanthanide Texaphyrins (All Values in ppm)

	La$^{III\,a}$	Ce$^{III\,a}$		Pr$^{III\,a}$		Nd$^{III\,a}$		Eu$^{III\,a}$		Yb$^{III\,b}$	
posn	δ	δ_{iso}	$\delta_c + \delta_{lc}$	δ_{iso}	$\delta_c + \delta_{lc}$	δ_{iso}	$\delta_c + \delta_{lc}$	δ_{iso}	$\delta_c + \delta_{lc}$	δ_{iso}	δ_{dip}
5^1	19.1	0.6	0.6	1.0	2.0	2.0	3.0	−4.9	−5.7	15.9	13.6
5^2	17.8	−0.8	−0.9	−2.1	−1.3	−2.1	−1.4	2.9	2.4	11.2	10.2
7	116.2	6.1	3.5	12.1	7.8	13.5	9.7	−27.2	−23.5	12.5	9.5
9^1	19.0	2.2	0.7	6.6	2.7	10.2	6.8	−10.1	−7.0	−12.21	−11.6
9^2	16.9	0.5	−0.6	2.3	−0.6	1.1	−1.4	0.1	2.3	−4.3	−8.4
10^1	10.2	2.6	0.8	8.3	3.1	7.7	3.6	−10.4	−6.4	−17.7	−16.5
12	142.1	−0.9	−6.9	−3.1	−19.7	−10.1	−19.1	16.3	28.5	−29.5	−28.4
15	99.6	1.8	1.7	9.3	10.1	15.1	18.4	−36.7	−37.6	25.1	25.9
16^2	56.8	−0.1	−0.1	0.0	0.4	−0.3	0.6	−0.2	−0.5	7.4	7.1
5	146.0			12.6	15.6	19.8	22.4	−35.1	−37.2		
6	151.6							3.4	0.0		
								−44.3^c	−47.7^c		
8	146.4							−39.2	−25.5		
								8.5^c	22.19^c		
9	149.4			31.6	22.4	37.6	29.7	−54.8	−47.6		
10	134.8										
11	158.0										
14	138.2			−6.9	−3.5	−5.4	5.4	−5.0	−8.6		
16	153.6			0.1	1.9	2.1	4.4	−5.1	−6.0		

[a] In bis(nitrate) texaphyrin complex. [b] In bis(diphenyl phosphate) texaphyrin complex. [c] Alternative assignment of positions 6 and 8 (see text for details).

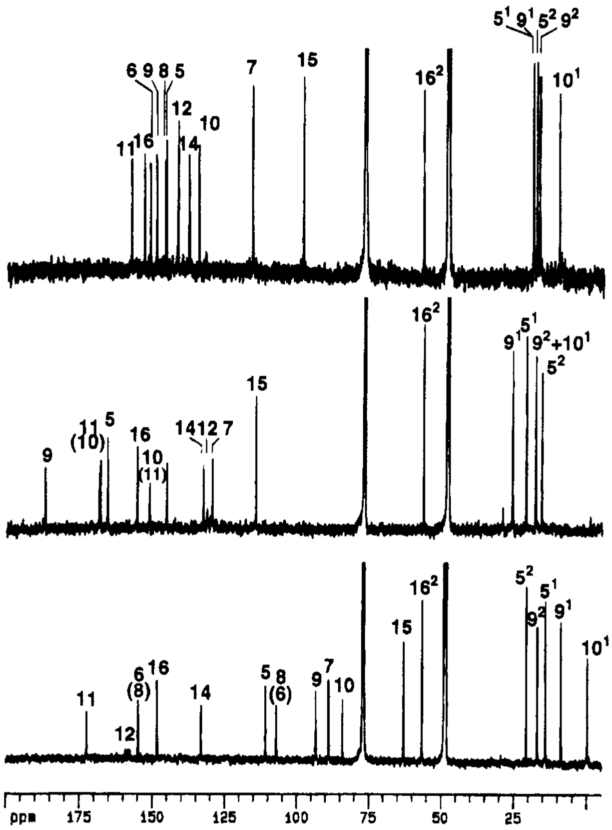

Figure 2. ^{13}C NMR spectra (296 K, $CDCl_3/CD_3OD$ (2:1)) of the **LaTx(NO$_3$)$_2$** (top), **NdTx(NO$_3$)$_2$** (middle), and **LnTx(NO$_3$)$_2$** (bottom) texaphyrin complexes.

case of paramagnetic systems, the use of these two methods has been very limited.[10] While this lack of previous use reflects a variety of factors, including instrumentation availability, it stems, at least to a certain extent, from the fact that in 2D spectroscopy involving paramagnetic systems (where the relevant relaxation processes are faster than in analogous diamagnetic compounds), magnetization is lost during the preparation and evolution periods.[4c,10–12] Fortunately, for at least some of the lanthanide texaphyrin complexes considered here, namely those involving Ce(III), Pr(III), Nd(III), Eu(III), and Yb(III) centers, the relaxation times were long enough to permit observation of at least some of the crosspeaks. This finding, in conjunction with the previously reported analysis of the ^{1}H NMR spectra, then allowed us to make the requisite carbon-13 assignments.

We started our analysis with the reference diamagnetic complex, **LaTx(NO$_3$)$_2$**. In this case, all the expected short- and long-range correlation crosspeaks were observed. A straightforward analysis of the HMQC spectrum (Table 1) thus enables an assignment of those carbon atoms that are bound to hydrogens.

Further assignment information was then obtained from the HMBC spectrum of this same diamagnetic complex (Figure 3). Generally, in HMBC spectra, several crosspeaks may be observed due to one-bond correlations (i.e., those already assigned on the basis of the HMQC spectrum) as well as two- and three-bond correlations (but not ones involving higher order). Given this, we began our analysis of the HMBC spectrum shown in Figure 3 by considering the signals associated with the benzo and imino protons (positions 15 and 12, respectively, in Figure 1). Here, both proton signals (cf. 1D spectrum at the top of Figure 3) were found to be correlated with the carbon signal at 138.2 ppm. This means that the latter can only correspond to position 14 (Figure 3). This, in turn, means that the other crosspeak associated with the benzo proton must arise from carbon 16 (153.6 ppm carbon shift), a conclusion that is supported by the finding that this particular carbon gives rise to the only crosspeak observed for the methoxy protons (designated by position 16^2 in Figure 1).

Continuing on with the analysis of the spectrum shown in Figure 3, one finds crosspeak connections between the carbon resonance at 149.4 ppm and the *meso* and methyl protons at

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(9) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093.

(10) (a) Timkovch, R. *Inorg. Chem.* **1991**, *30*, 37. (b) Banci, L.; Bertini, I.; Pierattelli, R.; Vila, A. J. *Inorg. Chem.* **1994**, *33*, 4338. (c) Turner, D. L.; Salgueiro, C. A.; Schenkels, P.; LeGall, J.; Xavier, A. V. *Biochim. Biophys. Acta* **1995**, *1246*, 24. (d) Turner, D. L. *Eur. J. Biochem.* **1995**, *227*, 829.

(11) (a) Emerson, S. D.; La Mar, G. N. *Biochemistry* **1990**, *29*, 1545. (b) Keating, K. A.; de Ropp, J. S.; La Mar, G. M.; Balch, A. L.; Shiau, F.-Y. *Inorg. Chem.* **1991**, *30*, 3258.

(12) Luchinat, C.; Steuernagel, S.; Turano, P. *Inorg. Chem.* **1990**, *29*, 4351.

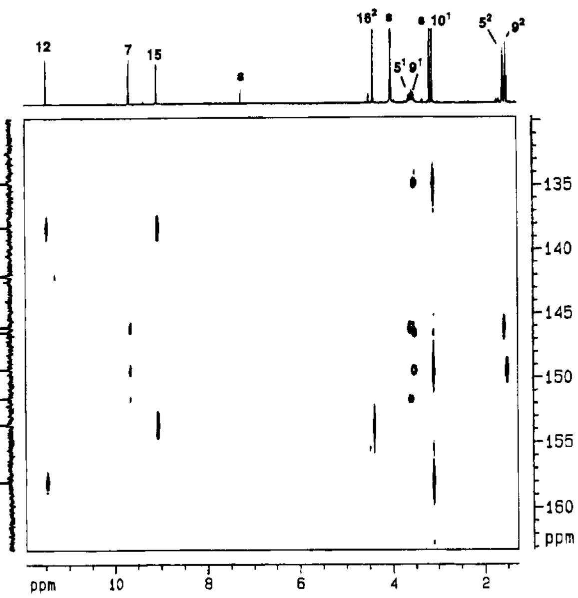

Figure 3. Portion of the HMBC spectrum (296 K, $CDCl_3/CD_3OD$ (2:1)) of the diamagnetic lanthanum(III) texaphyrin complex, **LaTx(NO_3)$_2$**. The ^{13}C NMR spectrum along the F1 axis was obtained *via* a separate 1D measurement.

positions 7 and 9², respectively. This allows this particular carbon signal to be assigned to position 9. Similarly, the presence of crosspeaks between the peak at 146.0 ppm and that for the methyl protons of position 5² allows this latter carbon signal to be assigned to position 5. One also finds, in the course of inspecting this HMBC spectrum, that the proton signal of methyl 10¹ is correlated to the carbon 9 (now assigned) and two other carbon resonances (at 158.0 and 134.8 ppm) that taken together must necessarily correspond to positions 10 and 11. Since the carbon signal at 158.0 ppm is also correlated to the imino proton signal, and the carbon signal at 134.8 ppm is correlated to the methylene 9¹ proton signal, the 158.0 ppm resonance can safely be assigned as corresponding to carbon 11, while that at 134.8 ppm can be assigned to carbon 10. With these assignments made, the remaining correlations (involving the proton signals of methylenes 5¹ and 9¹ to as-yet-unassigned carbon resonances) point to the carbon signals at 146.4 ppm and 151.6 ppm as corresponding to positions 8 and 6, respectively.

In the above analysis, it should be noted that some three-bond correlations lead to more intense crosspeaks than do the corresponding two-bond correlations involving the same proton signals. (The three-bond correlation between proton 7 and carbon 5, for instance, is more intense than that between this same proton and carbon 6.) This reflects the fact that in highly conjugated systems, such as, e.g., the texaphyrins, two-bond coupling constants, ^2J, can be smaller than three-bond ones (i.e., ^3J).[10,13]

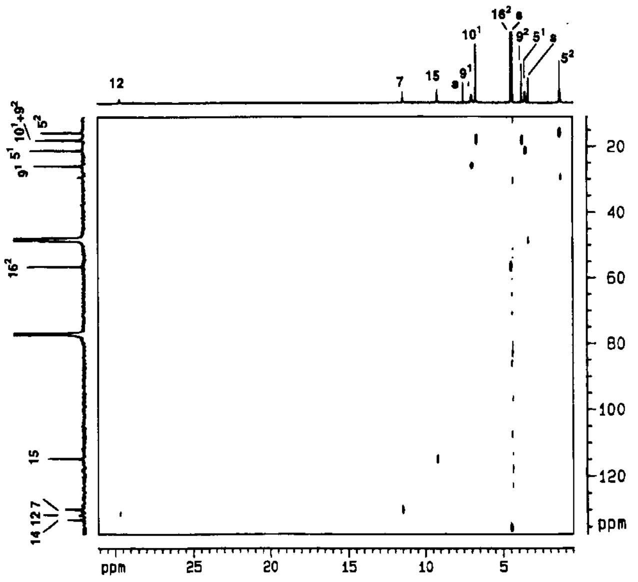

Figure 4. Portion of the HMQC spectrum (296 K, $CDCl_3/CD_3OD$ (2:1)) of the paramagnetic neodymium(III) texaphyrin complex, **NdTx(NO_3)$_2$**. The ^{13}C NMR spectrum along the F1 axis was obtained *via* a separate 1D measurement.

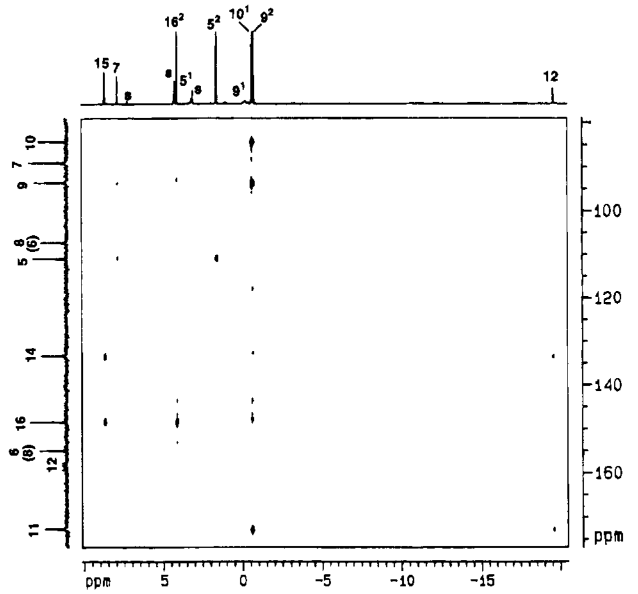

Figure 5. Portion of the HMBC spectrum (296 K, $CDCl_3/CD_3OD$ (2:1)) of the paramagnetic europium(III) complex, **EuTx(NO_3)$_2$**. The ^{13}C NMR spectrum along F1 axis was obtained *via* a separate 1D measurement.

In the case of the paramagnetic Ce(III), Pr(III), Nd(III), Eu(III), and Yb(III) texaphyrin derivatives, the HMQC spectra also allow for complete assignments. In fact, the relevant spectra display, gratifyingly, all the expected cross-correlations (cf., e.g., Figure 4 and also Table 1). On the other hand some of the crosspeaks seen in the case of the **LnTx(NO_3)$_2$** complex are missing from the HMBC spectra of the corresponding paramagnetic lanthanide texaphyrins. For instance, in the exemplary case of **EuTx(NO_3)$_2$** (Figure 5) the hoped-for correlations between methylene protons 5¹ and 9¹ and carbons 6 and 8, respectively, are no longer seen. Thus, a distinction within this particular pair of carbon-13 resonances cannot be made; in other words, two assignments are possible. Fortunately, the rest of the spectrum is clear and its analysis proceeds in analogy to that of the diamagnetic complex, **LaTx(NO_3)$_2$**, considered above. In the case of **PrTx(NO_3)$_2$** and **NdTx(NO)$_2$** even more crosspeaks are missing than in the case of **EuTx(NO_3)$_2$**. Thus assignments involving the quaternary carbon centers are less complete (Table 1).

Discussion of Contact Contributions in Proton and Carbon-13 Isotropic Shifts. In general, the values of contact shifts detected by paramagnetic NMR depend on (1) the extent of spin delocalization within the ligand framework and (2) the character of the bonds between the central metal ion and the ligating heteroatoms. In the subsections below, these two effects are discussed in turn. Also presented in the first of these

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(13) Summers, M. F.; Marzilli, L. G.; Bax. A. *J. Am. Chem. Soc.* **1986**, *108*, 4285.

subsections is a generalized discussion of the contact shift patterns for the various carbon-13 nuclei present in the lanthanide(III) texaphyrins.

Contact Shift Patterns in Lanthanide(III) Texaphyrins. Spin Delocalization Effects. It is well-known that, in the case of paramagnetic metalloporphyrins, contact shifts can arise as the result of two spin delocalization phenomena, namely those mediated through the σ- and π-bond frameworks, respectively (for review see ref 14). Thus, presumably, in the case of the texaphyrins, these two effects need to be considered as well.

Generally, σ-mediated spin delocalization effects are expected to drop off rapidly as the number of bonds increases.[4] Their influence is thus likely to be small in the case of the various texaphyrin protons (observed by, e.g., paramagnetic ^{1}H NMR spectroscopy) since most of these lie far from the paramagnetic center (i.e., several bonds away). Indeed, in previous work, involving an analysis of the ^{1}H NMR spectra of paramagnetic **LnTx(NO$_3$)$_2$** species, only the imino protons, three bonds away from the paramagnetic center, displayed a sizable contact contribution to the overall isotropic shift.[15] Specifically, for the complexes involved in the present study, i.e., the Ce(III), Pr(III), Nd(III), and Eu(III) texaphyrins, the values of these contact contributions were found to be 3.50, 9.61, 13.14, and −25.90 ppm, respectively.[3]

In contrast to the above, greater contact contributions to the isotropic shifts should be expected for the carbon signals of the paramagnetic lanthanide(III) texaphyrins than for the protons of the same complexes. This is due to the fact that, in general, the carbon are closer to the central lanthanide(III) centers (in terms of number of bonds) than the various periphery and substituent-bound protons.

The sum of the ligand-centered dipolar shift and contact shift for carbon can be obtained by subtracting the metal-centered dipolar shift from isotropic shift (eq 1). The former can be calculated on the basis of the eq 2,[4] where $D_1 = (\bar{c} - \chi_{zz})/2N$,

$$\delta_{\mathrm{dip}} = D_1G_1 + D_2G_2 = D_1\left(\frac{1 - 3\cos^2\theta}{r^3}\right) + D_2\left(\frac{\sin^2\theta\cos 2\varphi}{r^3}\right) \quad (2)$$

$D_2 = (\chi_{xx} - \chi_{yy})2N$, and χ_{xx} , χ_{yy}, and χ_{zz} are the principal components of the magnetic susceptibility tensor and r, θ, and φ are polar coordinates of a given proton. Here, the relevant geometric factors G_1 and G_2 are derived from the X-ray crystal structures of the **LnTx(NO$_3$)$_2$** complexes and the magnetic anisotropy parameters D_1 and D_2 are taken from the previous ^{1}H NMR analysis.[3] These calculations indeed show that the $\delta_{\mathrm{lc}} + \delta_{\mathrm{con}}$ term is sizable for the early lanthanide(III) texaphyrins and is actually dominant for **NdTx(NO$_3$)$_2$** and **EuTx(NO$_3$)$_2$** (Table 1). On the other hand, the isotropic shifts of **YbTx(P)$_2$** are strongly dominated by metal-centered dipolar contributions δ_{mc} (Table 1). As a result, a very close correspondence is observed between the measured carbon-13 isotropic shifts and the theoretical values obtained using the previously-reported ^{1}H NMR results as a starting point. This close correspondence is not surprising, since the relative theoretical ratio of δ_{con} to δ_{mc} (for a given position) in the present series of isostructural complexes, involving Ce(III), Pr(III), Nd(III), Eu(III), and Yb(III), should be 0.06:0.1:0.4:1:0.04 (values normalized to 1 for Eu(III)), respectively.[5,16,17] In other words, relatively high metal-centered dipolar contributions, δ_{mc}, are expected for Yb(III) complexes, while relatively larger contact shifts, δ_{con} (and hence, generally, also $\delta_{\mathrm{lc}} + \delta_{\mathrm{con}}$), are expected for complexes such as those of Nd(III) and Eu(III).

The data in Table 1 show that at a given carbon position, the ratios of the $\delta_{\mathrm{lc}} + \delta_{\mathrm{con}}$ terms in a series of Ce(III), Pr(III), Nd(III), and Eu(III) complexes are close to the calculated theoretical ratios of contact shifts,[17] namely −9.2:-27.8:-42.0:100, respectively. In particular, for the **NdTx(NO$_3$)$_2$** and **EuTx(NO$_3$)$_2$** complexes, where one would expect the highest relative contact contributions, the average ratio of these terms is −61.2:100. This indicates that for these complexes the sum δ_{lc} reflects mainly a contact contribution (i.e., $\delta_{\mathrm{lc}} < \delta_{\mathrm{con}}$). The values of the $\delta_{\mathrm{lc}} + \delta_{\mathrm{con}}$ term for **EuTx(NO$_3$)$_2$**, a complex which possesses the highest contact contribution, are presented in Figure 1.

A striking feature of the contact shift pattern in the texaphyrin case is the presence of both negative and positive shifts arranged in a rather regular manner. In many instances, the absolute value of the contact shifts for carbons two bonds away from the ligating nitrogen are higher than those of carbons but one bond away from the same nitrogen atom. For some carbon pairs, the signs of the contact shift values for neighboring atoms are the same, while for other they are opposite. This latter situation clearly points to the significance of spin correlation effects in the compounds under study.

For the σ mechanism of spin density delocalization, two possible scenarios need to be considered.[4] The first involves unpaired spin density that resides within a σ-type orbital possessing some nonzero contribution from the atom under observation. In this situation, the same sign in the observed isotropic shift (but sharply decreasing magnitude) is found in moving out from the coordinated paramagnetic metal center. By contrast, the second type of σ-based spin delocalization pathway involves spin polarization of σ-orbitals not directly involved in orbital containing unpaired electron. In this case, a decrease in the absolute magnitude of the contact shift value is also generally observed. However, the sign of this shift alternates along the pathway of the bonded atoms radiating out from the central paramagnetic atom.

In the case of π-type delocalization, the sign and magnitude of contact shifts can vary and are influenced by both the amount of unpaired spin density at a given carbon position as well as that at its neighbors. For instance the value of the contact shift for carbon C in the fragment C′−C(H)−C″ is given by the formula[18]

$$\delta_{\mathrm{con}} = \mathrm{const}[(S^{\mathrm{C}} + 2Q^{\mathrm{C}}_{\mathrm{CC'}} + Q^{\mathrm{C}}_{\mathrm{CH}})\varrho^{\mathrm{C}} + Q^{\mathrm{C}}_{\mathrm{C'C}}(\varrho^{\mathrm{C'}} + \varrho^{\mathrm{C''}}) \quad (3)$$

where, ϱ^{C} , $\varrho^{\mathrm{C'}}$, and $\varrho^{\mathrm{C''}}$ are the π spin densities at carbons C, C′, and C″ and S^{C}, $Q^{\mathrm{C}}{}_{\mathrm{CC'}}$, $Q^{\mathrm{C}}{}_{\mathrm{CH}}$, and $Q^{\mathrm{C}}{}_{\mathrm{C'C}}$ are known constants. Analogous expressions apply for other types of carbon atoms.[18]

The π spin density at a given carbon center is basically proportional to the square of the coefficient of the ligand-

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(14) La Mar, G. M.; Walker, F. A. in *The Porphyrins* vol. IV, chapter 2 Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, Chapter 2; pp 142−146.

(15) The unique large values of the contact shifts for the imino protons most likely derive from σ-type delocalization. Nonetheless, the possibility that they have their origin in π delocalization effects cannot be completely excluded at present. For this latter to be true, however, the coefficient of the π molecular orbital containing the unpaired spin would have to be exceptionally large at the imino position. On the basis of the previous calculations of the texaphyrin HOMOs and LUMOs, however, this appears unlikely to be the case (cf. Waluk, J.; Hemmi, G.; Sessler, J. L.; Michl, J. *J. Org. Chem.* **1991**, *56*, 2735). Further work using other, electronically modified lanthanide(III) texaphyrins could permit resolution of this issue.

(16) (a) Bleaney, B. *J. Magn. Reson.* **1972**, *8*, 91. (b) Bleaney, B.; Dobson, C. M.; Levine, B. A.; Martin, R. B.; Williams, R. J. P.; Xavier, A. V. *J. Chem. Soc., Chem. Commun.* **1972**, 791.

(17) Golding, R. M.; Halton, M. P. *Aust. J. Chem.* **1972**, *25*, 2577.

(18) Karplus, M.; Fraenkel, G. K. *J. Chem. Phys.* **1961**, *35*, 1759.

centered π orbital at that particular position. Thus, in the theory, it is possible to correlate the spin density distribution with the shape of the ligand-related frontier orbitals thereby finding which occupied or unoccupied orbitals are responsible for spin delocalization (and, possibly, bonding). This has been done successfully for, e.g., iron(III) and Ni(II) porphyrins.[19] Unfortunately, in the present instance, this approach breaks down since both σ- and π-based spin delocalization mechanisms could operate and the exact π-related spin density distributions cannot be found.

In spite of the above, some features of the shift pattern for the Eu(III) texaphyrin complex (presented in Figure 1) are still best interpreted in terms of the presence of substantial contact shifts arising from π-type delocalization. The reasons for this are as follows: First, the absolute magnitude of the $\delta_{\mathrm{lc}} + \delta_{\mathrm{con}}$ term (dominated by δ_{con} as discussed above) does not necessarily decrease in moving out from the paramagnetic Ln(III) center along all bond pathways. Second, positions that are similar in terms of distance and orientation relative to the central Eu(III) atom (e.g., the pyrrole α-carbons 6, 8, and 11) display different shift values. (For instance, the shifts of the pyrrole α-carbons are either equal to 0.0, −25.5, and 39.8 ppm or −47.7, 22.2, and 39.8, respectively, depending on the choice of alternative assignment for positions 6 and 8.) By contrast, for spin density delocalization mediated by a σ-type mechanism, a more even distribution of shifts at these positions would be expected. Also, the fact that different signs are observed for the shifts of carbon 12 and the attached imino proton is consistent with, but not a proof of, π-type delocalization.

Metal−Ligand Bonding Effects. One of the salient features of the texaphyrins is that they are porphyrin-like and aromatic. Because of this, it is of interest to determine if the nature of the ligands leads to any paramagnetic NMR effects that could reflect an unusual electronic structure of the lanthanide(III) complexes *in toto*. Specifically, it is tempting to ask whether the aromatic π-orbitals of the equatorial ligand interact with the metal ion and, more specifically, whether the lanthanide f-orbitals take part in covalent bonding.

In transition metal porphyrin complexes, π-type spin delocalization effects arise mainly as a result of direct interactions between the porphyrin π orbitals and those metal d orbitals that are of suitable symmetry. Since this generally occurs *via* π-orbital mediated donation or withdrawal of electron density to/from the metal ion, understanding these spin-related effects provides a means whereby π-electron density donation/withdrawal from the porphyrin ligand may be assessed.[14,19] This is useful since these latter electronic effects play a critical role in terms of stabilizing high and low oxidation states in coordinated metal centers.[20]

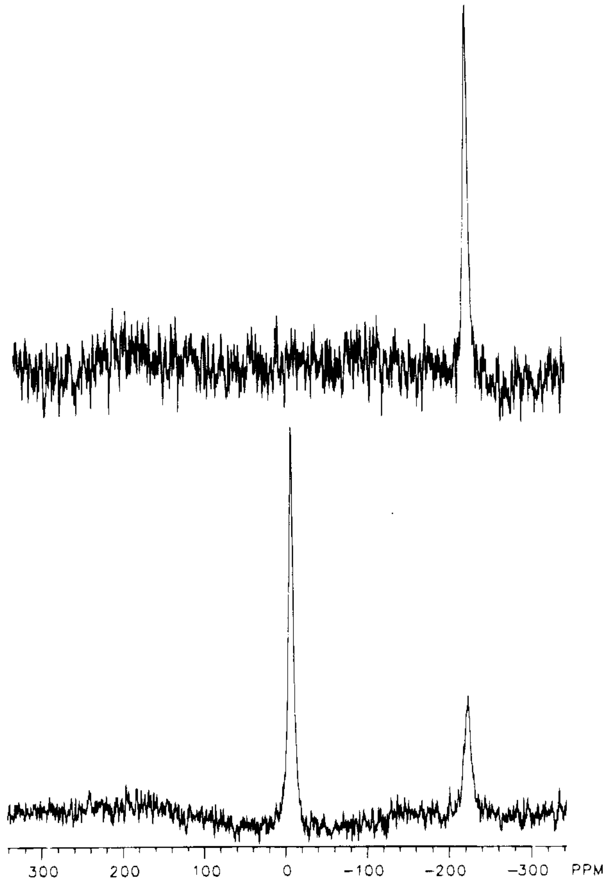

Figure 6. ^{31}P NMR spectra (296 K, $CDCl_3/CD_3OD$ (2:1)) of the paramagnetic erbium(III) texaphyrin species obtained after addition of 2 (top) and 4 (bottom) equiv of sodium diphenyl phosphate (**NaP**) to the starting nitrate adduct, **ErTx(NO$_3$)$_2$**. The signal at −222.1 corresponds to **ErTx(P)$_2$**, and that at −7.5 ppm, to a time-averaged signal derived from the free ligand **P**$^-$ with a small contribution from the monophosphate-ligated species, **ErTx(NO$_3$)(P)**.

In the case of paramagnetic lanthanide(III) texaphyrins, the situation is less clear. As noted above, π-delocalization effects are in fact observed. Thus, the simplest explanation of these effects would be in analogy to transition metal porphyrin situation: Direct orbital interactions serve to link the paramagnetic center to the ligand π-orbitals. However, in the case of the lanthanide(III) texaphyrins, such an explanation would necessarily require direct involvement of the "buried", spin-containing f-orbitals in bonding, and while this is not impossible,[21] it is certainly considered unlikely. One is thus left with a need to account for the π-delocalization effects *via* an indirect spin polarization mechanism. Such a mechanism could, for instance, involve participation of the lanthanide 5s orbitals. These latter orbitals would not be completely orthogonal to those of the texaphyrin π framework in complexes where the Ln(III) cation is pulled up out of the macrocyclic plane. As a result, interactions between these sets of orbitals are conceivable.[22]

^{31}P NMR Study. With the exception of the Gd(III), Sm(III), and Pm(III) adducts, ^{31}P NMR spectra were acquired for the whole series of lanthanide(III) diphenyl phosphate complexes, **LnTx(P)$_2$**. In most cases, two signals were observed in those samples containing an excess of free diphenyl phosphate monoanion (cf., e.g., Figure 6). In general, one of these signals, which does not vary in position with changes in free axial ligand concentration, corresponds to the phosphorus atom contained

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(19) For examples where spin π delocalization effects can be analyzed in terms of appropriate HOMOs and LUMOs of aromatic macrocycle, see e.g.: (a) Goff H. M. *J. Am. Chem. Soc.* **1981**, *103*, 3714. (b) Chatfield, M. J.; La Mar, G. N.; Parker, W. O., Jr.; Smith, K. M.; Leung, H.-K.; Morris, I. K. J. *Am. Chem. Soc.* **1988**, *110*, 6352. (c) Lin, Q.; Simonis, U.; Tipton, A. R.; Norvell, C. J.; Walker, F. A. *Inorg. Chem.* **1992**, *31*, 4216. (d) Lisowski, J.; Latos-Grazynski, L.; Szterenberg, L. *Inorg. Chem.* **1992**, *31*, 1933.

(20) For instance, π-donation of electron density from porphyrin molecular orbitals to empty d orbitals of suitable symmetry stabilizes species such as Fe(IV). In the case of low-valent complexes, the opposite effect, i. e., π-back-bonding with the participation of porphyrin π-orbitals, takes place.

(21) In at least one case involving cyclopentadiene−Eu(III) complexes, results of Mössbauer analyses indicate a substantial participation of f-orbitals in the formation of covalent bonds; cf.: Depaoli, G.; Russo, U.; Valle, G.; Grandjean, F.; Williams, A. F.; Long, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 5999.

(22) One can conceive of analogous alternative explanations involving, for instance, polarization of either the fully occupied 4d or completely unoccupied 5d orbitals.

within the coordinated axial ligand of the bis-ligated **LnTx(P)₂** adduct. The other signal, the relative intensity and exact position of which depends on the concentration of $\mathbf{P}^-$, derives from a time-averaging of signals originating from the free ligand, $\mathbf{P}^-$(diphenyl phosphate in the form of its sodium salt), and small amounts of the monoadduct **LnTx(NO₃)(P)**. As in the case of the macrocycle-based signals in the previously-reported ^{1}H NMR study, the first relevant exchange process (eq 4) is

$$LnTx(NO_3)_2 + P^- \rightleftharpoons LnTx(NO_3)(P) + NO_3^- \qquad (4)$$

$$LnTx(NO_3)(P) + P^- \rightleftharpoons LnTx(P)_2 + NO_3^- \qquad (5)$$

generally fast on the NMR time scale, while the second is slow (eq 5). Exceptionally, however, in the case of the Dy(III) and Tb(III) complexes both processes are fast on the NMR time scale and one broad phosphorus-31 signal, corresponding to a time-average of all three possible phosphorus-containing forms, namely $\mathbf{P}^-$, **LnTx(NO₃)(P)**, and **LnTx(P)₂**, is observed.

Turning to an analysis of the observed chemical shifts, it is again easiest to start the discussion with the diamagnetic complex, **LaTx(P)₂**. Here, the coordinated diphenyl phosphate anion is seen to give rise to a single phosphorus-31 signal at −27.0 ppm. This corresponds to a 17.8 ppm upfield shift as compared to the free ligand, $\mathbf{P}^-$. Presumably, this shift is caused in part by an aromatic ring current effect. Since here the two spectroscopically equivalent phosphorus atoms are located above (and below) the macrocycle plane, such an effect should indeed lead to a sizable upfield shift.

For the paramagnetic complexes, **LnTx(P)₂**, isotropic shift values of 53.2, 121.8, 129.0, −293.0, −85, −39, −215.8, −196.1, −36.2, and 6.9 ppm were observed for the Ce(III), Pr(III), Nd(III), Eu(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), and Yb(III) adducts, respectively.[23] From our previous ^{1}H NMR study, anisotropy parameter values are available for the Tb(III), Dy(III), Ho(III), Er(III), Tm(III), and Yb(III) complexes.[3] Using these, metal-centered dipolar shifts equal to 80.6, 105.6, −87.2, −32.5, 58.1, and 2.8 ppm, respectively, may be calculated.

A comparison of the two sets of values given above makes it clear that there is a substantial "mismatch". This indicates that for these complexes the phosphorus-based $\delta_{lc} + \delta_{con}$ term is sizable, just as it generally is in the case of the ^{13}C NMR spectra discussed earlier in this paper. This, in turn, again in analogy to the carbon-13 work, means that contact contributions to the isotropic shift effects are greater in the case of phosphorus than in the case of protons. Although not explicitly measured by experiment, we also predict that contact shift effects are likely to be dominant as well for the earlier lanthanide(III) derivatives, particularly **NdTx(P)₂** and **EuTx(P)₂**. This is because the theoretical relative ratios for the contact vs metal-centered dipolar shifts should vary predictably[16,17] along the series of paramagnetic lanthanide(III) texaphyrin complexes, as discussed for the case of carbon-13 above.

Conclusion

The present study complements the earlier one involving paramagnetic ^{1}H NMR effects. Together, these two studies paint a consistent picture of NMR spectroscopic properties of the lanthanide(III) texaphyrins. They also allow for a detailed analysis of shift mechanisms as they operate within this series of near-congruent series of lanthanide(III) complexes. Here of particular importance is the finding that dipolar shift effects are dominant in the case of protons but that contributions from both dipolar and contact shift effects mediate the isotropic shifts of carbon-13 and phosphorus-31. Also important is the finding that both the proton and phosphorus-31 chemical shifts are sensitive to changes in axial ligation. This means that paramagnetic spectroscopic analyses, such as those presented here, can be used to monitor these kinds of all-important changes. This could be useful as further efforts are made to understand the chemical and biomedical features of the texaphyrins.

Acknowledgment. Support for this work from the National Institutes of Health (Grant AI 28845) and Pharmacyclics Inc. is gratefully acknowledged.

IC950033T

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[23] For the Tb(III) and Dy(III) complexes, the given values actually correspond to that of the time-averaged signal since an extrapolation of the shift to zero concentration (of added ligand) was not possible due to experimental sensitivity.