**XAFS Study of Gadolinium and Samarium Bisporphyrinate Complexes**

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Received April 11, 2000

The comparative X-ray absorption spectroscopy study of gadolinium and samarium bisporphyrinate complexes represented by the formulas GdIII(H(oep)(tpp)), GdIII(oep)2, GdIII(H(tpp))2 and SmIII(H(oep)(tpp)), SmIII(oep)2, SmIIIH-(tpp)2 is reported. The XAFS spectra are recorded on the LURE-DCI storage ring (Orsay, France) in transmission mode on the microcrystalline samples at the Gd and Sm L3 edges. The local environment for Ln3+ ions has been reconstructed applying one-shell and two-shell XAFS analysis procedures. The protonated and nonprotonated bisporphyrinate complexes present different XAFS features. After our analysis on the title derivatives, the gadolinium ion (at 80 K) is found to be bonded: (i) to eight nitrogen atoms at R(Gd–N) 2.50 Å, for GdIII(oep)2 [Debye–Waller (DW) factor 0.004 Å2]; (ii) to seven nitrogen atoms at R(Gd–N) 2.49 Å, for GdIIIH(oep)(tpp) [DW factor 0.005 Å2] and one nitrogen at long distance; and (iii) to six nitrogen atoms at R(Gd–N) 2.50 Å [DW factor 0.006 Å2] and two nitrogen atoms at long distance for GdIIIH(tpp)2. A similar coordination sphere has been detected for the corresponding Sm derivatives. So, the samarium ion (at room temperature) is bonded: (i) to eight nitrogen atoms at R(Sm–N) 2.53 Å, for SmIII(oep)2 [DW factor 0.006 Å2]; (ii) to seven nitrogen atoms at R(Sm–N) 2.53 Å, for SmIIIH(oep)(tpp) [DW factor 0.006 Å2] and one nitrogen at long distance; and (iii) to six nitrogen atoms at R(Sm–N) 2.50 Å, for SmIIIH(tpp)2 [DW factor 0.006 Å2] and two nitrogen atoms at long distance. As far as concerns LnIII(oep)2 complexes, the increase of Ln–N distance in the series Gd3+ < Eu3+ < Sm3+ reflects an increase in the ionic radii, which are in good agreement with previously published XRD data on EuIII(oep)2. Moreover, the protonated LnIIIH(oep)(tpp) and LnIIIH(tpp)2 complexes possess systematically shorter distances of about 0.02 Å between the XAFS and XRD data. This difference is attributed to the asymmetry of the distribution concerning Ln–N distances.

**Introduction**

The concept that there exist some structural and electronic similarities between the bacterial photosynthetic reactional center and the porphyrin sandwich-like complexes1–2 gave rise to the synthesis of many lanthanide, actinide, Zr, and Hf porphyrin double-deckers.1–21 All that activity prompted us to synthesize gadolinium and samarium bisporphyrinate complexes with various ligands: LnIII(oep)2, LnIIIH(oep)(tpp), and LnIIIH(tpp)2.

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where oep = octaethylporphyrin and tpp = tetraphenylporphyrin, see also Figure 1), in an effort to be able to target derivatives which may be used as artificial batteries.

Buchler et al. have reported the structure and electronic properties of sandwich-like lanthanoid (LnIV and LnIII) bisporphyrinates.2,6–9 The formula LnIV(oep)2 (starting with CeIV as well as ZrIV, HfIV, ThIV, etc.) can be explained in terms of porphyrin ligands being present in the complexes as dianion (oep)2−, while the formula LnIII(oep)2 can only be explained in terms of one porphyrin ligand being present in the complexes as dianion (oep)2− and the other as radical monoanion (oep)−...

Sandwich-like lanthanoid bisporphyrinates have been thoroughly investigated, and their physicochemical characterization by UV, ESR, and Raman spectroscopies has been reported,1,3,6–20 but there are very few studies by EXAFS spectroscopy. Also spectroscopic studies like UV–visible, 1H NMR, FT-IR, and EPR as well as electrochemical experiments have been improved on them, in order to enhance their redox behavior and particularly the influence of the strong π−π interactions between the two macrocycles.1,3,6–20

We previously have reported the synthesis, electrochemical, and spectroscopic properties for analogous complexes.15–17 Unfortunately only on the asymmetrical GdIIIH(oep)(tpp) and SmIIIH(oep)(tpp) complexes were X-ray diffraction data obtained (see Figure 2). Single crystals suitable for X-ray diffraction analysis have not been obtained for the symmetrical gadolinium [GdIII(oep)] and GdIIIH(tpp)3 and samarium [SmIII(oep)3 and SmIIIH(tpp)3] dimers, despite the existence in the literature of crystallographic data for symmetrical Ce4+, Zr4+, and Eu3+ complexes, especially with the (oep) ligand.1,9,11 In fact, the crystallization of this kind of derivative is extremely difficult, and this is probably due to the incorporation of solvent molecules during the preparation–purification process and/or their two forms, the protonated form and the deprotonated form.

However, the questions concerning the determination of structural parameters for the noncrystallized derivative, as well as the influence of some factors such as temperature and the presence of protonated forms for our double-deckers, warrant further study.

Continuing the effort to investigate this family of derivatives, we report herein the comparative X-ray absorption spectroscopy study (EXAFS and XANES) of bisporphyrinate LnIII(oep)2.

analysis procedures with experimental phases and amplitudes as well as ab initio multiple scattering (MS) calculations; thus, we were able to obtain additional information about the structure of the first coordination shell of the protonated and nonprotonated complexes. We also attempted to analyze higher shells by including multiple scattering effects on the XAFS signals up to 5 Å, and the global results are discussed below.

**Experimental Section**

**General Information.** Dichloromethane (CH₂Cl₂) and 1,2,4-trichlorobenzene (1,2,4-tcb) were purchased from Riedel-de Haën and Aldrich, respectively, and used as received. Tetrahydrofuran (THF) was purchased from Merck and distilled under an argon atmosphere over a mixture of sodium—benzophenone. All syntheses were performed under an argon stream atmosphere using Schlenk-tube techniques. Pentane-dione [acac(H)] and all lanthanide salts in the form of chlorides or nitrates were purchased from Aldrich and used as received. The (tpp)H₂ free base was synthesized according to a reported method,²² (oep)H₂ was synthesized by a modified process,²³ and the metalation reactions were performed by the acetylacetonate method.²⁴

**Synthesis of Neutral Complexes LnIIIH(oep)(tpp) and LnIII, H(tpp)₂.** Lanthanide(III) monophosphinates, LnIII(tpp)acac, with Ln = Gd, Sm, were prepared according to well-established experimental procedures.²⁴ The synthesis of the corresponding homo- and heteroleptic double-deckers LnIIIH(tpp)₂ and LnIIIH(oep)(tpp) was carried out as follows: The freshly prepared LnIII(tpp)acac (0.500 g, 0.570 mmol) was refluxed in 1,2,4-tcb for 3–5 h with 0.350 g (0.654 mmol) of Li₂(oep), prepared in situ according to the method published for SmIII[H(oep)-(tpp)].¹⁶ The reaction mixture was then allowed to cool to room temperature (RT). The isolation of all the complexes was achieved in four column chromatography steps.¹⁵

**XAFS Measurements.** The Gd L₃ edge spectra were recorded on the XAS2 beamline in transmission mode at the LURE-DCI storage ring (ring current, 350–250 mA; beam energy, 1.85 GeV) at low (80 K) and room temperature. The Sm L₃ edge spectra were collected on the XAS13 beamline and only at room temperature. We used a Si-(311) double-crystal monochromator, and 50% of harmonic rejection was achieved by slightly detuning the two crystals from the parallel alignment. The experimental spectra were measured by two ionization chambers filled with air with a step of 1 eV, and a count rate of 2 sp per spectrum. The energy resolution (fwhm) being 2.0 eV. The white line edge positions were reproducible with a precision of 0.2 eV (see XANES in Figure 3). A white line characteristic of a 2p transition has been observed.

The microcrystalline powder samples were finely ground and pressed into a pellet supported with Kapton tape windows. The variations of the XAFS spectra related to the slit width were studied and adjusted in order to obtain spectra well defined for the data analysis.²⁵ The adjusted thickness of the sample permitted us to reach a value for the absorption jump between 0.5 and 1. So, a total of 4 scan data were recorded for each sample (about 2 h per spectrum), and each spectrum was individually checked before averaging.

**XAFS Data Analysis.** The following procedure was performed for our XAFS data analysis. First, the parameters for the LnIIIH(oep)(tpp) complex were found, and then the structural parameters for the symmetrical complexes LnIII(oep)₂ and LnIIIH(tpp)₂ were refined. As it is well-known,²⁶ in order to obtain structural parameters concerning the coordination sphere around a metal ion by using XAS techniques, it is necessary to know the backscattering phases and amplitudes. These two parameters could be obtained by two different approaches: the first one is measured from the experimental data on a related crystalline form, and the second one is from theoretical calculations that give directly these electronic functions, but here, there is a lack of knowledge of damping amplitude factors.

Quantitative analyses were performed with experimental and theoretical standards.²⁸ The experimental data were analyzed with the EXAFS data analysis software package “EDA,”²⁷ which has already been used in other cases.²⁸,²⁹ For the derivatives with known X-ray analysis data, we had to constrain the parameters in order to get integer values of occupation number, with the same DW factor for similar types of atoms, at similar distances from Ln.³⁰,³¹ Particular attention was devoted to the XAFS zero-line removal (background and multi-electron contributions) through the multistep polynomial/cubic-spline procedure.³² The obtained XAFS signals, χ(E), were converted to the k space of the photoelectron wavevector, defined as k = [(2mν²)(E - E₀)]¹², where (E - E₀) is the photoelectron kinetic energy measured. In the case of the L₃ edge of rare-earth elements, E₀ is located at 3.2 eV above the white line maxima. The experimental XAFS signal χ(k) was multiplied by a factor k² to compensate the decrease in its amplitude with the increase in the wavevector value (see Figure 4).

Figure 5 shows the Fourier transforms (FTs) of the experimental XAFS signals, with a Kaiser—Bessel window in the range 0.0–13.0 Å⁻¹. Modulus and imaginary parts of the FTs are not corrected for the

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photoelectron phase shift; therefore the positions of peaks differ from the true crystallographic values at about 0.5 Å. As one can see (Figure 5), four main peaks are present in the experimental FTs: first main peak located at 1.2–2.2 Å with a maximum at 1.94 Å (label A) representing the Ln–N first shell; two peaks located at 2.5–3.2 Å with maxima at 2.8 and 3.25 Å, respectively (labeled C1 and C2); and a smaller peak (labeled D) at longer distances around 3.9–4.9 Å with a maximum at 4.25 Å.

We will proceed by presenting step by step our analysis for text clarity. So, in this context we will start with the first shell XAFS signal analysis. The first shell XAFS signals were singled out by the back FT procedure in the range between 0.6 and 2.4 Å. Calculations of the XAFS function were based on the single scattering curved-wave formalism. The first shell XAFS signals were fitted using an anharmonic one-shell model by a cumulant expansion:33,34

\[ \chi(k) = \frac{N}{kR} f(\pi k) \exp(-2C_2k^2 + \frac{2}{3}C_4k^4) \sin\left(2kR - \frac{4}{3}C_3k^3 + \phi(\pi k)\right) \]

where \( N \) is the coordination number, \( R \) is the interatomic distance, and \( \sigma_i \) is the Debye-Waller (DW) factor (in harmonic approximation \( C_2 = \sigma_i^2 \)). The DW of the lanthanide complexes can be described as the sum of \( \sigma_{\text{dis}}^2 \) due to static disorder and \( \sigma_{\text{vib}}^2 \) due to thermal vibrations.35 The higher-order cumulants \( C_3 \) and \( C_4 \) characterize the deviation of the distribution of distances from a Gaussian shape. In a second step, we proceed to the decomposition of the first shell in a two-shell model. For this, we fitted using standard harmonics (\( C_1 \) and \( C_2 = 0 \)), in which the radial distribution function (RDF) is taken into account by a superposition of two Gaussian distributions.

The backscattering amplitude and phase functions were obtained using two approaches: the experimental and the theoretical one. The experimental backscattering amplitude \( f(\pi k) \) and phase \( \phi(\pi k) \) functions were extracted from the XAFS data of the LnIII(oep)2 derivatives: Gd–N (\( R = 2.50 \) Å, \( DW = 0.004 \) Å); Sm–N (\( R = 2.53 \) Å, \( DW = 0.006 \) Å). We expected for LnIII(oep)2 complexes an increase of Ln–N distance in the series Gd III < Eu III < Sm III according to the increase in the ionic radii: 1.06 < 1.07 < 1.09 Å. The calculated distances are in agreement with previously published XRD data by Buchler et al. for the Eu(oep)2 complex (Eu–N = 2.510 Å).5

The theoretical backscattering functions were calculated for the clusters as following: distorted antiprism LnN8 (first shell of the dimeric complexes) with the distance Ln–N (\( R = 2.50 \) Å), and the typical values of the muffin tin radii: \( R_{\text{mt}}(\text{Ln}) = 1.56, R_{\text{mt}}(\text{N}) = 0.71 \) Å. We must affirm here that the distorted antiprism LnN8 mimics the structure of the title complexes. Since the initial energy \( E_0 \) of the photoelectron is defined in the FEFF6 code40 relative to the Fermi level \( E_F \) and strongly depends upon the muffin tin radii, we chose the continuum threshold (3.2 eV above the white line maximum). The photoelectron mean free path contribution was automatically included in the scattering amplitude function using the complex Hedin–Lundqvist (HL) exchange and the correlation potential (ECP). A natural broadening was included through the core level width \( \Gamma_{\text{core-hole}} = 3.5 \) eV for the 2p1/2 level in the case of the Gd and Sm L3 edges.

MS XAFS Analysis. Considering the signatures observed beyond the first shell, we took care of the MS effects which are known to modify the amplitudes and phases of the XAFS signals. The MS calculations were performed using the FEFF6 code40 on the clusters with different dimensions, constructed from the crystallographic data of LnIII(oep)(tpp) derivatives.

The central Ln atoms of the clusters are stuck between two porphyrin macrocycles (see Figure 2, GdIII(oep)(tpp) complex) and bound to

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the eight nitrogen atoms with distances around 2.46–2.66 Å. The Ln position possesses \( \text{C}_4 \) symmetry, and the eight nitrogen atoms form a distorted square antiprism. The 16 pyrrole carbon atoms, named \( \text{C}_6 \) (3.42–3.61 Å), and the eight carbon atoms in meso positions, named \( \text{C}_5 \) (3.75–3.93 Å), create the second and third coordination shells, respectively. The last 16 carbon atoms of the pyroles, named \( \text{C}_7 \) (4.65–4.79 Å), form the fourth shell of Gd. The ligands ethyl and phenyl are further out from the central atom at 5.5 Å and are not included in the clusters; the distance is too long to be unambiguously extracted by XAFS analysis.

Therefore, we carried out MS calculations for the clusters of 32 atoms within the 4.5 Å radius and with the cluster of 48 atoms within the 5.0 Å radius, taking into account all SS and MS paths up to the third order and with the muffin tin radii: \( R_m(\text{Gd}) = 1.56 \) Å, \( R_m(\text{N}) = 0.70 \) Å, \( R_m(\text{C}) = 0.69 \) Å, \( R_m(\text{C}) = 0.70 \) Å, \( R_m(\text{C}) = 0.71 \) Å.

Sharp double-electron excitations have been observed in the studied XAFS spectra. They are illustrated by the peaks with a width of several electronvolts located in the XAFS spectra about 6 Å\(^{-1}\) (see Figure 4). In the case of the rare-earth \( \text{L}_3 \) edges, such signals have already been reported.\(^{37-39}\) As it was mentioned earlier, the presence of the double-excitation contribution modifies the fine structure beyond the absorption edge. This automatically leads to the distortion of the XAFS signal (and consequently its FT) and, accordingly, increases the error in the determination of structural parameters. However, our analyses confirm that the influence of such effects on the FT was analogous to the effect of the steplike function, i.e., it produces a significant contribution only in the FT range above 5 Å.

**Results**

**XANES Data.** Figure 3 represents the XANES spectra (shifted to the corresponding \( E_0 \) positions) of the studied gadolinium and samarium complexes. All spectra are normalized and displaced vertically for clarity. For the comparison, the well-known reference spectra of \( \text{Gd}^{3+} \) and \( \text{Sm}^{3+} \) aqua ions (0.2 M aqueous solutions) are shown. Finally, the spectrum of monoporphyrinate \( \text{Gd}^{3+}(\text{tpp})\text{acac} \) complex is also included. As one can easily distinguish within the two series (Gd and Sm), the white line (WL) maximum positions coincide with each other (experimental precision 0.2 eV).

The presence of two valence states (\( \text{Ln}^{2+} \) and \( \text{Ln}^{3+} \)) can easily be distinguished by XANES spectroscopy due to their different position of WL (about 8 eV) which corresponds to the transition to unoccupied 5d states.\(^{40}\) In our case, no traces of \( \text{Ln}^{2+} \) ions were detected: the arrow indicates the expected WL position of \( \text{Ln}^{3+} \) ions. Therefore, the obtained experimental XANES spectra (Figure 3) are in good agreement with the expected spectra concerning the +3 oxidation state.

All XANES spectra of the studied bisporphyrinates present a great similarity, which confirms the similarity of the structures of these complexes. A characteristic shoulder (A) is observed which has been attributed to the MS contribution. Previously, Natoli and co-workers\(^ {41} \) published the MS calculation on a known reference spectra of \( \text{Gd}^{3+} \) and \( \text{Sm}^{3+} \) ions. Therefore, the obtained experimental XANES spectra (Figure 3) are in agreement with the expected spectra concerning the +3 oxidation state.

Further research on the Ln bisporphyrinate polyhedron of \( \text{Ln}^{3+} \) is a square antiprism where the proton prefers residing on the macrocycle on the meso position, thus creating a distorted square antiprism polyhedron of \( \text{Ln}^{3+} \) is a square antiprism where the two porphyrin rings are rotated about 45°. On the ORTEP diagram of the \( \text{Gd}^{3+}(\text{oep})(\text{tpp}) \) (Figure 2), the coordination polyhedron of the \( \text{Gd}^{3+} \) is shown, which is a square antiprism with the two porphyrin rings, rotated by an angle of 45°.

However, an interesting question was how the symmetry compounds are packed. A reasonable answer for that can be given after the analysis of XANES curves. As we have stressed before, all the XANES spectra of the bisporphyrinates present a very similar form. Therefore, we can use the spectra of known complexes as a fingerprint for the identification of unknown structure. Note that feature A is very well defined in all spectra for our Gd and Sm bisporphyrinate derivatives. On the other hand, the XANES spectra of the \( \text{Gd}^{3+} \) and \( \text{Sm}^{3+} \) aqua ions (tricapped prism) and monoporphyrinate \( \text{Gd}^{3+}(\text{tpp})\text{acac} \) complex present a significantly smaller amplitude for the shoulder (A) in question. Therefore, we suggest that antiprism coordination is more favorable for the Gd and Sm bisporphyrinates studied.

Experimental XAFS spectra for the Ln \( \text{L}_1 \) edge of the \( \text{Ln}^{3+}, (\text{oep})_2, \) \( \text{Ln}^{3+}(\text{tpp})\text{acac} \) complexes in the crystalline state at low and room temperatures (for Gd and Sm) are presented in Figure 4. The XAFS spectra are very similar between the corresponding Gd and Sm complexes, and that confirms the similarity between those two series of complexes. Also, the XAFS spectra of Gd at low and room temperatures exhibit a normal temperature dependence (increase of the Debye–Waller factor with temperature); that confirms the reproducibility of the XAFS measurements.

Furthermore, the features of the XAFS signals are very similar in the protonated forms \( \text{Ln}^{3+}(\text{oep})(\text{tpp}) \) and \( \text{Ln}^{3+}(\text{tpp})_2 \) and different from those in \( \text{Ln}^{3+}(\text{oep})_2 \) complexes. Under the same conditions and inside the recorded sets of measurements, the same ratio between the oscillation amplitudes of the XAFS spectra (8:7:6 for the \( \text{Ln}^{3+}(\text{oep})_2, \text{Ln}^{3+}(\text{tpp})_2, \) and \( \text{Ln}^{3+}(\text{tpp})_2 \), respectively) has been observed.

The experimental XAFS spectra were Fourier transformed, and their FTs are presented in Figure 5. The first peak on the FTs corroborates the feeling about the XAFS amplitude: the \( \text{Ln}^{3+}(\text{tpp})_2 \) has an abnormally lower amplitude of its first peak in comparison to that of the \( \text{Ln}^{3+}(\text{oep})_2 \). Those differences are related to protonated and nonprotonated forms for the studied complexes as we will discuss below.

A recurrent phenomenon either with Gd or with Sm is the decreasing amplitude of the first peak from \( \text{Ln}^{3+}(\text{oep})_2 \) to \( \text{Ln}^{3+}(\text{tpp})_2 \) complexes. This fact has prompted us to investigate the influence of protonation or not of our complexes and its influence on the Ln–N distance. It appears that the proton has the tendency to displace the macrocycle on which it resides, providing one large distance Ln–N–N–H in the protonated species. The XRD provides for the \( \text{Ln}^{3+}(\text{oep})_2 \) (for the nonprotonated complexes, \( \text{Gd}^{3+}(\text{tpp})_2 \), \( \text{Sm}^{3+}(\text{tpp})_2 \), and \( \text{Ln}^{3+}(\text{tpp})_2 \), respectively) has been observed.

It was hitherto reported that the proton prefers residing on the more basic OEP nitrogen atom than that on TPP with a ratio \( \text{N}^{+} \) with \( \text{H}^{+} \) equal to 1:4.3 based on \( ^1 \)H NMR data.\(^ {17} \) That implies a Ln–N–N–H distance superior to the other Ln–N–N–H distances. We assume that the protonated bond Ln–N–N–H gives a weak contribution to XAFS spectra and creates an asymmetry in the radial distribution function. The above assumption also could explain the highest amplitude observed for the nonprotonated \( \text{Ln}^{3+}(\text{oep})_2 \) complex.

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XAFS Study of Gd and Sm Bisporphyrinate Complexes

Table 1. First Coordination Shell Structural Data Obtained from the Best-Fit Analysis of the Ln Complexes with the One- and Two-Shell Fitting Models

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<th>State</th>
<th>Gd–N</th>
<th>Sm–N</th>
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<tr>
<td>Ln(^{III})(oep):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LT(feff)</td>
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<td>2.45</td>
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<tr>
<td>LT(ref)</td>
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</tr>
<tr>
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</tr>
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<td>RT(ref)</td>
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<td>2.46</td>
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</table>

<table>
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<tr>
<th>Ln(^{III})(oep)(tpp)</th>
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<tbody>
<tr>
<td>LT(feff)</td>
<td>6.4</td>
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</tr>
<tr>
<td>RT(ref)</td>
<td>6.4</td>
<td>2.50</td>
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</table>

* The label (ffef) indicates theoretical while (ref) indicates experimental phases and amplitudes. N is the number of atoms located at the distance R from the Ln, σ^2 is the DW factor, and ε is the fitting error. The one-shell (ffef) absolute errors are ±0.5 Å 2 on σ, and ±0.001 Å 2 on σ^2. The relative error bars (ref) are lowered when we compare different measurements to ±0.3 Å 2 on R, and ±0.001 Å 2 on σ^2. The error bars for the two-shell fitting procedure are ±0.02 Å on R and ±0.001 Å 2 on σ^2 for the short distances and ±0.05 Å on R and ±0.003 Å 2 on σ^2 for the long distances. The reference compound. The mean bond lengths R(N–N) are calculated from the crystallographic data on the Eu\(^{III}\)(oep)(tpp) complex from ref 1. The DW factor is taken from the feff fitting procedure. The coordination numbers are fixed.


In the case now of the protonated compounds, two different factors could play an important role on the inter-ring distance: the presence of the proton moving the (oep) macrocycle away from the central Ln\(^{III}\) atom more than the (tpp) macrocycle, and the steric effect due to the phenyl substituents reducing the distance between the two porphyrinic rings and making the (tpp) cycle closer to the photoabsorber.

First Coordination Shell Fitting Results. The SS contributions, related to the first shell, were singled out by the back FT in the intervals 0.6–2.4 Å (ΔR = 1.8 Å). The best fit of the XAFS signal analysis was performed in the k range from 2.0 to 11.0 Å⁻¹ (Δk = 9.0 Å⁻¹). The maximum number of fitting parameters Nmax is about 12 (Δk = 9.0 Å⁻¹ and ΔR = 1.8 Å), and Nind is limited by the number of independent data points Nind = 2ΔkΔR/(π + 2). The number of fitting parameters is significantly smaller. For the Gd and Sm bisporphyrinate complexes, one-shell (Ln–N\(_1\)) and two-shell (Ln–N\(_1\), Ln–N\(_2\)) contribution models are used. The analysis with constant constraints was performed for the two-shell model. We took four fitting parameters as for one contribution (N, R, DW, C\(_1\)), and as for two contributions (R\(_1\), DW\(_1\), R\(_2\), DW\(_2\)). The above analysis with the two-shell model is in agreement with the analysis for the Gd and Sm complexes, and that for the eight nitrogen atoms of the bisporphyrins. In contrast, the one-shell model gave unreasonable coordination numbers for the protonated complexes, or great fitting error with reasonable coordination number (see for example Figure 6).

A summary of the best-fit analysis between the theoretical (ffef) and experimental (ref) phases and amplitudes for the first coordination shell is presented in Table 1. For convenience, the best fits obtained using one- and two-shell models for the Gd\(^{III}\)(oep)(tpp) complex are shown in Figure 6. The results of this analysis including asymmetry of the RDF (C\(_2\) cumulant) with the theoretical phases and amplitudes are presented in the Table S.1 as Supporting Information. Note that, in Table 1, only the fitting procedures labeled (ffef) give the absolute values of the structural parameters, while the fitting procedures label (ref) give the small fitting error and high accuracy of relative changes between the different samples.

On the basis of the fitting parameters, the radial distribution function (RDF) can be reconstructed according to the equation:

\[ \rho(r) = \frac{2}{\pi} \int_0^\infty \left[ \frac{1}{r^2} \frac{d}{dr} \left( r \frac{d}{dr} \chi(2kr) \right) - \frac{2}{r^2} \chi(2kr) \right] dr \]

Figure 6. Best fit of first shell using experimental phases and amplitudes: the experimental XAFS for the GdH(oep)(tpp) complex at LT (solid line); two-shell model fit with constraints N\(_1\) = 7, N\(_2\) = 1, and C\(_1\) = 0 and residual (dashed line); one shell model fit with constraints N = 8, C\(_1\) = 0 and residual (dotted line).

The mean bond lengths Ln–N calculated from the crystallographic data on the Eu\(^{III}\)(oep)(tpp) complex from ref 1. The DW factor is taken from the feff fitting procedure. The coordination numbers are fixed.

Figure 7. Reconstructed RDFs of the first coordination shell of the Gd complexes at LT. RDFs obtained from XAFS data [Ln\(^{III}\)(oep)(tpp) complex (dotted line), Ln\(^{III}\)(oep)(tpp) complex (dashed line), Ln\(^{III}\)(tpp) complex (long dashed line)] and based on the XRD data of Ln\(^{III}\)H(oep)(tpp) (full line).
MS XAFS Results. We present herein the MS calculations for a cluster of 32 atoms within a 4.5 Å radius around Ln and for a cluster of 48 atoms within a 5.0 Å radius, taking into account all SS and MS paths up to the third order. The comparison of MS and SS calculations for the clusters of different dimensions allowed us to assign different peaks on the experimental XAFS FT.

At this first step, we tried to understand qualitatively the nature of the peaks beyond the first coordination shell in the XAFS FTs and particularly about the MS contributions. As one can see in Figure 5, four main peaks are present in the experimental FTs: the first main peak located at 1.2–2.2 Å with a maximum at 1.94 Å (label A); two peaks located at 2.5–3.2 Å with maximums at 2.80 Å and at 3.25 (label C1 and C2, respectively); and the peak at 3.9–4.9 Å with a maximum at 4.25 Å (label D).

For the cluster of 32 atoms around the Gd, the SS and MS (total 112 paths) calculated spectra within the radius 4.5 Å are shown in Figure S1 in comparison with the experimental one. The SS calculation (32 paths) is surprisingly in good agreement with the experiment. The modulus and imaginary parts of these FTs coincide well too. The MS signals (80 paths) give only small distortion of the form of the SS contributions (Figure S1.a). The modulus (see Figure S2.a) and imaginary parts of these FTs coincide well too. The MS signals produce some contribution in the EXAFS region and to the FT peaks C1 and C2, but it seems that the MS signals produce small contribution in the experimental spectra. This result is mainly due to the interference effect between MS signals and, possibly, structural and/or thermal disorder. As one can see in Figure S1, the DS and TS signals present the opposite phase that leads to a decrease of the total MS signal amplitude. The most important MS signal generated within the Gd–N–Cn chains originates from the eight pyrrolic groups: 32 DS contributions with path lengths of 3.6–3.8 Å and amplitude ratio 6%.

For the cluster of 48 atoms around the Gd, the SS and MS (total 435 paths) calculated XAFS and FT spectra are shown in Figures S1.b and S2.b, respectively. The 16 peripheral carbon atoms Cβ (4.65–4.79 Å) generate SS contributions (15% amplitude), but also strong DS and TS contributions within near linear Gd–N–Cβ chains originate from the eight pyrrolic groups: 32 DS contributions with a path length about 4.8 Å and amplitude ratio 12% and 16 TS contributions with a path length about 4.8 Å and amplitude ratio 10%. The FT analysis shows that the D peak at 4.25 Å corresponds mainly to the MS contributions within Gd–N–Cβ chains. Note that the number of carbon atoms (Cβ) determined from the SS analysis of XAFS is three times less than the expected one. This result is mainly due to the interference effect between SS and MS signals. As a consequence, the fitting analysis of this region is complicated and beyond the scope of this paper.

To conclude MS analysis, we suggest that also on the experimental FTs the main first peak A corresponds to SS processes on the eight nitrogen atoms, the second and third ones (C1 and C2) correspond mainly to SS from the second and third shells around gadolinium ion formed by the 16 Cn and eight Cn carbon atoms, and, finally, peak D corresponds to MS contributions within near linear Gd–N–Cβ chains. Its amplitude is damped by the dispersion of the distances structural and thermal disorder.

Second and Third Coordination Shell Fitting Results. As previously mentioned, the C1 and C2 peaks of the FTs are attributed mainly to two SS contributions from the Gd surrounding second and third shells formed by 16 carbon (Cn) atoms at 3.23–3.52 Å and eight carbon (Cn) atoms at 3.6–3.8 Å, respectively. However, we verified that the DS signal (Gd–N–Cn) can also produce some small contribution.

We included only more important MS contribution: the DS contribution within the Gd–N–Cn chain. The fitted parameters for each contribution were distances and DW factors that give 6 varying parameters. Nevertheless, the fitting results show that, due to a high DW factor, and to the behavior of the MS scattering amplitude, rapidly going down with the increase of the photoelectron energy, the MS contribution is present mainly at the beginning of the XAFS signal (up to 4 Å−1). This allows to separate SS contributions from the MS one and to extract reliable information on the distances and DW factor of Cn and Cn atoms, whose XAFS signal is well isolated at high wave vector values (4–13 Å−1).

The contributions, related to the second and third shell, were singled out by the back FT in the intervals 2.3–3.7 Å (ΔR = 1.4 Å). The best fit analysis was performed in the k range from 4.0 to 12.0 Å−1 (Δk = 8.0 Å−1) taking into account two SS contributions (Gd–Cn and Gd–Cn) with 4 varying parameters. The fitted parameters for each contribution were distances and DW factors. The maximum number of fitting parameters Nfitted is about 8 (Δk = 8 Å−1 and ΔR = 1.4 Å). Thus, if we also take two fitting parameters per contribution, the maximum number of contributions which can be used is four.

The summary of the best-fit analysis is presented in Table 2 and compared with the crystallographic data for LnIII(oep)2 and LnIII(H(oep))(tpp). The XAFS values are in close agreement with the average mean bond lengths calculated from XRD data. The data from ref. Spyroulias et al. [15, 16]. The coordination numbers are fixed.

### Table 2. Second Coordination Shell Structural Data Obtained from the Best-Fit Analysis of the Gd Complexes at LT and Sm Complexes at RT

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* N is the number of atoms located in the ith shell at the distance R from the Gd, σi is the DW factor, and ε is the fitting error. Absolute errors are ±0.03 Å on R and ±0.002 Å2 on σi. This error bar is lowered when we compare different measurements to ±0.01 Å on R and ±0.001 Å2 on σi. The mean bond length Ln–Cn is calculated from the crystallographic data on the EuIII(oep)2 complex from ref. Buchler [1]. The data from ref. Spyroulias et al. [15, 16]. The coordination numbers are fixed.
disorder determined by XAFS $\sigma^2 = 0.004 \, \text{Å}^2$ for the distributions (Gd–C$_6$ and Gd–C$_7$) is slightly larger than the ones given by XRD. The obtained distances are in good agreement with previously published XRD data.

**Discussion**

**Ln$^{III}$**(oep)$_2$. Buchler et al.\(^1\)–\(^3\),\(^6\)–\(^10\) have described the synthesis and physicochemical characterization of sandwich-like lanthanoid bisporphyrinates Ln$^{III}$(oep)$_2$ and have emphasized that the presence of two porphyrin ligands with distinct negative charges $-1$ and $-2$ should cause different Ln–N bond lengths. However, the small differences (Eu$^{III}$–N: 2.514 and 2.506 Å) are not significant. Therefore, Buchler and co-workers have suggested either statistical disorder of two porphyrin ligands in different oxidation states or complete delocalization of the electron hole between the two cofacial $\pi$-electron systems of the porphyrin ligands.\(^1\) As it was mentioned before, for Ln$^{III}$(oep)$_2$ complexes the increase in Ln–N distance in the series Gd$^{III}$ < Eu$^{III}$ < Sm$^{III}$ must reflect an increase in the ionic radii: 1.06 < 1.07 < 1.09 Å, respectively.

The distances for the studied Gd$^{III}$(oep)$_2$ and Sm$^{III}$(oep)$_2$ complexes have been calculated from the X-ray structure of Eu$^{III}$(oep)$_2$. The results of fitting procedures (see Tables 1 and 2) are in good agreement with previously published XRD data.\(^1\) The gadolinium ion is strongly bonded to the eight nitrogen atoms at $R$(Gd–N$_{av}$) 2.50 Å with a small DW factor. The DW factor increases with temperature from 0.004 to 0.006 Å$^2$ in agreement with the increase of the thermal motions. The samarium ion is also bonded to the eight nitrogen atoms at the distance $R$(Sm–N$_{av}$) 2.53 Å (in accordance with the ionic radii of Gd$^{III}$ and Sm$^{III}$, the latter distance is larger) with the same DW factor 0.006 Å$^2$ at room temperature. Thus, we confirm the structural data obtained on Eu$^{III}$(oep)$_2$. Moreover, we exclude the proposed statistical disorder of two porphyrin ligands in different oxidation states stated by Buchler et al.\(^10\) In fact, the sensitivity of the DW factor to the temperature, and its low value at 80 K measurements, is not consistent with an important part of the structural disorder related to various electronic charges on porphyrin ligands. So, the second assumption from Buchler on a complete delocalization of the hole between the two cofacial $\pi$-electron systems of the porphyrin ligands seems preferential.

**Ln$^{III}$(H(oep))(tpp).** The XRD data is only available for the asymmetrical Gd$^{III}$(H(oep))(tpp) and Sm$^{III}$(H(oep))(tpp) complexes.\(^15\),\(^16\) At room temperature the mean bond length to the eight nitrogen atoms $R$(Gd–N$_{av}$) is 2.538 Å, while the distance to tpp porphyrin is a little shorter (2.524 Å) than for the oep porphyrin Gd–N(oep) (2.551 Å). At low temperature (21 K) as expected, the distances became smaller (2.516 and 2.548 Å, respectively) due to the thermal contraction. Concerning the longer Gd–N(oep) bond distance with respect to Gd–N(tpp), the authors have assumed the presence of the hydrogen in the oep ring. The one-shell model (jeff and ref) gives an unreasonable coordination number (7) for gadolinium as well as for samarium. The gadolinium ion is strongly bonded to the six nitrogen atoms at $R$(Gd–N$_{av}$) 2.49 Å with a small DW factor. The DW factor increases with temperature from 0.005 to 0.007 Å$^2$. The samarium ion is also bonded to the seven nitrogen atoms at expected larger distance $R$(Sm–N$_{av}$) 2.53 Å (according to the ionic radii of Gd$^{III}$ and Sm$^{III}$) with the same DW factor 0.006 Å$^2$ at room temperature.

We introduce the two-shell model to mimic dispersion of the distances and especially to take into account the presence of one nitrogen atom at about 2.65 Å that creates strong asymmetry of RDF. The model matches the experimental signal as well as the one-shell model, and in addition has reasonable coordination number with respect to known XRD structure of the bisporphyrins. After this described analysis we conclude that the gadolinium and samarium ions are strongly bonded to the eight nitrogen atoms, but one nitrogen atom is located at significantly larger distance.

From first analysis and calculations on the XRD data of the bisporphyrinate, it seems that the RDF of Gd–N distances is represented by two Gaussians separated about 0.03 Å: the Gd–N(tpp) distance is 2.516 Å and that for Gd–N(oep) 2.548 Å. The inspection of the reconstructed RDF (broadened with DW factor 0.003 Å$^2$) shows only one peak at 2.52 Å with pronounced asymmetry (see Figure 7). The maximum of the RDF (approximately seven atoms) is shifted, approximately 0.05 Å compared to the average distance, and one atom gives the additional peak at about 2.64 Å. This is due to the fact that bond lengths Gd–N(oep) are very dispersed from 2.459 to 2.655 Å and the first seven distances have an average distance 2.516 Å. The XRD distance Gd–N for seven nitrogen atoms differs from the EXAFS distance at about 0.02 Å. The difference can be attributed to the asymmetry of the distribution of distances Gd–N, as a single scattering EXAFS analysis is very sensitive to the asymmetry of that radial distribution function (RDF) and generally gives shorter distances.

The XAFS RDFs reconstructed using experimental phases and amplitudes are presented on the Figure 7. Note that, for Ln$^{III}$(H(oep))(tpp), the Ln–N(tpp) distances form a more symmetrical distribution, with a smaller DW factor, than protonated Ln$^{III}$(H(oep))(tpp) complexes. The widths of the distributions are in good agreement, and hence, obtained from the fitting procedure with the theoretical phases and amplitudes (FEFF6), the DW factors reproduce well at low temperature the static distribution of the distances (the antiprism is distorted). Moreover, a small increase of the DW factors at room temperature is due to the increase of thermal motions.

**Ln$^{III}$(H(tpp)).** As it was mentioned earlier,\(^15\),\(^16\) all attempts to obtain crystals suitable for an XRD study for this kind of symmetrical dimer and whatever is the rare earth concerned have failed so far. Therefore XAFS analysis gives for the first time the structural parameters for these complexes. The one-shell fitting procedures give an unreasonable coordination number (six) for gadolinium as well as for samarium ions. The gadolinium ion is strongly bonded to the six nitrogen atoms at $R$(Gd–N$_{av}$) 2.51 Å with a small DW factor. The DW factor increases with temperature from 0.006 to 0.008 Å$^2$. The samarium ion is bonded to the six nitrogen atoms at the distance $R$(Sm–N$_{av}$) 2.53 Å with the DW factor 0.006 Å$^2$ at room temperature. Here we also introduce the two-shell model to take into account the strong asymmetry of RDF (presence of two nitrogen atoms at about 2.65 Å). The model matches the experimental signal better than the one-shell model and has a reasonable coordination number in agreement with the structure of bisporphyrinates.

**Conclusions**

Our XAFS analysis gives consistent structural information about the poor crystalline symmetrical Gd and Sm complexes. The XANES spectra of studied complexes are in good agreement with the expected Ln$^{III}$ oxidation state.

The XAFS results show that we were particularly sensitive to the decreasing amplitude of the signals and light changes in the first coordination sphere bonding mainly due to the protonation but also to a contribution of steric effects. For the
Ln—nitrogen first-shell coordination, the fit was done using both experimental and theoretical (FEFF) amplitudes and phases of the photoelectron.

The fitted parameters were gathered by calculating the RDFs, and we observed a longer bonding effect for the protonated LnIIIH(oep)(tpp) and LnIIIH(tpp)₂ compounds, revealing a pronounced asymmetry with the displacement of the curves toward large distances. In contrast, the RDF of the nonprotonated complex LnIII(oep)₂ presents a Gaussian form. Nevertheless it was important to take care of disorder effects especially with LnIIIH(tpp)₂ (lowest amplitude of the signal, highest DW factors) for which the substituents may cause a large deformation of the ring. Concerning this family of LnIIIH(tpp)₂ complexes, the structural data presented here are original as no crystalline form had been obtained previously.

The MS analysis of the carbon atom peaks (C₁ and C₂) confirms the dominance of the SS signals generated by the sixteen Cₐ and eight Cᵢ carbon atoms. The fitting results show that for gadolinium and respectively for samarium complexes the two-atom distribution (Gd–Cₐ and Gd–Cᵢ) remains the same with the average distances \( R(Gd–Cₐ) = 3.46 \pm 0.03 \text{ Å} \) and \( R(Gd–Cᵢ) = 3.78 \pm 0.03 \text{ Å} \).

Considering the signatures observed beyond the first three shells, strong MS contributions within near linear Gd–N–Cᵢ chains are generated (peak D). We have reached the limits of the XAFS technique concerning the difficulty to include, while calculating theoretical amplitudes and phases, the atoms far from the absorbing one beyond 5 Å, in particular the ligands ethyl and phenyl. Therefore we will develop in the near future the MS calculations and analysis on these crowded macrocyclic complexes.

**Acknowledgment.** This research was supported by the Greek General Secretariat of Research and Technology. J.P. would like to thank the Laboratoire de Chimie Bioinorganique—Centre pharmaceutique Châteenay-Malabry Université Paris-Sud, for their hospitality during this work. We also gratefully acknowledge the LURE laboratory.

**Supporting Information Available:** Figure S1 (XAFS spectra) and Figure S2 (FTs XAFS), showing the comparison of the MS calculations (the cluster of 32 and 48 atoms around the Gd) and experimental XAFS signals for the GdH(oep)(tpp) complex. Table S.1, showing the first coordination shell best-fit analysis with the theoretical phase and amplitude label (feff) including the asymmetry of RDF (C₃ cumulant). This material is available free of charge via the Internet at http://pubs.acs.org.