Intramolecular Dynamics of Asymmetric Lanthanide(III) Porphyrin Sandwich Complexes in Solution

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Temperature dependencies of the ^{1}H NMR spectra of asymmetric double-decker complexes of DyH(oep)(tpp) (**I**) and LuH(oep)(tpp) (**II**), where tpp is tetraphenylporphyrin and oep is octaethylporphyrin, have been analyzed. The kinetic and thermodynamic parameters for intramolecular phenyl ring rotations have been determined. The rotation in (**I**) is characterized by $k(298\ \mathrm{K}) = 11.4\ \mathrm{s}^{-1}$, $\Delta H^{\ddagger} = 48.0 \pm 6.0\ \mathrm{kJ\ mol}^{-1}$, while in (**II**) the derived parameters are found to be $k(298\ \mathrm{K}) = 14.0\ \mathrm{s}^{-1}$, $\Delta H^{\ddagger} = 65.5 \pm 7.1\ \mathrm{kJ\ mol}^{-1}$. The possible reasons for the different characteristics of these complexes are discussed. The structural parameters calculated for **I** and YbH(oep)(tpp) (**III**), indicate close similarities between the complexes. Nevertheless, it appears that the principal values of the molar paramagnetic susceptibility tensor (χ_i) differ significantly in these complexes.

Introduction

A number of physico-chemical studies on sandwich-complexes containing lanthanide metal(III) or metal(IV) ions and porphyrin ligands have been reported in the literature. These studies have been carried out using techniques such as UV/Vis, CD[1a−1g], low-temperature NIR spectroscopy[2c,2d], NMR,[1a−1c,2b−2e,3b−3d] resonance Raman (RR),[4c,4d,5a−5d] and electron spin resonance[1c,3c,4d] spectroscopies, as well as electrochemistry,[1d,2,3a] photophysics,[4a,4b] and X-ray crystal structure studies[1b,1c,2d,6]. Presently, the thermodynamic, structural, and electronic properties of these complexes are well known, both in solution and in the solid state. Recently, a new phenomenon, involving intramolecular rotation of the decker rings about each other in symmetrical sandwich complexes has been discovered and studied using CD and NMR spectroscopies.[1f,1g] The investigation of the dynamic properties of double-decker complexes represents an interesting area in metalloporphyrin chemistry and attracts the interest of researchers.

Although intramolecular dynamic processes involving motions, like phenyl ring rotation, in lanthanide porphyrin sandwich complexes were partially investigated, this motion was not sufficiently elucidated and described. The phenyl rings rotation-rate has been determined for the symmetric YbH(tpp)$_2$ complex at room temperature by the analysis of NOESY cross-peaks intensities.[3e] However, the activation parameters of the phenyl ring rotation were not measured. In this report we use the dynamic NMR approach[7a−7d] to obtain the phenyl rings rotation rate and the activation enthalpy for this process in solution on the asymmetric double-decker complexes DyH(oep)(tpp) (**I**) and LuH(oep)(tpp) (**II**).[3d,3e] The schematic representation of the complexes structure is illustrated in Figure 1. In addition, the results obtained by using pseudo-contact shifts and lanthanide-induced enhancements of longitudinal relaxation rates experienced by some protons of paramagnetic DyH(oep)(tpp) and YbH(oep)(tpp) (**III**) reveal that the structures of the complexes are very similar, with only a slight decrease in distances between the planes of porphyrin ligands upon increase in the atomic number of the lanthanide ions. This result has been interpreted as being due to so-called lanthanide contraction.

Results and Discussion

We have already reported the complete ^{1}H NMR signal assignment of complexes **I-III**.[3d,3e] The signal assignment was based on 1D NOE technique as well as on 2D NOESY, ROESY, TOCSY, and COSY experiments.

The intramolecular phenyl ring rotation rate for complex **II** was determined from the measurements of the temperature dependence of its ^{1}H NMR spectrum. ^{1}H NMR spectra of complex **II** at different temperatures are shown in Figure 2. ^{1}H NMR signals corresponding to *endo*-*ortho*,

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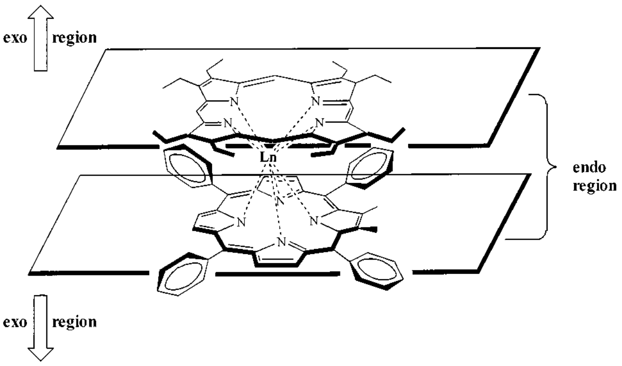

$Ln^{(III)}H(oep)(tpp)$

Figure 1. Schematic representation of the asymmetric LnH(oep)(tpp) complexes

exo-ortho, *endo-meta*, *exo-meta* protons are broadened with an increase in temperature, which is consistent with pairwise exchange between the sites: (*endo-ortho*) ⇄ (*exo-ortho*), and (*endo-meta*) ⇄ (*exo-meta*) (see Table 1). The first-order rate constant, k, for the intramolecular exchange processes was determined by comparison of calculated and observed temperature dependent linewidths of (*endo-ortho*), (*exo-ortho*), (*endo-meta*), and (*exo-meta*) ^{1}H NMR signals, according to a procedure reported for the uncoupled two-site exchange case.[7a,7e] Activation parameters were determined using the Eyring Kinetic Equation (1) from weighted least squares $\{\ln[k(T)/T]$ versus $1/T\}$[7a,7b,7e] where R is the gas constant, k_B is the Boltzmann constant and h is the Planck constant.

$$\ln[k(T)/T] = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R + \ln(k_B/h) \qquad (1)$$

The activation enthalpy of the phenyl rings rotation for **II** was found to be $\Delta H^{\ddagger} = 65.5 \pm 7.1$ kJ mol^{-1} with $k(298\text{ K}) = 14.0\text{ s}^{-1}$. We have also calculated the free energy of activation $\Delta G^{\ddagger} = 67.7 \pm 7.1$ kJ mol^{-1} at 95° C in order to compare it with data previously reported. The value obtained for the phenyl ring-flip activation free en-

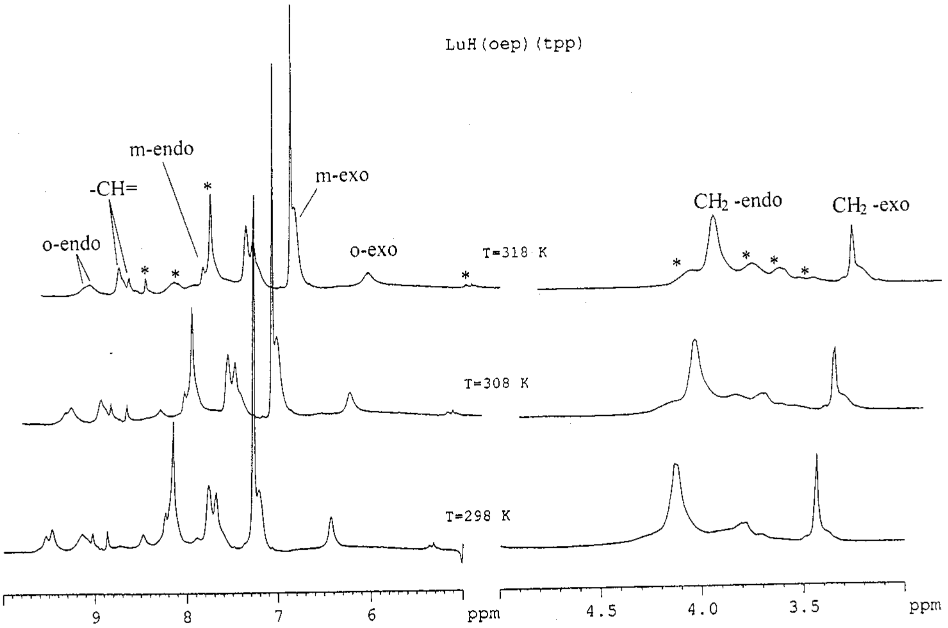

Figure 2. 500-MHz ^{1}H NMR spectra of LuH(oep)(tpp) (complex **II**) in $CDCl_3$ solution at various temperatures

Table 1. ^{1}H NMR observed chemical shifts (δ), hyperfine shifts (Δδ), longitudinal relaxation times (T_1) and calculated structural parameters of the LnH(oep)(tpp) complexes in $CDCl_3$ at 298 K

	Yb (**III**)[3e]				Dy (**I**)[3e]				Lu (**II**)[3d]
assignment	Δδ, ppm	Δδ/B(Yb)[a]	T_1,[b] ms	r/r(CH_3)[c]	Δδ, ppm	Δδ/B(Dy)[a]	T_1,[b] ms	r/r(CH_3)[c]	δ,[d] ppm
meso	30.4	0.78	8.0	0.76	−21.7	0.12	1.5	0.75	9.1
endo-CH_2	25.4	0.65	13.9	0.84	−6.6	0.037	7.2	0.96	4.1
exo-CH_2	17.4	0.44	18.7	0.88	−8.2	0.045	7.5	0.97	3.7
endo-ortho	1.3	0.033	21.7	0.90	−59.3	0.33	4.0	0.87	9.4
exo-ortho	3.7	0.094	34.0	0.97	16.2	−0.09	3.4	0.85	6.4
para	0.8	0.02	251.3	1.36	−9.6	0.05	52.6	1.34	7.6
endo-meta	−1.3	0.033	150.7	1.25	−21.9	0.02	31.9	1.23	8.1
exo-meta	−1.1	−0.028	157.6	1.26	−3.4	0.019	30.1	1.22	7.2
CH_3	2.4	0.06	40.2	1.0	−3.8	0.02	9.3	1.0	1.3
pyrrolic	−28.0	−0.71	9.3	0.78	−69.5	0.38	2.4	0.80	8.1

[a] B(Yb) = 39.2 and B(Dy) = −181.0, Bleaney's constants. – [b] Measured at 500 MHz. – [c] r – effective distance between the lanthanide cation and the resonated proton. – [d] Chemical shifts relative to TMS.

ergy in **II** is in good agreement with that found for the Ru(CO)(*i*Pr tpp) complex ($\Delta G^{\ddagger}$ = 77.8 kJ mol^{-1} at 95° C).[7e]

In order to compare the thermodynamic parameters of the phenyl ring flipping in LnH(oep)(tpp) complexes across the lanthanide series, including the activation enthalpy in the Lu complex, which is the last member of the series, the analogous parameters were determined for the Dy^{III} complex (**I**). The temperature dependence of ^{1}H NMR spectra of **I** within the temperature range 288 K to 306 K (data not shown) was investigated. No significant temperature dependent changes of the ^{1}H NMR linewidth were observed in addition to the Curie−Weiss dependence of the hyperfine shifts.[7b] This phenomenon can be explained by considering that the exchange rates between the sites (*endo-ortho*) ⇄ (*exo-ortho*), and (*endo-meta*) ⇄ (*exo-meta*) are smaller with respect to broadening of these signals due to lanthanide-induced enhancements of the relaxation rates (Table 1).

In order to determine the phenyl ring rotation rate constants for **I**, the temperature dependence of the 1D NOE spectra was investigated. The temperature variation of 1D NOE spectra of **I** is shown in Figure 3. The 1D NOE spectra were obtained by saturating *endo-ortho* and *endo-meta* signals. Upon saturation of *endo-ortho* and *endo-meta* signals, strong negative connectivities with signals *exo-ortho* and *exo-meta,* respectively, are observed. A temperature decrease results in a decrease of intensities of these negative peaks. This is consistent with the observed negative peaks being due to saturation transfer. We used these experimental data to evaluate the rate constants for the rotation of the phenyl rings. The time dependence of the longitudinal magnetization in an observed site at a transfer of saturated spins from the irradiated site is well known.[7a] During the irradiation the absorption intensity in the observed site [$\nu(t)$] falls off exponentially to a new steady state level [$\nu(\infty)$] due to transfer of saturated spins from the irradiated site. The rate of attainment of the new steady state, as well as its intensity, is determined by T_1 and the pre-exchange lifetime ($1/k$) of the observed site. Therefore, the rate constants were obtained using the following ratio [Equation (2)][7a] where $\nu(0)$ is the absorption intensity in the observed site without irradiation of another site.

$$k = [\nu(0) - \nu(\infty))/(\nu(\infty)\ T_1] \qquad (2)$$

The measured intensities of the saturation transfer spectra (Figure 3) allowed us to determine the phenyl ring-flip rate constant [k(298 K) = 11.4 s^{-1}] and the activation enthalpy for this process ($\Delta H^{\ddagger}$ = 48.0±6.0 kJ mol^{-1}).

An increase of the activation enthalpy along the series of lanthanide oep-tpp sandwich complexes reflects a larger steric barrier. Therefore, the differences in activation enthalpy of complexes **II** with respect to **I** may be related to a slight decrease of the porphyrin inter-plane distance. This is consistent with the ionic radius decrease along the series of lanthanide metals, known as *"lanthanide contraction"*.

In order to access this possibility, we have analyzed the available NMR and structural data on these complexes using Equation (3). It was assumed that the dipolar term dominates in the lanthanide-induced enhancements of spin-lattice relaxation rates on the ligand nuclei for **I** and **III**. The comparison of the calculated values of the structural parameter [$r(i)/r(\mathrm{CH_3})$], where r is distance between the lanthanide cation and the resonated proton,[10a−10c] (Table 1) for **I** and **III** reveals that the corresponding values in both complexes are rather similar although not identical.

$$r(i)/r(\mathrm{CH_3}) = [T_1(i)/T_1(\mathrm{CH_3})]^{1/6} \qquad (3)$$

The observed small differences between two complexes can be due either to an error in determination of $T_1(i)$ values or to minor structural differences.

A theoretical ratio has been previously reported for the variation of the pseudo-contact shifts in a series of isostructural Ln complexes.[11a,11b] In order to compare the hyperfine shifts of **I** with corresponding values of **II** (Table 1),

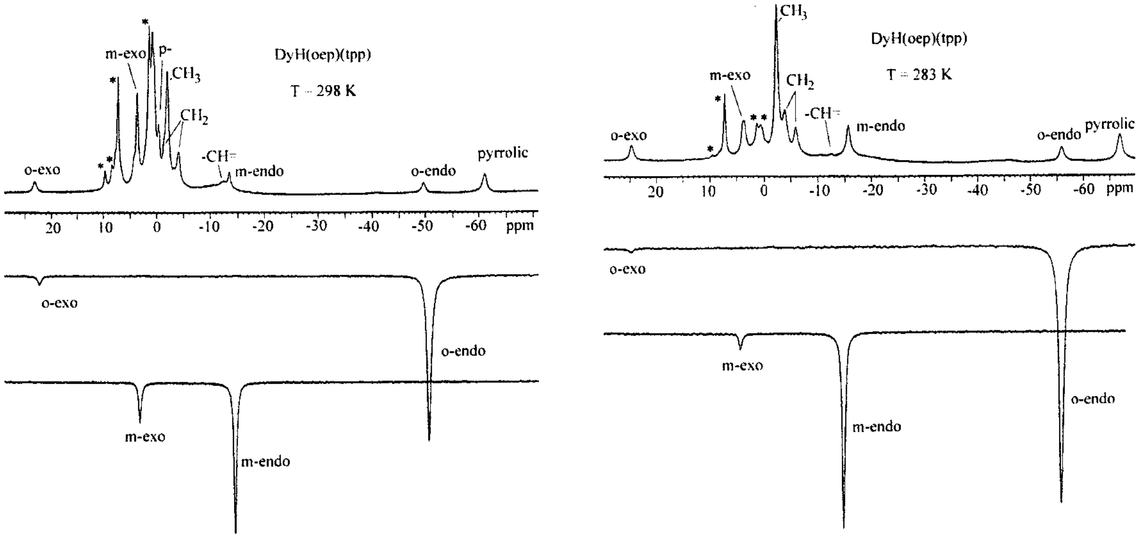

Figure 3. 500-MHz ^{1}H NMR 1D NOE difference spectra of DyH(oep)(tpp) (complex **I**) in CDCl$_3$ solution at various temperatures; assignment of diastereotopic phenyl proton peaks is reported; the asterisks indicate solvent or/and impurities

the parameters $\Delta\delta/B(\mathrm{Ln})$, where $\Delta\delta$ is the hyperfine shift and $B(\mathrm{Ln})$ is the Bleaney's constant,[11a,11b] were calculated. The analysis of Table 1 indicates that there is no correlation between the corresponding values of these parameters for complexes **I** and **III**. This means that the principal values (χ_i) of the molar paramagnetic susceptibility tensor change drastically from **I** to **III**, while only minor structural differences between these complexes occur. This behavior can be rationalized as due both to the effect of lanthanide contraction and to the macrocyclic nature (as basicity, planarity, etc.) of the ligand. These results are in rather good agreement with the study of complexes of macrocyclic polyether 18-crown-6 with paramagnetic lanthanide cations.[11b] The values of $(\chi_z - \chi_{av})/B(\mathrm{Ln})$ parameter are found to change monotonically three times with increase in the atomic number of Ln for Ln = Ce, Nd, and Pr with minor changes in the effective angle H−(18-crown-6)−Ln with C_2 axis of symmetry of the complexes. Therefore, the significant variation of molar paramagnetic susceptibility between complexes **I** and **III** are proposed to be related to a slight decrease of the distance between the planes of porphyrin ligands. This distance decreasing is relative to the increase in the number of lanthanide *f* electrons, which consequently results to lanthanide ionic radius contraction.

Experimental Section

Complexes **I**−**III** were synthesized according to the methods previously described.[1e,3d] Samples for NMR spectroscopy were prepared by dissolving **I**−**III** in deuterated chloroform. NMR spectra were recorded using MSL 200 and DRX 500 Bruker spectrometers operating at 200.13 and 500.13 MHz Larmor frequencies, respectively. Recycle delays and irradiation times ranged from 50 to 350 ms and from 20 to 200 ms, respectively. The spectra were calibrated by assigning the residual chloroform signal at 298 K to a shift from TMS of $\delta = 7.23$. 1D NOE spectra were recorded in difference mode using acquisition schemes previously described.[8a,8b] The chemical shift values of the diamagnetic LuH(oep)(tpp) complex[3d,3e] were used to calculate the hyperfine shifts for paramagnetic complexes **I** and **III**.

Longitudinal relaxation times were measured using a nonselective inversion recovery pulse sequence.[9a] The T_1 values were obtained from a two-parameter fit of the data to an exponential recovery function. In all cases the magnetization recovery was found to be exponential within the accuracy of the experiment, as expected for fast relaxing nuclei with little cross relaxation and favorable chemical exchange conditions.[9b]

Solution temperature was controlled using a Bruker B-VT 1000 temperature controller. Fourier-transformed spectra were subjected to complete line shape analysis[7a,7b,7d] on a Pentium-166 computer to obtain rate data for complexes **II**.

Supporting Information Available (see also footnote on the first page of this article): Temperature variations of ln(*k*) for DyH(oep)(tpp) in deuterated chloroform (Figure S1). Temperature variations of ln(*k*) for LuH(oep)(tpp) in deuterated chloroform (Figure S2).

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