Evidence of Protonated and Deprotonated Forms of Symmetrical and Asymmetrical Lutetium(III) Porphyrin Double-Deckers by ^{1}H-NMR Spectroscopy

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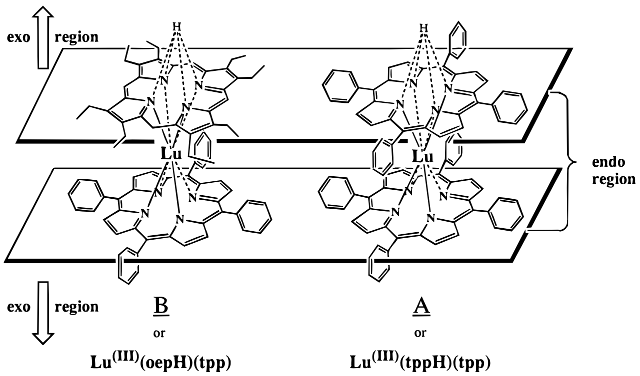
A number of physicochemical studies on double-deckers containing lanthanide metal(III) or metal(IV) ions and porphyrin ligands have been reported in the literature. Among these methods are included optical spectroscopy, electrochemistry,[1d,2,3a] NMR spectroscopy,[1a−c,2b−e,3b] photophysics,[4a,b] resonance Raman (RR) spectroscopy,[4c,d,5a−d] (and low-temperature NIR spectroscopy[2c,d,g,h]), electron spin resonance spectroscopy,[1c,3c,4d] and X-ray crystal structure studies.[1b,c,2d,6] Collectively, the above mentioned techniques assumed the existence, either of a sitting atop proton or of an equilibrium involving this proton on the porphyrin double-deckers in question. To date, however, there exists no direct evidence for the protonated form or its behavior in solution of the already known symmetrical or asymmetrical double-deckers.

As we have previously reported,[6] there are two possible formulas describing the protonated complexes in the asymmetrical (as well as the corresponding symmetrical with TPP ring) double-decker: $\mathrm{Ln^{(III)}(PorH)(Por')}$ or $\mathrm{Ln^{(III)}(Por)(Por'H)}$ [Por = Por′ for the symmetrical species]. The paramagnetic behavior, however, of 12 out of the 14 lanthanide metal ions could not allow a clear demonstration of the presence of the above-mentioned proton by ^{1}H-NMR spectroscopy. For this reason, the diamagnetic ion of lutetium was chosen and the $\mathrm{Lu^{III}H(TPP)(OEP)}$ and $\mathrm{Lu^{III}H(TPP)_2}$ complexes were prepared by the reaction of $\mathrm{(OEP)Li_2}$ or $\mathrm{(TPP)Li_2}$ with the isolated $\mathrm{(TPP)Lu^{III}(acac)}$ complex. The synthesis, purification, and isolation of these symmetrical and asymmetrical porphyrin double-deckers were carried out as previously reported.[6]

UV−visible spectroscopy confirmed the nature of these double-decker complexes. Different spectra were observed for the same complex in $\mathrm{CH_2Cl_2}$ and DMF solutions. The reason for this change of the spectrum has been attributed to an equilibrium between the protonated and deprotonated forms of the complexes.[6] The protonation process is solvent-dependent; in $\mathrm{CH_2Cl_2}$ the protonated form is present, while in basic solvents, such as DMF or pyridine the deprotonated form becomes dominant and the formula $\mathrm{[Lu^{III}(Por)(Por)]^-}$ can be postulated.

$$\underset{\text{protonated form}}{\mathrm{Lu^{(III)}H(Por)(Por')}} \xrightleftharpoons{\text{basic solvents, }-\mathrm{H^+}} \underset{\text{deprotonated form}}{\mathrm{Lu^{(III)}(Por)(Por')^-}}$$

Chart 1. Molecular Formulas and NMR Regions for Complexes **A** and **B**



Buchler et al.[1a,b,2b,d,e] have reported ^{1}H-NMR data for diamagnetic complexes of symmetrical Ce(IV), La(III), and Lu(III) double-deckers with TPP rings as well as asymmetrical Ce(IV) and La(III) double-deckers with TPP and OEP rings. Herein, we report on the direct evidence, by ^{1}H-NMR, of the localization of the proton in question on the title compounds. The unequal localization of this proton on both macrocycles is discussed in terms of the basicity of the macrocycle.

Considering the equilibrium presented beforehand, we carried out ^{1}H-NMR experiments in $\mathrm{CDCl_3}$ and DMF-d_7. The spectra suggest that $\mathrm{CDCl_3}$ favors the protonated form while DMF favors the corresponding deprotonated form, thus confirming the observations made by UV−visible spectroscopy. The chemical shifts for $\mathrm{Lu^{(III)}H(TPP)_2}$, **A**, and $\mathrm{Lu^{(III)}H(TPP)(OEP)}$, **B**, and the corresponding deprotonated forms are presented in Table 1.

In Figure 1 the ^{1}H-NMR spectrum in $\mathrm{CDCl_3}$ are shown. The N−H proton for **A** can be easily recognized in the high field region of the spectrum at −8.73ppm. Two well defined signals are also observed in the same region for **B**. Taking into consideration the chemical shifts of the nitrogen protons for the corresponding free bases (−3.74ppm for $\mathrm{OEPH_2}$ and −2.07ppm for $\mathrm{TPPH_2}$) and the chemical shift of the proton observed in the case of **A**, the observed peaks in **B** could be assigned as follows. The peak at −8.57 ppm corresponds to the proton contributed by TPP and that at −9.54 ppm corresponds to the proton contributed by OEP. Integration of the above two peaks confirms that the sum of the two areas corresponds to one proton. The ratio of the areas of the above mentioned peaks, $\mathrm{N{-}H_{TPP}/N{-}H_{OEP}}$, is 1:4.3. We should note that H−D exchange by ^{1}H-NMR experiments with complex **B** in $\mathrm{CDCl_3}$ support the above aspect and clearly confirms the labile character of the indicated proton for these double-deckers derivatives.

The data presented here strongly suggest that the proton in question prefers to reside on the more basic OEP nitrogen atom than that on TPP, contrary to literature data, which are based on indirect proofs.[3c] Therefore, the proton is unequally

Table 1. ^{1}H-NMR data for $\mathrm{Lu^{III}H(TPP)_2}$, **A**, and $\mathrm{Lu^{III}H(TPP)(OEP)}$, **B**, and Their Corresponding Deprotonated Forms [δ in ppm, TMS as Internal Reference, 400 MHz]

	ortho		*meta*								
complexes	endo	exo	endo	exo	*para*	pyr	N−H	CH	$\mathrm{CH_2}$	$\mathrm{CH_3}$	solvent
$\mathrm{Lu^{(III)}H(TPP)_2}$, **A**	9.45	6.54	8.05	7.24	7.84	8.26	−8.73				$\mathrm{CDCl_3}$
$\mathrm{[Lu^{(III)}(TPP)_2]^-}$	8.34	7.42	8.09	7.88	8.31	8.90					DMF-d_7
$\mathrm{Lu^{(III)}H(TPP)(OEP)}$, **B**	9.54 9.46	6.38	8.17	7.16	7.63 7.73	8.10	−9.54 −8.57	9.11 8.98	4.11 3.79	1.31	$\mathrm{CDCl_3}$
$\mathrm{[Lu^{(III)}(TPP)(OEP)]^-}$	8.35	7.83	8.12	7.88	8.30	8.82		10.38	4.21 4.08	1.95	DMF-d_7

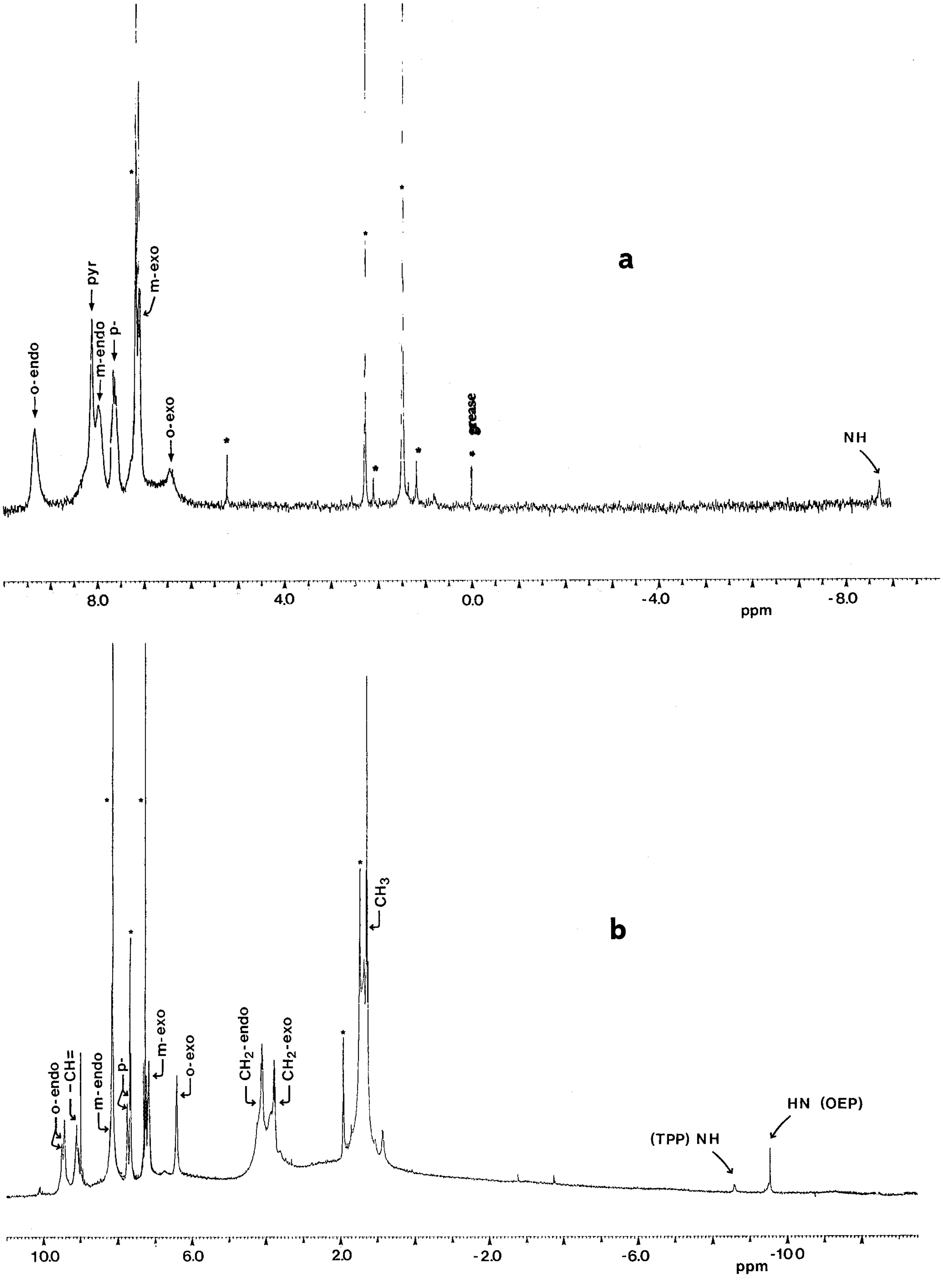


Figure 1. ^{1}H-NMR spectrum of (a) complex **A** (200 MHz, Bruker) and (b) complex **B** in $CDCl_3$ (400 MHz, Bruker). Peaks of the solvents are indicated by asterisks.

distributed between OEP and TPP nitrogen atoms. Consequently, this complex **B** could be described as a 1:4.3 mixture of the tautomers Lu^{III}(TPPH)(OEP) and Lu^{III}(TPP)(OEPH). Moreover, the observed upfield shift for the N−H protons of the OEP or TPP rings in **B** is most likely due to the shielding effect of the porphyrin rings. This effect is more pronounced when the proton is located on the OEP ring and is probably due to the increased basicity of this macrocycle with respect to the one containing two TPP rings (see also Chart 1).

From the data in Table 1, one can observe two sets of peaks for the *ortho*- endo protons and *para* protons of TPP (see also Figure 1, *ortho*-exo protons are located near the solvent peak) and, two peaks for the $-CH=$ of the OEP macrocycle. In the asymmetrical complex **B**, all of the proton resonances give broad, structureless signals, due to the flipping motion of the rings or to the equal contribution of the different positional isomers. However, for the deprotonated complex **A**, the *ortho*-endo protons are shielded and shifted upfield at 8.34 ppm. In the case of the corresponding deprotonated complex **B**, the above mentioned protons are shifted in the same region at ~8.35ppm, indicating that the major peak at 9.46ppm of the *ortho*-endo protons can be attributed to the TPP unit, which is free of the proton. That is in agreement with the integration ratio for the *ortho*-endo protons: *ortho*$_{\mathrm{TPPH}}$/*ortho*$_{\mathrm{TPP}}$ which is very similar to the integration ratio $N-H_{\mathrm{TPP}}$/$N-H_{\mathrm{OEP}}$.

COSY experiments were also run for complex **B** (data available in the Supporting Information). Connectivities between protons of the $-CH_3$ and $-CH_2-$ groups, *ortho* and *meta* protons of the phenyl groups and finally between the two diastereotopic protons in the $-CH_2-$ group have been observed, which clearly indicates there are two pairs of endo end exo protons. In addition, no connectivities were observed for the two N−H proton signals. Similarly, in the phase-sensitive NOESY spectrum (not shown), for the same N−H proton signals no correlations were observed with any other protons of complex **B**. Further TOCSY and ROESY experiments performed for complex **B** on a 500 MHz NMR apparatus confirm the attribution for each kind of proton as well as the presence of the N−H protons. From the TOCSY experiment (Figure 2a), one can observe that signals at ~9.5, 8.17, ~7.7, and 6.38 ppm are correlated, as well as, the $-CH_2-$ and $-CH_3-$ protons. In addition, ROESY experiment were carried out, in order to confirm the assignment in the aromatic region. So, in the ROESY spectrum two pairs of cross-peaks were observed at 9.5 and 6.38 ppm, due to saturation transfer. The two peaks at 9.5 and 8.17 ppm have been assigned to *ortho*-endo and *meta* protons respectively. The above attribution could be supported by the observed cross-peaks between *ortho* and *meta* protons and also by the cross-peak between *meta*- and *para* protons (see Figure 2b).

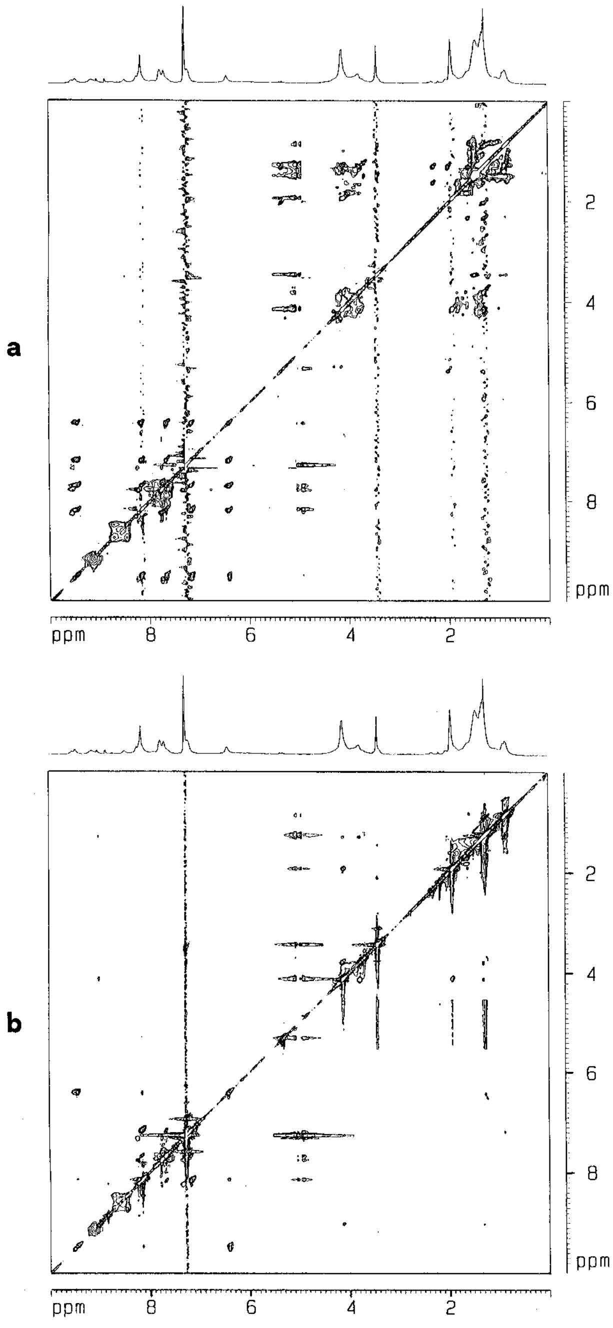


Figure 2. (a) TOCSY and (b) ROESY spectra of complex **B** in $CDCl_3$ (500 MHz, Bruker).

^{1}H-NMR experiments in DMF, on the other hand, confirm the proton abstraction in both complexes.The ^{1}H-NMR spectrum of the deprotonated complex **B**, in DMF-d_7, show that the *ortho*- and *meta*-endo protons of the TPP ring are shielded and thus shifted upfield, while all the other protons on the TPP and OEP rings are deshielded and shifted downfield (Table 1; spectra in Supporting Information). A similar shift is induced for the TPP protons of the deprotonated complex **A**.

From this study, using ^{1}H-NMR techniques and various solutions, of diamagnetic lutetium porphyrin double-deckers derivatives, we can deduce unambiguously that in fact, two forms could exist, the protonated and the deprotonated one. As the presence of the proton is solvent-dependent, the results

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concerning similar lanthanide double-deckers should be treated carefully, taking this fact into consideration.

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Supporting Information Available: Figure A, COSY spectra of complex **B,** (i) in the aromatic region (400 MHz, Bruker) and (ii) in the region of $-CH_2-$ and $-CH_3$ groups, in $CDCl_3$ (400 MHz, Bruker), Figure B, ^{1}H-NMR spectrum of the deprotonated form of complex **B** in DMF-d_7 (3 pages). Ordering information is given on any current masthead page.

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