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Inorganica Chimica Acta 275–276 (1998) 182–191

Inorganica Chimica Acta

Synthesis, UV–visible and electrochemical studies of lipophilic and hydrophilic lanthanide(III) bis(porphyrinates) [1]

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Received 7 April 1997; revised 28 July 1997; accepted 17 September 1997

Abstract

In a recent work we described the synthesis and some physicochemical properties of lanthanide(III) monoporphyrinate complexes. The increasing interest in cationic and/or anionic metalloporphyrins due to their biocompatibility with human tissues, their application as intercalating agents or as photochemical probes and NMR imaging agents, prompted us to extend our research to the synthesis and physicochemical study of hydrophilic lanthanide double-deckers. We present herein the synthesis of four new lanthanide(III) lipophilic 5,10,15,20-tetrapyridyl-bis(porphyrinates) and their easy conversion (upon methylation) to the corresponding water soluble double-deckers. Electrochemical studies were carried out using different polarity media while the optical properties of the complexes were studied in organic and aqueous media. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Electrochemistry; Lanthanide complexes; Porphyrinate complexes; Lipophilic complexes; Hydrophilic complexes

1. Introduction

In a recent work we described the synthesis and some physicochemical properties of lanthanide(III) monoporphyrinate complexes [1]. The increasing interest in cationic and/or anionic metalloporphyrins due to their biocompatibility with human tissues [2], their application as intercalating agents [3–5] or as photochemical probes [6,7] and NMR imaging agents [8], prompted us to extend our research to the synthesis and physicochemical study of the hydrophilic lanthanide 'double-decker' porphyrins.

Despite the synthesis of an enormous number of symmetrical or asymmetrical lipophilic lanthanide double-deckers (Ln(III) [9–43], Ac(IV) [33,37,44,45] and M(IV) (where M(IV) = Zr, Hf) [46–48]), only a limited number of hydrophilic complexes have been reported by Buchler and Nawra [9] and Machida and coworkers [10–12]. However, bis(porphyrinates) freely soluble in aqueous media, which could preserve the physicochemical properties of the analogous lipophilic complexes, have been reported only for Ce(IV) [9]. In addition, a thorough study of the electrochemical properties in various polar media has not been presented for such complexes.

Herein, we present the synthesis of four new lanthanide(III) lipophilic 5,10,15,20-tetrapyridyl-bis(porphyrinates), and their easy conversion (upon methylation) to the corresponding water soluble double-deckers (Scheme 1). Electrochemical studies were carried out in polar media while the optical properties of the complexes were studied in organic and aqueous media.

All the spectroscopic data presented for the lipophilic $[Ln^{III}(tpyp)_2]^-$ complexes are in close agreement with data for other homoleptic and heteroleptic Ln(III) complexes with tpp and oep complexes [25–29]. Small differences in the transition energy of the absorption bands and/or in the redox potential were observed and discussed in terms of the basicity of the tpyp ring [29]. The water soluble double-deckers exhibit a significantly red-shifted Soret band with respect to their precursors.

2. Experimental

Dichloromethane and 1,2,4-trichlorobenzene (1,2,4-tcb) were purchased from Riedel-de Häen and Aldrich, respec-

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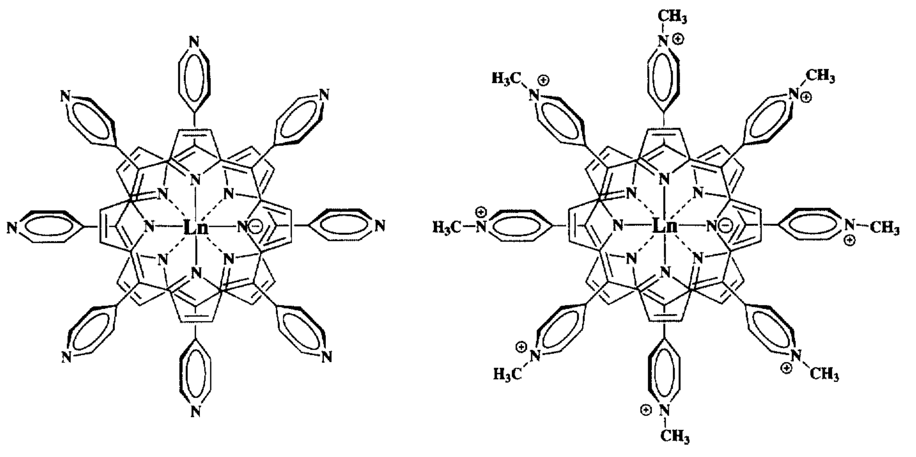
[1] Dedicated to our colleague and friend Professor I. Bertini.

0020-1693/98/$19.00
PII S0020-1693(97)06078-7



$[\mathrm{Ln^{III}(tpyp)_2}]^-$ $[\mathrm{Ln^{III}(tmepyp)_2}]^{+7}$

where $\mathrm{Ln^{III}}$ = La, Sm, Eu, Gd

Scheme 1. Structural formulae of lanthanide(III) lipophilic and hydrophilic bis(porphyrinates).

tively, and used as received. Tetrahydrofuran (THF) was purchased from Merck and was distilled under argon over sodium/benzophenone. Tetra-*n*-butylammonium perchlorate (TBAP) purchased from Fluka, was recrystallized from absolute ethanol and then dried under vacuum in an oven at 40°C. All synthetic procedures were performed under an argon stream.

Absorption spectra were collected on a Perkin-Elmer Lambda 6 grating spectrophotometer and ε measurements were recorded in MeOH, DMF or H_2O (solutions of 0.05×10^{-3} M).

Electrochemistry experiments were carried out with a home-made potentiostat interfaced with a PC-compatible microcomputer. The positive feedback (scan rate $>1\ \mathrm{V\ s^{-1}}$) or interrupt (scan rate $<1\ \mathrm{V\ s^{-1}}$) methods were used to compensate for uncompensated resistance (IR) drop. Electrochemical experiments were performed in an air-tight three-electrode cell connected to a vacuum/argon line. The cell was degassed and filled according to standard vacuum techniques. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge-compartment filled with a solution of the same supporting electrolyte in the same solvent as used in the cell. The counter-electrode was a spiral of $\sim 1\ \mathrm{cm^2}$ apparent surface area, made of an 8 cm long and 0.5 mm diameter platinum wire. The working electrode was a rotating disk electrode (RDE) with a 2 mm diameter Pt disk (Tacussel EDI), or an ultramicroelectrode consisting of a 100 μm diameter Pt disk.

All the lanthanide(III) monoporphyrinates, $\mathrm{Ln^{III}}$(tpyp)-acac, Sm, Eu, Gd were synthesized and purified according to well established experimental procedures [1]. The synthesis of the corresponding lipophilic and hydrophilic double-deckers was carried out as follows.

2.1. Hydrogen bis[5,10,15,20-tetrakis(4-pyridyl)-porphyrinato]lanthanum(III), $\mathrm{La^{III}H(tpyp)_2}$

To a solution of 350 mg (0.565 mmol) of $\mathrm{H_2}$(tpyp) in 30 ml of 1,2,4-tcb, 1000 mg (2.150 mmol) of $\mathrm{La^{III}(acac)_3\cdot xH_2O}$ was added and the mixture was brought to reflux for 6–8 h. After cooling the reaction mixture to room temperature, the solvent was distilled away under reduced pressure and the solid residue was dissolved in the minimum volume of CH_2Cl_2 and purified by aluminum oxide column chromatography, 5×5 cm (Al_2O_3, Basic, Grade I), prepackaged with CH_2Cl_2. The free base eluted first with CH_2Cl_2 while the desired $\mathrm{La^{III}H(tpyp)_2}$ complex was eluted using a mixture of CH_2Cl_2/CH_3OH 1:1, vol./vol. After evaporation to dryness, the purple crystalline powder was washed with $PhCH_3$ and Et_2O, and dried overnight in a vacuum oven (temperature not exceeding 50°C, yield 85%). *Anal.* Calc. for $C_{80}H_{49}N_{16}La$ (mol. wt. 1373.28): C, 69.70; H, 3.60; N, 16.32. Found: C, 69.05; H, 3.36; N, 16.45%.

2.2. Hydrogen bis[5,10,15,20-tetrakis(4-pyridyl)-porphyrinato]lanthanide(III), $\mathrm{Ln^{III}H(tpyp)_2}$ where Ln(III) = Sm, Eu, Gd

To a solution of 100 mg (0.115 mmol) of the corresponding monoporphyrinate, $\mathrm{Ln^{III}}$(tpyp)acac, in 20 ml of 1,2,4-tcb, 75 mg (0.120 mmol) of the free base $\mathrm{H_2}$(tpyp) was added and the mixture was brought to reflux for 24–72 h. Then the mixture was allowed to cool to room temperature, and the solvent was evaporated under reduced pressure. The solid residue was dissolved in the minimum volume of CH_2Cl_2 and was purified on an aluminum oxide chromatographic column, 6×5 cm (Al_2O_3, Basic, Grade I), prepackaged with CH_2Cl_2. The unreacted free base eluted as a first fraction, while the $\mathrm{Ln^{III}H(tpyp)_2}$ complexes eluted with CH_2Cl_2/CH_3OH 5–1:1, vol./vol.

Note. Great care is needed when one changes progressively the above ratio of solvents in order to avoid contamination of the double-deckers by the corresponding monoporphyrinates (which also begin to elute from the top of the column when high ratios of MeOH are used). The solvents were evaporated and the purple crystalline powder was selected (yields 40, 35 and 25% for Sm(III), Eu(III) and Gd(III) complexes, respectively), washed with $PhCH_3$ and Et_2O, and dried overnight in a vacuum oven (temperature not exceeding 50°C). *Anal.* Calc. for $C_{80}H_{49}N_{16}Sm$ (mol. wt. 1384.74): C, 69.39; H, 3.57; N, 16.18. Found: C, 68.90; H, 3.45; N, 16.40%. Calc. for $C_{80}H_{49}N_{16}Eu$ (mol. wt. 1386.34): C, 69.31; H, 3.56; N, 16.17. Found: C, 69.05; H, 3.30; N, 16.60%. Calc. for $C_{80}H_{49}N_{16}Gd$ (mol. wt. 1391.63): C, 69.05; H, 3.55; N, 16.10. Found: C, 68.15; H, 3.28; N, 16.80%.

2.3. Bis[5,10,15,20-tetrakis(1-methyl-4-pyridinio)-porphyrinato]Ln(III) heptaiodide, {$Ln^{III}(tmepyp)_2$}I_7 where Ln(III) = La, Sm, Eu, Gd

60 mg (0.043 mmol) of the above prepared double-deckers, $Ln^{III}H(tpyp)_2$, were dissolved in 30 ml DMF/MeOH 2:1, vol./vol. The mixture was stirred rigorously and heated at 50°C for 15 min in order to accelerate the solvation. The mixture was allowed to stand at room temperature before an excess (0.250 ml, 4.275 mmol) of CH_3I was added dropwise to the solution. The reaction was then stirred at ambient temperature for up to 6 h. Heating of the reaction mixture at 38°C for 0.5–1 h followed in order to complete the methylation process. The progress of the reaction was followed by UV–Vis spectroscopy. Once the reaction had been completed, the solvents were removed under vacuum and the solid residue recrystallized from CH_3OH/CH_2Cl_2 1:5, vol./vol. The solid was isolated by filtration (yields 75–80%) and the green-brown powder washed by methanol and diethyl ether while dried overnight in a vacuum oven. *Anal.* Calc. for $C_{88}H_{72}N_{16}I_7La$ (mol. wt. 2380.88): C, 44.39; H, 3.05; N, 9.41; I, 37.31. Found: C, 44.10; H, 3.00; N, 9.51; I, 37.92%. Calc. for $C_{88}H_{72}N_{16}I_7Sm$ (mol. wt. 2392.34): C, 44.18; H, 3.03; N, 9.37; I, 37.13. Found: C, 43.20; H, 2.88; N, 9.62; I, 36.54%. Calc. for $C_{88}H_{72}N_{16}I_7Eu$ (mol. wt. 2393.94): C, 44.15; H, 3.03; N, 9.36; I, 37.11. Found: C, 42.90; H, 3.00; N, 9.56; I, 37.63%. Calc. for $C_{88}H_{72}N_{16}I_7Gd$ (mol. wt. 2399.23): C, 44.05; H, 3.03; N, 9.34; I, 37.03. Found: C, 43.00; H, 2.93; N, 9.50; I, 37.57%.

3. Results and discussion

3.1. Synthesis

All the lanthanide(III) lipophilic monoporphyrinates and bis(porphyrinates) reported hitherto, were synthesized according to well established procedures [1,5,13,26,29] in 1,2,4-tcb at high temperatures, except in the case of La(III), where the metallation reaction yielded almost quantitatively the double-decker. The preparation of water soluble Ln(III) bis(porphyrinates) was carried out in three steps: (i) the synthesis of the Ln(III) monoporphyrinate [1]; (ii) synthesis of the lipophilic $Ln^{III}H(tpyp)_2$, where Ln(III) = Sm, Eu and Gd, by refluxing the corresponding monoporphyrinate in the presence of the free base, $tpypH_2$ [13–16,26,29]; (iii) transformation of the hydrophobic double-deckers to those with the ionic quaternized *N*-pyridyl group [1,4,5].

3.1.1. Lipophilic Ln(III) double-deckers

The reaction of 5,10,15,20-tetrakis(4-pyridyl)porphyrin, $(tpyp)H_2$, with the corresponding Ln(III) acetylacetonate, in boiling 1,2,4-tcb yields the monoporphyrinate $Ln^{III}(tpyp)$-acac in all cases, Eq. (1), except when the Ln(III) ion is La(III).

$$Ln^{III}(acac)_3\cdot xH_2O + (tpyp)H_2 \xrightarrow[215^{\circ}C,\ 3\ h]{1,2,4\text{-tcb}} Ln^{III}(tpyp)acac + 2Hacac \qquad (1)$$

$$Ln^{III}(tpyp)acac + (tpyp)H_2 \xrightarrow[215^{\circ}C,\ 24-72\ h]{1,2,4\text{-tcb}} Ln^{III}H(tpyp)_2 + Hacac \qquad (2)$$

Eq. (2) describes the synthesis of the corresponding tpyp double-deckers. The yield of the double-decker complexes decreases from Eu(III) to Gd(III) as the stability of the corresponding monoporphyrinate increases [13,15–18,23,26,29]. This has been reported previously for tpp or oep sandwich-like complexes [16,18,26,29], and has been discussed in terms of their electronic configuration and their ionic radius.

Attempts to obtain higher yields of double-deckers in shorter reaction times (6–12 h) using $Li_2(tpyp)$ free base, as has been reported for Ce(IV) by Buchler and Nawra [9] and Machida and coworkers [10–12], resulted in traces of $Ln^{III}H(tpyp)_2$. (Recovery of the free base, $(tpyp)H_2$, was observed even after prolonged reaction times of 12–24 h.)

All the reported lipophilic monoporphyrinates or bis(porphyrinates) were characterized by elemental analysis, UV–Vis spectroscopy, and cyclic voltammetry experiments.

3.1.2. Hydrophilic Ln(III) double-deckers

For the water soluble double-deckers, the standard procedure described above employing 1,2,4-tcb failed to yield the bis(porphyrinates) from the parent monoporphyrinate owing to the low solubility of the former. As reported by Buchler and Nawra [9], quaternization of the *N*-pyridyl groups with methyl *p*-toluenesulfonate, TosOMe, yielded the $[Ce^{III}(tpyp)_2](Tos)_7$ but the resulting product was very hydroscopic and difficult to handle. Also, according to the above mentioned method, long reaction times (~5 days) and high temperature (100°C) are needed for a successful methylation reaction. Furthermore, the methylation procedure reported by Machida and coworkers [10–12] using methyl iodide in $CHCl_3$ at 20°C for 20 h, does not lead to the fully methylated complex according to Buchler and Nawra [9]. On the contrary, for a thoroughly methylated product heating to 38°C for about 3 days was required.

It was desirable, therefore, to develop a new, alternative, synthetic methodology to overcome the hitherto mentioned drawbacks. In this regard, we report herein the methylation process already used by our group in the case of $\mathrm{Ln^{III}(tpyp)acac}$ [1], applied successfully to the bis(porphyrinates) (Eqs. (3) and (4)). The octa-*N*-methylated water soluble double-deckers $\{\mathrm{Ln^{III}(tmepyp)_2}\}\mathrm{I_7}$ were obtained in quantitative yields in DMF/MeOH 2:1, vol./vol. using 100 fold excess of methylating agent. According to our investigation the key to successful methylation which requires only a short time was the choice of the solvent. It should be noted that in the above mentioned solvents for the lipophilic double-deckers the non-protonated form $[\mathrm{Ln^{III}(tpyp)_2}]^-$ is dominant, as has been confirmed previously for lanthanide(III) tpp complexes (Eq. (3)) [26,29]. For this reason, the octamethylated double-deckers are denoted as $\{\mathrm{Ln^{III}(tmepyp)_2}\}^{7+}\{\mathrm{I_7}\}^{7-}$ or simply as $\{\mathrm{Ln^{III}(tmepyp)_2}\}\mathrm{I_7}$ with seven iodines as counter ions instead of eight.

$$\mathrm{Ln^{III}H(tpyp)_2} \xrightarrow[\mathrm{RT}]{\mathrm{DMF/MeOH}} [\mathrm{Ln^{III}(tpyp)_2}]^- + \mathrm{H}^+ \tag{3}$$

$$[\mathrm{Ln^{III}(tpyp)_2}]^- + 8\,\mathrm{CH_3I} \xrightarrow[38\,^{\circ}\mathrm{C}]{\mathrm{DMF/MeOH}} \{\mathrm{Ln^{III}(tmepyp)_2}\}\mathrm{I_7} + \mathrm{I}^- \tag{4}$$

All the lanthanide monoporphyrinates, $\mathrm{Ln^{III}(tpyp)acac}$, or bis(porphyrinates), $[\mathrm{Ln^{III}(tpyp)_2}]^-$, are less soluble in organic media than the corresponding tpp complexes. They exhibit medium solubility in THF, while they are freely soluble in MeOH, DMF or DMSO. For this reason the DMF/MeOH solvent system was chosen for the methylation reaction, Eq. (3). DMF is used together with methanol, because the resulting desired complex is not soluble in the latter solvent. It has been observed that the rate of the methylation reaction in neat methanol is seriously diminished and several times we were not able to reach complete methylation. For this reason, the above mixture of solvents was used and DMF played the role of the assisting solvent in the generation of the methylated complex, Eq. (4). The choice of the methylating reagent, $\mathrm{CH_3I}$, was based on the high methylating ability of the tetrapyridyl porphyrinic macrocycle [4,5], and high volatility (boiling point ~40°C), which greatly simplify the following purification process.

The significant red shift (~16 nm), the broadening of the Soret band of the ionic complexes formed and the decreased intensity of the Soret band of the complexes, were the only observed differences when the reaction process was followed by UV–Vis spectroscopy. The excess of $\mathrm{CH_3I}$ used resulted in fully methylated complexes with reaction times of 4–6 h. Any additional $\mathrm{CH_3I}$ had no effect on the optical features of the complexes. These features are also discussed in the following section with regard to checking the completeness of the reaction.

Both the lipophilic and hydrophilic complexes are quite stable toward acids. Progressive addition of diluted acid solution (0.32% HCl in MeOH) in 2×10^{-6} M MeOH solutions of the lipophilic complexes, results in water soluble pyridinio porphyrin salts instead of the demetallated product. Demetallation of both lipophilic and hydrophilic complexes was observed under the same experimental conditions (2×10^{-6} M MeOH solutions) using more concentrated acid solution (3.2% HCl) and only when the concentration of the acid became 10 times that of the complexes. Demetallation of the complexes was manifested in both cases by the appearance of a second Soret band (418 nm in $\mathrm{MeOH/H_2O}$ and 420 nm in $\mathrm{H_2O}$ for lipophilic and hydrophilic complexes respectively), which belongs to the free base. However, it should be noted that even when the concentration of the acid became 1000 times that of the complexes, the lanthanide porphyrins were not completely demetallated.

3.2. *UV–Vis spectroscopy*

A well established tool for the study and investigation of the strong π–π interactions between the two macrocycles of the title complexes is UV–Vis spectroscopy. For lipophilic double-deckers with Ln(III) [9–43] or M(IV) (where M(IV) = Ac, Zr, Hf) [33,37,44–48], it is well known that the appearance of new characteristic bands is related to this π–π interaction.

Those optical features could be used as a diagnostic tool for the nature of the face-to-face or sandwich bis(porphyrinate) derivatives. The interaction of the excited states or 'excitonic interactions' and the charge transfer transition phenomena involved, ring-to-ring charge transfer (RRCT) or ring-to-metal charge transfer (RMCT) [31,36,44], are two terms of the corresponding approaches, used to explain the UV–Vis features. In fact, the broad and blue-shifted Soret band of the bis(porphyrinates) as well as the appearance of some new bands throughout the visible region of the spectra are the main observable differences between the bis and their corresponding monoporphyrinates [13,14,30–32,34–37].

Prior to presenting the UV–Vis data of the title derivatives, it should be mentioned that optical spectra recorded in $\mathrm{CH_2Cl_2}$ or $\mathrm{PhCH_3}$ pertain to the protonated form, while those recorded in MeOH, DMF, DMSO or pyridine pertain to the deprotonated form, Eq. (1).

3.2.1. *Lipophilic double-deckers*

The optical characteristics of the lipophilic complexes in solvents like $\mathrm{CH_2Cl_2}$ and $\mathrm{PhCH_3}$ are not presented because of their low solubility. However, in order to confirm the aforementioned equilibrium (between protonated/deprotonated forms), a few derivatives were checked by UV–Vis spectroscopy in diluted solutions of $\mathrm{CH_2Cl_2}$ and $\mathrm{PhCH_3}$.

On the other hand, these complexes are freely soluble in DMF and therefore the optical properties of $[\mathrm{Ln^{III}(tpyp)_2}]^-$ were examined in this solvent and are presented in Table 1. For comparison, the UV–Vis data of the corresponding double-deckers with tpp ring are also included in Table 1. All the $[\mathrm{Ln^{III}(tpyp)_2}]^-$ complexes studied exhibit a single, sharp,

Table 1
UV–Vis data for lipophilic double-deckers of type $[Ln^{III}(tpyp)_2]^-$ and $[Ln^{III}(tpp)_2]^-$, where Ln = La,Sm,...,Gd in DMF (λ nm ($\log \varepsilon$ $dm^{-3} mol^{-1} cm^{-1}$))

	B-band	Q-bands					
$[Ln^{III}(tpyp)_2]^-$							
La	411	463	487	508	561	609	
	5.46	*3.84*	*3.69*	*3.54*	*3.65*	*3.58*	
Sm	409	469	492	521	561	616	
	5.48	*3.78*	*3.73*	*3.42*	*3.60*	*3.26*	
Eu	409	470	489	523	561	615	
	5.67	*3.79*	*3.74*	*3.43*	*3.61*	*3.25*	
Gd	408	471	491	521	561	617	624
	5.66	*3.79*	*3.73*	*3.43*	*3.60*	*3.23*	*3.42*
$[Ln^{III}(tpp)_2]^-$							
La [a]	412	459	485	524	565	615	
	5.68	*4.14*	*4.00*	*3.84*	*3.94*	*3.85*	
Sm [b]	410	469	490	524	562	614	
	5.67	*4.14*	*4.04*	*3.80*	*3.89*	*2.79*	
Eu [b]	409	467	491	524	561	613	
	5.67	*4.16*	*4.08*	*3.80*	*3.90*	*3.48*	
Gd [b]	408	470	491	524	561	616	
	5.66	*4.14*	*4.08*	*3.79*	*3.89*	*3.48*	

[a] Taken from Ref. [49].
[b] Taken from Ref. [29].

blue-shifted (with respect to the monoporphyrinic precursors) Soret band, with λ_{max} which varies from 411 nm in $[La^{III}(tpyp)_2]^-$, to 408 nm in $[Gd^{III}(tpyp)_2]^-$ (Fig. 1).

The above mentioned analogies can also be extended to the origin of the observed new bands in the annexe region. So, the bands at ~470 nm and at ~615 nm, from Sm^{III} to $[Gd^{III}(tpyp)_2]^-$, (see also Table 1) are of the same origin Q'' and Q', as those observed for deprotonated symmetrical lanthanide bis(porphyrinates) with tpp, $[Ln^{III}(tpp)_2]^-$ [9–43], Ac(IV) [33,37,44,45], Zr(IV) [46–48] and Hf(IV) [46,48]. Progressing along the series, from La(III) to Gd(III), the Q' band splits into two components, the first being the characteristic $Q(0,0)$ (observable also in monoporphyrinates), and the second a red shifted band above 620 nm. This splitting is observed in the case of tpyp-bis(porphyrinates) for the Gd complex, while in the case of tpp-bis(porphyrinates) [29] it appears only for the complexes involving heavier metal ions (from Tb(III) to Lu(III), see also Table 1). Both of the above mentioned Q'' and Q' bands have been proven to be extremely significant and characteristic of strongly coupled similar porphyrinic systems [31,36,44]. Their origin is attributed to charge transfer transitions between the two porphyrin rings (RRCT) or between the metal and the porphyrin ring (RMCT), rather than to the excitonic interaction between the two tetrapyrrole ligands [44].

Moreover, two ill defined bands of medium and low intensity are observed in the region between 485 and 530 nm for all the investigated tpyp complexes. Those bands do not seem to be affected by the metal ion along the series of studied derivatives, but their origin is difficult to pinpoint.

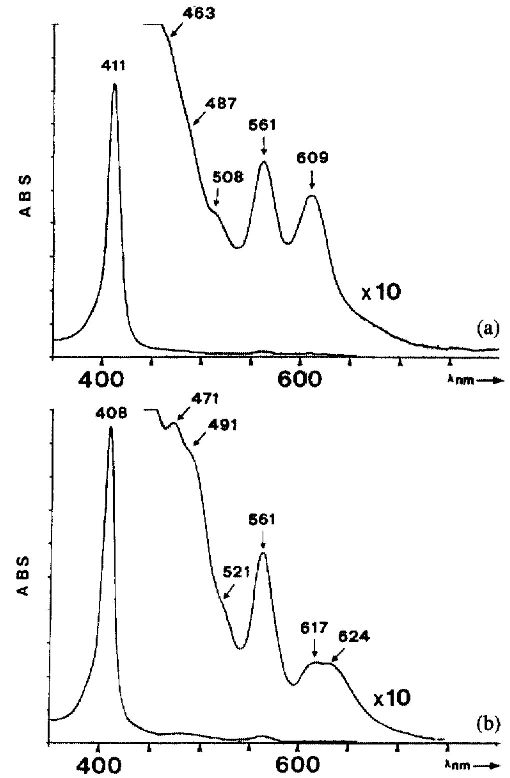


Fig. 1. UV–Vis spectra of (a) $[La^{III}(tpyp)_2]^-$ and (b) $[Gd^{III}(tpyp)_2]^-$ double-deckers in DMF.

3.2.2. *Hydrophilic double-deckers*

The UV–Vis spectra of the water soluble double-deckers show common features but also striking differences in comparison with their lipophilic precursors.

Among the similarities, we noticed that the Soret band is considerably broader and red shifted in both aqueous and non-aqueous media. In the region from 470 to 550 nm, only one band was observed. On the other hand, in the region from 550 up to 700 nm the same absorption bands, although broader, were observed as for the corresponding lipophilic complexes. The $Q(1,0)$ band at around 570 nm and the broad band at around 620 nm for $[La^{III}(tmepyp)_2]^{7+}$ (Fig. 2(a)), split into two components $Q(0,0)$ and Q' in the case of Gd (in DMF, Fig. 2(b), Table 2). The same features were also observed when H_2O was used as solvent (Fig. 3, Table 3) with the only difference being that the Q' band is split in both Eu and Gd derivatives.

As for differences, we noticed that they exhibit a single, but considerably broader and red shifted, Soret band in aqueous or non-aqueous media. Also, in the region from 470 to 550 nm only one band was observed. This band could be compared with Q'' discussed above for $[Ln^{III}(tpyp)_2]^-$ complexes but it is difficult to assign with certainty (owing to the lack of any other experimental and literature data).

3.3. *Electrochemistry*

In this section we present the electrochemical data for lipophilic derivatives. Several reasons have led us to this

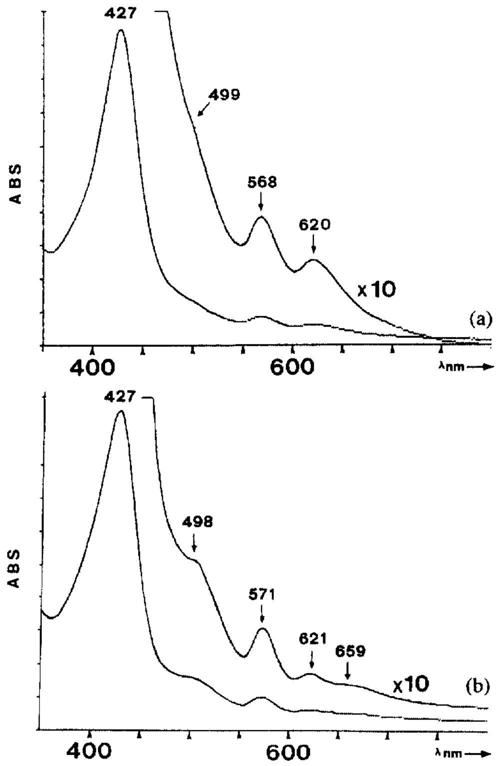


Fig. 2. UV–Vis spectra of (a) $[La^{III}(tmepyp)_2]^{7+}$ and (b) $[Gd^{III}(tmepyp)_2]^{7+}$ double-deckers in DMF.

Table 2
UV–Vis data for hydrophilic double-deckers of type $[Ln^{III}(tmepyp)_2]^{7+}$, where Ln = La,Sm,...,Gd in DMF (λ nm (log ε dm^{-3} mol^{-1} cm^{-1}))

$[Ln^{III}(tmepyp)_2]^{7+}$	B-band	Q-bands			
La	427	499	568	620	
	5.03	*3.93*	*3.68*	*3.54*	
Sm	427	505	570	620	
	5.02	*4.06*	*3.81*	*3.52*	
Eu	427	504	571	620	
	5.03	*4.00*	*3.81*	*3.53*	
Gd	427	498	571	621	659
	5.02	*4.04*	*3.81*	*3.54*	*3.44*

decision: adsorption phenomena during the investigation of the hydrophilic complexes were observed and thus it was difficult to extract direct information from the electrochemical processes involved. On the other hand, after solving the above problem by using various types of electrodes as well as electrochemical cells, we were not able to find a common system to study the title derivatives. Consequently, our results were not consistent with those of the tpyp precursors. In addition, the electrochemical processes are frequently coupled with chemical reactions, and we decided that they could be the subject of a separate study as they possess a completely different electrochemical behavior.

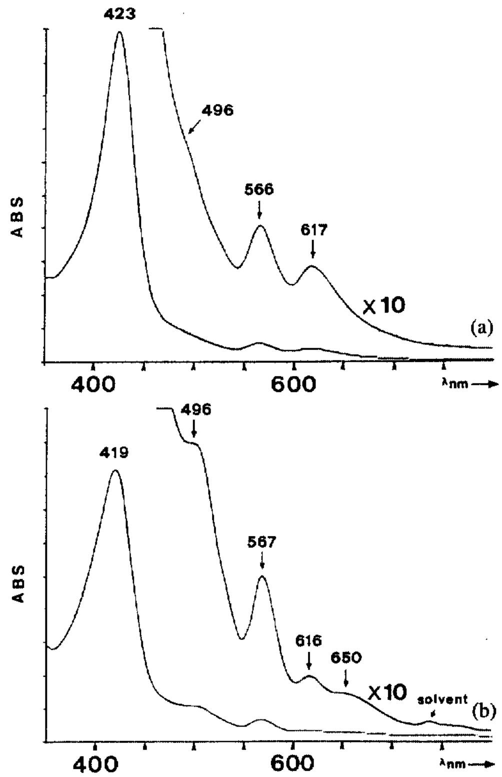


Fig. 3. UV–Vis spectra of (a) $[La^{III}(tmepyp)_2]^{7+}$ and (b) $[Gd^{III}(tmepyp)_2]^{7+}$ double-deckers in H_2O.

Table 3
UV–Vis data for hydrophilic double-deckers of type $[Ln^{III}(tmepyp)_2]^{7+}$, where Ln = La,Sm,...,Gd in H_2O (λ nm (log ε dm^{-3} mol^{-1} cm^{-1}))

$[Ln^{III}(tmepyp)_2]^{7+}$	B-band	Q-bands			
La	423	496	566	617	
	4.98	*3.76*	*3.59*	*3.42*	
Sm	421	496	567	617	
	5.00	*3.86*	*3.60*	*3.39*	
Eu	420	494	568	616	654
	5.04	*3.96*	*3.66*	*3.36*	*3.20*
Gd	419	496	567	616	650
	5.07	*4.03*	*3.78*	*3.36*	*3.21*

3.3.1. Lipophilic complexes

The electrochemical behavior of lipophilic lanthanide(III) porphyrin sandwich-like complexes were investigated in THF. Comparison with experiments in DMF and DMSO revealed that the former solvent was the best choice (good solubility, no adsorption of the complexes on the employed system of electrodes, etc.). As an example and for comparison, the redox properties of one lanthanide monoporphyrinate were also studied under similar experimental conditions (Sm^{III}(tpyp)acac: $E^{-3/-2} = -1.76$ V, $E^{-2/-1} = -1.24$, $E^{-1/0} = -0.90$, $E^{0/+1} = 1.02$).

The majority of the investigated complexes in THF undergo two oxidations (except in the case of La(III), where one oxidation process was observed). Upon reduction, all of the complexes undergo three reductions with respect to the limits of the solvent (Fig. 4). The measured half-wave potentials of the title complexes are summarized in Table 4. All of the processes, in reduction as well as in oxidation, correspond to one-electron transfer, exhibiting values $|E_{pa} - E_{pc}| = 65 \pm 5$ mV with a peak current proportional to $\nu^{1/2}$

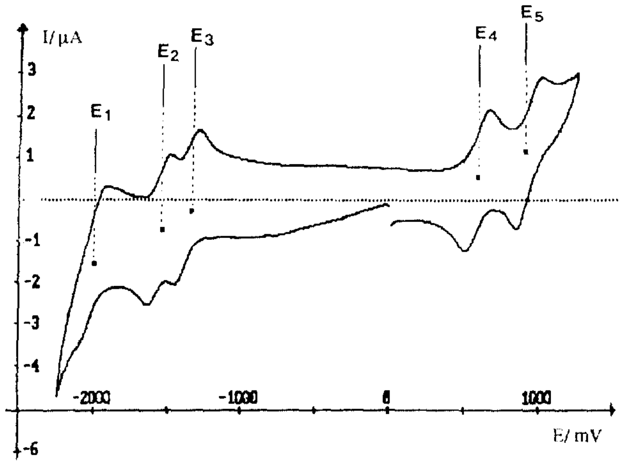


Fig. 4. Cyclic voltammogram of $[\mathrm{Eu^{III}(tpyp)_2}]^-$ in THF/NBu$_4$ClO$_4$ 0.1 M (Pt electrode 1 mm, scan rate 0.5 V s^{-1}, V vs. SCE, 21°C).

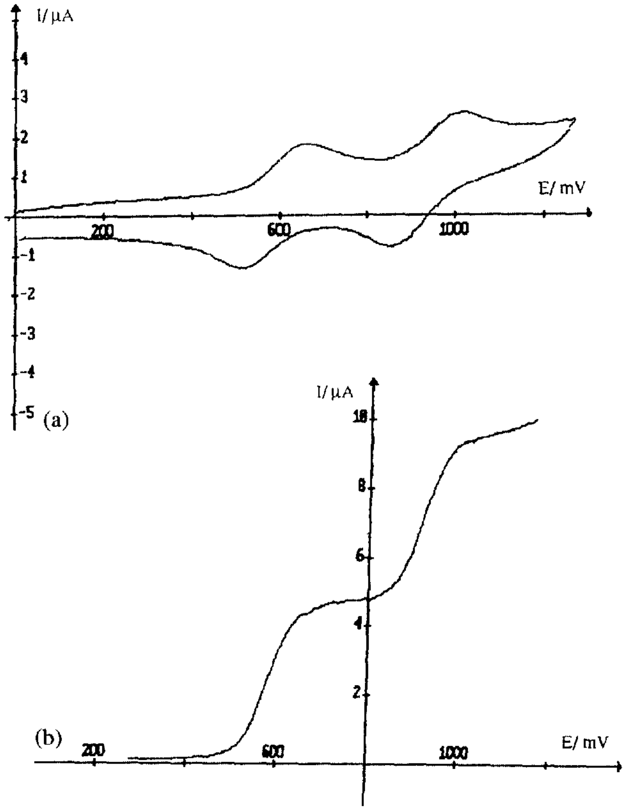


Fig. 5. (a) Cyclic voltammogram (Pt electrode 1 mm, scan rate 0.5 V s^{-1}, V vs. SCE, 21°C) and (b) linear voltammogram (Pt electrode 2 mm, rotation rate 1000 cycles min^{-1}, scan rate 5 mV s^{-1}, V vs. SCE, 21°C) of $[\mathrm{Eu^{III}(tpyp)_2}]^-$ in THF/NBu$_4$ClO$_4$ 0.1 M.

(Scheme 2). Linear voltammetry experiments for the above redox couples E_4 and E_5 were carried out (Fig. 5), and the data obtained confirm that these redox processes correspond to the two electro-oxidation reactions of the lipophilic complexes.

The general process depicted in Scheme 2 describes the overall electrochemical reactions which take place in solution and correspond only to the deprotonated form of these derivatives. Comparison between the $[\mathrm{Ln^{III}(tpyp)_2}]^-$ and the corresponding tpp double-deckers [29] indicates that the tpyp double-deckers oxidize considerably harder ($\sim$0.25 V) but reduce quite easily ($\sim$0.13 V), while the contrary should be anticipated for the complexes with the more basic tetrapyrrole (tpyp).

It is well known that for metalloporphyrins the half-way potentials $E_{\mathrm{1stOx}} - E_{\mathrm{1stRed}}$ correspond to the HOMO–LUMO energy difference. The HOMO–LUMO gap for the title lipophilic derivatives measured herein is the largest among the family of lanthanide(III) double-deckers [16,18,28,29]. As an example, for both Sm(III) homoleptic complexes with oep [16] or tpp [29] rings this HOMO–LUMO gap is 1.84 V, while for the corresponding heteroleptic complex (oep–tpp) the same gap is 1.73 V [28,29]. However, in the case of tpyp complexes this difference was measured to be 1.97 V (Scheme 3). The largest HOMO–LUMO energy difference in the series of $[\mathrm{Ln^{III}(tpyp)_2}]^-$ was measured for La(III), 2.14 V, while the other complexes of Eu(III) and Gd(III) showed an energy gap of 1.96 V. For the corresponding $[\mathrm{La^{III}(tpp)_2}]^-$ derivative this HOMO–LUMO energy gap was measured to be 1.85 V [49]. As has been mentioned already, for all the double-deckers hitherto reported [14,16,28,29,45,46,48,49], the HOMO–LUMO gap is manifested for all metalloporphyrins [51,52], and depends strongly on the inter-porphyrin distance. As this distance also depends on the ionic radius of the central ion (progressing along the series from La(III) to Lu(III) it becomes smaller), the complexes oxidize more easily [16,28,29,45,46,48,49] (see also Table 4 and Fig. 6) and consequently the HOMO–LUMO energy gap decreases. In Scheme 3 the HOMO–

Table 4

Half-wave potentials (V vs. SCE) for oxidation and reduction of lipophilic Ln$^{\mathrm{III}}$ double-deckers (where Ln = La,Sm,...,Gd) in THF/NBu$_4$ClO$_4$ 0.1 M (V vs. SCE)

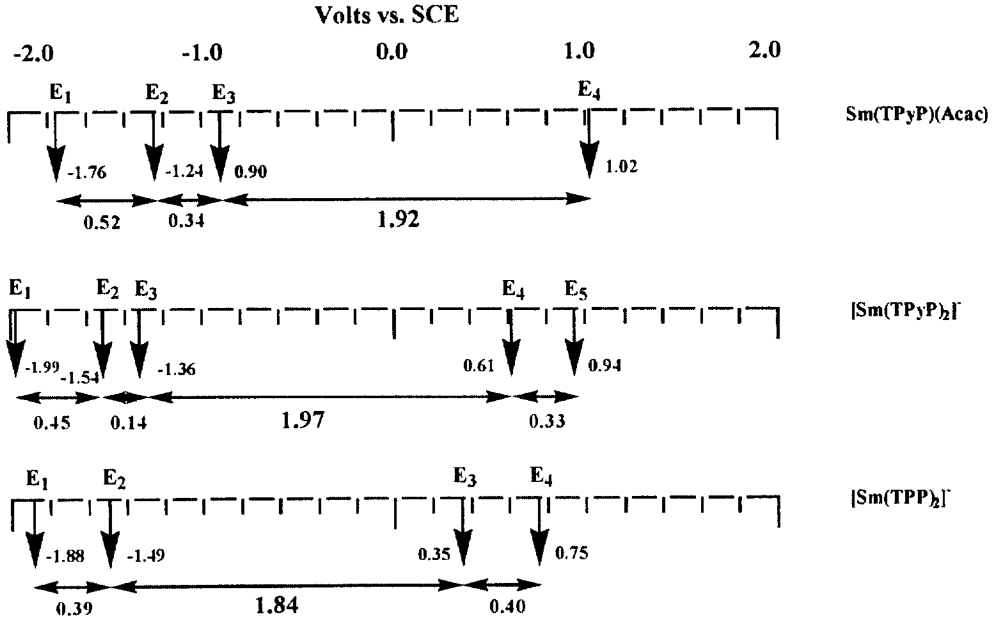
Ln	r_i (pm) [a]	E_1	E_2	ΔE_1 (E_2-E_1)	E_3	ΔE_2 (E_3-E_2)	E_4	E_5	ΔE_3 (E_5-E_4)	HOMO–LUMO gap
La [b]	117	−1.93	−1.48	0.45	−1.32	0.16	0.82			2.14
Sm	109	−1.99	−1.54	0.45	−1.36	0.18	0.61	0.94	0.33	1.97
Eu	107	−2.01	−1.56	0.45	−1.37	0.19	0.59	0.91	0.32	1.96
Gd	106	−2.00	−1.56	0.44	−1.37	0.19	0.59	0.92	0.33	1.96

[a] For coordination number 8. Taken from Ref. [50].

[b] HOMO–LUMO gap for $[\mathrm{La^{III}(tpp)_2}]^-$ in THF/NBu$_4$BF$_4$ 0.1 M (V vs. SCE) measured 1.85 V (from Ref. [49]).

$$[Ln(tpyp)_2]^{4-} \xrightleftharpoons[E_1]{-e} [Ln(tpyp)_2]^{3-} \xrightleftharpoons[E_2]{-e} [Ln(tpyp)_2]^{2-} \xrightleftharpoons[E_3]{-e} [Ln(tpyp)_2]^{1-} \xrightleftharpoons[E_4]{-e} [Ln(tpyp)_2]^{0} \xrightleftharpoons[E_5]{-e} [Ln(tpyp)_2]^{1+}$$

Scheme 2. Overall electrochemical reaction observed for lanthanide(III) lipophilic bis(porphyrinates).



Scheme 3. Potential difference between the electrochemical processes for $Sm^{III}(tpyp)(acac)$, $[Sm^{III}(tpyp)_2]^-$ and $[Sm^{III}(tpp)_2]^-$.

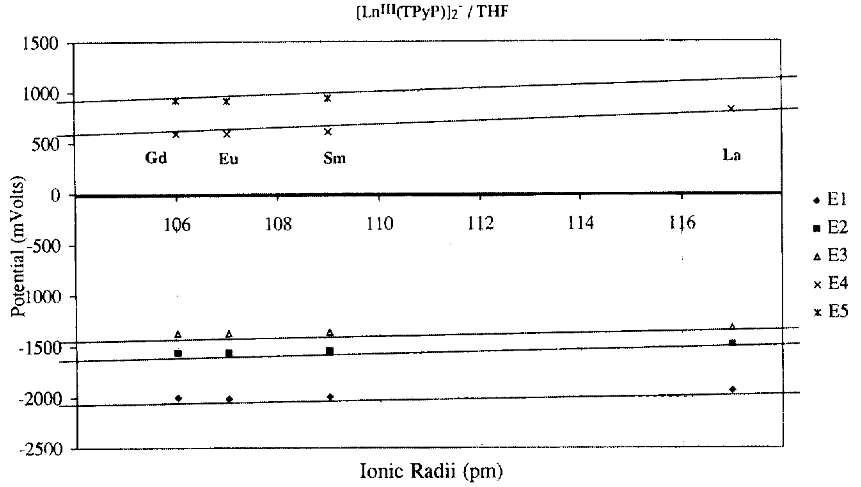


Fig. 6. Relationship between redox potential and ionic radius (in pm, and coordination number 8) of the metal ion in $[Ln^{III}(tpyp)_2]^-$ where Ln = La,Sm,...,Gd.

LUMO energy difference is shown for the monoporphyrinic precursor, $Sm^{III}(tpyp)acac$, the corresponding double-decker $[Sm^{III}(tpyp)_2]^-$ and $[Sm^{III}(tpp)_2]^-$. This observation is in good agreement with the analogous electrochemical data for tpp homoleptic [29] as well as oep–tpp heteroleptic [29] lanthanide(III) complexes.

The difference, however, between the second and the third electroreductions of $[Ln^{III}(tpyp)_2]^-$, ΔE_1, is of the order of 0.45 ± 0.01 V (see also Table 4), while the difference between the first and the second electroreductions, ΔE_2, is of the order of 0.18 ± 0.02 V. The latter is considerably smaller compared with the difference observed for the $[Ln^{III}(tpp)_2]^-$ [28,29] complexes (which is found to be 0.039 ± 0.03 V). On the other hand, the energy difference between the first and the second oxidation electron transfer processes of the lipophilic tpyp double-deckers, ΔE_2, was found to be 0.33 ± 0.01 V, which is slightly smaller than that for the corresponding $[Ln^{III}(tpp)_2]^-$ [28,29], 0.42 ± 0.03 V, and that of the asymmetrical $[Ln^{III}(oep)(tpp)]^-$ [28,29] complexes, 0.44 ± 0.04 V.

4. Conclusions

Regardless of the media used and in terms of UV–Vis spectroscopy, the following general observations can be made. The optical features of the complexes are less red shifted in aqueous than in organic media, Figs. 2 and 3. The optical features are strongly affected upon methylation: (i) the fine Soret band of $[Ln^{III}(tpyp)_2]^-$ which is located at around 410 nm, shifted 11–19 nm (depending on the medium) to the red, (ii) the three observed bands of the lipophilic complexes which were present in the region 450–530 nm practically disappear and only one of them is observed in the water soluble complexes $[Ln^{III}(tmepyp)_2]^-$, and (iii) the band analogous to Q' in the hydrophilic complexes is shifted up to ~660 nm, almost 35 nm red shifted when compared with the same band of the lipophilic compounds.

As for the electrochemical behavior of bis(porphyrinates) with respect to that of the corresponding monoporphyrinic precursors, the former reduce harder and oxidize more easily than the latter owing to the strong π–π interaction in the case of the double-deckers. Surprisingly, the HOMO–LUMO energy gap remains practically unchanged between the monoporphyrinates and bis(porphyrinates) (1.92 and 1.97 V respectively in the case of Sm(III) for example), although a smaller HOMO–LUMO difference has been observed in bis(porphyrinates) than in monoporphyrinates for all of the symmetrical or asymmetrical double-deckers reported above [29,49].

Finally, both physicochemical methods led us to conclude that the strong π–π interaction observed in the title complexes increases following the 'lanthanide contraction' trend.

Acknowledgements

This research was supported by the Greek General Secretariat of Research and Technology through Grant No 91 EΔ 442, the Centre National de la Recherche Scientifique and the Paul Sabatier University of Toulouse, France, 'Platon' grant for bilateral scientific and technological cooperation (France–Greece) and the Erasmus grant ICP-(92/97)-G-2002/13 for G.A.S.

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