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CATIONIC LANTHANIDE MONOPORPHYRINATES WITH Sm, Eu, Gd AND Tb, SYNTHESIS AND SPECTROSCOPIC PROPERTIES IN AQUEOUS AND NON-AQUEOUS MEDIA

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Abstract—The synthesis of a new series of cationic monoporphyrinates with "light" lanthanide ions is reported. The *meso*-tetrakis(4-pyridyl)porphyrin, (tpyp)H_2, was used as the tetrapyrrole ligand, and the metallation reaction with the lanthanide ions in acetylacetonato form, leading to Ln(tpyp)acac, where Ln = Sm, Eu, Gd and Tb, was carried out. The cationic monoporphyrinates, Ln(tmepyp)acac, were synthesized via the corresponding Ln(tpyp)acac. These complexes are freely soluble in aqueous and non-aqueous solutions, like MeOH, H_2O or *N*,*N*-dimethylformamide. Their spectroscopic properties in water and DMF solutions are reported. All the complexes were characterized on the basis of their UV–vis, IR and ESR data. No ESR spectra were obtained for cationic porphyrins in DMF for Sm, Eu and Tb, while the spectra of Gd(tmepyp)acac in DMF exhibits smaller ΔH_{pp} (103.1 G) among the spectra of Gd^{III} complexes. The unexpected broad signal of Eu(tmepyp)acac, $\Delta H_{pp} = 126.9$ G, in H_2O is discussed in terms of the formal oxidation state +2 for the central ion.

Lanthanide bis- and mono-porphyrinates have provided interesting properties as biomimetic models of photosynthetic reaction centres[1–4] and shift reagents.[5] Recently, a few attempts which involved lanthanide porphyrin complexes in catalytic reactions have also been reported.[6] In addition, cationic porphyrins have been studied for their interesting photochemical behaviour as potential agents in cancer phototherapy,[7] or intercalating agents to DNA.[8,9] Meunier *et al.*[10] have reported the selective cleavage of 35-mer single-stranded DNA containing the start code of the tat gene of HIV-1 by a tailored cationic manganese porphyrin conjugate.

With the increasing interest of interaction of various cationic, *meso*-substituted porphyrins with nucleic acids and DNA, as well as the perspective to study them as contrast complexes in NMR imaging,[11] we present in this work the synthesis of a few representative lanthanide complexes of *meso*-tetrakis(*N*-4-pyridyl)porphyrin, as well as their corresponding cationic complexes. The latter complexes were synthesized by methylation of their precursors, Ln^{III}(TpyP)acac, were Ln = Sm, Eu, Gd and Tb. Although Machida *et al.*[12a,b] reported the methylation of the novel sandwich-like complex, Ce$(tpyp)_2$, in 24 h, our procedure reported here produced the methylated product in a considerably shorter period of time (see Experimental section). As this manuscript was in preparation, Buchler and Nawra[13] reported that their attempt to access methylation according to the literature procedure[12a,b] did not yield any water-soluble material. The lanthanide porphyrin complexes with *meso*-tetraphenylporphyrin and metal ions

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Abbreviations: Por, unspecified porphyrinate^{2-}; tpp, *meso*-5,10,15,20-tetraphenylporphyrinate^{2-}; $(tpyp)_2$, *meso*-tetrakis(*N*-4-pyridyl)porphyrinate^{2-}; $(tmepyp)_2$, *meso*-tetrakis(*N*-4-methyl-pyridyl)porphyrinate^{2-}; Ln (por)acac, the general formula of lanthanide porphyrinate acatylacetonato; DMF, *N*,*N*-dimethylformamide; 1,2,4-Tcb, 1,2,4-trichlorobenzene; ΔH_{pp}, the peak-to-peak separation of ESR signal.

from neodymium to gadolinium are less stable than the corresponding complexes with "heavier" lanthanide ions,[14] such as terbium to lutetium ($4f^8$ to $4f^{14}$, respectively), and this is probably due to their size and/or to their electronic configuration (Nd^{III} $4f^3$, Gd^{III} $4f^7$). The analogous complexes with *meso*-tetrakis(*N*-4-pyridyl)porphyrin exhibit higher stability with respect to those with a tpp ring. This may be attributed to the different electron withdrawing character of the *N*-4-pyridyl group compared with the phenyl group.

The UV–vis spectra of the cationic complexes exhibit a significant red shift of the B-band (Soret band) due to their cationic character.[15] ESR spectroscopy revealed significant differences in solution or in the solid state between the cationic and the neutral tetrapyridylporphyrine complexes, as discussed below.

EXPERIMENTAL

Chemicals

All chemicals were reagent grade and were used without further purification, except as noted below. Alumina type basic I was activated at 150°C for at least 24 h. 1,2,4-Trichlorobenzene (Aldrich) was distilled and dried over molecular sieves. *N*,*N*-Dimethylformamide was distilled under nitrogen and over a complex of sodium–benzophenone. $Ln^{III}(acac)_3 \cdot xH_2O$ were prepared from the corresponding lanthanide(III) nitrate pentahydrate $[Ln^{III}(NO_3)_3 \cdot 5H_2O]$ (Aldrich) salts.

Methods and instruments

UV–vis spectra were recorded on a Lambda-6 Perkin–Elmer spectrophotometer or on an ORIEL diode-array visible spectrophotometer, using 5×10^{-3} mol dm^{-3} solutions of DMF or H_2O. Samples for IR measurements were prepared as 1% dispersions in CsI pellets or Nujol mulls and recorded on an FT-IR 1760 series Perkin–Elmer spectrophotometer. ESR spectra were recorded in a Bruker spectrometer at room temperature or at 90 K, in solution, in $MgSO_4$ (2%w/w) or as pure solid.

Synthesis and purification of the complexes

$(Por)H_2$ (0.700 g, ~1.13 mmol) was added to a round-bottomed flask (100 cm^3) equipped with an argon inlet and reflux condenser, together with 1.000 g (~2.10 mmol) of $Ln^{III}(acac)_3 \cdot xH_2O$ and 30 cm^3 of 1,2,4-Tcb. The above solution mixture was stirred for 4 h at reflux under a slow stream of argon. The 1,2,4-Tcb was removed by rotary evaporation and the resulting crude solid was dissolved in a minimum amount of CH_2Cl_2 and loaded into an aluminum oxide column (4 × 6 cm) using CH_2Cl_2 as eluent. The unreacted $(tpyp)H_2$ was eluted first. The last traces of the free base were eluted with a mixture of CH_2Cl_2–MeOH (100 : 1–10, v/v). Using MeOH first and then MeOH–DMF (3 : 1, v/v), the monoporphyrinate Ln^{III}(tpyp)acac is eluted. The above solvent mixtures, which contain only the desirable product, were collected together and removed by rotary evaporation. Recrystallization of the solid residue was carried out in a mixture of CH_2Cl_2–MeOH (5 : 1, v/v). The yields varied from 86 to 92%. [Sm(tpyp)acac] (**1**), 86%, [Eu (tpyp)acac] (**2**), 89%, [Gd(tpyp)acac] (**3**), 92%, [Tb(tpyp)acac] (**4**), 92%. Found: C, 62.1; H, 4.0; N, 13.7. Calc. for **1**, $C_{45}H_{32}N_8O_2Sm$ (mol. wt 867.20): C, 61.3; H, 3.7; N, 12.9%. Found: C, 61.9; H, 4.1; N, 13.7. Calc. for **2**, $C_{45}H_{32}N_8O_2Eu$ (mol. wt 868.76): C, 62.2; H, 3.7; N, 12.9%. Found: C, 61.2; H, 4.1; N, 13.8. Calc. for **3**, $C_{45}H_{32}N_8O_2Gd$ (mol. wt 874.05): C, 61.8; H, 3.7; N, 12.8%. Found: C, 61.1; H, 4.1; N, 13.3. Calc. for **4**, $C_{45}H_{32}N_8O_2Tb$ (mol. wt 875.73): C, 61.7; H, 3.7; N, 12.8%.

The synthesis of Ln^{III}(tmepyp)acac was achieved by methylation of the neutral complex as follows: in a round-bottomed flask equipped with a reflux condenser, 0.0750 g (~0.086 mmol) of the monoporphyrinate, Ln(tpyp)acac, was dissolved in 30 cm^3 of a solution of DMF–MeOH (2 : 1, v/v), and the mixture was heated at ~50°C. After 15 min, 0.2 cm^3 (~3.42 mmol) of CH_3I was added dropwise. The reaction was monitored by UV–vis spectroscopy and completed in 3 h. The solvents were evaporated under vacuum and recrystallization carried out using CH_2Cl_2–MeOH (5 : 1, v/v). The solid was filtered and washed several times with CH_2Cl_2–MeOH (3 : 1, v/v), in order to remove traces of demetallation products. The yields are as follows: $[Sm(tmepyp)acac]I_4$ (**5**), 84%, $[Eu(tmepyp)acac]I_4$ (**6**), 87%, $[Gd(tmepyp)acac]I_4$ (**7**), 90%, $[Tb(tmepy)acac]I_4$ (**8**), 96%. Found: C, 42.0; H, 3.1; N, 8.52. Calc. for **5** $C_{49}H_{44}N_8O_2I_4Sm$ (mol. wt 1434.96): C, 41.0; H, 3.1; N, 7.8%. Found: C, 41.1; H, 3.1; N, 8.4. Calc. for **6**, $C_{49}H_{44}N_8O_2I_4Eu$ (mol. wt 1436.52): C, 41.0; H, 3.1; N, 7.80%. Found: C, 41.3; H, 3.3; N, 8.4. Calc. for **7**, $C_{49}H_{44}N_8O_2I_4Gd$ (mol. wt 1441.81): C, 40.8; H, 3.1; N, 7.8%. Found: C, 41.2; H, 3.3; N, 8.4. Calc. for **8**, $C_{49}H_{44}N_8O_2I_4Tb$ (mol. wt 1443.48): C, 40.8; H, 3.1; N, 7.8%.

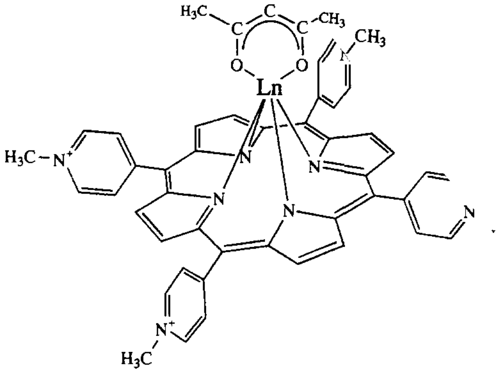
RESULTS AND DISCUSSION

The complexes of *meso*-tetrakis(*N*-4-pyridyl)-porphyrin are less soluble in comparison with the analogous complexes of *meso*-tetraphenyl-porphyrin with respect to the same organic solvents. The Ln^{III}(tpyp)acac complexes are freely soluble in solvents like MeOH and DMF, exhibit medium solubility in THF and are only slightly soluble in CH_2Cl_2. The neutral tetrakis(*N*-4-pyridyl) porphyrinic complexes exhibit higher stability than the analogous complexes of *meso*-tetraphenylporphyrin. The stability of Ln(tpyp)acac complexes compared with that of Ln(tpp)acac[14b] is surprising.

Electronic absorption and IR spectroscopy

The UV–vis data of neutral Ln^{III}(tpyp)acac complexes resemble the analogous tpp compounds. In Table 1 are listed the UV–vis data for Ln(tpyp)acac. All the complexes present absorption maxima of the Soret band at 430 nm and there are no significant differences of the extinction coefficient ε values. In the *Q*-region, three bands were observed from 510 to 600 nm. The absorption band at 560 nm exhibits the highest intensity. Figure 1 illustrates the spectrum of Gd(tpyp)acac.

In addition, in the UV–vis spectra of cationic complexes studied in aqueous or non-aqueous solutions, significant bathochromic shifts are observed compared with the neutral complexes. On the other hand, the same complexes exhibit a hypsochromic shift of the absorption maxima in aqueous solutions compared with the spectra obtained in DMF, but are still red shifted with respect to the neutral complexes. Figures 2 and 3 show the absorption spectra of Gd(tmepyp)acac in DMF and H_2O, respectively. A significant line broadening, especially concerning the Soret band, is observed for the cationic complexes. This is due to the cationic character of the porphyrin[15] (see Scheme 1). UV–vis data of cationic complexes in DMF and H_2O are presented in Table 2.



Scheme 1. Ln(tmepyp)acac.

IR spectroscopy of cationic and neutral complexes indicates that the band attributed to the ring C=N stretching mode of the pyridyl group has been hypsocromically shifted. This band, at 1598 cm^{-1} for Gd(tpyp)acac, appeared for the corresponding methylated compound at 1641 cm^{-1}. For all the complexes the above shifts varies between 46 and 53 cm^{-1}.

ESR spectroscopy

All the complexes were studied by ESR spectroscopy in the solid state or in frozen solutions. The complexes of tetrakis(*N*-4-pyridyl)porphyrin were studied in the solid state at room temperature, while the analogous cationic species were studied in solution (H_2O and DMF) at 290 K or at 90 K, respectively. In Table 3 the g values and the peak-to-peak separation, ΔH_{pp} (Gauss), are given. The complexes of tetrakis(*N*-4-pyridyl)porphyrin and tetrakis(*N*-4-methyl-pyridyl)porphyrin with metal ions, Ln = Sm, Eu and Tb, exhibit common features in the solid state at 290 K (see also Fig. 4) as

Table 1. UV–vis data for Ln(tpyp)acac complexes in *N*,*N*-dimethylformamide [λ, nm(log ε, $dm^{-3}mol^{-1}cm^{-1}$)]

Complexes	*B*-bands	*Q*-bands			Solvent
Sm(tpyp)acac	429 (5.41)	522 (3.62)	561 (4.50)	602 (3.80)	DMF
Eu(tpyp)acac	429 (5.49)	520 (3.70)	560 (4.55)	603 (3.83)	DMF
Gd(tpyp)acac	429 (5.51)	522 (3.72)	561 (4.52)	602 (3.81)	DMF
Tb(tpyp)acac	430 (5.48)	521 (3.72)	560 (4.49)	601 (3.73)	DMF

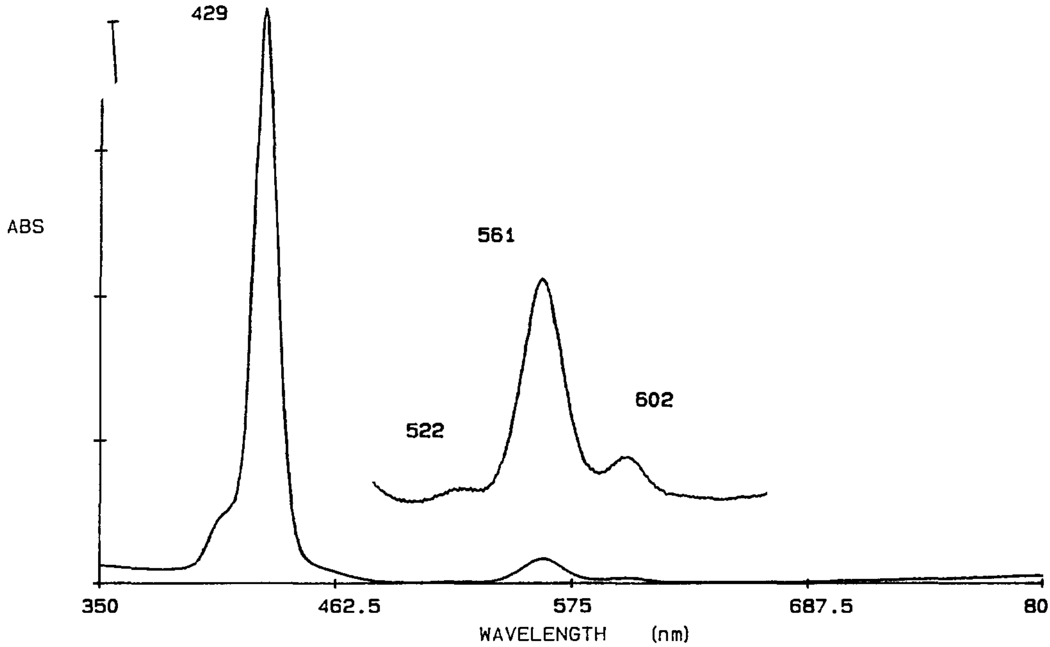


Fig. 1. UV–vis data for Gd(tpyp)acac in *N*,*N*-dimethylformamide.

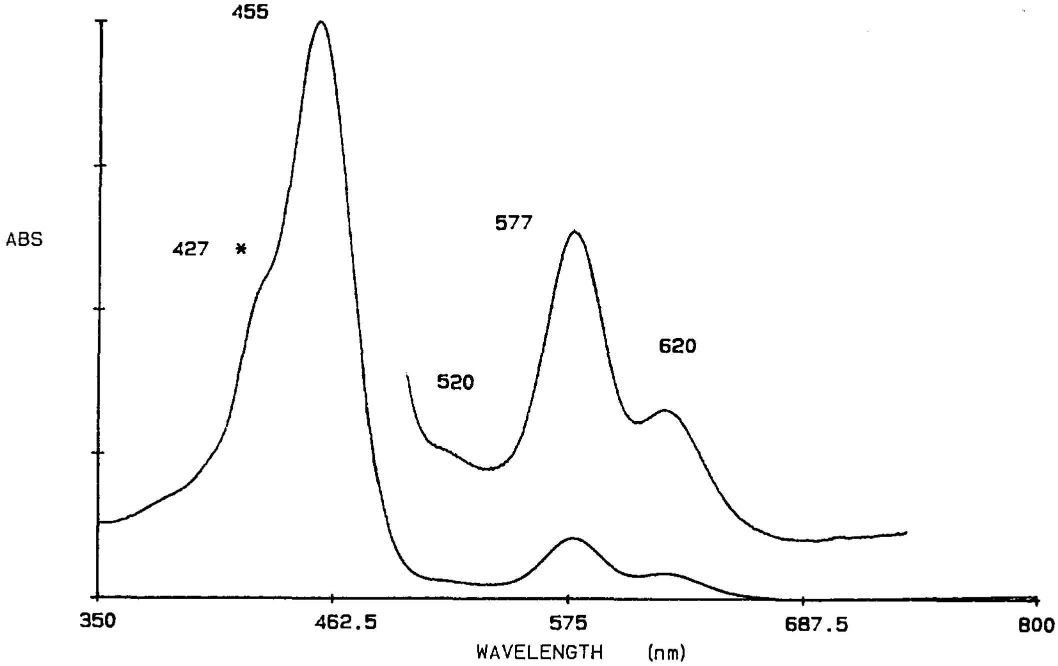


Fig. 2. UV–vis data for Gd(tmepyp)acac in *N*,*N*-dimethylformamide (asterisk indicates the presence of free base due to slight decomposition).

far as the *g* value ($\sim$2.00) and the hyperfine structure are concerned. The hyperfine coupling constant measured in these spectra is 16.9 G and seems not to be affected by the nature of the metal ion. This hyperfine structure has been observed for a whole variety of lanthanide mono- and bis-porphyrinates, the homoleptics, LnH(tpp)$_2$, or heteroleptics, LnH (oep)(tpp),[16a,b] and should be affected by the electron density on the nuclei that electron spin is delocalized on the macrocycle. Tpp and tpyp free radicals contain electron density primarily at the pyrrole nitrogen atoms and secondly at the methine bridge carbon atoms. The observed *g* value indicates a free radical, while the hyperfine

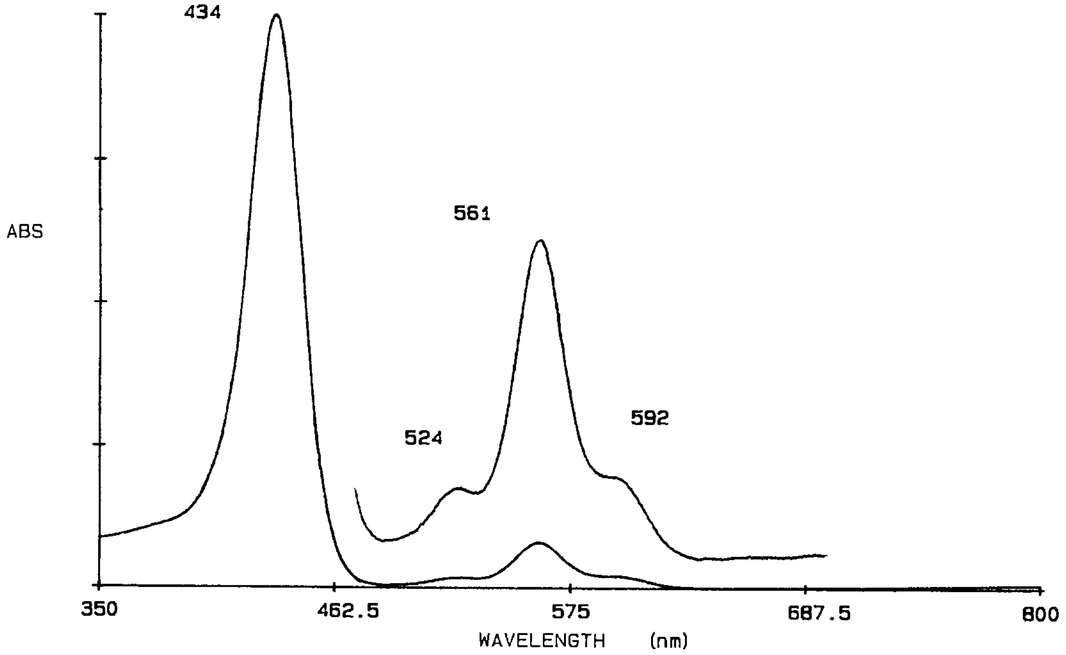


Fig. 3. UV–vis data for Gd(tmepyp)acac in H_2O at 90 K.

Table 2. UV–vis data for Ln(tmepyp)acac complexes in *N*,*N*-dimethylformamide and H_2O [λ, nm(log ε, $dm^{-3}mol^{-1}cm^{-1}$)]

Complexes	*B*-bands	*Q*-bands			Solvent
Sm(tmepyp)acac	438 (5.17)	520 (3.61)	564 (4.20)	600 (3.80)	H_2O
	452 (4.90)	522 (3.52)	575 (3.87)	619 (3.55)	DMF
Eu(tmepyp)acac	436 (5.19)	520 (3.70)	563 (4.15)	600 (3.71)	H_2O
	453 (4.92)	521 (3.53)	574 (3.88)	619 (3.59)	DMF
Gd(tmepyp)acac	434 (5.31)	524 (3.82)	561 (4.27)	592 (3.81)	H_2O
	455 (4.88)	520 (3.52)	577 (3.92)	620 (3.60)	DMF
Tb(tmepyp)acac	434 (5.28)	522 (3.75)	560 (4.21)	592 (3.79)	H_2O
	455 (4.98)	517 (3.57)	576 (3.95)	620 (3.64)	DMF

structure consisted of more than 20 lines (Fig. 4). As the unpaired electron density in the tpyp and tmepyp core is considered to be delocalized over the nitrogen atoms, a hyperfine splitting due to nitrogen atoms must be expected. The interaction of a free spin with the nitrogen nucleus should produce a hyperfine structure of nine lines (^{14}N, $I = 1$). However, the observed spectra consisted of more that 20 lines, with a hyperfine coupling constant of 16.9 G, which could be attributed to the hyperfine interaction of the free electron spin with ^{14}N nuclei rather than any other nuclei, such as ^{1}H ($I = 1/2$) and ^{16}O ($I = 0$) of the acetylacetonato ligand. The pattern of 20 lines could be attributed to the three sets of superimposed nine lines produced by the anisotropic signal. Anisotropy has been observed for a variety of metalloporphyrins studied at low temperature, in frozen solutions or in amorphous powder,[17a] exhibiting three *g* values and therefore three hyperfine couplings.

Table 3. ESR data of Ln(tpyp)acac and Ln(tmepyp)acac in different media (ΔH_{pp} in Gauss)

Complex, Ln(por)acac	Pure solid $g/\Delta H_{pp}$	In DMF $g/\Delta H_{pp}$	In H_2O $g/\Delta H_{pp}$
Sm(tpyp)acac	1.9946/14.6	—	—
Sm(tmepyp)acac	2.0009/14.6	*a*	*a*
Eu(tpyp)acac	2.0006/10.0	—	—
Eu(tmepyp)acac	2.0014/14.6	*a*	2.0765/126.9
Gd(tpyp)acac	1.9682/868	—	—
Gd(tmepyp)acac	1.9484/407.2	1.7022/103.1	1.6993/355.6
Tb(tpyp)acac	2.0037/14.6	—	—
Tb(tmepyp)acac	2.0037/13.6	*a*	1.9929/11.9

[a] Not observed.

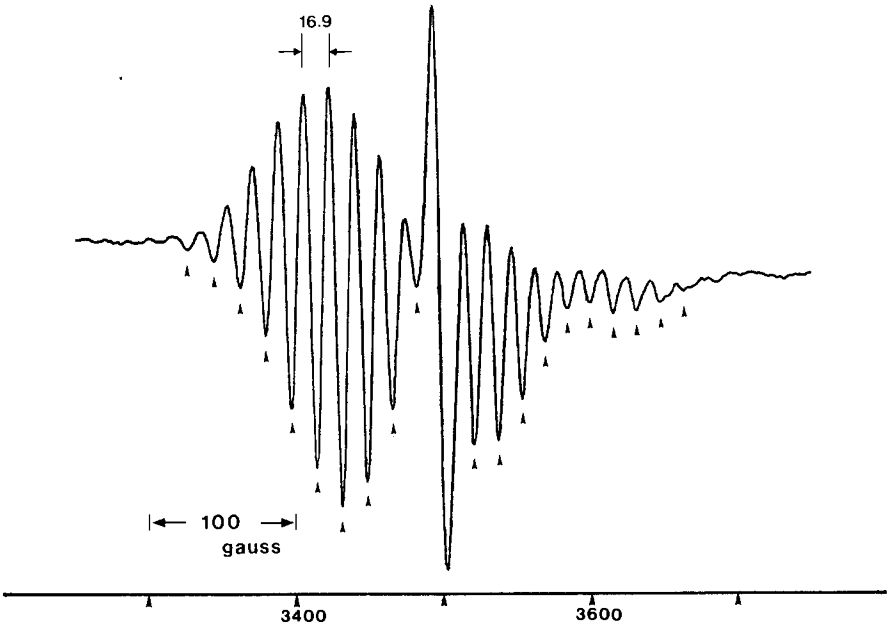


Fig. 4. ESR spectrum of Eu(tmepyp)acac in the solid state at 294 K.

The ESR spectra of cationic complexes of samarium, europium and terbium in the solid state exhibit the hyperfine structure that was discussed above. However, no hyperfine structure was observed for the same complexes studied in solution at low temperature. In order to discuss this difference, we have to focus our attention upon two cases. The first is the spectrum of Eu(tmepyp)acac in the solid state and in solution, while the second is the spectrum of Tb(tmepyp)acac in the same conditions. Both complexes are ESR inert in DMF (90 K) and no spectra were recorded. The cationic complex of Tb^{III} gave a single peak with a g value of 1.9929 (see Table 3), and a peak-to-peak separation of 11.9 G. No splitting was observed. This value is notably small among those of the other complexes studied in H_2O, but even smaller than for the same complex in the solid state (13.6 G). This behaviour is probably associated with the high dielectric constant of water and a possible contribution to the charged part of the molecule (N^+—CH_3 of the four pyridyl groups). A different electron density may be regarded for the cationic porphyrin core than for the non-methylated tpyp analogue. However, this aspect does not seem to explain the ESR spectrum of Eu(tmpyp)acac, which consisted of a broad intense signal with $g = 2.0765$ and $\Delta H_{pp} = 126.9$ G (Fig. 5). Two sets of symmetrical peaks are also observed flanking the intense peak.

This broadening of the main signal in Eu (tmepyp) acac can be discussed in terms of the

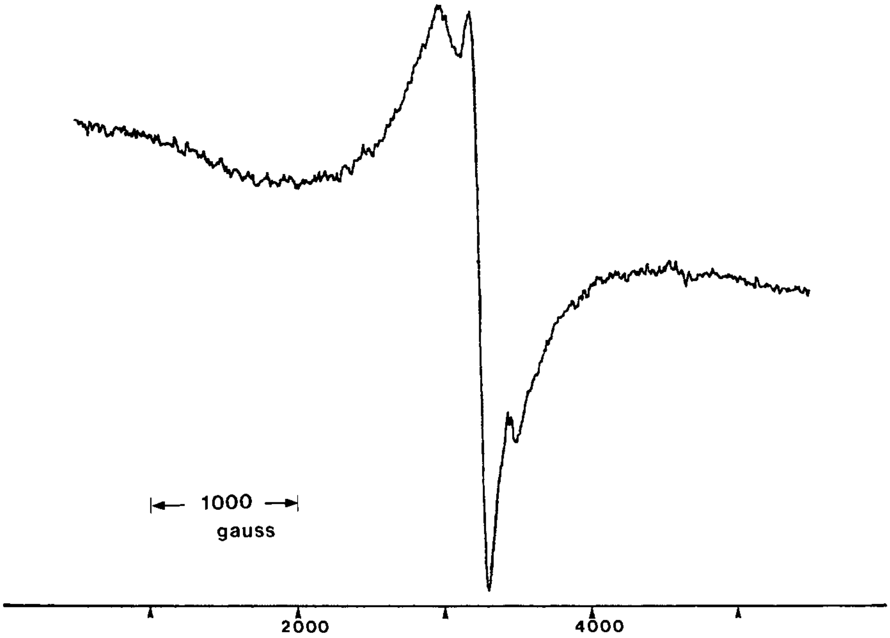


Fig. 5. ESR spectrum of Eu(tmepyp)acac in H_2O at 90 K.

presence of a formal oxidation state of +2 of the europium ion in aqueous solution. The Eu^{II} ion has an $^8S_{7/2}$ ground state (the same as Gd^{III}) and its magnetic hyperfine constants are considerably large. ESR studies of the Eu^{II} ion in salts such as CaF_2, $SrCl_2$ and SrS exhibited g-factors very close to 2.00 and also gave observable hyperfine splitting.[17b] In our case, the hyperfine structure may be superimposed due to the large peak-to-peak separation value, and only two lines were observed. Further spectroelectrochemical studies may shed light on this point.[18a,b]

The spectrum of Gd(por)acac exhibits striking differences compared with the spectra of the other lanthanide neutral or cationic porphyrins, either in the solid state or in solution. Gd^{III} also has an $^8S_{7/2}$ ground state and a long spin-lattice relaxation time, which allows its ESR signal to be observable at all temperatures. Its lowest orbital level is eight-fold degenerate in spin and as for other S-state ions is largely unaffected by crystal fields. Gd^{III} ESR has been studied for a variety of salts[17b] such as $Mg_3Gd_2(NO_3)_{12}\cdot 24H_2O$ and $Gd(EtSO_4)_3\cdot 9H_2O$, and its g value was isotropic, while no hyperfine structure has been observed. The ESR spectra of our complexes exhibit broad signals, with ΔH_{pp} which varied from 103.1 [Gd(tmpyp)acac in DMF at 90 K; see Table 3] to 868 G [Gd(tpyp)acac in the solid state at 290 K; see Fig. 6). Recently, studies of the complex $[Hg_2Gd(C_4H_6NO_2)(NO_3)_3]$[19] have been carried out considering two regions in order to study the anisotropy of the Gd^{III} signal. Anisotropy in g-factors has been observed in a variety of similar porphyrinic complexes that have also been synthesized in our laboratory,[16a,b] and although lines may narrow in magnetically concentrated materials, the smallest ΔH_{pp} value is observed in DMF solution and not in the solid state [the samples in the solid state consisted only of the Ln(por)acac derivative].

It is well known that the broadening of the peaks due to spin-lattice relaxation results from the interaction of the paramagnetic ions with the thermal vibrations of the lattice. Since relaxation times usually increase as the temperature decreases, many complexes of transition metals need to be cooled to liquid N_2, H_2 or helium temperatures before well-resolved spectra are observed. Although Gd^{III} is ESR active even at room temperature, this fact explains the narrowing of the line width in gadolinium complexes, from Gd(tpyp)acac (Fig. 6) at room temperature to Gd(tmepyp)acac at 90 K (Fig. 7). Another factor which plays an important role in the line width in ESR, as well as in NMR spectroscopy, is the spin–spin interaction. As this interaction is reduced, the line width becomes smaller. In Gd(tmepyp)acac in solution, the spin–spin interactions from the induced magnetic field that exist on neighbouring paramagnetic ions are expected to be smaller than in solid Gd(tmepyp)acac and Gd(tpyp)acac. However, no hyperfine structure is observed, while anisotropy of the g-factor is observed only in the case of Gd(tpyp)acac (Fig. 6). The observed g values for the Gd^{III} complexes vary from 1.6993 to 1.9682 (Table 3). Finally, the implication that no ESR spectra are observed for

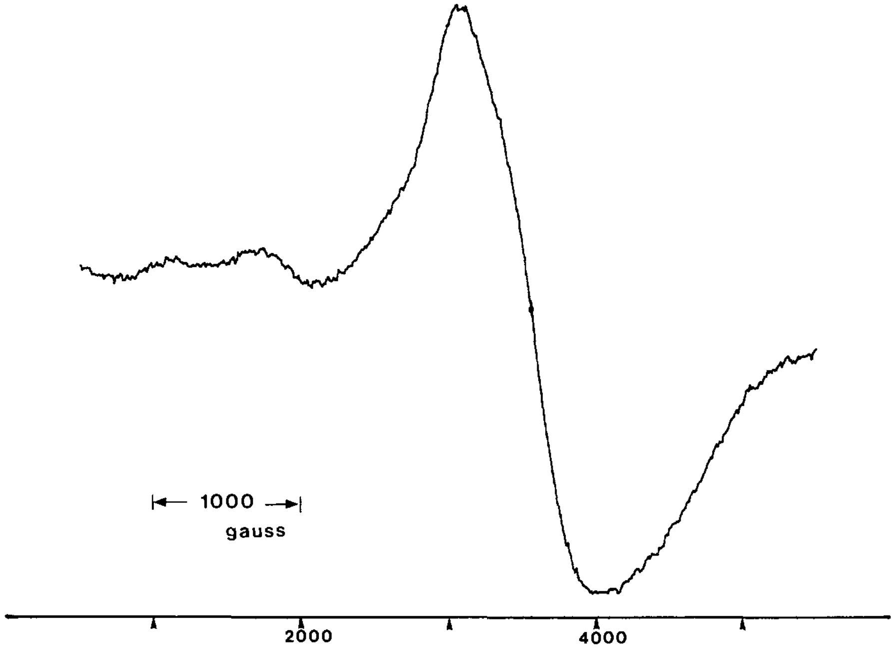


Fig. 6. ESR spectrum of Gd(tpyp)acac in the solid state at 294 K.

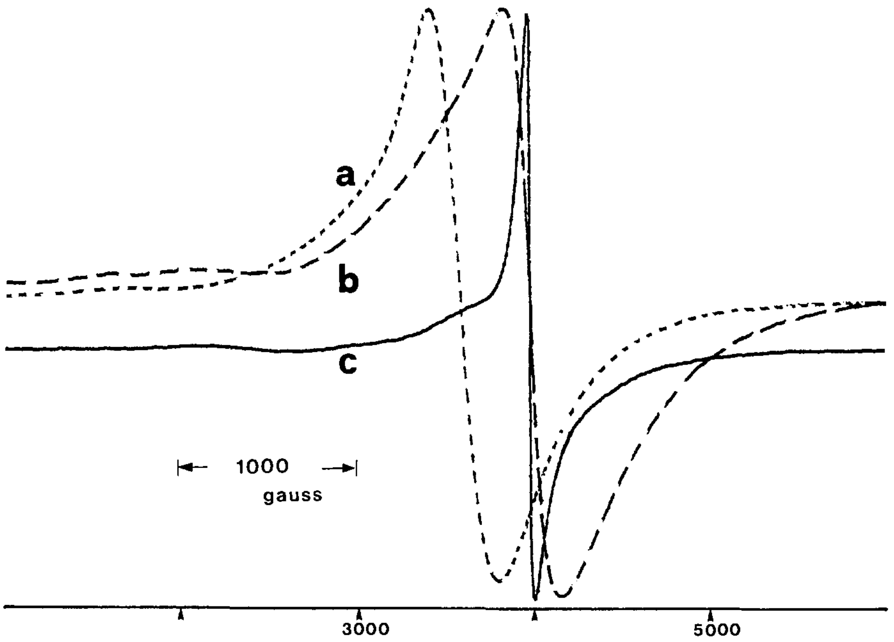


Fig. 7. ESR spectrum of Gd(tmepyp)acac: (a) pure solid at 290 K; (b) in H_2O at 90 K; (c) in DMF at 90 K.

Ln(tmepyp)acac, where Ln = Sm, Eu, Tb, in DMF due to an extreme broadening of the signal may be excluded as the cationic complex of gadolinium exhibits a smaller ΔH_{pp} value in frozen DMF.

The observed differences concerning the chemical behaviour of these "light" lanthanide monoporphyrins is prolonged in the case of gadolinium. However, for all the complexes studied, the solvent used plays an important role either in the stability or other properties. There is probably a direct influence on the primary coordination sphere of coordinated solvent molecules, either in aqueous or in organic media.

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