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SYNTHESIS AND SPECTROSCOPIC STUDIES OF LANTHANIDE MONOPORPHYRINATES WITH *MESO*-TETRA-ARYL PORPHYRINATE BEARING BROMINES ON THE β-PYRROLE POSITIONS OF FLUORINES ON PHENYL GROUPS

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Abstract—The metal derivatives of octabromotetraphenyl porphyrin with lanthanide (Sm to Lu) ions have been synthesized via the acetylacetonates and characterized by UV–vis, IR and ESR spectroscopies. These lanthanide complexes exhibit interesting electronic features compared with all the previously reported lanthanide monoporphyrinates. The stability of the complexes is discussed in terms of the already known related complexes. The *meso*-fluoro-aryl-substituted porphyrin with Sm^{III} has been synthesized and its spectroscopic behaviour compared with the above β-pyrrole octabromotetraphenyl complexes. IR studies indicate that the axial ligand is the acetylacetonate as has been observed for lanthanide monoporphyrinates synthesized by the acetylacetonate method. ESR spectroscopy of Ln(obp)acac† exhibit one intense peak with $g \sim 2.00$ and hyperfine splitting for Ln = Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu. The ESR spectrum of Gd(obp)acac exhibits an isotropic g-factor with a value of 2.3099 and it compared with the analogous complex of Gd(tpp)acac.

The catalytic activity of metalloporphyrins is well established by their biomimetic reactions[1] and/or their industrial applications.[2] For this purpose, a large variety of substituted metalloporphyrins has been used. An interesting and promising family of substituted porphyrins are the pentahalogenated tetraphenylporphyrins. These complexes have been considered as very efficient catalysts in the epoxidation process of organic substrates. Substitution at the β-pyrrole position with electron-withdrawing groups such as cyano or bromo produces great stability in the presence of strong oxygen donors as well as the induced shift for the ring oxidation or reduction of the porphyrin ring.[3]

In addition, lanthanide porphyrins have been considered as biomimetic models for photosynthetic reaction centres of purple bacteria[4] or as probes for NMR studies in biological molecules.[5] In recent years lanthanide porphyrins have also been proposed as probes of animal tumours[6] and as potential catalysts.[7] However, halogen-substituted lanthanide porphyrins have not been reported as far as we know. In this work we present the synthesis and the spectroscopic characterization of the acetylacetonate lanthanide(III) octabromotetraphenyl porphyrin with the lanthanide ions from Sm to Lu. In order to compare the spectroscopic properties of the above complexes with the cor-

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† Abbreviations: tpp: *meso*-5,10,15,20-tetraphenyl porphyrinate (2^-); tpfpp: *meso*-5,10,15,20-tetrakis (pentafluorophenyl) porphyrinate (2^-); obp: 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenyl porphyrinate (2^-); Ln(por)acac: the general type of lanthanide monoporphyrinate acatylacetonato; 1,2,4-Tcb: 1,2,4-trichlorobenzene; THF: tetrahydrofuran.

responding pentafluorophenyl porphyrins, the corresponding complex with Sm has also been synthesized. The optical, IR and magnetic properties of the above metalloporphyrins have been analysed and are discussed.

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 under molecular sieves and Ln $(acac)_3 \cdot xH_2O$ were prepared from the corresponding lanthanide(III) nitrate penta-hydrated $[Ln(NO_3)_3 \cdot 5H_2O]$ salts.

Methods and instruments

All manipulations of oxygen- and water-sensitive materials were performed by Schlenk-tube techniques under purified nitrogen or argon. UV–visible spectra were recorded on a Lambda-6 Perkin–Elmer spectrophotometer or an ORIEL diode-array visible spectrophotometer, using solutions of CH_2Cl_2 (5×10^{-3} mol dm^{-3}). 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 on a Bruker spectrometer at room temperature (298 K) or at 90 K, in $MgSO_4$ (2% in product) or as pure solid.

Synthesis and purification of the complexes

Synthesis of free-bases. (a) $(obp)H_2$: The 2,3,7,8 7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenyl porphyrin was synthesized according to Bhyrappa and Krishnan[8] with modifications as follows: Cu(tpp) (0.8875 g, 1.31 mmol) was dissolved in a mixture of $CHCl_3/CCl_4$ (1 : 1 v/v; 350 cm^3), Br_2 (2.18 cm^3; 6.79 g, 42.5 mmol) in $CHCl_3/CCl_4$(1 : 1 v/v; 90 cm^3) was then added over a period of 30 min at room temperature. The mixture was stirred for 4 h. Pyridine (5.38 cm^3) in a mixture $CHCl_3$/CCl_4 (1 : 1 v/v; 140 cm^3) was added next, over a period of 30 min. In order to prevent violent reaction, great care is required not only during the addition of bromine but also during the addition of pyridine. The solution remained for another period of 12 h. The reaction mixture was treated with a solution of $Na_2S_2O_5$ (20%; 350 cm^3), the organic phase was dried under $MgSO_4$, concentrated under rotary evaporation and chromatographed on a column of Al_2O_3 using $CHCl_3$ as the eluant. Pure Cu(obp) (73.5%; 1.26 g) was obtained by a second chromatography column. Cu(obp) (0.4 g) was dissolved in $CHCl_3$ (250 cm^3) and H_2SO_4 (20 cm^3) was added. After stirring for 15 min the solution was treated with 4 M NaOH. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. $(obp)H_2$ (0.257 g) was obtained (yield 68%).

[**Note:** An attempt to process the demetallation via treatment with perchloric acid failed and H_2SO_4 (95%) has been used]. UV–vis data in $CHCl_3$, λ_{max}, nm (log ε): 469 (5.32), 569 (4.02), 626 (4.15) and 745 (3.91).

(b) $(tpfpp)H_2$: The synthesis of *meso*-5,10,15,20 tetrakis(pentafluorophenyl) porphyrin has been synthesized with modifications to the literature method as follows:[9] to propionic acid (125 cm^3) was added pyrrole (1.76 cm^3, 25.5 mmol) and 2,3,4,5,6-pentafluorobenzaldehyde (5 g, 25.5 mmol). The mixture was refluxed for 2 h, the propionic acid distilled *in vacuo* and the crude solid dissolved in a minimum volume of CH_2Cl_2/petroleum ether (1 : 1, v/v). The solution was chromatographed on a column of neutral Al_2O_3 with a mixture of CH_2Cl_2/petroleum ether as eluant (3 : 7, v/v). Many fractions were collected and those containing only the desired free base (after control by UV–vis) were evaporated together. The residue was recrystallized in MeOH at +4°C overnight. After filtration, the solid was washed several times with hexane and dried *in vacuo*. UV–vis data in toluene, λ_{max}, nm (log ε): 416 (5.48), 508 (4.33), 583 (3.82) and 658 (3.46).

Synthesis of metallated complexes. (a) Synthesis of lanthanide(III) acetylacetonato-2,3,7,8,12,13, 17,18-octabromo-5,10,15,20-tetraphenylporphyrin, Ln^{III}(obp)acac. $(obp)H_2$ (0.10 g, 0.08 mmol) and $Ln(acac)_3 \cdot xH_2O$ (0.209 g, 0.42 mmol) were added in 1,2,4-trichlorobenzene (20 cm^3, tcb) and the mixture heated to reflux for 2 h. The tcb was distilled *in vacuo* and the crude solid dissolved in the minimum volume of toluene was chromatographed on an Al_2O_3 column, with toluene as eluant. The traces of Cu(obp) were eluted first. With CH_2Cl_2 as the eluant traces of free base eluted first, while the monoporphyrinate Ln(obp)acac eluted by a mixture of MeOH/DMF (10 : 3, v/v). The yields varied from 79 to 90%. Found: C, 39.1; H, 2.3; N, 4.5. Calc. for **1**: $C_{52}H_{35}N_5O_3Br_8Sm$ (mol.wt 1567.52): C, 39.8; H, 2.2; N, 4.5; Br, 40.8%. Found: C, 39.3; H, 2.1; N, 4.4; Br, 40.7. Calc. for **2**: $C_{52}H_{35}N_5O_3Br_8Eu$ (mol.wt 1569.08): C, 39.8; H, 2.2; N, 4.5; Br, 40.8%. Found: C, 39.7; H, 2.2; N, 4.4; Br, 40.6. Calc. for **3**: $C_{52}H_{35}N_5O_3Br_8Gd$ (mol.wt 1574.37): C, 39.7; H, 2.2; N, 4.4; Br, 40.6%. Found: C, 39.6; H, 2.2; N, 4.4; Br, 40.5. Calc. for **4**: $C_{52}H_{35}N_5O_3Br_8Tb$ (mol.wt 1576.05): C, 39.6; H, 2.2; N, 4.4; Br, 40.6%. Found: C, 39.6; H, 2.1; N, 4.3; Br, 40.5. Calc. for **5**: $C_{52}H_{35}N_5O_3Br_8Dy$ (mol.wt 1579.62): C, 39.5; H, 2.2; N, 4.4; Br, 40.8%. Found: C, 39.6; H, 2.2; N, 4.4; Br, 40.3. Calc. for **6**: $C_{52}H_{35}N_5O_3Br_8Ho$ (mol.wt 1582.05): C, 39.5; H, 2.2; N, 4.4; Br, 40.4%. Found: C, 39.5; H, 2.2; N, 4.3; Br, 40.5. Calc. for **7**: $C_{52}H_{35}N_5O_3Br_8Er$ (mol.wt 1584.38): C, 39.4; H, 2.2; N, 4.4; Br, 40.3%. Found: C, 39.5; H, 2.1; N, 4.3; Br, 40.4. Calc. for **8**: $C_{52}H_{35}N_5O_3Br_8Tm$ (mol.wt 1586.06): C, 39.4; H, 2.2; N, 4.4; Br, 40.3%. Found: C, 39.5; H, 2.1; N, 4.5; Br, 40.3. Calc. for **9**: $C_{52}H_{35}N_5O_3Br_8Yb$ (mol.wt 1590.16): C, 39.3; H, 2.2; N, 4.4; Br, 40.2%. Found: C, 39.9; H, 2.1; N, 4.5; Br, 40.2. Calc. for **10**: $C_{52}H_{35}N_5O_3Br_8Lu$ (mol.wt 1592.09): C, 39.8; H, 2.2; N, 4.4; Br, 40.1%.

(b) Synthesis of samarium(III) acetylacetonato-tetrakis(2,3,4,5,6-pentafluorophenyl) porphyrin, Sm^{III}(tpfpp)acac. (tpfpp)H_2 (0.150 g, 0.15 mmol) and $Sm(acac)_3 \cdot xH_2O$ (0.50 g, 1.05 mmol) were added in 1,2,4,-tcb (20 cm^3). The mixture was heated to reflux for 6–8 h, the tcb was distilled *in vacuo* and the crude residue was chromatographed on an Al_2O_3 column with toluene as the eluant. First eluted was the unreacted free base. With CH_2Cl_2 as the eluant part of the complex Sm(tpfpp)acac was collected, though contaminated by traces of free base. Mixtures of MeOH/DMF (10: 1–3, v/v) have been used and the monoporphyrinate compound, [Sm(tpfpp)acac][DMF], was in pure form, yield 94%. UV–vis in CH_2Cl_2, λ_{max}, nm (log ε): 417 (5.47), 507 (3.23), 548 (4.14), 583 (3.49). Found: C, 47.5; H, 1.9; N, 5.5. Calc. for $C_{52}H_{25}N_5O_3F_{20}Sm$ (mol.wt 1298.17): C, 48.1; H, 1.9; N, 5.4%.

RESULTS AND DISCUSSION

Although the octabromoporphyrin free base, (obp)H_2, has been found to be freely soluble in many organic solvents such as $CHCl_3$, CH_2Cl_2 and $PhCH_3$, it is also quite soluble in MeOH, THF and pyridine. In the same way, lanthanide complexes are very soluble in the former solvents but exhibit medium solubility in the latter solvents. As has been reported, the imino nitrogens of (obp)H_2 are relatively less basic than those of tetraphenylporphyrin, (tpp)H_2, and porphyrin, (p)H_2.[8,10] The acidic nature of (obp)H_2 is probably due to the electron-withdrawing bromines at the β-pyrrole positions. The first synthesized metal derivatives[8] exhibited surprising stability towards acids, in contrast to those of the lanthanides. During the chromatography procedure, a notable amount of complex is demetallated. For this reason, just before the application of the reaction mixture, the addition of triethylamine (1 cm^3) on the column of aluminum oxide is required.

For all the lanthanides used the reaction is completed in 1 or 2 h. This reaction time is the shortest known for the variety of porphyrin ligands that have been used so far. Comparatively, a reaction time of 6 h is needed for the metallation of tpp porphyrin, while a period of 4 h is required for the corresponding tppyp derivative.

Except for the activity of the imino hydrogens, probably the planarity of this dodeca-substituted porphyrin accelerates the reaction time. As has been reported by Smith and co-workers,[11] non-planarity affects the electronic absorption properties too. Recent studies on some dodeca-substituted porphyrins, such as 2,3,7,8,12,13,17,18-octaethyl-(5,10,15,20-tetraphenyl) porphyrin, showed a significant red shift of the absorption maxima compared with the octa- or tetra-substituted porphyrins. A significant bathochromic shift of (obp)H_2 in comparison to (tpp)H_2 is also observed.

In addition, the *meso*-tetra(pentafluorophenyl) porphyrin was metallated in 4–5 h and its metal derivatives are more soluble than the corresponding acetylacetonato complexes of tpp. A comparison of metal derivatives of (tpfpp)H_2 porphyrin with those of non-substituted tpp indicates that the fluorines on the phenyl groups affect not only the solubility but also the electronic properties.

Electronic absorption and IR spectra

The electronic absorption spectra of Sm(obp) acac is presented in Fig. 1, while the optical spectral data for all the lanthanide complexes are given in Table 1.

The free base (obp)H_2 exhibits three Q-bands, with that at 626 nm having the higher intensity ($569 < 626 > 743$ nm) in contrast to four, for tetra-substituted (tpp)H_2 or octa-substituted (oep)H_2. In the B region of the spectra an intense peak at 469 nm is observed (Soret band), while another one of medium intensity is present at 370 nm. As has been reported by Bhyrappa and Krishnan,[8] among the substituted porphyrins known so far, octabromo(tetraphenyl) porphyrin exhibits the largest red shift of B and Q bands. The metal derivatives that have been synthesized by the same group present a blue-shifted Soret band relative to the free base (obp)H_2. According to the above studies, a correlation between electronegativity of the metal ion and the corresponding induced red shift is discussed below.

The less electronegative metal produces the larger shift to the red region, relative to free base. As we

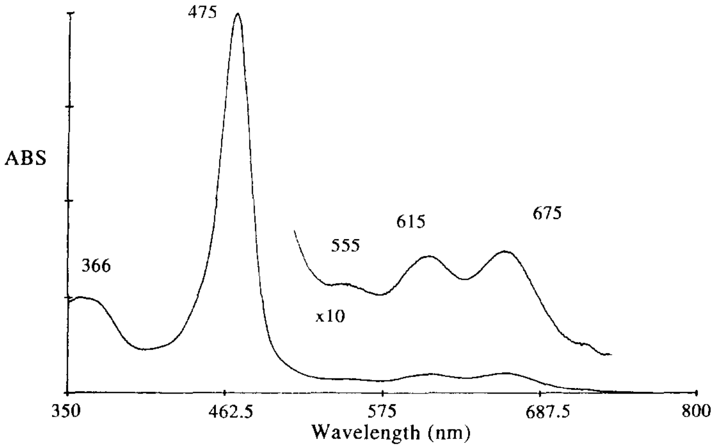

Fig. 1. UV–vis spectrum of Sm(obp)acac in CH_2Cl_2.

can deduce from Table 1, the samarium derivative exhibits B and Q bands to lower energy among the series of lanthanide octabromo complexes, while the complex of Lu exhibits bands at higher energy. According to the electronic absorption spectra obtained in CH_2Cl_2 there is a periodic red shift of λ_{max} from Lu to Sm. Therefore, the above red shift follows the electronegativity series of the lanthanide ions. Lu, the metal with the largest electronegativity, exhibits spectral features blue-shifted compared with the other complexes of this series.

Hence, the data obtained lead to the conclusion that the electronegativity influences the energy of electronic transitions in the same way as these are influenced by transition metal derivatives. Although the synthesized lanthanide octabromoporphyrins are a novel example of complexes with a red-shifted Soret band[12] with respect to free base, the most electronegative metal ion decreases the energy of the HOMO (a_{2u} orbitals) and shifts the λ_{max} to the blue of porphyrin complexes more than the less electronegative metals. This induced lowering of a_{2u} orbital energy is small, as is the electronegativity difference within the lanthanide series.

The UV–vis spectrum of Sm(tpfpp)acac is totally

Table 1. UV–vis data for Ln(obp)acac complexes in CH_2Cl_2 [λ (nm) (log ε dm^{-3} mol^{-1} cm^{-1})]

Ln(obp)acac	Soret		Annex			Solvent
Sm	366	475	555	615	675	CH_2Cl_2
	(4.10)	(4.80)	(3.39)	(3.52)	(3.63)	
Eu	365	474	554	615	675	CH_2Cl_2
	(4.25)	(4.72)	(3.45)	(3.55)	(3.62)	
Gd	370	474	555	615	672	CH_2Cl_2
	(4.12)	(5.00)	(3.48)	(3.71)	(3.82)	
Tb	357	474	552	612	669	CH_2Cl_2
	(4.44)	(4.65)	(3.48)	(3.42)	(3.50)	
Dy	362	473	557	612	668	CH_2Cl_2
	(4.24)	(4.80)	(3.30)	(3.50)	(3.58)	
Ho	362	473	555	612	668	CH_2Cl_2
	(4.10)	(4.79)	(3.32)	(3.50)	(3.56)	
Er	366	472	555	612	666	CH_2Cl_2
	(3.84)	(4.81)	(3.18)	(3.48)	(3.58)	
Tm	358	472	549	607	664	CH_2Cl_2
	(4.31)	(4.92)	(3.49)	(3.63)	(3.71)	
Yb	358	471	547	607	663	CH_2Cl_2
	(4.10)	(4.90)	(3.45)	(3.60)	(3.68)	
Lu	358	470	546	606	663	CH_2Cl_2
	(4.32)	(4.87)	(3.48)	(3.62)	(3.64)	

different compared with the corresponding octabromoporphyrin (Fig. 2). Although the absorption maxima exhibit a blue shift compared with lanthanide non-substituted tpp (see experimental), according to studies on halogenated *meso*-tetraphenyl porphyrin by Kim *et al.*[13] the substitution at the *ortho* position causes a decrease in the extinction coefficient. As has also been reported, substitution in other positions did not affect the optical properties. Although in our case where the two *ortho* positions are substituted, no significant change in optical properties is observed. In contrast, the coefficient ε of Sm(tpfpp)acac is considered among the higher in substituted or not, *meso*-tetraphenyl porphyrin lanthanide derivatives.

A large shift is observed for the N—H vibration in the case of (obp)H_2. The N—H vibration observed at *ca* 3290 cm^{-1} in (tpp)H_2 has been shifted up to 3634 cm^{-1} in (obp)H_2 due to the electron-withdrawing effect of bromine substituents on the pyrrole ring. A small shift is observed for the N—H vibration of (tpfpp)H_2 which is seen at 3317 cm^{-1}. IR spectroscopy indicates the coordination of the acetylacetonato ligand for both the halogenated complexes.

ESR spectroscopy

All the complexes with β-pyrrole octabromo- and *meso*-tetrakis(pentafluorophenyl) porphyrins have been studied by ESR spectroscopy in the solid state at room temperature and the metal derivatives of the octabromoporphyrin, except that of Gd^{III}, exhibit the same features. These are the g-factor values close to 2.00 and the observed hyperfine structure. The values of hyperfine coupling constants are not the same in all cases while only small differences are observed for peak-to-peak separation. The g value, ΔH_{pp} and hyperfine constants α, are given in Table 2.

Table 2. ESR data for Ln(obp)acac in the solid state [ΔH_{pp} (Gauss)]

Complexes	g	ΔH_{pp}	α
Sm(obp)acac	1.9975	13.35	18.46
Eu(obp)acac	1.9995	14.35	26.67
Gd(obp)acac	2.3099	172.80	[a]
Tb(obp)acac	1.9985	15.38	15.38
Dy(obp)acac	1.9995	15.46	25.25
Ho(obp)acac	2.0030	16.30	15.70
Er(obp)acac	2.0063	16.40	14.60
Tm(obp)acac	1.9995	15.38	15.38
Yb(obp)acac	2.0137	13.34	15.85
Lu(obp)acac	1.9985	16.40	18.50

[a] No hyperfine splitting observed.

As has been already discussed, gadolinium porphyrinates[14] give ESR signals different from those of the other lanthanide porphyrinates. It is clear according to our studies[14] that the ESR spectra of Gd^{III} are strongly dependent on the nature and the number of porphyrinic ligands (mono-bisporphyrinates and/or homo-heteroleptic double-deckers). In most cases, the ESR spectra of gadolinium porphyrinates are anisotropic. Recently water-soluble porphyrin with lanthanide porphyrins was reported to exhibit isotropic g factors.[15] Also, the spectrum with no anisotropic g was obtained in the case of Gd(obp)acac as a pure solid. However, two broad peaks from both sides of an intense signal may imply a superimposed hyperfine splitting (Fig. 3a). This ESR spectrum is totally different from the ESR spectrum of the corresponding gado-

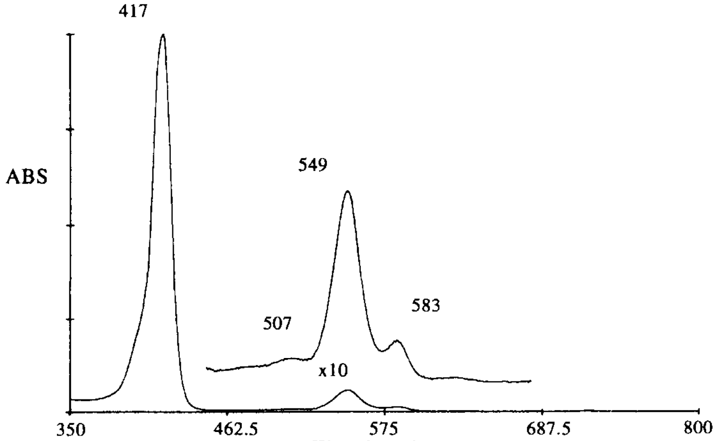

Fig. 2. UV–vis spectrum of Sm(tpfpp)acac in CH_2Cl_2.

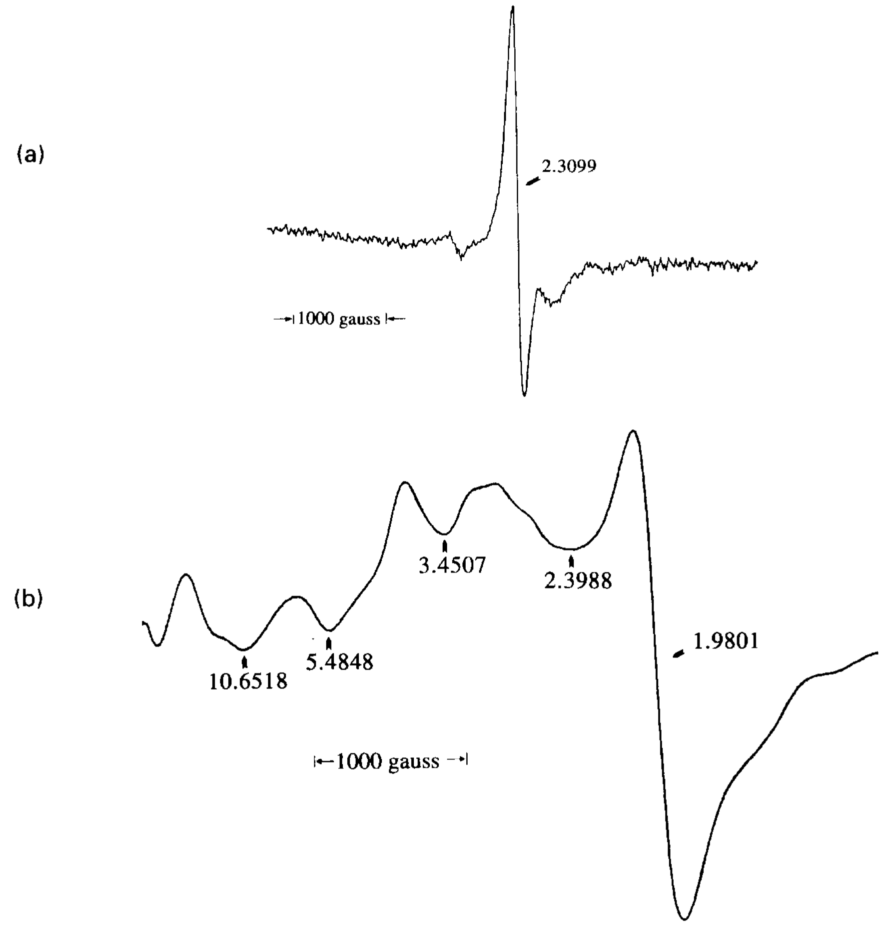

Fig. 3. ESR spectra of (a) Gd(obp)acac and (b) Gd(tpp)acac in the solid state (290 K).

linium(III) monoporphyrinate with the tpp macrocycle (Fig. 3b). The ESR spectrum of the latter complex, Gd(tpp)acac, exhibits a highly anisotropic *g* factor and consisted of six major peaks spread in the region 0–6000 Gauss. This spectrum is typical of an *S*-state ion (Gd^{3+} ground state $^8S_{7/2}$) with a large zero-field splitting. Gadolinium, with a half-filled *f* shell and no orbital angular momentum, is the only trivalent lanthanide ion whose ESR spectrum can be observed routinely at room temperature. However, the bromines on β-pyrrole seem to influence the a_{2u} orbitals (-tpp HOMOs possess a_{2u} symmetry) as the electron-withdrawing substituents on the pyrrole carbons would enhance conjugation with the ring, resulting in delocalization of the ring charge and hence a destabilization of the a_{2u} energy level. The single broad signal with *g* value of 2.3099 of Gd(obp)acac could be explained as due to line broadening as a result of spin–spin interactions. The difference in ESR spectra of Gd(tpp)acac and Gd(obp)acac could be attributed to the destabilization of the a_{2u} energy level of obp compared with tpp and hence to the interaction between porphyrin and metal orbitals.

The spectra of all the other Ln(obp)acac complexes consisted of one intense signal with a *g* value

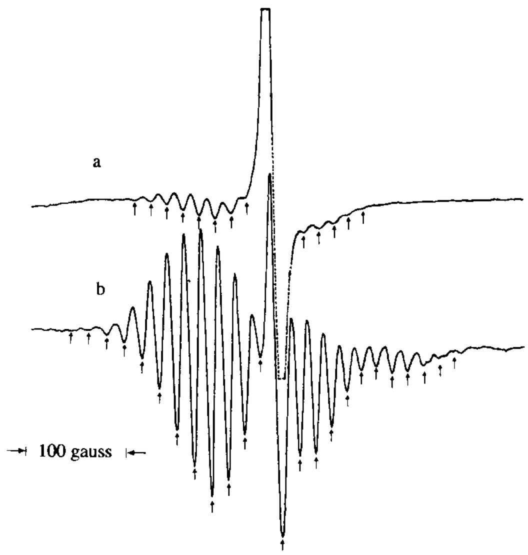

Fig. 4. ESR spectra of (a) Eu(obp)acac and (b) Eu(t-Mepyp)acac in the solid state (290 K).

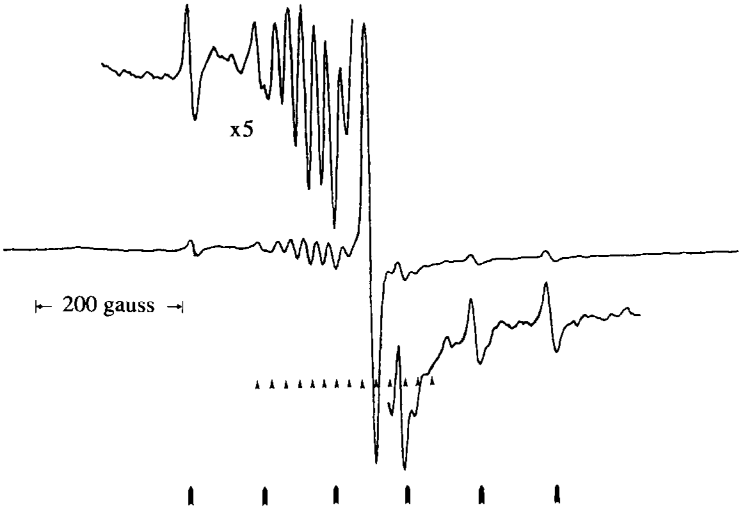

Fig. 5. ESR spectra of Sm(tpfpp)acac in the solid state (290 K).

that indicates the existence of a free radical. The observed hyperfine structure, as for a variety of substituted lanthanide porphyrins, arises by the delocalized unpaired electron density over the pyrrolic nitrogen atoms. Concerning the hyperfine structure between the lanthanide octabromo complexes and tetrakis(N-methyl) porphyrins, a difference has been observed: for the octabromo derivatives the number of lines decreases. This is probably due to the absence of hydrogen atoms in β-pyrrole positions and the perturbation to the unpaired electron density, caused by bromine substituents. The above is well represented in Fig. 4 for the europium complexes.

Fig. 5 illustrates the ESR spectrum of Sm(tpfpp)acac in the solid state at room temperature. Two types of hyperfine interactions are observed. The superhyperfine structure probably due to porphyrinic nitrogens exhibits a coupling constant, $\alpha = 18.5$ G, and peak-to-peak separation, $\Delta H_{pp} = 10.4$ G. The hyperfine structure consisting of six peaks with $\alpha = 101.28$ G and $\Delta H_{pp} = 12.8$ G is probably due to a manganese impurity.

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REFERENCES

1. (a) T. J. McMurry and J. T. Groves, in *Cytochrome P-450: Structure, Mechanism and Biochemistry* (Edited by P. Ortiz de Montellano), Ch. 1. New York (1986); (b) T. C. Bruice, in *Mechanistic Principles of Enzyme Activity* (Edited by J. F. Liberman and A. Greenberg), Ch. 8. VCH Publishers, New York, (1988).
2. (a) M. J. Tornaritis and A. G. Coutsolelos, *J. Polymer Sci.: Part A: Polymer Chem.* 1992, **30**, 2791; (b) M. J. Tornaritis and A. G. Coutsolelos, *Polymer* 1992, **33**, 1771.
3. (a) A. Giradeau, H. J. Callot and M. Gross, *Inorg. Chem.* 1979, **18**, 201; (b) A. Giradeau, H. J. Callot, J. Jordan, I. Ezhar and M. Gross, *J. Am. Chem. Soc.* 1979, **101**, 3857; (c) A. Giradeau, I. Ezhar, M. Gross, H. J. Callot and J. Jordan, *Bioelec. Bioenerg.* 1976, **3**, 519; (d) A. Giradeau, A. Lovati, H. J. Callot and M. Gross, *Inorg. Chem.* 1979, **20**, 769.
4. (a) C. Kirmaier and D. Holten, *Photosynth. Res.* 1987, **13**, 225; (b) D. Budil, P. Gast, M. Schyffer and J. R. Norris, *Ann. Rev. Phys. Chem.* 1987, **38**, 581; (c) L. K. Hancon, *Photochem. Photobiol.* 1988, **47**, 903; (d) R. A. Friesner and Y. Won, *Biochim. Biophys. Acta* 1989, **977**, 99.
5. (a) W. DeW. Horrocks Jr. and C.-P. Wang, *J. Am. Chem. Soc.* 1976, **98**, 7157; (b) W. DeW. Horrocks Jr. and E. G. Hove, *J. Am. Chem. Soc.* 1978, **100**, 4386; W. DeW. Horrocks Jr., R. F. Venteicher, C. A. Spilburg and B. L. Vallee, *Biochem. Biophys. Res. Commun.* 1975, **64**, 317.
6. W. Chau Chin, H. Wu Shiung, T. Yasuo, T. Jui Chang and C. C. Yin, *Nucl. Instrum. Methods Phys. Res., Sect.* 1993, **B75**, 195.
7. (a) A. N. Vedernikov, D. O. Kochnev and B. W. Solomonov, *Zh. Obshch. Khim.* 1993, **63**, 409; (b) A. N. Vedernikov, D. O. Kochnev, D. A. Suslov and B. N. Solomonov, *Dokl. Akad. Nauk.* 1993, **330**, 200.
8. P. Bhyrappa and V. Krishnan, *Inorg. Chem.* 1991, **30**, 239.
9. (a) C. K. Chang and F. J. Ebina, *J. Chem. Soc., Chem. Commun.* 1981, 778; (b) B. De Poorter and

B. Meunier, *Nouv. J. Chim.* 1985, **9**, 393; (c) J. P. Collman, T. Kodadek, S. A. Raybuck, J. I. Brauman and L. M. Papazian, *J. Am. Chem. Soc.* 1985, **107**, 4343.

10. (a) J. N. Phillips, *Rev. Pure Appl. Chem.* 1960, **10**, 35; (b) J. E. Falk, *Porphyrins and Metalloporphyrins*. Elsevier, Amsterdam (1964).
11. M. O. Senge, G. J. Medforth, L. D. Sparks, J. A. Shelnutt and K. M. Smith, *Inorg. Chem.* 1993, **32**, 1716.
12. F. D'Souza, A. Villard, E. Van Caemelbecke, M. Franzen, T. Boschi, P. Tagliatesta and K. M. Kadish, *Inorg. Chem.* 1993, **32**, 4042.
13. J. B. Kim, J. J. Leonard and F. R. Longo, *J. Am. Chem. Soc.* 1972, **94**, 3986.
14. G. A. Spyroulias, M. P. Sioumpara and A. G. Coutsolelos, *Polyhedron*, in press.
15. G. A. Spyroulias and A. G. Coutsolelos, unpublished results.