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Invited Paper

Metal Complexes with Tetrapyrrole Ligands. 47.[1] Yttrium(III) Bis(octaalkylporphyrinate)s: Synthesis and Electron Spin Resonance Spectra of Earth Metal Porphyrin Sandwich Compounds

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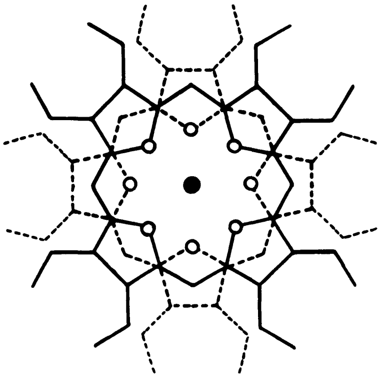
Reaction of tris(2,4-pentanedionato)yttrium(III) with octaethylporhyrin, H_2oep in refluxing 1,2,4-trichlorobenzene (TCB) produces a trace (2%) of the double-decker, Y(oep)$_2$ (**3A**) besides major amounts (72%) of the yttrium(III) monoporphyrinate, Y(oep)(acac) which are separated by chromatography. Appreciable yields of Y(oep)$_2$ (**3A**) (25%) are obtained from dilithium octaethylporphyrinate, Li$_2$(oep), formed in situ and Y(oep)(acac) in refluxing TCB. The constitution of the double-decker **3A** is proved by UV/VIS, IR, ^{1}H NMR, ESR, ENDOR, and mass spectra. The well-defined composition Y(oep)$_2$ requires that one of the porphyrin rings is electron-deficient, i.e. the charge of the Y^{III} ion is compensated by the normal porphyrinate dianion and a porphyrinate monoanion radical. The magnetic moment in the solid state, μ_{eff}=1.5 B.M. (5—100 K), demonstrates the radical nature of **3A** as well. Under the time resolution of the methods used, the unpaired electron is delocalized between the two porphyrin rings. The wavenumber of the internal charge transfer absorption band in the near infrared (λ_{CTI} 1175 nm) agrees well with the value expected for the ionic radius of Y^{III} according the linear relationship of the energy of the CTI band and the ionic radius which has been established for the series of lanthanoid octaethylporphyrinates, Ln(oep)$_2$ (Ln=La···Lu). **3A** can be reduced to the diamagnetic sandwich anion, [Y(oep)$_2$]$^-$. Y^{III} double-decker radicals Y(omp)$_2$ (**3B**; λ_{CTI} 1100 nm) or Y(hbp)$_2$ (**3C**, λ_{CTI} 1100 nm) containing octamethylporphyrin or hexadecahydrotetrabenzoporphyrin have also been prepared.

Sandwich like metal bis(tetrapyrrole)s are known since the first description of tin(IV) bis(phthalocyaninate), Sn(pc)$_2$,[2,3] and the sandwich nature was demonstrated by crystallography in the case of Sn(pc)$_2$ and the actinoid sandwich systems, An(pc)$_2$ (An=Th, U),[4] or the lanthanoid double-deckers, Ln(pc)$_2$.[5] The latter compounds are intensively studied as prospective materials for electrical devices such as semiconductors or color displays.[6]



A

● = M, central metal
○ = N, nitrogen atom

No.	1	2	3	4	5	6
M	Ce	Eu	Y	Ho	Er	Lu

Synthetic investigations on the corresponding porphyrin sandwich systems have been initiated with the cerium(IV) bis[tetra(*p*-tolyl)porphyrinate], Ce(ttp)$_2$, and praseodymium(III) hydrogen bis[tetra(*p*-tolyl)-porphyrinate], PrH(ttp)$_2$.[7] Due to the limited solubility of the former species, the further investigation of the corresponding octaethylporphyrin derivatives M(oep)$_2$ (**A**; M=Ln; Ln=La···Lu save Pm) has been undertaken.[8] The diamagnetic parent compound, the Ce^{IV} sandwich Ce(oep)$_2$ (**1A**) has been fully described and the square antiprismatic geometry shown in **A** demonstrated by X-ray crystallography.[9]

The same geometry obtains for the paramagnetic Eu^{III} sandwich, Eu(oep)$_2$ (**2A**).[1] As in **2A**, the porphyrin rings in all the Ln^{III} double-deckers Ln(oep)$_2$ occur in two different oxidation states: There is a normal (oep)$^{2-}$ dianion, and an electron-deficient radical anion, (oep·)$^{1-}$. These two rings show an internal charge transfer absorption band (CTI band) in the near infrared the energy of which is solely dependent on the ionic radius of the Ln^{III} ion.[10,11] As the radius of the Ln^{III} ion at coordination number 8 increases, the energy of the CTI band decreases,[11] and the redox potential of reaction (1) decreases likewise.[10,12]

$$\mathrm{Ln(oep)_2 + e^- \rightleftarrows [Ln(oep)_2]^-} \qquad (1)$$

Obviously, interelectronic repulsion is less pronounced when the two porphyrin rings have a larger distance. Hence, the electron-rich reduced species is the more stable the larger the Ln^{III} ion is.

The importance of the ionic radius in these double-deckers led to the hypothesis that yttrium(III) derivatives, e.g. Y(oep)$_2$ (**3A**), should be accessible and have redox potentials and energies of CTI bands close to those of Ho(oep)$_2$ (**4A**) or Er(oep)$_2$ (**5A**), because the ionic radii of these metal(III) ions are very similar: Y, 101.5 pm; Ho, 102 pm; Er, 100 pm.[13] Indeed, this idea has been realised. The synthesis and spectral properties of the yttrium(III) porphyrin sandwich compounds Y(oep)$_2$ (**3A**), Y(omp)$_2$ (**3B**), and Y(hbp)$_2$ (**3C**)[3] are described in this paper.

Experimental

Material and Methods. Chemicals and instruments used were the same as previously described[9] if not stated below. Y(acac)$_3$·H$_2$O was prepared following literature methods.[14] Octamethylporphyrin, H$_2$omp, was a gift of Professor R. Guilard, Dijon. Hexadecahydrotetrabenzoporphyrin, H$_2$hbp, was prepared as described by Fuhrhop.[15] Near infrared spectra (Fig. 1) were taken with a Zeiss spectrophotometer DMR 21. The ESR spectra [Fig. 2; Varian X-band, E-line spectrometer; 9.25 GHz; diphenylpicrylhydrazyl (g=2.0036) as calibrant] and the magnetic susceptibility of Y(oep)$_2$ (5—100 K; vibrating reed magnetometer[16]) were obtained by Mr. Weißenberger and Mr. F. Arenz at the Institut für Festkörperphysik, Technische Hochschule Darmstadt (courtesy of Professor B. Elschner). A 0.25 M (1 M=1 mol dm^{-3}) solution of sodium anthracenide in THF was prepared as described elsewhere.[17]

Synthesis of 2,4-Pentanedionato(2,3,7,8,12,13,17,18-octaethylporphyrinato)yttrium(III), Y(oep)(acac). 300 mg (0.56 mmol) octaethylporphyrin and 500 mg Y(acac)$_3$·H$_2$O (1.25 mmol) are heated to reflux in 50 ml TCB under a stream of nitrogen. After 5 h, the cherry-red solution is freed from TCB in vacuo, the residue dissolved in toluene, filtered and chromatographed at alumina (grade I, basic, column 4×6 cm). Elution with toluene yields Fraction 1: traces of Y(oep)(acac) and TCB. A second, red-brown Fraction 2 is eluted with toluene/methanol (100:1) and consists of H$_2$oep and Y(oep)$_2$. The alumina column is now deactivated with water,[8] dried and eluted with THF, whereupon the main product Y(oep)(acac) is obtained as Fraction 3 (bright red). This THF solution is diluted with dichloromethane and extracted several times with water for removal of THF. The dichloromethane phase is filtered, the solvent removed in vacuo and the red-violet powder of Y(oep)(acac) (290 mg, 72%) dried in vacuo. UV/VIS [λ_{max}]: 574 (I), 538 (II), 404 (III), 334 (IV) nm; rel. intens. III>IV≈I>II.[18] IR (KBr): 1605 and 1510 cm^{-1} (bands of the coordinated acetylacetonate ligand[19]). MS (FD): Calcd for Y(oep)(acac), M=720, Found M=720, Calcd for Y(oep)(OAc): M=680, Found M=680. (This peak is due to thermolysis of the coordinated acetylacetonate as observed previously with Sc(oep)(acac).[19])

Fraction 2 is rechromatographed at alumina (grade I, basic, 2×6 cm). With toluene, some H$_2$oep is eluted. With toluene–methanol (200:1), a brownish-red fraction containing 10 mg (2%) of Y(oep)$_2$ (**3A**; see below) is obtained.

Synthesis of Bis(2,3,7,8,12,13,17,18-octaethylporphyrinato)yttrium(III), Y(oep)$_2$ (3A). 4 ml of a 1.6 molar solution of butyllithium in hexane[8] is added dropwise to a solution of 135 mg (0.25 mmol) of H$_2$oep in 50 ml of TCB under argon. After stirring for 1 h at 20 °C, 180 mg (0.25 mmol) Y(oep)(acac) are added and heated to reflux under a rapid stream of argon. The color of the initially red-violet reaction mixture changes to brown after 5 h. The TCB is then removed in a high vacuum at 50 °C. The residue is chromatographed at an alumina column (grade I, basic, 4×8 cm) with toluene. After an orange-yellow forerun of unknown composition, a brown main fraction is eluted which at its end is increasingly contaminated with H$_2$oep. This eluate is evaporated to dryness and rechromatographed as above in order to remove the large amounts of H$_2$oep. The obtained solid is fractionately dissolved in benzene–TCB (5:1) leaving undissolved H$_2$oep which is filtered. Crystallization of the solution yields small black rhombs of **3A** (72 mg, 25%) which are dried in vacuo at 50 °C. Found: C, 74.12; H, 7.58; N, 9.68%. Calcd for **3A**, C$_{72}$H$_{88}$N$_8$Y: 1154.52: C 74.91; H 7.68; N, 9.70%. IR (KBr): 1535 cm^{-1} (oxidation state marker band[20]). MS(FD): Found, M=1154, Calcd for ^{89}Y, M=1153.6. UV/VIS [λ_{max}, (log ε), cyclohexane]: 674 (3.38), 538 (3.88), 374 (5.10), 340 (4.96). NIR [λ_{max} (log ε), cyclohexane]: 1175 (3.83). See also Fig. 1. TLC-R_f value: 0.68 (toluene).

Sodium Bis(2,3,7,8,12,13,17,18-octaethylporphyrinato)yttriate(III) in toluene/tetrahydrofurane. A solution of 5 mg (0.004 mmol) Y(oep)$_2$ (dried in vacuo at 50 °C) in 0.5 ml toluene-d_8 containing a trace of TMS was placed under Ar into a dry NMR tube and seald with a septum cap and Nescoe film. With a Hamilton syringe, 15 µl of 0.25 M sodium anthracenide in THF was added and a ^{1}H NMR spectrum taken (see Table 1); apart from the signals of [Y(oep)$_2$]$^-$, stronger signals of THF and weaker signals of anthracene, toluene, TMS, and H$_2$oep were noted. Afterwards, the red-brown solution was transferred (under air) to a cuvette for absorption spectroscopy. It did not show any absorption in the near infrared (900—2000 nm). UV/VIS (λ_{max}, toluene): 586 (I), 542 (II), 492 (III), 390 (IV) nm; rel. intens. IV>I>III>II. The relatively high intensity of band III is due to the presence of some H$_2$oep.

Synthesis of 2,4-Pentanedionato(2,3,7,8,12,13,17,18-octamethylporphyrinato)yttrium(III), Y(omp)(acac), and Bis(2,3,7,8,12,13,17,18-octamethylporphyrinato)yttrium(III), Y(omp)$_2$ (3B). As described for Y(oep)(acac), 300 mg (0.71 mmol) H$_2$omp and 600 mg (1.5 mmol) Y(acac)$_3$·H$_2$O are reacted and the reaction products separated. After 5 h, besides the expected Y(omp)(acac) (170 mg, 40%) a notable part of the reaction product consisted of **3B**. After chromatography, **3B** (98 mg, 16%) was obtained as a dark brown powder which could not be recrystallized due to its very limited solubility. UV/VIS [λ_{max}], Y(omp)(acac) [dichloromethane]: 574 (I), 538 (II), 404 (III), 334 (IV) nm; rel. intens. III>IV≈I>II. Y(omp)$_2$ [toluene]: 670 (I), 536 (II), 374 (III), 340 (IV) nm, rel. intens. III>IV>II>I. NIR [λ_{max}, toluene]: Y(omp)$_2$, 1100 nm (about the same intensity as the VIS band II). MS (FD), Y(omp)(acac): Found, M=608, Calcd ^{89}Y, M=608; Y(omp)$_2$: Found, M=929, Calcd ^{89}Y, M=929. A TLC-R_f value could not be determined for Y(omp)$_2$: A spot of Y(omp)$_2$ was not visible on attempted chromatography with toluene.

Synthesis of 2,4-Pentanedionato(hexadecahydrotetrabenzo[*b*,*g*,*l*,*q*]porphyrinato)yttrium(III), Y(hbp)(acac). As described for Y(oep)(acac), 300 mg (0.57 mmol) H$_2$hbp and

500 mg (1.25 mmol) $Y(acac)_3 \cdot H_2O$ are reacted and the products separated. Fraction 2 yields 20 mg (3%) $Y(hbp)_2$, Fraction 3 270 mg (66%) Y(hbp)(acac).—UV/VIS (λ_{max}, dichloromethane): 572 (I), 536 (II), 404 (III), 334 (IV); rel. intens. III>IV≈I>II.—MS(FD): Found, M=712; Calcd ^{89}Y, M=712.

Synthesis of Bis(hexadecahydrotetrabenzo[*b,g,l,q*]porphyrinato)yttrium(III), $Y(hbp)_2$ (3C). As reported for **3A**, 135 mg (0.25 mmol) H_2hbp, 4 ml of a 1.6 molar solution of butyllithium, and 180 mg (0.25 mmol) Y(hbp)(acac) are reacted and the products separated. The resulting **3C** is less soluble than **3A** in all usual organic solvents and is obtained as a dark brown powder (51 mg; 18%) by recrystallization from toluene. UV/VIS (λ_{max}, toluene): 670 (I), 536 (II), 374 (III), 340 (IV) nm; rel. intens. III>IV>II>I. NIR (λ_{max}, toluene): 1100 nm (about the same intensity as the VIS band II). TLC-R_f: see note for $Y(omp)_2$.

ENDOR Spectroscopy. A Bruker ER 420 spectrometer was attached to a Dietz 621 computer and equipped with an ENDOR facility described previously[21]. Measurements between 1 and 20 MHz were performed at about 10 K and a ESR frequency of 9.4804 GHz with a sample of $Y(oep)_2$ in frozen toluene solution and recorded in the first derivative mode. The pattern of the weakly coupled proton signals (10—20 MHz; see Fig. 3) was not significantly changed when the measurement were not done at g=2.002(4), but at the tails of the ESR signal.

Results and Discussion

(a) Chemistry. The reaction of lanthanoid acetylacetonates $Ln(acac)_3$ with porphyrins H_2p is normally achieved by heating the reactants in boiling trichlorobenzene for 1—4 h and then produces the monoporphyrin complexes Ln(p)(acac)[22] according Eq. 2.

$$Ln(acac)_3 + H_2p \longrightarrow Ln(p)(acac) + 2Hacac \qquad (2)$$

Prolonged heating (up to 20 h) yields the double-deckers in the tetraarylporphyrin series, e.g. $Ce(ttp)_2$[7] or the double-deckers $Ln(oep)_2$ with Ln=La···Tb[8—10,23] (Eqs. 3, 4).

$$Ln(p)(acac) + H_2p \longrightarrow LnH(p)_2 + Hacac \qquad (3)$$

$$4LnH(p)_2 + O_2 \longrightarrow Ln(p)_2 + 2H_2O \qquad (4)$$

The latter are accompanied by triple-deckers $Ln_2(oep)_3$[8—10,23] for Ln=La···Gd which emerge from reaction (5).

$$LnH(p)_2 + Ln(p)(acac) \longrightarrow Ln_2(p)_3 + Hacac \qquad (5)$$

Obviously, the tendency to form double- and triple-deckers decreases with decreasing ionic radius of the lanthanoid ion and increasing bulkiness of the porphyrin. The later members of the series $Ln(oep)_2$ where Ln=Dy···Lu are not accessible from $Ln(acac)_3$. They have to be prepared by a modified "raise-by-one-story" reaction sequence 6—7 similar to Eqs. 3 and 4 using the monoporphyrin Ln(oep)(acac) and the dilithium complex of octaethylporphyrin, $Li_2(oep)$, which is an unstable material but easily obtained in situ from H_2oep and an excess of butyllithium in inert solvents.[8,24]

$$Ln(oep)(acac) + Li_2(oep) \longrightarrow LnLi(oep)_2 \qquad (6)$$

$$4LnLi(oep)_2 + O_2 \longrightarrow 4Ln(oep)_2 + 2Li_2O \qquad (7)$$

Other feasible starting materials for the synthesis of lanthanoid sandwich complexes would be the lanthanoid dialkylamides. While a uranium(IV) double-decker cannot be made from $U(oep)(acac)_2$ and $Li_2(oep)$,[8] $U(tpp)_2$ has been prepared from $U(NEt_2)_4$ and H_2tpp in refluxing toluene.[25]

Yttrium being similar to Holmium and Erbium as regards their ionic radii, the formation of a double-decker in the reaction of $Y(acac)_3$ with any porphyrin H_2p was not expected. At first, therefore, the monoporphyrinates Y(p)(acac) where prepared from octaethylporphyrin, octamethylporphyrin, and hexadecahydrotetrabenzoporphyrin.[15] However, when $Y(acac)_3$ is reacted with the octaalkylporphyrins, surprisingly, small amounts of double-deckers $Y(p)_2$ (**3A—3C**) are found besides the monoporphyrins Y(p)(acac) [(p)=(oep), (omp), (hbp)]: 2% for **3A**, 16% for **3B**, 3% for **3C**. The obtained yield of **3B** was sufficient to characterize the compound. Therefore, only the synthesis of **3A** and **3C** was performed with the "butyllithium raise-by-one-story" method (Eqs. 3 and 4).[8]

The monoporphyrins Y(p)(acac) are formed in reasonable yields, but have not been fully characterized because Y(tpp)(acac)[26] and Y(oep)(acac)[18] have already been described. It is more probable, however, that all the monoporphyrinates Ln(p)(acac) rather have the composition $Ln(p)(acac)(H_2O)_2$ or similar octacoordinate geometries in view of the known crystal structures[5,27] of lanthanoid phthalocyanines with bidentate acetate or acetylacetonate ligands. Furthermore, bridged binuclear structures may be formed from these monoporphyrinates in solution which still show the molecular ion of Ln(p)(acac) in the mass spectrum after crystallization but give inconsistent elemental analyses for this composition.[28] Therefore, the formula Y(p)(acac) is only used for simplicity.

Equations 4 and 7 imply that an oxidation is involved in the formation of the double-deckers $Ln(p)_2$. For an earth metal ion like Y^{III}, no other oxidation state is available. The oxidation must then involve the porphyrin ligand. Evidence for the presence of a porphyrin radical in $Y(p)_2$ is presented in the later sections.

All the properties of the porphyrin radical vanish in $Y(oep)_2$ when it is reduced to the diamagnetic anion $[Y(oep)_2]^-$. This reduction according Eq. 1[1,8] is done with sodium anthracenide in THF and easily followed by NMR spectroscopy. The oxidation-reduction potential for the pair $Y(oep)_2/[Y(oep)_2]^-$ is −0.21 V (cyclic voltammetry, SCE, DMF, NBu_4PF_6).[10,12]

$Y(oep)_2$ closely resembles its cerium analog: **3A** is rather soluble even in alkanes. However, **3B** and **3C** only have a very limited solubility, like their parent porphyrins and the other metal complexes of the latter. This has precluded a more thorough investigation of **3B** and **3C**.

(b) Identification. Y(oep)$_2$ (**3A**), Y(omp)$_2$ (**3B**), and Y(hbp)$_2$ (**3C**) are identified by optical absorption (UV/VIS and NIR) and mass spectra. The optical absorption spectra of **3A**—**3C** do not have the "normal" appearence[29] of their cerium(IV) analogs, but are typical for species in which the porphyrin ligand is oxidized to a π-radical.[30] Specifically, the bands at 670 nm are reminiscent to strong absorption occurring in Mg(oep)ClO$_4$ (**7**) at about 660 nm.[30b] The bands found in **3A**—**3C** correspond well with those found with all compounds Ln(oep)$_2$ containing Ln^{III} ions.[11]

Furthermore, infrared spectra showing all the typical bands of octaethylporphyrin complexes lacking axial ligands, magnetic measurements and elemental analyses fully identify **3A**. As in the case of Lu(pc)$_2$[5a,31] and Lu(oep)$_2$ (**6A**),[8] the magnetic moment measured in the solid state clearly demonstrates the radical nature of Y(oep)$_2$: μ_{eff}=1.46—1.52 B. M. between 5.4 and 100 K (Curie-Weiss behavior, θ=1.5 K).

The most characteristical property of these double-decker radicals consisting of a noninteracting central metal ion M^{III} or M^{IV}, a porphyrinate dianion (p)$^{2-}$ and a porphyrinate monoanion radical (p$\cdot$)$^-$ is the NIR absorption band which occurs, e.g., for La(oep)$_2$ at 1480 nm,[10,11] Eu(oep)$_2$ at 1280 nm,[10,11,23] Lu(oep)$_2$ at 1135 nm,[10,11] [Ce(oep)$_2$]$^+$ at 1270 nm,[32] and [Ce(ttp)$_2$]$^+$ at 1340 nm.[32] This band is due to an internal charge-transfer complex (electron donor acceptor complex)[33] which is formed between the donor, (p)$^{2-}$, and the acceptor, (p$\cdot$)$^-$.[1,11] Donor and acceptor are combined in the same molecule. In an alternative view, these radicals could be "inverse mixed valence complexes," the mixed valencies not residing on two metals, but rather on two ligands.[1,11] The yttrium doubledeckers clearly fall into this class with their NIR bands for Y(oep)$_2$ (**3A**) at 1175 nm and Y(omp)$_2$ as well as Y(hbp)$_2$ at 1100 nm (see Fig. 1). The value for **3A** indeed coincides with the value for Er(oep)$_2$ (**5A**) at 1175 nm[11] and is very close to the value of Ho(oep)$_2$ (**4A**) at 1180 nm.[11]

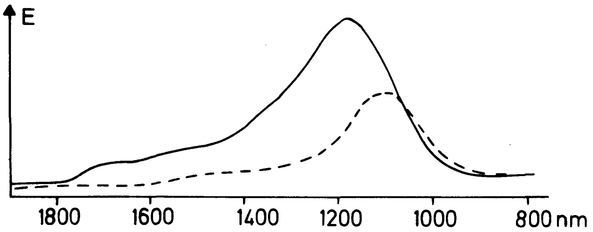


Fig. 1. Near infrared absorption spectra of Y(oep)$_2$ (**3A**) and Y(omp)$_2$ (**3B**) (extinction arbitrary).

A working hypothesis for a explanation of the lower wavelength found with **3B** and **3C** as compared with **3A** is the following: In the octamethyl or hexadecahydrotetrabenzo porphyrin sandwiches, the steric inter-ring repulsion is smaller than in the octaethyl porphyrin sandwich. Hence, the distance of the C$_{20}$N$_4$ mean planes is also smaller, and the electronic properties more closely resemble Lu(oep)$_2$ in which due to the smaller Lu^{III} ion the rings are forced more closely together.

The NIR band found in these double-deckers is reminiscent to the oxidized form [(BChl)$_2$]$^+$ of the "special pair" of bacteriochlorophyll b molecules (BChl)$_2$. [(BChl)$_2$]$^+$ is formed on illumination and has a NIR absorption at 1300 nm in Rhodopseumonas viridis.[34] The redox pair [(BChl)$_2$]$^+$/(BChl)$_2$ corresponds to the redox pairs [Ce(oep)$_2$]$^+$/Ce(oep)$_2$[32] or Y(oep)$_2$/[Y(oep)$_2$]$^-$ (see above). This relationship to the photosynthetic reaction center makes further studies of these double-deckers quite attractive.

(c) ^{1}H NMR Spectroscopy. The ^{1}H HMR spectrum of Y(oep)$_2$ (**3A**, data in Table 1) is much more complicated than the spectrum of Ce(oep)$_2$ (**1A**). This is seen in the chemical shifts and the linewidths of the signals. Most notable is a strong very broad peak at δ 3. This is reminiscent to a very broad peak in the spectrum of [Ce(oep)$_2$]$^+$ [32] at δ 2.25 and a similar peak in the spectrum of Lu(oep)$_2$ (**6A**) at δ 3.06. In fact, these two peaks are the only ones in the spectra of **3A** and **6A** which point to paramagnetism of the compounds. All the other signals appear in regions where the proton signals occur in the diamagnetic reference **1A**. A detailed interpretation of the NMR spectra of **1A** and **2A** is given elsewhere.[1,8,9]

Even the methine signals of **3A** are duplicated, indicating a sandwich system in which one porphyrin ring is slightly different from the other, a situation which is also found in the diamagnetic anions, [Y(oep)$_2$]$^-$ and [Lu(oep)$_2$]$^-$.[8] In the latter, the duplication of the methine signals is due to the formation of an ion pair with a THF-solvated Na$^+$ counter ion which is thought to coordinate to the pyrrole nitrogen atoms on one side of the sandwich system. In the absence of any charges and ions, the diamagnetic species present in **3A** could be a centrally vacant quadruple-decker [M(p)$_2$]$_2$ formed in an association equilibrium (8):

$$2\,\mathrm{M(p)_2} \rightleftharpoons [\mathrm{M(p)_2}]_2 \qquad (8)$$

Monoporphyrin π-radicals, e.g. [Zn(oep)]ClO$_4$,[35] tend to dimerize as well in concentrated solutions and thus form diamagnetic π-π-dimers. The diamagnetic component in the solution of **3A** (and **6A**[8]) can be removed by addition of the radical di-*t*-butyl nitroxide (*t*Bu)$_2$NO, which otherwise acts as a "spin relaxer".[36] Generally, the line width of the NMR spectra of organic radicals is reduced in the presence of

Table 1. ^{1}H NMR Data (300 MHz) of $Y(oep)_2$ (**3A**), Its Reduction Product $Na[Y(oep)_2]$, and $Lu(oep)_2$ (**6A**) Together with the Reference Data of $Ce(oep)_2$ (**1A**)

Compound	Chemical shifts δ, coupling constants J, or line widths $w(1/2)$[a]						
	CH= (e)[b]	CH= (i)[c]	CH_2 (i)	CH_2 (e, 1)[d]	CH_2 (e, 2)[d]	CH_3 (i)	CH_3 (e)
$Ce(oep)_2$	9.11			4.20	3.86		1.68
$[Y(oep)_2]_2$[e]	9.14	9.05	4.17	3.85		1.72	1.62
$Y(oep)_2$							3.00
$Y(oep)_2$[f]	26.8			22.3	14.5		3.16
$w(1/2)$	*125*			*150*	*110*		*68*
δ_{iso}(rad)[g]	17.7			18.3[h]	10.5[h]		1.48
$[Lu(oep)_2]_2$[e]	9.11	9.07	4.23	3.87		1.69	1.61
$Lu(oep)_2$[f]	30.1			23.0	15.0		3.06
$w(1/2)$	*702*			*414*	*234*		*68*
δ_{iso}(rad)[g]	21.0			19.0[h]	11.0[h]		1.38
$[Y(oep)_2]^-$	9.21	9.07	4.42; 4.02	4.30	3.90	1.77	1.60
M[i]	s	s	m m	m	m	t	t

a) δ [ppm] vs. int. TMS; J [Hz] or half widths $w(1/2)$ [Hz] (in italics). b) Methine protons of external (e) ring (outwards of the molecule). c) Methine protons of internal (i) ring (inwards to the molecule). d) 1 and 2 denote exo and endo methylene protons, respectively (assignment arbitrary). e) Presumed dimer present in the concentrated solution. f) Compound measured in presence of spin relaxer $(tBu)_2NO$. g) Isotropic shift of the radical $\delta_{iso}(rad) = \delta_{obs} - \delta_{ref}$ [$Ce(oep)_2$]. h) Reference is $1/2[\delta CH_2(e, 1) + \delta CH_2(e, 2)]$ because of ambiguity of assignment. i) Multiplicity of the signals observed.

other paramagnetic molecules acting as "spin relaxers". Hence, in the presence of $(tBu)_2NO$, the NMR spectrum of the radical **3A** alone becomes visible with all its four broad peaks that are to be expected in comparison to the diamagnetic **1A**. The assignments indicated in Table 1 are based on integrated intensity ratios. The multiplicity of the signals indicates only one set of methyl and two sets of diastereotopic methylene protons. On the NMR timescale, therefore, the two porphyrin rings are identical, and the π-electron hole seems to be delocalized.

The equilibrium (8) for **3A** obviously exists only in solution. Solid **3A** consists of paramagnetic monomers. Otherwise it should be diamagnetic (as is the solid phase of $La(oep)_2$[8]) and not exhibit an ESR spectrum as microcrystalline material in frozen matrices like **7**.[30b]

The isotropic shifts of the radical **3A** using **1A** as a diamagnetic reference are given in Table 1 as $\delta_{iso}(rad) = \delta_{obs} - \delta_{dia}$, along with the corresponding values of **6A**[8] and those calculated for the porphyrin radical contribution from the spectrum of **2A**.[1]

(d) Electron Spin Resonance and Electron Nuclear Double Resonance Spectra. ESR spectra of $Y(oep)_2$ at various temperatures in toluene or frozen toluene are shown in Fig. 2. With $g = 2.002(4)$, this is a typical signal of an organic radical. The line width ΔH_{pp} does not change very much on cooling to 70 K ($\Delta H_{pp} \simeq 4.11$ G at 70 K, 3.52 G at 290 K), but on cooling below 40 K, shoulders appear causing an increase of total spectral extent to ~28 G at 4.2 K together with a slight increase in ΔH_{pp} ($\simeq 4.76$) of the central line (see Fig. 2). The reason for the additional lines is unclear. The slight asymmetry of the shoulders with respect to the central line could be indicative of the presence of a second, chemically different species. ΔH_{pp} at 70 K is slightly larger than that of the signal of the monoporphyrin radical $[Mg(oep)]ClO_4$ (**7**) [$g = 2.0025$ at 223 K; $\Delta H_{pp} \approx 3.5$ G].[30b]

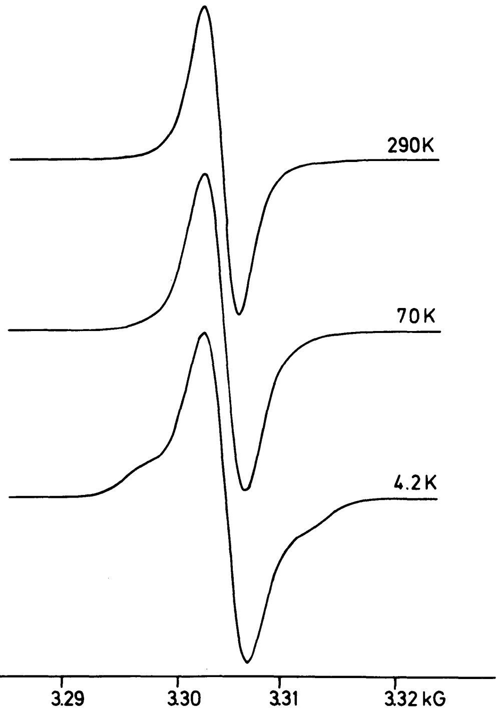


Fig. 2. Electron spin resonance spectrum of $Y(oep)_2$ (**3A**) (derivative mode).

While the spectrum of **7** shows a proton hyperfine structure (HFS) due to the methine H atoms [a_H=1.48 G=0.148 mT], such a fine structure is not distinguishable in the spectrum of **3A**. Under the assumption that the unpaired electron is delocalized between the two rings on the ESR time scale, a_H should be smaller for each contributing nucleus, and the total linewidth be reduced as compared with **7** although the number of contributing nuclei is doubled. The observed somewhat larger width of the signal of **3A** points to a coupling of the electron spin with another nucleus not present in **7**. This could be the ^{89}Y nucleus (100% natural abundance; spin 1/2; $\mu/\mu_N=-0.237$). Radicals derived from oep complexes, like **7**, bear the unpaired electron in the A_{1u} molecular orbital[30b)] which has nodal planes at the four porphyrin nitrogen atoms. There is no spin density at these atoms and hence no ^{14}N-HFS seen. Likewise, in **3A** a ^{14}N hyperfine splitting is not observable. Hence, **3A** is probably also an A_{1u} radical. This is consistent with the visible absorption spectrum.[30b)] Further investigations with meso-deuterated **3A** or Y(tpp)$_2$ would be useful, but the latter compound is hitherto not accessible via the butyllithium raise-by-one-story reaction.

The proton ENDOR spectrum is shown in Fig. 3. Three types of interaction can be distinguished. One is a sharp "matrix proton" line at the free nuclear frequency $\nu_n \simeq 14.5$ MHz; it gives no structural information. Next is a pair of lines displaced symmetrically about ν_n with a coupling of 0.45 MHz; its line shape indicates a dominantly isotropic interaction. The third coupling involves a broad, more powder-type anisotropic pair with 1.1 to 2.0 MHz. The absence of any larger interaction corroborates the notion of a distribution of spin density between the two porphyrin rings. The methine-H coupling in the monoporphyrin radical **7** translates into about 2.64 MHz for the double-decker **3A** whereas twice this value would be expected for the monoporphyrin radical.

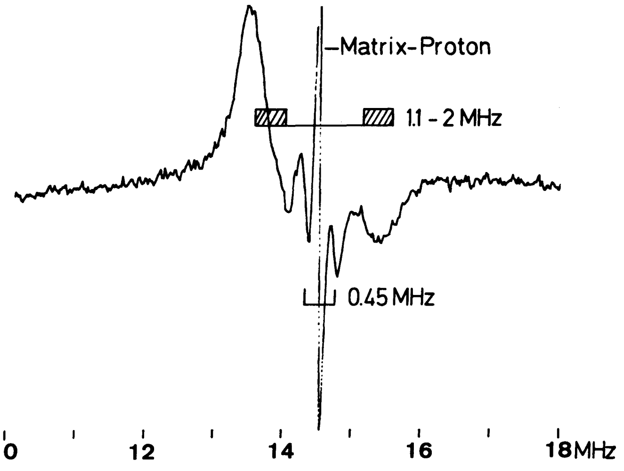


Fig. 3. Electron nuclear double resonance spectrum of Y(oep)$_2$ (**3A**) (proton range, 10—18 MHz).

If we assign the broad line pair in **3A** to the methine protons, the even lower observed (1.1—2.0 MHz) interaction again points to a contribution of the ^{89}Y nucleus onto which some spin density should be transferred. Such an interaction was looked for in the 1—10 MHz frequency region, but the data so far are not interpretable with reliability. The 0.45 MHz proton interaction could be due to the methylene protons of the ethyl groups.

(e) Conclusion. In view of the existence of yttrium(III) phthalocyaninate double-deckers Y(pc)$_2$[37)] and probably also triple-deckers Y$_2$(pc)$_3$,[38)] it is promising for further investigations to have the corresponding porphyrin sandwich **3A** which is much better soluble. With its NIR absorption, any redox reactions can be very easily followed. Indeed, not only the energies of the NIR absorption bands, but also the oxidation reduction potentials for the following steps (9a)—(9c) have been determined accurately in the

$$[\mathrm{M(oep)_2}]^+ \underset{(a)}{\rightleftarrows} \mathrm{M(oep)_2} \underset{(b)}{\rightleftarrows} [\mathrm{M(oep)_2}]^- \underset{(c)}{\rightleftarrows} [\mathrm{M(oep)_2}]^{2-} \qquad (9)$$

porphyrin series for M=Ln (Ln=La···Lu save Pm) and for M=Y (**3A**).[10,12)] The redox potentials associated with reactions (9a) [which is reaction (1) for M=Ln], (9b), and (9c) as well as the energy of the NIR band each lie on a straight line in the series M=La···Lu as the ionic radius decreases. The corresponding values obtained with **3A** fall onto these lines between Ho(oep)$_2$ (**4A**) and Er(oep)$_2$ (**5A**), demonstrating the importance of the ionic radius and the ring–ring distance in these sandwich systems.[10–12)]

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3) Abbreviations used: M, metal; (p)$^{2-}$, (oep)$^{2-}$, (pc)$^{2-}$, (tpp)$^{2-}$, (ttp)$^{2-}$, (omp)$^{2-}$, (hbp)$^{2-}$: dianions of a general porphyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin, phthalocyanine, 5,10,15,20-tetraphenylporphyrin, 5,10,15,20-tetra-

(*p*-tolyl)porphyrin, octamethylporphyrin, hexadecahydrotetrabenzoporphyrin, respectively; Ln: lanthanoid metal; Hacac, acetylacetone; DMF: *N*,*N*-dimethylformamide; HOAc, acetic acid; TCB, 1,2,4-trichlorobenzene; TLC, thin-layer chromatography; NIR, near-infrared; MS(FD), mass spectrum in the field ion desorption mode; THF: tetrahydrofuran; SCE: saturated calomel electrode.

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