

Synthesis, Characterization, and X-ray Study of a Heteroleptic Samarium(III) Porphyrin Double Decker Complex

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Introduction

Lanthanide and actinide porphyrin sandwich and triple-decker complexes of the type $[M^{III}H(por)_2]/[M^{III}(por)_2]^-$, $M^{IV}(por)_2$, and $M^{III}_2(por)_3$ have provided an ideal series of molecules for studying the electronic structure and dynamics of interacting porphyrin macrocycles.^{1,2} Complexes with dissimilar macrocycles are also known and have been studied for derivatives of Ce(IV),^{1m,2f,3,4} Eu(III),^{2c,5} Th(IV),^{2k,6} La(III),²ⁿ or U(IV),⁶ of which $Ce^{IV}(oep)(tpp)^{1m}$ is the only structurally characterized heteroleptic porphyrin double-decker complex. We have recently achieved, via an improved short route, the preparation and isolation of the whole family of "asymmetrical sandwich"

complexes with Lanthanide metal ions, $Ln^{III}H(oep)(tpp)$, where $Ln = Nd \dots Lu$.⁷ We present here the synthesis of $Sm^{III}H(oep)(tpp)$, the first single-crystal X-ray structural study of an asymmetrical double-decker with the metal ion in oxidation state +3 and its characterization by ¹H-NMR, UV-vis, IR, and EPR spectroscopy. These data are compared with those of other $Ln^{III}H(por)_2$ or $Ac^{IV}(por)_2$ complexes. In order to gain a better understanding of the nature of the double-decker, the corresponding oxidized complex has been studied and a comparative spectroscopic analysis is presented.

Experimental Procedures

Absorption spectra were collected on a Perkin-Elmer Lambda 6 (or a Perkin Elmer 330 for near-infrared region) grating spectrophotometer. Near-IR reflectance spectra were recorded on a Varian 2390 UV-vis-near-IR spectrophotometer. Spectra for ϵ measurements were recorded in CH_2Cl_2 (Riedel-de Haen spectral grade) (solutions of 0.05×10^{-3} M). Infrared spectra were recorded on a Perkin-Elmer FT series 1760 spectrophotometer in CsI pellets. ¹H-NMR spectra were recorded on a Bruker AC spectrometer (200 MHz for ¹H) in $CDCl_3$ solutions of 2×10^{-3} M. EPR spectra were recorded at X-band frequency with a Bruker spectrometer ER 200D-SRC at 298 or 77 K, as a pure solid and in CH_2Cl_2 or DMF solutions. Signal g values and intensities were calibrated with a standard diphenylpicrylhydrazyl (dpph) sample ($g = 2.0036$). Magnetic susceptibility measurements on pure solid were recorded on a QUANTUM DESIGN MPMS-5, squid magnetometer.

The complex $Sm^{III}H(oep)(tpp)$ was prepared by the following procedure: in a solution of 0.350 g (0.654 mmol) of $(oep)H_2$ in 30 mL of 1,2,4-tcb, 2.0 mL (3.2 mmol) of $n-BuLi$ (solution of 15% in hexane, Merck for synthesis) was added and the solution remained at room temperature under a slow stream of nitrogen for 15 min. Then, 0.500 g (0.57 mmol) of the monoporphyrinate $Sm^{III}(tpp)(acac)$, freshly prepared,⁸ was added. The solution was refluxed for 3 h. Upon cooling to room temperature, the reaction mixture was applied to a Al_2O_3 column (type Basic I, activated at 150 °C overnight, 4×10 cm), with toluene as eluent and five fractions were collected. The first fraction contained the symmetrical oep -complex while the free base, $(tpp)H_2$, and $Sm^{III}_2(oep)_3$ followed. The asymmetrical $Sm^{III}H(oep)(tpp)$ is obtained in the fourth fraction, though contaminated by traces of $(tpp)H_2$ and $Sm^{III}_2(oep)_3$. The last fraction containing $Sm^{III}H(tpp)_2$ is easily eluted with CH_2Cl_2 along with traces of unreacted $(oep)H_2$. In order to obtain analytically pure $Sm^{III}H(oep)(tpp)$ a second, chromatographic separation by a "dry" column of Al_2O_3 , (type Basic I, 4×8 cm) is carried out with the first eluent a mixture of petroleum ether/diethyl ether 8:2 and then 7:3 to elute double- and triple-deckers with oep ring and $(tpp)H_2$ while their remaining traces are finally removed by elution with diethyl ether/ CH_2Cl_2 (100:1). Elution with CH_2Cl_2 yields 0.156 g of pure $Sm^{III}H(oep)(tpp)$: yield 21% after recrystallization by slow evaporation of a saturated toluene solution. Anal. Calcd for $[Sm^{III}H(oep)(tpp)][PhCH_3]$, $C_{87}N_8H_{81}Sm$ (mol wt 1296.91): C, 75.23; H, 5.88; N, 8.07. Found: C, 75.50; H, 5.39; N, 8.61. UV-vis data for $Sm^{III}H(oep)(tpp)$: CH_2Cl_2 , (20 °C, $\times 10^{-3} dm^3 \cdot mol^{-1} \cdot cm^{-1}$ in parentheses) 400 (Soret) (161.38), 454 (15.77), 557 (8.49), 617

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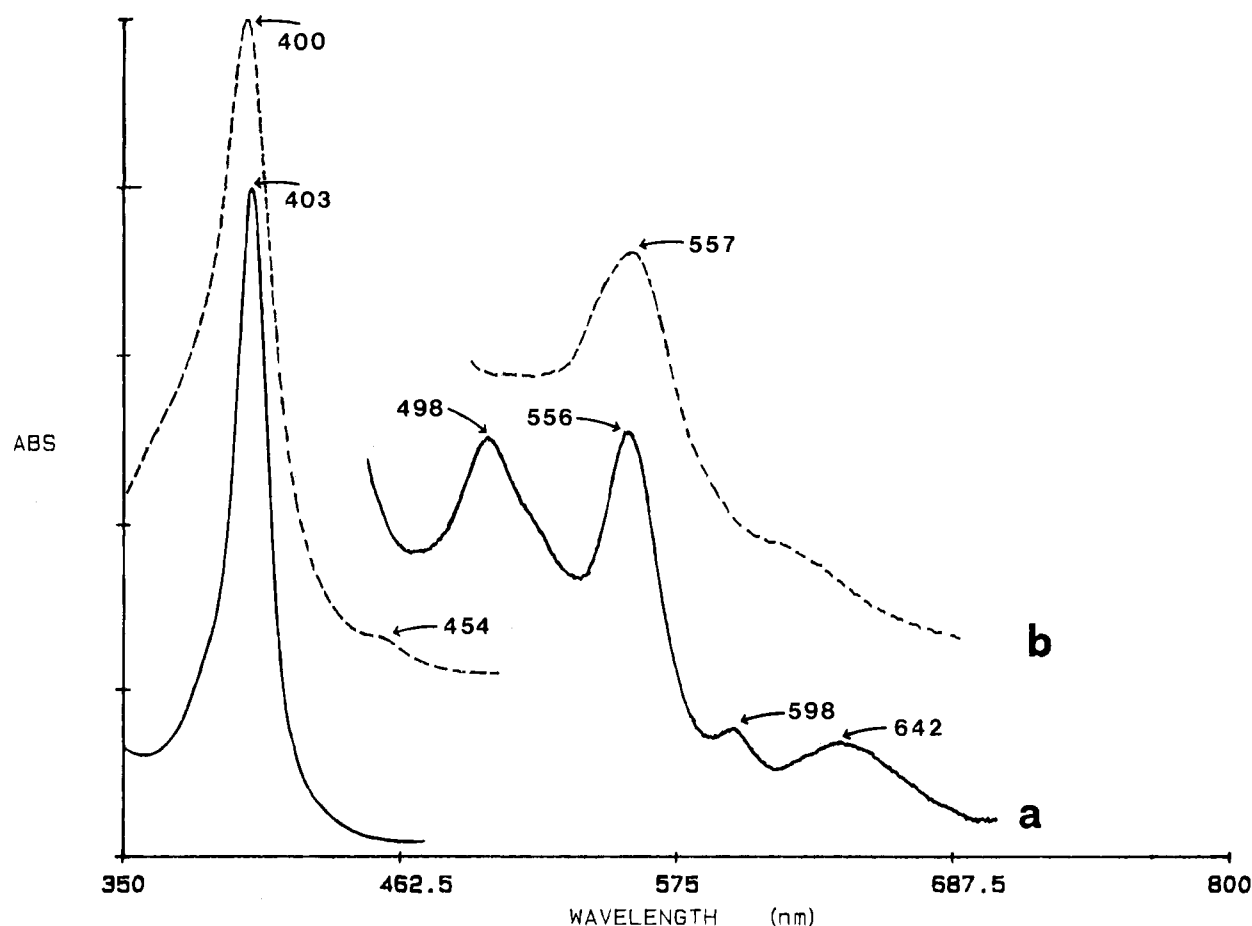


Figure 1. Absorption spectra in detail, of $\text{Sm}^{\text{III}}\text{H}(\text{oep})(\text{tpp})$ in DMF (a) and CH_2Cl_2 (b), respectively.

(3.30) and DMF (20 °C, $\times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in parentheses) 403 (Soret) (281.59), 498 (8.97), 556 (10.72), 598 (4.15), 641 (2.59). ^1H -resonance of $\text{Sm}^{\text{III}}\text{H}(\text{oep})(\text{tpp})$ spread over 45 ppm. The methylene hydrogens of the oep ring resonate at 28.2 and 20.2 ppm while the methine and the methyl hydrogens resonate at 28.9 and 3.9 ppm, respectively. The protons of the tpp ring give signals at 8.8 and 6.7 ppm (*o*-H) and 8.46 and 7.86 ppm (*m*-H), while *p*-H and pyr-H resonate at 8.31 and -16.9 ppm, respectively.⁹ The N-H vibration mode has been observed as a weak peak at 3258 cm^{-1} .

Results

In order to thoroughly investigate the electronic properties of the sandwich-like porphyrin complexes, asymmetrical complexes, with two different tetrapyrrolic ligands have been synthesized.

In CH_2Cl_2 the UV-visible spectrum of $\text{Sm}^{\text{III}}\text{H}(\text{oep})(\text{tpp})$ exhibits intermediate features of the two symmetrical double-deckers with oep and tpp rings with the Soret band at 400 nm. This band is blue-shifted (9 nm) compared to the $\text{Sm}^{\text{III}}\text{H}(\text{tpp})_2$ and red-shifted (21 nm) compared to the corresponding oep double-decker. Figure 1 shows in detail, the differences in the absorption spectra at the UV-visible region of this double-decker, in CH_2Cl_2 and DMF solutions respectively. A comparison with literature data^{2k,7} shows that the spectrum in DMF presents the same features as the corresponding actinide double-deckers, where the metal ion is at +4 oxidation state (both porphyrin ligands are dianions). The reason for this change of

the spectrum can be attributed to an equilibrium between the protonated and deprotonated forms of the complex. The protonation process is solvent-dependent; in CH_2Cl_2 the protonated form is present, while in basic solvents, such as DMF or pyridine (DMF's basicity probably is not due to itself but to one of its decomposition product, Me_2NH), the deprotonated form becomes dominant and the formula $[\text{Sm}^{\text{III}}(\text{oep})(\text{tpp})]^-$ can be postulated. No near-IR absorption band in the region between 800 and 1600 nm has been observed in CH_2Cl_2 for the above complex. At this point it should also be noted that the band at 454 nm is a common feature⁸ of all $\text{Ln}^{\text{III}}\text{H}(\text{oep})(\text{tpp})$ in CH_2Cl_2 , and it is not observed at the same wavelength for $\text{Ln}^{\text{III}}\text{H}(\text{tpp})_2$. The position of the Soret maximum of the oxidized sandwich complex, in CH_2Cl_2 , is blue shifted relative to those of the neutral species.

The $\text{Sm}^{\text{III}}\text{H}(\text{oep})(\text{tpp})$ is EPR active in the solid state, even at room temperature (Figure 2). It exhibits a hyperfine structure with two groups of eight non-symmetrical peaks with a peak to peak separation $\Delta p_p = 16.9 \text{ G}$. The proposed oxidation state for the central ion is also supported by the magnetic measurements. In the solid state, $\text{Sm}^{\text{III}}\text{H}(\text{oep})(\text{tpp})$ displayed a magnetic moment of $1.62 \mu_B$ at 300 K, and it is in good agreement with reported μ_B for Sm^{III} , 1.55–1.65,¹⁰ thus confirming the +3 oxidation state and $S = 5/2$. At 4.94 K, the magnetic moment drops to $0.828 \mu_B$. The formula of $\text{Sm}^{\text{III}}\text{H}(\text{oep})(\text{tpp})$ may be represented by the following two compositions: $[\text{Sm}^{3+}/(\text{oep})^{2-}/(\text{tppH})^-]$ or $[\text{Sm}^{3+}/(\text{tpp})^{2-}/(\text{oepH})^-]$. These formulas indicate the presence of a proton on the tpp or oep as has been mentioned before.

(9) According to our studies: ^1H -NMR $\text{Sm}^{\text{III}}\text{H}(\text{tpp})_2$ (CDCl_3 , 18 °C), δ 10.66 (*o*-endo H), 10.41 (*m*-endo H), 7.63 (*p*-H), 7.37 (*o*-exo H), 4.45 (*m*-exo H), -16.20 (pyrrole-H).

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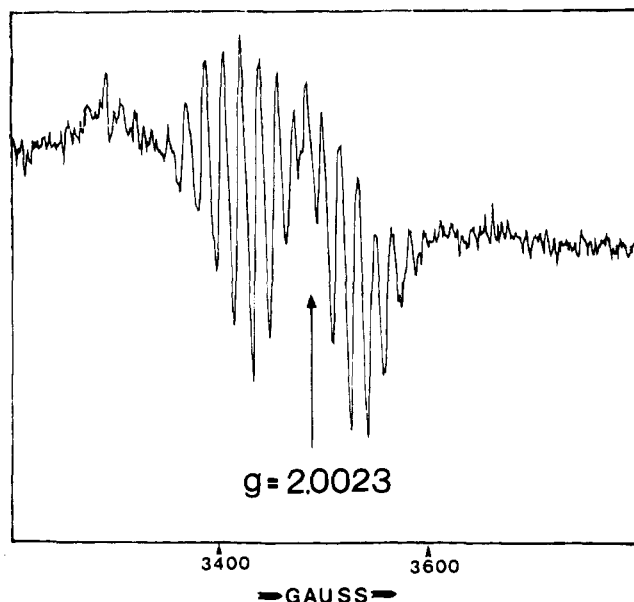


Figure 2. EPR spectra of $\text{Sm}^{\text{III}}\text{H}(\text{oep})(\text{tpp})$ in the solid state at 298 K at 10.0% in MgSO_4 .

The NMR spectrum of the complex (see Experimental Procedures), exhibits mixed features of the two symmetrical sandwich complexes.⁹ The extremely large shift of pyrrolic hydrogens has been observed in some other lanthanide sandwich complexes¹¹ and also for the $[(\text{tpp})_2\text{U}][\text{SbCl}_6]$ ¹¹ and $[\text{U}(\text{oep})(\text{tpp})][\text{SbCl}_6]$.⁷

The complex $\text{Sm}^{\text{III}}\text{H}(\text{tpp})(\text{oep})$ has also been structurally characterized by X-ray crystallography (Figure 3).¹² The asymmetric unit contains one discrete double-decker molecule and one toluene molecule. The packing diagram of $\text{Sm}^{\text{III}}\text{H}(\text{oep})(\text{tpp})$ displays the same interaction between perpendicularly oriented phenyl groups on neighboring molecules which is a common feature of a large class of lattice clathrates known as porphyrin sponges.¹³ The coordination polyhedron of the Sm^{III} is a square antiprism. The porphyrin rings are rotated by an angle of 45.016° (mean value) with respect to their eclipsed position. The mean bond length of $\text{Sm}-\text{N}(\text{tpp})$ is $2.538(4)$ Å and that for $\text{Sm}-\text{N}(\text{oep})$ is $2.563(4)$ Å (see supplementary

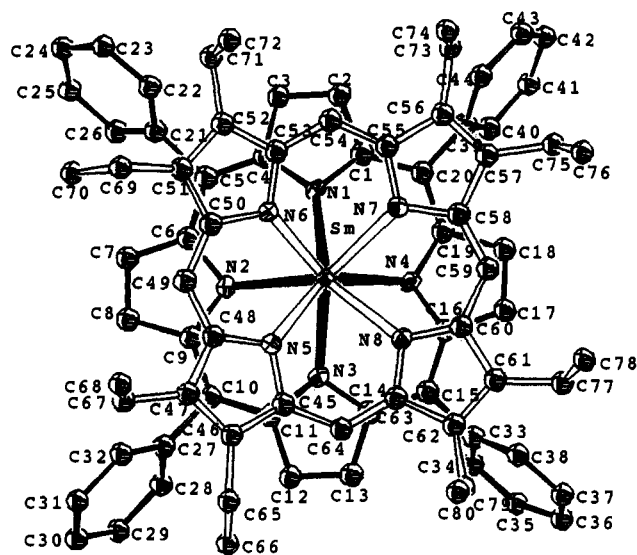


Figure 3. structure of $\text{Sm}^{\text{III}}\text{H}(\text{oep})(\text{tpp})$. Rotations: 2.0 about x , 6.0 about y , and 25.0 about z . Selected bond distances (Å): $\text{Sm}-\text{N}(1)$ 2.489(4), $\text{Sm}-\text{N}(2)$ 2.551(4), $\text{Sm}-\text{N}(3)$ 2.603(5), $\text{Sm}-\text{N}(4)$ 2.509(4), $\text{Sm}-\text{N}(5)$ 2.533(4), $\text{Sm}-\text{N}(6)$ 2.555(4), $\text{Sm}-\text{N}(7)$ 2.619(5), $\text{Sm}-\text{N}(8)$ 2.553(4).

material). The samarium ion lies at 1.470 and 1.516 Å from the $\text{N}_1\text{N}_2\text{N}_3\text{N}_4$ and $\text{N}_5\text{N}_6\text{N}_7\text{N}_8$ planes of tpp and oep respectively. The corresponding $\text{M}-\text{N}$ mean bond lengths for $\text{Ce}^{\text{IV}}(\text{tpp})(\text{oep})^{\text{Im}}$ are 2.480(1) and 2.471(1) Å; this reversal in the mean bond lengths suggests that the proton is residing on the oep ring and complex may be represented by the formula $\text{Sm}^{\text{III}}(\text{oepH})(\text{tpp})$. The separation of the two N_4 mean planes is 2.986 Å. The two mean planes $\text{N}_1\text{N}_2\text{N}_3\text{N}_4$ (tpp) and $\text{N}_5\text{N}_6\text{N}_7\text{N}_8$ (oep) are almost parallel, their dihedral angle being only 0.858° . The four pyrrole rings form the following dihedral angles with the $\text{N}_1\text{N}_2\text{N}_3\text{N}_4$ plane of the tpp : $\text{C}_1\text{C}_2\text{C}_3\text{C}_4\text{N}_1$, 18.129° ; $\text{C}_6\text{C}_7\text{C}_8\text{C}_9\text{N}_2$, 8.915° ; $\text{C}_{11}\text{C}_{12}\text{C}_{13}\text{C}_{14}\text{N}_3$, 5.223° ; $\text{C}_{16}\text{C}_{17}\text{C}_{18}\text{C}_{19}\text{N}_4$, 10.344° . For the oep the dihedral angles of the pyrrole rings with the $\text{N}_5\text{N}_6\text{N}_7\text{N}_8$ plane are as follows: $\text{C}_{45}\text{C}_{46}\text{C}_{47}\text{C}_{48}\text{N}_5$, 14.874° ; $\text{C}_{50}\text{C}_{51}\text{C}_{52}\text{C}_{53}\text{N}_6$, 17.305° ; $\text{C}_{55}\text{C}_{56}\text{C}_{57}\text{C}_{58}\text{N}_7$, 9.345° ; $\text{C}_{60}\text{C}_{61}\text{C}_{62}\text{C}_{63}\text{N}_8$, 17.433° . The distance d_{CN} of the C_{20}N_4 mean plane and the N_4 mean plane which is the measure of the observed doming in such complexes is 0.233 Å for the tpp and 0.316 Å for the oep indicating that the oep ring is somewhat more deformed. Thus, the two mean planes of the core atoms, C_{20}N_4 , of the individual macrocycles are 3.535 Å apart from each other. The average of the dihedral angles δ of the individual pyrrole rings with respect to the corresponding C_{20}N_4 mean plane are as follows: (tpp) 10.68° ; (oep) 14.69° . These values corroborate the stronger doming of the oep ring. The mean displacement of the core atoms from their mean plane is as follows: for the tpp ($\text{C}_1-\text{C}_{20}\text{N}_1-\text{N}_4$), 0.123 Å, and for the oep ($\text{C}_{45}-\text{C}_{64}\text{N}_5-\text{N}_8$) 0.175 Å. The individual pyrrole rings are planar within experimental error. The phenyl rings of the tpp form the following dihedral angles with the C_{20}N_4 plane: $\text{C}_{21}-\text{C}_{26}$, 66.373° ; $\text{C}_{27}-\text{C}_{32}$, 60.159° ; $\text{C}_{33}-\text{C}_{38}$, 77.027° ; $\text{C}_{39}-\text{C}_{44}$, 65.285° . They are situated just above and between neighboring ethyl groups of the oep ring, which is in agreement with the high-field shift of the methyl protons.

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- (11) -14.65 ppm for $\text{Nd}^{\text{III}}\text{H}(\text{tpp})_2$, and -15.7 ppm for $\text{Eu}^{\text{III}}\text{H}(\text{tpp})_2$.
 (12) X-ray crystal structure determination: slow crystallization from toluene yielded purple prismatic crystals. Diffraction measurements were made on a P2, Nicolet diffractometer upgraded by Crystal Logic using Zr-filtered Mo-radiation. The structure was solved by direct methods with SHELXS-86 and refined by full-matrix least-squares methods on F^2 using SHELXL-92. Crystal intensity collection and refinement data are given as follows: formula, $\text{C}_{87}\text{H}_{80}\text{N}_8\text{Sm}$; fw 1387.94; crystal system, triclinic; $a = 10.512(1)$ Å, $b = 13.285(1)$ Å, $c = 26.682(1)$ Å; $\alpha = 95.093(2)^\circ$, $\beta = 95.227(2)^\circ$, $\gamma = 107.495(2)^\circ$; $Z = 2$; $V = 3512.8(3)$ Å³; $d_{\text{calcd}} = 1.312$ mg·m⁻³; $\mu = 0.852$ mm⁻¹; space group, $P\bar{1}$; crystal size, $0.20 \times 0.18 \times 0.07$ mm; scan mode/speed, $\theta-2\theta/3.0$ deg/min; scan range, $2.4 + \alpha_1\alpha_2$ separation; θ range, $2.29-22.75^\circ$; temperature, 295 K; octants, $\pm h, \pm k, \pm l$; reflections collected/unique/used, 9673/9221 ($R_{\text{int}} = 0.0134$)/9220 (all data used in refinement based on F^2 except of one bad reflection rejected); $F(000)$ 1440; maximum absorption correction factor, 1.40; $[\Delta\sigma]_{\text{max}} = 0.045$; $[\Delta/\rho]_{\text{max}}/[\Delta/\rho]_{\text{min}}$, 1.872/−1.333 e/Å³; refining parameters 894; $R_1 = \sum|F_o - F_c|/\sum|F_o| = 0.0458$ [$I < 2\sigma(I)$]; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.1251$; GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2} = 1.114$; for all data, $R_1 = 0.0575$, $wR_2 = 0.1399$, GOF = 1.210; weighting scheme $W = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ $a = 0.0753$, $b = 6.5304$, $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$. Sheldrick, G. M. SHELXS-86 Structure Solving Program, University of Göttingen, Germany, 1986. Sheldrick, G. M. SHELXL-92 Program for Crystal Structure Refinement, University of Göttingen, Germany, 1992.
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surements, and Prof. C. E. Strouse and the two reviewers for their insightful comments. We are also grateful to John Boutari and Son Co. for financial support to C.P.R.

Supplementary Material Available: Tables of positional and equivalent thermal parameters, bond distances and angles, and positional

and isotropic thermal parameters of the hydrogen atoms for $\text{Sm}^{\text{III}}\text{H}(\text{oep})(\text{tpp})$ (12 pages). Ordering information is given on any current masthead page.

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