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Lanthanide porphyrazine sandwich complexes: synthetic, structural and spectroscopic investigations

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The synthesis of four novel lanthanide tetraazaporphyrin (porphyrazine) sandwich complexes is reported: $[Ce(OPTAP)_2]$ (**2**), $[Lu(OPTAP)_2]$ (**3**), $[Eu(OPTAP)_2]$ (**4**) and $[Eu_2(OPTAP)_3]$ (**5**) (OPTAP = 2,3,7,8,12,13,17,18-octapropyltetraazaporphyrinato). The structure of **2** has been unequivocally established by an X-ray crystallographic study. The π radical nature of **3** and **4** has been confirmed by UV-vis, IR, and EPR spectroscopy. Cyclic voltammetry results show that **2**–**5** are more easily oxidized than **1** (H_2OPTAP) by 0.41, 0.56, 0.48 and 0.40 V respectively.

Introduction

Sandwich-type metal complexes of tetrapyrrolic macrocycles have been known since 1936, with the first synthesis of a tin(IV) bis(phthalocyanine) by Linstead and co-workers,[1] and are of great interest because of their unique physical, spectroscopic and electrochemical properties. Bis(phthalocyaninato)-lutetium(III), for example, is the first intrinsic semiconductor in thin films and one of the most promising electrochromic display materials.[2] These characteristic features are a consequence of strong π–π interactions due to the close proximity by which the two macrocycles are held together through the metal ion. It is well-known that such interactions also play an important role in natural systems, and in particular porphyrin sandwich complexes have been studied as models for the photosynthetic "special pair".[3]

Homoleptic bis(phthalocyanines) of transition,[4] lanthanide[5,6] and actinide[7] metal ions have been described. Similarly, since Buchler's first synthesis of a Ce^{IV} bis(porphyrinate) in 1983,[3] sandwich compounds of transition,[8] lanthanide[9–12] and actinide[13] metal ions containing the same porphyrinato ligand have been extensively studied and structurally characterised. Also heteroleptic analogues with mixed phthalocyanines[14] and/or porphyrins[15,16] have received increased attention over the past decade. In contrast, sandwich complexes of the structurally related porphyrazine (tetraazaporphyrin) macrocycles are scarce and have only been reported with lutetium[17] and zirconium.[18,19]

Previously we reported the preparation of thioporphyrazines having n = 1 to 4 pyrrolodithiolates incorporated into the macrocycle and corresponding polymetallic complexes of these ligands.[20,21] More recently, we described the preparation of *chiral* porphyrazinols,[22] related aminoporphyrazines[23] and multimetallic complexes of the latter.[24] We have also reported a new family of tetraazamacrocycles in which one of the pyrrole rings is cleaved (seco-porphyrazines),[25] and the synthesis of *trans*-heterofunctionalized porphyrazine derivatives.[26] In continuation, herein we now report full experimental and spectroscopic data for the four novel octapropylporphyrazine sandwich complexes **2**–**5**. The structure of the cerium sandwich compound **2** has been unequivocally established by an X-ray crystallographic study.

Experimental

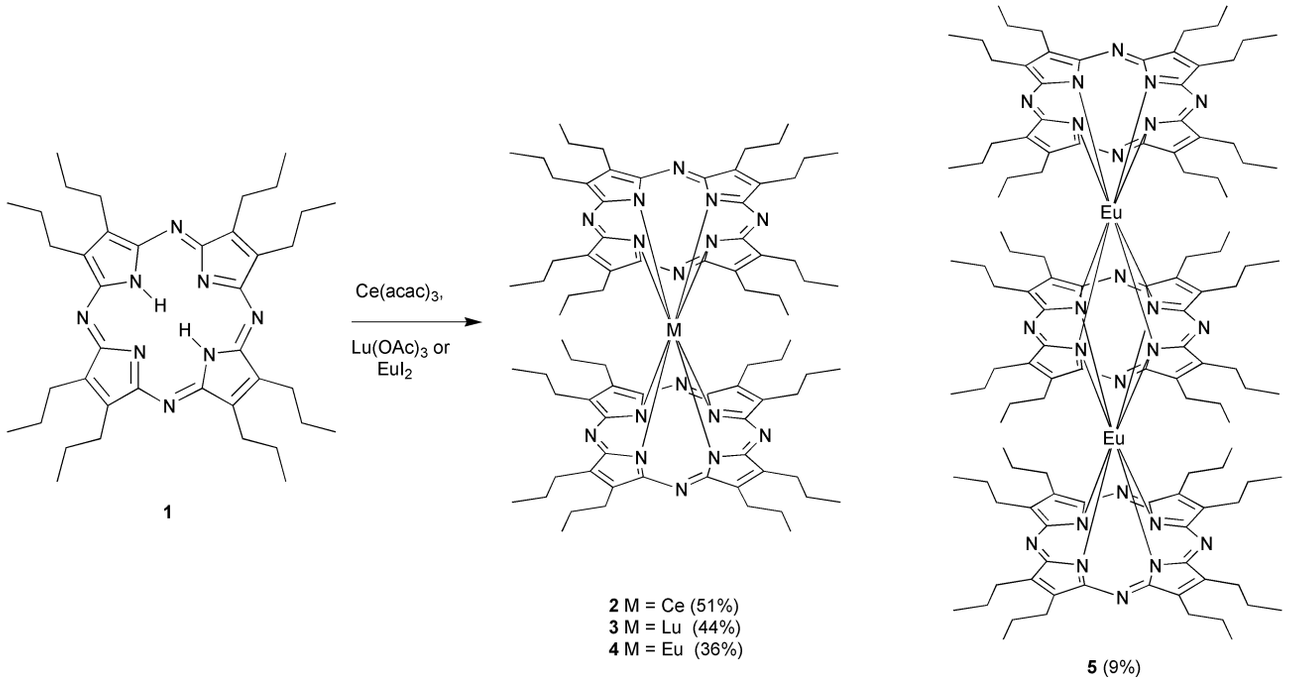
General procedures

All reactions were conducted in oven or flame dried glassware. Hexanes refers to the petroleum fraction with bp 40–60 °C. All other reagents were used as commercially supplied. TLC was carried out on E. Merck precoated silica gel 60 F_{254} plates which were visualized using UV radiation (254 nm). Chromatography refers to gravity chromatography on E. Merck silica gel 60, 40–60 μm. Size exclusion chromatography was performed on Bio-Beads SX3. The octapropylporphyrazine **1**[27] and phenoxathiin hexachloroantimonate[28] were prepared according to published procedures. Electron paramagnetic resonance (EPR) spectra were measured using a modified Varian E-4 X-band spectrometer.

Syntheses

Bis[2,3,7,8,12,13,17,18-octapropylporphyrazinato]cerium(IV) (2). To a suspension of octapropylporphyrazine **1** (20 mg, 31 μmol) in 1,2,4-trichlorobenzene (5 mL) was added $Ce(acac)_3 \cdot H_2O$ (6.8 mg, 15 μmol) and the mixture heated to reflux for 24 h under N_2. The reaction mixture was allowed to cool and filtered (Celite), and the solids were washed with CH_2Cl_2. Evaporation of the solvent under reduced pressure followed by chromatography (hexanes : CH_2Cl_2 9 : 1) and gel filtration (CH_2Cl_2) gave $Ce(OPTAP)_2$ **2** (11 mg, 51%) as a dark purple solid, mp >350 °C (MeOH, decomp); R_f 0.80 (hexanes : CH_2Cl_2 2.3 : 1); ν_{max}/cm^{-1} (CH_2Cl_2) 2959, 2932, 2870, 1463, 1364, 1255, 1150, 1088, 1012, 953; λ_{max}/nm (CH_2Cl_2) 326 (log ε 5.01), 470 (4.12), 584 (4.87); δ_H(300 MHz, $CDCl_3$) 1.22 (t, J = 7.3 Hz, 48H, $-CH_3$), 1.98–2.10 (m, 32H, CH_3-CH_2-), 3.57–3.62 (m, 16H, -C*H*H-TAP), 3.93–4.00 (m, 16H, -CH*H*-TAP); δ_C(75 MHz, $CDCl_3$) 14.9, 25.2, 28.3, 140.1, 158.1; MS (FAB) m/z 1437 ($M^{+\bullet}$); HRMS (FT-ICR) Calcd for $C_{80}H_{112}CeN_{16}$: ($M^{+\bullet}$), 1436.8286, found: ($M^{+\bullet}$), 1436.8048. Slow evaporation of a solution of sandwich complex **2** in acetone/water (1 : 1) at 4 °C gave iridescent purple crystals suitable for an X-ray crystallographic study.

Bis[2,3,7,8,12,13,17,18-octapropylporphyrazinato]lutetium(III) (3). To a suspension of octapropylporphyrazine **1** (40 mg, 62



1

2 M = Ce (51%)
3 M = Lu (44%)
4 M = Eu (36%)

5 (9%)

Scheme 1

μmol) in dry redistilled (from Mg) hexanol (10 mL) was added $Lu(OAc)_3 \cdot H_2O$ (11.5 mg, 31 μmol) and the mixture heated to reflux for 24 h under N_2. The reaction mixture was allowed to cool and filtered (Celite), and the solids were washed with CH_2Cl_2. Evaporation of the solvent under reduced pressure followed by chromatography (hexanes : CH_2Cl_2 9 : 1) and gel filtration (CH_2Cl_2) gave $Lu(OPTAP)_2$ **3** (20 mg, 44%) as a dark purple solid, mp >350 °C (MeOH, decomp); R_f 0.82 (hexanes : CH_2Cl_2 2.3 : 1); ν_{max}/cm^{-1} (film) 2957, 2928, 2869, 1736, 1453, 1356, 1297, 1234, 1150, 1087, 1011, 952; λ_{max}/nm (CH_2Cl_2) 318 (log ε 5.16), 496 (4.03), 588 (4.77), 789 (3.57); MS (FAB) *m/z* 1473 ($M^{+\bullet}$); HRMS (FT-ICR) Calcd for $C_{80}H_{112}LuN_{16}$: ($M^{+\bullet}$), 1471.8640, found: ($M^{+\bullet}$), 1471.8406.

Bis[2,3,7,8,12,13,17,18-octapropylporphyrazinato]-europium(III) (4) and tris[2,3,7,8,12,13,17,18-octapropylporphyrazinato]dieuropium(III) (5). To a suspension of octapropylporphyrazine **1** (10 mg, 15 μmol) in dry redistilled (from Mg) hexanol (10 mL) was added EuI_2 (6.1 mg, 15 μmol) and the mixture heated to reflux for 24 h under N_2. The reaction mixture was allowed to cool and filtered through a plug of silica, and the solids were washed with CH_2Cl_2. Evaporation of the solvent under reduced pressure followed by chromatography (hexanes : CH_2Cl_2 9 : 1) or gel filtration (CH_2Cl_2) gave $Eu_2(OPTAP)_3$ **5** (1 mg, 9%) as a dark purple solid, mp >200 °C (MeOH, decomp); R_f 0.80 (hexanes : CH_2Cl_2 2.3 : 1); ν_{max}/cm^{-1} (film) 2955, 2915, 2848, 1462, 1375, 1234, 1150, 1087, 1012, 951; λ_{max}/nm (CH_2Cl_2) 329 (log ε 4.82), 487 (3.90), 580 (4.40); MS (FAB) *m/z* 2250 ($M^{+\bullet}$); HRMS (FT-ICR) Calcd for $C_{120}H_{169}Eu_2N_{24}$: $(M + H)^+$, 2251.2404, found: $(M + H)^+$, 2251.2412, followed by $Eu(OPTAP)_2$ **4** (4 mg, 36%) as a dark blue solid, mp 240–50 °C (MeOH); R_f 0.74 (hexanes : CH_2Cl_2 2.3 : 1); ν_{max}/cm^{-1} (film) 2956, 2921, 2851, 1735, 1461, 1376, 1341, 1291, 1234, 1127, 1086, 1040, 1005; λ_{max}/nm (CH_2Cl_2) 320 (log ε 4.96), 595 (4.52), 783 (3.31); MS (FAB) *m/z* 1450 ($M^{+\bullet}$); HRMS (FAB) Calcd for $C_{80}H_{112}EuN_{16}$: ($M^{+\bullet}$), 1447.8444, found: ($M^{+\bullet}$), 1447.8586.

Electrochemistry

Cyclic voltammetry data were recorded with a Cypress Systems 2000 computer-controlled potentiostat. A three electrode configuration was employed: a platinum disk working electrode, a silver wire counter electrode, and a silver–silver chloride reference electrode. Measurements were made in CH_2Cl_2, freshly distilled from CaH_2, with $Bu_4N \cdot PF_6$ as the supporting electrolyte. All measurements were calibrated by addition of ferrocene as an internal reference, and $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 110 mV s^{-1}.

Crystallography

Crystal data for **2**: $C_{80}H_{112}CeN_{16}$, M = 1438.0, monoclinic, space group *Cc* (no. 9), a = 32.094(2), b = 9.617(1), c = 27.840(1) Å, β = 112.66(1)°, V = 7930.1(8) Å^3, Z = 4, D_c = 1.204 g cm^{-3}, μ(Cu-Kα) = 48.3 cm^{-1}, F(000) = 3048, T = 293 K; iridescent purple plates, 0.37 × 0.37 × 0.10 mm, Siemens P4/RA diffractometer, ω-scans, 5919 independent reflections. The structure was solved by the heavy atom method and the major occupancy non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give R_1 = 0.053, wR_2 = 0.127 for 4970 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 125°$] and 884 parameters. The polarity of the structure was unambiguously determined both by an R-factor test [R_1^+ = 0.053, R_1^- = 0.073] and by use of the Flack parameter [$x^+ = -0.01(1)$, $x^- = +1.01(1)$]. All computations were carried out using the SHELXTL PC program system.[29]

CCDC reference number 167399.

See http://www.rsc.org/suppdata/dt/b1/b103346h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and optical properties

The cerium sandwich complex **2** [$Ce(OPTAP)_2$] was readily obtained through reaction of octapropylporphyrazine **1** (H_2OPTAP) with $Ce(acac)_3 \cdot H_2O$ in a 2 : 1 molar ratio in 1,2,4-trichlorobenzene (TCB) at reflux (Scheme 1). Prolonged heating (>24 h) or the use of an excess of $Ce(acac)_3 \cdot H_2O$ resulted in lower yields due to decomposition. From reaction of compound **1** with lanthanum(III)-, europium(III)- or gadolinium(III)-acetylacetonate under analogous conditions only trace amounts of the corresponding sandwich complexes were detected (MS). On the other hand, treatment of H_2OPTAP **1** with a stoichiometric amount of $Lu(OAc)_3 \cdot H_2O$ in refluxing hexanol gave the corresponding sandwich complex **3**

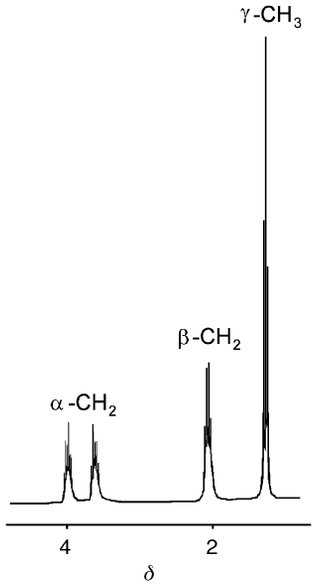


Fig. 1 ^{1}H NMR spectrum of Ce(OPTAP)$_2$ in $CDCl_3$.

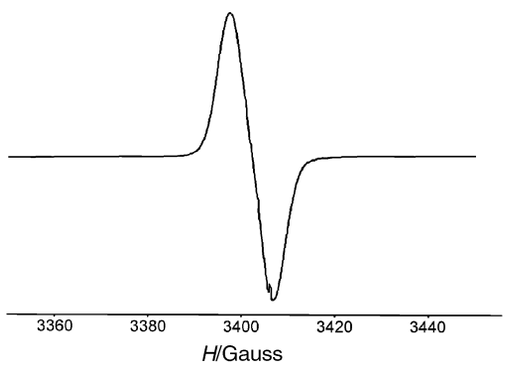


Fig. 2 X-Band solution EPR spectrum of sandwich complex **3**, recorded at 298 K.

[Lu(OPTAP)$_2$] in moderate yield (44%). Interestingly, reaction of **1** with EuI_2 under similar reaction conditions as above gave the sandwich complex **4** [Eu(OPTAP)$_2$] and the triple decker **5** [Eu$_2$(OPTAP)$_3$] in 36 and 9% yield respectively. When TCB was used as the solvent lower yields of both **4** and **5** were obtained and under neither conditions could a 1 : 1 complex be isolated. From reaction of **1** with Nd(OAc)$_3$, Sm(OAc)$_3$, SmI_2, YbI_2 or $EuCl_2$ again only trace amounts of the respective sandwich complexes were detected (MS) but were formed in insufficient quantities for isolation and characterisation. Prolonged reaction of porphyrazine **1** with these salts resulted only in decomposition.

It is well documented that porphyrinoid (P) sandwich complexes with lanthanide(III) cations exist as $Ln^{3+}(P^{2-})(P^{\bullet -})$, in which the unpaired electron delocalises in both of the macrocycles.[15,16] Thus, satisfactory NMR spectra of compounds **3** and **4** could not be obtained and trace amounts of paramagnetic impurities hampered the acquisition of a satisfactory spectrum of **5**. The proton NMR spectrum of the diamagnetic Ce(IV) complex **2** [$Ce^{4+}(OPTAP^{2-})_2$] in $CDCl_3$, however, showed all individual features of the porphyrazine including the expected set of well-resolved diastereotopic α-methylene signals (Fig. 1).[30] Further evidence for the π-radical anion ($OPTAP^{\bullet -}$) in Lu(OPTAP)$_2$ **3** and Eu(OPTAP)$_2$ **4** was obtained from IR and EPR (*vide infra*) spectroscopy. Phthalocyanine,[15] porphyrin[11] and porphyrazine[19] sandwich complexes show diagnostic π-radical IR "marker" bands that are not present in the dianions (P^{2-}). The IR spectra of compounds **3** and **4** contain intense bands at 1736 and 1735 cm^{-1} respectively which are absent in **1**, **2** and **5**. Thus, we assign these absorptions as

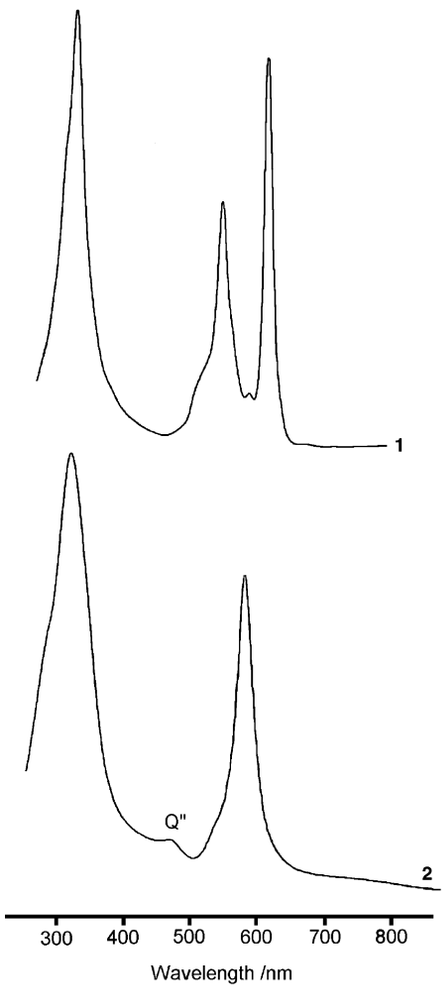


Fig. 3 UV-vis spectra for porphyrazines **1** and **2** in CH_2Cl_2.

the characteristic $OPTAP^{\bullet -}$ radical anion "marker" bands. The observation of such "marker" bands was initially used to determine empirically whether oxidation in monoporphyrins occurred at the metal or the porphyrin π system (porphyrin radical cation),[31] and has been extended to demonstrate the π radical character of porphyrin-type sandwich complexes (*vide supra*). EPR spectroscopy further confirmed the presence of an unpaired electron in sandwich complexes **3** and **4**. Spectra of **3** and **4** were recorded in dichloromethane/chloroform (1 : 1) and dichloromethane solutions respectively at 77 (only **3**) and 298 K, of which the latter is shown in Fig. 2. Both **3** and **4** exhibit a signal having a *g*-value of 2.00 with no hyperfine structure under both experimental conditions, consistent with a typical organic radical. However, the data obtained from magnetic susceptibility studies were not amenable to simple interpretation and could be attributed to the poor crystallinity of the materials.

Compounds **2**–**5** have electronic absorption spectra which are typical for sandwich complexes of this type. All display intense bands in the Soret region at 326, 318, 320 and 329 nm respectively. In accordance with strong π–π interactions, the bands are blue-shifted by 14, 22, 20 and 11 nm, respectively, when compared to the free base porphyrazine **1** (representative UV-vis spectra are shown in Figs. 3 and 4). The fact that the B-bands of **3** and **4** are of higher energy than those of **2** and **5** suggest that they couple more strongly due to their π-radical nature. In addition, compounds **2**–**5** display a single Q band (approximate D_{4h} symmetry) at 584, 588, 595 and 580 nm respectively. In contrast, the free base **1** shows a split Q band with peaks centered at 559 and 626 nm, consistent with a D_{2h} symmetry and in accordance with Gouterman's four orbital model.[32] Another characteristic of sandwich compounds is the appear-

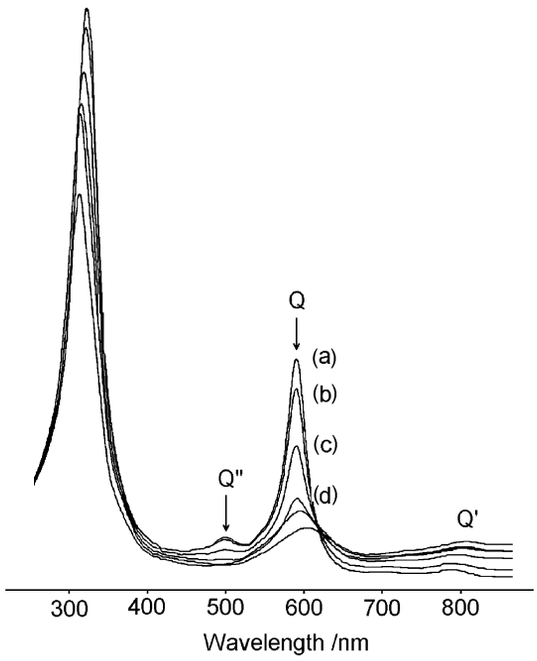


Fig. 4 UV-vis spectra of a sample of **3** in CH_2Cl_2 (a) and after the addition of phenoxathiin hexachloroantimonate in the same solvent. The initial concentration of **3** was 1.95×10^{-5} M. The concentration of the oxidant was 5.42×10^{-5} M. Each spectrum corresponds to the addition of (b) 0.1 equiv., (c) 0.4 equiv., (d) 0.7 equiv., (e) 1.0 equiv. and (f) 2.0 equiv. of the oxidant.

ance of absorption bands at lower and higher energies than the normal Q band. The new transitions are thought to result from orbitals delocalized over the two macrocycles and have been termed Q′ (red-shifted) and Q″ (blue-shifted). The bands of sandwich complexes **2**, **3** and **5** which appear at 470, 496 and 487 nm respectively are tentatively assigned as the Q″ transitions (Figs. 3 and 4). We assign additional bands at 789 and 783 nm, only observed in the lutetium and europium sandwich complexes **3** and **4**, as the Q′ band (Fig. 4). Upon addition of phenoxathiin hexachloroantimonate, the Soret bands of compounds **2**–**5** were blue shifted further by ≈10 nm, while the Q″ and Q bands decreased in intensity (see representative UV-vis titration in Fig. 4), consistent with the formation of cationic species such as $[Ln_m(OPTAP)_n]^+[SbCl_6]^-$ (Ln = Ce, Lu, Eu; $m = 1$ or 2; $n = 2$ or 3). Similar observations have been reported elsewhere.[19] Upon addition of hydrazine to the oxidized species in solution, the original electronic absorption spectra of the parent compounds **2**–**5** were restored, thus confirming the reversibility of the oxidation process. However, no changes in the UV-vis spectra of **2**–**5** were observed when treated with a methanolic hydrazine solution.

Crystal structure of 2

The complex is seen (Fig. 5) to have a structure very similar to that of the related 2,3,7,8,12,13,17,18-octaethylporphyrinato species.[9] The geometry at cerium is distorted square antiprismatic (Fig. 6) with a mean stagger of *ca.* 28°, a value noticeably less than that (of 42°) observed in the porphyrin complex. The Ce–N distances are in the range 2.411(9) to 2.430(9) Å, distances that are markedly shorter than those in the porphyrin structure which range between 2.467(3) and 2.483(3) Å. The porphyrazine ring has a dished geometry, the pyrrole rings being inclined by between 8 and 17° with respect to their associated central N_4 planes, away from the metal centre (the comparable values in the porphyrin structure are between 12 and 19°). The N_4 centroid · · · centroid distance between the porphyrazine rings is significantly shorter at 2.43 Å than in the porphyrin case (2.75 Å).

The molecules pack to form stepped stacks with a Ce · · · Ce separation of 9.62 Å and a lateral offset of 6.07 Å. This contrasts with a total absence of any stacking in the porphyrin complex, where the molecules are arranged "edge-to-face" in a parquet-like array.

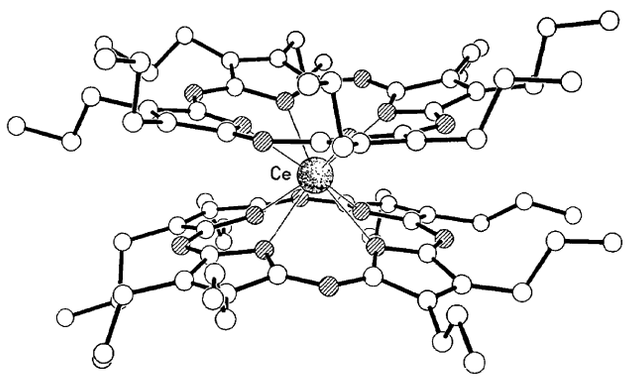


Fig. 5 The molecular structure of **2**, showing the distinct dishing of the two porphyrazine rings.

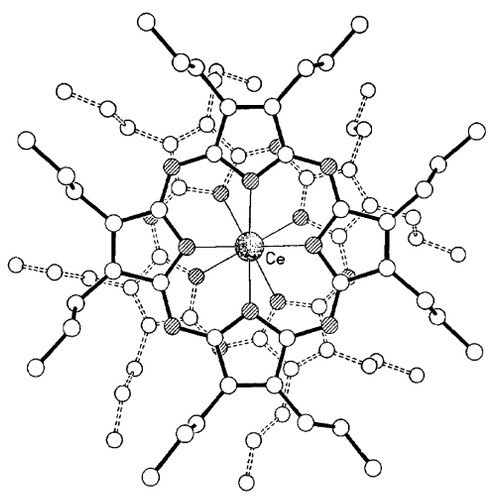


Fig. 6 View of **2** in parallel projection, perpendicular to the central N_4 ring planes, depicting the staggering of the two macrocycles. Selected bond lengths (Å) are: Ce–N(2) 2.424(10), Ce–N(7) 2.412(8), Ce–N(12) 2.430(9), Ce–N(17) 2.413(10), Ce–N(2′) 2.411(9), Ce–N(7′) 2.423(9), Ce–N(12′) 2.417(10), Ce–N(17′) 2.425(9).

Electrochemistry

The formal potentials of the reversible redox processes exhibited by compounds **1**–**5** are given in Table 1. The free base porphyrazine **1** exhibits one reversible ring oxidation centered at +0.68 V referenced *versus* ferrocenium/ferrocene, and one reversible ring reduction centered at −1.37 V.[21] When **1** is converted into sandwich complexes **2**–**5**, a distinct change in redox potential occurs; all are more easily oxidized by an average of ≈0.46 V than the parent porphyrazine **1**. The $E_{1/2}$ values for **2**–**5** are +0.27, +0.12, +0.20 and +0.28 V respectively (*vs.* Fc^+/Fc). This shift in oxidation potential has been observed for analogous porphyrin sandwich complexes, and it has been suggested that the π–π interactions between the two porphyrinic ligands stabilize higher oxidation states.[10,12] A similar shift in ring reduction is seen for the Lu and Eu sandwiches **3** and **4** in which reversible waves are observed at −0.53 and −0.39 V respectively, and in agreement with the fact that the redox potentials of tetrapyrrolic double deckers with tervalent lanthanides generally decrease for the oxidations and increase for the reductions with decreasing ionic radius across the series (lanthanide contraction).[6,12] Interestingly, the cerium sandwich **2** and europium triple decker **5** do not show the same shift, instead, an irreversible reduction, that can be attributed to the Ce^{IV}/Ce^{III} process is observed at −1.24 V for the former (Fig. 7)

Table 1 Comparison of half-wave potentials for compounds **1**–**5**

Compound	$[TAP]^{2+}/[TAP]^{+}$	$[TAP]^{+}/[TAP]$	$[TAP]/[TAP]^{-}$	Ref.
H_2OPTAP (**1**)	—	+0.68	−1.37	21
$Ce(OPTAP)_2$ (**2**)	+0.90	+0.27	−1.24 (Ce^{IV}/Ce^{III})	This work
$Lu(OPTAP)_2$ (**3**)	—	+0.12	−0.53	This work
$Eu(OPTAP)_2$ (**4**)	—	+0.20	−0.39	This work
$Eu_2(OPTAP)_3$ (**5**)	+0.61	+0.28	−1.43	This work

Couples are shown in units of volts. Measurements were done in CH_2Cl_2 with 0.1 M NBu_4PF_6 as the electrolyte using a Pt working electrode, Ag/AgCl reference electrode and are reported *versus* ferrocenium/ferrocene.

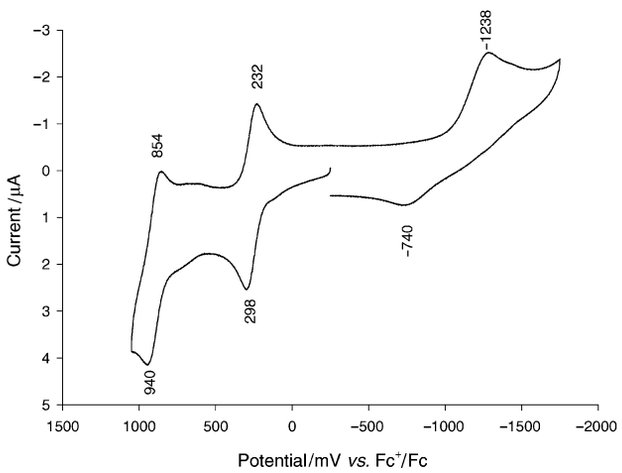


Fig. 7 Cyclic voltammogram of **2** in CH_2Cl_2.

and a reversible ring reduction centered at −1.43 V for the latter (*vs*. Fc^+/Fc). Such an irreversible reduction, which may be due to the Ce f orbital being so buried within the sandwich complex that the redox reaction is retarded, has also been observed for Ce porphyrin sandwich complexes.[10,12] In addition, a second quasi-reversible oxidation, only observed for **2** and **5** and centered at +0.90 and +0.61 V respectively (*vs*. Fc^+/Fc), reflects the dianionic nature of the porphyrazine ligands in the neutral complexes.[10]

Conclusions

We have successfully carried out the syntheses [$Ce(OPTAP)_2$, $Lu(OPTAP)_2$, $Eu(OPTAP)_2$ and $Eu_2(OPTAP)_3$] and the first X-ray crystal structure determination of a lanthanide porphyrazine sandwich complex [$Ce(OPTAP)_2$]. Examination of these compounds by electrochemical methods has shown that they are markedly easier to oxidize than the free base porphyrazine precursor, thus indicating the close proximity by which the macrocycles are held together by the central metal ions. This work provides initial structural and electronic information of rare sandwich complexes containing the porphyrazinato ligand as compared to the extensively studied porphyrin and phthalocyanines.

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