The First Electrochemistry of a Monomeric Europium Porphyrin. Reactions of (tpp)Eu(facam) (tpp is the dianion of tetraphenylporphyrin, facam⁻ is the trifluoroacetylcamphor ion)

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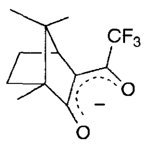
The overall two-electron oxidation and two-electron reduction of (tpp)Eu(facam) is monitored by cyclic voltammetry in several solvent/supporting electrolyte mixtures.

The most well-studied lanthanide porphyrins are those with double-decker[1–9] or triple-decker[1,4,10,11] structures of the form $(\mathbf{P})_2\mathrm{M}$ or $(\mathbf{P})_3\mathrm{M}_2$ where **P** is the dianion of a given porphyrin ring. Monomeric lanthanide porphyrins with acetylacetonate (acac^-) axial ligands have also been synthesized[12–16] but these complexes, represented as (**P**)M(acac) in which the acac^- ion acts as a bidentate ligand, have only moderate stability in solution.

The redox properties of both double- and triple-decker complexes are known[3,6,7,11] but there are no reports in the literature of the electrochemistry of a simple monomeric lanthanide porphyrin. This is perhaps due to the fact that numerous decomposition products are observed upon oxidation or reduction of the acac complex. We have now been able to change the bidentate ligand in order to obtain greater stability of the oxidized and reduced metalloporphyrin. This is reported in the present communication, which presents the first electrochemistry of a monomeric $\mathrm{Eu^{III}}$ porphyrin in nonaqueous media. The investigated compound is (tpp)-Eu(facam) (tpp = tetraphenylporphyrin dianion and facam^- = trifluoroacetylcamphor ion) **1**.

The (tpp)Eu(facam) derivative is monomeric as indicated by mass spectrometry and cryoscopy in benzene and this contrasts with lanthanide complexes having anionic bidentate ligands such as tris(2,2,6,6-tetramethyl)heptane-3,5-dionate (tmhd).[17,18] These latter compounds are dimeric in the solid



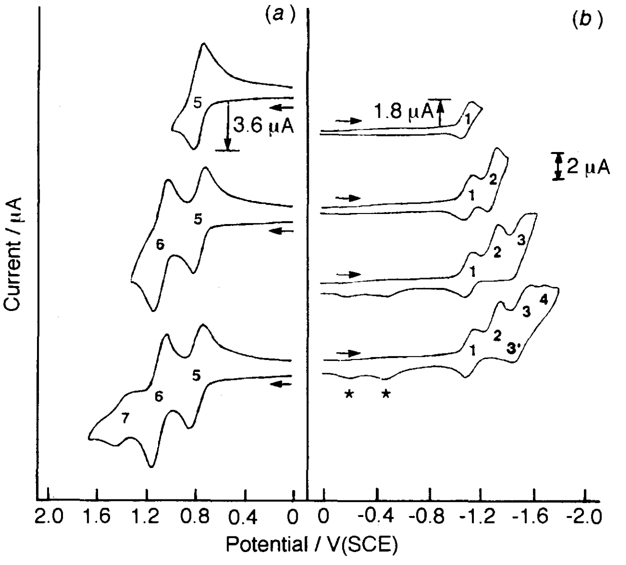
state but may dissociate in solutions of 10^{-4} mol dm^{-3} to give monomers of the type Eu(tmhd)$_3$ and Pr(tmhd)$_3$.[17]

The synthesis of (tpp)Eu(facam) was carried out from (tpp)Eu(acac)[15] in the following manner: to a solution of 0.4 g of 3-(trifluoroacetyl)camphor (1.6 mmol), 1.5 ml sodium hydroxide, 1 mol dm^{-3} (1.5 mmol) in 30 ml of ethanol–water (1 : 1 in volume), was added 0.4 g of (tpp)Eu(acac) (0.5 mmol) in 50 ml of benzene. The reaction mixture was allowed to stand for 24 h. The solvent was evaporated and the solid purified by chromatography on an alumina-packed column using dichloromethane–methanol (10 : 1) as eluent. After evaporation of the solvent, the resulting solid was used without further purification.†

Cyclic voltammograms of (tpp)Eu(facam) in PhCN and thf containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (tbap) are illustrated in Fig. 1 and 2 and a summary of half waves or peak potentials is given in Table 1. Four reductions (labelled 1–4) and three oxidations (labelled 5–7) are observed in PhCN at room temperature. The first two oxidations are characterized by a one-electron transfer wave shape of $|E_{pa} - E_{pc}| = 60 \pm 5$ mV and have a peak current, i_p, which is proportional to $v^{1/2}$. This is also the case for the first two reductions in PhCN or the first three reductions in thf and indicates diffusion-controlled electron transfers for each electrode reaction.

Controlled potential coulometry carried out at potentials negative to the first reduction (peak 1) gives 0.5 electrons added per mole of (tpp)Eu(facam). This contrasts with the first oxidation of (tpp)Eu(facam), which involves the abstraction of 1.0 electron during controlled potential electrolysis at +1.0 V (a value just positive of wave 5). The maximum peak current for oxidation of (tpp)Eu(facam) by cyclic voltammetry is double that of the reduction peak current (see Fig. 1) and this result is consistent with the coulometric data. In addition, the peak currents for the first and second oxidation of (tpp)Eu(facam) are identical, within experimental error, consistent with data from controlled potential coulometry, which gives an overall 2.0 electrons abstracted at +1.2 V. Two electrons are also added to the complex by controlled potential reduction at −1.6 V and this suggests that each of the four electroreduction steps shown in Fig. 1 involves a 0.5 electron transfer process.

The first two reductions of (tpp)Eu(facam) are well-defined in PhCN at a scan rate of 1.0 V s^{-1} (see Fig. 1) but one or more chemical reactions occur after peaks 2, 3 and 4, and these may or may not be observed on the cyclic voltammetric timescale. The occurrence of these reactions results in a decreased anodic peak current for processes 2 and 4 and the appearance of new oxidation peaks at $E_p = -0.45$ and -0.20 V for a scan rate of 1.0 V s^{-1} (see Fig. 1). Under these conditions, the reoxidation associated with reduction peak 3 is assigned as peak 3′. The potentials are almost identical for oxidation peaks 3′ and 3 but the electrode reactions are different in the presence or absence of a chemical reaction.



Scheme 1

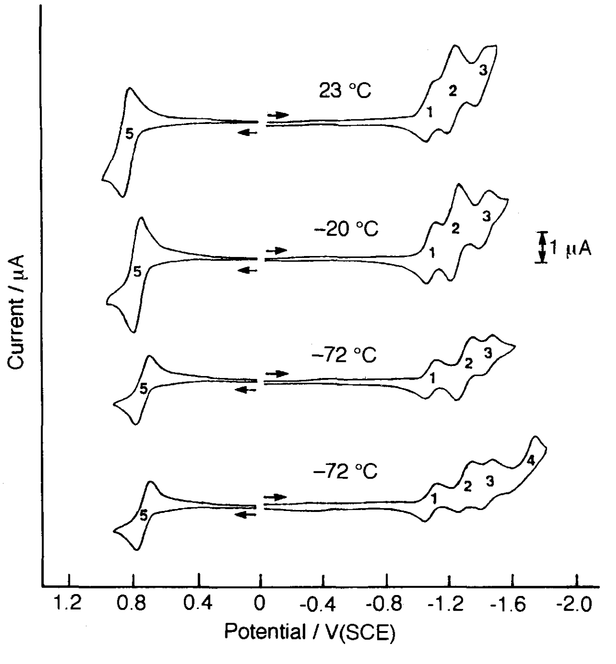


Fig. 1 Cyclic voltammograms illustrating the room temperature oxidation and reduction of (tpp)Eu(facam) in PhCN, 0.1 mol dm^{-3} tetrabutylammonium perchlorate at a scan rate of 1.0 V s^{-1}. The starred peaks are due to reoxidation products of the decomposed reduced porphyrin and are assigned to (tpp)Eu units lacking the facam axial ligand.

The chemical reaction that follows the third reduction of (tpp)Eu(facam) is slower in thf than in PhCN and the first three reductions are reversible at all temperatures between 23 and −72 °C. However, the chemical reaction that occurs after peak 4 cannot be cut off at either fast scan rate or low temperature. The cyclic voltammogram under these latter conditions is illustrated in Fig. 2 and was recorded at −72 °C.

The electrochemistry of (tpp)Eu(facam) in benzene containing 0.7 mol dm^{-3} tetrahexylammonium perchlorate is similar in some respects to that seen in thf or PhCN but differs significantly from these other solvents in that the peak currents for the first reduction and the first oxidation are approximately equal to each other (see Fig. 3). Three

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† (tpp)Eu(facam), ^{1}H NMR (400 MHz) δ (C_6D_6; rel. to $SiMe_4$): 7.76 (s, pyrrole H), 12.15, 8.66, 8.29 and 8.23 (broad signals, aromatic H), −1.59, −1.81, −2.66, −2.82, −4.36, −5.20 and −6.09 (broad singlets, facam H); UV–VIS data (CH_2Cl_2); 428 (Soret band), 519, 557 and 596 (Q bands); Mass spectral data (+FAB, *m*-nitrobenzylalcohol as matrix): 1012 (100%, [(tpp)Eu(facam)]$^+$), 765 (35%, [(tpp)Eu]$^+$); cryoscopic measurements (in benzene as solvent): M = 1090 ± 50.

Table 1 Half-wave and peak potentials (V *vs.* SCE) for reduction and oxidation of (tpp)Eu(facam)

		Reduction/V				Oxidation/V		
Solvent	T/°C	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	$E_p(4)^c$	$E_{1/2}(5)$	$E_{1/2}(6)$	$E_{1/2}(7)$
PhCN[a]	23	−1.17	−1.36	−1.55[e]	−1.73	0.72	1.04	1.31
THF[a]	23	−1.08	−1.22	−1.42	−1.66	0.84	[g]	[g]
	−20	−1.09	−1.25	−1.44	−1.69	0.77	[g]	[g]
	−72	−1.09	−1.30	−1.44	−1.75	0.74	[g]	[g]
Benzene[b]	50	−1.07	−1.34[d]	−1.50[f]		0.72	1.12	1.28

[a] Solvent containing 0.1 mol dm^{-3} tbap. [b] Solvent containing 0.7 mol dm^{-3} thap. [c] Anodic peak potential at scan rate of 0.1 V s^{-1}. [d] Cathodic peak potential at scan rate of 0.1 V s^{-1}. [e] Value obtained at scan rate ≥ 5 V s^{-1}. [f] E_p for broad wave consisting of several overlapping peaks 3, 3′ and 4. [g] Reaction occurs beyond solvent limit.

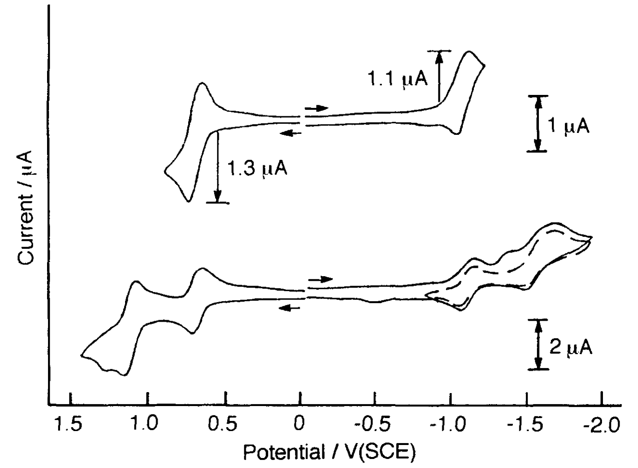

Fig. 2 Cyclic voltammograms illustrating the oxidation and reduction of (tpp)Eu(facam) at different temperatures in thf, 0.1 mol dm^{-3} tetrabutylammonium perchlorate at a scan rate of 0.1 V s^{-1}

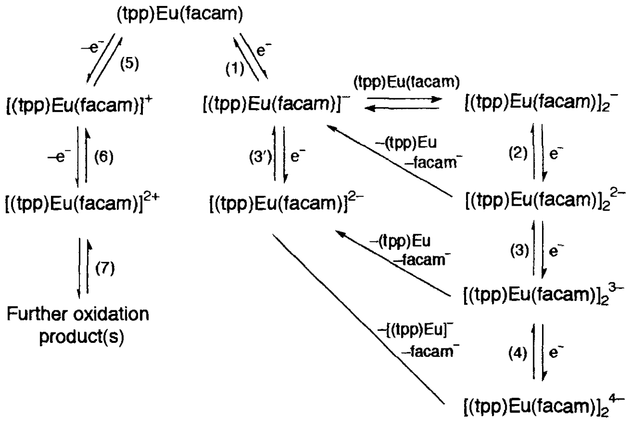

Fig. 3 Cyclic voltammograms of (tpp)Eu(facam) in benzene, 0.7 mol dm^{-3} tetrahexylammonium perchlorate at a scan rate of 0 1 V s^{-1}

reductions are obtained in benzene and these are located at $E_{1/2} = -1.07$, $E_p = -1.34$ and $E_p \simeq -1.50$ V for a scan rate of 0.1 V s^{-1}. The middle peak disappears upon a second potential sweep (see Fig. 3) as is also the case in thf or PhCN. Well-resolved peaks 3 and 4 are not observed in the voltammogram, and there is only a single broad cathodic peak located at $E_p \simeq -1.50$ V.

The resulting voltammetric and coulometric data for (tpp)Eu(facam) in PhCN, thf and benzene are self-consistent and suggest the presence of both monomers and dimers in solution. There is a global addition or abstraction of 2.0 electrons and the overall mechanism on the cyclic voltammetric timescale is postulated to occur *via* the oxidation–reduction shown in Scheme 1.

Evidence for the various pathways in Scheme 1 is given in large part by the coulometric values of 0.5, 1.0 and 2.0 electrons added during controlled potential reduction of (tpp)Eu(facam) in PhCN at potentials positive of peaks 1, 2 and 4. These values contrast with coulometric data for the first two oxidations (peaks 5 and 6) of the same compound where 1.0 and 2.0 electrons are abstracted, respectively.

The generated $[(tpp)Eu(facam)]_2^{2-}$ and $[(tpp)Eu(facam)]_2^{3-}$ dimers are stable on the rapid cyclic voltammetric timescale but decompose at slower scans to give several reduced forms of the monomeric europium porphyrin. The electrogenerated $[(tpp)Eu(facam)_2]^{4-}$ complex also rapidly decomposes and the products of all three chemical reactions are postulated to be reduced forms of the monomeric porphyrin, which are unligated by $facam^-$. These are assigned as (tpp)Eu and $[(tpp)Eu]^-$, which can be oxidized at $E_p = -0.45$ and -0.20 V. These oxidations correspond to the peaks labelled by* in Fig. 1 and are not included in Scheme 1, which concerns only those species ligated by $facam^-$.

The exact coordination geometries of the neutral and/or reduced monomeric europium porphyrins formed upon dissociation of the electroreduced dimer are not known at this time (the ClO_4^- supporting electrolyte may or may not be complexed) but a spectroscopic and electrochemical characterization of these derivatives, as well as attempts to structurally characterize (tpp)Eu(facam), are now both underway.

It will be of special importance to elucidate the site of electron transfer in the monomeric and dimeric derivatives and also to understand how changes in coordination geometry will relate to the thermodynamic potentials for oxidation or reduction of the europium complex in a given oxidation state. The absolute potential difference between the first oxidation and the first reduction of (tpp)Eu(facam) varies between 1.79 V in benzene and 1.89–1.92 V in PhCN or thf. These values are in agreement with a 1.81 V separation for oxidation and reduction of $(oep)_3Eu_2$ in CH_2Cl_2,[11] but are much smaller than the separation of 2.25 ± 0.15 V, which is generally observed when both the addition and abstraction of an electron occur at the porphyrin π ring system.[19] This could suggest the formation of either a Eu^{II} or a Eu^{IV} complex prior to a ring-centred redox reaction. This possibility is presently under investigation.

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