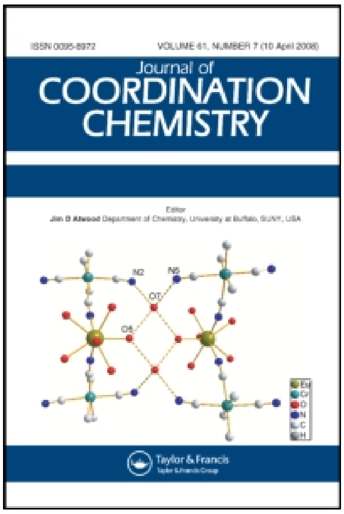

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

ELECTROCHEMICAL STUDIES OF PROTONATED AND DEPROTONATED FORMS OF HETEROLEPTIC AND HOMOLEPTIC EUROPIUM$^{(III)}$ AND DYSPROSIUM$^{(III)}$ PORPHYRIN DOUBLE-DECKERS

G. A. Spyroulias[a]; A. G. Coutsolelos[a]; D. de Montauzon[b]; R. Poilblanc[b]
[a] Laboratory of Bioinorganic Coordination Chemistry, Chemistry Department, University of Crete, Heraklion, Crete, Greece [b] Laboratoire de Chimie de Coordination, C.N.R.S., UPR 8241 liée par convention à l'Université Paul Sabatier et à l'Institut Polytechnique de Toulouse, Toulouse, cedex, France

To cite this Article Spyroulias, G. A. , Coutsolelos, A. G. , de Montauzon, D. and Poilblanc, R.(1996) 'ELECTROCHEMICAL STUDIES OF PROTONATED AND DEPROTONATED FORMS OF HETEROLEPTIC AND HOMOLEPTIC EUROPIUM$^{(III)}$ AND DYSPROSIUM$^{(III)}$ PORPHYRIN DOUBLE-DECKERS', Journal of Coordination Chemistry, 39: 1, 89 — 96

To link to this Article: DOI: 10.1080/00958979608028177

URL: http://dx.doi.org/10.1080/00958979608028177

J. Coord. Chem., 1996, Vol. 39, pp. 89–96
Reprints available directly from the publisher
Photocopying permitted by licence only

Note

ELECTROCHEMICAL STUDIES OF PROTONATED AND DEPROTONATED FORMS OF HETEROLEPTIC AND HOMOLEPTIC EUROPIUM$^{(III)}$ AND DYSPROSIUM$^{(III)}$ PORPHYRIN DOUBLE-DECKERS

G. A. SPYROULIAS, A. G. COUTSOLELOS*

Laboratory of Bioinorganic Coordination Chemistry, Chemistry Department,
University of Crete, P.O. Box 1470, 714 09-Heraklion, Crete, Greece

D. de MONTAUZON and R. POILBLANC*

Laboratoire de Chimie de Coordination, C.N.R.S., UPR 8241 liée par
convention à l'Université Paul Sabatier et à l'Institut Polytechnique de
Toulouse, 205 route de Narbonne, 31077-Toulouse cedex, France

(Received September 13, 1995)

The cyclic voltammetric oxidation, of heteroleptic and homoleptic lanthanide porphyrin double-deckers demonstrates the presence of equilibrium protonated/deprotonated species present in CH_2Cl_2, DMF, and THF.

Keywords: porphyrins; metalloporphyrins; lanthanide porphyrins; electrochemistry; cyclic voltammetry

Lanthanide "sandwich"-type porphyrins are those with double-decker[1–13] or triple-decker[2,5,14–16] structures of the form $M(por)_2$ or $M_2(por)_3$, where (por) is the dianion of the porphyrin ring. The redox properties of both homoleptic and heteroleptic complexes are known.[3,4,6,7,12,15–17] There are no reports, however, in the literature on

---

*Authors for correspondence.

the electrochemistry of the two forms, protonated and deprotonated, respectively, that exist for these double-decker complexes. The only example is for the case of $Pr^{(III)}H(oep)_2$,[17] an homoleptic compound with octaethylporphyrin (oep) rings. We have now been able to confirm by using electrochemical methods the presence of two forms of an heteroleptic complex, which are in equilibrium with each other, as was previously shown by other methods.[1,19] Evidence for the aforementioned equilibrium is reported in the present communication. The investigated heteroleptic compounds in the present study include $Eu^{(III)}H(oep)(tpp)$, $Dy^{(III)}H(oep)(tpp)$ and the corresponding homoleptic species with tetraphenylporphyrin (tpp) rings. Experiments were performed following procedures already describe.[20]

We have found that the deprotonation process is solvent-dependent,[1,19] in CH_2Cl_2 the protonated form **A** of the complex is present, while in basic solvents such as DMF or pyridine the deprotonated form **B** becomes dominant. The latter form can be described as $[Ln^{(III)}(por)(por')]^-$ (por = por′ for the homoleptic ones). It should also be noted that in THF, which possesses almost the same basicity as DMF,[17] the deprotonation process occurs at a slower rate. For reasons stated above, we decided to examine the electrochemical properties of the title complexes by cyclic voltammetry in three solvents, namely, CH_2Cl_2, DMF, and THF.

Considering the solvent-dependent nature of the proton in question for the examined double-deckers, it was appropriate to start by investigating cyclic voltammetry in CH_2Cl_2, followed by the addition of a strong base, such as Et_3N. Figure 1a shows the CV $Eu^{(III)}H(oep)(tpp)$ complex in CH_2Cl_2 and Figure 1b shows the CV of the same complex in CH_2Cl_2 after the addition of Et_3N. In the latter cyclic voltammogram only the reversible oxidations E_1, E_2, E_5 and E_6 are observed. These correspond to one electron transfer processes, exhibit values for $|\,Epa\text{-}Epc\,| = 60 \pm 5$ mV and have a peak current which is proportional to $v^{1/2}$. The same experiment (in Et_3N) carried out with a rotating disk electrode confirms that these waves correspond to one electron oxidations processes for the title complex. We can deduce *a priori* after comparison of the above two CV traces the mixture in Figure 1a gives rise to one porphyrinic species which gives common electrochemical behaviour, Figure 1b. Similar results were obtained when the same initial solution of **A** stays for a long time in the presence of the supporting electrolyte (see Figure 2). It is thus obvious that we can also follow this transformation, even in the absence of triethylamine, except that this process occurs slowly (supporting electrolyte play the base role). Due to the described behaviour it is very likely that initially we have an equilibrium mixture, composed of the

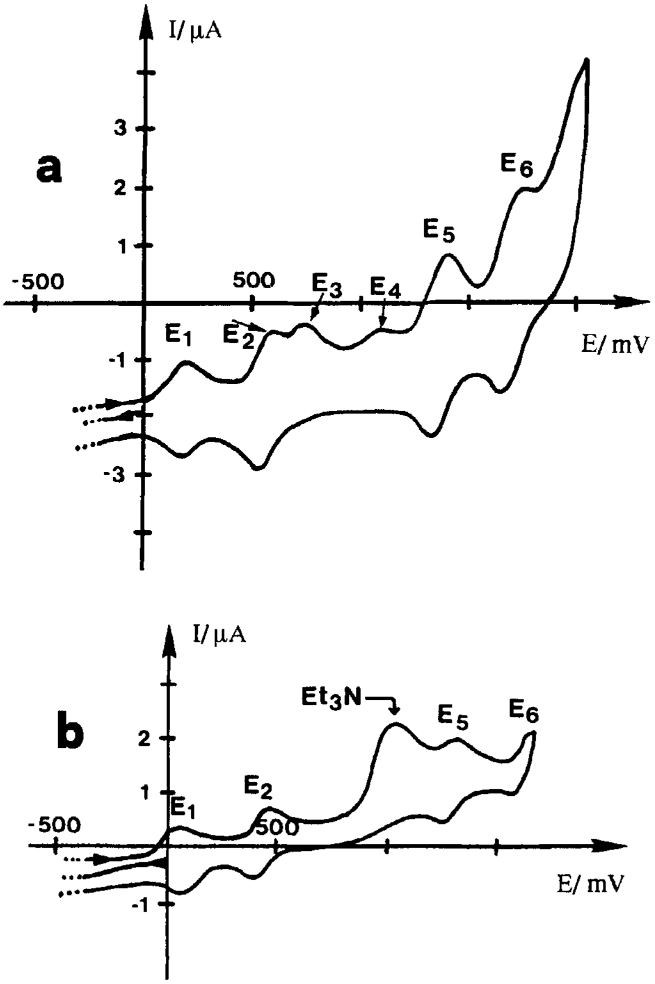

FIGURE 1 a) Cyclic voltammogram of $Eu^{(III)}H(oep)(tpp)$ in CH_2Cl_2; 0.1M NBu_4ClO_4; scan rate 0.1 Vs^{-1}; b) after addition of 60μL Et_3N in CH_2Cl_2; 0.1M $NBuBF_4$; scan rate $0.1Vs^{-1}$.

protonated **A** and deprotonated **B** forms of the title complexes. Consequently, addition of Et_3N or even the mere presence of the supporting electrolyte may shift the equilibrium to the left, towards the deprotonated form **B**, as follows.

$$\underset{\textbf{A}}{Ln^{(III)}H(por)(por')} \xrightleftharpoons{-H^+} \underset{\textbf{B}}{[Ln^{(III)}(por)(por')]^-}$$

$$\text{por} = \text{or} \neq \text{por}'$$

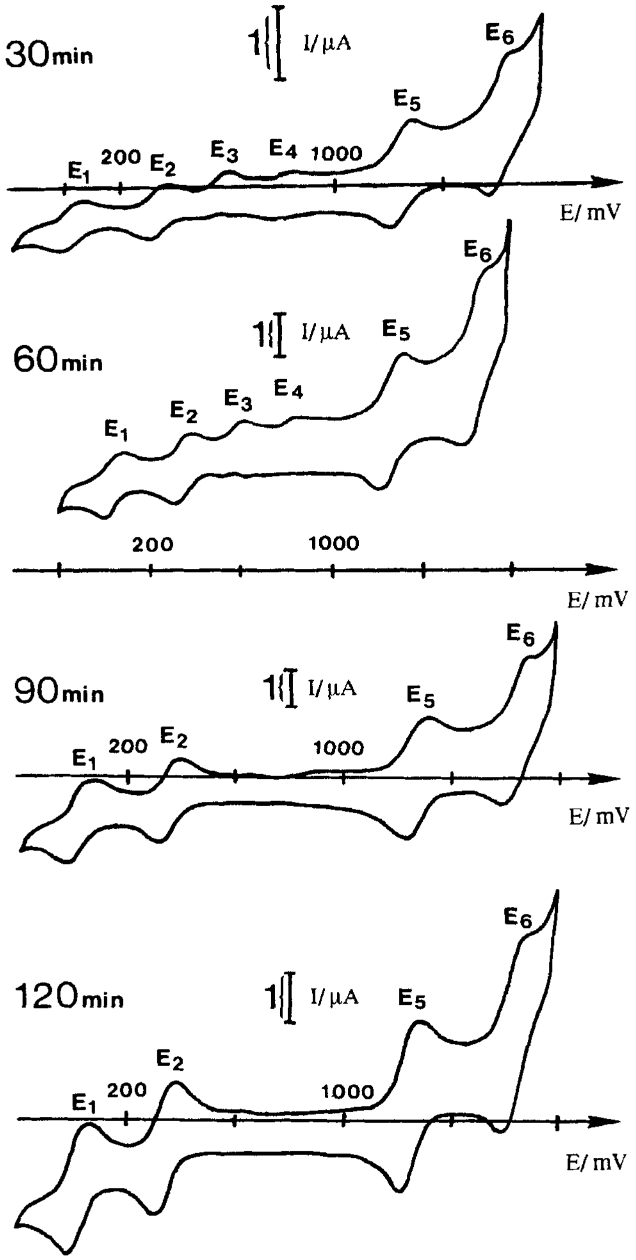

FIGURE 2 Cyclic voltammograms *versus* time at 30, 60, 90, and 120 min of $Eu^{(III)}H$ (oep)(tpp) in CH_2Cl_2; 0.1M NBu_4BF_4; scan rate $0.1Vs^{-1}$.

TABLE I Half-wave (E_1 and E_2) and peak potentials (E_5 and E_6) (V *vs* SCE) for oxidation of [Ln^{III}(Por)(Por')], (Ln = Eu, Dy and Por = or ≠ Por').

Complex	E_1	E_2	E_5	E_6	*Solvent*
[Eu(oep)(tpp)]$^-$	-0.08	0.36	1.17	1.51	CH_2Cl_2[a]
	0.03	0.44	d	d	CH_2Cl_2/Et_3N[b]
	0.19	0.58	1.29	e	THF[b]
	0.13	0.47	1.19	e	DMF[b]
[Dy(oep)(tpp)]$^-$	-0.11	0.33	1.18	1.55	CH_2Cl_2[a]
	0.09	0.52	1.28	e	THF[b]
	0.11	0.45	1.19	e	DMF[b]
[Eu(tpp)$_2$]$^-$	0.13	0.45	1.29	1.59	CH_2Cl_2[c]
	0.20	0.54	d	d	CH_2Cl_2/Et_3N[b]
	0.33	0.72	e	e	THF[b]
	0.36	0.60	1.31	e	DMF[b]
[Dy(tpp)$_2$]$^-$	0.07	0.39	1.27	1.62	CH_2Cl_2[c]
	0.34	0.75	e	e	THF[b]
	0.32	0.57	1.32	e	DMF[b]

[a]Solvent containing 0.1M NBu_4ClO_4 [b] Solvent containing 0.1M NBu_4BF_4 [c] Solvent containing 0.1M NBu_4BF_4 [d] Not measured [e] Not measured or reaction occurs beyond the limit of the solvent.

Table I presents half-wave potentials of the deprotonated double-deckers and data in Table II refers to the corresponding protonated species. In the case of the europium heteroleptic derivative, the protonated form **A** of the complex is in equilibrium with the corresponding deprotonated one **B**. $E_1 = -0.08$ and $E_3 = 0.50$V are the half-wave potentials ($E_{1/2}$) of the first oxidation, and $E_2 = 0.36$, $E_4 = 0.88$V the halfwave potentials for the second oxidation of the deprotonated and protonated forms, respectively. Beyond E_4, there is no other electrochemical process detected for the protonated species and the equilibrium is shifted to the deprotonated species [Ln(III)(por)(por')]$^+$ which exhibits two more resolved oxidations waves with potentials E_5 and E_6, respectively.

Figure 3 illustrates cyclic voltammograms of the complex [Eu$^{(III)}$(oep)(tpp)]$^-$ in THF (3a) and DMF(3b) containing 0.1M tetrabutyl

TABLE II Half-wave and peak potentials (V *vs* SCE) for the oxidation of Ln^{III}H(Por)(Por'),(Ln = Eu,Dy and Por = or ≠ Por').

Complex	E_3	E_4	*Solvent*
EuH(oep)(tpp)	0.50	0.88	CH_2Cl_2[a]
DyH(oep)(tpp)	0.49	0.84	CH_2Cl_2[a]
EuH(tpp)$_2$	0.63	0.97	CH_2Cl_2[b]
DyH(tpp)$_2$	0.60	0.91	CH_2Cl_2[b]

[a] Solvent containing 0.1M NBu_4ClO_4 [b] Solvent containing 0.1M NBu_4PF_6.

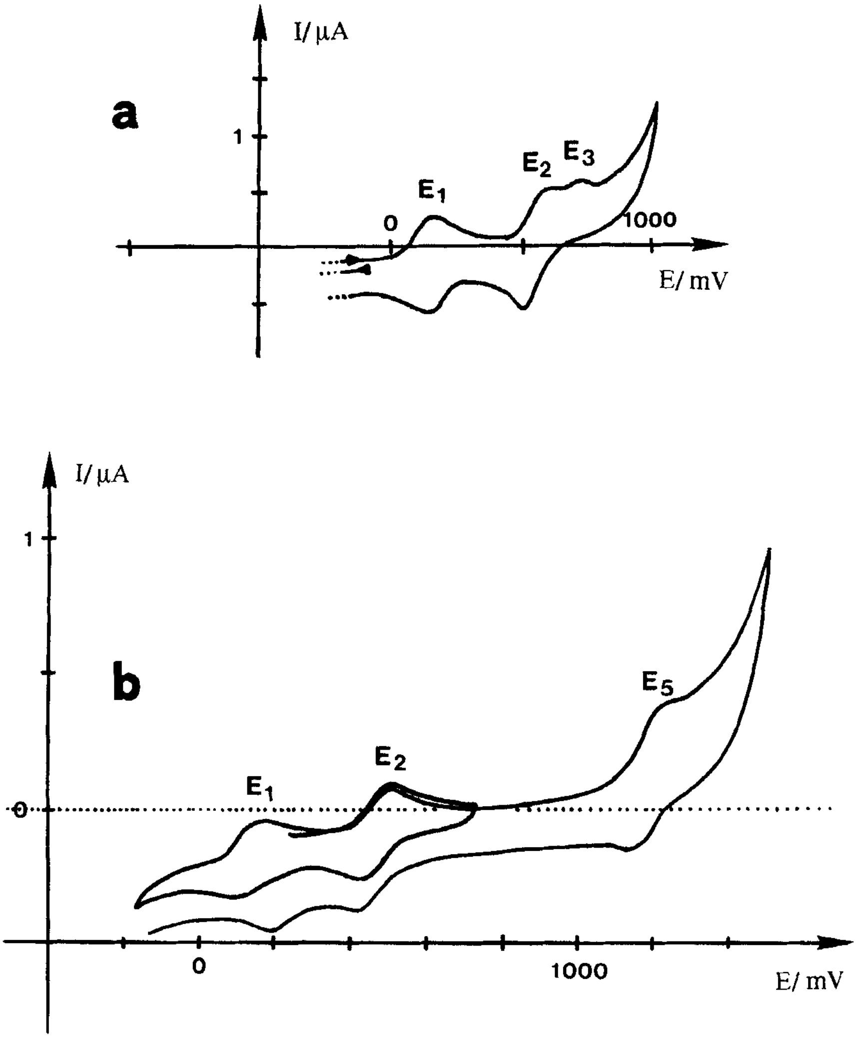

FIGURE 3 Cyclic voltammograms illustrating the oxidation of the complex $[Eu^{(III)}(oep)(tpp)]^-$ a) in THF, and b) in DMF, containing 0.1M NBu_4BF_4; scan rate 0.1 Vs^{-1}.

ammonium tetrafluoroborate. Closer examination of Figure 3a reveals the existence of a small quantity of the protonated form A for which the wave is not clearly defined under the present conditions of the CV run. As far as concerns the third oxidation in THF (that observed in the case of heteroleptic double-deckers), it should be noted that it is not observed in the case of the corresponding homoleptic complexes (see Table I). In the latter case the oxidation may take place beyond the limits of this solvent.

From the complexes examined herein, as well as the total number of heteroleptic and homoleptic lanthanide double-deckers investigated, the same behaviour was observed by cyclic voltammetry upon oxidation. All the steps described by potentials E_1, E_2, E_3, E_5 and E_6, are *quasi*-reversible, electrochemically. The processes that take place correspond to oxidation reactions on the porphyrin rings with no evidence for metal participation with respect to literature data.[12,13] Finally, the protonated form A of the complexes can only be observed in CH_2Cl_2 and it exhibits *quasi*-reversible behavior (E_4). The data presented herein support the use of cyclic voltammetry in clearly describing complex deprotonation of the title compounds in solution. Complete study of homoleptic complexes (with tpp, oep rings, and other non planar rings) and heteroleptic compounds from Nd to Lu is under way.

Acknowledgements

This research was supported by the Greek General Secretariat of Research and Technology through Grant No. 91 EΔ 442, the Centre National de la Recherche Scientifique and the Paul Sabatier University at Toulouse, France, a "Platon" grant for bilaterar scientific and technological cooperation (France-Greece) and an ERASMUS grant, ICP-92-G-2002/13.

References

[1] G. A. Spyroulias, A. G. Coutsolelos, C. P. Raptopoulou and A. Terzis, *Inorg. Chem.*, **34**, 2476 (1995).

[2] J. W. Buchler, A. De Cian, J. Fischer, M. Kihn-Botulinski, H. Paulus and R. Weiss; *J. Am. Chem. Soc.*, **108**, 3652 (1986).

[3] J. W. Buchler, K. Elsässer, M. Kihn-Botulinski and B. Scharbert, *Angew. Chem. Int. Ed. Engl.*, **25**, 286 (1986).

[4] J. W. Buchler and B. Scharbert, *J. Am. Chem. Soc.*, **110**, 4272 (1988).

[5] J. W. Buchler, A. De Cian, J. Fischer, M. Kihn-Botulinski and R. Weiss, *Inorg. Chem.*, **27**, 339 (1988).

[6] R. J. Donohoe, J. K. Duchowski, and D. F. Bocian, *J. Am. Chem. Soc.*, **110**, 6119 (1988).

[7] J. W. Buchler, A. De Cian, J. Fischer, P. Hammerschmitt, J. Löffler, B. Scharbert and R. Weiss, *Chem. Ber.*, **122**, 2219 (1989).

[8] J.-H. Perng, J.K. Duchowski and D. F. Bocian, *J. Phys. Chem.*, **94**, 6684 (1990).

[9] J. K. Duchowski and D. F. Bocian, *J. Am. Chem. Soc.*, **112**, 3312 (1990).

[10] J. K. Duchowski, and D. F. Bocian, *Inorg. Chem.*, **29**, 4158 (1990).

[11] R. Guilard, J.-M. Barbe, A. Ibnlfassi, A. Zrineh, V. A. Adamian and K. M. Kadish, *Inorg. Chem.*, **34**, 1472 (1995).

[12] J. W. Buchler, P. Hammerschmitt, I. Kaufeld and J. Löffler, *Chem. Ber.*, **124**, 2151 (1991).

[13] K. M. Kadish, G. Monimot, Y. Hu, D. Dubois, A. Ibnlfassi, J.-M. Barbe and R. Guilard, *J. Am. Chem. Soc.*, **115**, 8153 (1993).

[14] J. W. Buchler, M. Kihn-Botulinski, J. Löffler and M. Wicholas, *Inorg. Chem.*, **28**, 3770 (1989).

[15] J. K. Duchowski and D. F. Bocian, *J. Am. Chem. Soc.*, **112**, 8807 (1990).

[16] J. W. Buchler and J. Löffler, *Z. Naturforsch,* **45b**, 531 (1990).

[17] J. W. Buchler, M. Kihn-Botulinski and B. Scharbert, *Z. Naturforsch.*, **43b**, 1371 (1988).

[18] This is probably due to the fact that DMF's basicity is not only due to itself but also to one of its decomposition products, Me_2NH.

[19] G. A. Spyroulias and A. G. Coutsolelos, submitted for publication.

[20] J.-B. Tommasino, D. de Montauzon, X. He, A. Maisonnat, R. Poilblanc, J.-N. Verpeaux and C. Amatore, *Organometallics,* **11**, 4150 (1992).