

Chemical and Electrochemical Preparation of Low Oxidation State Niobium Porphyrinates

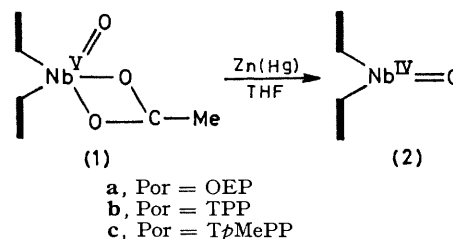
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Summary Zinc amalgam or electrochemical reduction of porphyrinatoniobium(v) oxide acetates leads to porphyrinatoniobium(IV) oxides, which are characterized by their *esr*, *ir*, and *uv-vis* spectra

We have reported in previous papers^{1,2} the synthesis of porphyrinatoniobium(v) oxide acetates, PorNbOAcO [Por = octaethylporphyrin (OEP), tetraphenylporphyrin (TPP), and tetra-*p*-tolylporphyrin (TpMePP)] (1). Trihalogeno-derivatives of niobium(v) tetraphenylporphyrins were prepared more recently by Green *et al.*³ We describe here the preparation of niobium(IV) porphyrins.

Reduction of the porphyrins (1) (0.35 mmol) in tetrahydrofuran (THF) (100 ml) by Zn(Hg) (1 g) leads to the niobium(IV) porphyrinates, PorNbO (2), which are isolated in good yield. The *esr* spectra of compounds (2) show the



10 lines which are to be expected for niobium(IV) complexes. The Nb=O *ir* vibration of compounds (2) is at *ca.* 1000 cm^{-1} , which is comparable with that for Ti=O in titanilporphyrins, which are also pentaco-ordinated. For compounds (1) the band appears near 900 cm^{-1} . A shift of the Soret band of $< 7\text{ nm}$ is observed when passing from (1) to (2). The

TABLE I Spectroscopic data for (1)–(3)

	E s r		ν_{max} (Nb=O) / cm^{-1}	λ_{max} /nm ($\epsilon \times 10^{-4}$)
	<i>g</i>	<i>a/G</i>		
(1a)			900	410 (14.0), 520 (0.6), 540 (1.0), 565 (1.7), 585 (1.1)
(2a)	1.9645	179	1020	403 (10.0), 455 (0.7), 538 (1.0), 577 (1.4)
(3a)	1.9416	144		
(1b)			890	425 (30.0), 534 (1.0), 555 (1.5), 601 (0.1)
(2b)	1.9657	178	1020	— ^a
(3b)	1.9380	144		
(1c)			900	428 (27.2), 535 (1.0), 554 (1.5), 602 (0.2)
(2c)	1.9657		1020	428 (19.5), 462 (0.9), 557 (1.5), 558 (0.35)
(3c)	1.9428	144		

^a Too insoluble to be measured

analyses and the mass spectra of (2) agree with the proposed structure, but they do not provide unambiguous information: the elemental analysis is not different enough from that of the oxidation products, (PorNb)₂O₃, and the molecular peak PorNbO⁺ of (2) appears at the same *m/e* value as that observed for the main fragment of (PorNb)₂O₃. The e.s.r., i.r., and u.v.-vis. characteristics are summarized in Table 1.

The *i*-*E* curves (rotating Pt electrode) of compounds (1) in THF [TBA⁺ ClO₄⁻ or TBA⁺ PF₆⁻ as supporting electrolyte (TBA⁺ = tetrabutylammonium)] show 3 reduction (A₁, B₁, and C₁) and either one ill-defined oxidation (D₁) or no oxidation waves (Table 2). As shown by cyclic voltammetry (Figure), wave A₁ is irreversible and corresponds to the cleavage of the acetate ligand with formation of (2); waves B₁ and C₁, which are reversible and whose half-wave potentials obey Furhop's relationship ($\Delta E_{1/2}$ ca. 0.4 V),⁴ are the waves of the porphyrin ring. Wave D₁, which is irreversible, probably corresponds to the oxidation of the ring. An example of *i*-*E* curves for the reduction is given in the Figure.

We have carried out controlled potential electrolyses at the potential of wave A (using a platinum grid). The results depend on the supporting electrolyte and on whether the anodic and the cathodic compartments are separated.

TABLE 2. Electrochemical data for (1)-(3).¹

	<i>E</i> _{1/2} (ox.)/V ^a		- <i>E</i> _{1/2} (red.)/V ^a		
	Wave D	Wave E	Wave A	Wave B	Wave C
(1a)	1.1 (i) ^b		1.10 (i)	1.25 (r)	1.66 (r)
(2a)	0.55 (i) ^b			1.20 (r)	1.60 (r)
(3a)	0.96 (i)		1.48 (i)	0.95 (r)	1.70 (r)
(1b)	1.24 (i) ^b		0.92 (i)	1.03 (r)	1.45 (r)
(2b)				0.96 (r)	1.44 (r)
(3b)	1.14 (i)		0.69 (r)	1.18 (r)	
(1c)	1.38 (i) ^b		0.90 (i)	1.01 (r)	1.48 (r)
(2c)		0.28 (i) ^b		0.91 (r)	1.42 (r)
(3c)	1.09 (i)		0.71 (i)	1.20 (r)	

^a i = irreversible; r = reversible. ^b Ill defined.

If TBA⁺ ClO₄⁻ is used, (2) is obtained after consumption of 1 F, with or without separation of the compartments. The *i*-*E* curve of (2) consists of 2 reduction (B₂ and C₂) and two oxidation (D₂, E₂) one-electron waves which correspond to the reduction and oxidation of the porphyrin ring (Table 2 and Figure). When TBA⁺ PF₆⁻ is used without separation of the half-cells, (2) is again obtained after consumption of 1 F, but it is slowly transformed (several hours) to give new compounds (3). Compounds (3) give rise to 10-line e.s.r. spectra, which are different from those of compounds (2) (Table 1), implying Nb^{IV} derivatives. They give rise to 3 (or 2) reduction waves (B₃, A₃ and C₃) and one one-electron oxidation wave (Table 2 and Figure). Wave A₃, irreversible, probably corresponds to the reduction of the metal. Waves B₃ and C₃ are reversible; they can be ascribed to the reduction of the ring. If the electrolysis is carried out in a

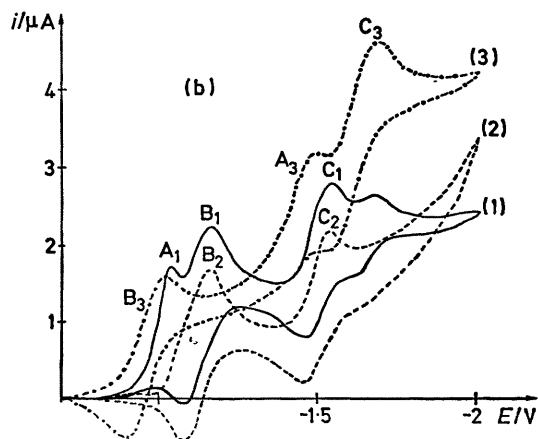
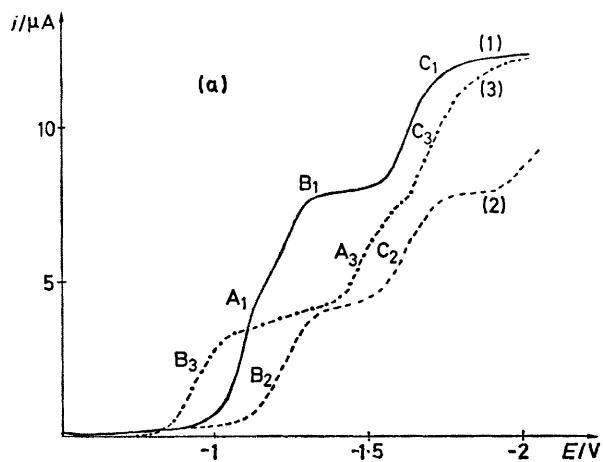
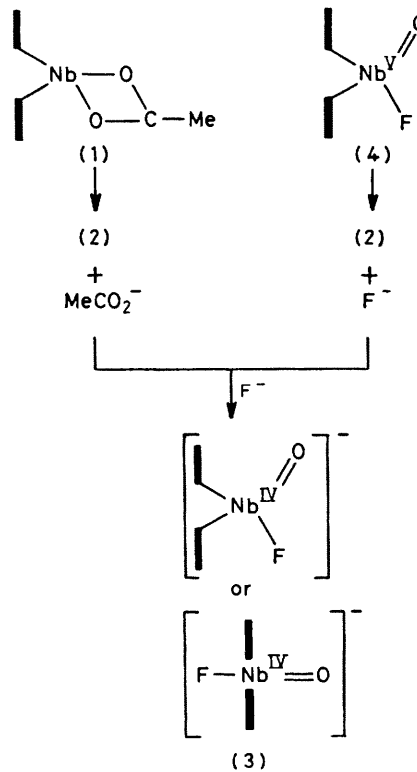


FIGURE. (a) *i*-*E* curves (rotating Pt electrode); (b) cyclic voltammograms (static Pt electrode). —, (1a); ---, (2a); ·····, (3a).



SCHEME

separated cell, (2) is formed and is not transformed, however, compound (3) appears slowly after the anolyte is mixed with the catholyte. Compound (3) is also obtained by electrolysis of OEPNbOF (4)⁵ with TBA⁺ClO₄⁻ as supporting electrolyte, (2) is obtained as an intermediate and slowly changes into (3). These results can be rationalized as shown in the Scheme. The fluoride ions are either generated on the anode by electrolysis of the hexafluorophosphate (1), or by reductive cleavage of (4). The conversion of (4) into (3)

can be explained by the ionic character of the Nb-F bond (*cf.* structure of the acetate)² which would result in a pre-dissociation yielding the fluoride ion, or by a rebonding of the fluorine atom to give a different type of co-ordination (Scheme).

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