Chemical and Electrochemical Preparation of Low Oxidation State Niobium Porphyrinates

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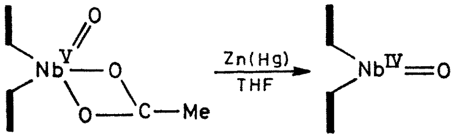
Summary Zinc amalgam or electrochemical reduction of porphyrinatoniobium(v) oxide acetates leads to porphyrinatoniobium(iv) oxides, which are characterized by their e s r , i r , and u v –vis spectra

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 (T*p*MePP)] (**1**) Trihalogenoderivatives of niobium(v) tetraphenylporphyrins were prepared more recently by Green *et al* [3] We describe here the preparation of niobium(iv) porphyrins



(**1**) (**2**)

a, Por = OEP
b, Por = TPP
c, Por = T*p*MePP

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 e s r spectra of compounds (**2**) show the 10 lines which are to be expected for niobium(iv) complexes The Nb=O i r vibration of compounds (**2**) is at *ca* 1000 cm^{-1}, which is comparable with that for Ti=O in titanylporphyrins, which are also pentaco-ordinated For compounds (**1**) the band appears near 900 cm^{-1} A shift of the Soret band of < 7 nm is observed when passing from (**1**) to (**2**) The

Table 1 Spectroscopic data for (**1**)—(**3**)

	E s r		ν_{max} (Nb=O) /cm^{-1}	λ_{max}/nm ($\epsilon \times 10^{-4}$)
	g	*a*/G		
(**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, $(PorNb)_2O_3$, and the molecular peak $PorNbO^{+\cdot}$ of (**2**) appears at the same *m/e* value as that observed for the main fragment of $(PorNb)_2O_3$. 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 [$TBA^+ ClO_4^-$ or $TBA^+ PF_6^-$ as supporting electrolyte (TBA^+ = tetrabutylammonium)] show 3 reduction (A_1, B_1, and C_1) and either one ill-defined oxidation (D_1) or no oxidation waves (Table 2). As shown by cyclic voltammetry (Figure), wave A_1 is irreversible and corresponds to the cleavage of the acetate ligand with formation of (**2**); waves B_1 and C_1, 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 D_1, 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.

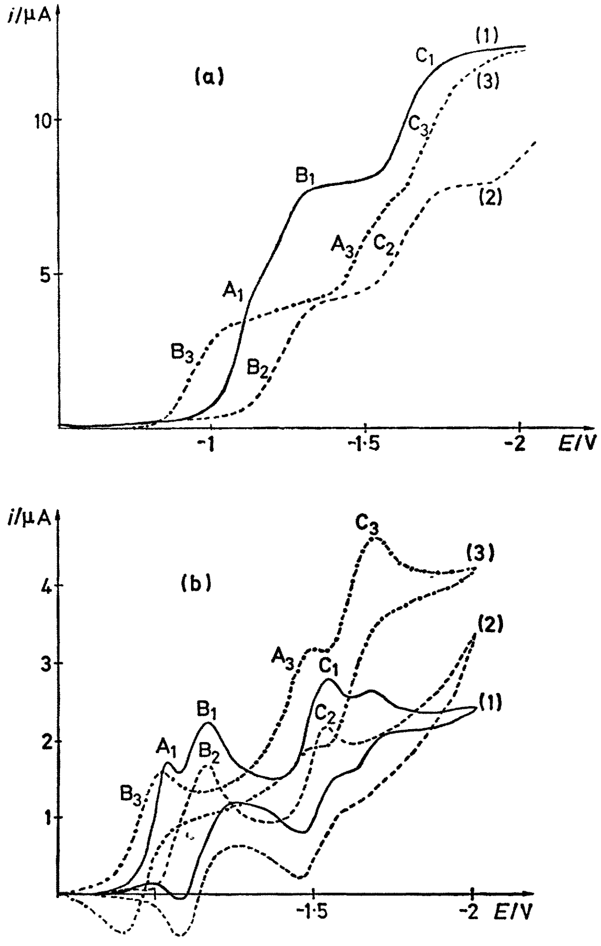


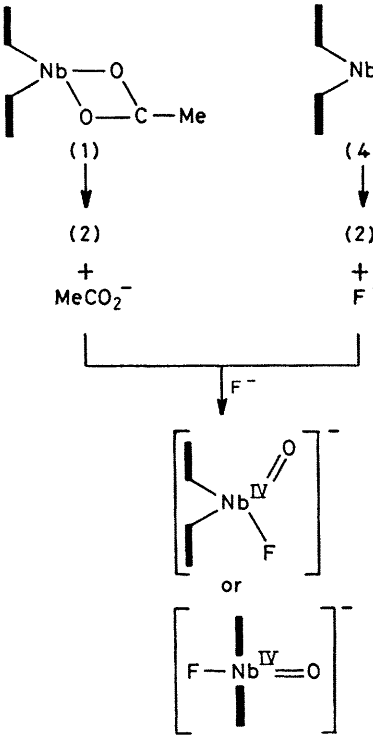
FIGURE. (a) *i–E* curves (rotating Pt electrode); (b) cyclic voltammogramms (static Pt electrode). ——, (**1a**); - - - -, (**2a**); -·-·-·-, (**3a**).

TABLE 2. Electrochemical data for (**1**)—(**3**).

	$E_{1/2}$(ox.)/V[a]		$-E_{1/2}$(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 $TBA^+ ClO_4^-$ 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 (B_2 and C_2) and two oxidation (D_2, E_2) one-electron waves which correspond to the reduction and oxidation of the porphyrin ring (Table 2 and Figure). When $TBA^+ PF_6^-$ 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 (B_3, A_3 and C_3) and one one-electron oxidation wave (Table 2 and Figure). Wave A_3, irreversible, probably corresponds to the reduction of the metal. Waves B_3 and C_3 are reversible; they can be ascribed to the reduction of the ring. If the electrolysis is carried out in a



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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 $TBA^+ClO_4^-$ 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 predissociation 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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