

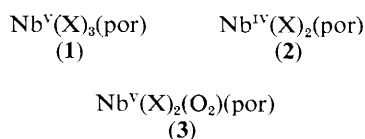
Synthesis and Characterization of Niobium(IV) Porphyrins. Formation and Spectroscopic Properties of Dioxygen Adducts of Niobium(IV) Porphyrins

Philippe Richard and Roger Guillard *

Laboratoire de Synthèse et d'Electrosynthèse Organométallique associé au C.N.R.S. (LA 33), Faculté des Sciences 'Gabriel,' 6, Bd Gabriel, 21100 Dijon, France

The niobium(IV) porphyrins $\text{Nb}^{\text{IV}}(\text{X})_2(\text{por})$ have been prepared from $\text{Nb}^{\text{V}}(\text{X})_3(\text{por})$ [por = meso-tetraphenylporphinato (TPP), meso-tetra-*m*-tolylporphinato (TMTP), or meso-tetra-*p*-tolylporphinato (TPTP); X = Cl or Br]; irreversible oxygenation of these low-valent porphyrins yields adducts such as $\text{Nb}^{\text{V}}(\text{X})_2(\text{O}_2)(\text{por})$ and e.s.r. and i.r. data show that the niobium- O_2 bonding in the dioxygen complexes is best described by the superoxide formalism.

The interaction of dioxygen with metalloporphyrins remains a topic of extreme interest and the subject has been extensively reviewed in recent years.¹ Irreversible oxygenation of Cr^{II} and reversible oxygenation of Fe^{II} and Co^{II} porphyrins yield species for which the metal- O_2 bonding is best described by the superoxide formalism; however, only a few complexes are correctly formulated as paramagnetic superoxides. We report here a convenient synthetic procedure for the isolation of niobium(IV) porphyrins by reduction of higher oxidation state halogeno derivatives and structural determination of these complexes. Our results concern the spectroscopic characterization of the niobium porphyrin dioxygen adducts as superoxide complexes.



- a**; X = Cl, por = TPP
b; X = Br, por = TPP
c; X = Cl, por = TMTP
d; X = Br, por = TMTP
e; X = Cl, por = TPTP
f; X = Br, por = TPTP

Reduction by zinc amalgam (1 g) of a dry oxygen-free tetrahydrofuran solution (50 ml) containing 500 mg of $\text{Nb}^{\text{V}}(\text{Br})_3(\text{TPP})^{\ddagger}$ (**1b**) led in a few minutes to a green precipitate. The solid was filtered off, washed with heptane, and dried [285 mg, 60% yield of $\text{Nb}^{\text{IV}}(\text{Br})_2(\text{TPP})$, (**2b**)]. The formation of (**2b**) is conveniently monitored by u.v.-visible spectroscopy; the absorption spectra of compounds (**1b**) and (**2b**) are of the 'normal' type and the Soret band appears respectively at 414 and 438 nm. Complexes (**2a**) and (**2c-e**) were obtained similarly from (**1a**) and (**1c-e**), and all complexes (**2**) in THF show a Soret band near 438 nm.

Hyperfine splittings in the e.s.r. spectra of compounds (**2**) at room temperature are typical of d^1 complexes; the spectra exhibit 10 hyperfine lines of an unpaired electron localized over a ^{93}Nb nucleus ($I = 9/2$) ($A_{\text{Nb}} = 147 \times 10^{-4} \text{ cm}^{-1}$, $g = 1.961$). Values of the g factor and hyperfine splitting are obtained from a comparison of experimental and simulated e.s.r. spectra.[‡]

[†] Abbreviations used: por = porphinato; TPP = meso-tetraphenylporphinato; TMTP = meso-tetra-*m*-tolylporphinato; TPTP = meso-tetra-*p*-tolylporphinato; THF = tetrahydrofuran.

[‡] Isotropic e.s.r. data (in THF) for $\text{Nb}^{\text{IV}}(\text{X})_2(\text{por})$, g , $A_{\text{Nb}} \times 10^{-4}$ in cm^{-1} : (**2a**), 1.962, 143; (**2b**) 1.962, 147; (**2c**), 1.962, 148; (**2d**), 1.962, 147; (**2e**), 1.962, 148; (**2f**), too insoluble to be measured.

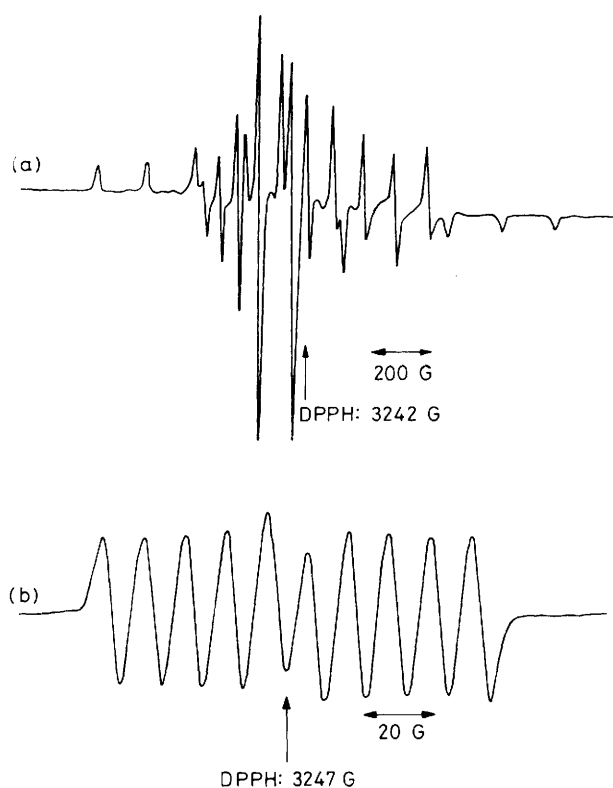
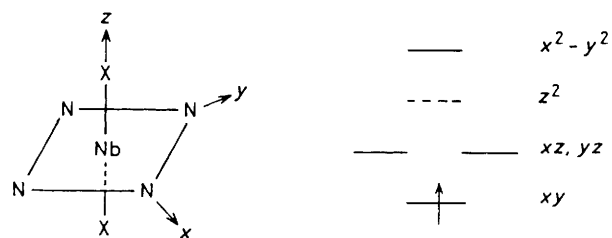


Figure 1. E.s.r. spectra: (a) of **(2e)** in frozen THF solution at 77 K; (b) of a solution of **(3b)** in THF at room temperature. DPPH = diphenylpicrylhydrazyl. $1 \text{ G} = 10^{-4} \text{ T}$.

Symmetrical ligation of two halogeno-ligands is consistent with either a *trans*- or a *cis*-co-ordination. E.s.r. spectra of these six-co-ordinate complexes in frozen solution (THF) allow a discrimination between the two possible configurations; the spectrum of **(2e)** [Figure 1(a)] exhibits two sets of hyperfine lines for a niobium(IV) complex with axial symmetry ($A_{\parallel} = 224 \times 10^{-4} \text{ cm}^{-1}$; $A_{\perp} = 112 \times 10^{-4} \text{ cm}^{-1}$; $g_{\parallel} = 1.942$; $g_{\perp} = 1.965$). Our experimental results are typical of a d^1 ion with the unpaired electron mainly in a d_{xy} orbital (Scheme 1).

Exposure of **(2b)** in THF to molecular oxygen leads to a red solution and gives rise to the e.s.r. spectrum shown in Figure 1(b).

Upon admission of O_2 , a new ten-line signal grows at lower field ($g = 2.002$) while the resonance of the d^1 complex **(2b)**



Scheme 1

decreases in intensity and disappears. The e.s.r. spectrum due to the molecular oxygen adduct is in reasonable agreement with the superoxo Nb^{V} formulation **(3b)**, for which a super-hyperfine (s.h.) coupling of an unpaired electron with the Nb nucleus is observed, the electron being mainly localized on an oxygen atom ($A_{s.h.} = 10.8 \times 10^{-4} \text{ cm}^{-1}$).[§] If nitrogen is passed through the red solution, the original niobium(IV) complex is not recovered. The adducts **(3)** are relatively stable at room temperature and under a dry atmosphere undergo slow degradation to yield tri- μ -oxo compounds, $\text{Nb}^{\text{V}}(\text{O})_3(\text{por})_2$.³

The i.r. spectrum of $\text{Nb}^{\text{IV}}(\text{Br})_2(\text{TPP})$ in Nujol was recorded after exposure to $^{18}\text{O}_2$. A new band at 1220 cm^{-1} increased with time. This band is consistent with an oxygen-oxygen stretching vibration of a superoxide ion,⁴ and this result is in good agreement with the e.s.r. data.

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[§] All compounds **(3)** in THF exhibit the same g and A constants within experimental error.