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LETTER

4-Fluorophenylimido osmium(VI) porphyrins. Isolation and characterization

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Although many transition metal imido complexes have been reported [1], the known imido metalloporphyrins are very few [2]. Buchler *et al.* obtained a phosphineimido manganese porphyrin by treatment of a nitrido manganese porphyrin with triphenylphosphine [2a]. Groves and Takahashi characterized an acylimidomanganese porphyrin from the reaction of a nitrido manganese porphyrin with trifluoroacetic anhydride [2b]. A hydrazido iron porphyrin containing an Fe–N multiple bond was isolated by Mansuy *et al.* from the O_2-dependent oxidation of 1-amino-2,2,6,6-tetramethylpiperidine in the presence of an iron porphyrin [2c]. We have recently reported the synthesis of tert-butylimido complexes of ruthenium(VI) and osmium(VI) porphyrins [3a]. Here the synthesis of two 4-fluorophenylimido osmium(VI) porphyrins are described.

We have synthesized bis(4-fluoroanilino)-osmium(IV) porphyrins, $Os(Por)(4\text{-}F\text{-}PhNH)_2$ (Por = TPP, **1**; 3,4,5-MeO-TPP, **2**)** by treatment of dinitrogen osmium(II) porphyrins with 4-fluoroaniline in tetrahydrofuran (THF) [3b]. Reflux for several hours of a solution of complex **1** or **2** in aerobic THF containing tert-butylamine results in the formation of (4-fluorophenylimido)oxoosmium(VI) porphyrins Os(Por)(O)(4-F-PhN) (Por = TPP, **3**; 3,4,5-MeO-TPP, **4**). Both **3** and **4** can be purified by chromatography on an Al_2O_3 column (Activity II) using CH_2Cl_2 as the eluent. Recrystallization from dichloromethane–heptane yields dark purple crystals (yield ~60%). *Anal.* **3**: Calc. for $C_{50}H_{32}N_5FOOs$: C, 64.71; H, 3.48; N, 7.55. Found: C, 64.22; H, 3.37; N, 7.25%. **4**: Calc. for $C_{62}H_{56}N_5FO_{13}Os$: C, 57.80; H, 4.38; N, 5.44. Found: C, 56.82; H, 4.42; N, 5.34%.

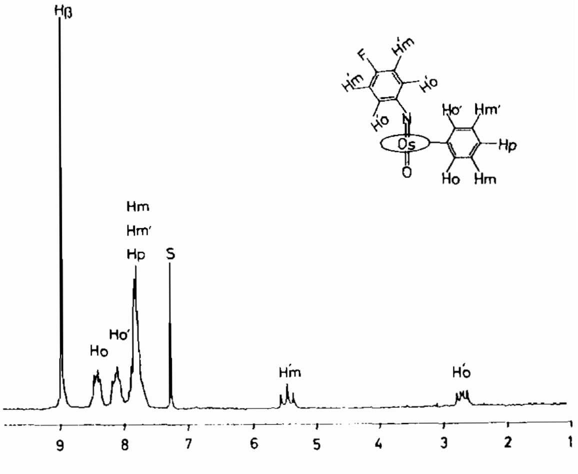

Fig. 1. ^1H NMR spectrum of Os(TPP)(O)(4-F-PhN) (90 MHz, $CDCl_3$, TMS).

Complexes **3** and **4** are characterized by ^1H NMR spectrometry†. The ^1H NMR spectrum of **3** is shown in Fig. 1. For both **3** and **4**, the pyrrolic protons (H_β) give a sharp singlet at a normal position, indicating that they are diamagnetic. The large H_β values (8.95 and 9.07 ppm for **3** and **4**, respectively) are in agreement with the +6 oxidation state of osmium (cf. $H_\beta = 9.13$ and 9.24 ppm for $Os(VI)(TPP)(O)_2$ [4] and $Os(VI)(3,4,5\text{-}MeO\text{-}TPP)(O)_2$ [3], respectively). The *ortho* proton resonances of the porphyrin ring appear as two well resolved multiplets for **3** or two well resolved doublets for **4**. Integration suggests that only one 4-fluorophenylimido group is coordinated to the Os(Por) moiety. All these are consistent with an asymmetric structure of **3** and **4** having slightly bent Os–N–C geometry which is required by the 18-electron rule [5]. It is apparent, from a comparison of the proton resonances of the axial 4-fluorophenyl group (H'_o and H'_m) of the amido complexes (**1**: $H'_o = 2.95$, $H'_m = 5.70$ ppm; **2**: $H'_o = 3.02$, $H'_m = 5.72$ ppm [3]) and the imido complexes (**3**: $H'_o = 2.65$, $H'_m = 5.42$ ppm; **4**: $H'_o = 2.73$, $H'_m = 5.49$ ppm), that the formation of the imido complexes leads to a considerable upfield shift of those proton resonances. This can be expected, since the Os–N bond in the imido complexes should be significantly shorter than that bond in the

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**Abbreviations: Por = porphyrinato dianion; TPP = *meso*-tetraphenylporphyrinato dianion; 3,4,5-MeO-TPP = *meso*-tetra-3,4,5-trimethoxyphenylporphyrinato dianion.

† ^1H NMR data (90 MHz, $CDCl_3$, TMS, δ, ppm): **3**: H_β 8.95(8H,s); H_o 8.41(4H,m); $H_{o'}$ 8.10(4H,m); H_m, $H_{m'}$, H_p 7.78(12H,m); N-C_6H_4F: H'_o 2.65(2H,qm); H'_m 5.42(2H,tm). **4**: H_β 9.07(8H,s); H_o 7.65(4H,d); $H_{o'}$ 7.34(4H,d); *m*-OCH_3 3.98(12H,s); *m′*-OCH_3 3.97(12H,s); *p*-OCH_3 4.20(12H,s); N-C_6H_4F: H'_o 2.73(2H,qm); H'_m 5.49(2H,tm).

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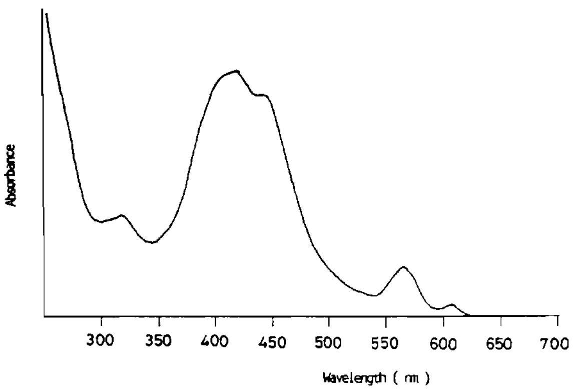

Fig. 2. UV–Vis spectrum of Os(3,4,5-MeO-TPP)(O)(4-F-PhN)(THF).

amido complexes, causing the protons in the 4-fluorophenylimido ligand to be closer to the porphyrin ring and thus more strongly affected by the ring current.

The structure of **3** and **4** is further confirmed by IR measurements. Firstly, the IR spectra of both **3** and **4** exhibit no N–H stretching bands. Secondly, a new intense band appears at 1229 cm^{-1} in the spectrum of **3**. This band is absent in the IR spectra of other *meso*-tetraphenylporphyrinato osmium porphyrins, such as Os(TPP)(CO)(MeOH), Os(TPP)-$(O)_2$ and complex **1** etc., and can be considered as the band characteristic of the imido ligand [5]. However, for complex **4**, this band is obscured by a strong band of the equatorial porphyrinato ligand. Thirdly, the Os=O stretching band (ν(Os=O)) is observed for both **3** and **4** (**3**: 835 cm^{-1} (very strong); **4**: 837 cm^{-1} (strong); cf. Os(TPP)$(O)_2$: 845 cm^{-1} (very strong) [4]; Os(3,4,5-MeO-TPP)$(O)_2$: 840 cm^{-1} (strong) [3]). Further, the 'oxidation state marker' band [6] appearing at 1019 and 1022 cm^{-1} for **3** and **4**, respectively, is consistent with the +6 oxidation state of osmium. This band is observed at 1021 and 1026 cm^{-1} for Os(VI)(TPP)$(O)_2$ and Os(VI)(3,4,5-MeO-TPP)$(O)_2$, respectively.

Complexes **3** and **4** give nearly the same UV–Vis spectra, whose structure closely resembles that of dioxoosmium(VI) porphyrins*. Figure 2 shows the UV–Vis spectrum of complex **4**. It is obvious that all bands, except the Soret band, of the imido complexes **3** and **4** are remarkably blue shifted as compared with the corresponding bands of the dioxoosmium(VI) porphyrins.

A solution of the imido complex **3** or **4** in dichloromethane is red–green, just like nitridoosmium(VI) porphyrins [7]. Both **3** and **4** are air-stable. During the oxidation of the amido osmium(IV) complexes by O_2, the existence of tertbutylamine is essential to the formation of the imido complexes **3** and **4**. Otherwise, only the dioxoosmium(VI) porphyrins are obtained.

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*Data of UV–Vis spectra (THF, λ_{max}): **3**: 319, 415 (Soret), 444 sh, 564, 602 nm; **4**: 318, 419 (Soret), 442 sh, 566, 606 nm; Os(TPP)$(O)_2$: 339, 393 (Soret), 456 sh, 580, 620 nm; Os(3,4,5-MeO-TPP)$(O)_2$: 331, 396 (Soret), 459 sh, 584, 625 nm.

Acknowledgements

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