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Preliminary communication

Trimethylphosphine complexes of iron(III) tetraphenylporphyrin; ^{1}H NMR studies of the electronic effect in paramagnetic haems

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Abstract

New low-spin ferric tetraphenylporphyrin-phosphine complexes were prepared in order to undertake a study by ^{1}H NMR spectroscopy of the sensitivity of the trimethylphosphine ligand to the *trans* effect, and to improve the understanding of the electronic structure of PMe_3-ligated haemo-proteins.

The binding of phosphine by haemoproteins is a subject of much current interest [1]. It has been reported that PMe_3, which is considerably bulkier than O_2 or CO, can serve as a sensitive ^{1}H NMR probe of the ligand binding in met-myoglobin (met-Mb) and in met-haemoglobin (met-Hb) [2]. For instance, separate ^{1}H NMR signals can be observed for the PMe_3 ligands bound to the α and β chains in met-Hb [2]. In order to provide information about the *trans*-electronic effect on trimethylphosphine binding, we have synthesised tetraphenylporphyriniron(III)-PMe_3 complexes. The spectroscopic properties (^{1}H NMR) of these complexes are compared with those of haemoprotein adducts.

Previous studies on model complexes have been undertaken at low-temperature on dissolved species [3,4], and a major difficulty that we have encountered in preparing trimethylphosphine ferric porphyrin derivatives has been the autoreduction of ferric porphyrin [5]. This difficulty has been circumvented by use of $Fe(TPP)ClO_4$ as starting material [6]. Addition of two equivalents of PMe_3 to 0.2 g of $Fe(TPP)ClO_4$ (0.26 mmol) in toluene (20 cm^3) under argon at 20 °C resulted in rapid formation of $Fe(TPP)(PMe_3)_2ClO_4$. The solution was set aside overnight and the fine crystals then filtered off (yield 88%). The electronic spectrum of $Fe(TPP)(PMe_3)_2ClO_4$ exhibits hyperspectra with two Soret bands (λ_{max} at 359 nm (ϵ 99 mM^{-1} cm^{-1}) and (λ_{max} at 440 nm (ϵ 128 mM^{-1} cm^{-1})) and a band at 618 nm (ϵ 45 mM^{-1} cm^{-1}). Hyperporphyrin spectra have been reported previously [3] for dimercaptide hemin and mercaptide-phosphine-hemin complexes [3]. Mixed

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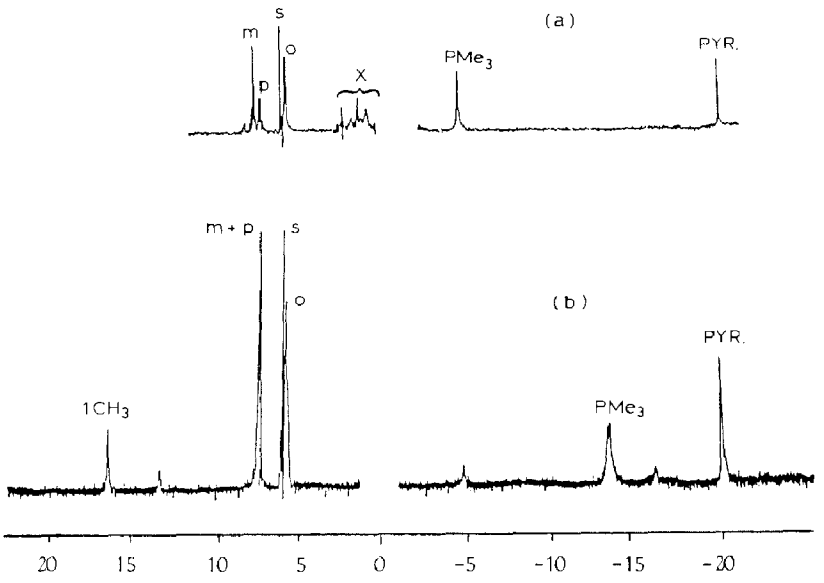

Fig. 1. ^{1}H NMR spectra of Fe(TPP)$(PMe_3)_2ClO_4$ (**1**) (a) and FeTPP(PMe_3)(1-MeIm)ClO_4 (**2**) (b). All spectra were obtained in CD_2Cl_2 at 20 °C. Assignments of the various resonances are indicated: S indicates the residual solvent peak and X indicate an impurity peak. Tetramethylsilane was used as internal reference.

hexacoordinated derivatives with PMe_3 and nitrogen bases as axial ligands have been synthesised; for example, progressive addition of 1.2 equivalents of PMe_3 in CH_2Cl_2 (5 cm^3, 20 °C, under argon) to 0.3 g of Fe(TPP)(1-MeIm)$_2ClO_4$ (0.32 mmol) [6] in CH_2Cl_2 (15 cm^3) gave Fe(TPP)(PMe_3)(1-MeIm)ClO_4, which was precipited by additional hexane (40 cm^3). The yield of the CH_2Cl_2 solvate was 0.25 g (78%), λ_{max} at 422 nm (ϵ 131 mM^{-1} cm^{-1}), 541 nm (ϵ 47 mM^{-1} cm^{-1}) and 568 nm (ϵ 46 mM^{-1} cm^{-1}).

The ^{1}H NMR spectra of Fe(TPP)$(PMe_3)_2ClO_4$ (**1**) and Fe(TPP)(PMe_3)(1-MeIm)ClO_4 (**2**) are shown in Fig. 1. The signal lying far upfield (ca. −20 ppm) can be assigned to the pyrrole proton atoms on the basis of data for low-spin porphyriniron(III) complexes [7]. The PMe_3 signal was unambiguously assigned by examination of $P(CD_3)_3$ complexes. Other information pertinent to assignments was gained from selective frequency decoupling experiments and by consideration of the relative integrations.

In order to characterize the electronic structure of the porphyriniron phosphine, the chemical shifts were analysed by empirical methods [7]. The isotropic chemical shifts were calculated by using diamagnetic Fe(TPP)$(PMe_3)_2$ and Fe(TPP)(PMe_3)(1-MeIm) complexes as references [8]. The geometric factor calculated values of the different porphyrin proton sites of Fe(TPP)$(PMe_3)_2ClO_4$ (**1**) and Fe(TPP)(PMe_3)(1-MeIm)ClO_4 (**2**), and ESR data were used to determine the corresponding dipolar shifts. We used the following well-known equation [7]:

$$(\Delta H/H)_{dip} = -\frac{\beta^2 S(S+1)}{9\,kT}\left(g_{\parallel}^2 - g_{\perp}^2\right)\frac{3\cos^2\theta - 1}{R^3}$$

The effective axial field permits the use of this equation with $g_\perp = [1/2(g_{xx}^2 + g_{yy}^2)]^{1/2}$ and $g_\parallel = g_{zz}$. ESR data measurement at 140 K in CH_2Cl_2 yield the

Table 1

Observed chemical shifts and separation of the isotropic shift into contact and dipolar contribution for $Fe(TPP)(PMe_3)_2ClO_4$ (**1**) and $Fe(TPP)(PMe_3)(1\text{-MeIm})ClO_4$ (**2**)

Proton type	$Fe(TPP)(PMe_3)_2ClO_4$				$Fe(TPP)(PMe_3)(1\text{-MeIm})ClO_4$			
	$(\Delta H/H)$	$^a(\Delta H/H)_{iso}$	$^b(\Delta H/H)_{dip}$	$(\Delta H/H)_{con}$	$(\Delta H/H)$	$^a(\Delta H/H)_{iso}$	$^c(\Delta H/H)_{dip}$	$(\Delta H/H)_{con}$
o-H	5.00	−2.91	−2.16	−0.75	5.03	−2.75	−2.77	0
m-H	6.78	−0.75	−0.92	+0.23	6.26	−1.23	−1.26	0
p-H	6.36	−1.17	−0.82	−0.29	6.2	−1.23	−1.13	0
pyrr-H	−19.6	−27.81	−4.08	−23.73	−19.45	−27.34	−5.24	−22.10
PMe_3	−5.00	−2.39	+10.93	−13.32	−12.95	−10.08	14.05	−24.10
Me(Im)					15.03	13.43 [d]	6.12	7.31
CH(Im)					12.18			
					−4.99			
					−15.72			

[a] Chemical shift in ppm at 20 °C with Me_4Si as internal reference (CD_2Cl_2). [b] Isotropic shift with diamagnetic $Fe(TPP)(PMe_3)_2$ complex as reference [8]. [c] Isotropic shift with diamagnetic $Fe(TPP)(PMe_3)(1\text{-MeIm})$ complex as reference [8]. [d] Isotropic shift with diamagnetic $Fe(TPP)(1\text{-MeIm})_2$ complex as reference [11].

following g values for **1**: 2.687, 2.088, 1.680 and for **2**: 2.890, 2.286, 1.542. The geometric factor for PMe_3 was calculated by use of structural data from our X-ray study of $Fe(TPP)(PMe_2Ph)_2$ [8]: $(3\cos^2\theta - 1)/r^3 = 0.01837$ Å^{-3}. The results are listed in Table 1. Both of the phosphine-complexes **1** and **2** have pyrrole proton resonances at very high-field ($\delta \approx -19$ ppm); this shift is typical of iron(III) in a low spin state and is attributed to the strong field character of the phosphine ligand. The large upfield pyrrole proton contact shifts agree with charge transfer from the porphyrin $3e\pi$ orbitals to the d_{xz} and d_{yz} orbitals of the metal [7].

Detailed analysis of PMe_3 isotropic shift for $Fe(TPP)(PMe_3)_2ClO_4$ (**1**) suggests that the contact shift and the dipolar shift have similar magnitudes but opposite signs. Thus the coordination of an alkylphosphine to the iron center leads to a complex with unpaired spin density on the methyl group of PMe_3. The influence of axial imidazole is clearly demonstrated in Fig. 1 by the presence of PMe_3 proton signal at stronger field (≈ -13 ppm). On going from $Fe(TPP)(PMe_3)_2ClO_4$ to $Fe(TPP)(PMe_3)(1\text{-MeIm})ClO_4$, the dominant hyperfine shift change observed for PMe_3 must involve the contact interaction (Table 1). This finding favors the interpretation that spin transfer in both species involves iron → $PMe_3\pi$ charge transfer, since this mechanism would be enhanced by the presence of an imidazole acting as a π donnor [9,10]. From consideration of the chemical shifts of PMe_3 protons in the present complex **2**, it seems reasonable to expect that the PMe_3 ligand in low-spin ferric haemoproteins should resonate upfield of the diamagnetic region. For met-myoglobin-PMe_3, and met-hemoglobin-PMe_3, proton resonances have been detected at ≈ -12 ppm (model complex **2**, $\delta = -13$ ppm) which can be safely attributed to PMe_3 [2]. The highfield shift of PMe_3 can thus be used as a probe for the haeme environments in haemoproteins. Application of this probe is currently under way.

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