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Preliminary communication

Unusually facile formation of a hexa-coordinated bisamine adduct by tetrakis(pentafluorophenyl)porphinatocobalt(II) and azaferrocene

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Abstract

An ESR study of axial coordination of azaferrocene to tetrakis(pentafluorophenyl)porphinatocobalt(II) is reported. It reveals that, in contrast to pyridine, azaferrocene readily coordinates easily at both axial sites of the cobalt center.

Cobalt(II) porphyrins (CoP) in the presence of amines (B) readily form the monoamine complexes **1** [1–5]. In the presence of a large excess of amine (and if the amine is a sufficiently strong σ-donor, e.g. quinuclidine or piperidine) bisamine adducts **2** are also formed. When dioxygen is present in the solution, an equilibrium between **1** and the η^1-dioxygen complex **3** is generally observed:

$$\begin{tikzcd}
\mathrm{CoP} \arrow[r, shift left, "\mathrm{B}"] & \mathrm{CoP(B)} \arrow[l, shift left] \arrow[r, shift left, "\mathrm{B}"] & \mathrm{CoP(B)_2} \arrow[l, shift left] \\
 & (1) \arrow[d, shift right, "\mathrm{O_2}"'] & (2) \\
 & \mathrm{CoP(B)(O_2)} \arrow[u, shift right] & \\
 & (3) &
\end{tikzcd}$$

We have recently become interested in the complexation by CoP of an organometallic amine, azaferrocene $(\eta\text{-}^5C_4H_4N)(\eta\text{-}^5C_5H_5)Fe$ (**4**), in an effort to develop new photosensitive oxygen carrier systems [6] and to provide further insight

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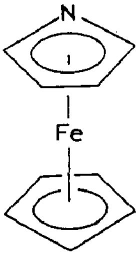
into the coordination chemistry of η^5-pyrrolyl complexes [7].



(4)

We previously found [8] that **4** readily forms adducts of types **1** and **3**; and that their physicochemical properties are similar to those of their pyridine-based counterparts, and confirmed that the *N*-ligating properties of azaferrocene and pyridine are similar. More recently, however, we showed [9] that photochemical properties of $CoP(4)(O_2)$ and $CoP(Py)(O_2)$ are different, the former being photolabile and losing O_2 on visible light irradiation, whereas the latter is photostable.

We report here another example of the striking difference between coordinating properties of **4** and Py. We have found that in toluene solutions and at low temperature **4** tends to form the bisamine adduct with the highly electrophilic CoP, tetrakis(pentafluorophenyl)porphinatocobalt(II) (hereafter denoted CoP_F), even at the molar ratio $CoP_F : 4 = 1:1$, whereas Py forms only monoamine adduct at a molar ratio CoP_F : Py of 1 : 10.

Figure 1a presents the ESR spectrum of CoP_F (5×10^{-4} *M*) and Py (5×10^{-3} *M*) in toluene glass at 100 K in the presence of air. This spectrum reveals the

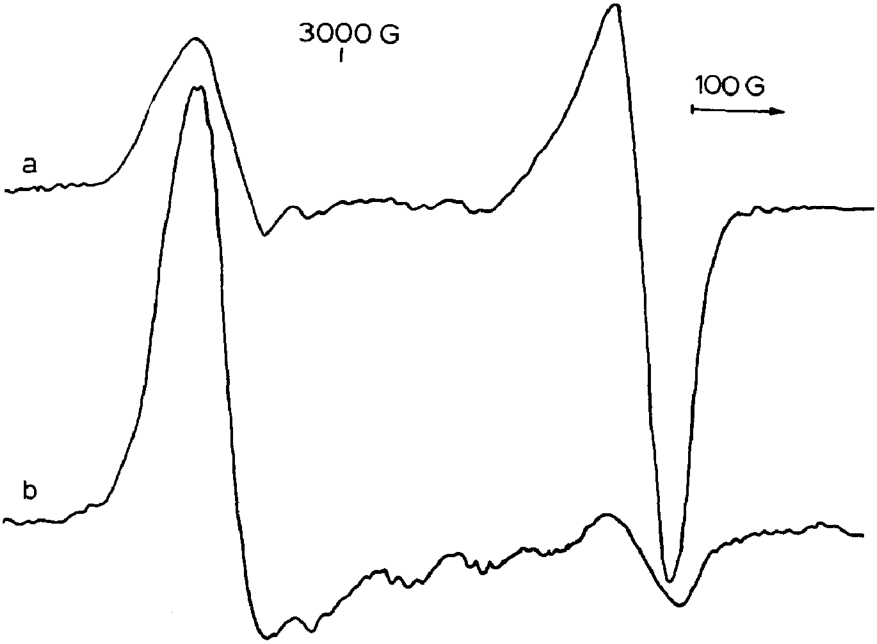


Fig. 1. ESR spectra (9.3 GHz) of CoP_F (5×10^{-4} *M*) and Py (5×10^{-3} *M*) in toluene glass at 100 K: (a) aerated sample; (b) sample purged with argon.

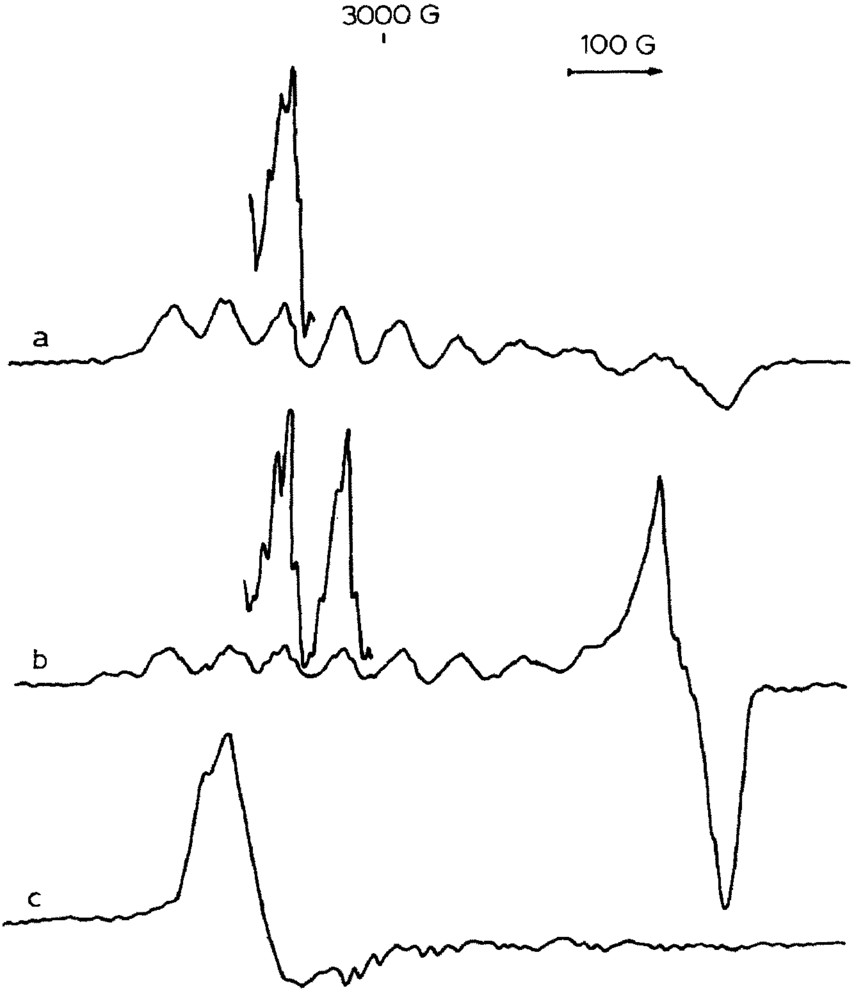


Fig. 2. ESR spectra (9.3 GHz) in toluene glass at 100 K in the presence of air: (a) CoP_F (5×10^{-4} *M*)+**4** (5×10^{-3} *M*); (b) CoP_F (5×10^{-4} *M*)+**4** (5×10^{-4} *M*); (c) sample (b) after photolysis (see in the text).

presence of the monoamine adduct $CoP_F(Py)$ and η^1-dioxygen complexes of type $CoP_F(Py)(O_2)$, or possibly $CoP_F(O_2)$. When the solution was deoxygenated by bubbling of argon the signal of η^1-dioxygen complexes diminished and the superhyperfine structure of $CoP_F(Py)$ was better resolved (Fig. 1b). The spectral parameters are: $g_\perp = 2.297$, $g_\parallel = 2.028$, $a_\parallel^{Co} = 83$ G, $a_\parallel^{N} = 18$ G for $CoP_F(Py)$, and $g_{iso} = 2.003$ for η^1-dioxygen complexes. The presence of one coordinated molecule of pyridine is unambiguously confirmed by the splitting of the parallel components into triplets. Thus even in the presence of a ten-fold excess of Py only monoamine adduct $CoP_F(Py)$ is formed.

When pyridine was replaced by azaferrocene the ESR spectrum changed completely (Fig. 2a). Only a small amount of the η^1-dioxygen complex was observed in the aerated sample, the major component being identified as $CoP_F(\mathbf{4})_2$. The eight lines of its spectrum shown in Fig. 2a correspond to the perpendicular component, the parallel one being much weaker and observable only at high signal gain. The measured spectral parameters are: $g_\perp = 2.234$, $g_\parallel = 1.838$, $a_\perp^{Co} = 62$ G, $a_\parallel^{Co} = 83$ G,

$a_{\perp}^{N} = 13$ G. The superhyperfine structure of the perpendicular lines confirms the presence of two coordinated molecules of azaferrocene (5 bands: 1.2.3.2.1, due to interaction of two ^{14}N with $I = 1$). Moreover, the formation of $CoP_F(\mathbf{4})_2$ accounts for the lack of η^1-dioxygen complexes (no coordination sites available).

This unusually facile formation of bis-amine adduct $CoP_F(\mathbf{4})_2$ prompted us to study in greater detail the behavior of the CoP_F–**4** system at various ratios of components. We have found that at 0.5 molar equivalent of **4** the ESR spectrum was similar to that shown in Fig. 1a. Accordingly, in this case $CoP_F(\mathbf{4})$ and η^1-dioxygen complexes were formed, probably $CoP_F(O_2)$ and $CoP_F(\mathbf{4})(O_2)$. Obviously "bare" porphyrin, CoP_F, could also be present, but its signal would be superimposed on the perpendicular component of the $CoP_F(\mathbf{4})$ signal. At 1 molar equivalent of **4** we observed the ESR spectrum (Fig. 2b) similar to that presented in Fig. 2a, but the signal corresponding to η^1-dioxygen complexes was markedly stronger. Thus, even at the molar ratio $CoP_F : \mathbf{4} = 1 : 1$ there is a strong preference for formation of $CoP_F(\mathbf{4})_2$. Finally, when the amount of **4** was increased from 1 to 10 equiv. there was a gradual decrease in the ESR signal of η^1-dioxygen species. This means that **4** gradually replaces O_2, to form $CoP_F(\mathbf{4})_2$.

Within the context of these observations it is relevant to note that the CoP_F–**4** system behaves like iron(II)-based systems FeP–B, which readily form bis-base complexes $FeP(B)_2$ (coordination of the second molecule of the base is easier than that of the first) [3,4].

We have also observed that irradiation with visible light (900 W Xe lamp and CS-051 filter) of the solution of CoP_F containing 1 equiv. of **4** at 200 K results in the disappearance of the signals of both $CoP_F(\mathbf{4})_2$ and the η^1-dioxygen species and the formation of $CoP_F(\mathbf{4})$ (Fig. 2c, $g_{\perp} = 2.305$, $g_{\parallel} = 2.030$, $a^{N} = 18$ G, $a^{Co} = 82$ G).

In conclusion, we have demonstrated, for the first time, that coordination chemistry of η^5-pyrrolyl complexes can be very different from that of pyridine. Such complexes may be therefore ligands of choice for constructing bi- and poly-nuclear complexes with unusual properties.

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