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Preliminary communication

Axial coordination of azaferrocene to a cobalt(II) porphyrin and alkylcobaloximes

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Abstract

A study of axial coordination of azaferrocene to tetra-*p*-tolylporphinatocobalt-(II) and alkylcobaloximes is reported. The ESR and O_2 binding data show that N-ligating properties of this organometallic nitrogen base are similar to those of pyridine.

Coordination of axial ligands (usually organic nitrogen bases such as pyridines or imidazoles) plays an important role in the chemistry of complexes related to vitamin B_{12}, namely cobalamines, cobaloximes and cobalt(II) porphyrins. For example, formation of five-coordinated adducts **1** (eq. 1) enables cobalt(II) porphyrins (CoP) to bind reversibly dioxygen [1] (eq. 2).

$$\mathrm{CoP} + \mathrm{L} \overset{K_1}{\rightleftarrows} \mathrm{CoP} \cdot (\mathrm{L}) \qquad (1)$$

(1)

$$\mathrm{CoP} \cdot (\mathrm{L}) + \mathrm{O_2} \overset{K_2}{\rightleftarrows} \mathrm{CoP} \cdot (\mathrm{L}) \cdot (\mathrm{O_2}) \qquad (2)$$

(2)

Furthermore, the reactivity of the cobalt–carbon bond in alkylcobaloximes (**3**) which are now frequently used as precursors of organic radicals [2], depends largely on the nature of the axial ligand L [3].

Here we report that an organometallic nitrogen base, azaferrocene (**4**, $pK_a = 4.5$) [4] also forms complexes of type **1–3**, which contain two metal centers (Co and Fe) bridged via the η^1,η^5-pyrrolyl ligand. We thought that investigation of such complexes would provide new insight not only into the coordinating properties of cobalt macrocyclic systems, but also into the chemistry of η^5-pyrrolyl metal complexes

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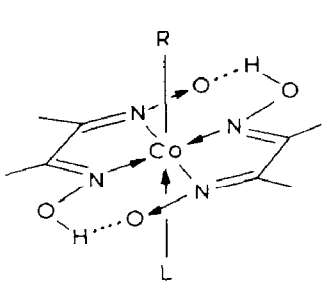
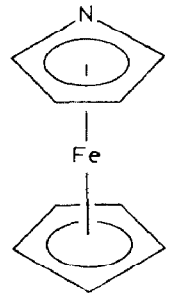


(3 ≡ R−Co(dmgH)$_2$L)



(4)

which have recently attracted considerable attention [5]. In this investigation emphasis is placed an comparison of *N*-ligating properties of **4** with those of pyridine (Py).

The addition of **4** to an argon-saturated solution of tetra-*p*-tolylporphinatocobalt(II) (CoTTP) results in changes in the visible spectrum, similar to those caused by the addition of pyridine (Fig. 1). These changes can be interpreted in terms of the reversible formation in both cases of the five-coordinated adducts **1** [6]. The non-isosbestic behaviour of the CoTTP · **4** system at higher concentration of **4** is undoubtedly due to the absorption by this ligand in the spectral region scanned. This absorption (the tail of the large band at 433 nm) hampered our determination of K_1 (eq. 1) for the above system, but we believe that it is close to that for CoTTP · (Py) (Log $K_1 = 2.742$) [7].

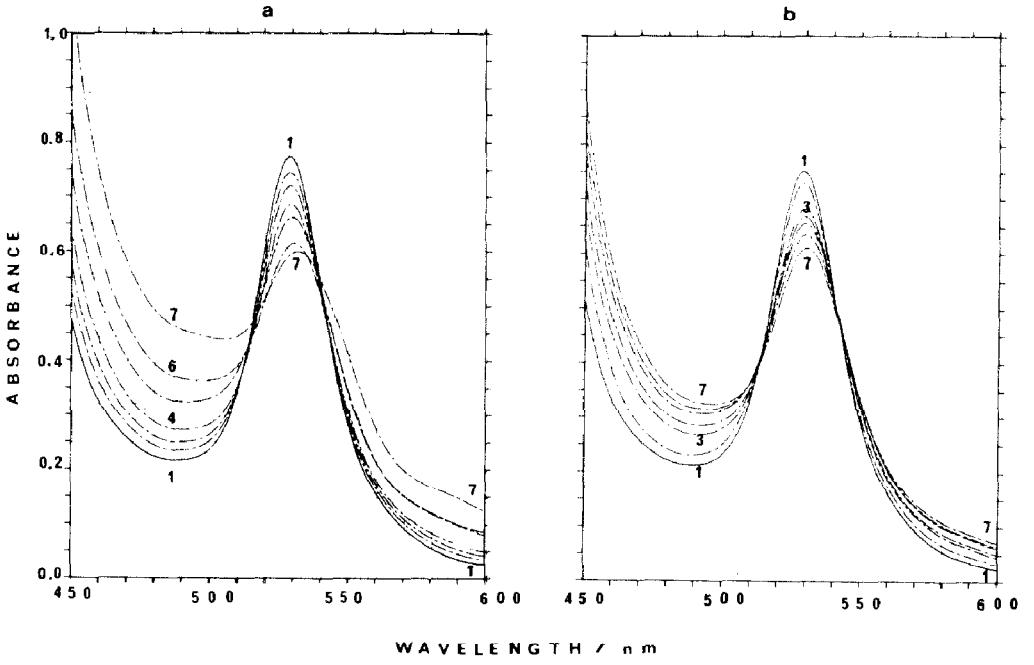


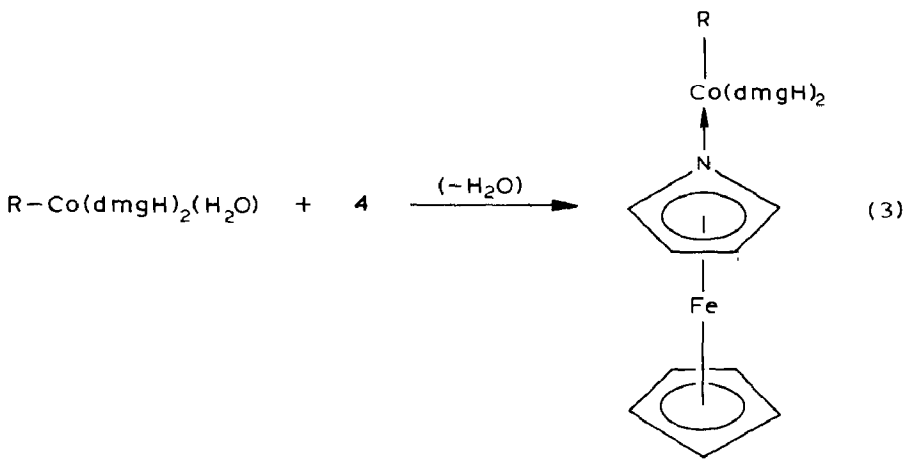
Fig. 1. Spectral changes observed when azaferrocene (a) or pyridine (b) are added to CoTTP (5×10^{-5} *M*) in toluene at 296 K. The curves 1–7 correspond to addition of 0, 1, 2, 4, 8, 16 and 32 equivalents of the ligand respectively.

The formation of the five-coordinated adduct CoTTP · **4** was also demonstrated by ESR spectroscopy. We found that a 1/1 mixture of CoTTP and **4** in deoxygenated toluene glass at 133 K displays the spectrum typical for cobalt(II) porphyrin-amine adducts [8], showing a superhyperfine splitting caused by the nitrogen atom of axially coordinated **4**. Surprisingly, the spectral parameters are practically the same as those observed, under the same conditions, for CoTTP · (Py) [9*]. This suggests similar *N*-ligating properties of **4** and Py and the absence of interactions between Co^{II} and Fe^{II} centres in the CoTTP · **4** complex.

In aerated (ambient pressure) toluene solutions of CoTPP and **4** an equilibrium between CoTTP · **4** and CoTTP · **4** · (O_2) was observed at 192–243 K (at lower temperatures the formation of the dioxygen complex was complete). By using the procedure described by Walker [10], we obtained values of ΔH -13.9 ± 1.5 kcal/mol and ΔS -58 eu. The analogous values obtained for the pyridine-type system are ΔH -13.0 ± 1.5 kcal/mol; ΔS -47 eu (lit. ΔH -9.30 kcal/mol ΔS -57 eu) [1a]. Since our measurements were carried out under the same conditions for both systems, it is evident that there is no substantial difference in their O_2 bonding abilities.

In contrast to cobalt(II) porphyrin amine adducts, which usually exist only in solution, alkylcobaloximes **3** (L = amine) are isolable and stable compounds. We have prepared a series of such complexes **5a**–**5c**, containing **4** such as the axial ligand by substitution of the coordinated water in the corresponding aquo compounds (eq. 3) [11*].

The complexes **5a** and **5b** are air-stable orange crystalline solids, whereas **5c** is an orange oil. Their structures were confirmed by ^1H NMR spectroscopy and by elementary analysis [12].



(3)

5a R = CH_3

5b R = $(CH_3)_2CH$

5c R = $CH_3(CH_2)_{15}$

* Reference number with asterisk indicates a note in the list of references.

We have found that irradiation with visible light of a solution of **5b** in $CHCl_3$ generates the isopropyl radical, identified as its adduct with nitrosodurene (g_{iso} 2.0073 ± 0.0001, a^N 14.36 ± 0.01 G, a^H 8.05 ± 0.01 G). Coordination of azaferrocene therefore does not affect the homolysis of the cobalt–carbon bond.

In conclusion, we have shown that azaferrocene can serve as a 2e donor ligand (through the nitrogen atom) for cobalt macrocyclic systems, and that its ligating properties are similar to those of pyridine.

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9 ESR parameters: CoTTP·**4**: $g_\perp$ = 2.3211 ± 0.0008, $g_\parallel$ = 2.0205 ± 0.0008, a^{Co} 83 ± 0.8 G, a^N 17.16 ± 0.7 G. CoTTP·(Py): $g_\perp$ = 2.3190 ± 0.0009, $g_\parallel$ = 2.0254 ± 0.0009, a^{Co} 84.7 ± 0.8 G, a^N 16.1 ± 0.8 G. CoTTP·(**4**)·$(O)_2$: g_{iso} = 2.0164 ± 0.0008, $a^{Co-O-O^{\cdot}}$ = 11.4 ± 0.8 G. CoTTP·(Py)·(O_2): g_{iso} = 2.0173 ± 0.0008 $a^{Co-O-O^{\cdot}}$ = 11.1 ± 0.8 G.

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11 Typically, a solution of an equimolar mixture (0.1–0.2 mmol) of $RCo(dmgH)_2(H_2O)$ and **4** in $CHCl_3$ (5–10 ml) was stirred at room temperature for 10 min. The orange solution was concentrated and chromatographed on silica gel with chloroform/ethyl acetate 1/1 as eluent. Analytical samples were prepared by recrystallisation from CH_2Cl_2/hexanes.

12 **5a** (86%): ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.63 (s, 3H, Me), 2.12 (s, 12H, Hdmg), 4.21 (s, 5H, Cp), 4.57 (s, 2H, β-pyrrolyl), 5.33 (s, 2H, α-pyrrolyl), 18.07 (s, 2H, OH). Anal. Found: C, 44.4; H, 5.3; N, 14.7. $C_{18}H_{26}N_5O_4CoFe$ calcd.: C, 44.0; H, 5.3; N, 14.3%. **5b** (90%): ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.48 (d, *J* 7 Hz, 3H, CH_3), 1.71 (m, 1H, CH), 2.13 (s, 12H, Hdmg), 4.23 (s, 5H, Cp), 4.63 (s, 2H, β-pyrrolyl), 5.39 (s, 2H, α-pyrrolyl), 18.10 (s, 2H, OH). Anal. Found: C, 46.4; H, 5.6; N 13.6. $C_{20}H_{30}CoFeN_5O_4$ calcd.: C, 46.3; H, 5.8; N, 13.5%. **5c** (82%): ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.88 (t, *J* 7 Hz, $CoCH_2$), 1.2 (31H, $CH_3(CH_2)_{14}$, 2.21 (s, 12 H, Hdmg), 4.23 (s, 5H, Cp), 4.63 (s, 2H, β-pyrrolyl), 5.42 (s, 2H, α-pyrrolyl), 18.21 (s, 2H, OH).