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Axial coordination of azaferrocene to transition metal macrocyclic complexes: photoactivation of the macrocycle

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Abstract

Azaferrocene, $(\eta^5-C_4H_4N)(\eta^5-C_5H_5)Fe$, coordinates to the axial sites of metal macrocylic complexes such as cobaloximes, metalloporphyrins and phthalocyanines. Despite the "three-dimensional" structure of this organometallic ligand, X-ray crystal data and electronic properties of the adducts reveal tight coordination. This may be due to significant π acceptor properties of azaferrocene. The photochemical properties of the macrocyclic complex–azaferrocene adducts (or macrocyclic complex in the presence of azaferrocene) have been examined. It has been established that the macrocyclic complex can be easily photoreduced either at the metal centre or at the macrocycle. This photoreactivity was attributed to the photoinduced electron transfer (PET) from azaferrocene to the macrocycle. The reverse transfer is hampered by fast decomposition of the azaferrocenium system (only in the case of methylcobaloxime complex was a reversible PET observed by laser flash photolysis). In all experiments azaferrocene proved much more efficient than classical organic electron donors (amines).

Keywords: Axial coordination; Azaferrocene; Cobaloximes; Metalloporphyrins; Phthalocyanines; Photochemistry

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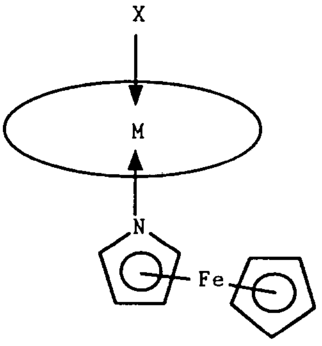
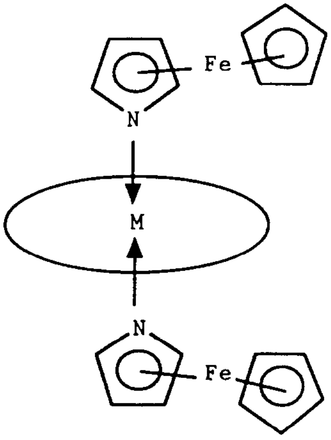
1. Introduction

The photochemistry of metal macrocyclic complexes such as metalloporphyrins, phthalocyanines etc. continues to attract a great deal of interest owing to its relevance to photosynthesis, solar energy conversion and photodynamic therapy of cancer [1]. Furthermore, the photochemistry of molecules comprising two or more redox-active metal-based centres which are covalently linked is a burgeoning topic within supramolecular photochemistry with applications in molecular electronic devices, sensors etc. [2].

A few years ago we became interested in polynuclear transition metal systems built up from a metal macrocyclic complex and axially coordinated with one or two molecules of an organometallic base, azaferrocene (AF). Such species (structures **A** and **B**) exhibit features of both aforementioned systems and we expected they would display interesting and unusual photochemical properties.



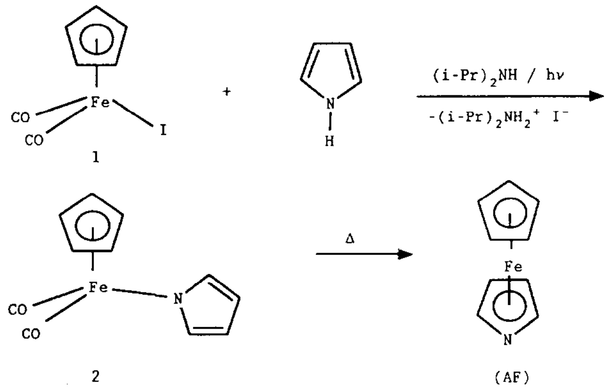
(A)



(B)

We have chosen the nitrogen system (phospha-, arsa- and even bismaferrocene have also been synthesized and can be considered as potential axial ligands for macrocyclic complexes; see for example Ref. [3]) because of the very important role played in nature by coordination of nitrogen bases (especially imidazole from the histidine residue) in haem proteins and related systems. Obviously, we were aware that there are no natural macrocyclic systems containing AF, but we wondered whether the principal properties of these natural complexes (spin state, electronic properties etc.) can be modelled in polynuclear organometallic systems. Moreover, we hoped that bi- and polynuclear complexes of the types **A** and **B** will display interesting photochemistry owing to possible photoinduced electron transfer (PET) between different redox sites (metals, macrocycle).

In this review we present the results of this research, but, before starting it, we would like to give to the reader some brief information concerning the synthetic methods leading to AF and describe some its chemical properties.



Scheme 1.

2. Synthesis and chemical properties of azaferrocene

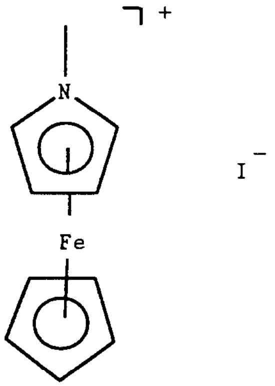
Azaferrocene and some of its alkyl derivatives were first prepared by reaction of ($\eta^5-C_5H_5$)Fe(CO)$_2$I (**1**) with the potassium salt of the corresponding pyrrole in boiling benzene [4]. This reaction involves formation of the intermediate η^1-*N*-pyrrolyl complex **2**, which was isolated in the case of unsubstituted pyrrole when the reaction was carried out under milder conditions (60 °C) [5]. The reported yield of AF was rather poor (22%).

We have recently reported a photochemical modification of this route [6,7]. Species **1** irradiated with visible light with pyrrole and diisopropylamine in toluene afforded **2** in relatively good yield (66%) (Scheme 1). The decarbonylation of **2** in boiling cyclohexane–toluene (12:1) gave AF in 92% yield. Consequently, this two-stage procedure affords AF in 61% overall yield. An important advantage of this approach is the replacement of dangerous potassium metal, used in the preparation of pyrrolylpotassium, by diisopropylamine.

More recently, another approach to azaferrocenes has been reported [8], but it was only checked for 2,3,4,5-tetramethylazaferrocene. Unfortunately, it can be expected that the coordinating properties of this complex will be significantly reduced owing to the steric hindrance around nitrogen.

In comparison with ferrocene, AF is considerably less stable thermally (it decomposes at 80 °C, whereas ferrocene is stable up to ca. 470 °C). It is somewhat air sensitive, especially in solution. However, solid samples of AF can be stored under argon at 0 °C and in the dark for several months without traces of decomposition.

The presence of the lone pair of electrons endows AF with basic and nucleophilic properties. In fact, the basicity of AF ($pK_a = 4.5$) is closely similar to that of quinoline ($pK_a = 4.65$) [4]. AF reacts with methyl iodide to afford the cationic *N*-methylpyrrole complex **3** [9] and coordinates through nitrogen to transition metals (vide infra).



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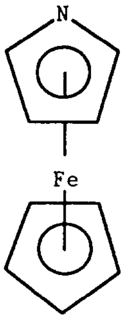
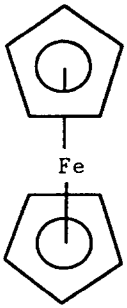
The redox properties of AF were studied by the cyclic voltammetry technique [10]. As expected, AF proved more difficult to oxidize ($Fe^{II} \rightarrow Fe^{III}$) and easier to reduce ($Fe^{II} \rightarrow Fe^{I}$) than ferrocene itself:





$E_{1/2}^{ox} = 0.60$ V $\quad$ $E_{1/2}^{ox} = 0.43$ V

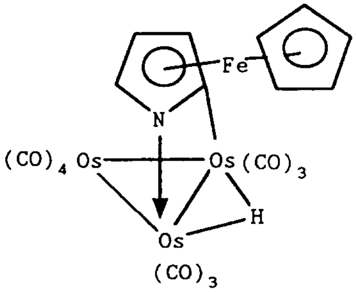
$E_{1/2}^{red} = -2.56$ V $\quad$ $E_{1/2}^{red} = -2.93$ V

(*vs.* SCE)

In striking contrast to the relatively stable ferrocinium cation, the azaferrocinium system proved highly unstable and reversible redox processes of AF were observed only at high potential sweep rates [10].

3. Coordination chemistry of azaferrocene

Azaferrocene behaves as a pyridine-like 2e donor ligand towards transition-metal centers. The first complexes to contain η^1-*N*-AF ligand were reported by Pyshnograeva et al. [11]: $M(AF)_2Cl_2$ (cis + trans), M = Pd, Pt. Another coordination mode of AF (cyclometallation) was recently reported by Deeming's group (structure 5) [12].



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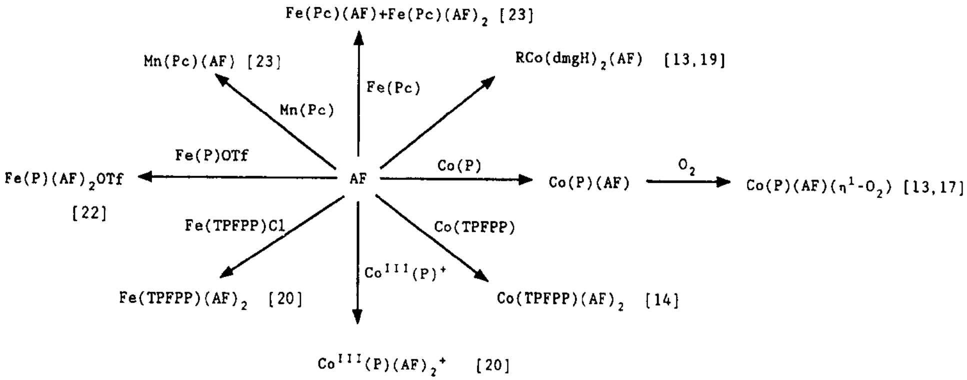
When beginning the work on the coordination of AF to metal macrocycles we thought that there would be severe steric interactions between the macrocycle and cyclopentadienyl hydrogen atoms if the pyrrolyl ligand plane is perpendicular to the macrocycle. Consequently, the system will probably adopt a sterically more favourable "tilted" orientation (Fig. 1).

Surprisingly, we have found that, despite the expected "tilting", AF readily coordinates to a variety of transition metal macrocyclic complexes (Scheme 2) [13–23].

In principle, AF forms the same types of complexes as do organic heterocyclic amines. However, in one case AF coordinates to a macrocycle more easily than an organic amine. Thus, according to electron paramagnetic resonance (EPR) spectra, CoTPFPP reacts with AF to give hexacoordinate $CoTPFPP(AF)_2$ (this adduct is formed even when equimolar amounts of CoTFPP and AF are mixed) [14]. Contrastingly, organic amines generally give rise only to pentacoordinate complexes CoP(B) and hexacoordinate species are formed only with strongly basic amines (e.g. piperidine) used in a very large excess (as a solvent) [24].

Fig. 1. Perpendicular and "tilted" coordination of AF to metal macrocycles.



Scheme 2.

Studying the coordination chemistry of AF one should take into consideration its reducing properties. An iron(III) porphyrin, Fe(TPFPP)Cl, reacts with AF in $CHCl_3$ at room temperature (RT) to give the hexacoordinate complex of the corresponding iron(II) porphyrin [21]:

$$\mathrm{Fe(TPFPP)Cl} \xrightarrow{\text{AF (excess)}} \mathrm{Fe(TPFPP)(AF)_2}$$

Neither Fe(TPP)Cl nor Fe(OEP)Cl reacts with AF under the same conditions. It therefore seems that this reaction takes place only with porphyrins displaying relatively high oxidizing properties to oxidize AF to $AF^{+\bullet}$. The reduction potentials (Fe^{III}/Fe^{II}) of Fe(TPP)Cl, Fe(OEP)Cl and Fe(TPFPP)Cl in DMF vs. a saturated calonel electrode (SCE) are −0.34 V [25], −0.52 V [25], and 0.04 V (a value calculated from the reported value of −0.46 V vs. Ag/Ag^+ [26]) respectively. These porphyrins therefore are not able to oxidize AF ($E_{1/2} = +0.60$ V [10]) in an outer sphere process. This is also confirmed by the fact that they do not react with the stronger outer sphere reductant ferrocene ($E_{1/2} = +0.43$ V [10]). Consequently, we think that reaction of Fe(TPFPP)Cl with AF involves formation of a complex by coordination of AF to the porphyrin. This renders the porphyrin iron(III) centre more prone to reduction. In fact, it is known that the coordination of pyridine markedly enhances the oxidizing properties of Fe(TPP)Cl (the reduction potential of Fe(TPP)Cl is −0.30 V vs. SCE in butyronitrile and +0.17 V in pyridine) [27]).

We propose the following mechanism for this reaction:

$$\mathrm{Fe^{III}(P)Cl + AF \rightarrow Fe^{III}(P)(AF)Cl}$$

$$\mathrm{Fe^{III}(P)(AF)Cl \rightarrow Fe^{II}(P) + AF^{+\bullet} + Cl^-}$$

$$\mathrm{Fe^{II}(P) + 2AF \rightarrow Fe^{II}(P)(AF)_2}$$

$$\mathrm{AF^{+\bullet} \rightarrow decomposition}$$

The lack of reactivity of Fe(TPP)Cl and Fe(OEP)Cl can be explained by assuming that the equilibrium concentration of $Fe^{III}(P)(AF)Cl$ is very low (the low rate of dissociation of Cl^- may constitute a kinetic barrier for the transformation of this adduct into a hexacoordinate species) [28]. The overall process is triggered by intramolecular electron transfer in $Fe^{III}(P)(AF)Cl$ if the porphyrin iron(III) centre displays sufficient oxidizing capabilities (FeTPFPP).

The reduction of iron(III) porphyrins by organic amines has already been reported [29]. This reaction takes place only when the amine is capable of binding to the iron(III) centre and contains the >CH—NH— moiety, which is oxidized to the imine function (>C=N—). Heterocyclic amines such as pyridine and imidazole are usually inert.

In contrast to the chlorides, the triflates Fe(TPP)OTf and Fe(OEP)OTf readily react with AF in chloroform solution at RT to afford hexacoordinate iron(III) porphyrin complexes [22]:

$$\mathrm{Fe(P)OTf} \xrightarrow{\text{AF (excess)}} \mathrm{[Fe(P)(AF)_2]OTf}$$

(P=TPP, OEP)

This reaction is in concert with the suggestion above concerning the role played by dissociation of the original axial ligand (triflate should dissociate more easily than chloride).

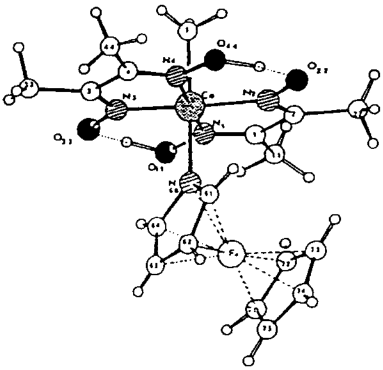
The X-ray crystal structures of three complexes, $Me(dmgH)_2(AF)$, $PhCH_2(dmgH)_2(AF)$ [19] and $FeTPFPP(AF)_2$ [21] are shown in Fig. 2.

In all these structures a tilted coordination of AF to a macrocycle was found. The dihedral angle between the pyrrolyl ligand plane and the plane of the macrocycle is 72° in $CH_3Co(dmgH)_2(AF)$, 71° in $PhCH_2Co(dmgH)_2(AF)$ [19] and 65° (67°) in $Fe(TPFPP)(AF)_2$ (the structure of the latter complex consists of two independent molecules) [21]. The azaferrocene moiety in these complexes exhibits a typical sandwich structure, the η^5-cyclopentadienyl and η^5-pyrrolyl ligands being planar and roughly parallel (dihedral angle, 3.5°–4.0°).

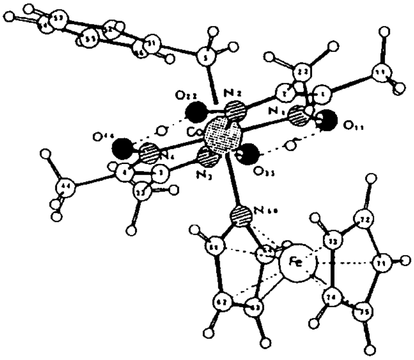
The axial Co—N and Co—C bonding distances in $CH_3Co(dmgH)_2(AF)$ and $PhCH_2Co(dmgH)_2(AF)$, together with the literature values for methyl- and benzylcobaloximes containing organic heterocyclic *N*-bases, are presented in Table 1.

Despite the "tilting", AF coordinates tightly to cobalt (especially in the methyl derivative). The axial Co—N distance in this complex is shorter than the same distance in its 2-methylimidazole and pyridine counterparts.

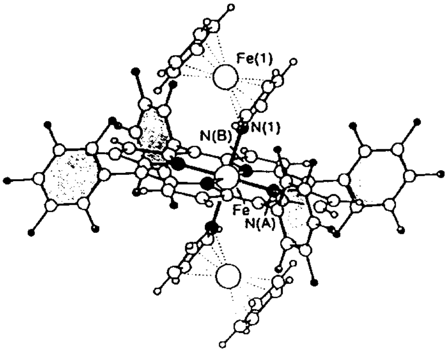
Relatively tight coordination of AF has also been found in $Fe(TPFPP)(AF)_2$ [21]. The axial Fe—N distance 2.05(2) Å in this complex is considerably shorter than the same distance in $Fe(TPP)(pip)_2$, 2.217(3) Å [31] (however, the different hybridizations of nitrogen, and the different geometries of the five- and six-membered rings and steric interactions between macrocycle and axial ligand, should be taken into account, in the direct comparison of these two complexes), and close to that in $Fe(TPP)(py)_2$, 2.037 (1) Å [32]. On the contrary, imidazoles coordinate more tightly to Fe(TPP) (2.004–2.012(4) Å) [33]. $Fe(TPFPP)(AF)_2$ exhibits a centrosymmetric structure with the iron atoms of the core lying in crystallographically imposed centres



$CH_3Co(dmgH)_2(AF)$ (19)



$PhCH_2Co(dmgH)_2(AF)$ (19)



Fe(TPFPP)$(AF)_2$ (21)

Fig. 2. X-ray structures of complexes of AF with metal macrocycles.

Table 1
The axial Co—N and Co—C distances in cobaloximes

Cobaloxime	Co—C (Å)	Co—N (Å)	Ref.
$CH_3Co(dmgH)_2(AF)$	2.018(5)	2.043(3)	[19]
$CH_3Co(dmgH)_2(MeIm)$	2.009(7)	2.058(5)	[30]
$CH_3Co(dmgH)_2(Py)$	1.998(5)	2.068(3)	[30]
$CH_3Co(dmgH)_2(Im)$	2.019(3)	1.985(3)	[30]
$PhCH_2Co(dmgH)_2(AF)$		2.066(3)	[19]
$PhCH_2Co(dmgH)_2(Py)$	2.064(4)	2.056(3)	[30]

of symmetry. Consequently, the three iron atoms lie on one axis forming an angle of 17.4–17.8° with the axis perpendicular to the tetrapyrrolic core.

The ligating properties of ligands are usually discussed in terms of their σ donor and π acceptor (donor) ability. The metal–ligand π bonding depends strongly on the electronic properties of the metal. Imidazoles are considered as π acceptors in their adducts with Co(II)porphyrins [34], whereas they act as π donors toward iron(II) and iron(III) porphyrins [35]. According to Walker [34] "the direction and the extent of π-bonding depend critically on the energies of the metal d_π and ligand π and π^* levels". The relative weak basicity of AF in comparison with for example imidazoles suggests that its coordinating properties can be due to high π acceptor ability. This nicely explains why AF coordinates more strongly to methyl- than to benzylcobaloxime, whereas pyridine displays the opposite preference. In fact, it can be expected that the stronger σ donor (methyl), increasing the electron density around cobalt, will favour coordination of π acceptor ligands.

Further evidence for "back bonding" from a metal carbonyl to AF was recently provided by a ^{57}Fe Mössbauer study [36]. The results are presented in Table 2.

It is seen that *N*-protonation and *N*-methylation which consist in simple σ donation significantly decrease the quadrupole splitting, indicating diminution of the electron density around iron. On the contrary, the quadrupole splitting in the $W(CO)_5$ complex of AF is close that of AF itself. Thus in $W(CO)_5$—AF σ donation is compensated by a reverse effect, "back bonding", and the total electron density around the iron atom in AF practically does not change on complexation.

Table 2
^{57}Fe Mössbauer parameters of AF and some of its derivatives at 78 K [36]

Complex	Isomer shift ($mm\ s^{-1}$)	Quadrupole splitting ($mm\ s^{-1}$)
AF	0.54(1)	2.51(1)
$AF(H^+)^a$	0.54(1)	2.36(1)
3	0.54(1)	2.36(1)
$AF—W(CO)_5$	0.58(1)	2.47(3)

[a] AF protonated in CF_3COOH.

The relatively strong ligating properties of AF have also been confirmed by the EPR spectra of [Fe(TPP) $(AF)_2$]OTf and [Fe(OEP) $(AF)_2$]OTf. These complexes exhibit "rhombic" low spin EPR spectra at low temperatures [22], which suggest a parallel alignment of two AF ligands. It is well established that such an alignment is characteristic of complexes of these porphyrins with strongly coordinating heterocyclic *N*-bases (unhindered, strongly basic imidazoles and pyridines). Otherwise, the perpendicular relative orientation of both axial ligands planes is observed, giving rise to highly anisotropic low spin spectra [37]. The "rhombic" spectra are characteristic of some cytochromes b, which contain iron(III) porphyrin core and two axial imidazole rings (from histidine) as a prosthetic group. These data show therefore that the coordination environment of iron in cytochromes b can be modelled by iron(III) porphyrins containing not only an organic but also an organometallic axial base.

4. Photochemistry of macrocyclic metal complexes containing axially coordinated AF

The photochemistry of polynuclear transition metal complexes attracts a great deal of attention owing to the possibility of a PET between metal centres [2]. We were therefore interested to know whether such a transfer is possible in macrocyclic transition metal complexes containing axially coordinated AF and, if so, how it will influence their photochemical properties. The direct evidence for PET between a metal centre in the macrocycle and an axial AF was provided by the nanosecond laser flash photolysis study of MeCo $(dmgH)_2(AF)$ and $PhCH_2Co$ $(dmgH)_2$ (AF) [18]. In contrast to their pyridine counterparts, these AF adducts irradiated at 353 nm display strong transient absorption at $\lambda > 600$ nm. The transient absorbance difference spectrum observed for the methyl complex is shown in Fig. 3, and the kinetic evolution of this absorbance at different monitoring wavelengths is shown in Fig. 4.

Almost the same behaviour was observed for the benzyl derivative. In the spectrum shown in Fig. 3 the absorption at 450–500 nm can be assigned to the formation of the cobalt(II) centre. However, the fact that the addition of nitrosodurene (spin trap for alkyl radicals) does not influence the lifetime of this absorbance suggests that formation of Co(II) does not involve the homolysis of the $Co-CH_3$ bond (a process which is typical for MeCo $(dmgH)_2(py)$, but proceeds much more slowly, and is strongly influenced by nitrosodurene [38]). On the contrary, absorption at $\lambda > 600$ nm can be assigned to the azaferrocenium chromophore. Although this chromophore is unstable on a longer time scale, and its electronic spectrum is unknown, one can expect that it should be closely similar to that of the ferrocinium cation, which absorbs at 600–650 nm ($e_{1u} \rightarrow e_{2g}$ ligand-to-metal charge transfer band) [39]. The absorption at longer wavelengths may indicate strong electronic interactions between Fe(III) and Co(II) in the transient species and may have metal-to-metal charge transfer (MMCT) nature. Mixed-valence (Fe(II)—Fe(III)) biferrocenes display similar, very broad, bands, tailing into the near-IR region, attributed to MMCT transitions [40].

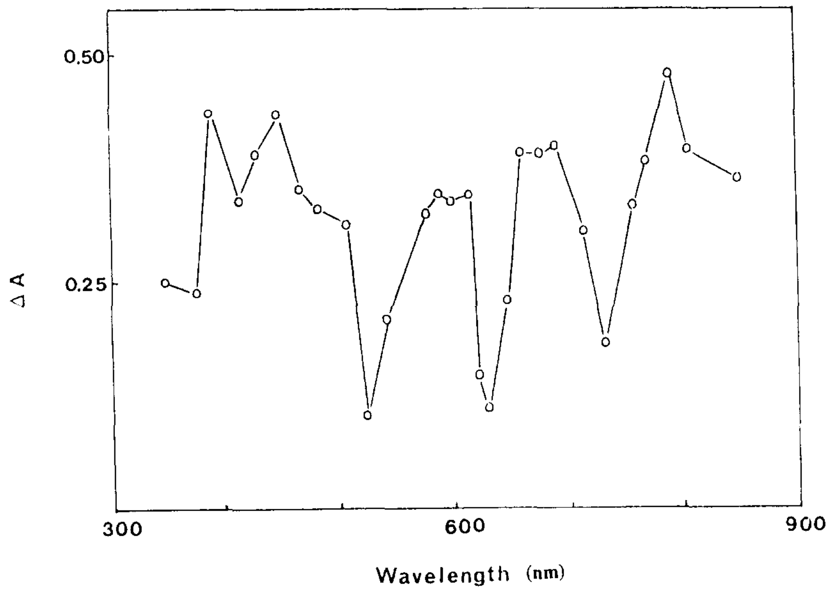


Fig. 3. Transient absorbance difference spectrum obtained 50 ns after excitation with a laser pulse (355 nm, 4 ns) of MeCo $(dmgH)_2(AF)$ in toluene. (With permission from Ref. [18].)

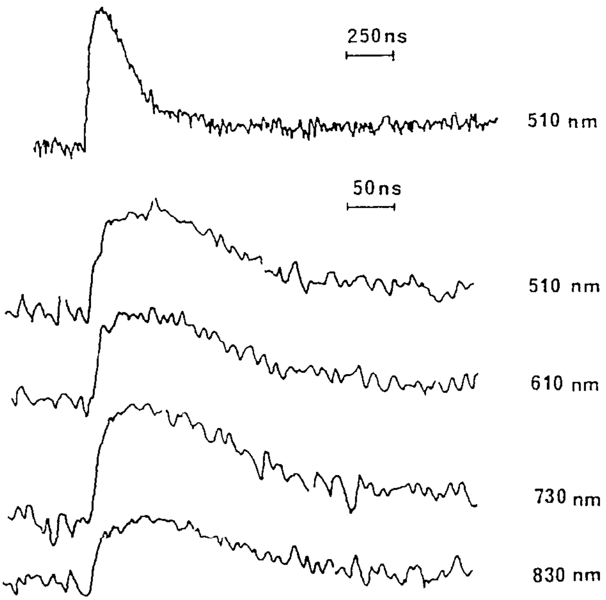


Fig. 4. Time dependence of the transient absorbance shown in Fig. 3 at different monitoring wavelengths. (With permission from Ref. [18].)

Considering all these facts, the formation of the azaferrocenium chromophore occurs simultaneusly with the formation of Co(II). This suggests PET as shown in Scheme 3.

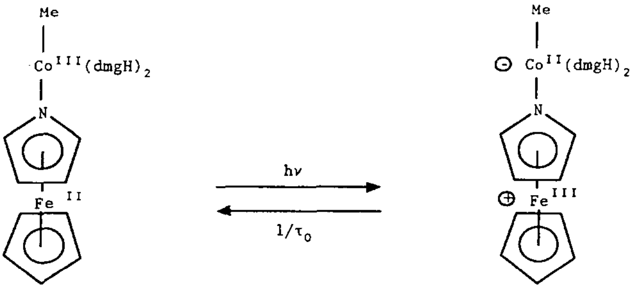
The transient species containing a Co(II)/Fe(III) redox couple decays exponentially with $k \approx 4 \times 10^6$ s^{-1}. The reverse electron transfer is therefore very efficient and cannot influence the photohomolysis of the Co—C bond.

The first example of net reaction photochemistry, due to axially coordinated AF was provided by the study of η^1-dioxygen adducts of Co(II) porphyrins [15]. Using EPR spectroscopy, it was observed that irradiation with visible light of cobalt porphyrin dioxygen complexes containing AF results in the ejection of triplet dioxygen, whereas the pyridine complexes proved photostable (Scheme 4).

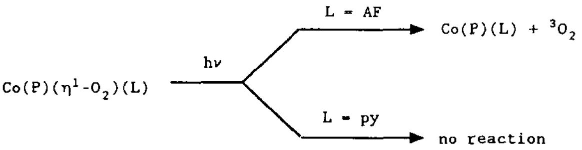
More detailed study showed that at the same intensity of irradiation, the rate of reaction decreases in the order P=TPP>TTP>*p*-MeOTPP. When the irradiation was stopped the reverse process, i.e. complexation of O_2 by Co(P) (AF), took place. Control experiments have shown that neither singlet dioxygen ($^1O_2$) nor superoxide anion ($O_2^{\bullet -}$) was formed.

The photoreactivity of the AF adducts can be explained by assuming PET between Co and Fe as shown in Scheme 5.

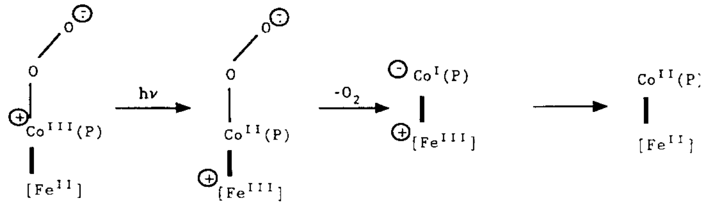
In fact, in our original paper we proposed PET in the opposite direction, i.e. from Co to Fe, but further experiments with complexes of Co(III) porphyrins with azaferrocene revealed the tendency of the macrocycle to reduction [20]. The hypothesis that PET occurs from Fe to Co is consistant with the observed reactivity order, which is the same as the expected order of reducibility of the Co centre. The destabilization of the dioxygen complex after photoreduction may be due to introduction of the electron on the π_v^* antibonding orbital. The reaction presented in Schemes 4 and 5 constitutes the first example of the photoejection of dioxygen from a



Scheme 3.



Scheme 4.



Scheme 5.

hexacoordinate dioxygen-amine adduct of a cobalt(II) porphyrin. Note also that the photoreversibility of dioxygen complexation is characteristic of natural dioxygen carriers, e.g. haemoglobin.

The photochemical behaviour of hexacoordinate complexes containing two molecules of AF depends strongly on the nature of the metal in the macrocyclic core. Thus, $[Co(TPP)(AF)_2](BF_4)$ undergoes photoreduction to Co(TPP) on irradiation with visible light in deoxygenated dimethylformamide solution [20], as monitored by electronic absorption (Fig. 5) and EPR spectroscopy.

The yield of Co(TPP) formed was 95% or more. There was no reaction in the dark, although subdued daylight was sufficient to produce detectable amounts of Co(TPP) in solutions of $[Co(TPP)(AF)_2](BF_4)$ before photolysis. The high photosensitivity of this AF adduct stands in sharp contrast to the behaviour of $[Co(TPP)(H_2O)_2](BF_4)$ and $[Co(TPP)(Im)_2](BF_4)$, which proved photostable under the same experimental conditions.

On the contrary, as indicated by EPR spectroscopy, the hexacoordinate complex of the fluorinated cobalt(II) porphyrin $Co(TPFPP)(AF)_2$ loses one AF molecule on irradiation with visible light in toluene solution at 180 K to afford Co(TPFPP)(AF) [17]. This result is interesting since the latter adduct cannot be obtained by simple mixing of equimolar amounts of Co(TPFPP) and AF (this procedure leads to a mixture of $Co(TPFPP)(AF)_2$ and Co(TPFPP)).

The plausible explanation of the photoreduction of Co(III) in $[Co(TPP)(AF)_2](BF_4)$ involves PET from Fe(II) to Co(III), followed by the loss of axial ligands and decomposition of $AF^{+\cdot}$ (Scheme 6).

The behaviour of $Co(TPFPP)(AF)_2$ seems more "classical" since there are reports of photoejection of amines from $Co(P)(B)_2$ complexes, leading to a mixture of penta- and tetracoordinate complexes. This reaction was studied using the laser flash photolysis technique [41].

The metallophthalocyanines are another class of metal macrocyclic complexes presenting a formidable challenge for photoredox chemistry initiated by coordination of AF. In fact, axial ligands (e.g. amines) coordinate to numerous phthalocyanines, and display rich redox chemistry, giving rise to a variety of products in which either the central metal atom or the macrocycle are oxidized or reduced [42,43].

The ligand AF coordinates to both iron(II) and manganese(II) phthalocyanine, $Fe^{II}Pc(2-)$ and $Mn^{II}Pc(2-)$ ($Pc(2-)$ denotes the phthalocyanine dianion), in solution in DMF or DMSO [23]. Analysis of the electronic spectra suggests that in the case of $Fe^{II}Pc(2-)$, two adducts, presumably $Fe^{II}Pc(2-)(AF)$ and $Fe^{II}Pc(2-)(AF)_2$

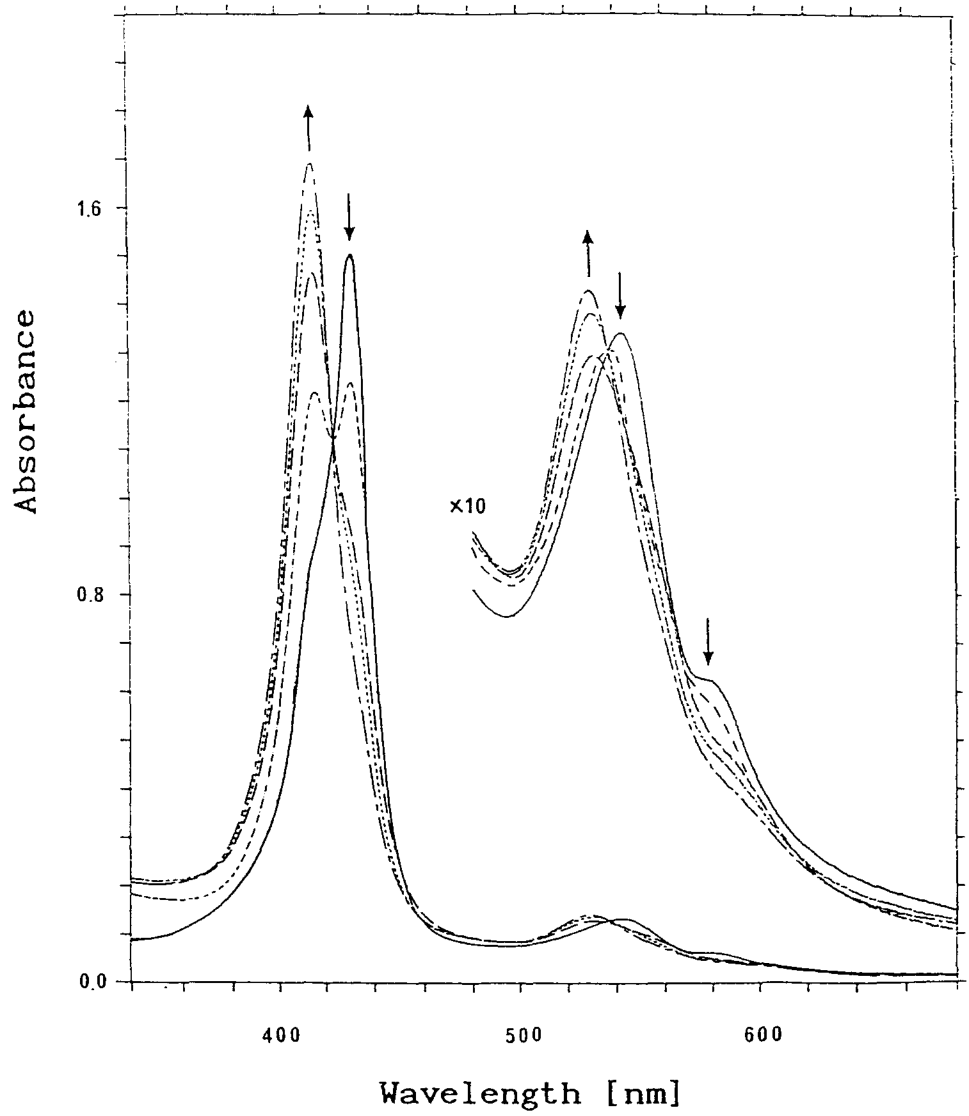
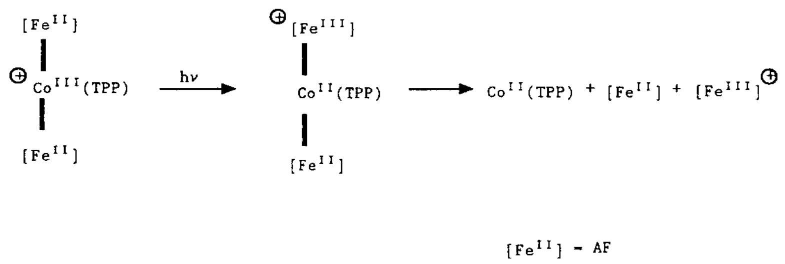


Fig. 5. Photolytic conversion of [Co(TPP) $(AF)_2$] (BF_4) into Co(TPP) in DMF. Arrows indicate the change in absorbance during irradiation at $\lambda > 350$ nm. (With permission from Ref. [20].)

are formed, whereas $Mn^{II}Pc(2-)$ cleanly gives the 1:1 adduct Mn^{II} Pc(2−) (AF). Deoxygenated solutions of these phthalocyanines containing AF are highly photosensitive. Brief irradiation with visible light ($\lambda > 400$ nm) of a solution of $Fe^{II}Pc(2-)$ and an excess of AF in DMSO (this solution contained mainly uncomplexed phthalocyanine and less than 10% of the AF adduct) resulted in a rapid colour change from



Scheme 6.

green to violet. The corresponding changes in the electronic absorption spectrum are shown in Fig. 6.

The species formed is photosensitive itself and prolonged irradiation results in photolytes displaying very broad spectra without discernible maxima and minima. It is also air sensitive and introduction of air brings about rapid return of a green coloration. The EPR spectroscopy showed that the species formed is $[\mathrm{Fe^IPc(2-)(AF)}]^-$ with an axial EPR spectrum (Fig. 7) ($g_\perp = 2.104$, $g_\parallel = 1.946$), and the parallel component split into a triplet by one axial nitrogen atom ($a^{\mathrm{N}} = 0.0013\ \mathrm{cm^{-1}}$).

This spectrum is closely similar to that reported by Lever and Wilshire for $[\mathrm{Fe^IPc(2-)(Py)}]^-$ [44].

The presence of organic bases such as pyridine, imidazole or triethylamine does not give rise to photoreduction of phthalocyanine, under the same conditions.

The photochemical behaviour of the paramagnetic $\mathrm{Mn^{II}Pc(2-)}$ in the presence of AF is more complicated. Before photolysis, this system showed only very broad, structureless EPR spectra in DMSO or DMF at 78 K. Irradiation with visible light resulted in the appearance of a violet coloration and much sharper, intense EPR signals. In DMSO an isotropic feature at $g = 2.133$ was assigned to $[\mathrm{Mn^IPc(3-)}]^{2-}$.

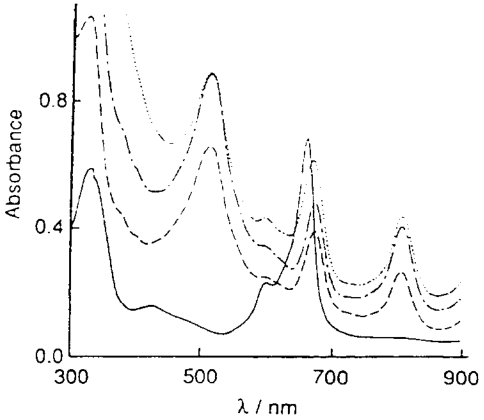


Fig. 6. The changes in electronic absorption spectrum of $\mathrm{Fe^{II}Pc(2\text{-})}$ in DMSO containing an excess of AF caused by irradiation with visible light: —, before irradiation; ---, after 5 s irradiation; —·—, after 10 s irradiation; ···, after 25 s irradiation. (With permission from Ref. [23].)

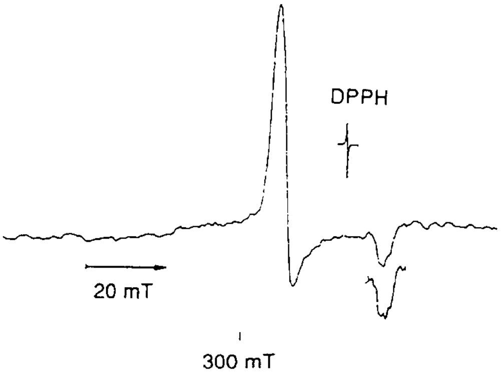


Fig. 7. The X-band EPR spectrum of a photolysed solution of FE$^{\mathrm{II}}$Pc(2−) in DMSO containing an excess of AF at 77 K. (With permission from Ref. [23].)

Annealing of this species to room temperature for a few minutes resulted in an "axial" spectrum ($g_{\perp} = 2.208$, $g_{\parallel} = 1.884$), corresponding to an as yet unknown species. When photolysis was carried out in DMF, the photolyte displayed the EPR spectrum shown in Fig. 8. This spectrum contains a single feature at $g = 2.001$ and features characteristic for a low spin manganese(II) in an axially symmetrical environment ($g_{\perp}^{\mathrm{av}} = 2.185$, $a_{\perp}^{\mathrm{Mn,av}} = 0.0013\ \mathrm{cm}^{-1}$, $g_{\parallel} = 1.875$, $a_{\parallel}^{\mathrm{Mn}} = 0.014\ \mathrm{cm}^{-1}$). The relative intensity of the single line increased with prolonged photolysis confirming its assignment to another species than that giving the other features. We can assign the anisotropic part of the spectrum to the product of the 2e reduction, i.e. [Mn$^{\mathrm{II}}$Pc(4−)]$^{2-}$ and the single feature to a product of deeper reduction, e.g. [Mn$^{\mathrm{I}}$Pc(5−)]$^{4-}$. Unfortunately, in the case of manganese complexes the EPR spectra do not provide direct information about the presence of axial ligands in reduced species (solvent, AF).

The mechanistic interpretation of the observed photoreductions is not straightforward since the irradiated solutions contained a mixture of various species absorbing light (phthalocyanines as a major species and their adducts with AF). However,

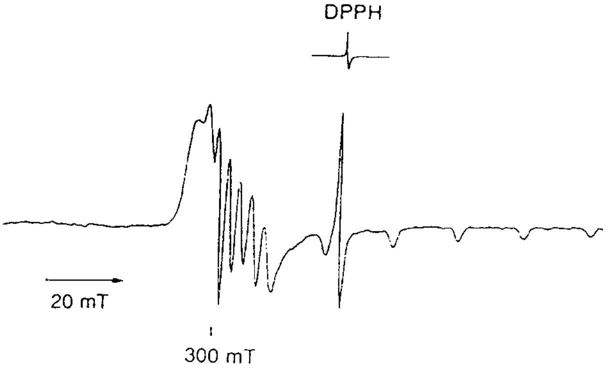


Fig. 8. The X-band EPR spectrum of a photolysed solution of Mn$^{\mathrm{II}}$Pc(2−) in DMF containing an excess of AF at 77 K. (With permission from Ref. [23].)

phthalocyanine photoreduction also occurs when red ($\lambda > 620$ nm) light is used [45], which means that excited AF is not involved (AF does not absorb at these wavelengths and consequently cannot be photoexcited). In this situation the observed photoreductions may involve either ground state macrocycle–AF adducts or exciplexes (excited macrocycle–AF). However, there is no photoreduction in the presence of ferrocene, which is a stronger reductant than AF, but is not capable of coordinating to phthalocyanine. Thus an outer sphere PET (i.e. PET in a collisional complex) is rather unlikely. However, another possibility is that an outer sphere PET occurs for AF and ferrocene, but in the latter case there is an efficient back electron transfer recovering the starting materials, as was observed for AlPcCl and ferrocene [46]. In the case of AF, the azaferrocenium system formed undergoes fast decomposition making back transfer impossible.

5. Conclusions

The results of the research presented here show that AF behaves as a relatively strongly coordinating ligand towards transition metal macrocyclic complexes. In some cases its ligating properties are closely similar to those of unhindered imidazoles. These strongly ligating properties are (at least in part) due to the π acceptor properties of AF (in this context it is worth noting that relatively strong π acceptor properties are also characteristic of phosphaferrocene [47]). The coordination of AF to metal macrocyclic complexes engenders high photochemical activity for the system. The typical photoreactions are expulsion of the axial ligand(s) and reduction of the macrocyclic complex (either at the metal or at the macrocycle). All photochemical reactions described in this review take place under conditions in which typical organic amines are completely unreactive. Finally, recent development in the chemistry of transition metal complexes containing η^5-pyrrolyl, phospholyl [47,48] and arsolyl [49] ligands suggest that many interesting structures displaying unusual structural and photochemical properties can be prepared by coordination of these complexes to macrocyclic systems.

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Appendix A: Nomenclature

AF	azaferrocene
DMF	dimethylformamide
dmgH	dimethylglyoximate
DMSO	dimethylsulphoxide
Im	imidazole
MeIm	2-methylimidazole
OEP	2,3,7,8,12,13,17,18-octaethylporphyrinate
P	porphyrinate (generally)
Pc	phthalocyaninate
p-MeOTPP	*meso*-tetrakis(*p*-methoxyphenyl)porphyrinate
Py	pyridine
TPFPP	*meso*-tetrakis(pentafluorophenyl)porphyrinate
TPP	*meso*-tetraphenylporphyrinate
TTP	*meso*-tetra(*p*-tolyl)porphyrinate

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