Metal–Ligand Bonding Properties of Double-sided Porphyrin Complexes: Influence of Bulky Ester Groups†

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Metal–ligand bonding properties of double-sided porphyrinato-iron(II) and -cobalt(II) complexes have been characterized by ESR, IR, and Mössbauer spectroscopy. The smaller A_N value for a 1-methylimidazole (mim) adduct of 5,10,15,20-tetra(2,6-dipivaloyloxyphenyl)porphyrinatocobalt(II) compared to that of 5,10,15,20-tetra(2,6-di-*tert*-butylacetoxyphenyl)porphyrinatocobalt(II) suggested that the cobalt–imidazole bond is weak. The ESR spectrum of the dioxygenated double-sided series in fluid toluene indicated that an electrostatic interaction between the bound dioxygen and the ester fences was rarely found. The relaxation of steric strain on the rear side of the ring plane for axial imidazole bonding resulted in a lowering of the bound CO and O_2 stretching frequencies of iron(II) complexes. This indicates that the π-back donation from the d_π orbital of the iron to the π* orbital of the bound gaseous ligand could be controlled by the strength of the iron–imidazole bonding, which is regulated by the structure of the rear pocket on the macrocycle. The co-ordination structure of various ligands in double-sided porphyrinatoiron complexes is also discussed by means of Mössbauer parameters.

The iron–ligand bonding properties of haemoproteins, such as haemoglobin (hb), myoglobin (mb) and cytochrome P-450 have been intensively studied because of interest in their abilities to transport or activate dioxygen. In these haemoproteins the axial base plays a very important role in the binding of gaseous ligand.[1,2]

Much effort has been made to clarify the nature of the characteristic bonding properties of the haemoproteins by using synthetic porphyrinatoiron(II) complexes.[3,4] Several highly modified porphyrinatoiron complexes with an appropriate cavity on the ring plane can bind dioxygen reversibly at 25 °C.[5–10] Typical of these highly modified porphyrins is the 'picket-fence' complex 5,10,15,20-tetra(*o*-pivalamidophenyl)-porphyrinatoiron [Fe(tpvp)], which forms a dioxygen adduct even if the fifth ligand is imidazole, pyridine,[6] or thiolate.[11] Thus the co-ordination geometry and the electronic nature of [Fe(tpvp)] and/or [Co(tpvp)] have been characterized by several physicochemical measurements [Mössbauer,[12] IR,[13] ESR,[14] and Raman spectroscopy,[15] X-ray structure analyses[16] and extended X-ray absorption fine structure (EXAFS),[17] *etc.*].

Recently, we reported that highly symmetric and bis-fenced porphyrin complexes (double-sided porphyrins) can form stable and reversible dioxygen adducts in toluene at 25 °C.[18] A unique feature of double-sided porphyrins compared to other models is their ability to block both axial sites of porphyrin complexes. That is, the bulky ester groups on both sides of the porphyrin plane impede the formation of an intermolecular μ-oxo dimer leading to irreversible oxidation. Furthermore, the relaxation of steric restraint between the axial base and the ester fences on the rear side resulted in an increase in the dioxygen binding affinities.[18c] This might be caused by enhancing favourable electron donation from the axial base. In the present study, the characteristics of metal–ligand bonding in the double-sided series have been analysed by various physicochemical measurements.

Experimental

Materials and Solvents.—The iron(III) complexes **1a′** and **2a′** and the cobalt(II) complexes **1b** and **2b** were prepared as described previously.[18b,c] The iron-57-labelled derivatives of **1a′** and **2a′**, used for Mössbauer measurements, were synthesised similarly.[18b] 1-Methylimidazole (mim) was purified before use by distillation *in vacuo* under reduced pressure. Toluene and benzene were purified immediately before use by distillation from sodium and benzophenone under argon.

Reduction of the iron(III) complexes was carried out by using $Na_2S_2O_4$ in a heterogeneous two-phase system under anaerobic conditions as previously reported.[18b]

ESR Spectroscopy.—The samples were prepared on a vacuum line by degassing solutions by the usual freeze–pump–thaw method. Concentrations were 5 mmol dm^{-3} for porphyrinatocobalt(II) in toluene. The tubes were then sealed and the ESR spectra were recorded on a JEOL JES-RE2X spectrometer equipped with a digital variable-temperature system (JEOL ES-DVT2) using liquid nitrogen. The magnetic field was calibrated with a JEOL ES-SCXA frequency meter and the field corrections for samples were made with MnO.

Infrared Spectroscopy.—The infrared spectra were taken with a double-beam type spectrometer (JASCO IR-810) in absorbance mode. The differential spectra were measured under $^{16}O_2$ *vs.* $^{18}O_2$ and $^{12}C^{16}O$ *vs.* argon atmospheres. The concentration of porphyrinatoiron was 10 mmol dm^{-3} in benzene and the cells used were precisely matched in terms of path length (0.1 mm) and NaCl window thickness.

Mössbauer Spectroscopy.—The Mössbauer spectra were recorded for ^{57}Fe-enriched porphyrinatoiron complexes under an argon, CO or O_2 atmosphere, respectively, at 77 K. The spectrometer was of the constant-acceleration type, the source consisted of *ca.* 10 mCi (3.7 × 10^8 Bq) of ^{57}Co-diffused palladium foil, and the absorber (thickness *ca.* 0.2 mg iron per cm^2) was kept at 77 K. The Doppler velocity was calibrated with natural iron foil kept at 25 °C and zero velocity was taken

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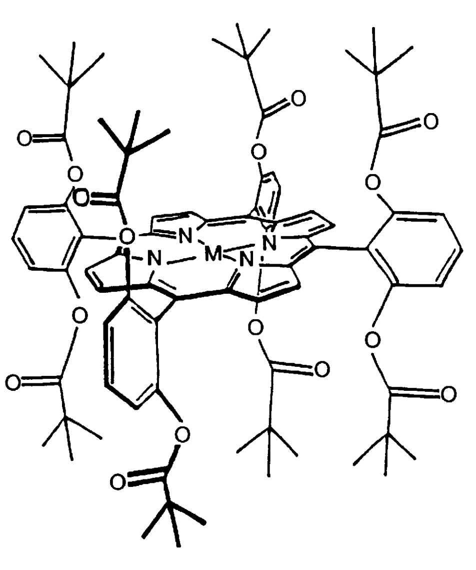
† *Non-SI unit employed:* G = 10^{-4} T.



M

1a′ $Fe^{III}Br$

1a Fe^{II}

1b Co^{II}

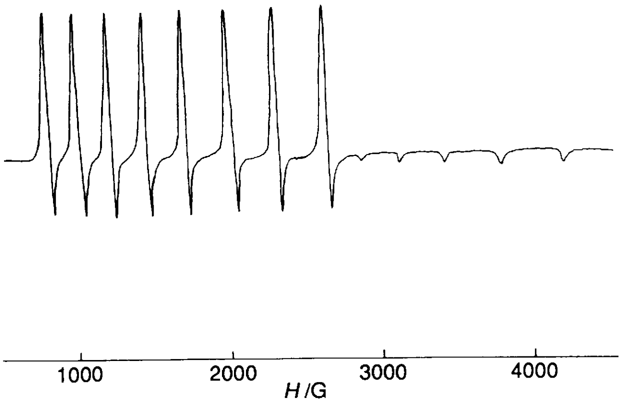


Fig. 1 The ESR spectrum of 5 mmol dm^{-3} complex **2b** in toluene glasses at 77 K

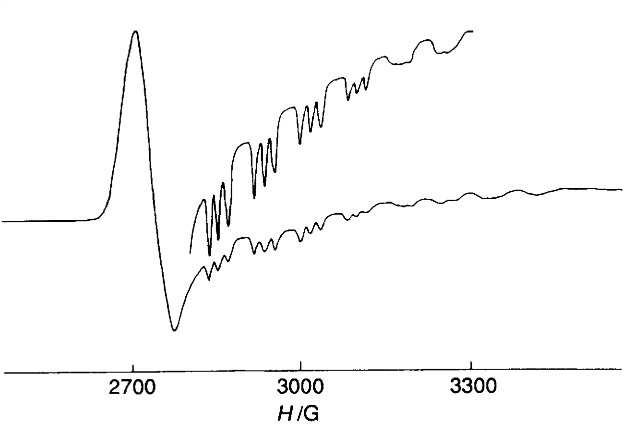
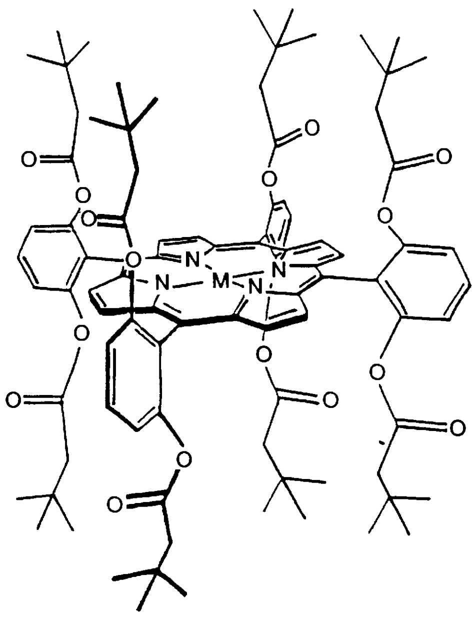


Fig. 2 The ESR spectra of 5 mmol dm^{-3} **2b**–mim in toluene glasses at 77 K



M

2a′ $Fe^{III}Br$

2a Fe^{II}

2b Co^{II}

as the centroid of its spectrum at 25 °C. The spectra were fitted to Lorentzian line shapes using a least-squares program.

Results and Discussion

ESR Measurements.—The ESR spectrum of double-sided porphyrinatocobalt in glassy toluene at 77 K was well resolved as shown in Fig. 1. The intense low-field pattern is composed of eight lines as expected from the magnetic interaction of the unpaired electron with the cobalt nucleus ($I = \frac{7}{2}$), and is very similar to that of the free base-diluted crystalline [Co(tpp)] (tpp = 5,10,15,20-tetraphenylporphyrinate). This phenomenon may be due to two reasons on the basis of our finding that the ester cavities constructed on the ring plane of **2a** prevent access of solvent molecules to the ligand binding site for O_2 and CO binding.[18c] First, the intermolecular Co ··· Co interaction was inhibited by the four bulky ester fences on both sides of the porphyrin plane. Secondly, the cobalt nucleus of the double-sided porphyrins was not affected by solvation.

The spectrum of complex **2b** in the presence of mim in glassy toluene ([Co]/[mim] = 1:20) at 77 K is shown in Fig. 2. Eight hyperfine lines in the parallel region due to the cobalt nucleus were observed. Further, these components show super-hyperfine (s.h.f.) splitting due to interaction with one nitrogen, indicating that the species is the mono mim ligated complex of **2b**. The ESR parameters of the porphyrinatocobalt complexes are summarized in Table 1. The order of A_N values for the five-co-ordinated complexes having different rear pocket-spaces for axial base binding is [Co(tpvp)] > **2b** > **1b**. In addition, the values of $A_\parallel$ decrease with increasing A_N. This result indicates that the unfavourable steric repulsion between the axial base and pivaloyloxy fences weakens the cobalt–imidazole σ bond.

When dioxygen was admitted to a sample tube containing a solution of **2b**–mim the spectrum at 77 K was typical of a O_2 complex in glassy toluene as shown in Fig. 3. There are substantial differences in the interpretation of the ESR properties of Co–O_2 complexes.[20–22] Participation of cobalt d_π orbitals through overlap with π^* orbitals is considered most likely to be responsible for the hyperfine structure in the O_2^- model.[20,21] On the other hand, spin-polarization mechanisms which imply indirect polarization of the pair of electrons in the bonding molecular orbital by the unpaired electron in O_2 have been suggested as a result of a number of conflicts based upon the Co^{III}–O_2^- structure.[22] The similarity of the ESR parameters of the dioxygen complex of **2b** to those of other porphyrinatocobalt–dioxygen complexes indicates that all the species have similar electronic configurations. Therefore, it

Table 1 ESR spectral data for cobalt(II) porphyrin complexes in toluene at 77 K

Complex	$g_\perp$	$g_\parallel$	$10^4 A_\perp/\mathrm{cm}^{-1}$	$10^4 A_\parallel/\mathrm{cm}^{-1}$	$10^4 A_\mathrm{N}/\mathrm{cm}^{-1}$
Deoxy					
1b–mim	—	1.993	—	78.6	15.0
2b–mim	—	2.032	—	77.6	16.1
[Co(tpvp)(mim)][a]	2.133	2.028	—	76.8	16.2
[Co(tpvp)(mim)][b]	2.31	2.04			
[Co(tmopp)(mim)][c]	2.314	2.033	12	75.9	16.3
O_2 Adduct					
1b–mim–O_2	1.993	2.068	6.9	14.6	—
2b–mim–O_2	1.991	2.075	7.4	16.1	—
[Co(tpvp)(mim)]·O_2	1.993	2.076	7.2	15.7	—
[Co(tpvp)(mim)]·O_2[b]	2.01	2.09			
[Co(tmopp)(mim)]·O_2[c]	2.002	2.080	9.8	16.2	—

[a] In $CHCl_3$, ref. 19. [b] From ref. 14. [c] From ref. 20; tmopp = 5,10,15,20-tetra(*p*-methoxyphenyl)porphyrinate.

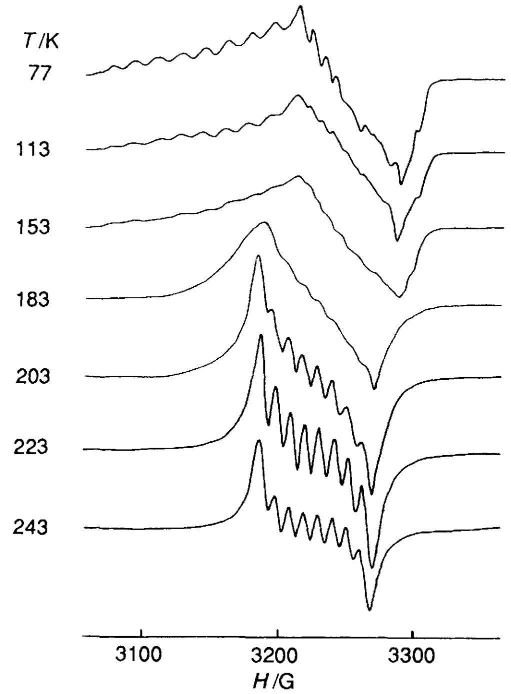


Fig. 3 The ESR spectra of 5 mmol dm^{-3} **2b**–mim–O_2 in toluene solution

seems reasonable to consider that the electron is transferred from cobalt to dioxygen and the electronic structure of the dioxygenated double-sided porphyrins be formulated as Co^{III}–O_2^-.

A series of ESR spectra for the dioxygen adduct of complex **2b** in toluene solution at various temperatures is shown in Fig. 3. At 77 K, as mentioned above, the spectrum showed a pattern typical of frozen dioxygen complexes. The anisotropic spectrum exhibited obviously parallel and perpendicular branches, because the sample was immobilized in glassy toluene. As the sample was warmed from 77 to 153 K the spectrum began to lose its resolution. When this sample was warmed up to 183 K the eight-line pattern was observed for Co–O_2 in solution, as reported previously.[21]

In the case of 5-(*o*-acetamidophenyl)-10,15,20-trisphenylporphyrinatocobalt, the ESR spectrum of the dioxygen adduct was not motionally averaged even in fluid solution.[23] Walker and Bowen[23] considered that an internal rotation of bound O_2 was prevented presumably by hydrogen-bond donation from the NH of the *o*-acetamide groups, as observed in oxy-Co–mb. Thus the averaging of the ESR signals of the **2b**–mim–O_2 complex in fluid toluene suggested the rotation of the O_2 moiety about the Co–O bond. It is therefore concluded that an electrostatic interaction between the bound dioxygen and the ester fences is rarely found in the ester-fenced porphyrins. This is in accord with our previous prediction that the low dioxygen binding affinities of double-sided porphyrins were due to the weakly polar ester fences which cannot have an interaction with bound dioxygen.[18c]

IR Measurements.—Difference spectra of the deoxy complex *vs.* the CO adduct and of $^{16}O_2$ *vs.* $^{18}O_2$ adducts were measured in the regions 2000–1800 and 1200–1000 cm^{-1} respectively, at 25 °C. The shifts in stretching frequencies of $^{16}O_2$ and $^{18}O_2$ adducts of iron(II) porphyrins were in accord with Hooke's law. The infrared data are summarized in Table 2. The $\nu(O_2)$ values for the dioxygen adducts of double-sided porphyrinatoiron complexes were close to that of O_2^- ion (1150–1100 cm^{-1}). Consequently, the dioxygen-co-ordinated structure of the double-sided series is considered to involve bent-on bonding like oxy-hb, oxy-mb, and the dioxygen adducts of other model haems.

The ν(CO) value of the **2a**–1-hexylimidazole(him) adduct (1964 cm^{-1}) is much lower than that of the **1a**–him complex (1979 cm^{-1}). In contrast to the difference in $\nu(O_2)$ among **1a**, **2a**, and [Fe(tpvp)],[13] significant differences in ν(CO) for the CO adduct of each complex were observed. Both CO stretching and Fe–C stretching frequencies are available from infrared and resonance-Raman studies of a large number of haem–CO adducts.[3,27] In general, stronger donor ligands increase the electron density at Fe and enhance π-back donation from iron d_π to CO π^* orbitals. This strengthens the Fe–C π bond and weakens the CO bond, as reflected in the lower ν(CO). We considered that the difference in ν(CO) for double-sided porphyrins is due to the electron-donating ability of the imidazole ligand. Since the bulky pivaloyloxy fences of **1a** weakened the co-ordination of imidazole, the electron donation from the axial base to the iron might be decreased compared to that in single-face hindered series such as [Fe(tpvp)].[18b] On the other hand, in **2a** there is no unfavourable steric repulsion on the rear side because of the more flexible *tert*-butylacetoxy groups.

Mössbauer Spectrum.—Mössbauer spectroscopy has been used extensively to characterize the electronic nature of porphyrinatoiron complexes. In order to probe the co-ordination structure of the double-sided series, we have prepared samples of **1a** and **2a**, 97% enriched with ^{57}Fe. Mössbauer data for double-sided porphyrinatoiron complexes in glassy toluene at 77 K are summarized in Table 3. The spectra of the deoxy form showed small δ and ΔE_Q values. These are easily assigned to iron(II) low-spin, six-co-ordinate species **2a**–2mim. For the CO adduct of **2a** both δ and ΔE_Q were smaller than those of the deoxy complex owing to π-back donation to the co-ordinated CO. Another reason for the decrease in ΔE_Q might be the large changes in iron–porphyrin binding. In the case of **1a** the strength of the imidazole co-ordination to the central

Table 2 Infrared spectral data (cm^{-1}) for iron(II) porphyrin complexes at 25 °C

Haem	Ligand	Solvent	O_2 Adduct $\nu(^{16}O-^{16}O)(\nu_{\frac{1}{2}})$	O_2 Adduct $\nu(^{18}O-^{18}O)$	CO Adduct $\nu(CO)(\nu_{\frac{1}{2}})$
1a	him	Benzene	1166(10)	1084	1979(12)
2a	him	Benzene	1161(12)	1082	1964(12)
[Fe(tpvp)]	him	Benzene	1159(10)	1075	1968(12)
[Fe(tpvp)][a]	mim	Nujol mull	1159(10)	1075	1969
hb		Water	1107(9 ± 1)[b]	1065	1951(12)[c]
mb		Water	1103(9 ± 1)[d]	1065	1945(8)[c]
O_2 or CO gas			1556		2143
O_2^-			1145		

[a] From ref. 13. [b] Ref. 24. [c] Ref. 25. [d] Ref. 26.

Table 3 Mössbauer parameters (mm s^{-1}) for iron(II) porphyrin complexes at 77 K

			Deoxy		O_2 Adduct		CO Adduct	
Haem	Ligand	Solvent	δ	ΔE_Q	δ	ΔE_Q	δ	ΔE_Q
1a	him	Toluene	0.44	1.00	0.25	2.02	0.25	0.32
2a	him	Toluene	0.44	0.98	0.28	2.07	0.29	0.35
[Fe(tpvp)][a]	him	Solid	0.44	1.02	0.27	2.04	0.27[b]	0.27[b]
hb[c]		Solid	0.92	2.37	0.26[b]	2.19[b]	0.26[b]	0.36[b]
mb[b,d]		Solid	0.90	2.20	0.27	2.32	0.27	0.37

[a] From refs. 6 and 12. [b] At 4.2 K. [c] Ref. 28. [d] Ref. 29.

iron was weakened by the steric repulsion on the rear side. Thus, a decrease in the electron flow from the bound imidazole to the iron should result in a decrease in the electron density on the iron. This leads to a reduction in π-back donation from the Fe d_π to the CO π* orbital. As described above, the π-bond strength of Fe–C might be in the order of **2a**, [Fe(tpvp)] > **1a**, according to the values of ν(CO). However, the differences in the Mössbauer parameters of these CO complexes are surprisingly small. For the dioxygen adduct of complex **2a** the Mössbauer spectrum showed only one species and the parameters were almost identical with those of [Fe(tpvp)]–mim–O_2.[12] It is noteworthy that the Mössbauer parameters of double-sided porphyrins are slightly complicated in contrast to the ESR and IR properties.

In conclusion, the results of the ESR, IR and Mössbauer spectroscopic measurements suggest that double-sided porphyrins are indeed capable of forming dioxygen complexes. The ESR spectra in fluid toluene indicated that an electrostatic interaction between the bound dioxygen and the ester fences was rarely found. This is in accord with our previous prediction that the low dioxygen binding affinities of double-sided porphyrins are attributed to the weakly polar ester fences which cannot have an interaction with bound dioxygen. Further, the π-back donation from the d_π orbital of the iron to the π* orbital of the bound gaseous ligand can be controlled by the strength of the iron–imidazole bonding, which is regulated by the structure of the rear pocket on the macrocycle.

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