Reaction of Sterically Hindered Imidazolate Complexes with Iron Porphyrins

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Reaction of sterically hindered copper(II) or nickel(II) imidazolate complexes derived from imidazole-2-carbaldehyde with iron porphyrins results in the formation of monoadducts which are dinuclear complexes. The spin states of the iron atoms in some of the adducts have been determined from variable-temperature magnetic susceptibility measurements to be admixed-intermediate spin or intermediate spin.

Recent work in our laboratory has centred on the synthesis of imidazolate-bridged di- and tri-nuclear complexes by the reaction of copper(II) and nickel(II) imidazolate chelates of H_2L^1 with metalloporphyrins. Metal complexes of these chelates contain a free, unhindered imidazolate N available for binding to a metalloporphyrin. This strategy has been used to produce dinuclear complexes in the case of monoligation of Zn(tpp),†[1] Co(tpp),[2] Mn(tpp),[3] and Cr(tpp)Cl[4] and trinuclear complexes in the case of bis ligation of Cr(tpp)(ClO_4),[4] Fe(tpp)[5] and Fe(tpp)($B_{11}CH_{12}$).[5]

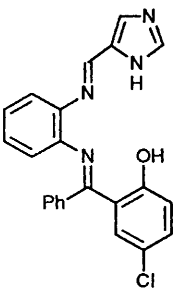
Our most recent effort focuses on the preparation of dinuclear complexes from the reaction of iron porphyrins with a metal imidazolate complex. Because of the greater thermodynamic stability of a low-spin bis adduct compared to the monoadduct, both iron(II)[6] and iron(III)[7] porphyrins generally bind two axial ligands [equations (1) and (2), n = 0 or 1]. The iron(II)

$$[\mathrm{Fe(por)}]^{n+} + \mathrm{L} \overset{K_1}{\rightleftharpoons} [\mathrm{Fe(por)L}]^{n+} \qquad (1)$$

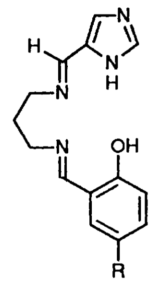
$$[\mathrm{Fe(por)L}]^{n+} + \mathrm{L} \overset{K_2}{\rightleftharpoons} [\mathrm{Fe(por)L_2}]^{n+} \qquad (2)$$

porphyrins are more sensitive to steric requirements as is evidenced by the fact that a monoadduct of Fe(tpp) has been obtained from the sterically hindered 2-methylimidazole while the bis adduct was obtained from the iron(III) porphyrin analogues.

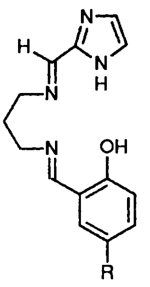
The absence of synthetic routes to simple monoimidazole or monoimidazolate complexes of iron(III) porphyrins is a long standing problem[8] in the porphyrin and haemoprotein area and has hindered efforts to prepare simple spin-state analogues of horseradish peroxidase[9] and cytochrome c′,[10] and to understand the factors that govern spin-state selection. This work investigates an approach to the control of the stoichiometry of axial ligation in which a small variation in the structure of the metal imidazolate complex provides sufficient steric constraints about the iron porphyrin binding site to prevent binding of a second ligand [reaction (2)] and thus promote formation of the monoadduct. This investigation provides information on the synthetic feasibility of preparing five-co-ordinate iron porphyrin dinuclear complexes and on spin-state selection of iron in the five-co-ordinate complexes. Dinuclear iron(III)–copper(II) complexes are also of interest in investigating imidazolate-mediated antiferromagnetic exchange, as has been observed in cytochrome c oxidase.[11]



H_2L^1



H_2L^2 R = H
H_2L^3 R = OMe



H_2L^4 R = H
H_2L^5 R = OMe

The imidazolate complexes used in this work are the nickel(II) and copper(II) complexes of the ligands H_2L^2–H_2L^5, where H_2L^4 and H_2L^5 are isomers of H_2L^2 and H_2L^3, respectively, in which imidazole-2-carbaldehyde was substituted for imidazole-4-carbaldehyde in the Schiff-base condensation reaction leading to the formation of the ligands. Each isomeric pair differs only in the degree of steric crowding about the 'backside' imidazolate N, which is the site for binding to a metalloporphyrin. The complexes ML^2 and ML^3 are unhindered about the imidazolate binding site while ML^4 and ML^5 are hindered due to the position of the imine H. Reaction of iron porphyrins with the hindered isomers produced only monoadducts, dinuclear complexes, while reaction with the unhindered isomers yielded bis adducts, trinuclear complexes, of the iron porphyrins. Herein we report the synthesis and variable-temperature magnetic susceptibility measurements of the dinuclear adducts of NiL^5 with [Fe(tpp)] and [Fe(tpp)(ClO_4)] and the solution characterization of the dinuclear adduct of CuL^4 with [Fe(ttpp)(OH)].

Experimental

General.—Toluene and tetrahydrofuran were distilled from sodium–benzophenone. Acetonitrile and dimethyl sulfoxide, spectra grade, were obtained from Aldrich. All reactions and manipulations of oxygen- or water-sensitive compounds were conducted under He in a Vacuum Atmosphere dry-box.

Spectra.—Visible spectra were obtained on a computer-controlled Perkin-Elmer Lamda 4 UV/VIS spectrometer using

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† Abbreviations used: tpp and ttpp are the dianions of 5,10,15,20-tetraphenyl- and 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)-porphyrin; thf and dmso are tetrahydrofuran and dimethyl sulfoxide, respectively.

software obtained from Softways, IR spectra on a Perkin-Elmer model 1750 FT IR instrument.

Magnetism.—The magnetic susceptibilities were measured between 80 and 300 K on a computer-controlled Faraday system which consists of a Cahn 2000 microbalance, Applied Magnetics electromagnet, Lake Shore Cryotronics temperature controller, platinum-resistance thermometer, and Abbess instrument cryostat. A Data Translation A/D board and AT computer were used to monitor the microbalance output and temperature readings. The instrument was calibrated with $HgCo(NCS)_4$.[12] The raw data were corrected for the susceptibility of the holder and the diamagnetism of the ligand atoms by Pascal's constants,[13] and converted into molar susceptibilities from which the magnetic moments were calculated as $\mu = 2.828(\chi_M T)^{\frac{1}{2}}$.

Porphyrins.—The complex $[Fe(tpp)(ClO_4)]\cdot C_6H_5Me$ was prepared from the reaction of [Fe(tpp)Cl] (Aldrich) with $AgClO_4$ (Aldrich) as described previously,[14] and [Fe(tpp)] was prepared by the reaction of $FeBr_2$ and $Fe(O_2CMe)_2$ (Alfa) with H_2tpp (Aldrich) as described previously.[15] The porphyrin H_2ttpp was prepared by Lindsey's method[16] and its iron(III) complex, [Fe(ttpp)Cl], by reaction of iron(II) chloride with H_2ttpp according to the method of Adler *et al.*[17] The complex [Fe(ttpp)(OH)] was prepared from [Fe(ttpp)Cl] as reported.[18]

Metal Imidazolate Complexes.—The metal imidazolate complexes were prepared by an adaptation of the method of Elder[19] as described previously.[20]

$[Fe(tpp)\cdot NiL^5]ClO_4$. The complex NiL^5 (0.021 g, 0.062 mmol) was dissolved in refluxing ethanol (10 cm^3) and filtered into a round bottom flask containing $[Fe(tpp)(ClO_4)]\cdot 5C_6H_5Me$ (0.505 g, 0.062 mmol) in thf (10 cm^3). The reaction mixture was refluxed for a few seconds and allowed to cool. A brown solid (0.021 g) precipitated during the next day.

$[Fe(tpp)\cdot NiL^5]$. The complex $[NiL^5]$ (0.021 g, 0.062 mmol) was dissolved in refluxing ethanol (10 cm^3) and filtered into a round bottom flask containing $[Fe(tpp)(thf)_2]$ (0.050 g, 0.062 mmol) in toluene (10 cm^3). Addition of heptane resulted in the precipitation of shiny purple crystals (0.016 g) within 3 h.

Neither of these compounds gave entirely satisfactory analysis data due to their extreme water and oxygen sensitivity.

$[Fe(ttpp)(N_3)]$. The complex [Fe(ttpp)(OH)] (0.065 g) was dissolved in toluene (20 cm^3) and NaN_3 (0.6 g) was dissolved in deionized water (10 cm^3). The two solutions were mixed and stirred vigorously overnight, by which time the UV/VIS spectrum of the toluene layer indicated complete conversion from [Fe(ttpp)(OH)] into $[Fe(ttpp)(N_3)]$. The toluene layer was removed by pipette and transferred to a dry-box to reduce the possibility of hydrolysis to [Fe(ttpp)(OH)] during work-up. The toluene was removed under vacuum with slight warming leaving a residue consisting of a purple solid with some white NaN_3. This mixture was recrystallized from methylene chloride to remove the sodium azide contaminant. Yield: 0.039 g, 58%.

Results and Discussion

Metal(II) *Imidazolate Complexes.*—A crystal structure of $[CuL^2]$ shows it to be a linear polymer with Cu atoms of adjacent molecules bridged by imidazolate groups, making each five-co-ordinate.[21] The magnetic moment is reported to vary from 1.63 at 80 K to 2.06 at 295 K, which indicates weak antiferromagnetic coupling. Analysis of the data using the Ising[22] model yielded J −15 cm^{-1}. A crystal structure is not available for the $[CuL^4]$ isomer; however, the magnetic data are very similar to those of $[CuL^2]$ with a moment which varies between 1.72 at 80 K and 1.80 at 295 K. Analysis of the data by the Ising model yields J −5.0 cm^{-1}. Both isomers are insoluble in toluene and do not react with metalloporphyrins except in co-ordinating solvents such as acetonitrile, dmso and acetone. This behaviour contrasts sharply with that of $[CuL^1]$, which is not an imidazolate-bridged polymer.[1–5] The insolubility of $[CuL^2]$ in toluene and lack of reactivity toward metalloporphyrins except in co-ordinating solvents are consistent with its polymeric structure since the polymeric linkages involve the imidazolate N used for binding to a metalloporphyrin. The similar magnetic behaviour, solubilities, and reactivities of $[CuL^2]$ and $[CuL^4]$ suggest that $[CuL^4]$ is also an imidazolate-bridged polymer.

Crystal structures for the diamagnetic nickel(II) complexes are not available. However, polymerization within the solid is not likely based on their solubilities and reactivities compared to those of the copper(II) complexes and the lesser tendency of square-planar nickel(II) to form a fifth bond. The complexes $[NiL^2]$–$[NiL^5]$ are soluble in toluene and tetrahydrofuran and form adducts readily with [Zn(tpp)] and $[Fe(tpp)(ClO_4)]$ in these solvents.

Use of [Fe(ttpp)(OH)].—For the purposes of the following discussion of iron(III) porphyrin spectra, class a spectra result from high- or intermediate-spin species and exhibit a visible maximum between 470 and 530 nm, class b result from low-spin species and exhibit two visible bands between 545 and 630 nm, and class c spectra resemble those of class b but result from high-spin species. The complex [Fe(ttpp)(OH)] was chosen for the investigation of the reaction between an iron(III) porphyrin and the copper complexes of H_2L^2 and H_2L^4 in co-ordinating solvents. The visible spectra of most five-co-ordinate iron(III) complexes, [Fe(tpp)X], in co-ordinating solvents and those expected for the monoadduct with a nitrogen-containing base are both class a. Therefore, a reaction between $[CuL^4]$ and $[Fe(tpp)(ClO_4)]$, for example, would not be apparent by visible spectroscopy. The complex [Fe(ttpp)(OH)] is a high-spin iron(III) porphyrin with a class c visible spectrum. Formation of a five-co-ordinate complex from this porphyrin would produce a class a spectrum, like that observed for [Fe(tpp)Cl], providing easily recognizable evidence for reaction. In addition, earlier studies in this laboratory demonstrated the displacement of OH^- in [Fe(ttpp)(OH)] by thiols and suggest that OH^- may be an easily displaced ligand for the present study.[23] The ttpp ligand stabilizes the hydroxide by preventing hydrolysis to the μ-oxo dimer, which is generally a problem with five-co-ordinate iron(III) porphyrins, and may also increase the effect of the steric factors favouring formation of a monoadduct with $[CuL^4]$.

Displacement Reactions of [Fe(ttpp)(OH)].—The displacement of hydroxide in [Fe(ttpp)(OH)] by anions and imidazole was examined for the purposes of determining (1) the potential usefulness of [Fe(ttpp)(OH)] as a synthetic starting material and (2) the plausibility of spectrally monitoring the formation of the desired monoadduct with $[CuL^4]$ in a reaction with [Fe(ttpp)(OH)]. Hydroxide ion in [Fe(ttpp)(OH)] was displaced by both azide and thiocyanate ions to give species which exhibit normal class a spectra in toluene, consistent with the formation of $[Fe(ttpp)(N_3)]$ and [Fe(ttpp)(SCN)]. To substantiate further the exchange of hydroxide for another ligand, the product of the reaction of [Fe(ttpp)(OH)] and NaN_3 was isolated as a solid. The magnetic moment of this compound is 5.90 and is temperature independent, which indicates a simple high-spin $S = \frac{5}{2}$ complex. The IR spectrum exhibited a strong sharp band at 2053 cm^{-1}, attributable to the presence of azide.[24]

The complex [Fe(ttpp)(OH)] reacted with excess of imidazole (Him) in toluene at spectroscopic concentrations (*ca.* 10^{-5} mol dm^{-3} porphyrin) to produce a species with a bis adduct spectrum similar to that observed for [Fe(tpp)(Him)(im)][25] and most likely due to the analogous complex [Fe(ttpp)(Him)(im)].

Reaction of $[CuL^2]$ *and* $[CuL^4]$ *with* [Fe(ttpp)(OH)].—Reaction of [Fe(ttpp)(OH)] with excess of $[CuL^2]$ in acetonitrile,

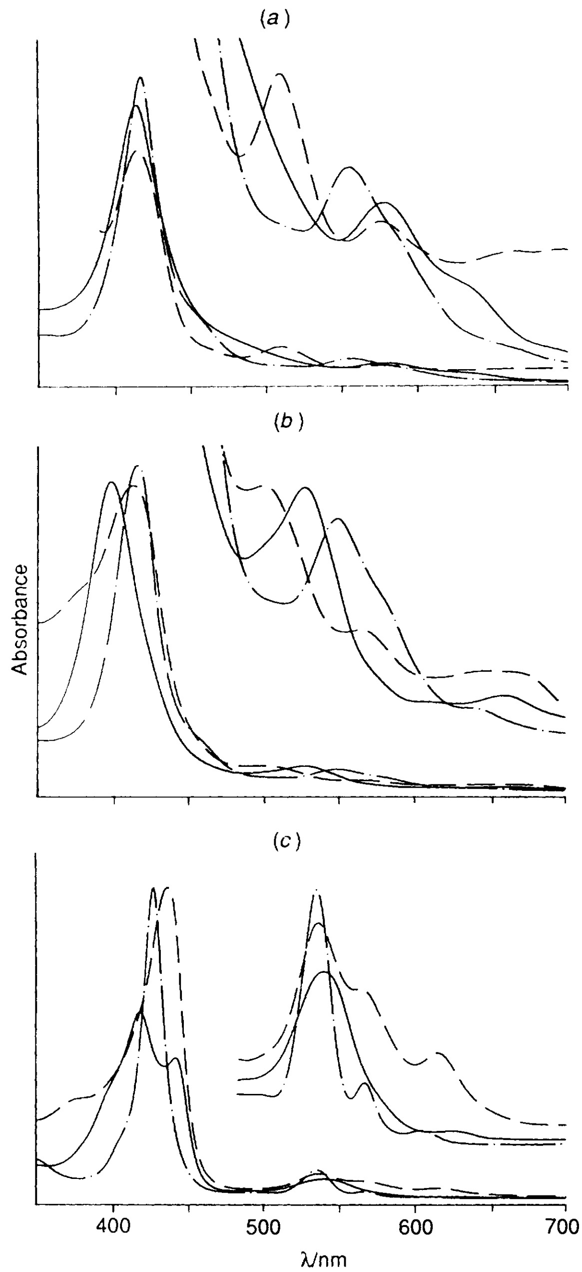

Fig. 1 The UV/VIS spectra of (*a*) [Fe(ttpp)(OH)] in acetonitrile (——), + [CuL^2] in acetonitrile (— · —) and + [CuL^4] in acetonitrile (– – –), (*b*) [Fe(tpp)(ClO_4)] in thf (——), + [NiL^3] in thf (— · —) and + [NiL^5] in thf (– – –) and (*c*) [Fe(tpp)] in toluene (——), + [NiL^3] in toluene (— · —) and + [NiL^5] in toluene (– – –)

dmso, or acetone solution produced spectral changes indicative of the formation of the bis adduct [Fe(ttpp)·2CuL^2]$^+$$OH^-$ as shown in Fig. 1(*a*) and as predicted for the reaction of an unhindered imidazolate complex.

The complex [CuL^4] reacted with [Fe(ttpp)(OH)] in acetonitrile, dmso, or acetone to produce a species which exhibits a normal class a spectrum [Fig. 1(*a*)]. This spectrum is consistent with the formulation, [Fe(ttpp)·CuL^4]$^+$$OH^-$, a dinuclear species in which a high- or intermediate-spin iron(III) is bridged by an imidazolate group to Cu^{II}. The complex could be either five- or six-co-ordinate with the sixth site occupied by hydroxide or solvent. Attempts at isolating this monoadduct have not yet been successful.

Reaction of [NiL^5] *with Iron Porphyrins.*—The UV/VIS spectra of the products of the reaction of [Fe(tpp)(ClO_4)] with

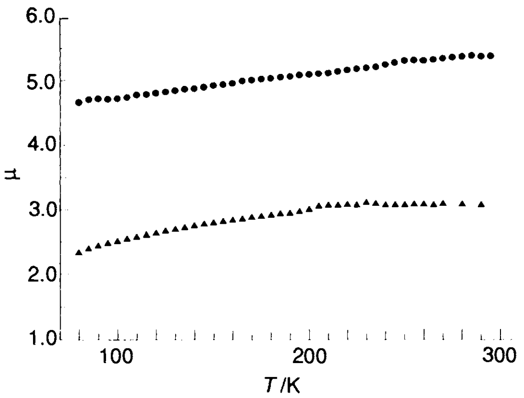

Fig. 2 Plot of magnetic moment *versus* temperature for [Fe(tpp)·NiL^5]ClO_4 (●) and [Fe(tpp)·NiL^5] (▲)

excess of [NiL^3] and [NiL^5] in thf are shown in Fig. 1(*b*). These nickel complexes were chosen over [NiL^2] and [NiL^4] because of their greater solubility in toluene and thf; [NiL^3] forms the bis adduct and [NiL^5] forms exclusively the monoadduct of [Fe(tpp)(ClO_4)]. Spectral identification of the monoadduct is hampered due to the small number of [Fe(tpp)L]$^+$ or [Fe(tpp)L]X systems in the literature. A monoimidazole adduct of [Fe(tpp)(SbF_6)] in toluene was observed by Valentine and co-workers,[25] who reported a red shift of the Soret band from 406 to 413 nm and a blue shift of the main visible band from 517 to 511 nm on monoligation. The class a spectrum of the adduct of [Fe(tpp)(ClO_4)] and [NiL^5], with a red-shifted Soret and a blue-shifted visible band, is consistent with monoadduct formation. Exposure of a solution of [Fe(tpp)·NiL^5]ClO_4 to air results in rapid hydrolysis to the μ-oxo dimer. The magnetic moment of the solid (Fig. 2) varies from 4.66 at 80 K to 5.36 at 295 K, which suggests an admixed-intermediate-spin state as is the case for a number of [Fe(tpp)X] complexes in which X is a weak-field anion.[14] The selection of the admixed-intermediate-spin state is attributed to extreme axial distortion, as would be expected for the present complex. The IR spectrum of [Fe(tpp)·NiL^5]ClO_4 reveals perchlorate bands at 1102 and 624 (sharp) cm^{-1} which differ from those of [Fe(tpp)(ClO_4)] (1170, 1148, 1120, 850 and 613w cm^{-1}) and more closely resemble those of free perchlorate as in [Fe(tpp)(1-mim)$_2$]ClO_4 (1-mim = 1-methylimidazole) (1085 and 620 cm^{-1}).

Fig. 1(*c*) shows the UV/VIS spectral changes observed in the reaction of [Fe(tpp)] with excess of [NiL^3] and [NiL^5] in toluene. Based on their similarity to the spectra of [Fe(tpp)(2-mim)] and [Fe(tpp)(1-mim)$_2$],[26] they indicate formation of a five-co-ordinate complex with [NiL^5] and a six-co-ordinate complex with [NiL^3]. Exposure of these solutions to air results in the formation of the μ-oxo dimer, rapidly for [NiL^5] and more slowly for [NiL^3]. The solid-state magnetic moment of [Fe(tpp)·NiL^5] (Fig. 2) varies from 2.3 at 80 K to 3.0 at 295 K, which suggests the $S = 1$ intermediate-spin state for iron. The intermediate-spin-state electron configuration $(t_{2g})^5(e_g)^1$ is due to destabilization of the $d_{x^2-y^2}$ orbital, which is promoted by extreme axial distortion. In the present case the sterically hindered, unsymmetrical [NiL^5] blocks bis adduct formation and stabilizes the intermediate-spin state through axial distortion. The $S = 1$ state has also been observed for [Fe(tpp)][26] and the bis(1-methylimidazole) adduct of an iron(II)-capped porphyrin.[27] The magnetic moments of these complexes are larger than that observed for the present example and have been explained by spin–orbit coupling between the ^3A ground state and a low-lying ^3E state. Calculations show that the coupling between these states is extremely sensitive to ligands along the z axis and that a weak interaction will lead to an increase in their separation.[28] The lower magnetic moment observed for [Fe(tpp)·NiL^5] may result from increased separation of the triplet states due to the axial distortion imposed by the NiL^5 ligand.

Conclusion

The preparation of the dinuclear complexes [Fe(tpp)·NiL^5]ClO_4 and [Fe(tpp)·NiL^5] and the observation in solution of the dinuclear [Fe(ttpp)·CuL^2]OH illustrate the utility of this method for control of the stoichiometry of axial ligation of iron porphyrins. The spin states of the iron atoms in the former two complexes are clearly in the admixed-intermediate and intermediate spin regimes, respectively. These spin states are favoured in cases of extreme axial distortion as should be provided by these ligands. While the dinuclear imidazolate-bridged [Fe(ttpp)·CuL^4] complex was not isolated, the solution evidence of its formation is clear and further work to prepare this or a similar complex is in progress. The complex [Fe(ttpp)(OH)] was found to be a valuable iron(III) porphyrin for spectral observation of axial ligation.

Acknowledgements

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