Chloro(N-p-nitrobenzoylimido-meso-tetraphenylporphyrinato)iron(III): a high-spin complex †

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The crystal structures of diamagnetic (methanol)(N-p-nitrobenzoylimido-meso-tetraphenylporphyrinato)zinc(ii) methanol solvate Zn(N-p-NCOC6H4NO2-tpp)(MeOH)·MeOH [or 4(MeOH)·MeOH] and paramagnetic chloro-(N-p-nitrobenzoylimido-meso-tetraphenylporphyrinato)iron(III) Fe(N-p-NCOC6H4NO2-tpp)Cl (5), were determined. Both are pentacoordinate complexes where the N-p-nitrobenzoylimido (NNB) moiety is inserted into a zinc–pyrrole (or iron–pyrrole) bond. The coordination geometry of the zinc (or iron) center is best described as a distorted trigonal bipyramid with the N(2), N(5), and O(4) [or N(2), N(5), and Cl(1)] atoms lying in the equatorial plane. The plane of the three pyrrole nitrogen atoms [i.e., N(1), N(2), and N(3)] strongly bonded to Zn in 4(MeOH)·MeOH (or FeCl3 in 5) is adopted as a reference plane, 3N. The porphyrin ring is severely distorted and the pyrrole ring N(4) is bonded to the NNB ligand making a dihedral angle of 30.0° (or 27.8°) with the 3N plane for 4(MeOH)·MeOH (or 5).

Solid state magnetic susceptibility and the effective magnetic moment data were measured for 5 from 300 to 5 K. In the higher temperature range ($T > 50$ K), the effective magnetic moment is constant and is equal to 5.87 $\mu_B$. This $\mu_{eff}$ value confirms that there is a high-spin ferric ($S = 5/2$) state for the iron atom in 5. The $g$ values of $9.5 \pm 0.4$, 4.2 and 1.1 measured from X-band EPR spectra were also consistent with a high-spin ferric iron in 5. The magnitude of zero field splitting, D, and the rhombic parameter, $\lambda$ ($= E_D$), in 5 were determined approximately as 0.79 cm$^{-1}$ and 0.29, respectively, by EPR spectroscopy and paramagnetic susceptibility measurements.

Introduction

Metalloporphyrins with a bridged structure between the central metal and one of the four pyrrole nitrogens are of great interest since an iron(III) porphyrin with an oxygen atom inserted into an Fe–N bond is postulated as one of the possible structures for the highly oxidized forms of some hemoproteins.1 Many bridged metalloporphyrins with metal–NTs–N linkages (metal = Zn,2 Ni,3 Fe,4 Hg,5 Ga,6 Ti,7 Ts = tosyl) have so far been reported. Callot et al.1 reported the synthesis and spectroscopic characterization of the metallation of N-p-nitrobenzoylimidomeso-tetraphenylporphyrin[N-p-HNCOC6H4NO2-tpp] (tpp = the dianion of meso-tetraphenylporphyrin) leading to mononuclear complexes of (N-p-nitrobenzoylimido-meso-tetraphenylporphyrinato)nickel(ii) Ni(N-p-NCOC6H4NO2-tpp) (1) and (N-p-nitrobenzoylimido-meso-tetraphenylporphyrinato)coppper(ii) Cu(N-p-NCOC6H4NO2-tpp) (2). We have recently reported the X-ray structures of two diamagnetic, mononuclear, and bridged metal complexes i.e., the four-coordinate compound of 1 and the six-coordinate complex of cis-acetatot(N-p-nitrobenzoylimido-meso-tetraphenylporphyrinato)thallium(III) Tl(N-p-NCOC6H4NO2-tpp)(OAc) (3).7

In this paper, we present the results obtained upon replacing Ni(ii) with Zn(ii) and Fe(iii) in 1 forming new compounds 4(MeOH)·MeOH and 5, respectively. This replacement increases the coordination number (CN) from 4 of 1 to 5 forming diamagnetic (methanol)(N-p-nitrobenzoylimido-meso-

Chloro(N-p-nitrobenzoylimido-meso-tetraphenylporphyrinato)iron(III) 5.

† Dedicated to Professor Rob Dunbar (Case Western Reserve University) on the occasion of his 60th birthday.

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through one-bond coupling and HMBC (heteronuclear multiple bond coherence) for two- and three-bond proton–carbon coupling.

The positive-ion fast atom bombardment mass spectrum (FAB MS) was obtained in a nitrobenzyl alcohol (NBA) matrix using a JEOL JMS–SX/SX 102A mass spectrometer. UV/Visible spectra were recorded at 25 °C on a HITACHI U-3120 spectrophotometer.

**Magnetic susceptibility measurements**

The solid-state magnetic susceptibilities were measured under helium on a Quantum Design MPMS5 SQUID susceptometer from 5 to 300 K at a field of 1 T. The sample was held in a Kel-F bucket. The bucket had been calibrated independently at the same field and temperature. The raw data for 5 were corrected for the molecular diamagnetism. The diamagnetic contribution of the sample was measured from an analogous diamagnetic metal complex, i.e. 4(MeOH)–MeOH.

**EPR spectroscopy**

EPR spectra were measured on an X-band Bruker EMX-10 spectrometer equipped with an Oxford Instruments liquid helium cryostat. Magnetic field values were measured with an NMR gaussmeter and the frequency calibrated with a digital counter.

**Crystallography**

Table 1 presents the crystal data for 4(MeOH)–MeOH and 5-CHCl₃. Measurements were taken on a Siemens SMART CCD diffractometer using monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The empirical absorption corrections were made for both complexes. The structures were solved by direct methods (SHELXTL PLUS) and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atoms were treated as riding. See http://www.rsc.org/suppdata/dt/b2/b202842p/ for crystallographic data in CIF or other electronic format.

**Results and discussion**

**Molecular structures of 4(MeOH)–MeOH ($S = 0$) and 5 ($S = 5/2$)**

The molecular framework is depicted in Fig. 1a for complex 4(MeOH)–MeOH and in Fig. 1b for 5-CHCl₃. Both the five-coordinate structures have metal atoms bonding with three
nitrogen atoms of the porphyrins and one extra nitrogen atom of the nitrene fragment in common, but they differ with an axial MeOH ligand for 4(MeOH)-MeOH and a Cl⁻ ligand in the axial site for 5-CHCl₃. In both 4 and 5, it appears that the p-nitrobenzoylimido (NNB) moiety is inserted into the Zn-N bond of (meso-tetraphenylporphyrinato)zinc(ii), Zn(nit), and the Fe-N bond of chloromeso-tetraphenylporphyrinato)iron(III), Fe(tpp)(Cl)₁⁴. The unusual metal–ligand bond distances, i.e., from the Zn(nit) and Fe(tpp) atoms to the ligand and the angles are summarized in Table 2.

Bond distances (Å) are Zn(1)-O(4) = 2.106(3) and the mean Zn(1)-N(p) = 2.029(3) for 4(MeOH)-MeOH; for 5 the Fe(1)-Cl(1) = 2.238(1) and the mean Fe(1)-N(p) = 2.048(3). The average Fe-N(p) distance of 2.048(3) Å in 5 is similar to that observed for the iron–pyrrole nitrogen bond of the high-spin (S = 5/2) iron(II) porphyrin complex Fe(N-Ts-tpp)Cl [Fe-N(p) = 2.036 Å], but it is substantially longer than the 1.993 Å value of intermediate-spin (S = 3/2) complexes. The Zn(1)-O(4)(MeOH) distance of 2.106(3) Å is slightly longer than the sum of the covalent radii of Zn and O (1.93 Å) but is significantly shorter than the sum of the van der Waals radii of Zn and O (2.90 Å). This Zn(1)-O(4) contact may be described as a weak covalent bond. The pyrrole nitrogen N(4) is no longer bonded to the zinc and iron as indicated by their longer inter-nuclear distances, 2.564(3) Å for Zn(1)·····N(4) and 2.434(3) Å for Fe(1)····· N(4).

The distortion in these five-coordinate complexes can be quantified by the “degree of trigonality” which is defined as τ = (β – α)/60°, where β is the largest and α the second largest of the θbasal-M-θbond angles.¹³.¹⁴ The limiting values are τ = 0 for an ideal tetrahedral geometry and τ = 1 for an ideal trigonal-bipyramid. In the present case, we find β = 164.61(¹°) [N(3)-Fe(1)-N(1)] and α = 125.33(⁹°) [N(5)-Fe(1)-Cl(1)] for 5, and β = 169.7(¹°) [N(3)-Zn-N(1)] and α = 130.5(¹°) [N(2)-Zn-O(5)] for 4(MeOH)-MeOH. Thus the value τ = 0.65 is obtained for both 4(MeOH)-MeOH and 5. The geometry around Zn(1) in 4(MeOH)-MeOH and Fe(1) in 5 are best described as a distorted trigonal bipyramid (or a square-based pyramidal) and the mean Fe(1)-N(p) distance in Fe(tpp)(Cl), in the equatorial plane for 4(MeOH)-MeOH (or 5). The τ values calculated for Fe(N-Ts-tpp(Cl⁴ and Ga(N-Ts-tpp(OAc)⁶ by the same methods are 0.72 and 0.68, respectively, and the coordination geometry for these two compounds is also distorted trigonal bipyramidal (or SBPDTBP). We adopt the plane of three strongly bound pyrrole nitrogen atoms [i.e., N(1), N(2), and N(3)] as a reference plane, 3N.

Fig. 2 shows the actual porphyrin skeleton of 4(MeOH)-MeOH and 5. Because of the larger size of Fe⁺, Fe(1) lies 0.27 Å below the 3N plane toward the chloride atom in 5, compared to 0.09 Å for Zn(1) in 4(MeOH)-MeOH [cf. 0.17 Å for N(i) in 1, 1.15 Å for T(iii) in 3, and 0.21 Å for Fe(iii) in Fe(N-Ts-tpp(Cl). (Fig. 2). The porphyrin macrocycle is indeed distorted because of the presence of the NB group (Fig. 2). Thus, the N(4) pyrrole rings bearing the NB group would mostly deviate from the 3N plane and orient separately in a dihedral angle of 30.0° for 4(MeOH)-MeOH and 27.8° for 5, whereas small angles of 17.7°, 9.3°, and 13.0° occur with N(1), N(2), and N(3) pyrrole for 4(MeOH)-MeOH and the corresponding angles are 6.3°, 2.1°, and 10.9° for 5. In the diamagnetic compound 4(MeOH)-MeOH, such a large deviation from planarity for the pyrrole N(4) is also reflected by observing a 13–15 ppm upfield shift in the ¹³C NMR spectrum of the C(19) (C19, C20) at 118.8 ppm compared to 134.1 ppm for C(5) (C5, C14), 132.6 ppm for C(6) (C9, C10), and 132.0 ppm for C(7) (C4, C15). Similar upfield shifts were also observed for the diamagnetic complexes of C(19) resonances due to the non-planarity of porphyrin with a magnitude of 12–19 ppm for Ni(N-p-NO₂C₆H₄NO₂-tpp) and 17–21 ppm for Tl(N-p-NO₂C₆H₄NO₂-tpp(OAc).⁷

The pyrrole ring nitrogen N(4) is in fact inclined towards the Zn and Fe atoms in 4(MeOH)-MeOH and 5, respectively. These distortions make the distances between opposite pyrrole nitrogen atoms unusual. The normal diameter of the “hole” in an

![Molecular configuration and atom-labeling scheme for (a) 4(MeOH)-MeOH and (b) 5-CHCl₃.](image-url)
The undistorted metalloporphyrin complex has been estimated to be 4.02 Å. The N(2) · · · N(4) distances of 4.468 Å in 4(MeOH)-MeOH and of 4.328 Å in 5 are unusually long, which is caused by the large deviation of the N(4) pyrrole in 4(MeOH)-MeOH and 5 from the 3N plane. Because of this distortion, the N(1) · · · N(3) distance is 4.113 Å in 4(MeOH)-MeOH and 4.126 Å in 5. Hence, in 4(MeOH)-MeOH (or 5), the zinc(tl) [or iron(tll)] atom is bound in an expanded porphyrinato (4N) core. The plane (P) defined by Zn(1), N(5), N(4), and C(45) in 4(MeOH)-MeOH, or by Fe(1), N(5), N(4), and C(45) in 5 is almost perpendicular to the 3N plane with an angle of 94.1° in 4(MeOH)-MeOH and 79.9° in 5. The p-nitrobenzoyl group (NB) [i.e., the plane for NB is C(46)-C(51)] is bonded to N(5) in 4(MeOH)-MeOH and 5 so that it lies above the macrocycle, orienting in a dihedral angle of 47.9° and 61.3° with the 3N plane in 4(MeOH)-MeOH and 5, respectively. The dihedral angles between the mean plane of the skeleton (3N) and the planes of the phenyl groups are 46.1° [C(24)], 49.3° [C(30)], 58.0° [C(36)], and 46.5° [C(42)] for 4(MeOH)-MeOH and the corresponding angles are 44.0°, 78.7°, 87.4°, and 42.2° for 5.

**Magnetic properties of complex 5**

The temperature dependence of the molar magnetic susceptibility, $\chi_M$, and the magnetic moment, $\mu_{\text{eff}}$, for the crystalline complex 5 is shown in Fig. 3. As can be seen in Fig. 3, the value of $\mu_{\text{eff}}$ varies from 5.87 $\mu_B$ at 300 K to 4.28 $\mu_B$ at 5 K. The magnetic moment clearly shows a plateau equal to 5.87 $\mu_B$ at high temperatures (300–50 K), which is close to the expected value of 5.92 $\mu_B$ for a sextet multiplet high-spin state ($S = 5/2$). Below 20 K, the magnetic moment drops rapidly, reflecting the large zero-field splitting of the ground state which is usual in high-spin iron(tlll) porphyrins. $^{17,28}$

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**Fig. 2** Diagram of the porphyrinato core (C$_2$N$_3$M, NB, Cl$^-$, and OMe) of (a) compound 4(MeOH)-MeOH and (b) compound 5. The values represent the displacements (in Å) of the atoms from the mean 3N plane [i.e., N(1), N(2) and N(3) for 4(MeOH)-MeOH and 5].

**Fig. 3** Temperature dependence of the molar paramagnetic susceptibility, $\chi_M$, and the magnetic moment, $\mu_{\text{eff}}$, for a microcrystalline sample of 5 in the range 5–300 K. Points are the experimental data; solid lines represent the least-squares fit of the data to eqn. (3).

**Fig. 4** $^1$H NMR spectrum of 5 at 599.95 MHz in CDCl$_3$ at 20 °C.

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$^1$H NMR spectroscopy of 5 in solution

The $^1$H NMR spectrum of 5 in CDCl$_3$ at 20 °C is shown in Fig. 4. The signals at 92.22, 88.11, 86.22, and –31.34 ppm have been assigned to the pyrrole protons (H$_5$). These four signals for H$_5$ indicate that complex 5 has effective C$_s$ symmetry in solution with a mirror plane running through the Cl(1)–Fe(1)–N(2)–N(5)–N(4) unit. The signals at 13.21, 11.89, 11.39, and 10.40 ppm are due to the meta protons of the phenyl group (m-H). The signals at 6.69, and 3.45 ppm are assigned to the para protons of the phenyl rings (p-H). The two broad signals at 5.35 and 4.35 ppm have been assigned to the ortho protons of the phenyl group (o-H), which are closer to the paramagnetic center compared to the meta protons. Thus, the NMR spectra show clear evidence of spin density delocalization onto the
ligand for the Fe(III) complex, giving the so-called contact shifts for the 1H spectra.\textsuperscript{18,20} Since signal assignment of the 13C NMR data is not simple for compound 5, it is difficult to see whether this spin delocalization effect is present in the 13C spectra or not.

**EPR spectra of 5**

The spin Hamiltonian \(H_s = \frac{1}{2} g \mu_B HS\) used to interpret the EPR data is\textsuperscript{21-23}

\[
H_s = H_e + H_{CF}\tag{1}
\]

where

\[
H_e = g \mu_B HS
\]

\[
H_{CF} = D \left[ S_z^2 - S(S+1)/3 \right] + E(S_x^2 - S_y^2)
\]

The first term \(H_e\) in the spin Hamiltonian \(H_s\) is the electronic Zeeman term, which describes the interaction of the electronic spin \(S\), with the external magnetic field \(H\). \(H_{CF}\) is the crystalline electric field, \(\mu_B\) is the Bohr magneton, \(g\) is the electronic \(g\)-tensor, and \(D\) and \(E\) are the axial and rhombic zero-field splitting (ZFS) parameters.

The rhombicity parameter, \(\lambda = \frac{E}{D}\), is a measure of the departure of the electronic environment of the iron center from axial symmetry. In an appropriate axis system, axial symmetry corresponds to \(\lambda = 0\) while a maximally rhombic symmetry corresponds to \(\lambda = 1/3\). For \(D \gg \hbar\nu\) (the energy of the microwave, \(\sim 0.32\) cm\(^{-1}\) at X-band), the three Kramers doublets of a \(S = 1/2\) system act approximately like independent \(S = 1/2\) systems with effective \(g\)-values that are dependent only on \(\lambda\).

The high degree of rhombicity of the iron center in 5 is demonstrated by the presence of the intense signal at \(g = 4.2\) in a powdered solid, as shown in Fig. 5. In the solid-state spectra, a reasonable estimate of the principal \(g\) values associated with the middle doublet may be obtained by using the minimum, maximum, and inflection points of the \(g = 4.2\) EPR absorption derivative as limits for the \(g\) values.\textsuperscript{22} The \(g\) value for the maximum \((g = 4.6)\), minimum \((g = 3.9)\), and inflection point \((g = 4.2)\) of the main signal at \(g = 4.2\) were close to the calculated values of \(g_5 = 4.53, g_1 = 4.03,\) and \(g_2 = 4.24\) derived from the transitions in the middle Kramers doublet (Fig. 6). As shown in Figs. 5 and 6, the \(g\) values with \(g_5 = 1.12\) and \(g_2 = 9.55\) calculated for the lowest Kramers doublet indeed agree semi-quantitatively with observed \(g_5 = 1.1\) and \(g_2 = 9.5 \pm 0.4\). The eigenvectors and energies of eqn. (1) with \(\lambda = 0.29\) in zero field \((D > 0)\) are

\[
|\phi_1^g\rangle = -0.1237 | \pm 5/2 \rangle + 0.902 | \pm 1/2 \rangle - 0.4129 | \mp 3/2 \rangle
\]

\[
|\phi_2^g\rangle = -0.1065 | \pm 5/2 \rangle + 0.4017 | \pm 1/2 \rangle + 0.9096 | \mp 3/2 \rangle
\]

\[
|\phi_3^g\rangle = 0.9865 | \pm 5/2 \rangle + 0.1568 | \pm 1/2 \rangle + 0.0465 | \mp 3/2 \rangle
\]

The paramagnetic susceptibility, \(\chi_m\), and effective magnetic moment, \(\mu_{eff}\), data shown in Fig. 3 for 5 were least-squares which fit to eqn. (3) to give the fitting parameters \(D = 0.79\) cm\(^{-1}\) and \(g = 2.39\).

\[
\chi_m = \frac{N g^2 \beta^2}{4kT} \left[ \frac{0.14 + 5.12e^{-2.23/T}}{1 + e^{-2.23/T}} + 23.85e^{-6.03/T} + e^{-8.03/T} + 0.1 + 4.12e^{-4.12/T} \right]	ag{3}
\]

In eqn. (3), \(X = DS/kT\), \(g\) is the average \(g\) value, and the other symbols have their usual meanings. Eqn. (3) is the simple theoretical susceptibility equation resulting from the axial and rhombic zero-field splitting (ZFS) for \(S = 1/2\) as governed by the spin Hamiltonian \(H_s\) in eqn. (1). Importantly, the energy splitting diagram for 5 with \(\lambda = 0.29\) shown in Fig. 6 and the eigenvectors shown in eqn. (2) are used in the derivation of eqn. (3). The solid lines in Fig. 3 represent this fit. This value of \(D\) means that the relative energies of the three Kramers doublets at zero magnetic field are 0.255, and 5.40 cm\(^{-1}\).

On consideration of all the experimental data combined, i.e., the magnetic moment \(\mu = 5.92 \mu_B\) at 300–50 K, the EPR signals at \(g = 9.5 \pm 0.4, 4.2,\) and 1.1 at 4 K, the Fe-N(p) distance 2.048(1) Å at 22 °C, and NMR shifts of the pyrrole protons \((\delta_H)\) \((\delta_H = 92.22, 88.11, 86.22, \sim 31.34)\) at 20 °C firmly establish a high-spin \((S = 1/2)\) state for complex 5. Although the characteristics of complex 5 are similar to those previously reported for the high-spin pentacoordinate iron(III) porphyrin complex Fe(N-N-Ts-tpp)Cl\textsuperscript{4,50} the fine structure of the EPR signals and paramagnetic susceptibility data allow us unambiguously to evaluate the parameters \(\lambda = 0.29\) and \(D = 0.79\) cm\(^{-1}\) for 5. This is
the first report applying the rhombicity evaluation by EPR methods to bridged metalloporphyrins with a Fe–NNB–N linkage.

In conclusion, we have investigated two pentacoordinate [one diamagnetic, 4(MeOH)•••MeOH, and one paramagnetic, 5], mononuclear, and bridged metal complexes of N-p-nitrobenzoylamido-meso-tetraphenylporphyrin having a M–NNB–N (M = Zn(II), Fe(III)) linkage, and established their X-ray structures. X-Band EPR spectroscopy and solid-state magnetic susceptibility data can be used to assess the zero-field splitting, D, and the rhombicity parameter, δ (= E/D), for 5.

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