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COMMUNICATION

Equatorial ligand plane perturbations lead to a spin-state change in an iron(III)porphyrin dimer

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A complete reversal of the spin state of iron(III) is observed upon a small change to the diporphyrin bridge from ethane to ethene by keeping all other factors intact. Combined analysis using single crystal X-ray structure determination, Mössbauer, variable-temperature magnetic, ¹H NMR and EPR studies have confirmed the spin states of iron(III) complexes both in solid and solution phases.

Despite having nearly identical heme prosthetic groups, the heme enzymes execute a large variety of biological functions which has continued to fascinate and perplex.^{1–4} Several chemical models based on iron porphyrins, in various geometries, oxidation and spin states, have been subsequently designed to reproduce the crucial intermediates in the catalytic cycles of both biological and abiological systems.^{1–9} In order to understand the function and catalytic activities of naturally occurring hemoproteins, the elucidation of the electronic structure of iron porphyrins bears prime importance. Comprehensive investigation on hemoproteins and their model systems have established that the ligand axially coordinated to the metal centre plays a pivotal role in determining the electronic structure and function of the chromophore.^{1,3–7} Moreover, it has also been shown that the porphyrin ring deformation affects the electronic structure of the iron(III) porphyrin complexes.^{3–8} Recently, we have shown that secondary interactions, such as H-bonding interactions, can cause a spin-flip in iron(III) porphyrins.^{6a} One of the key steps in cytochrome P450 catalysis is the spin-state crossing from low to high-spin upon substrate binding and subsequent reduction of the heme.¹⁰ Clearly, a weak perturbation in the

P450 enzyme mediates a spin-state crossing, which is still poorly understood. In the present work, we demonstrate the complete reversal of the iron spins using small environmental perturbation just by changing the bridge between the heme centres in a single molecular framework.

Scheme 1. Complexes investigated in this work; 1•X has been reported earlier⁷.

We report the synthesis and characterization of complexes 2•X (X: perchlorate, picrate), Scheme 1, and compare the structure and properties with the recently characterized complex 1•X.⁷ The sets of structures are identical apart from the linking bridge unit. When the ethane bridge is replaced by ethene, the Soret band in the UV-visible spectrum red-shifts for perchlorate, whereas it is blue-shifted in the case of picrate. In addition, the ethane-bridged complex shows a split in the Soret band (Fig. 1 and Fig. S1, Electronic Supporting Information).

Dark brown crystals of 2•perchlorate were grown by slow diffusion of benzene into the dichloromethane solution of the

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Electronic Supplementary Information (ESI) available: synthesis and characterization of all complexes. Instrumentation, experimental and computational details, spectroscopic characterization, computational results. CCDC-1813531 and 1813532 contain X-ray crystallographic details in CIF format. See DOI: 10.1039/x0xx00000x

complex at room temperature in air and the crystal structure is a benzene disolvate.¹¹ The complex has two iron centres each in a five coordinate square-pyramidal geometry that are in *trans* configuration (Fig. 2). The iron atom is displaced by 0.27 Å from the least-squares plane of C₂₀N₄ porphyrinato core (Δ_{24}^{Fe}) and the average Fe-N_{por} distance is found to be 1.996(4) Å while the Fe-OCIO₃ distance is 2.056(3) Å. The structural parameters such as the Fe-N_{por} and Δ_{24}^{Fe} distances are characteristic³⁻⁹ for a five-coordinate iron(III) porphyrin with intermediate spin state ($S = 3/2$), which we assign for **2**•perchlorate. By contrast, the average Fe-N_{por} distances are 2.062(9) (core-I) and 2.057(9) Å (core-II) for the high-spin complex, **1**•perchlorate while the corresponding Fe-O distances are 1.873(9) and 1.940(7) Å, respectively (Table 1).^{7a} It is, however,

Fig. 1 UV-vis spectra (in CHCl₃ at 295 K) using polycrystalline samples of **1**•picrate (red line) and **2**•picrate (blue line).

interesting to note that the reverse trends are seen for the Fe-N_{por} and Fe-O distances between **1**•perchlorate and **2**•perchlorate. Similar spin reversal upon going from ethane to ethene-bridged porphyrin dimer is observed with trinitrophenolate (picrate) as axial ligand. Dark purple crystals of **2**•picrate were grown by slow diffusion of hexane into dichloromethane solutions of the complex at room temperature in air (Fig. 2).¹¹ The iron atom is displaced by 0.45 Å from the least-squares plane of C₂₀N₄ porphyrinato core and the average Fe-N_{por} distance is found to be 2.046(3) Å while the Fe-O(TNP) distance is 1.916(3) Å. These results correspond to a high-spin iron(III) state (Table 1). By contrast, in **1**•picrate, the iron is in the intermediate-spin state as Fe-N_{por} distances of 1.972(3) Å and Δ_{24}^{Fe} is 0.23 Å.^{7b}

Table 1. Selected geometrical parameters of complexes **1**•X^e and **2**•X

	1 •perchlorate		2 •perchlorate	1 •picrate	2 •picrate
	Core I	Core II			
Fe-O[Å]	1.873(9)	1.940(7)	2.056(3)	2.000(2)	1.915(3)
Fe-N _{por} ^a [Å]	2.062(9)	2.057(9)	1.996(4)	1.972(3)	2.047(3)
$\Delta_{24}^{\text{Fe},b}$ [Å]	0.44	0.42	0.27	0.23	0.45
Fe...Fe ^c [Å]	10.04		10.11	9.39	10.28
Δ_{24}^{d} [Å]	0.11	0.11	0.10	0.26	0.10
Spin state	H. S. (5/2)		I. S. (3/2)	I. S. (3/2)	H. S. (5/2)

^aAverage value. ^bDisplacement of iron from the least-squares plane of C₂₀N₄porphyrinato core. ^cNonbonding distance between two Fe centers in a molecule. ^dAverage displacement of atoms from the least-squares plane of C₂₀N₄ porphyrinato core. ^eTaken from ref 7.

Fig. 2 Perspective views (at 100 K) of (A) **2**•perchlorate, and (B) **2**•picrate showing 50% thermal contours for all non-hydrogen atoms (H atoms have been omitted for clarity).

Fig. 3 Out-of-plane displacement (in units of 0.01 Å) of the porphyrin core atoms of **1**•picrate (black line), and **2**•picrate (red line) from the least-squares plane of the C₂₀N₄ porphyrinato core. The horizontal axis represents the bond connectivity between atoms.

Generally, the porphyrin macrocycles are more distorted in **1**•X as compared to **2**•X, which is reflected by the out-of-plane displacement plots in which the bridging *meso*-carbon atoms are seen to be displaced the most (Figs. 3 and S2). Due to the highly flexible ethane-bridge in **1**•X, the two heme units come closer to each other leading to stronger interactions (which results in more ring-distortion) between them as compared to **2**•X where the heme centres are more separated using a sufficiently rigid ethene-spacer. Porphyrin ring distortion, well-known⁵⁻⁹ to control the spin states of Fe(III) porphyrins, is responsible for such a spin-flip between ethane and ethene bridged complexes reported here. Packing diagrams of the complexes **2**•perchlorate and **2**•picrate are shown in Figs. S3 and S4 in the Electronic Supporting Information.

In order to establish the spin-states of the complexes unequivocally, Mössbauer spectra were recorded. Fig. 4 compares the Mössbauer spectra of the microcrystalline samples of **1**•picrate and **2**•picrate at 100 K. Both complexes show a doublet signal with a large quadrupole-splitting [δ (ΔE_Q): 0.27 (2.70) mms⁻¹ for **1**•picrate and 0.30 (0.58) mms⁻¹ for **2**•picrate. These results correspond to intermediate-spin ($S = 3/2$) and high-spin ($S = 5/2$) states of iron, respectively. The Mössbauer spectrum of **2**•perchlorate was also recorded and gives a large quadrupole-splitting [δ (ΔE_Q): 0.28 (2.67) mms⁻¹] (Fig. S5, Electronic Supporting Information) demonstrating an intermediate-spin ($S = 3/2$) state for iron(III). The magnetic moments of the polycrystalline samples of **2**•perchlorate and **2**•picrate are found to be independent of temperature over the range from 5 to 300 K (Figs. S6 and S7, Electronic

Supporting Information). The magnetic moment of **2**•perchlorate is found to be 3.96 μ_B per iron at 298 K which is quite close to the spin only value of 3.87 μ_B expected⁷ for $S = 3/2$ complex whereas for **2**•picrate it has been found to be 5.95 μ_B per iron at 298 K that resembles the spin-only value of 5.92 μ_B expected⁷ for an $S = 5/2$ complex.

Fig. 4. Left, Mössbauer spectra (obtained at 100 K) and right, EPR spectra (obtained at 120 K) of (A) **1**•picrate, (B) **2**•picrate.

To obtain more conclusive evidence for the spin state, EPR spectroscopy studies were carried out for the complexes in both solid and solution phases. All the spectra are axially symmetric (Fig. 4) with $g_{\perp} = 4.28$ and $g_{\parallel} = 2.01$ for **1**•picrate and $g_{\perp} = 6.05$ and $g_{\parallel} = 1.97$ for **2**•picrate in dichloromethane at 120 K. Similar g values are also obtained for the molecules in solid state. Consistent with the X-ray structure, SQUID and Mössbauer results, **2**•perchlorate and **2**•picrate give a pure intermediate ($S = 3/2$) and high-spin ($S = 5/2$) state, respectively.

Fig. 5. ^1H NMR spectra of (A) **1**•perchlorate, (B) **2**•perchlorate, (C) **1**•picrate, and (D) **2**•picrate at 295 K in CDCl_3 .

The solid state structures are also preserved in solution as reflected in their ^1H NMR spectra (Fig. 5). In complex **1**•perchlorate, the methylene peaks are found at $\sim +40$ ppm while the two *meso*-proton signals are observed in a 2:1 intensity ratio in the far up-field region at -35.2 and -52.4 ppm which is typical for high-spin iron(III)porphyrins of octaethylporphyrin (OEP)-type.^{7a} However, the eight methylene signals for **2**•perchlorate are observed $\sim +20$ ppm region (from $\delta = 16.0$ to 21.4 ppm; with average of 18.2 ppm) while the two *meso*-peaks appear at -3.9 and 15.7 ppm and consequently refer to a more likely intermediate-spin state of iron(III). A similar spin state reversal is also observed with picrate as axial ligand upon replacing the bridge from ethane to ethene. For the intermediate-spin complex **1**•picrate, eight sharp $-\text{CH}_2$ proton signals are observed in a narrow region (from $\delta = 16.1$ to 20.4 ppm; with average of 17.5 ppm) while two *meso*-signals are in 1:2 intensity ratio but are found in the up-field region at -5.1 and -15.6 ppm.^{7b} However, for **2**•picrate the eight diastereotopic methylene resonances are observed at $\sim +40$ ppm region (from $\delta = 35.5$ to 55.4 ppm) while the *meso*-signals occur in the high up-field region at -22.0 and -43.7 ppm. This demonstrates that iron(III) is most likely in a high-spin state (Fig. 5). The *meta*-H peak for axially coordinated picrate species is observed at 52.4 ppm and was assigned through a ^1H - ^1H COSY spectrum (Fig. S8, Electronic Supporting Information). Chemical shifts of the methyl protons of the ethyl substituents are also known to be sensitive to the spin state of the metal: $S = 5/2$ complexes usually exhibit signals more down-field than $S = 3/2$ complexes because the unpaired electrons can be delocalized to $-\text{CH}_3$ protons through σ -bonds in the $S = 5/2$ complexes.¹² Methyl signals of **1**•perchlorate appear at 6.5 and 6.7 ppm while in case of **2**•perchlorate, they are found at 2.6 , 2.7 and 2.8 ppm. Similarly, the methyl proton peaks of **1**•picrate are located at 2.7 , 2.8 and 3.0 ppm while they move to 5.9 , 6.7 , 7.7 and 8.4 ppm in **2**•picrate. On the basis of the above results, the spin on iron is found to be similar in solution as compared to the solid state.

Fig. 6. OPBE/BS1 optimized geometries of structures **12**•perchlorate and **112**•picrate in the antiferromagnetic singlet spin state with $S = 3/2$ on **12**•perchlorate and ferromagnetic spin state with $S = 5/2$ on **112**•picrate. Bond lengths are in angstroms.

To gain further insight into the structure and spin-state ordering of the iron(III)porphyrin dimers **1•X** and **2•X** upon axial ligand binding, we ran a series of density functional theory calculations on these systems with either an axial perchlorate or picrate ligand as calibrated before on an analogous system.¹³ We used two models, namely **1A•X/2A•X**, where the side-chains of porphyrin were abbreviated to H-atoms, but also the full model, labelled **1•X/2•X** (Scheme S1) (Figs. S9 to S14, Tables S3 to S7). Fig. 6 gives OPBE optimized geometries of ¹¹**2•picrate** and ¹²**2•perchlorate** {3/2} in the ferro and antiferromagnetic spin state, respectively. The optimized geometries, particularly Fe-O and average Fe-N_p distances for the large model are in excellent agreement with the crystal structure described in Fig. 2. The calculations find the antiferromagnetically coupled intermediate spin state to be the ground state for structure **2•perchlorate** by $\Delta E = 2$ kcal mol⁻¹ with respect to the antiferromagnetically coupled high-spin state (Table S3). In the gas-phase, therefore, the correct spin-state ordering of structure **2•X** is reproduced with the calculations.

In general, whether the axial ligand is perchlorate or picrate we find the two spin states within a couple of kcal mol⁻¹ from each other and small external perturbations, such as solvent, the binding of anions, or the additions of substituents on the periphery of the porphyrin affect the ordering and relative energies, see Electronic Supporting Information for a detailed benchmark study on these complexes. Furthermore, the spin state energies are also sensitive to the density functional method applied here as also seen previously.^{13,14} With picrate as an axial ligand, at the $\Delta E + \text{ZPE}$ level of theory the calculations for model **1A•picrate** predict an intermediate-spin state ground state, whereas the high-spin state is lower for structure **2A•picrate** (Table S5). A similar trend is seen for the larger models that also give stabilization of the high-spin state with the ethene bridge complex (Table S7). As such the computational modelling on perchlorate *versus* picrate binding as axial ligand support the experimental observations that spin state orderings are affected by the nature of the axial ligand.

In summary, an extensive spectroscopy, crystallography and computational study shows a spin-flip between ethane and ethene bridged iron(III)porphyrin dimer with the same axial ligand. In the case of highly flexible ethane-bridged complex, two heme units come closer to each other leading to stronger interactions between them as compared to their ethene-bridged analogue in which the heme units are more separated due to rather rigid ethene-spacer. This has resulted in more distorted heme centres in the ethane-bridged complex which is well-known to play a significant role in controlling the spin states in Fe(III) porphyrins. It is possible that Nature utilizes such environmental perturbations as a powerful tool to mediate large change in the electronic structure and properties needed for the functioning of the large series of heme proteins.

Conflicts of interest

There are no conflicts to declare.

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- 11 Crystal data for **2•perchlorate**: triclinic, space group *P*-1, *Z*=1, *a*=10.8619(12) Å, *b*=13.5788(15) Å, *c*=15.2373(18) Å, α =64.626(2)°, β =78.507(2)°, γ =71.060(2)°, *V*=1915.9(4) Å³. *d*_{calcd}= 1.349 Mg/m³; *T* = 100(2) K, no. of independent reflections = 7006, $\theta_{\max}$ = 25.50°, goodness of fit on *F*²=1.027; *R*₁=0.0691 (for *I* > 2σ(*I*)), *wR*₂ (all data)= 0.1998; largest diff. peak and hole; 1.118 and -0.738 e.Å⁻³. For **2•picrate**: triclinic, space group *P*-1, *Z*=1, *a*=12.077(5) Å, *b*=13.443(5) Å, *c*=14.103(5) Å, α =62.358(5)°, β =74.156(5)°, γ =72.733(5)°, *V*=1912.0(13) Å³. *d*_{calcd}= 1.439 Mg/m³; *T* = 100(2) K, no. of independent reflections = 7129, $\theta_{\max}$ = 25.50°, goodness of fit on *F*²=1.039; *R*₁=0.0664 (for *I* > 2σ(*I*)), *wR*₂ (all data)= 0.1770; largest diff. peak and hole; 1.271 and -0.384 e.Å⁻³. CCDC-1813531, and 1813532 contains the supplementary crystallographic data of **2•picrate** and **2•perchlorate**, respectively, for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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