Proton mediated spin state transition of cobalt heme analogs

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The spin state transition from low spin to high spin upon substrate addition is one of the key steps in cytochrome P450 catalysis. External perturbations such as pH and hydrogen bonding can also trigger the spin state transition of hemes through deprotonated histidine (e.g. Cytochrome c). In this work, we report the isolated 2-methylimidazole Cobalt(II) [Co(TPP) (2-MeHIm)] and [Co(TPP)(2-MeHIm)], and the corresponding 2-methylimidazolate derivatives where the N−H proton of axial 2-MeHIm is removed. Interestingly, various spectroscopies including EPR and XAFS determine a high-spin state ($S = 3/2$) for the imidazolate derivatives, in contrast to the low-spin state ($S = 1/2$) of all known imidazole analogs. DFT assisted stereoelectronic investigations are applied to understand the metal-ligand interactions, which suggest that the dramatically displaced metal center allowing a promotion $e_g(d_{π}) \rightarrow b_{1g}(d_{x^2−y^2})$ is crucial for the occurrence of the spin state transition.
Spin state transition of hemes that is usually accompanied by metal displacement and conformational changes widely exists in biochemical processes, e.g., oxygenation of myoglobin (5c, HS (5c = five-coordinate, HS = high-spin) towards 6c, LS (6c = six-coordinate, LS = low-spin))\(^{12,13}\), and the starting step of Cytochrome p450 catalysis (6c, LS towards 5c, HS)\(^{14,15}\), both involved with ligand (un)binding. Besides this, spin state transition can also be controlled by (weak) external perturbations such as pH and hydrogen bonding\(^5\). The proximal His18 of Cytochrome c (or microperoxidases) can be deprotonated at high pH (> 11) to trigger the pH-dependent spin state transition (HS towards LS)\(^5\) regardless of the steric hindrance of the axial ligands\(^20\). This is contrasted to iron(II) analogs, the use of hindered imidazole is necessary to prepare the five-coordinate iron(II) porphyrinates, all of which known so far are high-spin (3d\(^6\), S = 2)\(^{17}\).

Here, we report the first examples of imidazolate ligated Co(II) porphyrinates [K(222)][Co(TPP)(2-MeIm\(^{−}\))] (222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) and [K(222)][Co(TTP) (2-MeIm\(^{−}\))] (TTP = tetraphenylporphyrin, TTP = tetraphenylporphyrin), which are prepared by the reaction between [Co(TPP)] (or [Co(TTP)]) and [K(222)](2-Mel\(^{−}\)) (cryptand 222 is used to stabilize the K\(^{+}\) cation) (Supplementary Figs. 1–4). Two corresponding imidazole derivatives [Co(TPP)(2-MeHIm)) and [Co(TTP)(2-MeHIm)) are also isolated for comparison (Supplementary Table 1). The labeled ORTEP diagrams of the TPP and TTP derivatives are given in Fig. 1 and Supplementary Figs. 5 and 6. Quantitative information that shows the displacements of each atom from the 24-atom mean plane and the orientations of the axial ligands are available in Supplementary Fig. 7. “Shoestring” diagrams illustrating the core conformation and cobalt displacement from the N\(_{ax}\) mean plane are given in Supplementary Fig. 8. It is seen that [Co(TPP) (2-MeHIm)] shows the most distorted porphyrin core with saddled conformation among the four new structures, which can be attributed to the strong steric repulsion between imidazole and N\(_{ax}-Co-N_{im}\) planes evidenced by the smallest \(\varphi\) angle (8.5\(^{\circ}\)) between them (Supplementary Fig. 7). The key structural parameters of all known imidazole(ate) ligated cobalt(II) porphyrinates are given in Table 1. Also given are the parameters of three pairs of 2-methylimidazole(ate) ligated iron(II) analogs. It is seen all the cobalt(II) complexes with neutral imidazole ligands including the new two structures have (Co–N\(_{p}\))\(^{av}\) thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms, [K(222)]\(^{+}\) and solvent molecules are not shown for clarity.

**Results**

**Single crystal structures.** Cobalt and iron hemes are analogous in many aspects, including the oxygen bonding ability\(^{16–18}\). Recently, we have reported the [Co(TpivPP)(R-Im)(O\(_2\))\(_2\)] (R-Im: 1-EtIm or 2-MeHIm; TpivPP = α, α, α-tetraakis(α-pivalamidophenyl)porphyrinato) complexes using imidazole cobalt(II) porphyrinates as the starting material, which are all five-coordinate due to the destabilization of the six-coordinate compound by the singly populated \(d_\alpha\) orbital\(^{19}\). Remarkably all the imidazole cobalt(II) porphyrinates are low-spin state (3d\(^6\), S = 1/2) regardless of the steric hindrance of the axial ligands\(^20\). This is contrasted to iron(II) analogs, the use of hindered imidazole is necessary to prepare the five-coordinate iron(II) porphyrinates, all of which known so far are high-spin (3d\(^6\), S = 2)\(^{17}\).

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**Fig. 1** ORTEP diagrams. a [Co(TPP)(2-MeHIm)]. b [Co(TPP)(2-Me\(^{−}\)). c [Co(TTP)(2-MeHIm)] (one of the two orientations is shown for the axial imidazole). d [Co(TTP)(2-Me\(^{−}\)). Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms, [K(222)]\(^{+}\) and solvent molecules are not shown for clarity.
are available in Supplementary Figs. 9 and 10. The authors suggested that the different geometrical features (e.g., small metal displacements and shorter (Co–Np)av distances \( \leq 2.0 \) Å) of the imidazole(ate) ligated cobalt/iron porphyrinates show consistent axial symmetric spectra with \( \Delta g = 2.0 \) (\( A_{ij} = 79.2 \) G), which are characteristic of high-spin Co(II)\(^{31-33}\). The authors also pointed out that the difference in the structural features caused the varying degree of electronic con

\[
\left\{ \begin{align*}
\Delta_{2s} & \text{ in the plane of the closest Np} \\
\Delta_{2d} & \text{ perpendicular to the plane of the closest Np}
\end{align*} \right.
\]

Electron paramagnetic resonance. The dramatically different structural parameters between imidazole and imidazolate species indicate different spin states of the Co(II) center. To confirm this, electron paramagnetic resonance (EPR) experiments have been conducted on the four new complexes. The experimental and simulated spectra of crystalline [Co(TPP)(2-MeHIm)] and [Co(TPP)(2-MeIm)]\(^{15}\) are given in Fig. 2. Multitemperature measurements on crystalline samples, solution samples with different equivalents of ligands, as well as those of TPP derivatives are available in Supplementary Figs. 9–16. As can be seen, the two imidazolate derivatives ([Co(TPP)(2-MeHIm)] and [Co(TTP)(2-MeHIm)]) show consistent axial symmetric spectra with \( \Delta g = 2.3 \), \( g_y = 2.0 \) (\( A_{ij} = 79.2 \) G), which are typical for a five-coordinate low-spin Co(II)\(^{31-33}\), in accordance with the single crystal structural features (e.g., small metal displacements and shorter (Co–Np)av distances). In contrast, the two imidazolate derivatives ([Co(TPP)(2-MeIm)]\(^{−}\) and [Co(TTP)(2-MeIm)]\(^{−}\)) show characteristic resonances at 6.0, 4.0, and 2.0 (\( A_{ij} = 82.0 \) G) and 5.4, 3.9, 2.0, respectively, (Supplementary Figs. 15b and 16b), which corresponds to a high-spin Co(II)\(^{2−}\) (\( S = 3/2 \))\(^{36-38}\), in agreement with the dramatically different structural parameters from the low-spin counterparts. The zero value \( E/D \) yielded by simulations confirmed the axial system where the \( \pm 3/2 \) Kramers doublet is the excited state and resonances at 4.0 (3.9) and 2.0 come from the ground \( \pm 1/2 \) doublet\(^{39}\). Notably, signals at \( \approx 2.3 \), which appear weak in solid while strong in solution samples, are observed in the spectra of imidazole derivatives (the asterisk in Fig. 2b, Supplementary Figs. 9, 10, 13, and 14). To understand this, reactions of [Co(TPP)] (or [Co(TTP)]) with different equivalents of [K(222)(2-MeIm)]\(^{−}\) in PhCl (or THF) were monitored and the spectra are given in Supplementary Fig. 13 (Supplementary Fig. 14). It is seen when 1 eq. of 2-MeIm\(^{−}\) was added to the [Co(TPP)] solution, resonances belonging to HS species (4.9–5.5 and 3.6–3.8) and a strong signal at \( \approx 2.3 \) became available immediately. Further addition of 2-MeIm\(^{−}\) (3, 5, and 7 eq.) has led to the increase of HS resonances, which suggests the equilibrium [Co(TPP)(2-MeIm)]\(^{−}\) product was generated gradually. In contrast, the signal at \( \approx 2.3 \), though decreasing relatively, was apparent even at the saturated solution (7 eq.). Hence, an intermediate of [Co(TPP)(2-MeIm)]\(^{−}\) with weakly bonding axial ligand, which is generated once 2-MeIm\(^{−}\) is added, is proposed to exist in the solution. Such a weak Co(II)\(^{−}\) interaction

### Table 1 Selected structural parameters of imidazole(ate) ligated cobalt/iron porphyrinates

| Complex          | Method | \( \Delta_{2s}^{ab} \) | \( \Delta_{2d}^{ab} \) | (M–Np)_av \( \leq 2.0 \) Å | M–Np | M–NpCm(2) | M–NpCm(4) | \( \phi_{e}^{ab} \) | \( \psi^{ab} \) | Refs. |
|------------------|--------|------------------------|------------------------|-----------------------------|------|-----------|-----------|----------------|-------------|------|
| Cobalt(II) complexes |
| [Co(TPP)(2-MeIm)] | SC     | 0.26                    | 0.17                    | 1.975(4)                    | 2.177(3) | 132.2(2)  | 124.2(2)  | 4.5            | 6.2          | 23   |
| [Co(TTP)(2-MeIm)] | SC     | 0.15                    | 0.14                    | 1.979(3)                    | 2.145(3) | 132.0(3)  | 123.1(3)  | 3.5            | 6.2          | 23   |
| [Co(TPP)(2-MeHIm)] | SC    | 0.14                    | 0.13                    | 1.977(3)                    | 2.157(2) | 127.8(3)  | 126.4(3)  | 4.1            | 7.1          | 23   |
| [Co(TEP)(1-MeHIm)] | SC    | 0.16                    | 0.13                    | 1.961(1)                    | 2.151(5) | 127.1(1)  | 126.1(1)  | 9.7            | 1.7          | 24   |
| [Co(OCOP)(1-MeHIm)] | SC    | 0.13                    | 0.12                    | 1.985(6)                    | 2.132(3) | 129.2(3)  | 126.6(3)  | 15.6           | 2.6          | 25   |
| Iron(II) complexes |
| [Fe(TPP)(2-MeIm)] | SC     | 0.66                    | 0.56                    | 2.118(11)                   | 2.0739(13) | 132.48(10) | 123.58(10) | 4.5            | 6.2          | 26   |
| [Fe(TPP)(2-MeIm)] | SC     | 0.65                    | 0.56                    | 2.113(4)                    | 2.069(2) | 136.6(2)  | 120.0(2)  | 37.4           | 3.6          | 15   |
| [Fe(TPP)(2-MeHIm)] | SC     | 0.65                    | 0.52                    | 2.106(20)                   | 2.002(15) | NA^4      | NA^4      | 14.7           | 5.1          | 27   |
| [Fe(TPP)(2-MeIm)] | SC     | 0.32                    | 0.32                    | 2.073(9)                    | 2.127(2) | 131.3(3)  | 122.9(2)  | 24.0           | 8.3          | 28   |
| [Fe(TPP)(2-MeIm)] | SC     | 0.46                    | 0.34                    | 2.077(7)                    | 2.135(2) | 131.3(3)  | 122.4(3)  | 19.5           | 6.9          | 29   |
| [Fe(TTP)(2-MeIm)] | SC     | 0.38                    | 0.35                    | 2.076(6)                    | 2.113(3) | 128.5(2)  | 125.7(3)  | 23.3           | 8.3          | 30   |

*Values in angstroms

*Displacement of metal atom from the 24-atom (\( \Delta_{2s} \)) or the four pyrrole nitrogen atoms (\( \Delta_{2d} \)) mean plane. The positive numbers indicate a displacement towards the axial ligand

*Average distance between the metal and porphyrin nitrogen atoms

*Distance between the metal and the axial nitrogen atom

*Angle values in degrees

*M–NpCm–CIm angle with CIm being the 2-carbon of the ligand ring, sometimes methyl substituted

*M–NpCm–CIm angle with CIm being the 4-carbon of the ligand ring

*Dihedral angle between the ligand plane and the plane of the closest Np–Np (illustrated in Supplementary Fig. 7)

*The tilt of the M–Np vector off the normal to the 24-atom mean plane

*Value not available

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does not draw the metal out of porphyrin plane as much as the axial bond of isolable [Co(TPP)(2-MeIm−)]− crystal; it is however similar to the longer axial bond of [Co(TPP)(2-MeHIm)], which shows low-spin signal at ~2.3 (vide infra). The intermediate also explains the weak signals observed in the crystalline samples since it can accompany the isolated crystals through the mother liquor as reported in other cases40, and/or be generated during grinding processes (Supplementary Fig. 9).

Magnetic susceptibility. Additional evidence for the spin state determination of the four complexes comes from temperature dependent (2 ≤ 30 K) magnetic susceptibility measurements, which are given in Fig. 3. As can be seen, the product of the molar susceptibility (χM) and temperature (T) of the two imidazolate complexes are 2.03 and 1.93 cm3 K/mol, close to that expected for the HS state (1.88 cm3 K/mol). This is contrasted to the two imidazole derivatives, which show χM/T at 0.49 and 0.54 cm3 K/mol, close to that expected for the LS state (0.38 cm3 K/mol). Hence, the magnetic susceptibility measurements are well consistent with the EPR results, both of which confirm the high- and low-spin states for imidazolate and imidazolide derivatives, respectively.

X-ray absorption spectroscopy. X-ray absorption spectroscopy (XAS) studies have been conducted on [Co(TPP)(2-MeHIm)] and [Co(TPP)(2-Mel−)]− to give more insights into the electronic structures. The pre-edge features of Co K-edge X-ray absorption near edge structure (XANES) of Co(II) porphyrinates. The changes appear unexpected because the imidazolate has been accepted as a strong ligand, which would induce LS species, e.g., in the alkaline transition5–7. Thus, we have conducted DFT calculations to investigate the products’ electronic configurations (Supplementary Figs. 22–25 and Supplementary Data 1). M06/6-31G(d)/TZVP level of theory has predicted 2.6 and 5.7 kcal/mol more stable LS [Co(TPP)(2-MeHIm)] and HS [Co(TPP)(2-Mel−)]−, respectively, in agreement with the experimental results. Qualitative diagrams showing the d-orbital energy ordering are illustrated in Fig. 5. The MOs of low and high-spin [Co(TPP)(2-Mel−)]− are compared in Fig. 5b. The dramatically lowered dxy, dxz, dyz, dz2 and dx2−y2 orbitals of HS state, which is consistent with the short axial bond distance and large metal displacement are obvious (Table 1). Close examinations also found the anti-bonding interaction between the imidazolate π orbital and the β orbital of dxy in LS state, which is 0.364 eV higher in energy than the α orbital of dx2−y2 in HS state (gray arrow). These electronic features are also consistent with the experimentally observed HS state of [Co(TPP)(2-MeHIm)] and the electronic structures of LS [Co(TPP)(2-MeHIm)] are given in Fig. 5a. The higher dxz and dxy energy differences between dxz and dxy are seen, which is consistent with the small metal displacements of LS cobalt(II) (0.17 and 0.26 Å). Moreover, the near-degenerate dxz and dxy

As has been seen, the removal of N−H proton of 2-MeHIm has led to dramatic changes in both geometric and electronic structures of Co(II) porphyrinates. The changes appear unexpected because the imidazolate has been accepted as a strong ligand, which would induce LS species, e.g., in the alkaline transition5–7. Thus, we have conducted DFT calculations to investigate the products’ electronic configurations (Supplementary Figs. 22–25 and Supplementary Data 1). M06/6-31G(d)/TZVP level of theory has predicted 2.6 and 5.7 kcal/mol more stable LS [Co(TPP)(2-MeHIm)] and HS [Co(TPP)(2-Mel−)]−, respectively, in agreement with the experimental results. Qualitative diagrams showing the d-orbital energy ordering are illustrated in Fig. 5. The MOs of low and high-spin [Co(TPP)(2-Mel−)]− are compared in Fig. 5b. The dramatically lowered dxy, dxz, dyz, dz2 and dx2−y2 orbitals of HS state, which is consistent with the short axial bond distance and large metal displacement are obvious (Table 1). Close examinations also found the anti-bonding interaction between the imidazolate π orbital and the β orbital of dxy in LS state, which is 0.364 eV higher in energy than the α orbital of dx2−y2 in HS state (gray arrow). These electronic features are also consistent with the experimentally observed HS state of [Co(TPP)(2-MeHIm)] and the electronic structures of LS [Co(TPP)(2-MeHIm)] are given in Fig. 5a. The higher dxz and dxy energy differences between dxz and dxy are seen, which is consistent with the small metal displacements of LS cobalt(II) (0.17 and 0.26 Å). Moreover, the near-degenerate dxz and dxy

Discussion

As has been seen, the removal of N−H proton of 2-MeHIm has led to dramatic changes in both geometric and electronic structures of Co(II) porphyrinates. The changes appear unexpected because the imidazolate has been accepted as a strong ligand, which would induce LS species, e.g., in the alkaline transition5–7. Thus, we have conducted DFT calculations to investigate the products’ electronic configurations (Supplementary Figs. 22–25 and Supplementary Data 1). M06/6-31G(d)/TZVP level of theory has predicted 2.6 and 5.7 kcal/mol more stable LS [Co(TPP)(2-MeHIm)] and HS [Co(TPP)(2-Mel−)]−, respectively, in agreement with the experimental results. Qualitative diagrams showing the d-orbital energy ordering are illustrated in Fig. 5. The MOs of low and high-spin [Co(TPP)(2-Mel−)]− are compared in Fig. 5b. The dramatically lowered dxy, dxz, dyz, dz2 and dx2−y2 orbitals of HS state, which is consistent with the short axial bond distance and large metal displacement are obvious (Table 1). Close examinations also found the anti-bonding interaction between the imidazolate π orbital and the β orbital of dxy in LS state, which is 0.364 eV higher in energy than the α orbital of dx2−y2 in HS state (gray arrow). These electronic features are also consistent with the experimentally observed HS state of [Co(TPP)(2-MeHIm)] and the electronic structures of LS [Co(TPP)(2-MeHIm)] are given in Fig. 5a. The higher dxz and dxy energy differences between dxz and dxy are seen, which is consistent with the small metal displacements of LS cobalt(II) (0.17 and 0.26 Å). Moreover, the near-degenerate dxz and dxy

![Fig. 2 Experimental and simulated X-band EPR spectra. a [Co(TPP)(2-MeHIm)] and b [Co(TPP)(2-Mel−)]−. The asterisk represents trace amount of [Co(TPP)(2-MeHIm)]− intermediate](image-url)
orbitals, which is in agreement with the axial EPR resonances and longer axial distance, suggest the weaker imidazole ligation.

The spin state transition happened only to cobalt(II) porphyrinates in contrast to invariable high-spin states of 2-methylimidazole(ate) iron(II) analogs, although both pairs of counterparts are mediated by N−H proton of imidazole. Steroelectronic analysis on interplays between imidazole(ate) and metal centers would reveal the differences between the two systems. It is suggested that 3d^6 iron(II), one electron less than 3d^7 Co(II), is in favor of stronger \( \sigma \) donation of imidazole(ate) through \( d_{z^2} \), which would draw the metal more out of the porphyrin plane, lower the \( d_{x^2-y^2} \) orbital and make the HS states accessible. It is important to note that the steric hindrance is not required here because five-coordinate iron(II) porphyrinates with non-hindered imidazole (e.g., 1-MeIm) were also reported to be HS, which suggests the large iron displacement is induced mainly by strong axial bonding. Interestingly, the switchable spin states of Co(II) analogs suggest 3d^7 Co(II), which always has one electron on \( d_{z^2} \), has weaker tendency to the \( \sigma \) donation of axial ligand than 3d^6 iron(II). For the imidazole ligand, the relatively

**Fig. 3** \( \chi_T \) vs. T in an external magnetic field of 1000 Gauss. **a** [Co(TPP)(2-MeHIm)] (black circles), [Co(TPP)(2-MeIm)]\(^-\) (red circles). **b** [Co(TTP)(2-MeHIm)] (black circles), [Co(TTP)(2-MeIm)]\(^-\) (red circles).

**Fig. 4** Comparisons of experimental and theoretical Co K-edge XANES and EXAFS. **a** K-edge XANES of [Co(TPP)(2-MeHIm)] (black line: Experiment, red line: Simulation). **b** K-edge XANES of [Co(TPP)(2-MeIm)]\(^-\) (black line: Experiment, red line: Simulation). **c** EXAFS of [Co(TPP)(2-MeHIm)] (black line: Experiment, red circles: Fitting). **d** [Co(TTP)(2-MeIm)]\(^-\) (black line: Experiment, red circles: Fitting).
weak axial bonding only induced small metal displacements (e.g., $\Delta d$: 0.12–0.17 Å of [Co(Porph)(Im)] vs. 0.32–0.35 Å of [Fe(Porph)(2-MeHIm)] and 0.52–0.56 Å of [Fe(Porph)(2-Melim)])$^{-}$, Table 1), so that the $d_{2-y^2}$ orbital is not drawn lower enough for the access of HS. This is true for both hindered and non-hindered imidazole as seen in Table 1, consistent with the LS states of all known five-coordinate [Co(Porph)(Im)] complexes. In contrast, the 2-methylimidazolate, a stronger ligand, has induced much shorter axial bonds and dramatically displaced Co(II), which drew the $d_{2-y^2}$ lower enough and made the $[(d_{xy})^2(d_y)^3(d_{yz})^1(d_{xz})^1] (4E_g)$ configuration to be accessible.

Strategies to obtain a high-spin cobalt(II) heme complex have been proposed for many years. As early as 1983, Scheidt and Gouterman$^{50}$ predicted this to be achieved in five coordination with the metal out of plane, as this lowers the $d_{2-y^2}$ energy ($\epsilon_4(d_y) \rightarrow b_{1g}(d_{2-y^2})$). Later, DiMaggio and coworkers$^{51}$ reported extremely electron-deficient $\beta$-octaluoro-meso-tetraarylporphyrins F$_{28}$TPP, which reduced porphyrin ligand and stabilized $d_{2-y^2}$ orbital. Nevertheless, a HS product in solid state has never been isolated and characterized.

In summary, comprehensive spectroscopic characterizations on four isolated cobalt(II) heme complexes demonstrate the removal of N–H proton of axial 2-MeHIm has changed the metal centers from LS to HS, thus mimicking spin state transition of heme systems. The single crystal data highly promote stereoelectronic studies on the mechanisms of spin state transition, which reveal different response of iron(II) and cobalt(II) to the axial imidazole(ate) ligands and underline the stronger ligand field of imidazole. The work also provides quantitative values for the metal displacements of hemes (e.g., $\Delta d_{2}$ and $\Delta d_{4} \geq 0.2$ Å, Table 1), which usually accompany with spin state transitions (and/or d-orbital reconstructions) that are physiologically important and can be triggered by charge changes of proximal ligands. To the best of our knowledge, this is the first examples of synthetic metalloporphyrins that can switch spin states through one proton of proximal ligands.

Methods

General procedure. All reactions and manipulations were carried out under argon using a double-manifod vacuum line, Schlenkware, and cannula techniques unless otherwise noted. Tetrahydrofuran, chlorobenzene, and hexanes were dried and degassed by standard techniques. General considerations on the measurements and experiments, as well as some experimental details are described in the Supplementary Information.

X-ray structure determinations. Single crystal experiments were carried out on a BRUKER D8 QUEST system with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). The crystal samples were placed in inert oil, mounted on a glass fiber attached to a brass mounting pin, and transferred to the cold dinitrogen gas (100 K). Crystal data were collected and integrated using a Bruker Apex II system. The structures were solved by direct method (SHELXS-2014) and refined against $\mathcal{F}^2$ using SHELXL-2014$^{52}$.

EPR measurements and simulations. EPR were carried out on a Bruker EMX plus 10/12 CW X-band EPR spectrometer, equipped with High-Q cylindrical cavity and Oxford ESR910 continuous flow liquid helium cryostat. The EPR spectra were simulated with the EasySpin package$^{53}$, which is operated in MATLAB. Typically, ~5 mg of crystal sample was transferred into an EPR tube in a dry-box. After the sample was ground into crystalline powder by a quartz pestle, the tube was sealed for measurements. A solution with a concentration of 2.98 × 10$^{-3}$ mmol/mL is used for measurements.

Magnetometry. Variable-temperature magnetic susceptibility measurements were performed on Quantum Design SQUID-PPMS3 (1–1000 Hz) magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal’s tables) and background of the sample holder.
The X-ray absorption fine structure spectroscopy. Experimental data were recorded at beamline 20 BM of Advanced Photon Source at Argonne National Laboratory, using the Si (111) double crystal monochromator to scan the energy. The spectra were collected in transmission mode and energy calibration were done using Co foil as references. Data analysis was performed at 1W1B and 1W2B, Beijing Synchrotron Radiation Facility.

Electronic structure. The G09 program package, was used to optimize the structures and for frequency analysis. The model complex for [Co(TPP)-(2-MeIm)] and [Co(TPP)-[2-MeHim]] were fully optimized without any constraints by using the Hybrid-GGA functional U-M065 and U-B3LYP6,7.

Data availability. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Center (CCDC), under deposition numbers 176508 and 176509. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)223-336-033; or deposit@ccdc.cam.ac.uk. All the other data that support the findings of this study are available within Supplementary Information and are available from J.L. (jil@usas.ac.cn) upon request.

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Author contributions
J.L. conceived and designed the experiments. Jianping Z. and Q.W. performed the experiments. Q.P., H.X., and Z.W. performed the DFT calculations. H.-L.S. and F.M. performed the SQUID measurements. W.X., Jiyoung Z., and C.-J.S. performed the XAS experiments. Jianping Z., Q.P., W.X., H.X., H.-L.S., E.M., Jiyoung Z., C.-J.S., Jianzhang Z., and J.L. analyzed the data. Jianping Z., Q.P., and J.L. wrote the manuscript. Jianping Z. and Q.P. contributed equally.

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