



Journal of Coordination Chemistry



ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

# Metal complexes of a phenol-tailed porphyrin with different hydrogen bonds

Caifen Ou, Huan Liu, Ben Ma & Chuanjiang Hu

To cite this article: Caifen Ou, Huan Liu, Ben Ma & Chuanjiang Hu (2016) Metal complexes of a phenol-tailed porphyrin with different hydrogen bonds, Journal of Coordination Chemistry, 69:15, 2308-2317, DOI: 10.1080/00958972.2016.1206656

To link to this article: <u>http://dx.doi.org/10.1080/00958972.2016.1206656</u>

0	_	1
	Т	
	Т	Г
	Т	

Accepted author version posted online: 27 Jun 2016. Published online: 12 Jul 2016.



🖉 Submit your article to this journal 🗹

Article views: 42



View related articles 🗹



View Crossmark data 🗹

Full Terms & Conditions of access and use can be found at http://www.tandfonline.com/action/journalInformation?journalCode=gcoo20



# Metal complexes of a phenol-tailed porphyrin with different hydrogen bonds

### Caifen Ou<sup>†</sup>, Huan Liu<sup>†</sup>, Ben Ma and Chuanjiang Hu

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, PR China

#### ABSTRACT

Hydrogen bonds are very common and important interactions in biological systems, they are used to control the microenvironment around metal centers. It is a challenge to develop appropriate models for studying hydrogen bonds. We have synthesized two metal complexes of the phenol-tailed porphyrin, [Zn(HL)] and [Fe(HL)(C<sub>6</sub>H<sub>4</sub>(OH)(O))]. X-ray crystallography reveals that the porphyrin functions as a dianion HL<sup>2-</sup> and the phenol OH is involved in hydrogen bonds in both structures. In [Zn(HL)], an intramolecular hydrogen bond is formed between the carbonyl oxygen and OH. In [Fe(HL) (C<sub>6</sub>H<sub>4</sub>(OH)(O))], the unligated O(5) of the ligand is involved in two hydrogen bonds, as a hydrogen bond donor and a hydrogen bond acceptor. The overall electronic effect on the ligand could be very small, with negligible impact on the structure and the spin state of iron(III). The structural differences caused by the hydrogen bonds are also discussed.



#### **ARTICLE HISTORY**

Received 17 January 2016 Accepted 16 May 2016

#### **KEYWORDS**

Porphyrin; hydrogen bond; phenol; crystal structure

#### Introduction

Hydrogen bonds are common in biological systems. They are generally considered as noncovalent interactions, used to control the microenvironment around metal centers. Porphyrin is a versatile functional group, playing important roles in many biological systems. Hydrogen bonds are widespread in many heme proteins, such as myoglobin, horseradish peroxidase, cytochrome P450, etc. For example, hydrogen bonding interactions in myoglobin involve the distal histidine, which can stabilize the iron

**CONTACT** Chuanjiang Hu Scjhu@suda.edu.cn <sup>†</sup>These authors contributed equally.

bound oxygen [1]. In horseradish peroxidase [2], there is a strong hydrogen bond between the proximal histidine (His170) and a highly conserved aspartate group Asp247. It is believed that this hydrogen bond increases the basicity of the His170 proximal ligand, thus stabilizing high oxidation state intermediates [2(b)]. Hydrogen bonds have also been investigated in many model systems. For example, Walker *et al.* reported that forming a hydrogen bond to the NH of coordinated imidazole led to a substantial increase in the magnitude of the corresponding binding constant [3]. Hu *et al.* studied the hydrogen bonding effect on the spin state of five-coordinate iron(II) porphyrinates [4]. Their studies suggest strong hydrogen bonds to the coordinated ligand could cause different spin states of iron(II). Recently, Rath and coworkers studied the impact of hydrogen bonding interactions on the electronic structure of a five-coordinate iron(III) octaethyltetraarylporphyrin chloride. They found the spin state of iron(III) switch reversibly between high ( $S = \frac{5}{2}$ ) and intermediate spin ( $S = \frac{3}{2}$ ) with hydrogen bonds to the axial ligand [5]. Though there are many model systems developed, it is still a challenge to develop models for studying hydrogen bonds of ligands.

We have been working on porphyrin-related hydrogen bonds [4, 6], recently synthesizing  $H_3L$  (shown in scheme 1) with a hanging phenol group [7]. The free base porphyrin  $H_3L$  is a triprotonic acid, which contains two inner NH and one phenol OH. When the porphyrin is metallated, there are two cases: (1) all three hydrogens are deprotonated to form  $L^{3-}$ ; (2) two inner NH are deprotonated but the phenol OH is not, forming  $HL^{2-}$ . For the second case, the phenol OH could provide a hydrogen bonding site. If the corresponding hydrogen bonds are associated with the ligand, we are interested in their effect on the structure and spin state of the metal. Herein, we synthesized two new complexes as shown in scheme 1, one is a zinc(II) complex, [Zn(HL)] and the other is an iron(III) complex with catechol as axial ligand, [Fe(HL)( $C_6H_4$ (OH)(O))]. Both have also been characterized by X-ray crystallography and <sup>1</sup>H NMR. Their structures reveal that in both complexes, the porphyrin is  $HL^{2-}$  and the phenol OH is involved in different hydrogen bonds.

#### 2. Experimental

#### 2.1. Materials and general methods

H<sub>3</sub>L and [FeL] were prepared according to our previous method [7]. Other chemicals were used without purification. <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer in the



Scheme 1. Synthetic route to [Zn(HL)] and [Fe(HL)(C<sub>6</sub>H<sub>4</sub>(OH)(O))].

2310 🔄 C. OU ET AL.

solvents indicated with tetramethylsilane as the internal standard. UV–vis spectra were measured on a Shimadzu UV-3150 spectrometer. Mass spectra were taken with an Agilent 6220 Accurate-Mass TOF LC/MS. Fluorescence emission spectrum of [Zn(HL)] was measured in toluene on a FLS920 spectrometer. EPR spectrum of polycrystalline sample of [Fe(HL)(C<sub>6</sub>H<sub>4</sub>(OH)(O))] was obtained on a EMX 10/12 EPR spectrometer operating at X band at 25 °C at Nanjing University.

# 2.2. Synthesis of [Zn(HL)]

To a solution of H<sub>3</sub>L (0.30 g, 0.37 mmol) in chloroform (100 mL), a solution of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.16 g, 0.74 mmol) in methanol (10 mL) was added. The mixture was refluxed for 3 h, then cooled. The mixture was washed with water (3 × 300 mL), the organic layer was separated and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, then purified with silica gel chromatography (CH<sub>2</sub>Cl<sub>2</sub>: petroleum = 3:1 as eluent) to give [Zn(HL)] (0.29 g, yield 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.92 (d, 2H), 8.87 (d, 1H), 8.81 (d, 2H), 8.67 (d, 2H), 8.63 (d, 2H), 8.38 (d, 1H), 8.32 (m, 3H), 8.09 (t, 1H), 8.03 (m,4H), 7.79 (m, 3H), 7.70 (m, 4H), 7.65 (m, 2H), 7.49 (t, 1H), 7.18 (d, 1H), 6.07 (t, 1H), 5.83 (t, 1H), 5.76 (d, 1H), 2.94 (d, 1H), 2.05 (s, 1H). LC-ESI-MS: *m/z* Calcd for C<sub>55</sub>H<sub>34</sub>N<sub>4</sub>O<sub>3</sub>Zn 862.19; found 863.20 [M + H]<sup>+</sup>. UV–vis, nm ( $\epsilon$  × 10<sup>-3</sup> M<sup>-1</sup> cm<sup>-1</sup>): 428 (538), 557 (20), 598 (5), in CH<sub>2</sub>Cl<sub>2</sub>. Anal. Calcd for C<sub>55</sub>H<sub>34</sub>N<sub>4</sub>O<sub>3</sub>Zn 1.3CH<sub>2</sub>Cl<sub>2</sub>: C, 69.38; H, 3.78; N, 5.75. Found: C, 69.13; H, 3.72; N, 5.59. X-ray quality crystals were obtained by liquid diffusion of methanol into the toluene solution in 8 mm diameter glass tubes.

# 2.3. Synthesis of [Fe(HL)(C<sub>6</sub>H<sub>4</sub>(OH)(O))]

[FeL] (40 mg, 0.047 mmol) and catechol (36 mg, 0.33 mmol) were mixed in toluene (4 mL) and stirred for 30 min at room temperature. X-ray quality crystals were obtained by liquid diffusion of hexane into the toluene solution in 8 mm diameter glass tubes. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  92.78, 89.92, 87.22, 81.16, 79.76, 12.21, 11.98, 11.50, 11.28, 10.78, 10.56, 8.92, 8.56, 8.07, 7.16, 6.75, 6.57, 6.04, 4.47, 103.90, 105.21. UV–vis, nm ( $\epsilon \times 10^{-3} \,\mathrm{M^{-1}\,cm^{-1}}$ ): 327 (34), 421 (110), 501 (11), 564 (5), 647 (4) in CH<sub>2</sub>Cl<sub>2</sub>. Anal. Calcd C<sub>61</sub>H<sub>39</sub>FeN<sub>4</sub>O<sub>5</sub>·3.5H<sub>2</sub>O: Calcd C, 71.35; H, 4.52; N, 5.46%. Found: C, 71.32; H, 4.46; N, 5.34%.

# 2.4. X-ray crystallography

X-ray data collections were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo K $\alpha$  ( $\lambda$  = 0.071073 nm) radiation at 223(2) K. Structures of [Zn(HL)] and [Fe(HL) (C<sub>6</sub>H<sub>4</sub>(OH)(O))] were solved by direct methods and refined on  $F^2$  using full matrix least-squares with SHELXTL version 97 [8]. All non-hydrogen atoms were refined anisotropically. All hydrogens were idealized with the standard SHELXL-97 idealization methods. Complete crystallographic details, atomic coordinates, anisotropic thermal parameters, and hydrogen coordinates are given in the cif file. For [Fe(HL)(C<sub>6</sub>H<sub>4</sub>(OH)(O))], the structure has badly disordered solvate molecules. SQUEEZE [9] was used to model the disordered solvate molecules. The residue electron count in the interporphyrin voids is 73 electrons per unit-cell (corresponding roughly to 0.8 molcules of toluene). A summary of the key crystallographic information of the complex is given in table 1.

# 3. Results and discussion

[Zn(HL)] was obtained by reaction of  $H_3L$  with Zn(OAc)<sub>2</sub>. The new iron complex [Fe(HL)(C<sub>6</sub>H<sub>4</sub>(OH)(O))] was prepared by reaction of [FeL] with excess catechol.

# 3.1. Molecular structure

Both complexes have been characterized by X-ray crystallography. Their ORTEP diagrams are presented in figures 1 and 2. The crystal structure of [Zn(HL)] was solved in P2<sub>1</sub>/c space group. One asymmetric

**Table 1.** Crystallographic data for  $[Zn(HL)] \cdot CH_2CI_2$  and  $[Fe(HL)(C_6H_4(OH)(O))]$ .

Compound	[Zn(HL)]·CH <sub>2</sub> Cl <sub>2</sub>	[Fe(HL)(C <sub>6</sub> H <sub>4</sub> (OH)(O))]
Empirical formula	C <sub>56</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>3</sub> Zn	C <sub>61</sub> H <sub>39</sub> FeN <sub>4</sub> O <sub>5</sub>
Formula weight (g mol <sup>-1</sup> )	949.16	963.81
Temperature (K)	223(2)	223(2)
Wavelength	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2,/c	<i>P</i> -1
Unit cell dimensions	a – 20.295(4) Å	a = 11.197(3) Å
	<i>b</i> = 11.429(2) Å	b = 13.209(3) Å
	c = 23.118(10) Å	c = 20.223(5) Å
	$\alpha = 90^{\circ}$	$\alpha = 107.126(5)^{\circ}$
	$\beta = 122.42(2)^{\circ}$	$\beta = 95.400(5)^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 91.023(3)^{\circ}$
Volume (ų)	4526(2)	2842.5(12)
Ζ	4	2
ho (g cm <sup>-3</sup> )	1.393	1.126
F (0 0 0)	1952	998
Crystal size (mm <sup>3</sup> )	$0.50 \times 0.40 \times 0.30$	$0.60 \times 0.50 \times 0.40$
Theta range for data collection	3.02°-25.00°	3.02°-25.00°
Limiting indices	$-22 \le h \le 24$	$-13 \le h \le 13$
	$-13 \le k \le 12$	$-15 \le k \le 15$
	–27 ≤ <i>l</i> ≤ 19	$-24 \le l \le 24$
Reflections collected/unique	21,653/7946	21,059/9876
Completeness to $\theta = 25.00^{\circ}$	99.6%	98.5%
Data/restraints/parameters	7946/22/538	9876/0/630
GOF	1.129	1.028
$R_1, wR_2[>2\sigma(I)]$	$R_1 = 0.0791$	$R_1 = 0.0662$
	$wR_2 = 0.2038$	$\dot{WR}_{2} = 0.1970$
$R_1, wR_2$ (all data)	$R_1 = 0.1120$	$R_1 = 0.0801$
	$wR_2 = 0.2341$	$wR_2 = 0.2122$
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.923 and -0.805	0.996 and -0.362

 $\overline{a^{a}w = 1/[\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP]}$  where  $P = (F_{o}^{2} + 2F_{c}^{2})$ .



Figure 1. ORTEP view for [Zn(HL)] at 50% probability thermal ellipsoids. The hydrogens except H(3) and two phenyl groups have been omitted for clarity.

unit contains one porphyrin and one methylene chloride molecule. There are one naphthyl and three phenyl groups at the *meso*-positions of the porphyrin. The phenol group is covalently bonded to the porphyrin at the eight-position of naphthyl group. Zinc(II) is five-coordinate with four pyrrole nitrogens and one phenol oxygen. Since there is no ion in the crystal structure, the porphyrin complex is neutral.



**Figure 2.** ORTEP view for [Fe(HL)( $C_{e}H_{4}(OH)(O)$ )] at 50% probability thermal ellipsoids. The hydrogens (except H(3O) and H(5O)) and two phenyl groups have been omitted for clarity.

Corresponding to zinc(II), the porphyrin should be the dianion, HL<sup>2-</sup>, in order to maintain neutrality. Obviously, the two inner NH groups are deprotonated, then four pyrrole nitrogens are coordinated to zinc. The axial ligand is from the phenol tail in which oxygen is protonated.

Selected bond distances are listed in table 2. The Zn–O distance is 2.368(4) Å and the average Zn– Np distance is 2.041(16) Å; these values are similar to that in the reported 4-chlorophenol ligated zinc porphyrinate [10]. Zinc is out of the porphyrin plane with a displacement of 0.17 Å, which is also typical for five-coordinate zinc porphyrinates.

The OH is not only coordinated to zinc, but also functions as a hydrogen donor to form an intramolecular hydrogen bond with the carbonyl O(1). The corresponding O···O distance is 2.660 Å and the O–H···O angle is 152.3°, while the corresponding O···O distance is much longer in H<sub>3</sub>L (4.575 Å) or [FeL] (2.936 Å) when there is no hydrogen bond between these two oxygens.

For  $[Fe(HL)(C_6H_4(OH)(O))]$ , the crystal structure was solved in the *P*-1 space group. Iron is five-coordinate with four pyrrole nitrogens and one oxygen. Different from [FeL], the axial ligand is from the catechol, not the covalent bonded phenol.

The coordinated catechol is on the same side as the phenol tail with the crystal structure revealing that hydrogen bonds contribute to this geometry. The catechol is bonded to iron by the deprotonated O(4) and behaves as a -1 charged ion. Corresponding to iron(III), the porphyrin moiety should be  $HL^{2-}$ . So there is one OH group for either the catechol or the tailed phenol. Both OH groups are involved in hydrogen bonds. As shown in figure 3, the uncoordinated catechol O(5) is involved in two types of hydrogen bonds in the crystal structure: (1) one is an intramolecular hydrogen bond formed with carbonyl O(1); (2) another is an intermolecular hydrogen bond formed with the tailed phenol OH from

**Table 2.** Selected bond lengths (Å) and angles (°) for [Zn(HL)] and  $[Fe(HL)(C_{e}H_{A}(OH)(O))]$ .

[Zn(HL)]				
Zn(1)–N(1)	2.040(4)	Zn(1)–N(2)	2.048(4)	
Zn(1)–N(3)	2.019(4)	Zn(1)–N(4)	2.057(4)	
Zn(1)–O(1)	2.368(4)	C(1)–O(3)	1.208(6)	
C(1)–O(2)	1.333(6)			
[Fe(HL)(C <sub>6</sub> H <sub>4</sub> (OH)(O))]				
Fe(1)–N(1)	2.073(2)	Fe(1)–N(2)	2.080(3)	
Fe(1)-N(3)	2.078(2)	Fe(1)–N(4)	2.077(2)	
Fe(1)–O(4)	1.835(2)	C(1)–O(1)	1.185(5)	
C(1)–O(2)	1.344(5)			



**Figure 3.** Packing diagram showing hydrogen bonds in [Fe(HL)( $C_6H_4(OH)(O)$ )]. Symmetry transformations used to generate equivalent atoms: A -x + 2, -y + 2, -z + 2.

the neighboring porphyrin unit. The corresponding distances and angles are listed in table 3. These hydrogen bonds cause porphyrin molecules to form dimers in the solid state. Different from Rath's case [5], the coordinated O(4) is not involved in hydrogen bonds. So the hydrogen bond is far from the metal center.

For this new iron(III) complex, selected bond distances are listed in table 2. The average Fe–Np distance (2.077(3) Å), Fe–O distance (1.835(2) Å) and the displacement of iron out of the porphyrin plane (0.48 Å) are similar to values for [FeL]. The Fe–Np distance and the displacement of iron are much larger than those in five-coordinate low-spin iron(III) porphyrinates but typical for five-coordinate high-spin iron(III) porphyrinates [11]. The above structural feature suggests [Fe(HL)(C<sub>6</sub>H<sub>4</sub>(OH)(O))] is a high-spin iron(III) species as was [FeL]. Such spin state is also confirmed by NMR spectroscopy.

O(5) of the ligand is involved in two hydrogen bonds, a hydrogen bond donor in one and a hydrogen acceptor in the other. So the net electronic effect on the catechol could be very small, with negligible impact on the structure and the spin state of iron(III).

We are also interested in the structural differences caused by coordination bonds and hydrogen bonds. For both [FeL] and [Zn(HL)], the ligand is from the covalent bonded phenol group, causing the overall structure to be strained, such as the tilted M–O bond and the displacement of the *meso* carbon (C(m1)) out of the porphyrin plane. The tilted angle is the angle between M–O bond and the normal direction of porphyrin. For [Fe(HL)(C<sub>6</sub>H<sub>4</sub>(OH)(O))], the Fe–O bond is almost perpendicular to the heme plane, with a very small angle between Fe–O and the normal direction of porphyrin (2.5°). But the corresponding angle is 7.5° for [FeL] and 12.2° for [Zn(HL)]. Such tilt is caused by the constraint due to covalent bonding of phenol to the porphyrin. Another result of the constraint is the positive displacement of *meso*-carbon (C(m1)) out of the porphyrin plane. The displacement is 0.09 Å for [Zn(HL)] and 0.23 Å

**Table 3.** Bond lengths (Å) and angles (°) for hydrogen bonds in  $[Fe(HL)(C_{6}H_{4}(OH)(O))]$ .

D–H…A	d(D–H)	d(H···A)	d(D…A)	<(DHA)
O(5)-H(5O)···O(1)	0.83	2.18	2.855(4)	138.2
O(3)–H(3O)···O(5A)	0.83	2.08	2.717(4)	133.6

Note: Symmetry transformations used to generate equivalent atoms: A -x + 2, -y + 2, -z + 2.

#### 2314 😧 C. OU ET AL.

		Four-nitrogen plane	Covalently bonded phenyl plane
COO plane	H,L	24.6	44.1
	[FeL]	23.7	55.2
	[Zn(HL)]	19.4	37.5
	[Fe(HL)(C <sub>6</sub> H <sub>4</sub> (OH)(O))]	31.0	76.6

Table 4. Dihedral angles (°) between the COO plane and four nitrogen porphyrin plane (or covalently bonded phenyl plane).

for [Fe(HL)], towards the carboxylate group. For [Fe(HL)] without such constraint, the corresponding displacement is -0.10 Å, away from the carboxylate group.

For these compounds, hydrogen bonds cause different dihedral angles between the COO plane and porphyrin plane (or the covalently bonded phenyl plane) as shown in table 4. For  $H_3L$  and [FeL], the corresponding dihedral angles between the COO group and four-nitrogen porphyrin plane are 24.6° and 23.7°, respectively. These angles are close to that in ENTPP (23.2°) [12]. But for [Zn(HL)], due to the intramolecular hydrogen bond between O(1) and coordinated O(3), the corresponding angle decreases to 19.4°. Such hydrogen bond also causes the dihedral angle between the COO plane and the covalently bonded phenyl plane to be much smaller in [Zn(HL)]. For [Fe(HL)], O(1) is hydrogen bonded to O(5), the uncoordinated atom, which causes the corresponding dihedral angle to be much larger (31.0°), not smaller.

Notably, the orientation of the tailed phenol plane in  $[Fe(HL)(C_6H_4(OH)(O))]$  is also different from others. For [Zn(HL)], the dihedral angle between the porphyrin plane and the phenol plane is 29.3°, similar to  $H_3L$  and [FeL]. But for  $[Fe(HL)(C_6H_4(OH)(O))]$ , since the coordinated catechol is on the same side as the tailed phenol, the covalent bonded phenol forms a dihedral angle of 88.1° with the porphyrin plane, much greater than in the other cases. Such orientation also causes the tailed phenyl to form a dihedral angle of 18.95° with the coordinated catechol. The corresponding centroid to centroid distance is 4.43 Å, which indicates there is a weak offset  $\pi$ - $\pi$  interaction between the coordinated catechol and the tailed phenol [13].

#### 3.2. <sup>1</sup>H NMR studies

The <sup>1</sup>H NMR of [Zn(HL)] is shown in figure 4(b). Since the phenol is located above the porphyrin plane, the ring current effect will generally cause their signals to shift upfield [14]. For the case of  $H_3L$  [7], these protons are located at 2.54, 3.41 and 5.43 ppm as shown in figure 4(a). Compared with them, the signals at 6.07, 5.83, 5.76 and 2.94 ppm with 1:1:1:1 ratio for [Zn(HL)] are assigned to the CH proton of the substituted phenol. For [Zn(HL)], the signal of OH is at 2.05 ppm. But for  $H_3L$  there are no observable signals for OH and NH protons. One possible reason is that fast exchange occurs between them. Similar case has also been reported by Liang *et al.* [15].

<sup>1</sup>H NMR spectrum of [Fe(HL)( $C_6H_4(OH)(O)$ )] is shown in figure 4(d). In this case, since iron(III) is paramagnetic, the signals are broader and expanded. The spectrum also shows resonances in the far-upfield and far-downfield region. Similar to those of [FeL] [7] (figure 4(c)), the signals at 79.76 and 87.22 ppm are assigned to the pyrrole protons according to their positions and intensities, which are typical for five-coordinate high-spin (tetraphenylporphyrinato)iron(III) complex [16]. Besides those pyrrole proton signals, there are also resonances at 89.92 and -105.21 ppm. Compared with those in phenolate (porphyrinate)iron(III) complexes [16], the far-downfield resonance at 89.92 ppm is assigned to *meta*-protons (H<sub>b</sub> and H<sub>d</sub>) of the coordinated phenol group, the far-upfield resonances at -105.21 ppm are assigned to *ortho*- and *para*-protons (H<sub>a</sub> and H<sub>c</sub>). So the <sup>1</sup>H NMR spectrum suggests that [Fe(HL)( $C_6H_4(OH)(O)$ )] has the same spin state as [FeL]. For the new iron complex, there are also extra peaks in the far-upfield and far-downfield region, which could be caused by the uncoordinated phenol ring.

#### 3.3. Fluorescence spectrum

The fluorescence spectrum of [Zn(HL)] was measured in toluene. As shown in figure 5, there are two absorption peaks at 602 and 649 nm in the emission spectrum. Compared with those for



Figure 4. <sup>1</sup>H NMR spectra of (a) H<sub>3</sub>L<sub>7</sub> (b) [Zn(HL)], (c) [FeL] and (d) [Fe(HL)(C<sub>6</sub>H<sub>4</sub>(OH)(O))] in CDCl<sub>3</sub>. \*, signal from impurity of grease.



Figure 5. Fluorescence emission spectrum of [Zn(HL)] in toluene. Concentration:  $2.0 \times 10^{-7}$  mol L<sup>-1</sup>. Excitation wavelength: 425 nm.



**Figure 6.** X-band EPR spectrum of polycrystalline sample of [Fe(HL)( $C_6H_4(OH)(O)$ )] at 25 °C.

tetraphenylporphyrin [17], these peaks are blue-shifted. These positions are similar to those in some other zinc porphyrinates containing phenols as axial ligands [18], which suggest that [Zn(HL)] is coordinated by phenol in solution. It is consistent with the <sup>1</sup>H NMR results.

#### 3.4. EPR study

The spin state of the Fe(III) in [Fe(HL)( $C_6H_4(OH)(O)$ )] is further confirmed by EPR spectrum. The spectrum was recorded at room temperature. As shown in figure 6, though the signal-to-noise ratio was not very good, the spectrum clearly showed the feature at g = 5.2, which is a typical value for high-spin Fe(III) heme, similar to those for the reported Fe(III) heme [19]. The result is consistent with its structure and <sup>1</sup>H NMR results.

# 4. Conclusion

We have synthesized and characterized two new complexes of the phenol-tailed porphyrin, [Zn(HL)] and [Fe(HL)( $C_6H_4(OH)(O)$ )]. X-ray crystal structures reveal the porphyrins function as dianions and the phenol OH is hydrogen bonded in both complexes. Different hydrogen bonds cause different orientations of the tailed phenol group. For [Fe(HL)( $C_6H_4(OH)(O)$ )], the unligated O(5) of the ligand plays double roles in two hydrogen bonds, one as a hydrogen bond donor and another as a hydrogen bond acceptor. The overall contribution on the ligand is small, causing negligible impact on the structure and the spin state of iron(III). Our studies confirm the tailed phenol forms hydrogen bonds with the axial ligand. Further studies on other ligands are ongoing.

#### **Supplementary material**

CCDC 1426124 and 1426126 contain the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or by application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk.

#### **Disclosure statement**

No potential conflict of interest was reported by the authors.

# Funding

This work was supported by the Natural Science Foundation of China [grant number 21271133]; State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials; the Priority Academic Program Development of Jiangsu Higher Education Institutions.

#### References

- (a) K.D. Egeberg, B.A. Springer, S.A. Martinis, S.G. Sligar, D. Morikis, P.M. Champion. *Biochemistry*, **29**, 9783 (1990); (b)
   S. Adachi, S. Nagano, K. Ishimori, Y. Watanabe, I. Morishima, T. Egawa, T. Kitagawa, R. Makino. *Biochemistry*, **32**, 241 (1993); (c) B.A. Springer, S.G. Sligar, J.S. Olson, G.N. Phillips Jr. *Chem. Rev.*, **94**, 699 (1994); (d) G.D. Depillis, S.M. Decatur, D. Barrick, S.G. Boxer. *J. Am. Chem. Soc.*, **116**, 6981 (1994).
- [2] (a) M. Gajhede, D.J. Schuller, A. Henriksen, A.T. Smith, T.L. Poulos. *Nat. Struct. Biol.*, 4, 1032 (1997); (b) G.I. Berglund, G.H. Carlsson, A.T. Smith, H. Szöke, A. Henriksen, J. Hajdu. *Nature*, 417, 463 (2002).
- [3] F.A. Walker, M.-W. Lo, M.T. Ree. J. Am. Chem. Soc., 98, 5552 (1976).
- [4] (a) C. Hu, B.C. Noll, P.M. Piccoli, A.J. Schultz, C.E. Schulz, W.R. Scheidt. J. Am. Chem. Soc., 130, 3127 (2008); (b) C. Hu, C.D. Sulok, F. Paulat, N. Lehnert, A.I. Twigg, M.P. Hendrich, C.E. Schulz, W.R. Scheidt. J. Am. Chem. Soc., 132, 3737 (2010).
- [5] D. Sahoo, M.G. Quesne, S.P. de Visser, S.P. Rath. Angew. Chem. Int. Ed., 54, 4796 (2015).
- [6] (a) W. Huang, J. Jiang, Z. Feng, X. Kai, C. Hu, H. Yu, W. Yang. J. Coord. Chem., 64, 2101 (2011); (b) J. Jiang, Z. Feng, B. Liu, C. Hu, Y. Wang. Dalton Trans., 42, 7651 (2013); (c) J. Jiang, X. Fang, B. Liu, C. Hu. Inorg. Chem., 53, 3298 (2014).
- [7] B. Ma, J. Jiang, C. Hu. Z. Anorg. Allg. Chem., 639, 676 (2013).
- [8] G.M. Sheldrick. SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany (1997).
- [9] A.L. Spek. J. Appl. Crystallogr., 36, 7 (2003).
- [10] M.P. Byrn, C.J. Curtis, Y. Hsiou, S.I. Khan, P.A. Sawin, S.K. Tendick, A. Terzis, C.E. Strouse. J. Am. Chem. Soc., 115, 9480 (1993).
- [11] (a) W.R. Scheidt, M.G. Finnegan. Acta Crystallogr., Sect. C, 45, 1214 (1989); (b) T. Ikeue, Y. Ohgo, A. Uchida, M. Nakamura, H. Fujii, M. Yokoyama. Inorg. Chem., 38, 1276 (1999); (c) R.A. Ghiladi, R.M. Kretzer, I. Guzei, A.L. Rheingold, Y.M. Neuhold, K.R. Hatwell, A.D. Zuberbuhler, K.D. Karlin. Inorg. Chem., 40, 5754 (2001); (d) B. Song, K. Park, B. Yu. J. Kor. Chem. Soc., 41, 495 (1997); (e) M.O. Senge. Acta Crystallogr., Sect. E, 61, m399 (2005).
- [12] J. Yang, J. Jiang, W. Fang, X. Kai, C. Hu, Y. Yang. J. Porph. Phthal., 15, 197 (2011).
- [13] M.D. Curtis, J. Cao, J.W. Kampf. J. Am. Chem. Soc., 126, 4318 (2004).
- [14] C.J. Medforth. In *The Porphyrin Handbook*, K. Kadish, K. Smith, R. Guilard (Eds.), Vol. 5, Chap. 35, pp. 1–80, Academic Press, New York, NY (2000).
- [15] Y. Liang, C.K. Chang, S.-M. Peng. J. Mol. Recognit., 9, 149 (1996).
- [16] (a) H.M. Goff, E.T. Shimomura, Y.J. Lee, W.R. Scheidt. *Inorg. Chem.*, 23, 315 (1984); (b) E.W. Ainscough, A.W. Addison, D. Dolphin, B.R. James. *J. Am. Chem. Soc.*, 100, 7585 (1978); (c) H. Sugimoto, N. Ueda, M. Mori. *Bull. Chem. Soc. Jpn.*, 55, 3468 (1982); (d) H. Nasri, J. Fischer, R. Weiss, E. Bill, A. Trautwein. *J. Am. Chem. Soc.*, 109, 2549 (1987); (d) A.M. Helms, W.D. Jones, G.L. Mclendon. *J. Coord. Chem.*, 23, 351 (1991); (e) N. Ueyama, N. Nishikawa, Y. Yamada, T. Okamura, A. Nakamura. *Inorg. Chim. Acta*, 283, 91 (1998); (f) D. Kanamori, Y. Yamada, A. Onoda, T. Okamura, S. Adachi, H. Yamamoto, N. Ueyama. *Inorg. Chim. Acta*, 358, 331 (2005); (g) A. Chaudhary, R. Patra, S.P. Rath. *Eur. J. Inorg. Chem.*, 33, 5211 (2010); (h) G. Peychal-Heiling, G.S. Wilson. *Anal. Chem.*, 43, 550 (1971).
- [17] G. Peychal-Heiling, G.S. Wilson. Anal. Chem., 43, 550 (1971).
- [18] G.D. Bajju, S. Kundan, M. Bhagat, D. Gupta, A. Kapahi, G. Devi. *Bioinorg. Chem. Appl.*, 2014, 782762 (2014). doi:http:// dx.doi.org/10.1155/2014/782762.
- [19] (a) M.R. Cheesman, V.S. Oganesyan, N.J. Watmough, C.S. Butler, A.J. Thomson. J. Am. Chem. Soc., 126, 4157 (2004);
  (b) E.L. Bominaar, X.-Q. Ding, A. Gismelseed, E. Bill, H. Winkler, A.X. Trautwein, H. Nasri, J. Fischer, R. Weiss. Inorg. Chem., 31, 1845 (1992).