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# Synthesis and characterization of tetraphenylporphyrin iron(III) complexes with substituted phenylcyanamide ligands

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### Abstract

Several five coordinate complexes of [(TPP)Fe<sup>III</sup>(L)] in which TPP is the dianion of tetraphenylporphyrin and L is the monoanion of phenylcyanamide (pcyd) (1), 2,5-dichlorophenylcyanamide (2,5-Cl<sub>2</sub>pcyd) (2), 2,6-dichlorophenylcyanamide (2,6-Cl<sub>2</sub>pcyd) (3), and 2,3,4,6-tetrachlorophenylcyanamide (2,3,4,6-Cl<sub>4</sub>pcyd) (4) have been prepared by the reaction of [(TPP)Fe<sup>III</sup>Cl] with appropriate thallium salt of phenylcyanamide. Each of the complexes has been characterized by IR, UV–Vis and <sup>1</sup>H NMR spectroscopic data. Dark redbrown needles of [(TPP)Fe<sup>III</sup>(2,6-Cl<sub>2</sub>pcyd)] (C<sub>51</sub>H<sub>31</sub>Cl<sub>2</sub>FeN<sub>6</sub> · CHCl<sub>3</sub>) crystallize in the triclinic system. The crystal structure of Fe(III) compound shows a slight distortion from square pyramidal coordination with the 2,6-dichlorophenylcyanamide ligand. In non-coordinating solvents, such as benzene or chloroform, these complexes exhibit <sup>1</sup>H NMR spectra that are characteristic of high-spin (S = 5/2) species. The X-ray crystal structure parameters are also consistent with high-spin iron(III) complexes. The iron(III) phenylcyanamide complexes are not reactive toward molecular oxygen; however, these complexes react with HCl and produce TPPFe<sup>III</sup>Cl. © 2006 Elsevier B.V. All rights reserved.

Keywords: Iron(III)phenylcyanamide; Tetraphenylporphyrin; X-ray; Paramagnetic <sup>1</sup>H NMR

# 1. Introduction

Material engineering adopted to generate new electronic, magnetic and photonic devices is an active field [1–6]. To obtain high conductivity as well as strong effective magnetic coupling, expansion of the  $\pi$ -electronic molecular structure is one of the most important and promising approaches [7– 9]. For example, [TPPMn][tetracyanoethylene] · 2PhMe has shown to act as molecule-based magnet [10–13] and (2,5dimethyl-*N*,*N'*-dicyanoquinone diimine)<sub>2</sub>Cu (DCNQI) has shown to exhibit extremely high conductivity of 500000 S cm<sup>-1</sup> at 3.5 K [14]. Crutchley [15] has investigated phenylcyanamide (ligands as analogue of DCNQI's) in both neutral and anionic forms with metals, such as Ag<sup>I</sup>, Cu<sup>I</sup>, Cu<sup>II</sup>, Ni<sup>II</sup>, Pd<sup>II</sup>, Ru<sup>II</sup>, Co<sup>II</sup>, W<sup>III</sup> and Mn<sup>II</sup>.

Moreover, the biological and chemical importance of iron porphyrins make the nature of the metals–ligand linkage in these complexes of considerable interest [16– 19]. Numerous structural and physical characterizations of iron porphyrin with different axial groups have been reported during the last decades. One of the aims of these investigations is to couple large  $\pi$ -conjugated system of porphyrins into a large  $\pi$ -conjugate system in phenylcyanamide via bridged iron metals, which hybrid coordinate with organic  $\pi$ -stack systems, to produce building blocks for molecular materials. So, we here wish to report the first example of preparation and characterization of phenylcyanamide-ligated tetraphenylporphyrin iron(III) (L) complexes (1–4). It has become clear that <sup>1</sup>H NMR

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spectroscopy in paramagnetic iron porphyrin species is a valuable tool [20–25] for studying the electronic and magnetic properties of these compounds. In this report, we have shown, by using NMR spectroscopy, that phenylcyanamides are capable of long electron/spin transfer. These complexes were also characterized by electronic and IR spectroscopy. The structure of 2,6-dichlorophenylcyanamidotetraphenylporphyrin iron(III) was determined by single-crystal X-ray diffraction technique.

### 2. Experimental

### 2.1. Reagents and materials

Caution: Thallium is toxic. Dichloromethane, N,Ndimethylformamide, methanol, p-chloranil, benzene, n-hexane, benzaldehyde, benzophenone, I2, Na and Mg were all of reagent grade and purchased from Merck. Pyrrole was purchased from Fluka. Prior to use, dichloromethane and methanol were distilled over  $P_2O_5$  and  $Mg + I_2$ , respectively. n-Hexane and benzene were distilled over Na and benzophenone, respectively. All reactions involving phenylcyanamide coordination to iron(III)porphyrin were carried out under nitrogen using standard schlenk technique. Tetraphenylporphyrin (TPPH<sub>2</sub>) and TPPFeCl were synthesized according to Lindsey's [26] and Adler's methods [27], respectively. Extra care was necessary to exclude traces of impurity of u-oxo dimer from TPPFe<sup>III</sup>Cl by pre-treatment of TPPFeCl with HCl. Thallium salts of phenylcyanamide ligands (pcyd<sup>-</sup>Tl<sup>+</sup>) were prepared following the previously reported procedure [28].

# 2.2. Physical measurements

### 2.2.1. Spectroscopy

UV–Vis spectra were obtained on a shimadzu 2100 spectrometer in benzene at room temperature. Infrared spectra  $(4000-600 \text{ cm}^{-1})$  of solid samples were taken as 1% dispersion in KBr pellet using a Shimadzu-470 spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Bruker AC-300 MHz spectrometer operating in the quadrature mode. The spectra were collected over a 50-kHz bandwidth with 16 K data points and a 5-µs 45° pulse. For a typical spectrum, between 1000 and 5000 transients were accumulated with a 50-ms delay time. The signal-to-noise ratio was improved by apodization of the free inducting decay. Elemental analysis was performed using a Heraeus CHN–O rapid analyzer.

# 2.2.2. X-ray structural determination of [TPPFe<sup>III</sup>(2,6-Cl<sub>2</sub>pcyd)] · CHCl<sub>3</sub> (3)

Needle-like dark red-brown crystals of [TPPFe<sup>III</sup>(2,6-Cl<sub>2</sub>pcyd)] · CHCl<sub>3</sub> (**3**) were grown by slow evaporation of CHCl<sub>3</sub> solution in a temperature range of 20–25 °C under N<sub>2</sub> atmosphere. Crystal data are shown in Table 1. Single-crystal diffractions were collected on a Nonius Kappa CCD instrument fitted with an Oxford Cryosystems Series

Table 1	
Crystal data for [TPPFe(2.6-Cl_pcvd)] · CHCl <sub>2</sub> (3)	

Empirical formula	C51H31Cl2FeN6 · CHCl3
Formula weight	973.94
Crystal system	triclinic
Space group	$P\overline{1}$
<i>a</i> (Å)	10.985(1)
$b(\mathbf{\dot{A}})$	11.350(1)
c (Å)	18.824(2)
$\alpha$ (°)	95.834(6)
β (°)	100.852(6)
γ (°)	101.253(5)
$V(Å^3)$	2237.2(5)
Z	2
$D_{\rm calc} ({\rm Mg}{\rm m}^{-3})$	1.446
$T(\mathbf{K})$	123(2)
$\lambda$ (Mo Ka) (Å)	0.71073
Maximum and minimum transmission	0.482 and -0.558
<i>R</i> factor <sup>a</sup>	0.056
$R_{\rm w}$ factor <sup>b</sup>	0.141
<sup>a</sup> $R = \sum   F_0  -  F_c   / \sum  F_0 $ .	

<sup>b</sup>  $R_{\rm w} = (\sum w(|F_{\rm o}| - |F_{\rm c}|)^2 / \sum w|F_{\rm o}|^2)^{1/2}.$ 

700 Cryostream low-temperature device with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Total number of 114 frames were collected with two oscillation modes ( $\phi + \omega$ ) at 1.7° oscillation angle and exposure time of 200 s per frame, affording a selected redundancy of 2. The data were integrated using DENZO SMN [29] and processed using DENZOX. Absorption effects were corrected by Gaussian quadrature. Full-matrix least-squares refinement on  $F^2$  was carried out using SHELXL97 [30] with no applied constraints applied. All calculations were carried out using the WINGX software package [31]. The results are summarized in Table 1.

# 2.3. Preparation of $[TPPFe^{III}(2,6-Cl_2pcyd)]$ (3)

TPPFeCl powder (50.0 mg, 0.071 mmol) and thallium salt of 2,6-Cl<sub>2</sub>pcyd (83.0 mg, 0.213 mmol) were placed in a two-neck round-bottomed flask. After 30 min under vacuum, the flask was placed under N2 atmosphere (schlenk technique). Dichloromethane was transferred to the reaction flask and stirred for 24 h at room temperature. Then, the mixture was filtered and the volume of the filtrate was reduced to approximately 10 ml. Then, dried *n*-hexane (50 ml) was added slowly to the reaction flask while stirring. The precipitate was removed by filtration and dried while standing in air. Other compounds (2) and (4) were prepared by the same procedure, except that 2,6-Cl<sub>2</sub>pcyd was replaced by appropriate phenylcyanamide derivatives. Compound 1 was prepared by the above procedure, except that dry dichloromethane and 2,6-Cl<sub>2</sub>pcyd were replaced by dry benzene and phenylcyanamide, respectively.

IR, UV–Vis data and yields of products are summarized in Table 2. *Anal.* Calc. for 1,  $C_{51}H_{33}FeN_6$  (785.718): C, 77.9; H, 4.2; N, 10.7. Found: C, 76.5; H, 4.1; N, 10.2%. *Anal.* Calc. for 3,  $C_{51}H_{31}Cl_2FeN_6$  (854.602): C, 71.6; H, 3.6; N, 9.8. Found: C, 71.0; H, 3.8; N, 9.0%. *Anal.* Calc. for 4,  $C_{51}H_{29}Cl_4FeN_6$  (923.492): C, 66.3; H, 3.2; N, 9.1.

Table 2 UV–Vis electronic absorption<sup>a</sup> and IR data<sup>b</sup> for TPPFe-L complexes and thallium salts of phenylcyanamide

Complex	UV–Vis <sup>c</sup>		v(NCN) <sup>d,e</sup>		Yield
	Soret band	Q bands	Thallium salt	Complex	(%)
TPPFeC1	416.5	509, 657			
TPPFe(pcyd)	417.5	509, 572	2050	2080	65
TPPFe(2,5-Cl <sub>2</sub> pcyd)	416	503, 632	2105	2115	76
TPPFe(2,6-Cl <sub>2</sub> pcyd)	415.5	512, 648	2050	2065	68
$TPPFe(2,3,4,6-Cl_4pcyd)$	414.5	512, 654	2090	2125	73

<sup>a</sup> In nm.

<sup>b</sup> In cm<sup>-1</sup>.

<sup>c</sup> In benzene.

<sup>d</sup> KBr disk.

<sup>e</sup> Strong.

Found: C, 67.7; H, 3.6; N, 8.7% (while %C is not very satisfactory, fractional solvent could improve the fit and  $^{1}$ H NMR support the purity of the compounds).

# 3. Results and discussion

Until the present work, to the best of our knowledge, no studies of phenylcyanamide derivatives of iron were reported in the literature, where we described the first synthesis, spectroscopic and X-ray characterization of iron(III) porphyrin phenylcyanamide derivatives.

The Fe<sup>III</sup>porphyrin complexes of phenylcyanamide derivatives were synthesized in generally good yields by following metathesis reaction in refluxing dry benzene or dichloromethane. This reaction was very sensitive to moisture and a lesser extent to molecular O<sub>2</sub>. Exposure of traces of water resulted in the formation of  $\mu$ -oxo dimer, TPPFe-O-FeTP.  $\mu$ -Oxo dimer impurity is hard to remove, since chromatography on silica gel or aluminum oxide may lead to its additional formation. The reaction yields were quantitative for phenylcyanamide and chloro substituted phenylcyanamides (1–4).



A different mixture of TPPFe-Cl, TPPFe-O-FeTPP and TPPFe(phenylcyanamide) was obtained in each preparation, when an electron donating substituent, such as methyl or mesithyl substituted phenylcyanamide was employed. In such cases, we were not able to separate and isolate a pure desired compound and thus we are not reporting the results in this paper. The reaction yields for compounds 1–4 were quantitative, although during the process of precipitation and isolation 20–30% of the products were lost. These products are less sensitive to moisture or molecular oxygen after formation. So, no effort was made to exclude air or moisture for spectroscopic studies; however, crystals of **3** were grown under dry N<sub>2</sub> atmosphere at room temperature. All compounds are fairly soluble in non-coordinating solvents, except saturated hydrocarbons. Phenylcyanamide derivative complexes readily react with HCl and result in the formation of starting TPPFeCl.

#### 4. Spectroscopic characterization

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

The <sup>1</sup>H NMR spectra of chloro substituted phenylcyanamide complexes are shown in Fig. 1 and full assignments of signals for compounds 1-4 are shown in Table 3. Resonance assignments have been made on the basis of relative intensity, line width, previous assignments of TPPFe-X moiety in high-spin Fe(III)complexes and direct comparison of signals in compounds 1-4.

For example, trace of **4** in Fig. 1 shows two signals at 75.9 and 25 ppm, which are assigned, respectively, to the  $\beta$ -pyrrole hydrogens and the only hydrogen present in meta position of phenylcyanamide ligands. Trace of **3** in Fig. 1 has shown a new signal high field region at -47 ppm with half intensities of signal in 30 ppm. So this signal in -47 ppm has been assigned to 4-H for compound **3**. These assignments were reconfirmed with the traces of **2** and **1**. In



Fig. 1. <sup>1</sup>H NMR spectra of iron(III)porphyrin complexes: TPPFepcyd (1), TPPFe(2,5-Cl<sub>2</sub>pcyd) (2), TPPFe(2,6-pcyd) (3), and TPPFe(2,3,4,6-Cl<sub>4</sub>pcyd) (4), in  $C_6D_6$  at 300 K.

Table 3 <sup>1</sup>H NMR spectral data of TPPFe-L complexes<sup>a</sup>

<sup>a</sup> In C<sub>6</sub>D<sub>6</sub>, data in ppm vs. TMS reference at 0.00 ppm at 300 K.

addition, new broad signals around -58 ppm in compounds **1** and **2** were assigned to the only hydrogens left to be assigned in 2 and 6 positions (*ortho*) of coordinated phenylcyanamides. Signals of phenyl of tetraphenyl porphyrins have been seen in almost the same place for TPP-FeCl, Table 3. The effect of temperature on the <sup>1</sup>H NMR spectrum of hydrogens of phenylcyanamide for **3** in chloroform solution is shown in Fig. 2, where the chemical shifts for the pyrrole protons, 3,5-H and 4-H, are plotted versus 1/T (K<sup>-1</sup>). Each resonance shows linear behavior. This is consistent with the presence of a monomeric paramagnetic complex.

<sup>1</sup>H NMR spectroscopy has been uniquely shown to be a definitive method for detecting and characterizing iron por-

these compounds have an admixed spin state with a fairly high degree of S = 5/2 character.

Crutchley has suggested that phenylcyanamides are expected to be the same as pseudo halide [15]. Pyrrole position of phenylcyanamide derivatives here confirms that the strength of phenylcyanamide is slightly weaker than halides and psuedo halide ligands [33,34].

# 4.2. IR and UV-Vis studies

Cyanamide group, a three atom  $\pi$ -system, is a poor  $\pi$ -acceptor system but it is a good  $\pi$ -donor of nitrile ligands. Three modes of coordination have been recognized for phenylcyanamide metal complexes, A, B and C [35–38].



phyrins. The hyperfine shift patterns are sensitive to the iron oxidation, spin and ligation state. Particularly, pyrrole protons provide a direct probe of the porphyrins macrocycle [32]. Magneto chemical series proposed by Reed et al. is based on the degree of S = 5/2, 3/2 spin state admixture engaged by axial ligands in TPPFe-X type complexes [33,34]. <sup>1</sup>H NMR  $\beta$ -pyrrole shift with the given range of -62 ppm for pure intermediate spin state, S = 3/2, to +80 ppm for high spin, S = 5/2, species at 25 °C was used as an indicator of the degree of admixture. The pyrrole chemical shift for 1–4 around 77–75 ppm indicates that



Fig. 2. Plot of the chemical shift vs. 1/T (K) for the pyrrole (a), 3,5-H; (b) and 4-H (c) resonances of **3** in chloroform solution.

IR spectroscopy can be used to identify which coordination mode of phenylcyanamide binds to the metal com-It can differentiate nitrile plexes. versus amide coordination in both anionic and neutral form of phenylcvanamides [39]. Neutral phenylcyanamide, A, has shown  $v(C \equiv N)$  around 2225–2250 cm<sup>-1</sup> [20,24] and coordinated nitrile in Fe<sup>III</sup>-CN complexes was reported at 2129 cm<sup>-1</sup> [23]. The Coordination of anionic phenylcyanamide ligand via nitrile nitrogen produced a characteristic strong bond in the frequency lower than  $2150 \text{ cm}^{-1}$  in both thallium salts and compounds (1-4), Table 2. In each case, the  $v_{\rm CN}$  absorption is consistent with the presence of resonance form of C. The v(N=C=N) in iron(III) phenylcyanamide complexes has consistently shifted around  $5-35 \text{ cm}^{-1}$  to higher frequency relative to the thallium salts. The same trend was observed for tetraphenylporphyrin manganase(III) complexes of phenylcyanamides [40].

Differentiation of the nature of axial ligands of iron(III) porphyrin is often possible by UV–Vis spectra [41]. Fig. 3 shows UV–Vis spectra of compounds 1 and 4 in benzene in comparison to TPPFeCl. These spectra and the results for other compounds in Table 2 indicate similarity of electronic spectra of prepared compounds. The  $\lambda_{max}$  values of the phenylcyanamide-ligated species are in the same range

Table 4



Fig. 3. UV–Vis spectra of TPPFeCl (—), TPPFe-pcyd (---) (1) and TPPFe-(2,3,4,6-Cl<sub>4</sub>pcyd) (...) (4),  $10^{-6}$  M in benzene.

to those of the Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup> and NCS<sup>-</sup> iron porphyrin species in the soret region. These data confirm the existence of high-spin iron(III) oxidation and spin states, since the UV–Vis spectra of metalloporphyrins are sensitive to the oxidation and spin state of metals [42]. Fig. 3 also shows higher absorption coefficients of 1 and 4 due to coordination of longer  $\pi$ -conjugated axial ligand.

# 4.3. X-ray diffraction studies

The structure of TPPFe(2,6-Cl<sub>2</sub>pcyd) (**3**) has been studied by X-ray diffraction. Two views of **3** with heavy atom numbering are shown in Fig. 4. Selected bond lengths and angles are presented in Table 4. Iron is five-coordinate in slightly distorted square pyramidal environment with the 2,6-dichlorophenylcyanamide in the axial position. The bond distances for Fe–N<sub>eq</sub> are 2.063(5) Å and the displacement of iron from the plane of core porphyrin 24 atoms is 0.47(1) Å. These parameters are consistent with the parameter observed for high-spin five-coordinated iron(III) porphyrins [43]. For example, bond length Fe–N<sub>eq</sub> and displacement of iron(III) for TPPFeI and TPPFeNCS are 2.060, 0.53 Å and 2.065, 0.49 Å, respectively [44].

There are many crystal structures of monodentate phenylcyanamide ligands showing coordination through the cyano-nitrogen, but there are no examples of amide–nitrogen coordination [15]. The anionic cyanamide group of the ligand cyanamide is shown to be planar with the phenyl group due to strong  $\pi$ -coupling between them. A significant degree of  $\pi$  bonding between the cyanamide group and Fe(III) d-orbital is indicated with the angle of 154° observed in the iron with axial NC and short bond length of Fe–N<sub>5</sub> (1.905 Å). For the TPPMn(4-Mepcyd), the Mn–NC axial angle of 135.8° and the metal axial ligand distance of 2.075 Å have been reported [40]. NCN moiety is almost linear with the N(5)–C(57)–N(6) angle of 171.1°.

Fe-axial ligand distances in high-spin 5-coordinated iron porphyrins range from 1.957 Å in TPPFeNCS to 2.554 Å in TPPFeI. Shorter distances between iron and axial ligands for intermediate spin complexes such as



Fig. 4. (a) Atom-numbering scheme and (b) molecular structure of TPPFe(2,6-Cl<sub>2</sub>pcyd) (3). Displacement ellipsoids at 50% for (a) and 30% for (b) probability level.

Selected bond lengths (Å) and angles	<sup>a</sup> (°) for [TPPFe(2,6-Cl <sub>2</sub> pcyd)] · CHCl <sub>3</sub>
(3)	

(-)			
Bond lengths		Bond angles	
Fe-N(1)	2.071(6)	Fe-N(5)-C(57)	154.2(6)
Fe-N(2)	2.057(5)	N(5)-C(57)-N(6)	171.1(7)
Fe-N(3)	2.066(6)	C(57)-N(6)-C(51)	129.3(7)
Fe-N(4)	2.059(5)	N(1)–Fe–N(2)	87.1(2)
Fe-N(5)	1.905(6)	N(2)-Fe-N(4)	155.9(2)
N(5)-C(57)	1.183(9)	N(4)-Fe-N(3)	87.0(2)
C(57)–N(6)	1.269(10)	N(3)-Fe- $N(1)$	151.4(2)
N(6)-C(51)	1.398(9)	N(2)-Fe-N(3)	87.4(2)
C(51)-C(52)	1.395(11)	N(1)-Fe-N(4)	86.7(2)
C(51)–C(56)	1.400(10)	N(1)-Fe-N(5)	106.8(2)
		N(3)-Fe-N(5)	101.8(2)
		N(4)-Fe-N(5)	103.8(2)
		N(2)-Fe-N(5)	100.2(2)

<sup>a</sup> Estimated SDs are in parentheses. Torsion angle C(57)-N(6)-C(51)-C(56), 29.41(2).

TPPFe(OClO<sub>3</sub>) of Fe–O = 2.029, TPPFe(SbF<sub>5</sub>) of Fe– F = 2.105 and TPPFe(B<sub>11</sub>CH<sub>12</sub>) of H–Fe = 1.82 were observed. A relatively short distance of Fe–N<sub>ax</sub> in the iron phenylcyanamide complex in 2 may be an indication for small population of intermediate spin in these systems.

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