Contents lists available at ScienceDirect

Inorganica Chimica Acta



journal homepage: www.elsevier.com/locate/ica

Synthesis and structural determination of new octaethylporphyrin iron(III) complexes containing cyanamide derivatives as axial ligand

Mozhgan Khorasani-Motlagh^{a,*}, Nasser Safari^b, Meissam Noroozifar^a, Hashem Shahroosvand^a, Brian O. Patrick^c

^a Department of Chemistry, University of Sistan & Baluchestan, P.O. Box 98147-155 Zahedan, Iran

^b Department of Chemistry, Shahid Beheshti University, Tehran, Iran

^c Department of Chemistry, University of British Columbia, Vancouver, Canada

ARTICLE INFO

Article history: Received 10 April 2008 Received in revised form 12 June 2008 Accepted 13 June 2008 Available online 1 July 2008

Keywords: Octaethylporphyrin Iron(III) Cyanamide X-ray Electrochemistry

ABSTRACT

The reactions of heme, [OEPFeCI] where OEP is the dianion of octaethylporphyrin, with phenylcyanamide (pcyd) ligands have been studied. Four new porphyrin complexes, [OEPFe(L)] (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**)), have been isolated and characterized by spectroscopic methods. ¹H NMR spectroscopy reveals that the species [OEPFe(L)] are paramagnetic and iron is five-coordinate. The structure of [OEPFe(pcyd)] (**2**) has been determined by X-ray diffraction analysis. The four Fe–N, bond distances have average values of 2.062 Å. The average displacement of the iron(III) atom from the mean porphinato core is 0.45 Å. Electrochemical of [OEPFe(L)] (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**)) have been studied by cyclic voltammetry.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The coordination chemistry of iron porphyrins has been extensively investigated in order to understand the ability of this macrocyclic to sustain a variety of biological functions including the transport and storage of dioxygen, and in the activation of dioxygen towards reduction [1,2]. Moreover, the biological and chemical importance of iron porphyrins makes the nature of the metals-ligand linkage in these complexes of considerable interest. Numerous structural and physical characterizations of iron porphyrin with different axial groups have been reported during the last decades [3–6].

Phenylcyanamide ligands (pcyd) are interesting ligands from the synthetic and magnetic point of view. An extensive π conjugation between the cyanamide group and the phenyl ring provides an energetically favorable means by which a metal ion can couple into a conjugated organic π system. The evident relationship with other pseudohalide ligands which in the last few years have provided a great variety of structural topologies and magnetic properties, including ferro, antiferro, (homogeneous or alternating) or in some few cases, ferrimagnetic systems [7–9].

Here we report the synthesis of four new heme analogues with phenylcyanamide ligands, [OEPFe(L)] (L = pcyd (**2**), 2-Clpcyd (**3**), 2-

Mepcyd (**4**), 2,4-Me₂pcyd (**5**)). Complexes **2–5** have been characterized with vibrational and NMR spectroscopes as well as elemental analyses. These phenylcyanamide ligands could stabilize five-coordinate iron (III) with a high-spin electronic configuration. [OEPFe(L)] (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**)) are stable in air, and these complexes react with HCl and produce [OEPFeCl] (**1**). The electrochemistry of dichloromethane solution of [OEPFe(L)] (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**4**), 2,4-Me₂pcyd (**5**)) have been studied by cyclic voltammetry.

2. Experimental

All solvents were dried by refluxing for several days over Na and benzophenone under Ar and distilled immediately before use. Purified N₂ (99.99%) was used without further treatment. All reagents and solvents used in this study were obtained from Merck or Aldrich Chem. Co. All phenylcyanamide derivatives and their thallium salts were synthesized following the general synthetic procedure described by Crutchley and Naklicki [10]. *Caution*! Thallium is extremely toxic.

IR spectra were recorded using KBr disks on a Shimatzu IR instrument. UV–Vis spectra were recorded on an analytikjena SPE-CORD S100 spectrometer with photodiode array detector. NMR experiments were recorded at room temperature in CDCl₃ on a Bruker AV-500 spectrometer using an internal deuterated solvent lock.



^{*} Corresponding author. Tel.: +98 541 244 6565; fax: +98 541 244 6888. *E-mail address*: mkhorasani@chem.usb.ac.ir (M. Khorasani-Motlagh).

^{0020-1693/\$ -} see front matter @ 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2008.06.029

2.1. Synthesis of [OEPFe(L]) (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**))

The four compounds were prepared as following procedure: Thallium phenylcyanamide salt (0.80 mmol) was added to dichloromethane solution of [OEPFeCl] (1) (25 mg, 0.04 mmol) under N₂ atmosphere. The reaction mixture was stirred for 1 h to produce brown-red solution. The mixture was filtered and the resulting clear solution was evaporated to dryness under vacuum to give a brown-red residue. The resulting solid was recrystallized by dissolving it in a minimum volume of dichloromethane and slowly adding *n*-hexane to precipitate the product as dark red crystals. Yields for the five compounds are around 85%. Elemental Anal. Calc. for C₄₃H₄₉N₆Fe (2): C, 73.17; H, 6.99; N, 11.91. Found: C, 73.02; H, 6.85; N, 11.79%. UV–Vis absorption: λ_{max} nm (ϵ , $cm^{-1}\,M^{-1}$), 373 (5.4×10^4) , 397 (6.2×10^4) , 509 (7.1×10^3) , 538 (7.3×10^3) , 634 (5.3×10^3) . IR (KBr): v (NCN) = 2195 cm⁻¹. Elemental Anal. Calc. for C₄₃H₄₈N₆FeCl (**3**): C, 69.76; H, 6.53; N, 11.35. Found: C, 69.63; H, 6.42; N, 11.27%. UV–Vis absorption: λ_{max} , nm (ϵ , cm⁻¹M⁻¹), 375 (5.6×10^4), 396 (6.3×10^4), 507(7.1×10^3), 540 (7.1×10^3), 629 (5.4×10^3) . IR (KBr): $v(NCN) = 2114 \text{ cm}^{-1}$. Elemental Anal. Calc. for C₄₄H₅₁N₆Fe (**4**): C, 73.41; H, 7.14; N, 11.67. Found: C, 73.34; H, 7.07; N, 11.54%. UV–Vis absorption: λ_{max} , nm (ϵ , $cm^{-1} M^{-1}$), 371 (5.6 × 10⁴), 397 (6.4 × 10⁴), 505 (7.2 × 10³), 537 (7.3×10^3) , 639 (5.3×10^3) . IR (KBr): $v(NCN) = 2106 \text{ cm}^{-1}$. Elemental Anal. Calc. for C₄₅H₅₃N₆Fe (**5**): C, 73.64; H, 7.27; N, 11.45. Found: C, 73.47; H, 7.09; N, 11.32%. UV–Vis absorption: λ_{max} , nm (ϵ , $cm^{-1} M^{-1}$), 373 (5.5 × 10⁴), 397 (6.1 × 10⁴), 509 (7.1 × 10³), 540 (7.2×10^3) , 636 (5.2×10^3) . IR (KBr): $v(NCN) = 2090 \text{ cm}^{-1}$.

2.2. Crystallography

Crystallization of [OEPFe(pcyd)] (**2**) at room temperature by diffusion of *n*-hexane into its saturated dichloromethane solutions yielded black, tablet-shaped crystals. Measurements were made on a Bruker X8 APEX diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$). The data were collected at a temperature of -100 ± 0.1 °C to a maximum 2θ value of 55.7°. The structures were solved by direct methods [11] and expanded using Fourier techniques [12]. The non-H-atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but were not refined. The standard deviation of an observation of unit weight was 1.00. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.37 and $-0.32 \, e/Å3$, respectively.

A perspective view of complex **2** is shown in Fig. 3. Some details of the collection are given in Table 2. Selected interaction distances and angles are given in Table 3.

2.3. Electrochemical measurement

Cyclic voltammograms were recorded on a Electroanalyzer system Model Sama 500 (Sama research center, Esfahan, Iran) in a three electrode cell. The working electrode was a platinum disk with a diameter of 2 mm. Before each experiment the electrode was polished with fine carborundum paper and 0.5 mm alumina slurry in sequence. The electrode was then sonicated in order to remove the trace of alumina from the surface, washed with water and dried. A SCE served as the reference electrode. The auxiliary electrode was a platinum electrode. An initial background scan was run to check the purity of the reagents and to establish the solvent anodic potential range. The electrochemical measurements were carried out at a thermostated temperature of 25.0 ± 0.1 °C. Tetrabutylammonium perchlorate was used as supporting electrolyte.

3. Results and discussion

3.1. Formation of [OEPFe(L]) (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**))

The results presented here show that phenylcyanamide anions react with heme, $[OEPFe^{III}CI]$ (1), in air to produce five-coordinate products, [OEPFe(L)] (L = pcyd (2), 2-Clpcyd (3), 2-Mepcyd (4), 2,4-Me₂pcyd (5)) (Scheme 1). The solutions and solids of 2–5 complexes are air stable, and these complexes react with HCl and produce [OEPFeCI] (1).

[OEPFe(L)] (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**)) are soluble in a the range of solvents: chloroform, dichloromethane, hexane, pyridine. Their behavior in non-coordinating solvents, particularly dichloromethane and chloroform, are similar. The UV–Vis spectra of dichloromethane solutions of **2–5** show typical heme features [13,14] with intense Soret bands in the range of 370–397 nm and Q-bands, low energy absorption, in the range of 505–640 nm. The electronic absorption spectra obtained from



Fig. 1. The UV–Vis absorption spectra of a dichloromethane solution of [OEPFe^{III}CI] (blue line) and [OEPFe(2,4-Me₂pcyd)] (5) (purple line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

dichloromethane solutions of [OEPFe(L)] (L = pcyd (2), 2-Clpcyd (3), 2-Mepcyd (4), 2,4-Me₂pcyd (5)) are similar to electronic absorption spectra of the known high-spin iron (III) porphyrins such as, [OEPFeCI] and [TPPFeCI] [13,14] but Soret bands were found to be broadened and split. Fig. 1 shows the electronic absorption spectra of $[OEPFe(2,4-Me_2pcyd)]$ and [OEPFeCI] in dichloromethane for comparison. The arrangement of macrocycles in aggregates generally fall into two types, "J" (edge-to-edge) and "H" (face-to-face). Each type, J and H, have distinctive spectral features that can be exploited or utilized [15]. The split Soret band together with the broadened in the optical spectra suggest both types of interaction in the dichloromethane solution [15,16].

The [OEPFe(L)] (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**)) were characterized also by infrared spectroscopy.

IR spectroscopy is a proper tool for characterization of phenylcyanamide metal complexes. It can differentiate nitrile versus amine coordination in both anionic and natural form of phenylcyanamide. Neutral phenylcyanamide (pcyH) has shown C \equiv N stretch in the range of 2225–2249 cm⁻¹, where coordination of anionic phenylcyanamide ligands seems to occur via nitrile nitrogen and produce a strong bond in the frequency lower than 2150 cm⁻¹ [10]. Infrared data for **2** show one strong absorption band at 2195 cm⁻¹ that is close to absorption band of CN triple bond (resonance form A), but for **3–5** ν (CN) are 2090, 2106, 2114 cm⁻¹, respectively, that is consistent with the presence of the resonance form B (Eq. (1)).

All resonances in the ¹H NMR spectra of [OEPFe(L)] (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**)) species are well spread out and were assigned on the basis of their intensities, line



Fig. 2. Paramagnetic ¹H NMR (500 MHz) in CDCl₃ at room temperature of (a) [OEPFe(2-Clpcyd)], (b) [OEPFe(2-Mepcyd)], (c) [OEPFe(pcyd)], (d) [OEPFe(2,4-Me₂pcyd)].

Table 1		
¹ H NMR data	for 2-5	complexes

Complex	CH ₂	CH ₂	CH ₃	Meso	H_2^a	H ₃	H ₄	H ₅	H ₆
[OEPFe(pcyd)] (2)	42.25	39.94	6.22	-51.57	-47.47	33.09	-46.04	33.09	-47.47
[OEPFe(2-Clpcyd)] (3)	43.82	39.63	6.42	-52.00	-	35.85	-42.60	23.82	-47.30
[OEPFe(2-Mepcyd)] (4)	41.39	38.39	6.15	-55.00	40.50 ^b	25.74	-47.23	25.74	-47.23
[OEPFe(2,4-Me ₂ pcyd)] (5)	40.71	38.13	6.04	-56.10	43.46 ^b	39.96	61.37 ^b	26.95	-47.20



widths, and chemical shifts at room temperature. The paramagnetic shifts of protons are the same as typical paramagnetic shifts of protons for high-spin five-coordinate ferric porphyrin, OEPFeCI [17]. Fig. 2 shows, the ¹H NMR spectra of [OEPFe(L)] (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**)) species in CDCl₃ at 25 °C.

The methylene and methyl protons (eight ethyl groups in OEP) show strong paramagnetic shifts that place them in the downfield region. A special feature is the doubling of the methylene peak for example at 38.13, 40.71 ppm for [OEPFe(2,4-Me₂pcyd)] (5). One broad methyl resonance is seen in the range of 5.8-6.22 ppm. In the case of the natural porphyrins, the broad lines generally do not permit resolution of the nonequivalent methyls resonances. One meso (four methine hydrogens in porphyrin ring) resonance in the high field region (about -51 to -57 ppm) observed in the spectrum of each of these complexes which is consistent with the fact that they are the protons closest to the iron center and hence that they are the most affected by dipolar relaxation. Worth mentioning also is that the line widths increase in the order methyl > methylene > meso. This is consistent with a dominant dipolar contribution to the line width [18] since the distance between the porphyrin protons and the iron center follow an inverse order. These spectra are consistent with the structure shown in Scheme 1, in which the iron is five-coordinate and each of the two methylene protons of the eight unique ethyl groups is chemically distinct and hence there are two methylene resonances. In addition, based on comparison of the pattern of signals in

Table 2	
Crystallographic Data	for $[OFPFe(pcvd)](2)$

Empirical formula	C43H49N6Fe
Fw	705.73
Crystal color, habit	black, tablet
Crystal system	monoclinic
Dimension (mm)	$0.15 \times 0.30 \times 0.50$
Space group	P 2 ₁ /c (#14)
a (Å)	12.6428(7)
b (Å)	13.5119(7)
c (Å)	22.0756(12)
β(°)	102.923(2)
V (Å ³)	1949.4(2)
Ζ	4
T (K)	173.0(1)
D_{calc} (g/cm ³)	1.275
F(000)	1500.00
μ (cm ⁻¹)	4.50
Total data collected	37493
Number of unique data (R _{int})	8696 (0.042)
Final R indices $(I > 2\sigma(I)]$	$R_1 = 0.042; wR_2 = 0.094$
Final R indices (for all data)	$R_1 = 0.075; wR_2 = 0.109$
Goodness-of-fit	1.00

 $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|, \ wR_2 = \sqrt{\sum (w(F_0^2 - F_c^2)^2) / \sum w(F_0^2)^2}.$

phenylcyanamide complex **2–5**, assignment of ¹H NMR signals for **2–5** complexes are shown in Table 1.

The [OEPFe(L)] (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**)) species are paramagnetic. In chloroform solution at 25 °C, as measured by the Evans technique [19], **2**, **3**, **4** and **5** have magnetic moment of 5.65, 5.52, 5.61, 5.58 μ_{B} , respectively. This is consistent with a high-spin (*S* = 5/2) electronic configuration of iron in these species.

3.2. *Molecular structure*

The structure of [OEPFe(pcyd)] (**2**) has been determined by X-ray crystallography and some of the crystallographic data are summarized in Table 2. ORTEP diagrams of the monoclinic [OEP-Fe(pcyd)] (**2**) is shown in Fig. 3. Fig. 4 shows the molecular packing of **2**. Selected bond distances and angles [OEPFe(pcyd)] (**2**) are given in Table 3.

The Fe– N_{eq} bond distances have average value of 2.062 Å which is close to that observed for OEPFeCl (2.071 Å). The displacement of the iron(III) atom from the mean porphinato core is 0.45 Å and shorter than that of OEPFeCl (0.494 Å) [20]. These structural parameters are typical for five-coordinate, high-spin, iron(III) porphyrins [2].



Fig. 3. Perspective view of [OEPFe(pcyd)] (2). Porphyrin hydrogen atoms are omitted for clarity. The atoms were drawn with 50% probability ellipsoids.



Fig. 4. An overview of the molecular packing in the crystal structure of [OEPFe(pcyd)] (2).

Table 3	3
---------	---

Selected bond lengths	(Å) and	l angles (°) for	[OEPFe(pcyd)]] (2)
-----------------------	---------	------------------	---------------	-------

Bond length	
N(1)-Fe(1)	2.0626(17)
N(2)-Fe(1)	2.0592(17)
N(3)-Fe(1)	2.0665(17)
N(4)-Fe(1)	2.0597(17)
N(5)-Fe(1)	1.9678(17)
C(37)–N(5)	1.139(3)
C(37)–N(6)	1.268(3)
C(38)–N(6)	1.407(3)
C(1)-C(20)	1.377(3)
C(1)-N(1)	1.382(3)
Bond angle	
N(1)-Fe(1)-N(3)	154.45(7)
N(4)-Fe(1)-N(3)	87.44(7)
N(2)-Fe(1)-N(3)	87.21(7)
N(5)-Fe(1)-N(3)	102.44(7)
N(4)-Fe(1)-N(1)	87.33(7)
N(2)-Fe(1)-N(1)	87.28(7)
N(5)-Fe(1)-N(1)	103.11(7)
N(2)-Fe(1)-N(4)	155.52(7)
N(5)-Fe(1)-N(4)	101.08(7)
N(5)-Fe(1)-N(2)	103.40(7)
C(37)–N(5)–Fe(1)	168.53(18)
C(37)-N(6)-C(38)	124.9(2)
N(5)-C(37)-N(6)	171.7(3)
C(39)–C(38)–N(6)	123.6(2)
C(43)-C(38)-N(6)	117.3(2)

Cyanamide ligands have a coordination configuration that depends primarily on the nature and oxidation state of the metal atoms. The bond angle between a cyanamide group and a metal ion is largely determined by resonance: of 180°. Coordination of resonance structure B to a metal ion ought to result in an ideal bond angle of 120°. Coordination of the anionic cyanamide group to a strongly polarizing metal ion should increase the contribution of resonance structure B, and if the metal ion has significant π acceptor properties, the preferred bond angle will be close to 180°. In this regards, Ru(III), a strong π acceptor, has been shown to coordinate to 2,3-Cl₂pcyd⁻ with a bond angle 171° and Cu(II) has far weaker π acceptor properties has Cu(II)-cyanamide bond angles between 141° and 165° [21]. Here, the bond between the anionic cyanamide group and Fe(III) is almost linear, having an angle of C(37)–N(5)–Fe(1)=168.53°, and is shorter, with Fe– N_{ax} = 1.9678(17) Å. This indicates a significant degree of π -donation to Fe(III).

By reference to the Cambridge Structural Database, the C(37)–N(5) bond length of 1.139(3) Å is very close to that of a CN triple bond [22]. There is conformity between X-ray and Infrared data: Infrared data show one strong absorption band at 2195 cm⁻¹ that is close to absorption band of CN triple bond. This bond lengths are 1.183 and 1.171 Å for [TPPFe(2,4-Cl₂pcyd)] [23] and [TPPMn(4-Mepcyd)] [24], respectively, with non linear bond between the anionic cyanamide group and M(III).

Free anionic phenylcyanamide ligands are expected to be planar in the absence of the steric effects due to the strong coupling of the cyanamide group with the phenyl ring system. This interaction is apparently maintained upon coordination to Fe(III), the torsion angle C(37)–N(6)–C(38)–C(39), 4.3°, shows that the phenyl ring is approximately planar with cyanamide to optimize the interaction between the phenyl ring and cyanamide group. NCN is almost linear, having an angle of N(5)–C(37)–N(6) = 171.7(3)°.

The relative (inward/outward) orientations of the eight ethyl groups are different; two consecutive ethyl groups on each porphyrin are directed outwards relative to the cyanamide, whereas the remaining six ethyl groups are directed inwards.

The molecular packing in the crystal structure of [OEPFe(pcyd)] (**2**) is shown in Fig. 4. It is worth noticing that, the angle between the phenyl mean planes of two neighboring molecules is zero and two phenyl groups are exactly parallel.

The porphyrins macrocycle with Fe(II) is nearly planar [25], in distinct contrast as seen in Fig. 5 of Ref. [26], the Fe(III) porphyrin complexes have highly distorted, ruffled macrocyclic cores with atomic displacements up to 0.68 Å away from the porphyrin mean plane. However, here for Fe(III) porphyrins, [OEPFe(pcyd)] (**2**), the maximum of out-of plane displacements of the porphyrin core atoms is 0.103 Å.

3.3. Electrochemical measurements

The electron transfer properties of porphyrin complexes have been extensively reported in the literature [27]. Electrochemical of [OEPFeCI] was studied in nonaqueous media by Kadish et al. [28,29], they reported that Fe(III)/Fe(II) couple was obtained as an irreversible wave at -0.42 V versus SCE in dichloromethane.



If only sigma bonding interaction to the terminal cyanamide nitrogen are considered, resonance structure A (Eq. (1)) will coordinate to a metal *via* the nitrile lone pair, resulting in an ideal bond angle We have reported previously, electrochemical of [OEPFeL] $(L = BF_4, SbF_6, AsF_6)$ [30]. Here, electrochemical of dichloromethane solution of [OEPFe(L)] (L = pcyd (2), 2-Clpcyd (3),



Fig. 5. Cyclic voltammograms of [OEPFe(2,4-Me₂pcyd)] (**5**) on platinum electrode at various scan rates; (a) 25, (b) 100, (c) 200, (d) 500, (e) 1000, (f) 2000 mV s⁻¹. Inset, the correlation between the cathodic and anodic currents with $v^{1/2}$.

Table 4

Half-wave potentials (mV) for the first reduction of [OEPFeL] in dichloromethane at scan rate $100 \mbox{ mV/s}$

L	Fe(III)/Fe(II)
2,4-Me ₂ pcyd (5)	-300
2-Mepcyd (4)	-290
pcyd (2)	-270
2-Clpcyd (3)	-240

2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**)) have been studied on platinum electrode.

Each porphyrin undergoes two reductions and two oxidations at potentials between -1.50 and 2.00 V. One of the two one electron oxidation is being assigned to an Fe(III)/Fe(IV) couple and the other one to an oxidation of the conjugated porphyrin macrocycle [31].

Here, we concentrate on the first reduction waves. Half-wave potentials for the first reduction, Fe(III)/Fe(II), of [OEPFe(L)] have been reported in Table 4. Fig. 5 shows the first reduction of [OEPFe(2,4-Me₂pcyd)] (**5**) on platinum electrode at various scan rates in the range of 0.00 to -1.00 V. As is seen from Fig. 5, there is a linear correlation between the cathodic current and $v^{1/2}$, suggesting that the kinetics of the overall process is controlled by mass-transport. Fe(III)/Fe(II) couple for [OEPFe(L)] (L = pcyd (**2**), 2-Clpcyd (**3**), 2-Mepcyd (**4**), 2,4-Me₂pcyd (**5**)), was obtained as a quasi-reversible wave at (-300) to (-240) mV in dichloromethane. As seen in Table 4 the reduction of [OEPFe(L)] becomes more difficult by 60 mV as electron-donating substituents replace electron-withdrawing groups on the phenylcyanamides. Kadish et al. reported that the shift of the potential for the first reduction ob-

served in CH_2Cl_2 of iron porphyrins depends on the binding strength of anionic ligands in OEPFe-L. Here, half wave potential of Fe(III)/Fe(II) couple is close to the potential for the first one electron reduction of metal center of high-spin porphyrin complexes, [OEPFeX] (X = Br⁻, Cl⁻). This is consistent with similar binding ability of cyanamide derivatives (pseudo halides) with Br⁻, Cl⁻ anions [28].

Acknowledgement

We thank University of Sistan and Baluchestan (USB) for financial support, (GN: 85g02).

References

- S.J. Bertini, H.B. Gray, A.B.P. Lippard, J.S. Valentine, Bioinorganic Chemistry, University Science Books, Mill Valley, California, 1994.
- [2] W.R. Scheidt, C.A. Reed, Chem. Rev. 81 (1981) 543.
- [3] J. Wojaczynski, L. Latos-Grazýnski, Coord. Chem. Rev. 204 (2000) 113.
- [4] H. Fujii, Coord. Chem. Rev. 226 (2002) 51.
- [5] K. Nakamoto, Coord. Chem. Rev. 226 (2002) 153.
- [6] W.R. Scheidt, in: K.M. Kadish, R. Guilard, K.M. Smith (Eds.), The Porphyrin Hand Book, vol. 6, Academic press, San Diego, 2000, p. 49.
- [7] R.J. Crutchley, Coord. Chem. Rev. 219–221 (2001) 125.
- [8] A. Escuer, F.A. Mautner, N. Sanz, R. Vicente, Polyhedron 23 (2004) 1409.
- [9] M.A. Fabre, J. Jaud, J.J. Bonvoisin, Inorg. Chim. Acta 358 (2005) 2384.
- [10] R.J. Crutchley, M.L. Naklicki, Inorg. Chem. 28 (1989) 1955.
- [11] A. Altomare, M.C. Burla, G. Cammalli, M. Cascarano, C. Gaiacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, A. Spanga, J. Appl. Crystallogr. 32 (1999) 115.
- [12] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. Gelder, R. Israel, J.M.M. Smiths, The DIRDIF94 Program System, Technical Report of Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
- [13] H. Ogoshi, E. Watanabe, Z. Yoshida, J. Kincaid, K. Nakamato, J. Am. Chem. Soc. 95 (1973) 2845.
- [14] R. Quinn, M. Nappa, J.S. Valentine, J. Am. Chem. Soc. 104 (1982) 2588.

- [15] (a) N.C. Maiti, S. Mazumdar, N. Periasamy, J. Phys. Chem. B 102 (1998) 1528;
 (b) C.A. Hunter, J.K.M. Sanders, J. Am. Chem. Soc. 112 (1990) 5525;
 - (c) K. Kano, H. Minamizono, T. Kitae, S. Negi, J. Phys. Chem. A 101 (1997) 6118;
 (d) R. Purrello, L. Monsu' Scolaro, E. Bellacchio, S. Gurrieri, A. Romeo, Inorg. Chem. 37 (1998) 3647.
- [16] (a) W. Xu, H. Guo, D.L. Akins, J. Phys. Chem. B 105 (2001) 1543;
- (b) X. Gong, T. Milic, C. Xu, J.D. Batteas, C.M. Drain, J. Am. Chem. Soc. 124 (2002) 14290.
- [17] G.N. La Mar, G.R. Eaton, R.H. Holm, F.A. Walker, J. Am. Chem. Soc. 95 (1973) 63.
- [18] T.J. Swift, In NMR of Paramagnetic Molecules, Academic Press, New York, 1973. p. 23.
- [19] D.F. Evans, J. Chem. Soc. (1959) 2003.
- [20] M.O. Sengo, Acta. Crystallogr., Sect. E 61 (2005) m399.
- [21] R.J. Crutchley, R. Hynes, E.J. Gabe, Inorg. Chem. 29 (1990) 4921.
- [22] F.H. Allen, O. Kennard, Chem. Des. Automation News 8 (1993) 31.

- [23] H. Chiniforoshan, N. Safari, J. Mohammad Nezhad, H. Hadadzadeh, A.H. Mahmoudkhani, Inorg. Chim. Acta 359 (2006) 2101.
- [24] N. Safari, B. Notash, J. Mohammad Nezhad, H. Chiniforoshan, H. HadadzadehAli R. Rezvani, Inorg. Chim. Acta 358 (2005) 2967.
- [25] S.P. Rath, M.M. Olmstead, A.L. Balch, Inorg. Chem. 43 (2004) 7648.
- [26] S.P. Rath, M.M. Olmstead, A.L. Balch, J. Am. Chem. Soc. 126 (2004) 6379.
- [27] K.M. Kadish, in: A.B.P. Lever, H.B. Gray (Eds.), Iron Porphyrin, Part 2, Addison-Wesley, Reading, MA, 1983. (Chapter 4).
- [28] K.M. Kadish, L.A. Bottomley, S. Kelly, D. Schaeper, L.R. Shiue, Bioelectrochem. Bioenergetic 8 (1981) 213.
- [29] K.M. Kadish, L.A. Bottomley, Inorg. Chem. 19 (1980) 832.
- [30] M. Khorasani-Motlagh, M. Noroozifar, A. Moodi, J. Porphyr. Phthalocyan. 11 (2007) 691.
- [31] K.M. Kadish, E.V. Caemelbecke, E. Gueletii, S. Fukuzumi, K. Miyamoto, T. Suenobu, A. Tabard, R. Guilard, Inorg. Chem. 37 (1998) 1759.