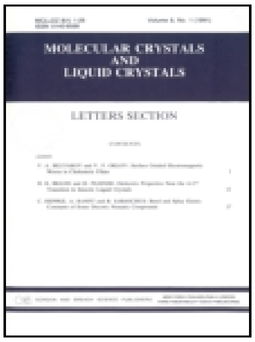

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Two Zinc Porphyrin Complexes Obtained by One-port Reaction

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Two zinc porphyrin complexes were synthesized by one-port reaction. Compound ***1*** *is a mononuclear complex. The zinc ion is bound in the cavity of the ligand and it is coordinated by five atoms in a square pyramidal geometry. Whereas in* ***2****, the metal ion is coordinated by six nitrogen atoms in an octahedral conformation. The porphyrin ligand is coordinated to three zinc ions with a* $\eta1$–$\eta1$–$\eta4$–$\mu3$ *coordination mode. Six neighboring zinc atoms constitute a six-numbered ring in a chair structure. Besides, three neighboring zinc atoms form another triangle helical structure and the structure extends into a three-dimensional metallic polymer.*

Keywords Coordination; crystal structure; porphyrin ligand; zinc(II) complex

1. Introduction

In the past decades, the chemistry of macrocyclic molecules and their derivatives has been the subject of a very active research field because they can bind metal ions in their cavities with special conformations and find their application in separation and transport, catalysts and enzyme mimics, sensoring and switching and medical applications [1–8]. Functionalized by several groups, such as cyanoethyl [9,10], prop-2-ynyl [11,12], phosphanylmethyl [13,14], carbonylmethyl [15,16], carboxyethyl [17,18] and heterocyclic groups, including pyridylmethyl [19,20], bipyridyl [21], terpyridyl [22,23] and acridinylmethyl [24,25], on the secondary N-sites, macrocyclic and macrobicyclic compounds show novel properties in coordination, electro-, photoluminescent, and catalytic chemistry. Hence, this study aims to prepare functionalized macrocyclic complexes constructed from functionalized polyaza ligands and to investigate their coordination behavior.

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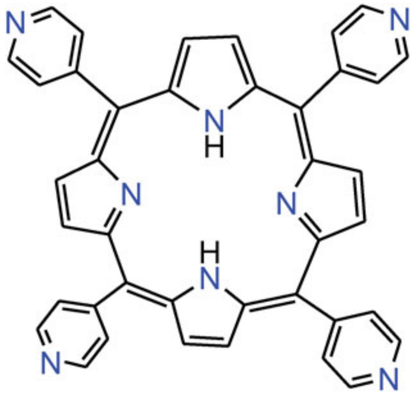

L

Scheme 1. Schematic diagram of ligand L.

Herein we report the syntheses, structures of two zinc complexes of a porphyrin ligand (L), $[H_4ZnL(H_2O)]^{4+}(NO_3)_4(CH_4O)(H_2O)_2$ (**1**) and $\{[ZnL]\cdot CH_4O\cdot (H_2O)_2\}_n$ (**2**), where L is 5,10,15,20-tetra(4-pyridyl)porphyrin (H_2L), which were synthesized by a one-port reaction.

2. Experimental

All reagents used in experiments were analytical or purified by standard method. 5,10,15,20-tetra(4-pyridyl)porphyrin (L) was purchased from Aldrich and Strem and used as received.

2.1. Synthesis of Zinc Porphyrin Complexes (1) and (2)

In a 100 cm^3 flask fitted with funnel, H_2L (0.124 g, 0.2 mmol) was dissolved in 40 cm^3 of a 1:3 mixture of methanol and dichloromethane. Into it, 20 cm^3 of a solution of $Zn(NO_3)_2\cdot 6H_2O$ (0.060 g, 0.20 mmol) in methanol was added dropwise for a period of 1 hr, stirred for 15 hr and refluxed for 3 hr. After cooling down, it is filtered off and a purplish solid (0.078 g) and a purple solution were obtained. The solid was recrystallized from water by natural evaporation and red purple crystals of **1** were obtained, which were suitable for X-ray analysis. Evaporation of filtrate led to the formation of purple crystals of complex **2** (0.031 g), which were also suitable for X-ray analysis.

2.2. Single-crystal X-ray Structure Determination

Single crystals of **1** and **2** were obtained as indicated above. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-Kα (λ 0.71073) radiation. Data were collected using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT [26] on all the observed reflections. Absorption corrections were applied using SADABS [26]. Structures were solved by direct methods by using the SHELXS-97 package [27] and refined with SHELXL-97 [28]. All hydrogens were inserted in calculated positions. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed. CCDC 935180 and 935181 contain the supplementary crystallographic data for

Table 1. Crystallographic data of complexes **1** and **2**

Compound	**1**	**2**
Formula	$C_{41}H_{38}N_{12}O_{16}Zn$	$C_{41}H_{32}N_8O_3Zn$
Formula Weight	1020.20	750.12
Crystal system	Triclinic	Trigonal
Crystal size(mm)	0.41 × 0.32 × 0.30	0.30 × 0.15 × 0.10
Space group	$P-1$	$R-3$
a(Å)	8.9290(8)	32.9790(15)
b (Å)	15.1568(13)	32.9790(15)
c (Å)	16.4368(14)	9.3210(9)
α (°)	88.344(4)	90
β (°)	78.149(4)	90
γ (°)	84.340(4)	120
V (Å^3)	2166.4(3)	8779.5(10)
Z	2	9
D_{calc} (Mg m^{-3})	1.564	1.277
μ (mm^{-1})	0.656	0.677
F(000)	1052	3492
$\theta_{\max}$, $\theta_{\min}$ (°)	28.37, 2.53	25.50, 2.14
Index range h	$-11 \rightarrow 11$	$-39 \rightarrow 39$
k	$-17 \rightarrow 20$	$-39 \rightarrow 39$
l	$-21 \rightarrow 21$	$-9 \rightarrow 11$
No.of independent reflections	10771 [$R_{\text{int}} = 0.0241$]	3636 [$R_{\text{int}} = 0.0506$]
No. of observed reflections	9245	2913
No. of variables	723	250
R	0.0580	0.0458
wR	0.1750	0.1678
GOF	1.015	1.018
Largest diff. peak*(hole) (e Å^{-3})	1.899 (−1.140)	0.737 (−0.610)

Note. *Largest peak(hole) in difference Fourier map.
$R = \sum||F_o|-|F_c||/\sum|F_o|$ $wR = \{\sum[w(F_o{}^2 - F_c{}^2)^2] / [\sum w(F_o{}^2)^2]\}^{1/2}$.

this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via w.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

Details of the crystal parameters, data collections, and refinements of complexes **1** and **2** are summarized in Table 1. The selected bond lengths and angles of the two complexes are listed in Tables 2 and 3. The hydrogen bond geometry for complexes **1** and **2** (Å,°) is shown in Tables 4 and 5, respectively.

Table 2. Selected bond lengths (Å) and angles (°) of complex **1**

	Zn(1)-N(1) 2.058(2)	Zn(1)-N(4) 2.060(2)	Zn(1)-N(2) 2.066(2)
Zn(1)-N(3)	2.070(2)	Zn(1)-O(1)	2.129(2)
N(1)-Zn(1)-N(4)	88.84(9)	N(1)-Zn(1)-N(2)	89.48(9)
N(4)-Zn(1)-N(2)	161.60(9)	N(1)-Zn(1)-N(3)	166.35(9)
N(4)-Zn(1)-N(3)	88.82(9)	N(2)-Zn(1)-N(3)	88.51(9)
N(1)-Zn(1)-O(1)	96.23(9)	N(4)-Zn(1)-O(1)	99.29(9)
N(2)-Zn(1)-O(1)	99.11(9)	N(3)-Zn(1)-O(1)	97.42(9)

Complex **1** is a zinc nitrate complex with a porphyrin ligand which contains four pyrrole groups and four pyridyl groups. The structure of **1**, illustrated in Fig. 1, crystallized in the triclinic system with space group $P-1$. There are two molecules $[H_4ZnL(H_2O)]^{4+}(NO_3)_4(CH_4O)(H_2O)_2$ in one unit cell. The central zinc ion is bound in the cavity of the ligand and every Zn^{2+} ion is coordinated by five atoms, four nitrogen atoms (N(1), N(2), N(3), and N(4)) from the four pyrrole groups of the ligand and one oxygen atom from a coordinated water molecule (O(1)), forming an irregular square pyramidal ZnN_4O structure as it is determined by the angles among the nitrogen, oxygen atoms and the zinc central ions (Fig. 1). The average bond length of the central zinc ion and the four nitrogen atoms is 2.064 Å in a range of 2.058–2.070 Å, shorter than that of the central ion and the coordinated oxygen atom (2.129(2) Å), indicating that the bound zinc ion has a stronger coordination with the four nitrogen atoms of the ligand in comparison with the oxygen atom because of the structure of the ligand. These values also show that the bond lengths of Zn(1) and these nitrogen atoms are close rather than equal, meaning that the zinc ion is not located in the symmetric center of the ligand. The ligand binds just one zinc ion in its cavity and its four pyridyl groups are protonated by four nitrate counterions from the zinc ion of this molecule and that of complex **2**. The four pyridyl groups are not coordinated to any zinc ion because of the protonation.

This irregular polyhedron ZnN_4O was found in several zinc porphyrin complexes, in which, the coordinated second ligand is water, ethanol or DMF [29–33]. In those complexes, the Zn—N bond lengths are also variable and the range is 2.048–2.079 Å (average 2.061 Å), 2.065–2.069 Å (2.067 Å), 2.052–2.071 Å (2.059 Å), 2.054–2.066 Å (2.060 Å), and 2.066–2.093 Å (2.078 Å), respectively. The range of average bond length of Zn—N in **1** is in the middle of the sequence of those in the reported structures. The variations of the bond lengths might be caused by the differences of structures of the complexes or

Table 3. Selected bond lengths (Å) and angles (°) for complex **2**

	Zn(1)-N(1) 2.066(3)	Zn(1)-N(2) 2.079(3)	Zn(1)-N(3) 2.341(3)
N(1)A-Zn(1)-N(1)	180.00(15)	N(1)A-Zn(1)-N(2)	91.40(13)
N(1)-Zn(1)-N(2)	88.60(13)	N(2)-Zn(1)-N(2)A	180.00(17)
N(1)-Zn(1)-N(3)A	87.26(12)	N(2)-Zn(1)-N(3)A	95.95(12)
N(1)-Zn(1)-N(3)	92.74(12)	N(2)-Zn(1)-N(3)	84.05(12)
N(3)A-Zn(1)-N(3)	180.00(12)		

Table 4. Hydrogen bond geometry of the complex **1** (Å,°)

D—H—A	D—H	H–A	D–A	D—H–A
O(1)—H(1E) ..O(9)	0.85	2.24	2.8402	128
O(1)—H(1E) ..O(13)	0.85	2.43	2.8836	114
O(1)—H(1F) ..O(7a)	0.85	1.92	2.7684	174
N(5)—H(5C) ..O(61)	0.86	1.91	2.7541	166
N(6)—H(6C) ..O(17b)	0.86	2.14	2.7955	133
N(6)—H(6C) ..O(50**b**)	0.86	2.33	2.9626	131
N(7)—H(7C) ..O(60c)	0.86	1.82	2.6514	162
N(8)—H(8C) ..O(9d)	0.86	1.98	2.8058	161
N(8)—H(8C) ..O(12e)	0.86	1.97	2.7840	157
N(8)—H(8C) ..O(13d)	0.86	2.15	2.8723	141
N(8)—H(8C) ..N(13d)	0.86	2.43	3.2620	163
O(60)—H(60A) ..O(65b)	0.93	2.32	2.6472	100
O(60)—H(60B) ..O(2f)	0.85	2.16	2.7902	130
O(65)—H(65E) ..O(3)	0.85	2.40	2.9382	121
C(2)—H(2A) ..O(3c)	0.93	2.54	3.4459	163
C(7)—H(7A) ..O(5a)	0.93	2.58	3.3621	142
C(7)—H(7A) ..O(6a)	0.93	2.55	3.4424	160
C(9)—H(9A) ..O(6g)	0.93	2.33	3.0798	137
C(10)—H(10A) ..O(7g)	0.93	2.55	3.4337	158
C(101)–H(10D) ..N(6b)	0.96	2.16	3.0876	163
C(101)–H(10F) ..O(51)	0.96	2.43	2.7697	100
C(101)–H(10F) ..O(60b)	0.96	1.96	2.6516	127
C(13)—H(13A) ..O(15h)	0.93	2.44	3.1841	137
C(17)—H(17A) ..O(12)	0.93	2.57	3.0703	114
C(18)—H(18A) ..O(11i)	0.93	2.54	3.1989	128
C(19)—H(19A) ..O(17)	0.93	2.35	3.1033	137
C(19)—H(19A) ..O(51)	0.93	2.55	3.2683	134
C(20)—H(20A) ..O(11)	0.93	2.53	3.4618	175
C(23)—H(23A) ..O(65b)	0.93	2.59	3.4137	148
C(27)—H(27A) ..O(2f)	0.93	2.38	3.1170	137
C(28)—H(28A) ..O(50c)	0.93	2.57	3.0926	116
C(32)—H(32A) ..O(7j)	0.93	2.57	3.2242	127
C(38)—H(38A) ..O(11k)	0.93	2.59	3.0804	114
C(39)—H(39A) ..O(4a)	0.93	2.44	3.2565	147

Notes. Symmetry codes: (a) $1-x$, $1-y$, $-z$; (b) $-x$, $1-y$, $1-z$; (c) x,y, $-1+z$; (d) $1-x$, $-y$, $-z$; (e) $2-x$, $-y$, $-z$; (f) $1-x$, $1-y$, $1-z$; (g) $2-x$, $1-y$, $-z$; (h) $1-x$, $-y$, $1-z$; (i) $1+x$, y,z; (j) $-1+x$, y,z; (k) $-x$, $1-y$, $-z$.

the coordinated auxiliary ligands (water, ethanol, or DMF), since the four pyridyl groups in the two examples are coordinated to four silver ions [31] or four cobalt ions [33].

Single crystal X-ray analysis illustrates that **2** is an interesting polymeric metallamacrocyclic complex as shown in Fig. 2. It crystallized in centrosymmetric space group and the asymmetric unit presents half of the molecule because of the symmetry of the molecule. There is only one crystallographic independent Zn^{2+} ion and it is coordinated

Table 5. Hydrogen bond geometry of the complex **2** (Å,°)

D−H—LA	D−H	H—LA	D—LA	D−H—LA
O(1)−H01E ..O(1a)	0.85	2.27	2.8452	126
O(1)−H01F ..N(4b)	0.85	1.97	2.7982	166
O(2)−H02E ..O(1)	0.85	1.96	2.6351	135
C(5)−H5B ..O(2)	0.93	2.39	3.2863	163

Notes. Symmetry codes: (a) $y, -x+y, -z$; (b) $x, y, -1+z$.

by six nitrogen atoms, four from the four pyrrole groups at the ligand and two from the two neighbouring ligand, in a octahedronal ZnN_6 geometry. The average bond length of the central zinc ion and the four nitrogen atoms from the four pyrrole groups of the ligand is 2.073 Å in a range of 2.066–2.079 Å, shorter than that of the central ion and the two coordinated nitrogen atoms from the two pyridyl groups at the two neighbouring ligands (2.341(3) and 2.341(3) Å, respectively), indicating that the bound zinc ion has a stronger coordination with the four nitrogen atoms of the ligand in comparison with the two nitrogen atoms from the two neighboring ligands. Every ligand shows a $\eta1$–$\eta1$–$\eta4$–$\mu3$ coordination mode to bind one zinc ion in its cavity as a tetradentate ligand and coordinate to other two

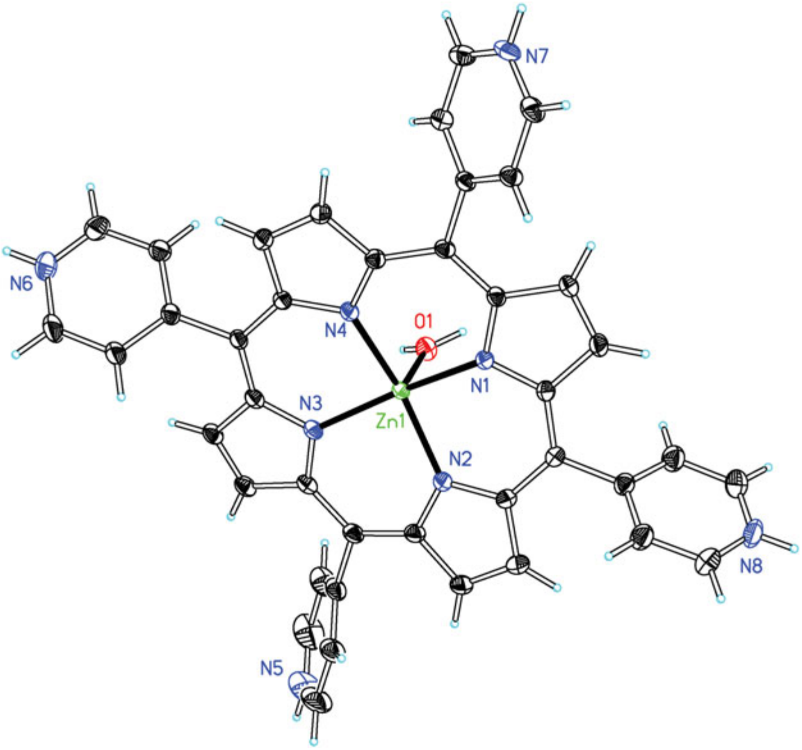

Figure 1. Thermal ellipsoid plot, drawn at the 50% probability level, of $[H_4ZnL(H_2O)]^{4+}(NO_3)_4(CH_4O)(H_2O)_2$ (**1**) with atomic numbering scheme.

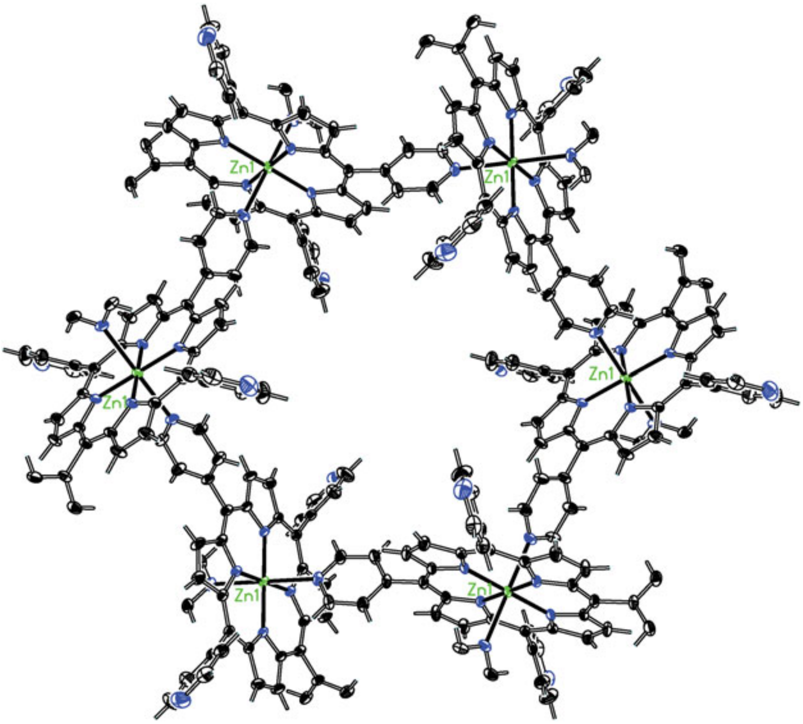

Figure 2. Thermal ellipsoid plot, drawn at the 50% probability level, of $\{[ZnL]{\cdot}CH_4O{\cdot}2H_2O\}_n$ (**2**) with metal ion numbering scheme.

zinc ions bound in the cavities of two neighbouring ligands by its two pyridyl groups in the *trans*-positions as a monodentate ligand. The distances between every two of the three zinc atoms coordinated by one ligand are 10.014, 10.014, and 20.028 Å, respectively. By such a conformation, the structure extends into a three dimensional metallic polymer.

The most striking feature of **2** is that its structure is built from two interesting metallacycle units. Six neighbouring zinc atoms constitute a six-numbered ring with ZnL—ZnL—ZnL—ZnL—ZnL—ZnL subnetwork in a chair structure with a side length of 10.014 Å, which is the distance between every two neighboring zinc atoms. The distances between every zinc atom and other three zinc atoms at diagonal positions of the six-numbered ring are 16.489, 19.292, and 16.489 Å, respectively. Besides, among the lines of these six-numbered rings, there are lines of triangles, which are formed by three neighboring zinc atoms. These triangles are equilateral because the symmetry of the structure and they are an extended helical ZnL—ZnL—ZnL subnetwork with the side length of 10.014 Å and a distance of 9.321 Å of the two neighboring zinc atoms in the helical direction, as shown in Fig. 3. Two similar structures were reported [34,35], in which one acetic acid or a chloroform molecule is included in the structures as the guests, respectively. A square-grid coordination networks of zinc(II) with the ligand in its clathrate with two guest molecules of 1,2-dichlorobenzene was also reported [36].

The structure of **1** presents no intermolecular π–π interactions but several X-H . . . Cg (π-Ring) interactions, between several hydrogen atoms at the pyrrole or pyridyl groups of the ligand and their neighboring rings. Three kinds of Y-X . . . Cg (π-Ring) interactions are also observed in the structure between the three oxygen atoms at the nitrates (O4, O5,

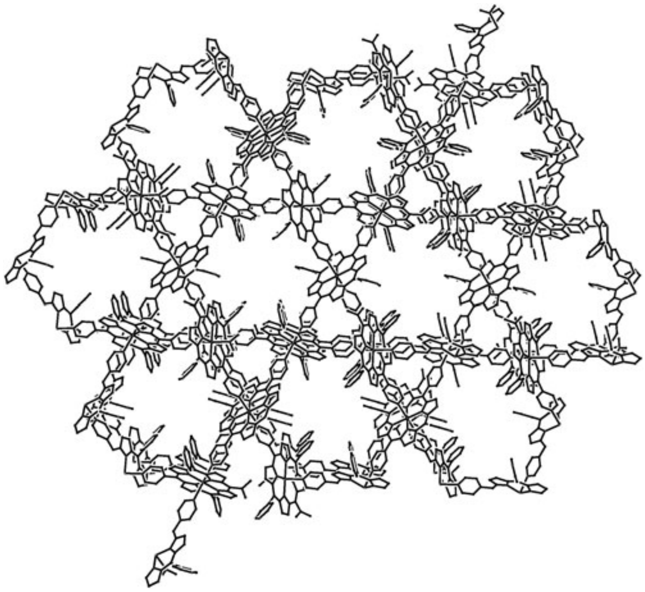

Figure 3. The packing of $\{[ZnL]\cdot CH_4O\cdot 2H_2O\}_n$ (**2**).

and O7) and the three neighboring rings constituted by N5—C18—C17—C16—C20—C19, N8—C8—C7—C6—C10—C9, and N1—C1—C2—C3—C4 with atom-centroid distances (X—Cg) of 3.1822, 2.9885, and 3.3765 Å, respectively. Many hydrogen bonds exist in the structure (see Table 4), between hydrogen atoms at water, methanol, the protonated pyridyl, or the carbon atoms of the pyrrole, pyridyl groups of the ligand, since several guests molecules are contained in the structure, including one coordinated water, two uncoordinated water and one methanol. Two nitrate counterions are in disorder and one of them occupies two positions. In **2**, one water and one methanol molecules are contained in the lattice of the structure as guests and four kinds of hydrogen bonds present in the structure, between a hydrogen at the water and another neighbouring water, methanol and the water molecule, methanol and one pyridyl group of the ligand, and a pyridyl and methanol (see Table 5). Several short ring interactions (Cg–Cg distances) exist in the structure in the range of 3.82–5.84 Å, along with several X-H... Cg (π-Ring) interactions between the hydrogen atoms at the pyrrole or pyridyl groups of the ligand and their neighbouring rings in the range of 2.50–3.34 Å (H..Cg distances), which also help to consolidate the three-dimensional structure.

4. Conclusion

5,10,15,20-tetra(4-pyridyl)porphyrin appears as a convenient N,N,N,N-tetrapodal or N,N,N,N,N,N-hexapodal ligand source towards the easy synthesis of zinc complexes with interesting structures. Two Zn(II) complexes with such a ligand were obtained by a simple one-port reaction with zinc nitrate. The zinc complexes thus prepared show interesting structures. The work provides good candidates for further synthetic and structural studies and deserves to be extended to other substituted macrocyclic zinc complexes on attempting to study substituent effects and to establish relationships.

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