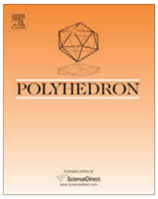
Polyhedron 28 (2009) 3907–3914

Contents lists available at ScienceDirect

Polyhedron

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



Metal complexes of tetradentate and pentadentate *N*-*o*-hydroxybenzamido-*meso*-tetraphenylporphyrin ligand: M(*N*-NCO(*o*-OH)C_6H_4-tpp) (M = Zn^{2+}, Ni^{2+}, Cu^{2+}) and M′(*N*-NCO(*o*-O) C_6H_4-tpp) (M′ = Mn^{3+}) (tpp = 5, 10, 15, 20-tetraphenylporphyrinate)

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ARTICLE INFO

Article history:
Received 24 August 2009
Accepted 1 September 2009
Available online 18 September 2009

Keywords:
Manganese porphyrin
Zero field splitting
EPR spectra
Magnetic susceptibility

ABSTRACT

The crystal structures of *N*-*o*-hydroxybenzimido-*meso*-tetraphenylporphyrinatozinc(II) toluene solvate [Zn(*N*-NCO(*o*-OH)C_6H_4-tpp)·$C_6H_5CH_3$; **4**·$C_6H_5CH_3$], *N*-*o*-hydroxybenzimido-*meso*-tetraphenylporphyrinatonickel(II) chloroform solvate [Ni(*N*-NCO(*o*-OH)C_6H_4-tpp)·0.6$CHCl_3$; **5**·0.6 $CHCl_3$], *N*-*o*-hydroxybenzimido-*meso*-tetraphenylporphyrinatocopper(II) toluene solvate [Cu(*N*-NCO(*o*-OH)C_6H_4-tpp)·$C_6H_5CH_3$; **6**·$C_6H_5CH_3$] and *N*-*o*-oxido-benzimido-*meso*-tetraphenylporphyrinato(-κ^4,N^1,N^2,N^3,N^5,κO^2) manganese (III) methylene chloride·methanol solvate [Mn(N-NCO(*o*-O)C_6H_4-tpp)·CH_2Cl_2·MeOH; **8**·CH_2Cl_2·MeOH] were established. The coordination sphere around Zn^{2+} ion in **4**·$C_6H_5CH_3$, (or Ni^{2+} ion in **5**·0.6 $CHCl_3$ or Cu^{2+} ion in **6**·$C_6H_5CH_3$) is a distorted square planar (DSP) whereas for Mn^{3+} in **8**·CH_2Cl_2·MeOH, it is a distorted trigonal bipyramid (DTBP) with O(1), N(1) and N(3) lying in the equatorial plane for **8**·CH_2Cl_2·MeOH. The g value of 8.27 measured from the parallel polarization of X-band EPR spectra at 293 K is consistent with the high-spin mononuclear manganese(III) (S = 2) in **8**. The magnitude of axial (D) zero-field splitting (ZFS) for the mononuclear Mn(III) in **8** was determined approximately as 3.0 cm^{-1} by the paramagnetic susceptibility measurements and conventional EPR spectroscopy.

1. Introduction

Previously, we reported the two-stage formation of (*N*-*o*-chlorobenzamido-*meso*-tetraphenylporphyrinato)zinc (II) (**1**) [1]. Compound **1** is a zinc complex of *N*-NHCO(*o*-Cl)C_6H_4-Htpp (**2**) (Scheme 1). In **2**, when the ortho chlorine is replaced by hydroxyl ligand, a new free aminated porphyrin is formed namely *N*-*o*-hydroxy benzamido-*meso*-tetraphenylporphyrin [*N*-NHCO(*o*-OH)C_6H_4-Htpp; **3**] (Fig. 1a) [2]. Compound **3** is a N-substituted porphyrin [3]. A carbonyl group in the ortho position of **3** shifts the phenolic proton absorption to the range of about δ 12.0–δ 10.0 ppm in CD_2Cl_2 because of intramolecular hydrogen bonding [4]. Thus, compound **3** shows a peak at about δ 11.95 in CD_2Cl_2 at 20 °C almost completely invariant with the concentration. It is worth to note the structure of porphrin ligand **3** as the presence of hydroxyl ligands plays a role in somewhat artificially increasing the coordination-number when **3** is coordinated to the metal ions. We explored coordination properties of *N*-*o*-hydroxy benzamido-*meso*-tetraphenylporphyrin. A thorough literature review reveals that there is no report on the metal complex of **3**. Depending on the metal ion choice two principal structural motifs have been detected. In the first case [copper(II), zinc(II), Ni(II)] the N-substituted porphyrin acts as tetradentate macrocycle using three pyrrolic and one amidate nitrogen (Scheme 2).The trivalent metal ions [gallium(III), manganese(III)] preserve the pattern of the equatorial coordination but in addition the apical position is occupied by the phenoxy moiety of the N-substituent (Scheme 2).

The complexation of Zn^{2+}, Ni^{2+} and Cu^{2+} classified as divalent B acids into **3** retains the intramolecular hydrogen bonding and

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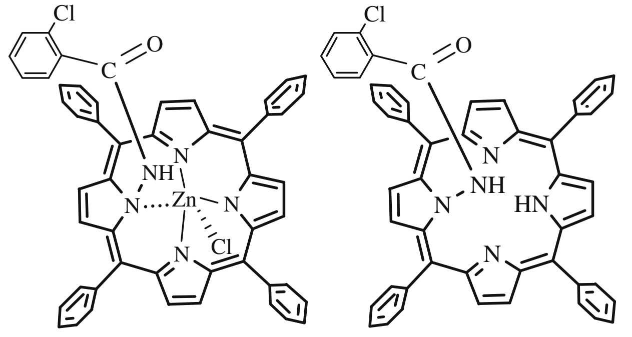
doi:10.1016/j.poly.2009.09.009



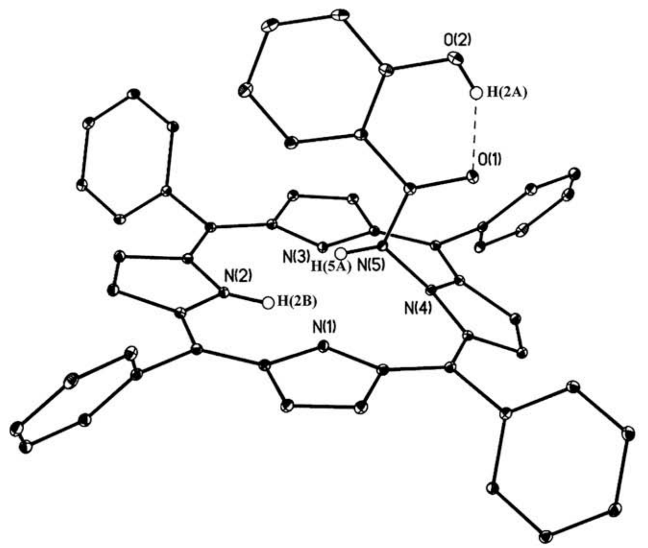
1

2

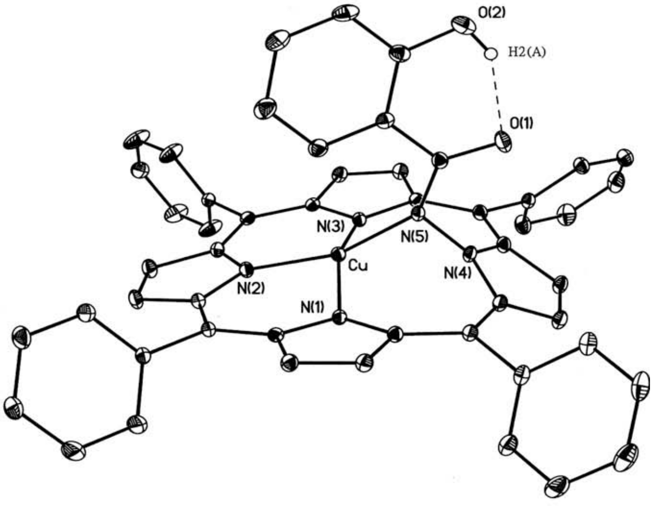
Scheme 1.

forms four-coordinate zinc(II) (**4**), nickel(II) (**5**) and copper(II) (**6**) complexes (Scheme 2) [5–7].[1]

Moreover for Ga^{3+} and Mn^{3+} with the coordination-number (CN) = 5 and a higher *Z* are trivalent E acids [6]. A strongly attractive electrostatic interaction between the gallium [Ga^{3+}] (or Mn^{3+}) and oxygen atom [i.e., $O(2)^-$] in **7** [or $O(1)^-$ in **8**] destroy intramolecular hydrogen bonding O(1)· · ·H(2A) in **3** and rotate (*o*-O)BA ligand along the C(45)–C(46) bond in **7** [or C(50)–C(51) bond in **8**] and finally stabilize the five-coordinate gallium(III) (**7**) [or manganese (III) (**8**)] complexes (Scheme 2) [2]. The lack of study on metal complexes of ligand **3** prompted us to undertake the synthesis and structural investigations of the zinc(II), nickel(II), copper (II) and manganese(III) complexes. In this paper, we describe the X-ray structural investigation on the metallation of **3** leading to the zinc complex of *N*-*o*-hydroxybenzimido-*meso*-tetraphenylporphyrinatozinc(II) toluene solvate [Zn(*N*-NCO(*o*-OH)C_6H_4-tpp)·$C_6H_5CH_3$; **4**·$C_6H_5CH_3$], nickel complex of *N-o-hydroxybenzimido-meso*-tetraphenylporphyrinatonickel(II) chloroform solvate [Ni(*N*-NCO(*o*-OH)C_6H_4-tpp)·0.6 $CHCl_3$; **5**·0.6 $CHCl_3$], copper complex of *N*-*o*-hydroxybenzimido-*meso*-tetraphenylporphyrinatocopper(II) toluene solvate [Cu(*N*-NCO(*o*-OH)C_6H_4-tpp)·$C_6H_5CH_3$; **6**·$C_6H_5CH_3$] and manganese(III) complex of *N*-*o*-oxido-benzimido-*meso*-tetraphenylporphyrinato -($-\kappa^4$,N^1,N^2,N^3,N^5,κO^2) manganese (III) methylene chloride·methanol solvate [Mn(*N*-NCO(*o*-O)C_6H_4-tpp)·CH_2Cl_2·MeOH; **8**·CH_2Cl_2·MeOH]. The reported diamagnetic compound **7** is used as a diamagnetic correction for paramagnetic complex **8** in the solid-state magnetic susceptibility measurements [2,7]. We also focus on the details of manganese (III) electronic structure of **8**. Studies of temperature dependence of magnetic susceptibility and effective moment show that S = 2, is the ground state for high-spin mononuclear Mn^{3+} in **8** at 20 °C. Application of the Bleaney–Bowers equation permits evaluation of D and an average *g* value for powder samples of **8** [8].



(a) **3**



(b) **6**·$C_6H_5CH_3$

Fig. 1. Molecular configuration and atom-labeling scheme for (a) **3** [2] and (b) [Cu(*N*-NCO(*o*-OH)C_6H_4-tpp)·$C_6H_5CH_3$; **6**·$C_6H_5CH_3$], with 30% thermal ellipsoids. Hydrogen atoms and solvent $C_6H_5CH_3$ for **6**·$C_6H_5CH_3$ are omitted for clarity.

2. Experimental

2.1. Zn(**N**-NCO(o-OH)C_6H_4-tpp) (**4**)

A mixture of **3** (0.051 g, 0.068 mmol) in CH_2Cl_2 (20 cm^3) and $Zn(OAc)_2$·$2H_2O$ (0.05 g, 0.228 mmol) in MeOH (5 cm^3) was refluxed at 60 °C for 3 h. After concentration, the residue was dissolved in CH_2Cl_2 and dried with anhydrous Na_2SO_4 and filtered [2,3]. The filtrate was concentrated yielding purple solid which was again dissolved in CH_2Cl_2 and layered with MeOH to get purple solid of **4**·$C_6H_5CH_3$ (0.043 g, 0.053 mmol, 78%). Compound **4**·$C_6H_5CH_3$ was dissolved in toluene and layered with hexane to afford purple crystals for single-crystal X-ray analysis. ^1H NMR (599.95 MHz, CD_2Cl_2, 20 °C): δ 11.49 [s ($\Delta\nu_{1/2}$ = 1 Hz, OH], where (*o*-OH)BA = *o*-hydroxybenzamido ligand; 9.09 [d, $H_\beta(2,13)$, $^{3J(\mathrm{H-H})}$ = 4.8 Hz]; 8.92 [s, $H_\beta(7,8)$]; 8.92 [d, $H_\beta(3,12)$, ^3J(H–H) = 3.6 Hz]; 7.79 [s, $H_\beta(17,18)$]; 8.40 [d, *o*-H(22,32), ^3J(H–H) = 6.6 Hz]; 8.11 [d, *o*-H(26,28), ^3J(H–H) = 7.2 Hz];11.49 [s, (*o*-OH)BA-OH]; 6.16 [t, (*o*-OH)BA-Ph-H_4,

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[1] Zhang suggested a scale for the Lewis acid strengths that has been calculated from the dual parameter equation $Z = \frac{z}{r_k^2} - 7.7\chi_z + 8.0$ [5,6]. One parameter, $\frac{z}{r_k^2} = P =$ (polarizing power), where *z* is the charge number of the atomic core and r_k is the ionic radius, is related to electrostatic force. Another parameter, the electronegativity of elements in valence states, χ_z is related to covalent bond strength. The metal ions in which there is clear dominance by the electrostatic force $\frac{z}{r_k^2}$ have *Z* values higher than 0.66. They call these acids large electrostatic acids or simply E acids. The metal ions in which there is clear dominance by the electronegativity χ_z, i.e. with a large covalent property and have *Z* values lower than zero. They call these acids large covalent acids, or simply C acids [6]. The metal ions lying between E and C acids and having *Z* values higher than zero and lower than 0.66 are border acids, or simply B acids. Although scales by Zhang which have been less widely used [6], we tried to coordinate the metal ions with B and E acids to ligand **3** and figure out the structural parameters that control the formation of these four-coordinate and five-coordinate porphyrin metal complexes. The cations were selected on the basis of differences in *Z* of the metal cations. The cations selected were Cu^{2+} (B acid), Ni^{2+} (B acid), Zn^{2+} (B acid), Ga^{3+} (E acid) and Mn^{3+} (E acid), for which *Z* = 0.177, 0.293, 0.656, 1.167 and 1.698, respectively.