

Structural and electrochemical properties of β -tetrabromo-*meso*-tetrakis(4-alkyloxyphenyl)porphyrins and their metal complexes

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Abstract. Crystal structure of 2,3,12,13-tetrabromo-5,10,15,20-tetrakis(4-butyloxy phenyl)porphinato copper(II) tetrahydrofuran solvate was examined and it features enhanced non-planar distortion of the porphyrin ring. The normal coordinate structural decomposition (NSD) analysis for the out-of-plane displacement of atoms of the macrocyclic ring in $\text{CuT}(4\text{-C}_n\text{P})\text{PBr}_4$ ($n = 4, 6$) indicates mainly saddled distortion combined with small contribution from wave conformation. The electrochemical studies on $\text{MT}(4\text{-C}_n\text{P})\text{PBr}_4$ ($M = 2\text{H}, \text{Cu(II)}, \text{Zn(II)}$) revealed cathodic shift in redox potentials in contrast to the corresponding brominated porphyrins, MTPPBr_4 . This is perhaps due to non-planarity of the porphyrin ring and the positive inductive effect of the alkyloxy groups.

Keywords. Porphyrins; metalloporphyrins; substituted porphyrins; crystal structure; electrochemical redox potentials.

1. Introduction

Non-planar porphyrins are of continued interest owing to their use in models of naturally occurring tetrapyrrole pigments.^{1–3} Besides, these highly functionalized porphyrins exhibit unique physico-chemical properties. Porphyrins with varying number of similar substituents at the β -pyrrole positions of MTPPs have been reported in the literature.⁴ Notably, halogenated high-valent metalloporphyrins serve as robust catalysts for the oxidative transformation of organic substrates in presence of strong oxygen donors.⁵ The mixed substitution at the β -pyrrole positions of the MTPPs showed interesting optical absorption, electrochemical redox and structural properties.^{6–9} The mixed substitution at the β -pyrrole positions produce modulation of the electrochemical redox and stereochemical properties of the porphyrin ring.⁸

Porphyrins are the potentially attractive molecular synthons for various material applications because of their large extended π -system, synthetic versatility, diverse coordination chemistry and high thermal stability. In recent years, there has been growing interest in various material applications of functionalized porphyrins¹⁰. In our previous report, we

examined the effect of non-planarity of the macrocyclic ring on the liquid crystalline behaviour of tetrabrominated tetraalkyloxyphenylporphyrins.¹¹ The present work reports the effect of antipodal β -pyrrole bromination on the stereochemistry of the 2,3,12,13-tetrabromo-5,10,15,20-tetrakis(4-alkyloxy phenyl)porphinato copper(II) and electrochemical redox properties of a series of alkoxy porphyrins (figure 1).

2. Experimental

Free base porphyrins, 2,3,12,13-tetrabromo-5,10,15,20-tetrakis(4-*n*-alkyloxyphenyl)porphyrins ($\text{H}_2\text{T}(4\text{-C}_n\text{P})\text{PBr}_4$) ($n = 4, 8$ and 10) and their metal ($\text{Cu(II)}, \text{Zn(II)}$) complexes were prepared using reported procedures.¹¹ All the solvents employed in this study were of analytical grade and used as received.

3. Methods

Single crystal X-ray structure data collections were performed on a Bruker AXS Kappa Apex II CCD diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystals were coated with inert oil, mounted on a glass capillary, transferred to the cold nitrogen gas stream of the diffrac-

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tometer, and crystal data was collected at 173 K. The reflections with $I > 2\sigma(I)$ were employed for structure solution and refinement. The SIR92¹² (WINGX32) program was used for solving the structure by direct methods. Successive Fourier synthesis was employed to complete the structures after full matrix least-squares refinement on $|F|^2$ using SHELXL97¹³ software. Fourier syntheses led to the location of all the non-hydrogen atoms. For the structure refinement, all data were used including negative intensities. Non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms in the porphyrin structure could be located in the difference map. However, the hydrogen atoms were geometrically relocated at chemically meaningful positions and were given riding model refinement. Crystals of $\text{CuT}(4\text{-C}_n\text{P})\text{PBr}_4$ ($n = 4, 6$) were grown at room temperature by diffusion of methanol vapour to the solution of the porphyrin in tetrahydrofuran over a period of five days.

Crystal structure of $\text{CuT}(4\text{-C}_4\text{P})\text{PBr}_4\cdot\text{THF}$ complex: $\text{C}_{64}\text{H}_{64}\text{N}_4\text{O}_5\text{Br}_4\text{Cu}$, Mr = 1352.37, crystal dimensions: $0.3 \times 0.2 \times 0.2$ mm, brown, monoclinic, space group, $P2_1/c$, $a = 18.5355$ (11) Å, $b = 16.8498$ (10) Å, $c = 18.0802$ (10) Å, $\beta = 97.674$ (3)°, $v = 5596.2$ (6) Å³, $Z = 4$, $d_{\text{calc}} = 1.605$ mg/m³, $(\text{MoK}\alpha) = 0.71073$ Å, $\theta_{\text{max}} = 27.7^\circ$, $R_1 = 0.0804$; $W_{R2} = 0.2090$ for 62069, 9610 unique reflections.

Crystal structure of $\text{CuT}(4\text{-C}_6\text{P})\text{PBr}_4\cdot\text{THF}$ complex: $\text{C}_{72}\text{H}_{80}\text{N}_4\text{O}_5\text{Br}_4\text{Cu}$, Mr = 1464.58, crystal dimensions: $0.26 \times 0.23 \times 0.21$ mm, brown, monoclinic, space group, $P2_1/c$, $a = 19.413$ (3) Å, $b = 17.559$ (3)

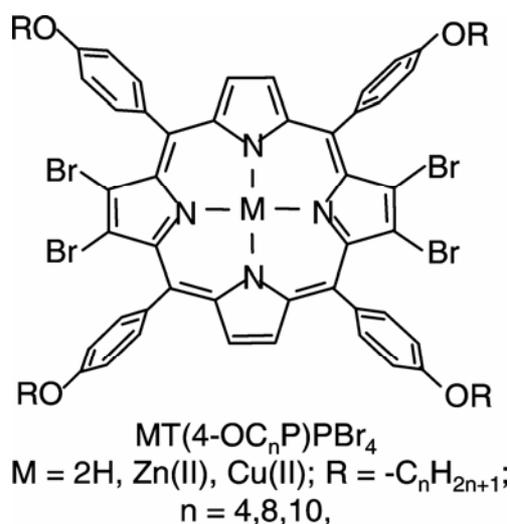


Figure 1. Chemical structures of brominated alkyloxy-porphyrins and their metal complexes.

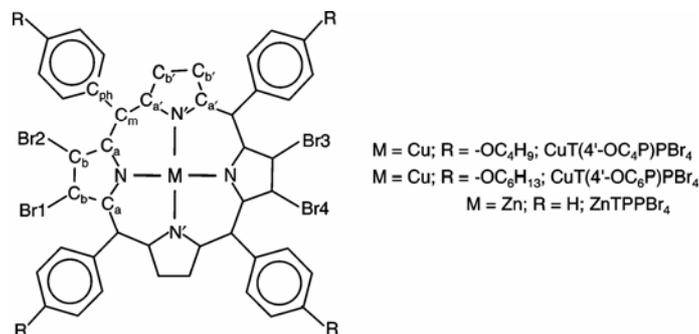
Å, $c = 18.765$ (3) Å, $\beta = 91.917$ (7)°, $v = 6393.3$ (17) Å³, $Z = 4$, $d_{\text{calc}} = 1.522$ mg/m³, $(\text{MoK}\alpha) = 0.71073$ Å, $\theta_{\text{max}} = 26.5^\circ$, $R_1 = 0.0820$; $W_{R2} = 0.2179$ for 58795, 11524 unique reflections.

The crystallographic data (excluding structure factors) of the $\text{CuT}(4\text{-C}_4\text{P})\text{PBr}_4\cdot\text{THF}$ and $\text{CuT}(4\text{-C}_6\text{P})\text{PBr}_4\cdot\text{THF}$ complexes have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 663139 and CCDC 639835, respectively. Copies of the data can be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Cyclic voltammetric measurements on the porphyrins were performed using CH instruments (USA) model 660B. The three electrode electrochemical cell assembly employed is described elsewhere.^{8a} The concentrations of the porphyrins employed were ~ 1.0 mM. All the measurements were performed at 298 K in CH_2Cl_2 under argon atmosphere using 0.1 M tetrabutylammonium hexafluorophosphate, TBAHFP as the supporting electrolyte.

4. Results and discussion

The crystal structure of non-mesogenic, $\text{CuT}(4\text{-OC}_4\text{P})\text{PBr}_4$ and mesogenic, $\text{CuT}(4'\text{-OC}_6\text{P})\text{PBr}_4$ complexes have been examined. The ORTEP diagrams of both complexes showing the top, side views and also the mean plane displacement of atoms are shown in figures 2 and 3. Both the $\text{Cu}(\text{II})$ -complexes showed four coordinate geometry with a lattice THF solvate. The selected bond lengths and geometrical parameters of the $\text{CuT}(4\text{-OC}_n\text{P})\text{PBr}_4\cdot\text{THF}$ ($n = 4, 6$) structures are listed in table 1. In our earlier report, we have examined the crystal structure of $\text{CuT}(4\text{-OC}_6\text{P})\text{PBr}_4\cdot\text{THF}$ complex.¹¹ For comparison, the reported $\text{ZnTPPBr}_4(\text{CH}_3\text{OH})\cdot\text{DMF}$ structure is also incorporated to the table 1. Interestingly, Cu-N bonds are longer than the $\text{Cu-N}'$ bond distances indicating the decreased electron density of the pyrrolic nitrogens bearing β -pyrrole bromo groups. The observed core Cu-N bond distances are comparable to the data reported for CuTPP (1.981 (7) Å)¹⁴, 2, 3, 7, 8, 12, 13, 17, 18-octabromo-5, 10, 15, 20-tetrakis (2, 3, 4, 5, 6-pentafluorophenyl) porphyrinato copper(II) (1.971 (6) Å)¹⁵ and 2, 3, 7, 8, 12, 13, 17, 18-octabromo-5, 10, 15, 20-tetrakis(2,6-dibromo-3,5-dimethoxy phenyl)porphyrinato copper(II)

Table 1. Selected bond lengths and geometrical parameters of β -brominated tetraalkoxyphenylporphyrins.

	CuT(4-OC ₄ P)PBr ₄ ·THF	CuT(4-OC ₆ P)PBr ₄ ·THF	ZnTPPBr ₄ (CH ₃ OH)·DMF ^a
Bond length (Å)			
M–N	2.040 (8)	2.030 (6)	2.115 (3)
M–N'	1.965 (8)	1.954 (7)	2.026 (3)
N–C _a	1.379 (12)	1.379 (10)	1.375 (4)
N'–C _a '	1.383 (12)	1.380 (10)	1.370 (4)
C _a –C _b	1.452 (14)	1.436 (11)	1.448 (5)
C _a '–C _b '	1.440 (14)	1.422 (11)	1.446 (4)
C _b –C _b	1.355 (14)	1.367 (12)	1.350 (5)
C _b '–C _b '	1.331 (14)	1.349 (11)	1.344 (5)
C _a –C _m	1.388 (14)	1.413 (11)	1.409 (4)
C _a '–C _m	1.389 (14)	1.391 (11)	1.401 (5)
ΔC _b (Å)	0.57	0.59	0.40
Bond angle (°)			
C _a –N–C _a	108.5 (8)	105.7 (7)	108.2 (3)
C _a '–N'–C _a '	105.9 (8)	106.3 (6)	106.8 (3)
C _a –C _m –C _{Ph}	120.5 (9)	121.2 (8)	119.7 (3)
C _a '–C _m –C _{Ph}	116.3 (9)	115.8 (7)	115.8 (3)
C _a –C _b –Br1(Br4)	129.5 (7)	131.4 (7)	129.6 (3)
C _a –C _b –Br2(Br3)	128.9 (7)	129.5 (8)	129.2 (2)

^aData taken from ref. 18

crowded β -octabrominated tetraarylporphyrins reported in the literature.⁴

In case of CuT(4-OC_nP)PBr₄·THF structures, the peripheral alkoxy groups show some positional disorder for the carbon atoms. In CuT(4-OC₄P)PBr₄ structure, all the four alkyl chains showed a moderately bent structure while in case of CuT(4-OC₆P)PBr₄ structure, the two opposite chains are bent and other two chains show fairly linear geometry. The *meso*-phenyl rings are almost planar with an average dihedral angle of 66.1(2)° and 70.5(2)° to the mean plane of the 24-atom core for CuT(4-OC₄P)PBr₄ and CuT(4-OC₆P)PBr₄ structures, respectively. Moreover, the adjacent bromo groups of the same pyrrole ring are tilted up and down from the mean plane of

the pyrrole rings to prevent steric repulsion between them. In case of CuT(4-OC₄P)PBr₄·THF complex, the intermolecular close contacts show β -pyrrole bromide interaction with the phenyl carbon of the adjacent molecule via C13–Br4...C64 = 3.355(9) Å (C–Br... π) interactions and Br...O (Br3...O5 = 2.949(13) Å) contacts. Similarly, CuT(4-OC₆P)PBr₄·THF complex shows C–H...Br (C31–H31A...Br3 = 2.76 Å) hydrogen bonding and C65–H65B...O4 = 2.45 Å and Br2...O5 = 2.986(12) Å contacts. Such intermolecular contacts are reported in the literature.²¹ The increase in distortion of the porphyrin rings in these systems is possibly arise from the core Cu(II) ion and the intermolecular interactions. Earlier crystal structure of the H₂T(4-OC₄P)PBr₄²²

Table 2. Electrochemical redox potentials^a of tetrabrominated tetra(4-alkyloxy phenyl) porphyrins and their metal complexes.

Porphyrin	Oxidation		Reduction		$\Delta E_{1/2}$ (V)	$Q(0,0)$ (eV) ^c
	I	II	I	II		
H ₂ TPPBr ₄		1060	1160	-900	-1.96	1.81
H ₂ T(4-OC ₄ P)PBr ₄	845	980	-910	-1050	1.76	1.76
H ₂ T(4-OC ₈ P)PBr ₄	840	985	-890	-1020	1.73	1.77
H ₂ T(4-OC ₁₀ P)PBr ₄	840	985	-900	-1040	1.74	1.77
ZnTPPBr ₄	930	1100	-1080	-1300	2.01	2.03
ZnT(4-OC ₄ P)PBr ₄	795	1020	-1070	-1345	1.86	2.05
ZnT(4-OC ₈ P)PBr ₄	785	1010	-1100	-1360	1.88	2.04
ZnT(4-OC ₁₀ P)PBr ₄	800	1015	-1135 ^b	-1330	1.93	2.04
CuTPPBr ₄	1020	1450	-1010	-1240	2.03	2.08
CuT(4-OC ₄ P)PBr ₄	860	1355 ^b	-985	-1080	1.85	d
CuT(4-OC ₈ P)PBr ₄	825	1050	-1060	-1240	1.89	2.06
CuT(4-OC ₁₀ P)PBr ₄	895	1365	-1020 ^b	-1290	1.91	2.06

^aError: ± 10 mV; ^birreversible; $\Delta E_{1/2} = I_{\text{oxn}} - I_{\text{redn}}$; $Q(0, 0)$, longest wavelength band; d, $Q(0, 0)$ band not observable

revealed enhanced distortion when compared to nearly planar H₂TPPBr₄ structure.²³

Electrochemistry of a wide variety of MTPPs bearing β -pyrrole substituents has been reported in the literature.²⁴ The redox potentials of the porphyrin π -system are influenced by the non-planar conformation, core metal ion and the peripheral substituents. In an effort to examine the role of tetraalkyloxy substituents on the electrochemical redox potentials, a few MT(4-OC_nP)PBr₄ (M = 2H, Cu(II), Zn(II)) derivatives have been studied by cyclic voltammetry. Figure 3 shows the cyclic voltammograms of ZnT(4-OC₁₀P)PBr₄ complex. Table 2 lists the electrochemical data for the MT(4-OC_nP)PBr₄ derivatives. Under similar conditions, the corresponding MTPPBr₄ were also examined and the observed potentials of MTPPBr₄ are similar to the reported values.^{18,25,26} MT(4-OC₁₀P)PBr₄s exhibited two successive one-electron electrochemical redox potentials. These potentials are found to be reversible and involve one electron process. Interestingly, the MT(4-OC_nP)PBr₄ derivatives exhibited approximately ~ 50 – 200 mV cathodic shift in the first ring oxidation and 30 – 80 mV in first ring reduction potentials relative to the corresponding MTPPBr₄ derivatives. Cu(II) derivatives showed easier reduction and difficulty in oxidation when compared to corresponding Zn(II) derivatives indicating the role of electronegativity of the core metal ion. The ease of first ring redox potentials may be attributed to the electron donor alkoxy groups at the peripheral posi-

tions and non-planarity of the porphyrin ring. The non-planar conformation^{27,28} of the porphyrin ring and the inductive effect of the alkoxy groups are responsible for the cathodic shift of redox potentials.²⁹ A comparison of $\Delta E_{1/2}$ (HOMO-LUMO gap) from the redox potential data is made with the longest wavelength absorption band ($Q_x(0, 0)$)^{11,30} for the MT(4-OC_nP)PBr₄ ($n = 4, 8, 10$) and the data show reasonably good correlation (table 2).³⁰

5. Conclusions

Crystal structures of CuT(4-OC_nP)Ps ($n = 4, 6$) were examined and they feature significant changes in non-planar conformation of the macrocyclic ring in contrast to the reported ZnTPPBr₄(CH₃OH)•DMF complex. Normal structure decomposition analysis for the out-of-plane displacement on both the complexes features essentially saddled combined with minor wave conformation. The electrochemical redox potentials of brominated alkyloxy porphyrins are cathodic relative to the unsubstituted MTPPBr₄ derivatives. This is perhaps due to the combined effect of non-planarity of the macrocyclic ring and the electron donor alkoxy groups.

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