Structural investigation of 5,10-A_2B_2-type porphyrins – Palladium(II) and zinc(II) complexes of 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin

Authors

Mathias O. Senge[a]* and Monika Zawadzka[a]

[a]School of Chemistry, SFI Tetrapyrrole Laboratory, Trinity Biomedical Sciences Institute, Trinity College Dublin, 152-160 Pearse Street, Dublin, 2, Ireland

Correspondence email: sengem@tcd.ie

Synopsis A comparison of 5,10- and 5,15-dibromoporphyrins indicates differences in the contributions of individual macrocycle distortion modes.

Abstract The analysis of (5,10-dibromo-15,20-bis(4-methylphenyl)porphyrinato)palladium(II) [$C_{34}H_{22}Br_2N_4Pd$] and methanol(5,10-dibromo-15,20-bis(4-methylphenyl)porphyrinato)zinc(II) [$C_{35}H_{26}Br_2N_4OZn$] reveals a small but localized influence of the bromine residues on the macrocycle conformation. A comparison of the 5,10-dibromo substituent pattern with literature data for 5,15-dibromoporphyrins shows similar in-plane distortions in both but a different mix of out-of-plane distortion modes for the different regiochemical arrangements.

1. Introduction

The structural chemistry of porphyrins is one of best investigated areas of coordination chemistry. Many studies are available on metal coordination (Scheidt, 2008), aspects of macrocycle modification (Chmielewski & Latos-Grazynski, 2005), supramolecular chemistry (Beletskaya *et al.*, 2009) and nonplanar systems (Senge, 2006). The latter have been the focus of conformational analyses which highlighted the flexible character of the porphyrins macrocycle, esp. in the case of highly substituted systems; *i.e.* porphyrins with large or sterically hindered substituents. For the simple, symmetric, meso 5,10,15,20-tetrasubstituted porphyrins (A_4-type) several thousand crystal structures are available (Senge, 2000). Yet much less is known about the structural chemistry of porphyrins with few meso substituents or the impact of different regiochemical arrangements thereof. In part, this has been

hampered by the only recently overcome synthetic inaccessibility of components of the A_x- and ABCD-type porphyrins (I) (where ABCD refers to meso substituents) (Senge, 2011).

For example, the structural impact of a 5,10- *versus* a 5,15-disubstitution pattern has not been investigated in detail. This has now become possible with the advent of general syntheses for 5,10-disubstituted porphyrins (Ryppa *et al.*, 2005). These have been used to develop $5,10-A_2-10,20-B_2$-type porphyrins (II) for optical applications due to the altered orientation of the intramolecular dipole moment compared to the well-known $5,15-A_2-10,20-B_2$ systems (III) (Senge *et al.*, 2011; Zawadzka *et al.*, 2013a). Here we use 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin (IV) and its palladium(II) (V) and zinc(II) complex (VI) for a comparative analysis of their structural properties.

2. Experimental

2.1. Synthesis and crystallization

The compounds were prepared *via* metallation of the respective free base (III) (Senge *et al.*, 2011), as described earlier (Zawadzka *et al.*, 2013b). Crystals were grown by liquid diffusion of methanol into a solution of the porphyrins in methylene chloride using crystallization tubes (5 × 200 mm). Crystals formed within two weeks at room temperature. Crystals were handled as outlined by Hope (1994).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Hydrogen atoms, except for the methanol –OH in (VI), were located in a difference map and then treated as riding in geometrically idealized positions, with C-H = 0.95 (aromatic) or 0.98 Å (methyl), and with $U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for the methyl groups, and 1.2 for all other H atoms. For the palladium(II) complex (V) the residual electron density was located close to the metal center. In the refinement of (VI) no hydrogen atom was included for the OH group of the axial methanol molecule. The methyl group exhibited high librational movement.

3. Results and discussion

Views of the molecular structures of the palladium(II) (V) and zinc(II) (VI) porphyrin complexes are shown in Figures 1 and 2, respectively. The structure of the free base (IV) was reported earlier (Senge *et al.*, 2011). Both compounds crystallized in the triclinic space group P-1 with one molecule in the asymmetric unit. The palladium complex is characterized by a typical four-coordinate Pd-center with average Pd-N bond lengths of 2.009(3) Å. The Pd-N21 bond [2.001(6) Å] is slightly shorter than the other three [average: 2.012(6) Å]. A similar situation is encountered in the zinc(II) complex. Compound (VI) crystallized as the methanol adduct, which a methanol molecule coordinated as the axial ligand to the zinc(II) ion [Zn-O1A = 2.027(3) Å], which is penta-coordinated. Here the Zn-N24

bond length is 2.033(3) Å, compared to an average value of 2.059(3) Å for the other three Zn-N bonds. Note, that Zn-N22 is also somewhat shorter than Zn-N23 and Zn-N24.

Further evidence for structural differences between the meso-bromo quadrants and the meso-tolyl quadrants can be derived from an inspection of the relevant C_a-C_m-C_a angles (Table 2). In both the metal complexes and the free base the C_a-C_m(Br)-C_a angles are larger than the C_a-C_m(tolyl)-C_a ones. This is most pronounced in the case of the palladium(II) complex where the respective average values are 128.1(7)º versus 123.3(7)º. Thus, the presence of the bromo residues results in a partial flattening of this bond, which is in agreement with a localized conformational effect of the bromine atoms (Senge, 2000).

Packing forces can only partially account for these differences. Both the palladium(II) complex (Figure 3) and the zinc(II) complex (Figure 4) form layers of porphyrins molecules with only minimal π-overlap. For example, in (V) the interplanar separation of the two 4N planes of the porphyrin rings is 3.87(1) Å and the closest intermolecular contact observed was a Pd-Br interaction (3.734(6) Å). In addition, H15C and Br2 form a close contact [D…A = 3.759(6) Å, D-H…A = 149º, i = -1+x, -1+y, z]. In the case of compound (VI) the closest intramolecular contacts observed were Zn-Br1 (3.578(4) Å) and Br1-H20D (3.053(4) Å).

In order to investigate the conformation in more detail the compounds were analysed using the normal-structural-decomposition (NSD) method (Jentzen *et al.*, 1997). This method allows an identification of the major out-of-plane and in-plane distortion modes and their individual contributions. An overall measure of the degree of conformational distortion, if any, is obtained by the determination of the average of in-plane distortion (Dip) and of out-of-plane distortion (Doop). As listed in Table 2 all three compound are nonplanar, i.e., have significant Doop values and the free base and zinc(II) complex have measurable in-plane distortions. Figure 5 shows a graphical representation of the individual contributions of the main distortion modes. The pattern and degree of out-of-plane distortion is very similar in all three compounds. They all have B2u, B1u and A2u contributions, which in descriptive terms mean saddling, ruffling and doming contributions. The latter is atypical for (IV) and (V) as it is mostly observed in porphyrins with penta-coordinated metal centers. Only one in-plane distortion mode (A1g) contributes significantly in the free base and zinc(II) complex. This one is related to the macrocycle breathing.

In order to investigate the influence of the regiochemistry, i.e. the 5,10-dibromo substituent pattern on the conformation we tried to identify suitable compounds for comparison. Only three other crystal structures with meso-bromo residues were found. One, (5-bromo-10,20-diphenylporphyrinato)nickel(II) (Arnold *et al.*, 1997) was omitted due to the nickel-induced ruffling and the absence of a comparative structure in our analysis here. Two more related ones are the free bases (VII) and (VIII). Both are 5,15-dibromo substituted porphyrins with a hexyl and

trimethoxyphenyl residue (Senge *et al.*, 2010). Their NSD analysis (Figure 5) indicates a similar overall degree of in-plane distortion (Dip ~0.21 Å for both) and different degrees of out-of-plane distortion (Doop = 0.353 Å and 0.893 Å for (VII) and (VIII), respectively). In terms of the contributions of individual distortion modes both are characterized by an A1g contribution for the in-plane distortion, similar to the compounds reported here. More differences between the 5,10- and 5,15-dibromo substituent pattern are observed in the out-of-plane distortion modes. The doming contribution is almost absent in the latter, the degree of ruffling is significantly reduced, while minor contributions of wave distortions (Eg) are present. Thus, differences in the 'mix' of distortion modes are associated with the two substituent pattern.

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Table 1   Experimental details

	(V)	(VI)
Crystal data		
Chemical formula	$C_{34}H_{22}Br_2N_4Pd$	$C_{35}H_{26}Br_2N_4OZn$
M_r	752.78	743.79
Crystal system, space group	Triclinic, P–1	Triclinic, P-1
Temperature (K)	123	108
a, b, c (Å)	9.396 (4), 10.558 (5), 15.129 (7)	10.280 (3), 11.637 (4), 14.052 (4)
α, β, γ (°)	95.157 (8), 103.433 (8), 107.007 (8)	110.195 (2), 95.785 (2), 105.564 (4)
V (Å^3)	1375.7 (10)	1484.6 (8)
Z	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	3.61	3.56
Crystal size (mm)	0.35 × 0.25 × 0.07	0.60 × 0.40 × 0.30
Data collection		
Diffractometer	Bruker Apex II diffractometer	Saturn724 (2x2 bin mode) diffractometer
Absorption correction	Empirical (using intensity measurements) program *SADABS*	ψ scan ψ scan, (North et al., 1968)
T_{min}, T_{max}	0.365, 0.786	0.224, 0.415
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10757, 4833, 3628	22765, 5140, 4320

R_{int}	0.041	0.086
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595	0.595
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.063, 0.180, 1.06	0.041, 0.110, 1.01
No. of reflections	4833	5140
No. of parameters	372	391
No. of restraints	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.50, −1.36	0.90, −0.94

Computer programs: Bruker *SMART*, Bruker *SAINT* (Bruker, 2005), *CrystalClear* (Rigaku/MSC., 2005), *SHELXTL*, *SHELXS97* (Sheldrick, 2008), *SHELXTL97* (Sheldrick, 2008).

Table 2   Selected geometrical parameters (Å,°)

Compound	(IV)	(V)	(VI)
M-N21	–	2.001(6)	2.061(3)
M-N22	–	2.012(6)	2.053(3)
M-N23	–	2.012(6)	2.063(3)
M-N24	–	2.011(5)	2.033(3)
C_a-C5-C_a	127.9(6)	127.9(7)	128.6(4)
C_a-C10-C_a	127.0(6)	128.4(7)	128.9(4)
C_a-C15-C_a	125.7(6)	123.3(7)	125.2(4)
C_a-C20-C_a	125.5(6)	123.2(7)	125.2(4)
Dip	0.2095	0.0291	0.1759
Doop	0.8956	0.732	0.6363

Figure 1 View of the molecular structure of (V) in the crystal. Hydrogen atoms have been omitted for clarity; thermal ellipsoids are drawn at 50 % probability level.

Figure 2 View of the molecular structure of (VI) in the crystal. Hydrogen atoms have been omitted for clarity; thermal ellipsoids are drawn at 50 % probability level.

Figure 3 View of the molecular packing of (V) in the crystal. Hydrogen atoms have been omitted for clarity.

Figure 4 View of the molecular packing of (VI) in the crystal. Hydrogen atoms have been omitted for clarity.

Figure 5 Graphical representation of the displacements along the lowest-frequency coordinates that best simulate the free base (IV), palladium(II) (V) and zinc(II) structures (VI) and comparison with structures (VII) and (VIII). (normal structural decomposition analysis).

Supporting information

Figure S1 Graphical representation of the displacements along the lowest-frequency coordinates that best simulate the structures (VII) and (VIII) (normal structural decomposition analysis).