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A Tin(IV) Porphyrin with Two Axial Organometallic NCN-Pincer Platinum Units

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Dedicated to Professor Wolfgang Beck on the Occasion of his 75th Birthday

Abstract. A tin(IV) porphyrin was combined with two axial NCN-pincer platinum(II) fragments by utilizing the oxophilicity of the apical positions on the tin atom and the acidic nature of the NCN-pincer platinum derived benzoic acid. The solid-state structure determined by X-ray crystallography revealed some close contacts between the pincer complexes and the *meso-p*-tolyl subsitutents of the porphyrin. It was shown by ^{1}H NMR spectroscopy that these close contacts were not present in solution and that this compound can potentially act as a novel building block for supramolecular architectures.

Keywords: Tin; Platinum; Tin(IV) porphyrin; NCN-pincer platinum(II); Supramolecular building block; X-ray structure; UV/Vis spectroscopy

1 Introduction

The use of the axial positions of metalloporphyrins provides ample opportunities to build two- and three-dimensional structures through supramolecular chemistry. While most research focuses on complexation of nitrogen and phosphorus ligands to the axial positions of diverse metalloporphyrins, the number of investigations into the supramolecular applications of tin(IV) porphyrins are gradually increasing in number [1]. There are several reasons, which make tin(IV) porphyrins such interesting building blocks, the most important being the high oxophilicity of the hard tin(IV) atom. This is in contrast to the commonly studied metalloporphyrin complexes of the middle and late transition metals, which generally display a higher affinity for binding to ligands with nitrogen and/or phosphorus donor atoms [1−3].

After the seminal investigations into the axial coordination chemistry of tin(IV) porphyrins by *Arnold* and co-workers [4−6], especially *Sanders* [7−12], and *Hunter* [13] employed them in a very elegant way in supramolecular studies. *Maiya* and co-workers used tin(IV) porphyrins to axially connect other metalloporphyrins by Lewis base/Lewis acid interactions [14, 15]. Very recently, a tin(IV) porphyrin was used to interconnect two carboxy-functionalized fullerene moieties and the resulting porphyrin-fullerene complex showed strong interactions between its components [16].

In this paper, we will focus on the axial, oxophilic chemistry of tin(IV) porphyrins as a means to attach additional functional groups that allow for further structural extension in a facile manner. One such way is by coordination chemistry, which, in order to be compatible with the dioxidotin(IV) porphyrin building block, should rely on an orthogonal metal-ligand interaction. In this respect, the ECE-pincer metal unit (with ECE-pincer being the potentially tridentate, monoanionic ligand $[2,6\text{-}(ECH_2)_2C_6H_3]^-$) [17−19] has become an increasingly useful organometallic construction tool. SCS-pincer Pd, and NCN-pincer Pd and Pt groups with functional *para*-substituents suited for covalent or non-covalent binding, have been applied by several researchers as building blocks for supramolecular systems such as coordination dendrimers [20−22], coordination polymers [23, 24], and giant macrocycles [25, 26]. Here, we report on the synthesis and characterization of a new supramolecular building block, in which two NCN-pincer Pt^{II} units are linked to a tin(IV) porphyrin through a Sn-O bond to the tin center of a tin(IV) porphyrin dication.

2 Experimental Section

2.1 Materials and methods

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques and were shielded from ambient

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light using aluminium foil. $CHCl_3$ and $CDCl_3$ were distilled from CaH_2 prior to use and stored in the dark. Compounds **1** [27] and **2** [5, 28] were synthesized according to literature procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300 and 75 MHz, respectively, on a Varian 300 spectrometer operating at 298 K. Resonances were referenced to residual solvent signals (δ_H = 7.26 ppm for $CHCl_3$ in $CDCl_3$ and δ_C = 77.16 ppm (central peak) for $^{13}CDCl_3$ in $CDCl_3$). UV/Vis spectra were recorded on a Cary 50 scan UV-visible spectrophotometer and ESI-MS measurements were performed by the Department of Biomolecular Mass Spectrometry, Bijvoet Centre for Biomolecular Research, Utrecht University. Elemental microanalyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Müllheim a/d Ruhr, Germany.

2.2 *Synthesis of* 3

Compound **2** (18.0 mg, 21.9 μmol) and molecular sieves (4 Å, 1.0 g) were added to a light yellow suspension of **1** (24.5 mg, 44.0 μmol) in dry $CHCl_3$ (8 mL). The resulting, clear purple solution was heated to reflux for 3 h, cooled to room temperature and filtered through anhydrous Na_2SO_4. The filtrate was concentrated to 5 mL and hexanes (40 mL) were added to induce precipitation of **3** as a purple microcrystalline solid. Yield: 40.6 mg (97 %). Anal. Calcd. for $C_{74}H_{72}I_2N_8O_4Pt_2Sn$: C 46.78, H 3.82, N 5.90, Sn 6.25 %; found: C 46.71, H 3.85, N 5.86, Sn 6.19 %. X-ray quality crystals were obtained by layering a concentrated solution of **3** in $CDCl_3$ with Et_2O. Dark red cubes were formed during 12 h.

^{1}H NMR ($CDCl_3$): δ = 9.17 (s, $^4J_{SnH}$ = 15.0 Hz, 8H, *β-H*), 8.06 (d, $^3J_{HH}$ = 7.8 Hz, 8H, Ar$H_{p\text{-tolyl}}$), 7.58 (d, $^3J_{HH}$ = 7.8 Hz, 8H, Ar$H_{p\text{-tolyl}}$), 4.25 (s, 4H, Ar*H*), 3.28 (s, $^3J_{PtH}$ = 40.8 Hz, 8H, CH_2N), 2.84 (s, $^3J_{PtH}$ = 37.5 Hz, 24H, N(CH_3)$_2$), 2.73 (s, 12H, ArCH_3); **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 164.0, 153.0, 147.4, 141.4, 138.5, 138.1, 134.7, 132.6, 128.0, 127.8, 121.8, 118.8, 76.1, 56.1, 21.8; **IR** /cm^{-1}: 2917, 1640, 1583, 1468, 1451, 1345, 1304, 1265, 1221, 1070, 1032, 1013, 840, 800, 790, 755;

2.3 *X-ray crystal structure determination of* 3

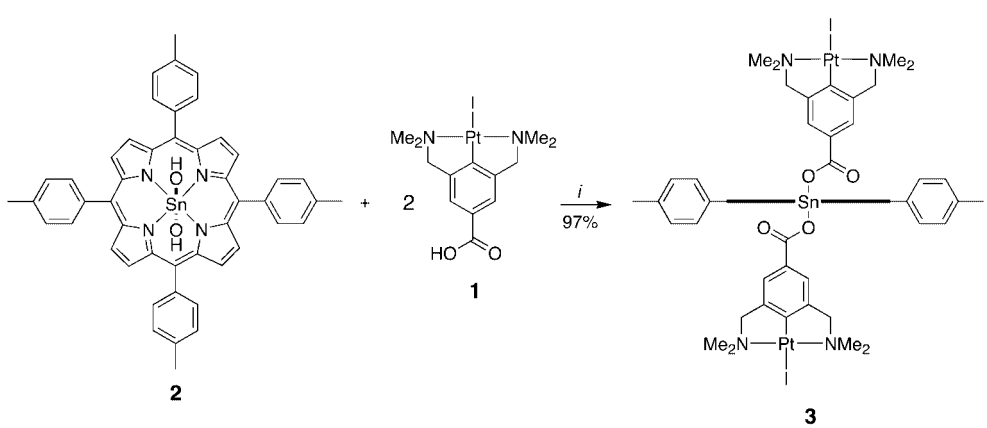
$C_{74}H_{72}I_2N_8O_4Pt_2Sn$, Fw = 1900.07, dark red plate, 0.30 × 0.12 × 0.03 mm, monoclinic, $P2_1/c$ (no. 14), a = 11.72(3), b = 23.30(3), c = 13.98(5) Å, β = 117.2(3)°, V = 3395(18) Å^3, Z = 2, D_x = 1.859 g/cm^3, μ = 5.44 mm^{-1}. 39792 Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) at a temperature of 150 K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.56 Å^{-1}. Intensities were integrated with EvalCCD [29] using an accurate description of the experimental setup for the prediction of the reflection contours. An analytical absorption correction was applied. 4988 Reflections were unique. The structure was solved with the program DIRDIF-99 [30] using automated Patterson Methods. The structure was refined with SHELXL-97 [31] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 418 Parameters were refined with 36 restraints. R1/wR2 [I > 2σ(I)]: 0.0585/0.1453. R1/wR2 [all refl.]: 0.0909/0.1648. S = 1.071. Residual electron density between −1.78 and 2.16 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program [32].

3 Results and Discussion

3.1 *Synthesis and characterization*

The synthesis of tin(IV) porphyrins with two axial carboxylato ligands usually involves the reaction of a dihydroxidotin(IV) porphyrin, in which the four pyrrolic nitrogen atoms of the dianionic porphyrin ring occupy the equatorial and two hydroxido ligands occupy the axial positions on tin, with two equivalents of an appropriate carboxylic acid. We recently reported the synthesis of 3,5-bis[(dimethylamino)methyl]-4-iodoplatino(II) benzoic acid **1** [27, 33, 34]. The pK_a of the carboxylic acid group is higher compared to that of benzoic acid, because the iodoplatino(II) group acts as a strong electron donor that is comparable to a dimethylamino substituent [34]. However, **1** is still expected to be able to protonate the hydroxy groups of dihydroxidotin(IV) porphyrins. This would make it a suitable building block for the construction of the corresponding dicarboxylatotin(IV) porphyrin according to the mechanism proposed by *Sanders* et al. [7]. Thus, dihydroxido[*meso*-tetrakis(*p*-tolyl)porphyrinato]tin(IV) **2** [28] was reacted with **1** in refluxing $CHCl_3$ in the presence of molecular sieves (4 Å) to give **3** in 97 % yield (Scheme 1).

The ligand exchange process was easily observed because **1**, which is rather insoluble in $CHCl_3$ and appeared as a yellowish powder in the reaction mixture, immediately dis-



Scheme 1 Synthesis of **3**. The horizontal bar in the structural formula of **3** represents an edge-on view of the porphyrin ring. *i*) 4 Å molecular sieves, $CHCl_3$, Δ.

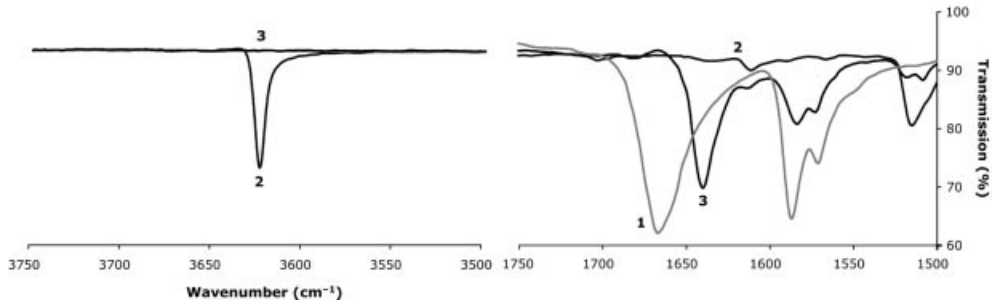


Figure 1 Comparison of the O−H and C=O regions of the IR spectra of **1**, **2**, and **3**.

solved upon addition of dihydroxidotin(IV) porphyrin **2**. ^{1}H NMR spectroscopy ($CDCl_3$) corroborated the formation of **3** as the signals corresponding to the two hydroxy protons of **2** at $\delta = -7.40$ had disappeared. Moreover, the protons of the pincer groupings showed upfield shifts that are typical for protons in the vicinity of the magnetically anisotropic porphyrin ring. In **3**, the two protons of the pincer-aryl ring are present as a singlet at $\delta = 4.25$, which is 3.19 upfield to the chemical shift position of these protons in **1**. The resonances belonging to the benzylic CH_2 and dimethylamino groupings ($\delta = 3.28$ and 2.84, respectively) are upfield shifted by 0.68 and 0.24 ppm, respectively. In addition, the aromatic protons of the *p*-tolyl groups on the porphyrin showed upfield shifts of 0.16 and 0.03 ppm for the *ortho*- and *meta*-protons, respectively.

The formation of **3** was also supported by IR measurements. Characteristic for **2** is the peak at 3621 cm^{-1} corresponding to the O−H stretching vibration of the hydroxyl groups bonded to the tin(IV) center. The IR spectrum of **3** does not show this absorption band (Figure 1). It does, however, show a strong C=O stretch absorption at 1640 cm^{-1}, which is situated at 1667 cm^{-1} in the parent acid **1** (Figure 1).

Substitution of the two hydroxyl groups for NCN-pincer Pt-benzoato monoanions leads to a very small hypsochromic shift in the UV/Vis spectra from 428 to 426 nm (Figure 2), which is in line with the reported values for the corresponding bis(benzoato) complex [1]. The effect of the electron-releasing properties of the iodoplatino(II) pincers on the electronic properties of the tin(IV) porphyrin entity apparently is small, pointing to a small interaction between the tin(IV) porphyrin and NCN-pincer platinum components in **3**. Exposure of a solution of **3** to gaseous SO_2, which is known to selectively bind to NCN-pincer platinum centers [35, 36], did not lead to notable changes in its UV/Vis spectrum. Probably, this is again indicative of the lack of electronic interaction between the pincer platinum and tin porphyrin centers. The ability of the *para*-carboxylato NCN-pincer PtI moiety to bind SO_2 was verified by the reaction of **1** with gaseous SO_2, which immediately led to the orange coloration diagnostic for pincer-derived Pt−SO_2 complexes [36].

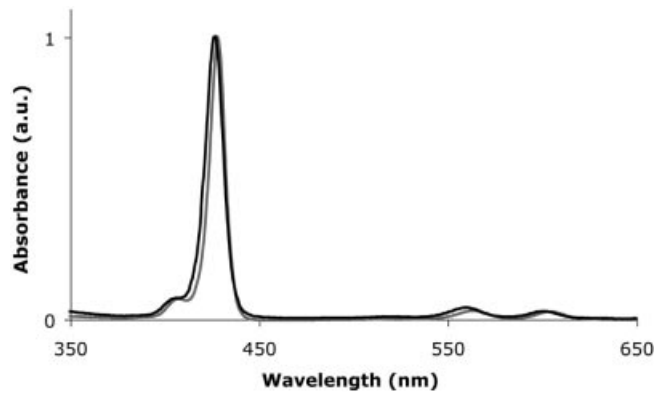


Figure 2 Comparison of the UV/Vis spectra of **2** (grey) and **3** (black).

3.2 X-ray crystallography

Final proof of the molecular structure of **3** was provided by a single crystal X-ray structure determination on single crystals of **3** that were obtained by layering a concentrated solution of **3** in $CDCl_3$ with Et_2O. Compound **3** crystallizes as a centro-symmetric system with the tin atom located on an inversion center (Figure 1).[1)] The tin atom is found in a slightly distorted octahedral ligand environment in which the apical Sn-O bond lengths are 2.096(10) Å. The four pyrrolic nitrogen atoms of the porphyrin system form the basal square plane of the Sn^{IV} atom, with two different Sn-N bonds of 2.109(13) (N1) and 2.069(10) Å (N2). A small tilt from the vertical was noted for the Sn-O bonds with respect to the porphyrin plane. The N1-Sn-O1 and N2-Sn-O1 angles amount to 91.1(4)° and 87.0(4)°, respectively. The dihedral angle between the *meso*-phenyl ring attached

[1)] Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre under CCDC 644930. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code (1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

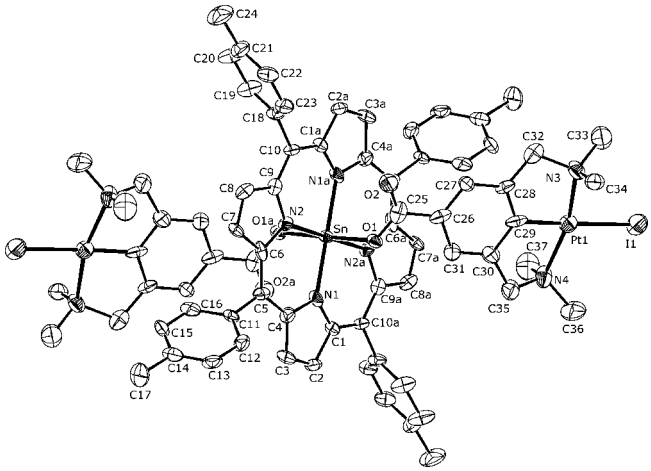


Figure 3 ORTEP representation of the crystal structure of **3** with displacement ellipsoids at the 50 % probability level. Symmetry operation a: 1−x, −y, 1−z.

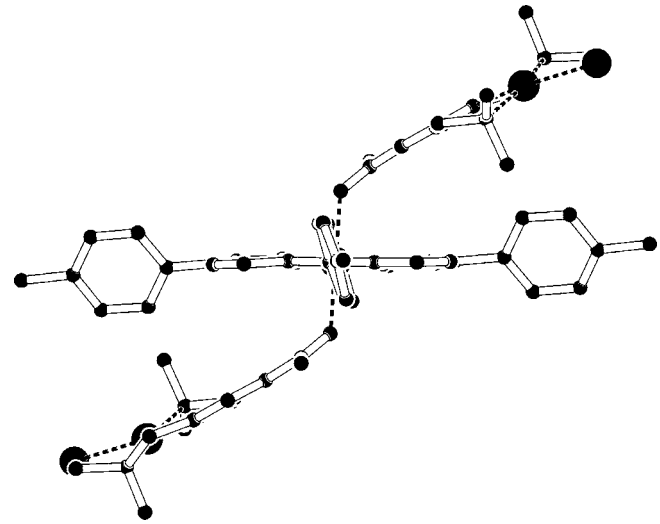


Figure 5 View of the crystal structure of **3** along C10a-C10 direction.

through C10 and the porphyrin ring is 69.7(6)°; for the other *meso*-phenyl ring this value amounts to 64.6(5)°.

Two side views perpendicular to the porphyrin plane, one running in the N1-Sn-N1a and the other in the N2-Sn-N2a direction, respectively, are given in Figure 4. Whereas it is usually found that in the crystal, the benzoato groups in bis(benzoato) tin porphyrin adducts adopt upward positions, *i.e.* with the plane of the phenyl group almost perpendicular to the porphyrin plane, the angle between the least square planes of the porphyrin and pincer aryl rings in **3** is only 32.06°. Indeed, a short C−H···π interaction is observed between the tolyl *o*-hydrogen atom and the phenyl ring of the NCN-pincer complex (distance C−H···Cg = 3.65 Å, angle C−H···Cg = 164°). A view along the C10-C10a direction is shown in Figure 5.

Closer inspection of the structure shows that the porphyrin ring adopts a wave-type conformation wherein the two *p*-tolyl groups at C5 and C5a bend towards the NCN-pincer PtI groups by 7.9(5)°, while the C17-C5-Sn angle is 180° (see Figure 5). The pincer fragment also assumes a non-planar shape, *i.e.* the C(O)O planar is not completely co-planar with the pincer aryl ring; the angle between the least square planes is 2.5(9)°. Moreover, the angle between the C25-C26 bond and the Pt-I bond is 12.4(8)°. Hence, it seems as if there is an interaction between the tolyl group on the porphyrin ring and the NCN-pincer PtI group. In the solid state, there was no evidence for the existence of intermolecular interactions between individual molecules of **3**.

To investigate whether the close contacts between the pincer groups and the *meso*-aryl rings are also present in solution, we used the ring current effect model recently published by *Fukazawa* et al. [37] for the structural elucidation of the bis(carboxylato) complexes of tin(IV) porphyrins. Comparison of the ^{1}H NMR spectra of **3** to the contour maps of induced NMR shift values indicated that in the case of **3**, close contacts between the *p*-tolyl and NCN-

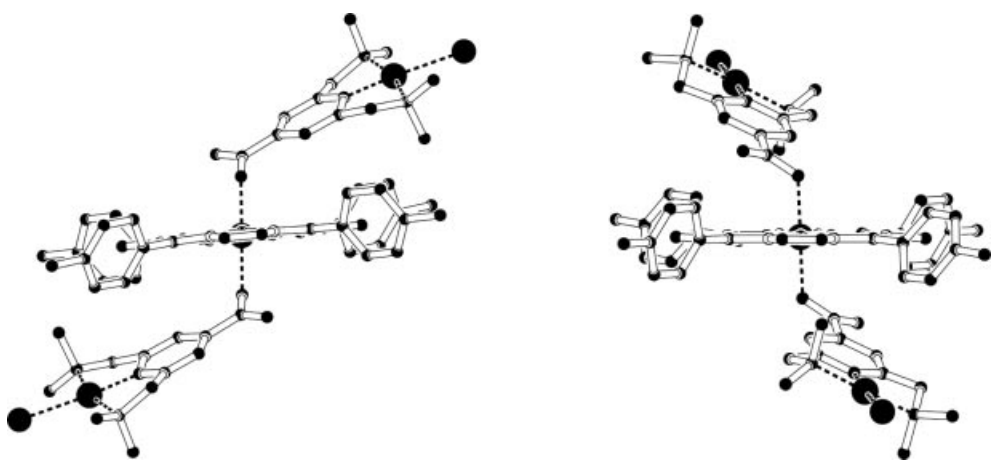


Figure 4 Different views of the molecular structure of **3** in the crystal along the N1−Sn−N1a direction (left) and the N2−Sn−N2a direction (right).

pincer platinum groups are not present in solution. In addition, low temperature NMR studies failed to show preferences for specific conformations due to preferred rotamer distributions as a result of restricted rotation about the C-O and/or Sn-O bond.

4 Conclusions

The results discussed above show that, although it has a relatively high pK_a, the NCN-pincer PtI benzoic acid can be nicely used for complexation to the apical positions of a tin(IV) porphyrin dication. The resulting bis(NCN-pincer platinum)benzoatotin(IV) porphyrin **3** adopts a peculiar structure in the solid state. Most notably, the benzoate rings adopt a more "flattened" orientation with respect to the porphyrin ring in contrast to the perpendicular orientation in the parent, unsubstituted bis(benzoato)tin(IV) porphyrins. Although the crystal structure shows some interesting close contacts between the pincer and tolyl groups, these were not observed in $CDCl_3$ solution. UV/Vis experiments furthermore provided no evidence for electronic communication between the apical NCN-pincer Pt sites and the porphyrin. The combination of the coordination and physical properties of ECE-pincer metal complexes and metalloporphyrins make compound **3** and analogues thereof interesting building blocks in supramolecular chemistry.

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