Coordination and structural studies of crowned-porphyrins†‡§

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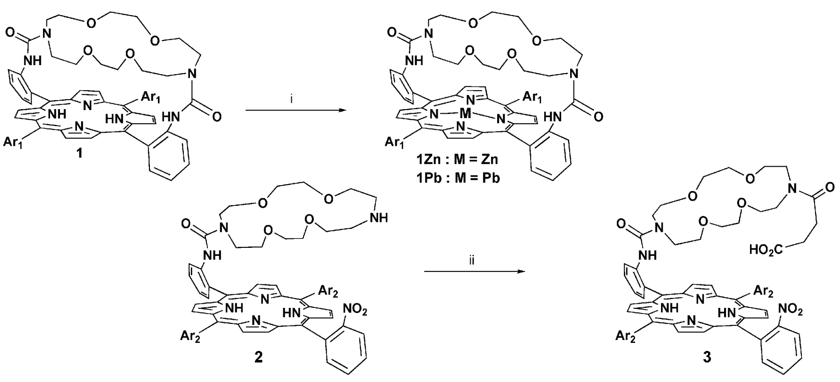
Simple chelating agents have been synthesized using a porphyrin and a covalently linked crown-ether. Depending on the relative spatial arrangement of both motifs, the resulting ligands, either a macrotricycle or bis-macrocycles, differ one from another by their flexibility or their aptitude to chelate bivalent or trivalent cations. The coordination chemistry as well as the structural study of these ligands and complexes are reported. In the particular case of the macrotricycle, the crown-ether motif, perpendicular to the porphyrin induces a side selectivity for the coordination of lead(II) outside the cavity. Furthermore, the coordination of zinc(II) implies a change of conformation of the ligand in which the crown-ether is parallel to the porphyrin.

Introduction

The design and synthesis of macrocyclic ligand frameworks for the sequestration of various elements has been investigated for several decades and still remains an active area of research.[1] Within this field, ligands of different types could exhibit a synergy for the recognition of host molecules. For instance, in crown-ether porphyrin molecules,[2] it has been shown that the stability of a supramolecular porphyrin–fullerene conjugate was obtained by means of 'two-point' recognition.[3] Moreover, metalloporphyrins were found to be efficient for multi-point recognition.[4] Regarding the role of water coordination in biological systems,[5] zinc strapped porphyrins were also studied as water molecule multi-point binding systems.[6] Furthermore, cofacial tetraazamacrocycles maintained in a cofacial geometry on a porphyrin are adequate ligands for studying the possible interactions between two transition metals.[7] Accordingly, it was reasoned that for larger elements such as those of Groups 13–15 or lanthanides, such assemblies could be suitable for the binding of a cation if each element—the porphyrin and the crown-ether—were maintained in a geometry such that each macrocycle could interact with the cation for binding purposes. Indeed, such complexes are expected to be attractive in the domains of imaging and therapy.[8]

Thus, the possible synthesis of various macromolecules in a simple reaction mixing a porphyrin and 1,4,10,13-tetraoxa-7,16-diaza-cyclooctadecane (Kryptofix-2,2) was recently investigated.[9] Four different macromolecules were purified and identified as a macrotricycle, a bis-macrocycle, a tris-macrocycle and a cryptand. Two major products—macrotricycle **1** and bis-macrocycle **2** (Scheme 1)—were obtained in ratios dependent on the reaction conditions. In this work, the study of these ligands in the coordination of several cations (Zn, Pb, Bi, La) as well as the structural characterisation of **1**, **1Zn** and **1Pb** are reported.



Scheme 1 Syntheses of crown-porphyrins. Ar$_1$ = 3,5-dimethoxyphenyl, Ar$_2$ = 2,4,6-trimethylphenyl. (i) Zn(OAc)$_2$, THF, RT, overnight or Pb(OAc)$_2$, pyridine, 50 °C, 1 h; (ii) succinic anhydride, aluminium oxide, CH$_2$Cl$_2$, RT.

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§ Electronic supplementary information (ESI) available: NMR and mass spectrometry data for all new compounds. See DOI: 10.1039/b701889d

Results and discussion

Synthesis of ligand precursors

Two different methods to optimize the yield of either **1** or **2** independently of the nature of Ar (Scheme 1) were reported.[9] For this study, the univocal reaction of Kryptofix-2,2 with a single *ortho*-amino phenyl porphyrin (Ar_2 = 2,4,6-trimethylphenyl) to obtain bis-macrocycle **2** with a yield of 88% was chosen. Opposite to **1**, in which the crown-ether cycle cannot escape from its apical position to the porphyrin, **2** can be considered as a freely hinged ligand in which the distance between the two macrocycles may change. Therefore, **2** is expected to be more flexible than **1**. Additionally, the remaining secondary amine function of **2** can be further functionalised to obtain a new ligand **3** which possesses a carboxylic pendant arm. Indeed, this simple strategy proved to be efficient to increase the kinetics of metallation of bismuth in tetra-aryl porphyrins.[10] The succinic motif was selected on the basis of its length which appears sufficient to allow the terminal carboxylic acid to coordinate a large cation inside the porphyrin. Thus, **2** reacts easily at room temperature with succinic anhydride leading to **3** in 81% yield. Where **1** or **2** are expected to stabilize bivalent metals with the dianionic porphyrin ligand, this new ligand **3** can supply intramolecularly a third counter-anion to a trivalent element such as bismuth or a lanthanide. From the proton NMR data of **1** and **2**, as expected, in solution, the crown-ether macrocycle is less shielded in **2** than in **1**. Moreover, in the latter, the mean planes of the two macrocycles are on average parallel as revealed by the three singlets of the crown-ether integrating for 8 protons each at 2.56, 1.94 and 0.49 ppm. The study of the new bis-macrocycle **3** could supply additional information about the effective pre-organisation of the bis-macrocylic scaffold common in **2** and **3**. For instance, the proton NMR crown-ether signature in **2** is composed of 3 broad singlets at 2.88, 2.38 and 1.97. In **3**, it appears roughly as the same 3 broad signals at 2.80, 2.75 and 2.42 ppm. The shift to lower field for one signal can be attributed to the change of the secondary amine of **2** to the withdrawing electron amide group of **3**. The pendant succinamic residue of **3** leads to two poorly resolved triplets at 2.39 and 2.26 ppm. These chemical shifts can be compared with those of the analogous compound in which the succinamic acid is tethered directly on the meso aromatic group of the porphyrin at 1.99 and 1.64 ppm.[11] From this light deshielding, it can be concluded that the pendant succinamic acid is located further away with no specific orientation towards the porphyrin. However, the basic concept of this type of ligand was to probe the possibility of an effect of the crown-ether *via* an interaction of its oxygen donor atoms on the insertion of large cations into the ligand. In such an eventuality, the crown-ether as well as the pendant arm would move closer to the porphyrin.

Structural studies

It has been previously reported that a bis-crown-ether porphyrin was not able to cooordinate bismuth. This observation was explained by the strength applied on each side of the porphyrin by the linked crown-ether.[12] This is, in part, why the coordination of bismuth on a mono-crown-ether porphyrin such as **1** was also investigated. Unfortunately, the metallation process, using bismuth nitrate or bismuth chloride, even at 100 °C, was not more successful. Some explanations are supplied by the structural resolution of the free-base porphyrin **1**. Indeed, crystals suitable for X-ray analysis were obtained from slow diffusion of methanol in a chloroform solution of **1**.¶ Unexpectedly, and in contrast to the structure in solution, the crown-ether residue in **1** is orthogonal to the mean porphyrin plane (Fig. 1, Table 1) with an angle of 89° between the two planes.* This specific orientation is maintained by two hydrogen bonds between O5 and N8 and O4 and N5 with respective bond lengths of 2.98 Å and 3.00 Å. The distances from the porphyrinic mean plane to O4 and O5 are 3.10 Å and 2.95 Å, respectively. Knowing that the average out-of-plane distance for a Bi^{III} atom in a porphyrin is 1.2 Å,[13] this specific geometry of **1** could rationalize why the metallation process is disfavoured for bismuth. Additionally, the distortion of the porphyrin plane observed in **1** is almost a pure ruffled distortion with a torsion angle Cα–N4–N2–Cα = 11.5°. This distortion is not compatible with the domed distortion required for a bismuth porphyrin.[14] Indeed, the two meso carbon atoms C10 and C20 are pulled outside the plane of the porphyrin towards the crown-ether and the four nitrogen atoms are located below the plane of the porphyrin. With such a

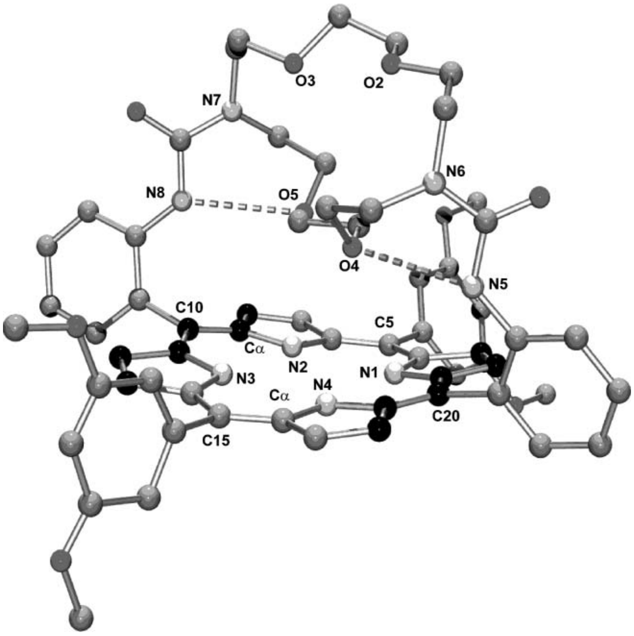

Fig. 1 X-Ray structure of **1** (black spheres depict atoms above the mean porphyrin plane, the four nitrogen atoms are located below this plane. Vertical positions relative to the plane in Å: C5: −0.19, C10: 0.26, C15: −0.17, C20: 0.18).

¶ This structural study was rather difficult to solve and refine due to a poor diffracting sample, presence of solvents and disorder in a chain. Furthermore it appears that this structure is not really centrosymmetrical (*C*2/*c*) but *Cc*. Considering the *Cc*space group, two porphyrins are found in the asymmetric unit with disorder in only one molecule. However, as we are very close to centrosymmetry, correlations exist in the refinement matrix, hence a poor quality of the geometry for the two moieties and non-positive definite atoms. This pseudo centrosymmetry also explains illogical intermolecular distances for a solvent molecule.

* The mean porphyrin plane is composed of the 24 atoms of the macrocycle. For the metalloporphyrins, the coordinated metal is not considered. In the case of the crown-ether, the mean plane was calculated only considering the six heteroatoms of the macrocycle but not the carbon atoms.

Table 1 Details of data collection, structure solution and refinement for **1**, **1Zn**, **1Pb** (refinement method: full-matrix least squares (F^2))

Compound	**1**	**1Zn**	**1Pb**
Empirical formula	$C_{62}H_{62}N_8O_{10}\cdot 0.5C_5H_{12}\cdot C_2H_5OH$	$2(C_{62}H_{60}N_8O_{10}Zn\cdot H_2O)\cdot CH_2Cl_2$	$C_{62}H_{60}N_8O_{10}Pb\cdot 2CHCl_3\cdot(0.5H_2O)_2$
M_r	1161.35	2406.12	1541.16
T/K	100(1)	120(1)	120(1)
CCDC n°	292378	296454	628337
λ/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2/a$	$P21/n$
a/Å	14.8938(7)	23.755(1)	17.2553(4)
b/Å	22.5940(7)	8.6928(4)	20.8665(5)
c/Å	35.296(2)	30.912(1)	18.5943(5)
α/°	—	—	—
β/°	101.776(4)	108.134(1)	101.284(2)
γ/°	—	—	—
V/Å^3	11628(1)	6066.2(4)	6566.2(3)
D_c/Mg m^{-3}	1.327	1.401	1.559
Z	8	2	4
μ/cm^{-1}	0.91	6.05	28.79
F(000)	4936	2664	3104
Crystal size/mm	0.25 × 0.12 × 0.12	0.35 × 0.20 × 0.16	0.25 × 0.15 × 0.08
θ Range/°	2.53–26.00	2.53–26.00	2.91–32.22
Index ranges hkl	0 to 18, 0 to 27, −43 to 43	0 to 29, 0 to 10, −38 to 38	−22 to 25, −31 to 27, −25 to 26
Reflections collected	80307	41065	60218
Independant reflections (R_{int})	11076 (0.0555)	11877 (0.0612)	20640 (0.0545)
Completeness to θ_{max} (%)	96.8	99.4	88.9
Absorption correction	None	None	None
Data/restraints/parameters	11076/0/762	11877/0/777	20640/0/820
Goodness-of-fit on F^2	1.145	0.861	0.998
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1098$	$R1 = 0.0430$	$R1 = 0.0483$
	$wR2 = 0.3292$	$wR2 = 0.0996$	$wR2 = 0.1351$
R Indices (all data)	$R1 = 0.1682$	$R1 = 0.0995$	$R1 = 0.0917$
	$wR2 = 0.3518$	$wR2 = 0.0.1073$	$wR2 = 0.1417$
$\Delta\rho_{max, min}$/e Å^{-3}	2.385, −1.015	1.388, −0.670	2.692, −1.959

distortion, bismuth cannot be coordinated inside the cavity of the macrotricycle in as much as bismuth would require an additional nitrato residue as counter-anion.

These results prompted us to investigate the possible coordination of bismuth by ligands **2** and **3**. As ligand **1** appears to be sterically over-crowded, **2** and **3** are more freely hinged and less congested bis-macrocycles, **3** further exhibiting an intramolecular counter-anion for bismuth inside the porphyrin. Thus, bismuth insertion was investigated in **2** and **3** with either $Bi(NO_3)_3$ or $BiCl_3$ (10 equiv.) in pyridine at various temperatures from 50 °C up to 100 °C overnight. Higher temperatures were not tested as the structural integrity of the ligands would be affected by atropisomerisation of the meso nitro-phenyl group. The failure of bismuth insertion at 100 °C is in favour of a lack of interaction of the crown-ether motif. Therefore, it is logical that bismuth insertion requires higher temperatures than 100 °C just as in unfunctionalized porphyrins.[15] To confirm this result, the insertion of lanthanum was also studied. Indeed, with a coordination number of 8, which would be expected in **3**, Bi^{III} and La^{III} exhibit the same effective ionic radius (EIR) of 116 pm.[16] Unfortunately, with $La(CF_3SO_3)_3\cdot H_2O$ (10 equiv.) in pyridine, lanthanum insertion in **3** remained unsuccessful too, even at 100 °C overnight. As La^{III} usually exhibits coordination numbers (CN) from 6 to 12, and as ligand **3** can formally allow a CN = 9, this result indicates that bis-macrocycles such as **3** are not suitable for the coordination of large trivalent cations such as Bi^{III} or La^{III}, presumably because of a too large distance between the two building blocks, namely the porphyrin and the crown-ether.

Conversely, in macrotricycle **1**, the steric hindrance—particularly emphasized by the possible conformation of the crown-ether found in the X-ray structure—is possibly the crucial factor that explains why no coordination of bismuth(III) occurs. This behaviour could be different for bivalent cations such as zinc(II) or lead(II), which is isoelectronic with bismuth(III). Obviously, zinc(II), known to be usually five-coordinate in porphyrins, is much smaller than bismuth(III) with an EIR = 68 pm. Lead(II), which also exhibits a similar lone-pair character to bismuth(III), also has a smaller EIR = 98 pm with a CN = 4 in porphyrins.

Thus, zinc insertion was sucessfully performed at room temperature according to well established methods.[17] In solution, by proton NMR spectroscopy, the chemicals shifts of the signals from the methylene groups of the crown-ether in **1Zn** were shown to be 2.17, 1.66 and 1.07 ppm. The difference between the most shielded and the least shielded protons is 1.1 ppm where this difference in the free-base compound is 2.1 ppm. In light of the known structure of **1**, this observation is consistent with a crown-ether more parallel with the porphyrin in **1Zn** than it is in **1**. Crystals suitable for X-ray analysis were obtained by slow diffusion of methanol into a solution of **1Zn** in chloroform and revealed two different porphyrins in the structure (Fig. 2, Table 1). The first striking difference with **1** is the parallel arrangement of the crown-ether with the porphyrin. Indeed, in both motifs (A) and (B), the angles between the porphyrin and the crown-ether are 0.0° and 3.4°, respectively. This geometry is the result of the coordination of a water molecule on the zinc atom. This water molecule is stabilized by two hydrogen bonds with two oxygen atoms diametrically

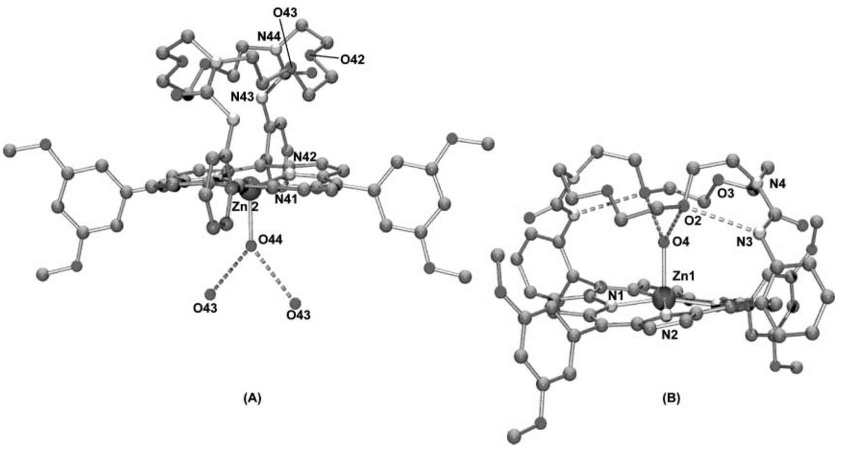

Fig. 2 X-Ray structure of the aqua complex of **1Zn**. The two independent zinc complexes each have crystallographically imposed twofold symmetry, with the Zn1–O4 and Zn2–O44 bonds on the two fold axes (MP: mean porphyrinic plane, distances in Å; O43–O44 = 2.959, Zn2–O44 = 2.143, Zn2–MP = −0.355, O4–O2 = 2.723, Zn1–O4 = 2.064, Zn1–MP = 0.189, Zn1–Zn2 = 16.757).

located in the crown-ether. In motif (B), the axial water molecule (O4) is coordinated inside the macrotricyclic cavity with hydrogen bonds to O2 atoms. In porphyrin (A), the axial water molecule (O44) is coordinated outside the macrotricyclic pocket and is held by two hydrogen bonds to O43 atoms from the crown-ether of another molecule. Both Zn–O and hydrogen bonds are shorter in motif (B) than in motif (A) (Fig. 2 caption). In motif (A) in which the intermolecular hydrogen bonds form a wire in the crystal, it is worth noting that Zn2 is −0.355 Å below the mean porphyrin plane. This distance is much shorter in motif (B) (0.189 Å) in which the hydrogen bonds are intramolecular. It should be underlined that in both motifs (A) and (B), the polyhedron of coordination of zinc with the weakly bound axial water molecule induces a parallel conformation of the system at least in the solid state.

The same experiment was carried out with lead using lead acetate in pyridine at 50 °C for the metallation reaction. After 1 h, the metallation was complete. On one hand, in solution, the proton NMR chemical shifts of the methylene groups from the crown-ether in **1Pb** are observed at 2.57, 1.83 and 0.91 ppm. They are almost the same as those of the free-base compound (2.56, 1.94 and 0.49) with the exception of the most shielded signal. Thus, this similitude is in favour of a position of the crown-ether perpendicular to the porphyrin in **1Pb**. On the other hand, in the solid state, it is known from previous X-ray studies that lead(II) in porphyrins remains four-coordinate out of the plane of the porphyrin.[18]

As for **1** and **1Zn**, crystals suitable for X-ray analysis by slow diffusion of methanol into a chloroform solution of **1Pb** were obtained (Fig. 3, Table 1). The same spatial arrangement of the crown-ether present in **1** is found in **1Pb**, with the crown-ether orthogonal to the mean porphyrin plane (88°) and the existence of two hydrogen bonds between two adjacent oxygen atoms O2 and O3 of the crown-ether and the two nitrogen atoms N5 and N8 from the amide groups of the porphyrin. As expected, lead(II) is four-coordinate, 1.417 Å out of the plane of the porphyrin but outside the macrotricyclic cavity. The lengths of nitrogen-to-lead bonds are comparable with those reported for the “roof” porphyrin.[18a] The porphyrin adopts a domed distortion with the β pyrrolic carbon atoms on the side of the crown-ether and the α pyrrolic carbon atoms as well as the nitrogen atoms on the side of lead. Therefore, the perpendicular conformation of the crown-ether excludes the “inside” coordination of lead. This observation is consistent with an interaction of the lone pair of lead with those of O2 and O3 or directly with the scaffold of the crown-ether.[19] It is also possible that the linkage of the crown-ether induces a distortion—as seen in **1**—which is favourable to a coordination of lead outside the cavity of the macrotricycle.

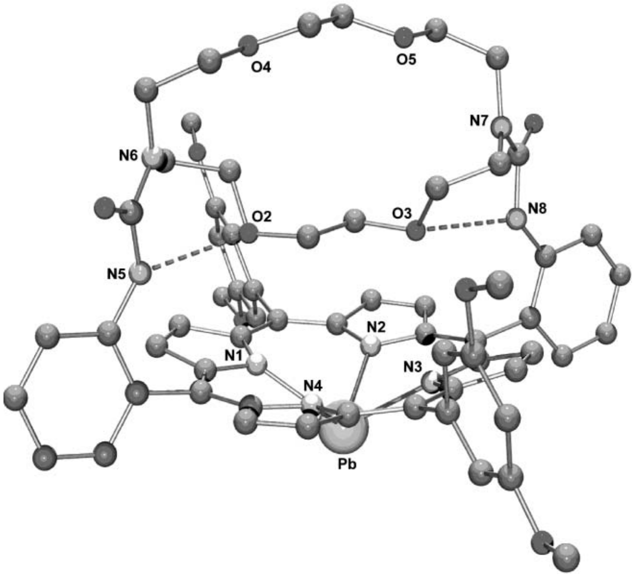

Fig. 3 X-Ray structure of **1Pb** (MP: mean porphyrinic plane, distances in Å; Pb–MP = 1.417, N5–O2 = 2.916, N8–O3 = 2.905, N1–Pb = 2.409, N2–Pb = 2.386, N3–Pb = 2.394, N4–Pb = 2398).

Experimental

(i) General considerations

^{1}H (500.13 MHz, 300.13 MHz) and ^{13}C (125 MHz, 75 MHz) NMR spectra were recorded on Bruker Avance spectrometers and referenced to the residual protonated solvent. Mass spectra were performed on a MS/MS ZABSpec TOF spectrometer at the University of Rennes I (C.R.M.P.O.). UV-visible spectra were recorded on an Uvikon XL spectrometer. Infrared spectra were recorded on Bruker IFS28 spectrometer. All solvents (ACS for analysis) were purchased from Carlo Erba. THF was distilled over potassium metal whereas methanol was distilled over magnesium turnings. CH_2Cl_2 was used as received. Triethylamine was distilled over CaH_2. The starting materials were generally used as received (Acros, Aldrich) without any further purification. All reactions were performed under an argon atmosphere and monitored by TLC (silica, CH_2Cl_2–MeOH). Column flash chromatography was performed on silica gel (Merck TLC-Kieselgel 60 H, 15 µm).

(ii) Ligand precursors

Ligands **1** and **2** were synthesized as previously described.[9]

4-(16-{2-[α-15-(2-Nitro-phenyl)-10,20-bis-(2,4,6-trimethyl-phenyl)-porphyrin-α-5-yl]-phenylcarbamoyl}-1,4,10,13-tetraoxa-7,16-diaza-cyclooctadec-7-yl)-4-oxo-butyric acid 3. In a 50 mL flask, **2** (24 mg, 22.9 µmol) and aluminium oxide (2.3 mg, 22.9 µmol) were dissolved in 10 mL of dry CH_2Cl_2. Then succinic anhydride (3.4 mg, 34.4 µmol) was added and the reaction was stirred at room temperature. After 3 h, the solution was evaporated to dryness and the residue dissolved in a minimum of $CHCl_3$ to be poured onto a silica gel chromatography column. Product **3** was eluted with a 0.1 : 12 : 87.9 acetic acid–CH_3OH–$CHCl_3$ mixture and obtained in 81% yield (21 mg, 18.5 µmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.86 (d, J = 4.5 Hz, 2H, βpyr), 8.72–8.70 (m, 4H, βpyr), 8.62 (m, 3H, βpyr + aro), 8.45 (d, J = 8.5 Hz, 1H, aro), 8.23 (d, J = 8.2 Hz, 1H, aro), 8.02 (t, J = 8.0 Hz, 1H, aro), 7.97 (t, J = 8.0 Hz, 2H, aro), 7.83 (bs, 1H, NH), 7.76 (t, J = 7.8 Hz, 1H, aro), 7.37 (t, J = 7.8 Hz, 2H, aro), 7.31 (bs, 4H), 3.10 (bs, 4H, $–CH_2–$), 3.00–2.00 (bs, 12H, $–CH_2–$), 2.74 (bs, 4H, $–CH_2–$), 2.65 (s, 6H, $–CH_3$), 2.43 (bs, 4H, $–CH_2–$), 2.40 (m, 2H, $–CH_2–$), 2.26 (bs, 2H, $–CH_2–$), 1.86 (s, 6H, $–CH_3$), 1.83 (s, 6H, $–CH_3$), −2.56 (s, 2H, NHpyr). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.9, 135.1, 131.1, 129.7, 129.5, 127.9, 123.9, 120.3, 119.1, 48.4, 30.5, 27.7, 21.6, 21.5, 21.4. ESI-HRMS: calcd m/z = 1169.5113 [M + Na]$^+$ for $C_{67}H_{70}N_8O_{10}Na$, found 1169.5112. FTIR (KBr, cm^{-1}): 1710 $(CO)_{acide}$, 1670 $(CO)_{amide}$, 1660 $(CO)_{urea}$, UV-vis (CH_2Cl_2) λ, nm ($10^{-3}\varepsilon$, $dm^3\ mol^{-1}\ cm^{-1}$): 421 (202.8), 515 (10.2), 550 (5.1), 592 (5.1), 647 (4.1).

(iii) Complex syntheses

1Zn. To a solution of porphyrin **1** (23.2 µmol, 25 mg) in THF (10 mL) was added zinc acetate (0.185 mmol, 41 mg) and sodium acetate (0.185 mmol, 15.2 mg). The mixture was stirred overnight at room temperature, then solvent was removed under vacuum. The resulting powder was dissolved in chloroform and washed with water, dried over $MgSO_4$ and concentrated under vacuum. The resulting powder was dissolved in chloroform and directly loaded onto a silica gel chromatography column. The expected compound eluted with 4% MeOH–$CHCl_3$ was obtained in 82% yield (22 mg). ^1H NMR ($CDCl_3$, 298 K, 300 MHz): δ = 8.98 (4H, d, J = 4.5 Hz, βpyr), 8.85 (4H, d, J = 4.5 Hz, βpyr), 8.46 (2H, d, J = 7.2 Hz, aro), 7.98 (2H, d, J = 8.1 Hz, aro), 7.72 (2H, t, J = 7.5 Hz, aro), 7.54 (2H, t, J = 7.5 Hz, aro), 7.41 (2H, s, aro), 7.20 (2H, s, aro), 6.92 (2H, br s, aro), 5.69 (2H, s, NHCO), 4.01 (6H, s, OCH_3), 3.88 (6H, s, OCH_3), 2.17 (8H, s, CH_2), 1.66 (8H, s, CH_2), 1.07 (8H, br s, CH_2). ^{13}C NMR ($CDCl_3$, 298K, 75 MHz): δ = 158.8, 150.0, 140.9, 132.8, 131.6, 129.3, 121.8, 121.3, 114.9, 113.3, 99.5, 77.2, 69.2, 56.6, 48.6. ESI-HRMS: calcd m/z = 1140.3724 $[M]^{+\bullet}$ for $C_{62}H_{60}N_8O_{10}Zn$, found 1140.3743. UV-vis (CH_2Cl_2): λ, nm ($10^{-3}\varepsilon$, $dm^3\ mol^{-1}\ cm^{-1}$): 427 (440.1), 559 (16.6), 591 (5.6), 601 (6.4).

1Pb. In a 50 mL flask, 16 mg (14.8 µmol) of **1** were dissolved in 4 mL pyridine. The solution was warmed up to 50 °C before 6.2 mg (16.3 µmol) of $Pb(OAc)_2\cdot 3H_2O$ were added. After 1 h of heating, the solvent was evaporated and dissolved in a minimum of $CHCl_3$ to be poured onto a silica gel chromatography column. Complex **1Pb** was eluted with a 0.5% CH_3OH–$CHCl_3$ mixture and obtained in 84% yield (16 mg, 12.5 µmol). ^1H NMR ($CDCl_3$, 298 K, 500 MHz): δ = 9.11 (4H, d, J = 4.0 Hz, βpyr), 8.92 (4H, d, J = 4.0 Hz, βpyr), 8.54 (2H, br s, aro), 7.95 (2H, d, J = 7.5 Hz, aro), 7.77 (2H, t, J = 7.5 Hz, aro), 7.56 (2H, br s, aro), 7.39 (4H, br s, aro), 6.92 (2H, br s, aro), 5.67 (2H, s, NHCO), 4.00 (12H, s, OCH_3), 2.57 (8H, s, CH_2), 1.83 (8H, br s, CH_2), 0.91 (8H, br s, CH_2). ^{13}C NMR ($CDCl_3$, 298K, 125 MHz): δ = 158.9, 158.7, 149.1, 140.6, 134.3, 132.4, 131.8, 129.2, 121.2, 114.2, 99.8, 68.6, 55.6, 49.6. ESI-HRMS: calcd m/z = 1285.4277 [M + H]$^+$ for $C_{62}H_{61}N_8O_{10}Pb$, found 1285.4287. UV-vis (CH_2Cl_2): λ, nm ($10^{-3}\varepsilon$, $dm^3\ mol^{-1}\ cm^{-1}$): 354 (20.4), 468 (156.3), 606 (6.2), 654 (8.1).

(iv) Crystallographic method

The samples were studied on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized Mo-Kα radiation. The data collections were performed with CrysAlis.[20] The structures were solved with SIR-97[21] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms may be found with a Fourier Difference. Atomic scattering factors were taken from ref. 22, ball and stick views were realised with PLATON98[23] and Pov-RAY. The whole structures were refined with SHELXL97[24] by the full-matrix least-squares techniques (use of F^2 magnitude, x, y, z, β_{ij} for C, Cl, N, O, Pb and Zn atoms, x, y, z in riding mode for H atoms).

Conclusions

In this work, the coordination properties of a macrotricycle and two different bis-macrocycles towards the possible chelation of various elements such as bivalent cations (Zn, Pb) and trivalent cations (Bi, La) were studied. Although the structure of both bis-macrocycles is expected to be more flexible, none of them is able to coordinate bismuth(III) or lanthanum(III). In contrast to tetra-aryl porphyrins, a pendant-armed succinamic acid attached to the crown-ether does not improve the coordination of large trivalent cations. It is plausible that the urea linkage between the two macrocycles represents a too rigid hinge and that the crown-ether motif cannot interact together with the porphyrin in the metalation process. On the other hand, the rigid macrotricycle exhibits an interesting behavior towards the chelation of bivalent cations. Indeed, it has been shown that, relative to the porphyrin plane, the crown-ether can switch from an orthogonal conformation to a parallel position. Accordingly, the coordination of lead(II) occurs outside the macrotricycle in which the orthogonal conformation of the crown-ether is locked by two hydrogen bonds with the amide groups of the porphyrin as in the free-base compound. In contrast, the coordination of zinc(II) implies a change of conformation of the ligand in which the crown-ether is parallel to the porphyrin. This phenomenon is due to an axially coordinated water molecule twice hydrogen-bound to two diametrically located oxygen atoms of the crown-ether.

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