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COMMUNICATION

Translocation-coupled transmetalation at the origin of a dinuclear lead porphyrin complex: implication of a *hanging-atop* coordination mode†

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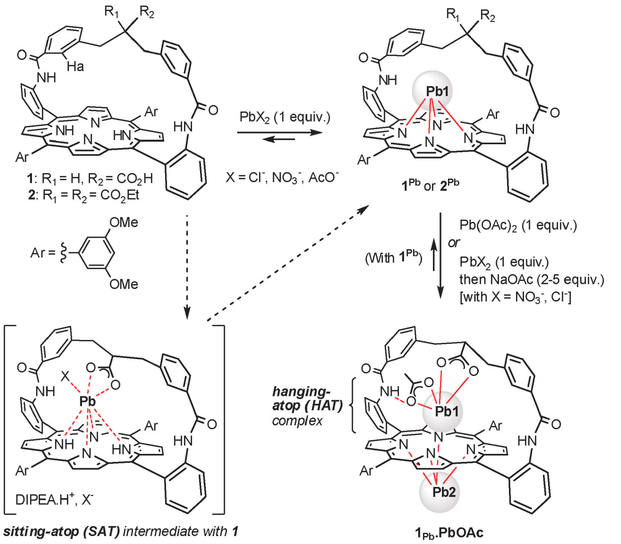
Translocation of a lead cation from the N-core of a porphyrin to a hanging carboxylate group is coupled to a transmetalation process with a second lead cation, leading to a dinuclear species. A novel *hanging-atop* coordination mode is responsible for the dynamic and stereocontrolled binding of lead to the porphyrin core.

Multimetal porphyrin entities have demonstrated indisputable utility in the building of functional supramolecular assemblies with cooperative or responsive properties, in the design of materials for light-energy conversion, or in the study of biomimetic systems.[1] In this context, a fine control of metalation processes in porphyrins appended with another metal binding site is of primary importance for the design of novel metallo-architectures. To our knowledge, translocation of a metal ion from the porphyrin N-core to an appended binding site remains unknown.[2]

Coordination chemistry of porphyrins towards Pb(II) cation is largely unexplored, and structural data available so far are limited to a few examples.[3] 1 : 1 complexes have been described in the crystalline state in which the 4-coordinate Pb(II) ion is significantly *out-of-plane*, 1.30–1.44 Å away from the mean plane of the macrocycle.[4] Such a displacement is due to the large ionic radius of Pb(II) (0.98 Å with a coordination number of 4) and to the stereochemically active $6s^2$ lone pair that points away from the porphyrin core and acts as a phantom ligand. We have recently described a unique coordination mode occurring in a dinuclear centro-symmetrical complex provided by the adjunction of overhanging carboxylate groups.[5] Each Pb(II) ion is σ-linked to a nitrogen atom of the N-core and to an oxygen atom of the COO$^-$ function, in a *cis* geometry, and is located 1.795 Å out of the porphyrin mean plane. We were interested in structural variations of the ligand and particularly in an intermediate situation in which a single carboxylate group dangles over the porphyrin core. As developed hereafter, such an environment allowed a case study of the dynamic and stereocontrolled binding of lead with a coupled translocation–transmetalation process.



Scheme 1 Complexation of Pb(II) by ligands **1** and **2** (DMSO-d_6 solution, 15 equiv. DIPEA).

The singly strapped, mono-carboxylic acid, porphyrin **1** (Scheme 1) was obtained from the corresponding diethyl malonate derivative **2** upon treatment with KOH in refluxing ethanol (ESI†). Complexation properties of **1** towards Pb(II) were studied at 25 °C by ^{1}H NMR titration experiments in DMSO-d_6 with an excess of diisopropylethylamine (DIPEA). The addition of 1 equiv. of $PbCl_2$ to **1** led to the quantitative formation of a C_s symmetrical species (Fig. 1a). No change in the spectrum was observed with an excess of this salt, indicating the formation of a mononuclear complex. The Soret band in the corresponding UV-vis spectra is red-shifted by 52 nm which is consistent with a classic *out-of-plane* coordination.[4d] The fact that equilibria are reached instantaneously at room temperature clearly contrasts with harsh metalation conditions required for 'naked' porphyrins (*e.g.* refluxing pyridine).[4] This strongly suggests that the binding is assisted by the deconvolution[6] of a chloride anion by the carboxylate of the strap, leading to the side-selective formation of a *sitting-atop* (SAT) intermediate prior to metal insertion (Scheme 1). Thus, in the

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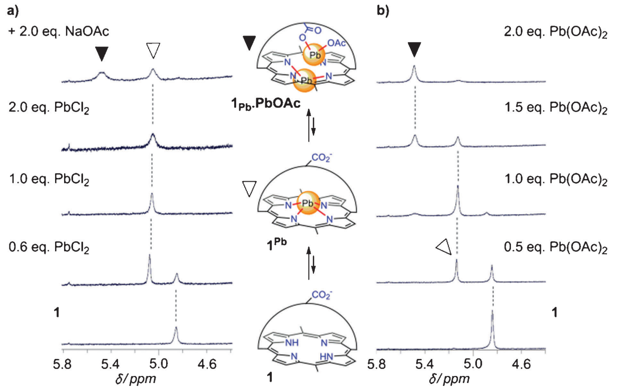

Fig. 1 ^{1}H NMR spectra for the complexation of Pb(II) by ligand **1** (DMSO-d_6, 500 MHz, 15 equiv. DIPEA, region of the Ha signal). (a) Titration with PbCl$_2$, and subsequent addition of NaOAc; (b) titration with Pb(OAc)$_2$.

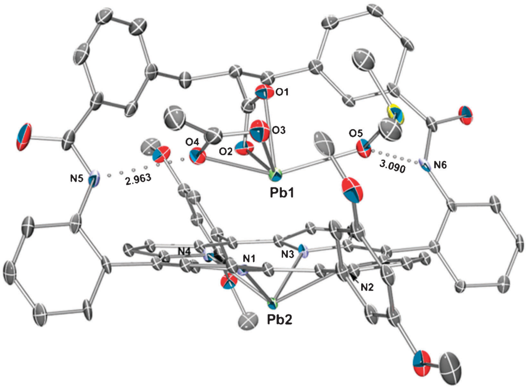

Fig. 2 X-Ray crystal structure of **1$_{\mathbf{Pb}}$·PbOAc**: ORTEP view at the 30% probability level (hydrogen atoms omitted, dashed lines indicate H-bonds). Distances [Å]: Pb1–Pb 2 3.727; Pb2(/Pb1) to 24-atom mean plane 1.383(/2.323); Pb1–O1 2.449, Pb1–O2 2.380, Pb1–O3 2.587, Pb1–O4 2.432, Pb1–O5 2.596, Pb2–N1 2.399, Pb2–N2 2.413, Pb2–N3 2.405, Pb2–N4 2.381.

mononuclear complex, the lead cation is likely located in an *inside* position relative to the strap, with the hanging COO$^-$ group being no longer coordinated (**1$^{\mathbf{Pb}}$**, Scheme 1).[7] This conclusion is strengthened by the X-ray structure of the mononuclear lead complex **2$^{\mathbf{Pb}}$** obtained with the diethyl malonate precursor of **1** (ESI†). The Pb(II) cation is out-of-plane 4-coordinate to the N-core; however, at the opposite of another nonrelated strapped porphyrin,[4c] the metal is in an *inside* position relative to the strap (Scheme 1). In DMSO-d_6 solution, Pb(II) was inserted into **2** upon standing overnight at room temperature (ESI†). This, as in **1$^{\mathbf{Pb}}$**, is consistent with the participation of the hanging group in the metalation process.

Similarly, Pb(NO$_3$)$_2$ led to **1$^{\mathbf{Pb}}$** as the major species even with an excess of the metal salt (ESI†). Conversely, a second complexation process was observed when Pb(OAc)$_2$ was used for the titration of **1**. Besides the formation of **1$^{\mathbf{Pb}}$**, addition of up to 3 equiv. of this metal salt led to the quasi-quantitative formation of a new species (Fig. 1b). The same species was formed upon addition of a slight excess of NaOAc to a 2 : 1 mixture of PbCl$_2$ or Pb(NO$_3$)$_2$ and **1** (Fig. 1a, ESI†). A ROESY 2D NMR experiment revealed that one acetate counteranion belongs to this new complex (ESI†). The high field shift of ~1.60 ppm for the CH$_3$ protons indicates a bound acetate located above the porphyrin plane. The overall process with Pb(OAc)$_2$ is compatible with the successive formation of mono- and dinuclear complexes and is characterized by the apparent association constants $K_{a_1} = 1.3 \times 10^4\ \mathrm{M}^{-1}$ and $K_{a_2} = 9.3 \times 10^4\ \mathrm{M}^{-2}$, respectively (ESI†).[8]

Single crystals were successfully grown from the NMR sample resulting from the titration of **1** by Pb(OAc)$_2$. X-Ray diffraction analysis confirmed the bimetallic nature of the complex, namely **1$_{\mathbf{Pb}}$·PbOAc** (Scheme 1). The crystal structure is depicted in Fig. 2. One lead cation (Pb2) is 4-coordinate to the N-core of the porphyrin, *opposite* to the strapped side and 1.383 Å out of the porphyrin mean plane. The other lead cation (Pb1) is not bound to the porphyrin N-core (average Pb1–N = 3.243 Å), but is hanged at 2.323 Å above the porphyrin mean plane. Its coordination sphere involves two dihapto carboxylate ligands, an intramolecular one from the strap and an exogenous one, and is completed by one DMSO ligand, with lead at the apex of a distorted pyramid. This strongly hemidirected distribution of the ligands is ascribed to the lone pair of lead which, as shown below, points towards the N-core of the macrocycle. Both the exogenous acetate and DMSO ligands are oriented at almost 90° relative to the carboxylate of the strap and are H-bonded to one amide NH group (dashed lines in Fig. 2). The Pb–Pb distance of 3.727 Å amounts to 92% of the sum of lead van der Waals radii, which indicates no metal–metal interactions. It is noteworthy that very similar inter-molecular Pb–Pb distances are found in mononuclear lead porphyrin complexes stacked in a closely related arrangement.[4b] From these structural data, the Pb1 ion appears as "floating" above the porphyrin, in what we define as a *hanging-atop* (HAT) coordination mode.

The formation of **1$_{\mathbf{Pb}}$·PbOAc** from **1$^{\mathbf{Pb}}$** is instantaneous at room temperature. This, again, strongly contrasts with the prolonged heating required for lead insertion into unfunctionalized porphyrins. Low activation energy could be due to the deformation of the porphyrin macrocycle induced by the *out-of-plane* coordination of lead in **1$^{\mathbf{Pb}}$**, similarly to what is described in transmetalation processes with unfunctionalized porphyrins.[9] A distortion-mediated mechanism related to that involved in chelatase-catalyzed insertions of metal ions into porphyrins[10] was presumably observed with a closely related ligand in the case of Pb(II) → Bi(III) transmetalation.[11] Therefore, the second lead ion (Pb2) is expected to approach from the naked side, opposite to the first lead atom Pb1 (transmetalation process), the latter being picked back up by the carboxylate group of the strap to yield **1$_{\mathbf{Pb}}$·PbOAc** (translocation process, Scheme 1). In the overall mechanism leading to **1$_{\mathbf{Pb}}$·PbOAc**, transmetalation and translocation are however coupled and do operate in a strong cooperative way (no translocation, no transmetalation). In other words, insertion of Pb2 and departure of Pb1 are assisted by the carboxylate of the strap, only if a suitable counteranion as acetate is present in the media. This unique HAT coordination mode thus allows a lead cation to be stereo-selectively coordinated to the N-core of the porphyrin, *i.e.* either *inside* or *outside* the strap, in an apparent switching process.

The counteranion dependence of the dinuclear complex, and the high field shift of the Pb1-bound acetate observed in the ^{1}H NMR spectrum of **1$_{\mathbf{Pb}}$·PbOAc**, are consistent with the

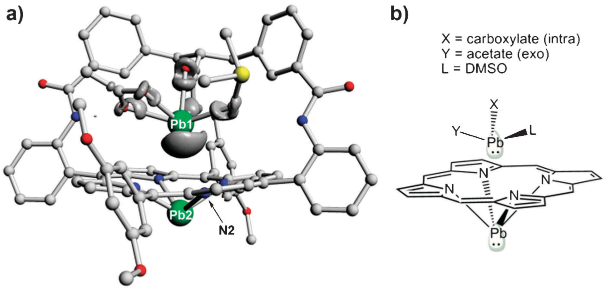

Fig. 3 (a) DFT-optimized structure of $\mathbf{1_{Pb}\cdot PbOAc}$ (hydrogen atoms removed) and deformation electron-density isosurface for the coordination sphere of Pb1 (contour value: $+0.008$ e bohr^{-3}). (b) Structural type observed for $\mathbf{1_{Pb}\cdot PbOAc}$ (second coordination sphere omitted).

inward orientation of Pb1 in solution as in the crystal structure. Density functional calculations (DFT) were performed to probe the role of the lone pair of the lead cations in this new HAT binding mode. Calculations were carried out at the B88P86/LANL2DZ[12,13] level of theory using Gaussian09.[14] A full *in vacuo* geometry optimization of $\mathbf{1_{Pb}\cdot PbOAc}$ was first performed starting from the X-ray structure. The computed geometry does not show significant modifications of the complex (Fig. 3a). The lone pair of each lead cation was indirectly localized using the deformation electron-density map.[15] In a hemidirected coordination geometry, the observed residual electron density in the vicinity of a lead atom is attributed to a *trans* deformation of the lone pair orbital relative to the proximal ligands.[16] Logically, the lone pair of Pb1 and Pb2 points towards and away from the N-core of the macrocycle, respectively (Fig. 3a, ESI†). Because of a quasi-symmetrical N4 environment, the lone pair of Pb2 keeps an axial symmetry whereas that of Pb1 appears distorted and slightly directed towards the N2 atom, but without effect on Pb1–N2 length. Therefore, there is evidence neither for a specific interaction between the lone pair of Pb1 and the N-core of the macrocycle, nor for any repulsion, and a faithful structural type for $\mathbf{1_{Pb}\cdot PbOAc}$ can be drawn as in Fig. 3b. The role of the counteranion was also investigated by DFT. First, the H-bonding interaction between the AcO^- and the NHCO was evaluated to be ~10 kcal mol^{-1}. Second, the bound AcO^- was replaced by a nitrate and DFT calculations of the complex $\mathbf{1_{Pb}\cdot PbNO_3}$ did not evidence significant differences with $\mathbf{1_{Pb}\cdot PbOAc}$, the bound nitrate being at a distance of the strap compatible with H-bonding interaction with the NHCO (ESI†).[17] In contrast, in the optimized structure of a hypothetical complex $\mathbf{1_{Pb}\cdot PbCl}$, the chloride anion is standing ~6 Å away from the NHCO of the strap and does not exhibit any intramolecular stabilizing interactions. Therefore, this second sphere of coordination defined by the intramolecular H-bond with the strap could be stronger with the AcO^-, if not specific, and explains why the formation of a dinuclear complex relies on the presence of this counterion.

In summary, we have described a new *hanging-atop* (HAT) coordination mode in a dinuclear lead complex with an overhanging carboxylic acid porphyrin. The HAT lead cation does not interact with the N-core but adopts an *inward* geometry stabilized through a second sphere of coordination with the strap. This intramolecular secondary interaction is best achieved with an acetate counterion, and is established owing to the 6s^2 stereochemically active lone pair that favorably orients the bound anion. The out-of-plane, *outside-the-strap* geometry, binding of Pb2 should favour the *inward* orientation of the HAT Pb(II), of which the 6s^2 lone pair can 'accommodate' in the dome-shaped porphyrin core. This coordination mode is responsible for a unique translocation-coupled transmetalation process, in which a lead cation bound to the N-core can be formally switched from an *inside* to an *outside* position, or in other words, can be stereoselectively incorporated in the strapped macrocycle, in a dynamic way. The hanging carboxylic acid approach provides a new opportunity to further extend the frontiers of porphyrin-like coordination chemistry.

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7 $\mathbf{1^M}$ ($\mathbf{1_M}$) refers to a metal ion coordinated in an *inside* (*outside*) position relative to the strap.

8 HRMS (ESI-TOF) measurements: at a 1 : 1 **1**/Pb(OAc)$_2$ ratio (negative ion mode), *m*/*z* calcd for $C_{66}H_{49}N_6O_8Pb$: 1261.3384 [**1**-3H + Pb]$^-$; found: 1261.3389. At a 1 : 3 **1**/Pb(OAc)$_2$ ratio (positive ion mode), *m*/*z* calcd for $C_{66}H_{49}N_6O_8Pb_2$: 1469.3143 [**1**-3H + 2Pb]$^+$; found: 1469.3149 (AcO^- is loss in the ionisation process).

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