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FOCUS ARTICLE

Compartmentalized *vs.* Non-Compartmentalized Translocations in Metal Porphyrin Complexes

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Double translocation processes in homo- and heterobimetallic bis-strap porphyrin complexes rely on the coexistence of two different coordination modes namely out-of-plane (OOP, bound to the N-core) and hanging-atop (HAT, bound to the strap). Two different dynamics were encountered: (i) the metal ions stay on their respective side of the macrocycle while exchanging between the strap and N-core binding sites (compartmentalized process); (ii) the metal ions exchange between the two sides of the porphyrin and maintain their OOP/HAT coordination modes (non-compartmentalized process). Various stimuli were used to tune these dynamic bimetallic systems (allosteric effector, acid-base conditions, dynamic constitutional evolution, light exposure).

1. Introduction

Besides being implied in the pigments of life in Nature porphyrins appear to be one of the most versatile ligands, with widespread utilization in the construction of bioinspired models[1] as well as supramolecular assemblies.[2] In Nature, porphyrins lead exclusively to monometallic species with the metal cation bound either in-plane or out-of-plane depending on the number of axial ligands and the spin state. Generally, the out-of-plane displacement does not exceed 0.5 Å. In synthetic chemistry and with regular (non N-alkylated) porphyrins, bimetallic complexes, although scarce, were reported with rhenium(I) and thallium(I), respectively by Tsutsui[3] and Smith,[4] some forty years ago. In these homobimetallic complexes, the porphyrin acts as a bridging ligand between the two cations as evidenced by X-ray structures.[4,5] Each cation "escapes" from the N-core with an out-of-plane (OOP) displacement of *ca.* 1.6 Å, resulting in only three nitrogen-metal bonds among the four possible ones. This type of coordination can be seen as midway between the regular N4-coordination sphere and Fleischer's sitting-atop intermediate with only two bonds to the N-core (SAT complex).[6]

Although much work has been devoted to the metallation mechanism of porphyrins,[7] few studies have focused on the possible entrance/departure of a metal at will, in order to confer and exploit a dynamic character to the N-core-metal interaction.[8] In this vein, transmetallation reactions have been investigated, mostly with non-functionalized porphyrins, focusing on the kinetic of the entering metal.[9] However, no attention has been paid to the fate of the leaving metal,

released in the medium. As reviewed in this Focus Article, an interesting situation has emerged from porphyrins appended with another binding site such as an overhanging carboxylic acid group (porphyrins **1-3**, Figure 1). For instance, translocation of a N-core bound metal to this second binding site can indeed occur in a dynamic (reversible) way. The vacant N-core upon translocation is likely to be occupied by an entering metal, affording new types of bimetallic complexes that are formed and disrupted in a dynamic way or undergo degenerate exchange reactions. In general, metal translocations triggered by external stimuli are not so widespread in supramolecular coordination chemistry,[10] although such processes could lead to new types of molecular
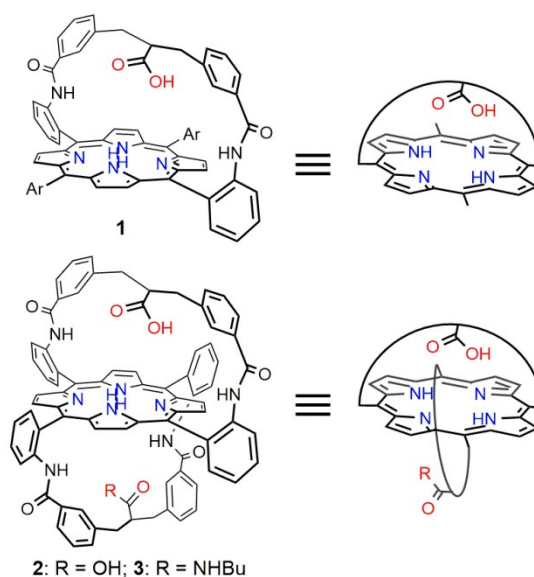

Figure 1. Structure of porphyrins **1**, **2** and **3** (Ar = 3,5-dimethoxyphenyl).

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switches and devices.[11] Usually, the different binding sites are not compartmentalized (there is no hurdle between them) and are thus 'freely' accessible. In the specific case of porphyrins, if the two sides of the macrocycle form two binding sites, the porphyrin can represent a hurdle depending on the size of the metal and its ability to funnel through the N-core. This can drastically affect exchange mechanisms, involving intermolecular or intramolecular pathways. Herein, such dynamic coordination processes are discussed and bimetallic porphyrin complexes exhibiting double translocation processes are reviewed.

2. Dynamic Stereoselective Metalation

When the two sides of the porphyrin are not equivalent as in all hemoproteins, both the relative location and the possible migration of the N4-bound cation are crucial. A timely example is the iron cation bound out-of-plane (0.3 Å) towards its fifth ligand (His F8) in deoxymyoglobin. Upon dioxygen binding, the cation moves in the plane to accommodate the resulting diamagnetic six-coordinate complex but is never found on the other (distal) side.[12]

2.1 Spontaneous *vs.* triggered migration through the ring

Formally, once a metal cation in the plane of the C_2-symmetric bis-strap porphyrin **2** (Figure 1), it could be displaced towards any of the two sides of the macrocycle, each delivering an
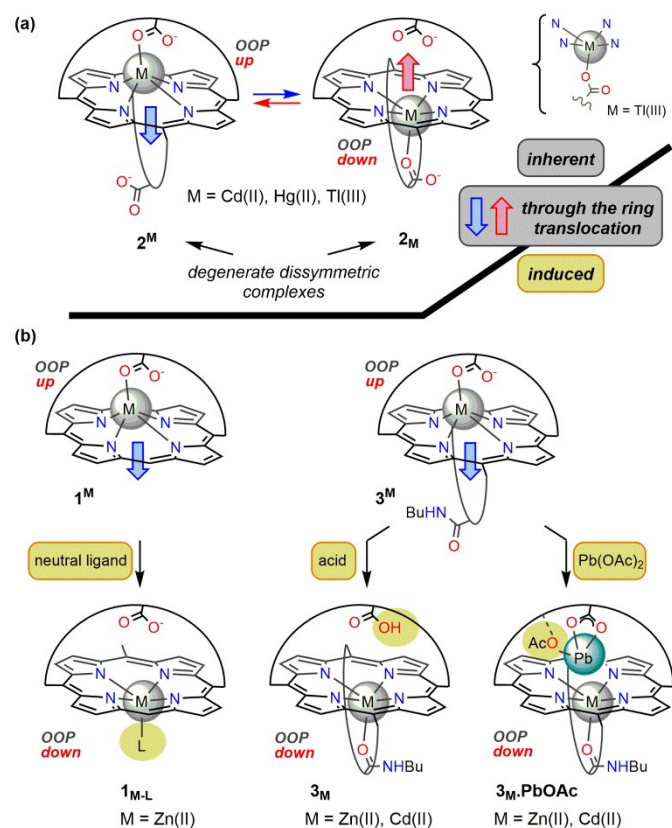
overhanging carboxylic acid group as potential intramolecular axial ligand. Although this scenario does not exist in Nature, it is instructive with synthetic complexes.

Porphyrin **2** readily forms monometallic complexes with Cd(II),[13] Hg(II),[14] and Tl(III)[15] the metallation processes being instantaneous at room temperature (**2^M**, Scheme 1a). The X-ray structures of the cadmium and thallium complexes revealed an out-of-plane coordination with respectively a dative coordination bond from the carbonyl function of one of the two overhanging carboxylic groups (Cd(II) OOP displ. = 0.856 Å), or a σ-bond from the carboxylate group (Tl(III) OOP displ. = 0.914 Å), leading to dissymmetric structures. Since the two straps are equivalent, the monometallic complexes exist as equimolar mixtures of two degenerate forms **2^M**/**2$_M$** (Scheme 1a; "M" superscripted/subscripted indicates the up/down position of the metal). In solution, under adequate basic conditions, these degenerate forms are in a fast exchange regime on the NMR time scale, as revealed by their C_2-symmetric signatures. Exchange correlation peaks in the 2D ROESY map between protons of the two straps were also observed below the coalescence temperature.[15] The metal exchange process between the two sides occurs via a migration through the ring of the porphyrin (Scheme 1a). This exchange has to be intramolecular by exclusion of any other possible intermolecular process that would imply *de facto* the free-base ligand. Indeed, proton NMR spectra of 1:1 mixtures of **2** and **2^M** revealed two well-differentiated C_2-symmetric traces even at high temperatures, which correspond to fast exchange regimes for the side-to-side migration process and to slow exchange regimes for the binding to the N-core, therefore ruling out any intermolecular process.[13,15]

In contrast to this inherent side-to-side funnelling, controlled translocation can be achieved by different means with dissymmetric ligands such as **1** and **3**, affording stereoselective metallations (Scheme 1b). Considering Zn(II) incorporation in **1**,[16] X-ray structure of the monometallic complex (**1^{Zn}**) indicates that the cation is located 0.51 Å out-of-plane on the strapped side with the intramolecular carboxyl group π-bound as a fifth ligand. The opposite "down" stereoselectivity can be triggered by addition of a competitive axial ligand, *i.e.* 4-dimethylaminopyridine (DMAP). A new complex is formed (**1$_{Zn-DMAP}$**) in which Zn(II) is located on the opposite side of the macrocycle with DMAP as its fifth ligand. Translocation of Zn(II), presumably through N-core, occurs because DMAP cannot bind from the strapped side for steric hindrance reasons. In the case of **3**, stereoselectivity of Zn(II) and Cd(II) relies on the protonation state of the overhanging COOH group. Considering the following order of affinity for the carbonyl group as a fifth ligand, COO$^-$ > CONH > COOH, the metal ions translocate from upper to lower side (**3^M** -> **3$_M$**) upon changing from basic to acidic medium (Scheme 1b).[16] Besides, the addition of a second metal ion to **3^M** ('PbOAc', see below) which binds selectively to the overhanging COO$^-$ group, also triggers the migration of Zn(II) or Cd(II) that are 'forced' to bind to the overhanging butylamide group (**3$_M$.PbOAc**, Scheme 1b).[16]

Scheme 1 Side-to-side inherent (a) and induced (b) metal migration processes through the porphyrin N-core.

2.2 Translocation-coupled transmetallation owing to a new 'hanging-atop' coordination mode

With a larger metal ion as Pb(II), which cannot funnel through the N-core,[17] a stereoselective metallation of **1** was also achieved but in a different way (Scheme 2).[18] In solution, the addition of one equivalent of lead acetate supplied the monometallic complex **1^{Pb}** as a major species. The metal insertion is instantaneous at room temperature suggesting that the binding is assisted by a deconvolution process[19] from the carboxylate group of the strap, leading selectively to an "up" Pb(II) ion (without any bond with the intramolecular carboxylic group). With a second equivalent of Pb(OAc)$_2$, the bimetallic complex **1$_{Pb}$.PbOAc** was formed (Scheme 2) with a Pb(II) OOP-bound to the N-core on the naked side ("down" stereoselectivity, Pb(II) OOP displ. = 1.383 Å) and a second one as a PbOAc moiety bound to the carboxylate group of the strap, without interaction with the N-core (hanging-atop coordination mode, HAT). The most plausible pathway explaining the formation of **1$_{Pb}$.PbOAc** from **1^{Pb}** is a translocation-coupled transmetallation process (Scheme 2). The second cation ('Pb2') approaches the porphyrin by its naked side (transmetallation) while the N-core bound 'Pb1' is picked back up by the intramolecular carboxylate group (translocation).
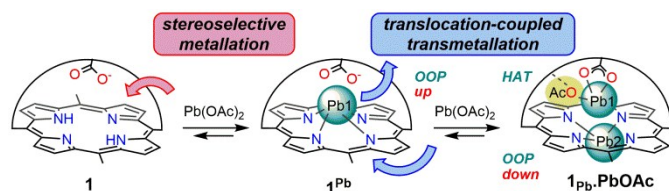

Scheme 2 Successive formation of mono- and bimetallic Pb(II) complexes of **1** with an opposite stereoselectivity for the OOP Pb(II) ion.

3. Double translocation processes in bimetallic complexes

3.1 Homobimetallic complexes: compartmentalized translocations

The above mentioned translocation-coupled transmetallation process was transposed to the C_2-symmetric ligand **2**, which led to a unique fluxional behaviour. The dissymmetric bimetallic complex **2$_{Pb}$.PbOAc**, incorporating OOP and HAT Pb(II) ions on opposite sides, was readily obtained either by addition of two equivalents of Pb(OAc)$_2$ to **2** or by the addition of acetate ions to the C_2-symmetric bimetallic complex **2Pb$_2$** with both Pb(II) bridged by the N-core (Scheme 3).[20,21] This complex exists as two degenerate forms, depending on which side is located the OOP Pb(II) (**2$_{Pb}$.PbOAc**/**2^{Pb}.PbOAc**). NMR data revealed an equilibrium between these two states: (i) the 2D ROESY NMR spectrum showed exchange correlations between protons of the two straps, corroborated by (ii) variable temperature NMR studies evidencing a coalescence of the signals of the two straps, leading to a C_2-symmetric NMR pattern upon heating. In addition, the coalescence temperature for the exchange process is independent of the concentration of Pb(II) in the medium. All these data indicate an

intraligand exchange process, the Pb(II) ions remaining on their respective side while undergoing a coupled exchange of coordination modes: OOP -> HAT / HAT-> OOP (Scheme 3, the exchange of the bound acetate follows an intermolecular pathway). This compartmentalized double translocation process resembles the motion of spheres in a Newton's cradle device, with the correspondence "lifted sphere" / "metal HAT" and "resting sphere" / "metal OOP" (Scheme 3). The dynamics of this bimetallic system depends on the presence of acetate ions in the medium, acting as allosteric effectors. Indeed, the binding of an acetate to **2Pb$_2$** ("resting" state) modifies the coordination spheres of both metal ions, thereby triggering the degenerate exchange reaction ("active" state, Scheme 3). An activation barrier of 13.7 kcal.mol^{-1} has been calculated for this double translocation process with Pb(II), corresponding to an oscillation frequency of about 500 Hz at 298 K. From a structural point of view, the distance of Pb to the mean plane of the porphyrin in **2Pb$_2$** (1.79 Å) is midway between those of the OOP and HAT Pb in **2$_{Pb}$.PbOAc** (1.38/2.32 Å). Hence, a motion of *ca.* 1 Å for a Pb(II) ion occurs while exchanging from HAT to OOP coordination.
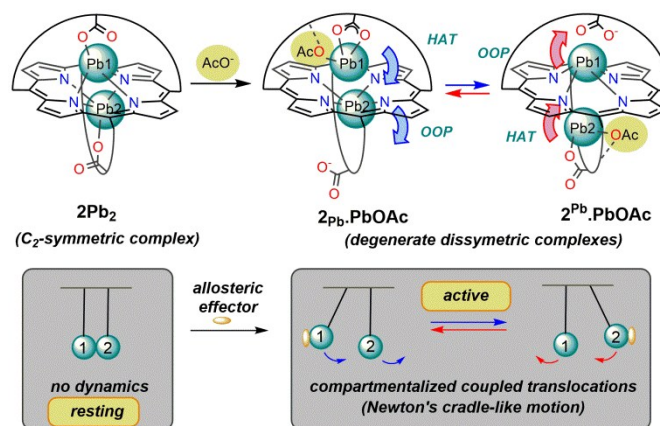
Scheme 3 Allosterically controlled double translocation process in bimetallic Pb(II) complexes of **2**.

Other homobimetallic complexes of the strapped porphyrin **2** were found to undergo such a compartmentalized double translocation process. For instance, the metallation of **2** with Cd(OAc)$_2$ gave a bimetallic dissymmetric complex with HAT and OOP Cd(II) ions on opposite sides.[13] NMR studies revealed an equilibrium between the two degenerate states proceeding *via* an intraligand metal exchange. Although Cd(II) can funnel through the porphyrin N-core (Scheme 1), it does not happen in this homobimetallic system. Indeed, an exchange process of the metals involving a funnelling through the N-core would imply an intermolecular pathway for the second metal. Thus, a compartmentalized double translocation process of the metals, similar to that observed for Pb(II) (Scheme 3), takes place also with Cd(II) with however a lower energy barrier (11.5 kcal.mol^{-1}). An allosteric control was achieved as well through the addition of acetate ions to a C_2-symmetric Cd(II) bimetallic complex, *i.e.* the Cd(II) counterpart of **2Pb$_2$**.

In general, bimetallic complexes featuring double translocation processes are scarce. Following different approaches with other ligands than porphyrins, two systems have been reported, one by Fabbrizzi, Pallavicini and coworkers under acid-base control,[22] and a second by Reinaud and coworkers under redox control[23] (Scheme 4a,b). In these two cases, the translocation processes likely follow intermolecular pathways (non-compartmentalized exchange), which drastically differ from the working principle of the Cd(II) and Pb(II) homobimetallic complexes of **2** (compartmentalized, Scheme 4c).
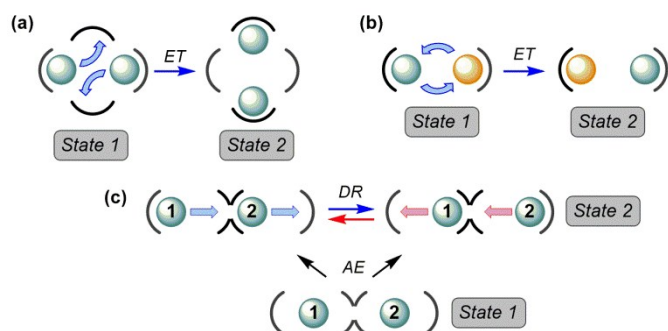
Scheme 4 Comparison of double translocation processes in some bimetallic complexes: (a,b) non-compartmentalized *vs.* (c) compartmentalized (ET = external trigger, AE = allosteric effector, DR = degenerate reaction).

The scene is slightly different with a large trivalent metal ion as Bi(III). The metallation of **2** with an excess of $Bi(OAc)_3$ supplied a mixture of two bimetallic complexes (Scheme 5), a C_2-symmetric one with both Bi bridged by the N-core (**2(BiOAc)$_2$**) and a dissymmetric one with an OOP Bi on one side and a HAT Bi on the other (**2$_{Bi}$.Bi(OAc)$_2$**).[20] The latter also exists as two degenerate states in equilibrium (**2$_{Bi}$.Bi(OAc)$_2$ ⇆ 2^{Bi}.Bi(OAc)$_2$**), as revealed by 2D ROESY NMR experiments. The exchange process is *a fortiori* intramolecular: (i) since the large Bi(III) cation cannot funnel through the N-core,[17] an intermolecular pathway would imply a release and binding of both Bi(III) ions, which would be energetically costly; (ii) no exchange correlations were detected between protons of the two straps of the corresponding monometallic Bi(III) complex, reflecting a high association constant. Hence, the degenerate exchange process between **2$_{Bi}$.Bi(OAc)$_2$** and **2^{Bi}.Bi(OAc)$_2$** is likely a two-step process involving **2(BiOAc)$_2$** as intermediate through the release and binding of an acetate (Scheme 5). The distance of Bi to the mean plane of the porphyrin in **2(BiOAc)$_2$** should be midway between that of the OOP Bi (1.31 Å) and that of the HAT Bi (2.58 Å).[20] This behaviour contrasts with the above described Pb(II) and Cd(II) bimetallic complexes, since the C_2-symmetric species (*e.g.* **2Pb$_2$**) was not observed in the presence of acetate, but is likely a transition state in the double translocation process. In addition, we also observed that the ratio of **2(BiOAc)$_2$** and **2$_{Bi}$.Bi(OAc)$_2$** was dependent on acid-base conditions, *e.g.* 5:95 and 85:15 ratios of these two species were respectively found in the presence and without DIPEA. Hence, this dynamic coordination of bismuth leads also to compartmentalized translocations with a

possible acid-base control over the population of "resting" and "lifted" states (green/purple arrows in Scheme 5).
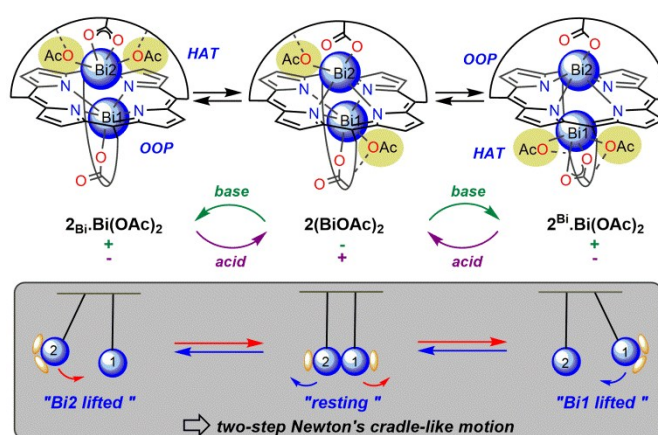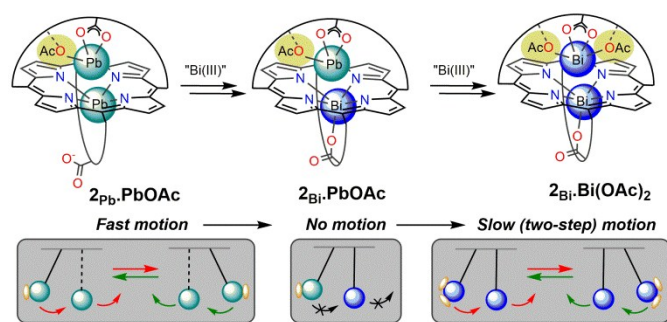

Scheme 5 Acid-base controlled double translocation process in Bi(III) bimetallic complexes of **2**.

3.2 Heterobimetallic complexes: no translocation or non-compartmentalized translocations

Moving from homobimetallic complexes of **2** to heterobimetallic ones led to very different scenarios. The first reported example of a heterobimetallic complex incorporating a HAT metal was **2$_{Bi}$.PbOAc** (Scheme 6, middle).[20] Formally, metallation of **2** by an equimolar mixture of bismuth and lead salts could deliver three types of heterobimetallic coordination isomers depending on which metal is OOP or HAT: Bi(OOP)/Pb(HAT), Bi(OOP)/Pb(OOP), Bi(HAT)/Pb(OOP). By analogy with the NMR chemical shift of the HAT acetate in **2$_{Pb}$.PbOAc**, and confirmed by an X-ray structure, **2$_{Bi}$.PbOAc** is exclusively obtained (Scheme 6, middle). Various experimental conditions for the coordination of these two cations failed to evidence other coordination isomers of this heterobimetallic complex. Also, exchange correlations between protons of the two straps were not observed in a 2D NMR NOESY spectrum. In other words, equilibrium between the two degenerate forms could not be detected. By analogy with the corresponding homobimetallic Pb/Bi complexes, **2$_{Bi}$.PbOAc** appears as a frozen lifted state of an inactive Newton's cradle device.

Selective Pb(II)-to-Bi(III) transmetallations were used to tune the dynamic of the system (Scheme 6).[20] Indeed, the addition of Bi(III) to **2$_{Pb}$.PbOAc** led to the successive formation of **2$_{Bi}$.PbOAc** and to the mixture of **2(BiOAc)$_2$** and **2$_{Bi}$.Bi(OAc)$_2$** (for experimental details, see Ref. 20). This allowed shifting from a system displaying fast double translocations on the NMR time scale, to a "frozen" system, to a system displaying 'two-step' translocations on the NMR time scale.

The situation was somewhat different when **2** was metallated in the presence of a base (DIPEA) by either mercury or cadmium, and subsequent treatment with lead acetate. These metallation reactions led very selectively to the formation of heterobimetallic complexes in which Pb(II) is the HAT-bound metal and the other metal (Hg(II) or Cd(II)) is OOP-bound to the N-core with an apical

Scheme 6 Double translocation processes in Pb(II)/Bi(III) bimetallic complexes of **2** tuned by successive Pb(II)-to-Bi(III) transmetallations.
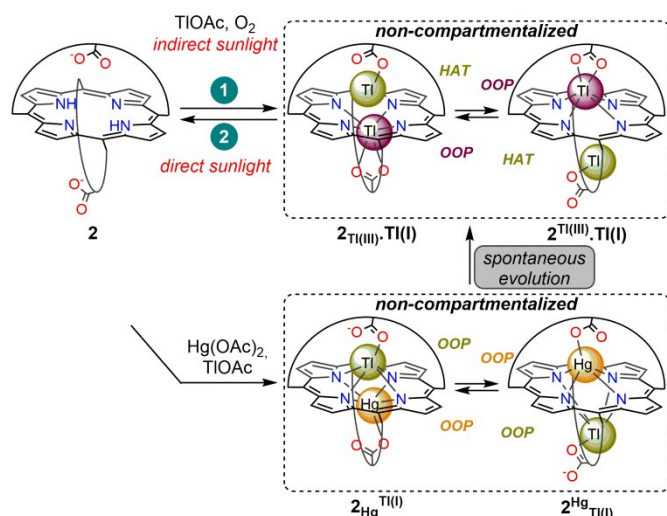

Scheme 7 Double translocation processes in Pb(II)/Hg(II) bimetallic complexes of **2** tuned by a dynamic constitutional evolution of the system.

bond to the carbonyl of the overhanging COO⁻ group (*e.g.* **2Hg.PbOAc**, Scheme 7 top).[24] Similarly to **2Bi.PbOAc**, no other coordination isomer was detected. Conversely, 2D NMR ROESY spectra as well as variable temperature NMR studies evidenced an equilibrium between the two degenerate states of the Hg/Pb and Cd/Pb heterobimetallic complexes (*e.g.* **2Hg.PbOAc** ⇌ **2^Hg.PbOAc**, Scheme 7 top). A compartmentalized double translocation process as in **2Pb.PbOAc** (Scheme 3) is precluded, as it would give a coordination isomer (which does not exist) instead of the second degenerate state. As cadmium and mercury can readily funnel through the plane of the porphyrin (Scheme 1a), the most plausible scenario is an intraligand side-to-side exchange of Hg(II) and Cd(II) through the N-core, combined to an intermolecular pathway for 'PbOAc' (Scheme 7 top). Thus, in contrast to their homobimetallic counterparts **2Pb.PbOAc** and **2Bi.Bi(OAc)₂**, the double translocation process is not compartmentalized: both cations change their location from one side to the other but remain in the same coordination mode, in a so-called "defective" Newton's cradle motion. In **2Pb.PbOAc** and **2Bi.Bi(OAc)₂**, the cations change both their location and their coordination but do remain on the same side of the macrocycle. The energy barrier of the exchange **2M.PbOAc ⇌ 2^M.PbOAc** with M = Cd(II) is higher than that with M = Pb(II) (15.1 *vs.* 13.7 kcal.mol⁻¹), probably as a result of the intermolecular pathway for the 'PbOAc' translocation in the former system.

In the case of the heterobimetallic complex **2Hg.PbOAc**, a dynamic constitutional evolution of the system was accomplished, which constitutes a proof-of-concept towards new types of adaptative systems (Scheme 7).[24] The addition of an excess of DMAP to this complex led very selectively to the formation of the corresponding homobimetallic complexes **2Hg₂-DMAP** and **2Pb.PbOAc**; this is due to (i) to the higher affinity of DMAP for **2Hg₂**, and (ii) to the agonist relation between the Hg(II) and Pb(II) homobimetallic complexes *vs.* the antagonist relation between the homo and heterobimetallic complexes. Such a dynamic constitutional evolution process allows to tune the compartmentalized *vs.* non-compartmentalized nature of the double translocations processes between degenerate states. More recently, the formation of a possible homobimetallic complex between **2** and thallium was investigated. When the monometallic complex **2^TI(III)** (Scheme 1a) was treated with an excess of Tl(OAc)₃, no other species was detected. Conversely, the addition of TlOAc
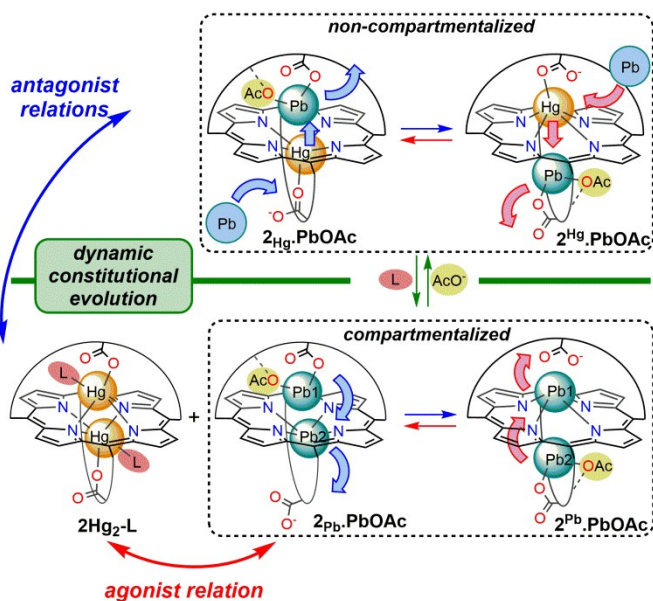
led to a significant modification of the proton NMR spectrum, clearly indicating the complexation of Tl(I), and thus the formation of the first mixed valence Tl(III)/Tl(I) porphyrin complex.[15] An X-ray structure of this species, namely **2TI(III).Tl(I)** was resolved and confirmed the existence of a HAT Tl(I) cation (Scheme 8, top). In the absence of base, its ¹H NMR spectrum is dissymmetric at 298 K, and a 2D NMR ROESY experiment showed exchange correlations between the protons of the two straps, indicating that the metal ions exchange their position relatively to the porphyrin plane. Similarly to **2Hg.PbOAc**, a double translocation takes place with an intramolecular motion of the OOP-bound Tl(III) through the porphyrin ring combined with an intermolecular motion of the HAT-bound Tl(I) from one strap to the other one (non-compartmentalized exchange process). Two unexpected ways were found to obtain the mixed valence complex **2TI(III).Tl(I)**:

(i) through the exposure to (*indirect*) sunlight of a solution of **2** and TlOAc in the presence of oxygen (Scheme 8, top).[15] Photosensitization of O₂ by the porphyrin is indeed responsible for a Tl(I)-to-Tl(III) oxidation process. Also, exposure of **2TI(III).Tl(I)** to (*direct*) sunlight led to a dissociation of the complex, presumably owing to the formation of Tl(0), leading to the free base **2** very cleanly (Scheme 8, top). Thus, a photo-control over the formation and disappearance of a dynamic bimetallic thallium complex was demonstrated.

(ii) through the formation and spontaneous evolution of a heterobimetallic Hg(II)/Tl(I) complex (**2Hg^TI(I)**, Scheme 8 bottom).[25] Conversely to **2TI(III).Tl(I)**, the two metal ions are bridged by the N-core (OOP coordinations) but the complex also undergoes equilibrium between its two degenerate forms through a non-compartmentalized double translocation process (funnelling of Hg(II) through the porphyrin ring; intermolecular exchange of Tl(I)). The spontaneous Tl(I)-to-Tl(III) oxidation in dark is mediated by an equimolar amount of Hg(II), without need of oxygen, which

enlarges the tool-box to control the dynamics of such bimetallic porphyrin complexes.

Scheme 8 Top: sunlight controlled formation/disappearance of a mixed valence Tl(III)/Tl(I) bimetallic complex of **2** featuring a non-compartmentalized double translocation process. Bottom: spontaneous evolution of a dynamic bridged Hg(II)/Tl(I) bimetallic complex of **2** into its Tl(III)/Tl(I) counterpart.

4. Conclusion

Owing to simple strapped porphyrin ligands, it has become possible to achieve the instantaneous and easy-to-control formation of various bimetallic species featuring new coordination modes and dynamics, thereby opening a new chapter in supramolecular coordination chemistry of porphyrins. Either spontaneous or triggered, these bimetallic complexes can undergo double translocation processes of two main types: (i) the metal ions stay on their respective side of the macrocycle while exchanging between coordination to the strap and to the N-core, which corresponds to a compartmentalized process; (ii) the metal ions exchange between the two sides of the porphyrin (and retain their coordination mode) with migration of one of the metals through the porphyrin ring, the process is not compartmentalized anymore. It can be expected that new functional systems would emerge by simply playing and adjusting these different dynamics and coordination modes together in related porphyrinoids. For instance, switchable catalysts can be envisioned with the reactivity of a metal centre addressed by a translocation event between the strap and N-core binding sites.

Acknowledgements

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Strapped porphyrin ligands exhibit instantaneous and easy-to-control formation of various bimetallic species featuring new coordination modes and dynamics.