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Hg(II)-Mediated Tl(I)-to-Tl(III) Oxidation in Dynamic Pb(II)/Tl Porphyrin Complexes

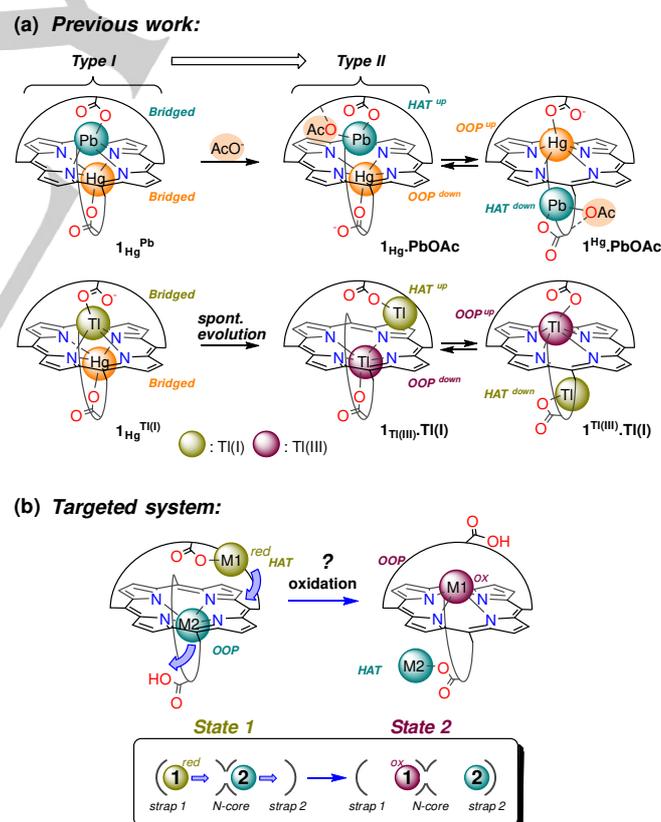
Stéphane Le Gac,^{*[a]} Victoria Ndoiyom,^[a] Luca Fusaro,^[b] Vincent Dorcet,^[a] and Bernard Boitrel^{*[a]}

Abstract: Compared to their purely organic counterparts, molecular switches based on metal ion translocations have been underexplored and, more particularly, it remains challenging to control the translocation of several particles in multisite receptors. Recently, bimetallic complexes undergoing double translocation processes have been developed with bis-strapped porphyrin ligands and in order to implement a redox control for these systems, we have investigated herein the formation of heterobimetallic lead/thallium complexes, with thallium stable in the +I and +III oxidation states. Two different complexes were characterized: (i) a Pb(II)/Tl(I) complex with both metal ions interacting with the N-core on its different sides; (ii) a Pb(II)/Tl(III) complex with Tl(III) selectively bound to the N-core and Pb(II) selectively bound to the strap opposite to Tl(III). These two complexes undergo an equilibrium between their two degenerate forms (same coordination of the metal ions but on opposite sides), according to different intra or intermolecular translocation pathways. In addition, conversion of the Pb(II)/Tl(I) complex into its Pb(II)/Tl(III) counterpart was achieved by addition of a stoichiometric amount of Hg(II) salt as a sacrificial electron acceptor. These results further contribute to the elaboration of devices featuring redox-controlled compartmentalized double translocations.

Introduction

Whereas the versatility of the regular porphyrin skeleton to form monometallic complexes with a wide range of elements is without equivalent, its ability to bind two metal ions at the N-core site remains unusual.^[1] Some bimetallic porphyrin complexes are however readily accessible upon relatively simple molecular design, opening the way to a new area in supramolecular coordination chemistry.^[2] For instance, porphyrins decorated with one or two straps, delivering so-called overhanging carboxylic acid groups from each side of the N-core, have shown a great versatility in the formation of bimetallic species with large metal ions propitious for out-of-plane complexation, as

Cd(II), Hg(II), Tl(I/III), Pb(II) and Bi(III).^[3] Fast and quantitative metalation at room temperature,^[4] control of the nuclearity and of the out-of-plane stereoselectivity,^[5-7] coupled translocation of two metal ions,^[8,9] dynamic constitutional evolution of homo/heterobimetallic species,^[10] as well as unexpected reactivities,^[11,12] were recently evidenced. These features underlie new functions to the porphyrin skeleton that could become part of a molecular device in which metal-to-porphyrin exchange plays a key role to obtain switchable states. Typically, molecular devices^[13] inspired by the compartmentalized motion of spheres in a macroscopic two-ball Newton's cradle can be foreseen (Scheme 1b),^[8,9] involving the translocation of a metal ion^[14] from a strap to the N-core ("M1-strap1" → "M1-N-core") coupled the opposite process on the other side of the ligand ("M2-N-core" → "M2-strap2"), and thus giving rise to two different states. Ideally, such a process could be controlled by



Scheme 1. (a) Illustration of three different binding modes ('Bridged', 'HAT' and 'OOP') found in two types of bimetallic complexes of ligand 1 and two possible ways for converting them. (b) Targeted systems featuring redox-controlled compartmentalized double translocations, based on bimetallic porphyrin complexes.

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changing the oxidation degree of one of the metal ions, triggering preferential binding at the level of the strap or the N-core.

From C_2 -symmetric bis-strap porphyrin ligand (**1**, Figure 1), we have recently described heterobimetallic complexes of different types with either Pb(II) and Hg(II)^[10] or Tl(I) and Hg(II),^[12] (Scheme 1a). In “type I”, both metal ions are bound to the N-core (the porphyrin acts as a bridging ligand, “bridged” coordination), while in type II, only one metal ion is bound to the N-core (*out-of-plane* coordination, OOP), the second metal ion being bound to the strap (*hanging-a-top* coordination, HAT). These dissymmetric complexes exist as two degenerate forms in equilibrium, *i.e.* the initial and final states are related by symmetry and thus equivalent in structure and energy. More precisely, the metal ions exchange their position relative to the porphyrin plane and retain their respective coordination modes (coupled translocation processes, *i.e.* HAT^{up} → HAT^{down} coupled to OOP^{down} → OOP^{up}). Type I-to-type II conversion was readily achieved by different means (Scheme 1a): addition of acetate ions in the first case,^[10] whereas in the second situation, spontaneous evolution of the Hg(II)/Tl(I) complex into a mixed valence Tl(III)/Tl(I) species was observed.^[11,12] The latter process, an Hg(II) mediated Tl(I)-to-Tl(III) oxidation, is well suited in the above mentioned context. Herein, we have expanded our investigations to Pb/Tl heteromultimetallic complexes, targeting Pb/Tl(I) and Pb/Tl(III) complexes, either directly or by means of Tl(I)-to-Tl(III) oxidation.

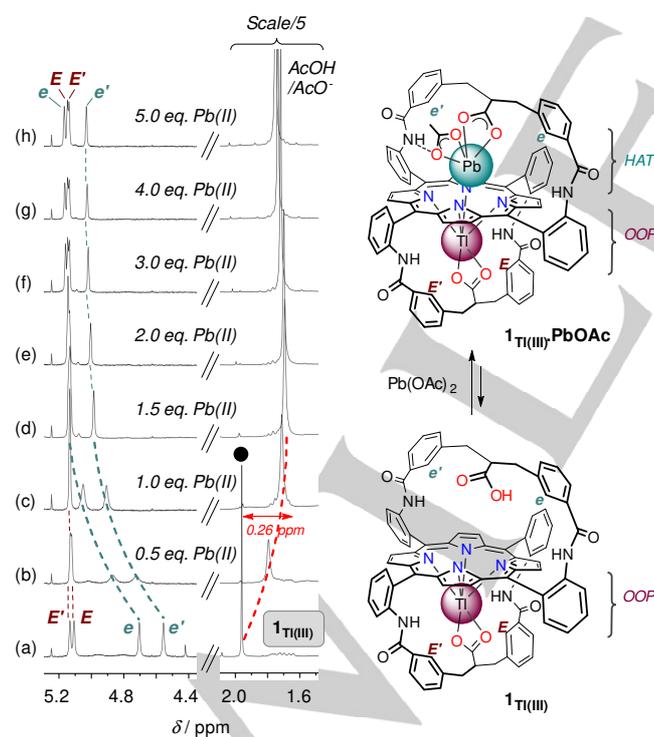


Figure 1. ^1H NMR titration experiment of $1_{\text{Tl(III)}}$ (a) with $\text{Pb}(\text{OAc})_2$ (b-h) (9:1 $\text{CDCl}_3/\text{CD}_3\text{OD}$, 298 K, 500 MHz, selected region); •: AcOH/AcO^- .

Results and Discussion

1. Formation of a Pb(II)/Tl(III) bimetallic complex

In a first set of experiments, we have investigated the formation of Pb(II)/Tl(III) bimetallic complex(es) with **1**. The monometallic complex $1_{\text{Tl(III)}}$ was quantitatively and instantaneously formed at room temperature by addition of 1.5 equiv. of $\text{Tl}(\text{OAc})_3$ to **1** (9:1 $\text{CDCl}_3/\text{CD}_3\text{OD}$ solution, Figure 1),^[11] and then submitted to ^1H NMR titration with $\text{Pb}(\text{OAc})_2$. Drastic changes were observed, attesting the binding of Pb(II) in a fast exchange regime at 298 K (Figure 1 and Figure S5; no trace of known lead complexes of $1_{\text{Tl(III)}}$ were observed). Also, the addition of Pb(II) led to a new ^{205}Tl NMR signal at 2509 ppm, highfield shifted by *ca.* 40 ppm (Figure S6). The new species displays a dissymmetric ^1H NMR pattern, evidencing two different sides of the ligand, and 2D NMR spectra allowed complete assignment of the ^1H chemical shifts. Notably, eight doublets of doublets are observed for the β -pyrrolic protons, with average coupling constants of *ca.* 5 Hz (3J H-H) and 63 Hz (4J H-Tl), as determined by 2D NMR and ^{205}Tl -decoupled ^1H NMR experiments (Figures S7 and S8). The latter coupling value remains close to those of $1_{\text{Tl(III)}}$,^[11] and is characteristic of a Tl(III) ion bound to the N-core of the porphyrin. The CH and CH_2 protons of the “thallium strap” also experience a coupling constant with Tl(III): ~ 30 Hz (5J H-Tl) and ~ 10 Hz (4J H-Tl). This confirms the binding of the overhanging COO^- group to Tl(III). The two He and He' aromatic protons of the “free strap”

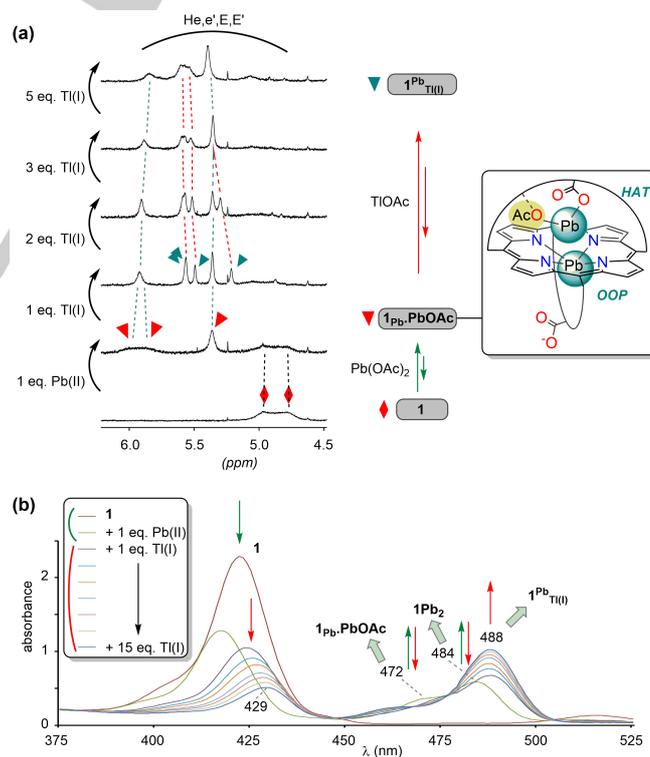


Figure 2. Titration experiment of **1** with $\text{Pb}(\text{OAc})_2$ (1 equiv.) and TlOAc (excess) monitored by (a) ^1H NMR spectroscopy ($\text{CDCl}_3/\text{CD}_3\text{OD}$ 9:1, DIPEA, 298 K, selected region: aromatic protons of the straps) and (b) UV-vis absorption spectroscopy ($\text{CHCl}_3/\text{CH}_3\text{OH}$ 9:1, DIPEA).

of $1_{\text{Tl(III)}}$ at 4.70 and 4.56 ppm are strongly deshielded by the addition of lead while those of the “thallium strap” HE and HE' are almost not affected (Figure 1). This is consistent with the binding of Pb(II) to the free strap of $1_{\text{Tl(III)}}$. Indeed, lead binding to the strap is expected to generate a more tilted strap experiencing a less shielding environment. Furthermore, highfield shift (up to 0.26 ppm) of the signal of the “free” acetates (Figure 1) together with a significant broadening at low temperature (down to 223 K) suggest that these anions participate to an exchange process involving their binding above the porphyrin plane, as seen previously with related compounds.^[7,8,10] In UV-vis spectroscopy, only a 2 nm red shift of the Soret band of $1_{\text{Tl(III)}}$ was observed upon addition of lead (437 to 439 nm, the solution remains reddish). It means that the coordination sphere of Tl(III) is not affected, except for a small variation of OOP displacement if any. All of these data are consistent with the formation of the complex $1_{\text{Tl(III).PbOAc}}$ (Figure 1) through the binding of a ‘PbOAc’ moiety in the so-called hanging-atop coordination mode. The temperature dependence of the ^{207}Pb NMR signal of $1_{\text{Tl(III).PbOAc}}$ (highfield shifted at low temperature) is also in accordance with this coordination mode.^[10]

2. Formation of a Pb(II)/Tl(I) trimetallic complex

In a second set of ^1H NMR experiments, we have investigated the formation of Pb(II)/Tl(I) bimetallic complex(es) with **1**, starting first with Pb(II) and Tl(I) acetate salts. Thus, in the presence of base (N,N-diisopropylethylamine, DIPEA), addition of 1 equiv. of $\text{Pb}(\text{OAc})_2$ to **1** in 9:1 $\text{CDCl}_3/\text{CD}_3\text{OD}$ led to a 1:1 mixture of **1** and $1_{\text{Pb.PbOAc}}$ (structure in inset Figure 2a),^[8] and this solution was subjected to titration with TIOAc (Figure 2a). This led to the

instantaneous formation of a new species displaying a dissymmetric NMR spectrum at 298 K (labeled with green triangles), but this process could not be brought to completion. The same titration experiment monitored by UV-vis spectroscopy (Figure 2b)^[15] showed the disappearance of the Soret bands at 422 and 472 nm, the latter corresponding to the OOP coordination of Pb(II) in $1_{\text{Pb.PbOAc}}$, together with the appearance of a Soret band at 488 nm which is typical for bridged bimetallic complexes with large metal ions such as Pb(II) and Tl(I).^[1e,3a] These data suggest the formation of a heterobimetallic Pb(II)/Tl(I) complex with both metal ions interacting with the N-core, namely $1_{\text{Pb.Tl(I)}}$ (*vide infra*, Figure 3).

We reasoned that the presence of acetate ions in solution could be a drawback for the complexation of Tl(I) since these anions contribute well to the binding of the ‘PbOAc’ moiety to the strap of **1**. Therefore, in order to introduce 1 equiv. of Pb(II), without acetate ions and to circumvent the low solubility of Pb(II) salts in 9:1 $\text{CDCl}_3/\text{CD}_3\text{OD}$ solution, we decided to work with a 1:1 mixture of **1** and 1_{Pb_2} (Figure 3b) and to use Tl(I) triflate. Accordingly, the ^1H NMR titration of **1** with TlOTf was first realized in basic conditions (DIPEA) (Figure 3a). A two-step binding event was observed: (i) first, the free base **1** is involved in a fast exchange process on the NMR time scale, without noticeable color change of the NMR tube (Figure 3a, red dotted lines). The corresponding NMR pattern is relatively broad and ill-defined C_2 -symmetric signature is formed in a slow exchange regime (Figure 3a, green dotted lines). A red-to-green color change is associated to this second process. An X-ray structure obtained from slow evaporation of the NMR tube solution

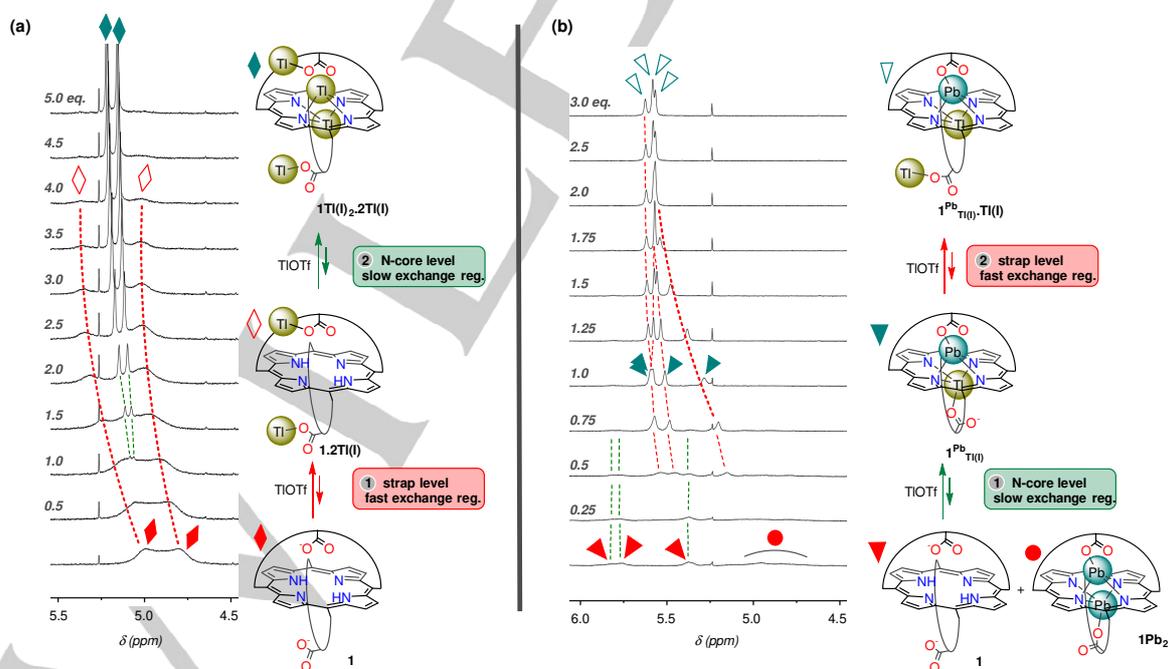


Figure 3. (a) Complexation behavior of **1** with TlOTf, monitored by ^1H NMR spectroscopy. (b) Complexation behavior of a 1:1 mixture of **1** and 1_{Pb_2} with TlOTf, monitored by ^1H NMR spectroscopy. Conditions: $\text{CDCl}_3/\text{CD}_3\text{OD}$ 9:1, DIPEA, 298 K, 500 MHz, selected signals (He, e, E, E').

(described below) evidenced the formation of a tetrametallic species, namely $1\text{Tl(I)}_2\cdot 2\text{Tl(I)}$ (Figure 4a), with two Tl(I) ions bridged by the N-core and one Tl(I) ion bound to COO^- group of each strap. Therefore, hypothesizing a higher affinity of Tl(I) for the strap vs. the N-core binding sites, the NMR titration is interpreted as follow: Tl(I) cations bind “first” to the strap in a fast exchange regime, and “second” to the N-core in a slow exchange regime, the latter process being responsible for the green color of the solution (Figure 3a).

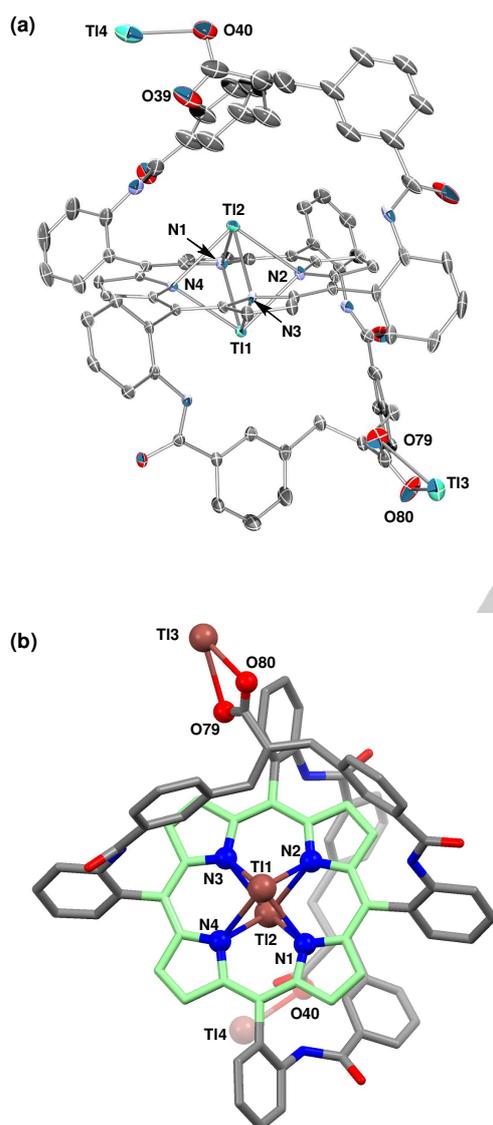


Figure 4. Crystal structure of $1\text{Tl(I)}_2\cdot 2\text{Tl(I)}$ (H atoms and solvents of crystallization were removed for clarity): (a) perspective ORTEP view with ellipsoids set at 30 % probability and (b) top view from the side of Tl3 (ball and stick representation with depth perspective, porphyrin coloured in green). Selected distances (Å): Tl1-24MP 1.7354(15), Tl2-24MP 1.7373(14), Tl1-Tl2 3.4774(4), Tl1-N1 2.679(6), Tl1-N2 2.641(6), Tl1-N3 2.642(6), Tl1-N4 2.742(6), Tl2-N1 2.698(6), Tl2-N2 2.741(6), Tl2-N3 2.688(6), Tl2-N4 2.673(6), Tl3-O79 2.638(8), Tl3-O80 2.529(8), Tl4-O40 2.478(11), Tl4-O39 2.757(14) (24MP = porphyrin 24-atom mean plane).

The X-ray structure of $1\text{Tl(I)}_2\cdot 2\text{Tl(I)}$ evidences a dissymmetric complex (Figure 4). The two Tl(I) cations Tl1 and Tl2 are bound to the N-core, on opposite sides, with important out-of-plane displacement of ca. 1.73 Å. Given the narrow range of their distances to the nitrogen atoms of the porphyrin (2.64 to 2.74 Å), they are considered 4-coordinate to the N-core. The Tl-Tl distance of 3.477 Å does not provide indication of Tl(I)-Tl(I) interaction.^[1e] The porphyrin macrocycle is slightly distorted, with only a moderate tilt of pyrrole-N4. This coordination mode is quite different from that of the unique crystal structure of a bridged bis-Tl(I) porphyrin complex reported by Smith et al.^[1e] In this latter complex, the Tl(I) cations are 3-coordinate to the N-core, and display a short Tl-N distance (2.129 Å) with a strongly tilted pyrrole.

The two other Tl(I) cations Tl3 and Tl4 are bound to the carboxylate groups of the straps that adopt a “broken W shape” conformation, in contrast to the “W shape” conformation displayed by related complexes with a hanging-atop coordination mode.^[6,7,8,11] Whereas the latter conformation orients a metal ion towards the porphyrin macrocycle, Tl3 and Tl4 are projected away from it. This solid state conformational preference of the straps corresponds to the formation of a 1D extended network involving Tl(I) ions with two types of bridges: (i) centrosymmetric dimers that have a Tl_2O_2 core and (ii) weaker amide $\text{O}\cdots\text{Tl}$ interactions that link dimers in a 1D chain.

Following this, titration of a 1:1 mixture of **1** and 1Pb_2 with Tl(I) triflate was performed in the presence of a base (DIPEA). The addition of TlOTf to this mixture led to a two-step binding process (Figure 3b), different to that observed with **1** alone: (i) according to a slow exchange regime, 1 equiv. of Tl(I) gave rise instantaneously and quasi-quantitatively to a single species displaying a dissymmetric NMR pattern (Figure 3b, green dotted lines/filled green triangles). Furthermore, a drastic red-to-green color change of the solution was associated with this process; (ii) with an excess of Tl(I) (up to 3 equiv.), the latter species undergoes a fast exchange process on the NMR time scale, leading quantitatively to a second dissymmetric species, the NMR tube solution retaining a deep green color (Figure 3b, red dotted lines/empty green triangles). Concomitant UV-vis spectroscopic monitoring showed appearance of a new Soret band at 488 nm during the *first step* of the process (Figure S20). These data are consistent with the following interpretation: in the first step, the bimetallic complex $1\text{Pb}_{\text{Tl(I)}}$ (Figure 3b) is formed, with both metal ions bridged by the N-core of the porphyrin. Their expected important out-of-plane displacement is responsible for the green color of the solution. In the second step, Tl(I) binds in a fast exchange regime to the “free” COO^- group of $1\text{Pb}_{\text{Tl(I)}}$, in a similar manner to the binding mode observed in the X-ray structure of $1\text{Tl(I)}_2\cdot 2\text{Tl(I)}$, leading to trimetallic complex $1\text{Pb}_{\text{Tl(I)}}\cdot \text{Tl(I)}$ (Figure 3b). In other words, in the presence of Pb(II), the affinity of Tl(I) is higher for the N-core than for the strap binding sites.

Comparison of the two titration experiments of Figure 3 highlights a remarkable cooperativity in the formation of the bridged Pb(II)/Tl(I) heterobimetallic complex $1\text{Pb}_{\text{Tl(I)}}$. Indeed, it is formed quasi-quantitatively at 1 equiv. of Pb(II) and Tl(I), with no Pb(II) or Tl(I) homobimetallic species observed.

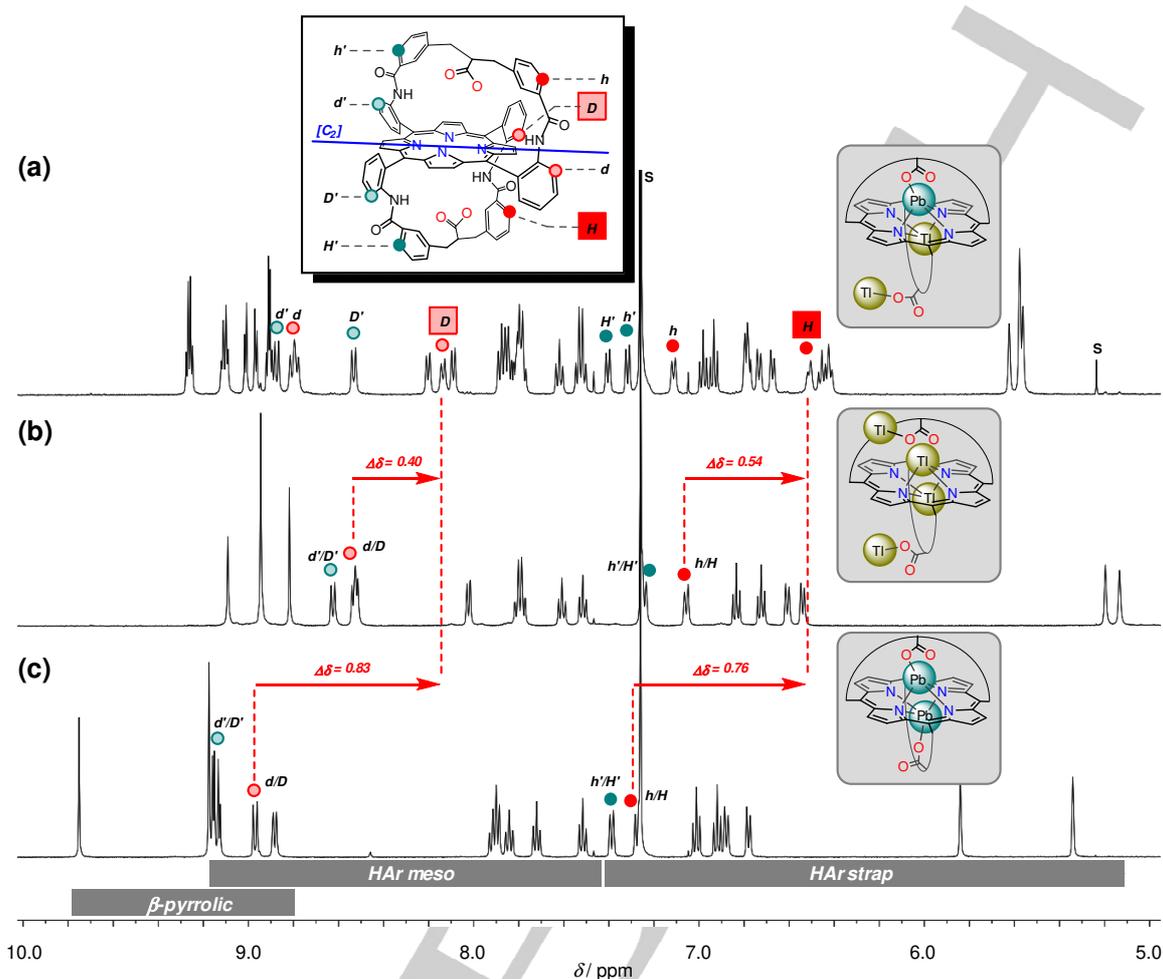


Figure 5. Selected region of the ^1H NMR spectra of (a) $1^{\text{PbTi(II)}}\text{.Ti(I)}$, (b) $1^{\text{Ti(II)}_2\text{.2Ti(I)}}$ and (c) 1^{Pb_2} . Conditions: $\text{CDCl}_3/\text{CD}_3\text{OD}$ 9:1, DIPEA for (a) and (b), 298 K, 500 MHz. S = residual solvents (CHCl_3 , CH_2Cl_2).

The ^1H NMR spectra of $1^{\text{PbTi(II)}}\text{.Ti(I)}$, $1^{\text{Ti(II)}_2\text{.2Ti(I)}}$ and 1^{Pb_2} are all well-defined at 298 K (Figure 5). That of the heterotrimeric species is logically dissymmetric while those of the homo(bi/tetra)metallic species display C_2 -symmetric patterns. All signals were assigned through 2D NMR experiments (SI), and comparison of the three species revealed unusual chemical shifts for protons of “one half” of the two straps of $1^{\text{PbTi(II)}}\text{.Ti(I)}$. More precisely, protons labeled “D” and “H” belonging respectively to a *meso* aromatic ring and to its amide connected aromatic ring (Figure 5a, red frames), are strongly highfield shifted vs. their homologues in the homo(bi/tetra)metallic complexes (see $\Delta\delta$ values above the red arrows). This shielding is associated to the second binding process, thus to the binding of Ti(I) to the “free” carboxylate group of the intermediate complex $1^{\text{PbTi(II)}}$. Having in mind the “broken W-shape” conformation of a strap observed in the X-ray crystal structure of $1^{\text{Ti(II)}_2\text{.2Ti(I)}}$ (Figure 4), this shielding experienced by $1^{\text{PbTi(II)}}\text{.Ti(I)}$ is likely due to a related “unusual” conformation of the strap.

3. Dynamics of $1^{\text{Ti(III)}}\text{.PbOAc}$ and $1^{\text{PbTi(II)}}\text{.Ti(I)}$

The complex $1^{\text{Ti(III)}}\text{.PbOAc}$ was further analyzed by 2D ROESY NMR experiments (Figure 6a). The ROESY spectrum showed exchange correlations between protons of the two sides of the ligands (*i.e.* between Ha and HA and between Ha' and HA'), evidencing an equilibrium between the two degenerate forms $1^{\text{Ti(III)}}\text{.PbOAc}$ and $1^{\text{Ti(III)}}\text{.PbOAc}$ (Figure 6b). It corresponds to a double translocation of the metal ions that exchange concomitantly between the two sides of the porphyrin while retaining their coordination modes. We have shown previously that in $1^{\text{Ti(III)}}$, the metal ion exchanges between the two sides of the ligand *via* a funneling through the N-core of the porphyrin (intramolecular motion), based on markedly different exchange regimes on the NMR time scale for degenerate equilibrium and equilibrium with free base.^[11] Therefore, the double translocation in $1^{\text{Ti(III)}}\text{.PbOAc}$ likely follows combined intra- and intermolecular exchange processes (funneling vs. dissociation-association), respectively for Ti(III) and Pb(II) ions (Scheme 2a), in a similar way as it proceeds for the related Cd(II)/Pb(II) and Hg(II)/Pb(II)

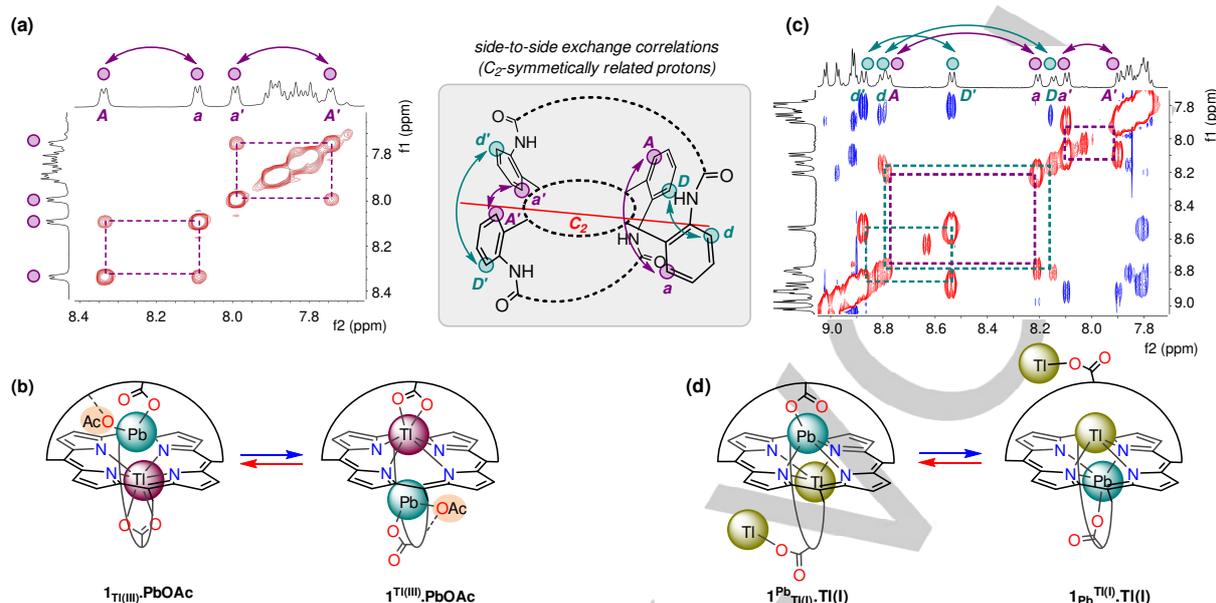


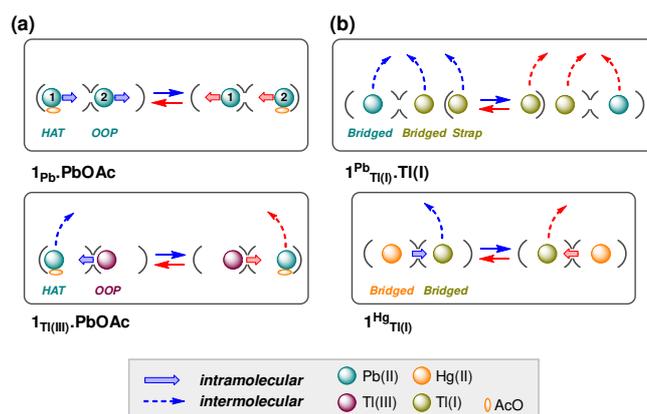
Figure 6. 2D ROESY NMR spectrum of (a) $1_{\text{Ti(III)}}\cdot\text{PbOAc}$ and (c) $1^{\text{PbTi(II)}}\cdot\text{Ti(I)}$ (selected regions; 9:1 $\text{CDCl}_3/\text{CD}_3\text{OD}$, 298 K, 600/500 MHz; blue/red cross peaks: NOE/exchange correlations). Equilibrium between the two degenerate forms of (b) $1_{\text{Ti(III)}}\cdot\text{PbOAc}$ and (d) $1^{\text{PbTi(II)}}\cdot\text{Ti(I)}$.

complexes (non-compartmentalized exchange process).^[10] Conversely, it contrasts with the parent homobimetallic complex $1_{\text{Pb}}\cdot\text{PbOAc}$ featuring coupled intraligand motion of Pb(II) ions (compartmentalized motion, the metal ions remain on the same side of the porphyrin, Scheme 2a),^[8] the double translocation in $1_{\text{Ti(III)}}\cdot\text{PbOAc}$ is a non-compartmentalized exchange process. Thus, changing the nature and especially the size of the OOP cation (Pb(II) vs. Ti(III)) has a deep influence on the degenerate exchange reaction.

It is noteworthy that the binding of 'PbOAc' to the strap of $1_{\text{Ti(III)}}$ slows down the funneling of Ti(III). Indeed, in the presence of a base (DIPEA), a fast side-to-side exchange of Ti(III) occurs on the NMR time scale in the case of the monometallic complex, in line with the deprotonation of the free carboxylic acid group,^[11] leading to a broad ^1H NMR spectrum at 298 K. Conversely, in the same experimental conditions, a slow side-to-side exchange of Ti(III) occurs on the NMR time scale with $1_{\text{Ti(III)}}\cdot\text{PbOAc}$, the bimetallic complex displaying a sharp dissymmetric NMR spectrum at 298 K (Figure S9). 'PbOAc' is thus somehow "caging" the COO group slowing down the intraligand exchange of Ti(III).

Similarly to $1_{\text{Ti(III)}}\cdot\text{PbOAc}$, the 2D ROESY spectrum of complex $1^{\text{PbTi(II)}}\cdot\text{Ti(I)}$ showed exchange correlations between protons of the two sides of the porphyrin (Figure 6c). For instance, selective correlations are observed between the C_2 -symmetrically related *meso* aromatic protons d,d',a,a' and respectively D,D',A,A' (green and purple arrows). It means that, according to a triple translocation process, Pb(II) and Ti(I) metal ions exchange their locations relative to the porphyrin plane (Figure 6d). In other words, there is equilibrium between the two degenerate forms of the heterotrimetallic complex. Considering

the large size of these cations, precluding their funneling through the N-core, an intramolecular pathway is ruled out for the exchange process, thus comprising all-intermolecular components (Scheme 2b). It is also interesting to compare the dynamics of $1^{\text{PbTi(II)}}\cdot\text{Ti(I)}$ with that of the related bridged complex $1^{\text{HgTi(II)}}$.^[12] For the latter, a non-compartmentalized degenerate exchange reaction occurs in a fast exchange regime at 298 K, with Hg(II) funneling through the N-core (Scheme 2b). It gives a C_2 -symmetric NMR pattern, even at low temperature (263 K). Conversely, with the larger Pb(II), a sharp dissymmetric NMR pattern is observed even at high temperature (330 K).



Scheme 2. Simplified representation of selected bimetallic porphyrin complexes of **1** undergoing degenerate equilibrium: comparison of the metal ion exchange pathways for (a) $1_{\text{Pb}}\cdot\text{PbOAc}$ vs. $1_{\text{Ti(III)}}\cdot\text{PbOAc}$ and (b) $1^{\text{PbTi(II)}}\cdot\text{Ti(I)}$ vs. $1^{\text{HgTi(II)}}$.

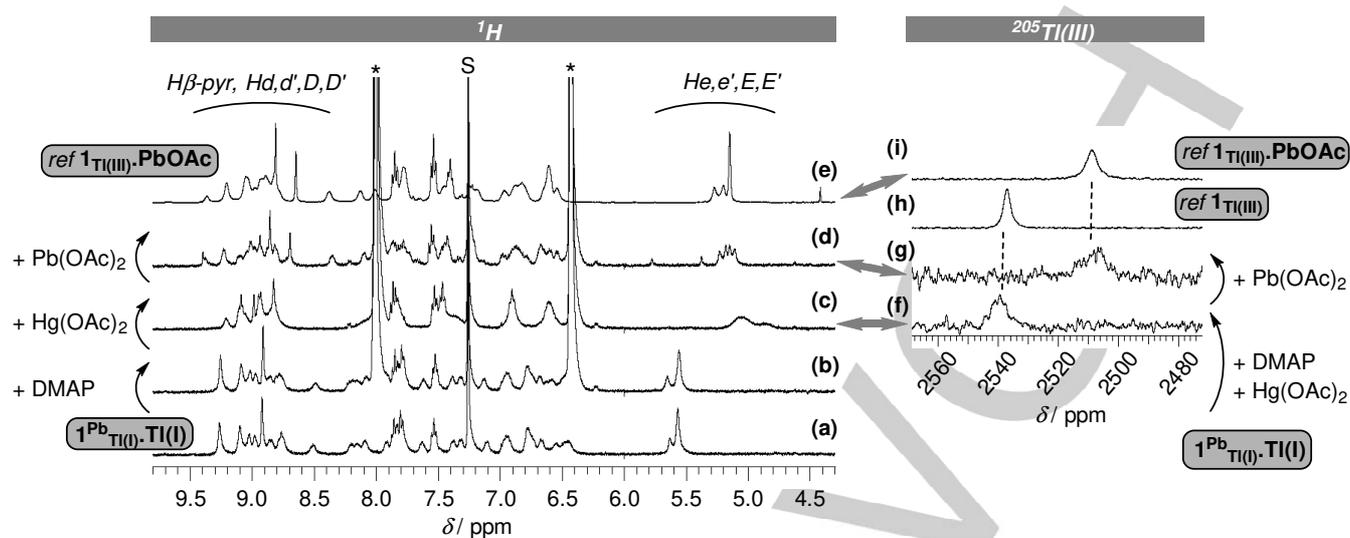


Figure 7. ^1H and ^{205}Tl NMR study (9:1 $\text{CDCl}_3/\text{CD}_3\text{OD}$, 298 K) for the transformation of $1^{\text{Pb}}_{\text{Tl}(\text{II})}\text{-TI}(\text{I})$ into $1_{\text{Tl}(\text{III})}\text{-PbOAc}$. Left: ^1H NMR spectrum of $1^{\text{Pb}}_{\text{Tl}(\text{II})}\text{-TI}(\text{I})$ before (a) and after (b-d) the successive addition of DMAP, $\text{Hg}(\text{OAc})_2$ and $\text{Pb}(\text{OAc})_2$; (e) reference ^1H NMR spectrum of $1_{\text{Tl}(\text{III})}\text{-PbOAc}$. S = solvent, * = DMAP. Right: (f) ^{205}Tl NMR spectrum obtained after addition of DMAP and $\text{Hg}(\text{OAc})_2$ to $1^{\text{Pb}}_{\text{Tl}(\text{II})}\text{-TI}(\text{I})$, (g) then after addition of $\text{Pb}(\text{OAc})_2$; (h) and (i): reference ^{205}Tl NMR spectra of respectively $1_{\text{Tl}(\text{III})}$ and $1_{\text{Tl}(\text{III})}\text{-PbOAc}$.

It highlights very different rates of metal ion exchanges, in line with their different “all inter” and “combined inter-intra” processes.

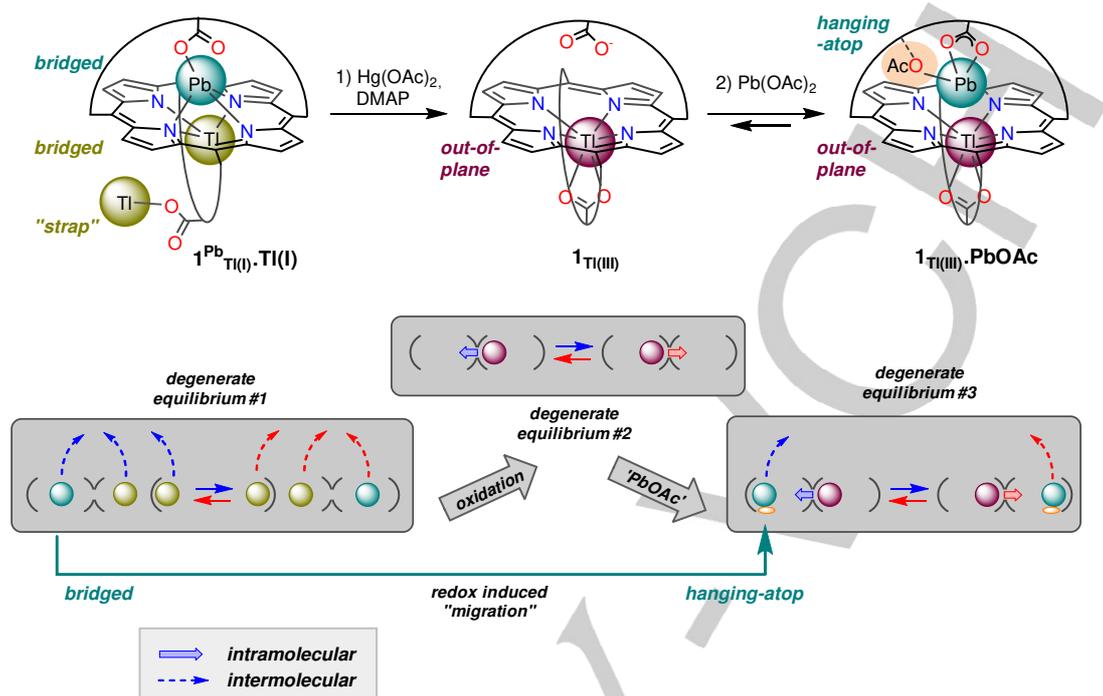
4. Conversion of $1^{\text{Pb}}_{\text{Tl}(\text{II})}\text{-TI}(\text{I})$ into $1_{\text{Tl}(\text{III})}\text{-PbOAc}$

From above, it appears that the combination of lead and thallium affords two redox-related heterobi(tri)metallic complexes of **1**, with thallium in the +I or +III oxidation states. Aiming at redox-controlled systems, we next attempted to generate the TI(III) species starting from the TI(I) one. Indeed, we have recently reported different strategies for such an oxidation of TI(I) porphyrin complexes, either by photosensitization of oxygen^[11] or by treatment with Hg(II) ions.^[12] Whereas the first strategy, consisting in the exposure of an NMR tube of $1^{\text{Pb}}_{\text{Tl}(\text{II})}\text{-TI}(\text{I})$ to light, remained unsuccessful, the second strategy revealed more efficient. In the presence of 4-dimethylaminopyridine (DMAP),^[16] addition of 1 equiv. of $\text{Hg}(\text{OAc})_2$ to $1^{\text{Pb}}_{\text{Tl}(\text{II})}\text{-TI}(\text{I})$ led instantaneously to the formation of a new species displaying a broad NMR signature (Figure 7 left, a-c), related to that of $1_{\text{Tl}(\text{III})}$ (Scheme 3). A ^{205}Tl NMR spectrum was recorded and displayed a broad signal at 2539 ppm, fitting well with the ^{205}Tl chemical shift of $1_{\text{Tl}(\text{III})}$ (2538 ppm) (Figure 7 right, vs. h).^[17] A UV-vis analysis of the NMR solution also evidenced the formation of $1_{\text{Tl}(\text{III})}$ (Figure S22). Since ca. 3-4 equiv. of $\text{Pb}(\text{OAc})_2$ were needed to quantitatively form $1_{\text{Tl}(\text{III})}\text{-PbOAc}$ from $1_{\text{Tl}(\text{III})}$, we reasoned that the oxidation process from $1^{\text{Pb}}_{\text{Tl}(\text{II})}\text{-TI}(\text{I})$ could not lead to $1_{\text{Tl}(\text{III})}\text{-PbOAc}$ as only 1 equiv. of Pb(II) is present in a competitive medium. Thus, to the NMR tube of $1_{\text{Tl}(\text{III})}$ formed by the addition of $\text{Hg}(\text{OAc})_2$ to $1^{\text{Pb}}_{\text{Tl}(\text{II})}\text{-TI}(\text{I})$, 5 equiv. of $\text{Pb}(\text{OAc})_2$ were then introduced. To our delight, this led instantaneously to the ^1H and ^{205}Tl NMR spectra of the targeted complex $1_{\text{Tl}(\text{III})}\text{-PbOAc}$ (Figure 7 left, d vs. e and right, g vs. i; Scheme 3). The ^{205}Tl NMR chemical shift of 2508 ppm is indeed in very good agreement

with that of the reference complex (2509 ppm). To the best of our knowledge, such a Pb(II)/TI(I)-to-Pb(II)/TI(III) transformation is unprecedented.

Interestingly, the Hg(II)-mediated formation of $1_{\text{Tl}(\text{III})}\text{-PbOAc}$ is not sensitive to the order of introduction of the reactants. Indeed, in a different experiment, $\text{Hg}(\text{OAc})_2$, $\text{Pb}(\text{OAc})_2$ and DMAP were successively added to $1^{\text{Pb}}_{\text{Tl}(\text{II})}\text{-TI}(\text{I})$, leading instantaneously and quantitatively to the targeted complex $1_{\text{Tl}(\text{III})}\text{-PbOAc}$ (Figure S21). Also, it is noteworthy that the Hg(II) mediated TI(I)-to-TI(III) oxidation process is much faster in the present case (ca. instantaneously) than in the previous study involving the spontaneous evolution of a Hg(II)/TI(I) bimetallic complex of **1** (ca. 2 hours, Figure 1a).^[12] This observation is in good agreement with a proposed mechanism where the reactive species does not involve a Hg(II) ion bound to the N-core. Instead, ‘free’ Hg(II) ions are expected to interact at the level of the strap where TI(I) is bound, leading to a transient Hg(II)-TI(I) association.^[12]

The Pb(II)/TI(I)-to-Pb(II)/TI(III) transformation highlights communication of the metal ions between the two sides of the porphyrin. Indeed, oxidation of TI(I) forces Pb(II) cation on the opposite side to change its coordination mode from *bridged* to *hanging-atop*, thus to migrate between two different coordination sites. This is an attractive feature in the context of the engineering of new multimetallic devices whose working principle would imply the controlled and compartmentalized motion of metal ions as depicted in Scheme 1b. In summary, this Pb/TI/1 redox system appears more complex than it was foreseen, as different dynamics involving metal motions/migrations/translocations are found (Scheme 3): (i) degenerate multiple translocations (combined intra/inter vs. all



Scheme 3. Hg(II)-mediated transformation of a Pb(II)/Tl(I) heterotrimetallic complex of **1** into its heterobimetallic Pb(II)/Tl(III) counterparts.

inter processes); (ii) a redox-induced migration of Pb(II) (bridged → hanging-atop).

Conclusions

The formation of Pb/Tl heterobimetallic complexes from C_2 -symmetric bis-strap porphyrin **1**, with thallium either in +I or +III oxidation state, has been successfully achieved. On the one hand (**1**_{Tl(III)}.PbOAc), Tl(III) is selectively bound to the N-core of the porphyrin (out-of-plane coordination), and allows a 'PbOAc' moiety bound to a carboxylate of a strap on the opposite side (hanging-atop coordination). On the other hand (**1**_{Pb}Tl(I)), Tl(I) and Pb(II) cations are bridged by the N-core of the macrocycle, and a second Tl(I) cation interacts with a carboxylate of a strap located on the side of the first Tl(I). These two redox-related complexes are intrinsically dynamic: they undergo equilibrium between their two degenerate forms, meaning that the metal ions exchange their positions relative to the porphyrin mean plane. Besides, we have demonstrated that conversion of **1**_{Pb}Tl(I) to **1**_{Tl(III)}.PbOAc can be readily achieved in smooth conditions by an original Hg(II)-mediated Tl(I)-to-Tl(III) oxidation process. The results presented here constitute a key step towards redox controlled multimetallic complexes featuring coupled and compartmentalized double translocations, as depicted in Scheme 1b. They further extend the "tool-kit" of supramolecular coordination chemistry with regular porphyrins.

Experimental Section

Experimental part is given in the Supporting Informations.

Acknowledgements

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Keywords: Porphyrinoids • Lead • Thallium • Bimetallic complexes • Supramolecular chemistry

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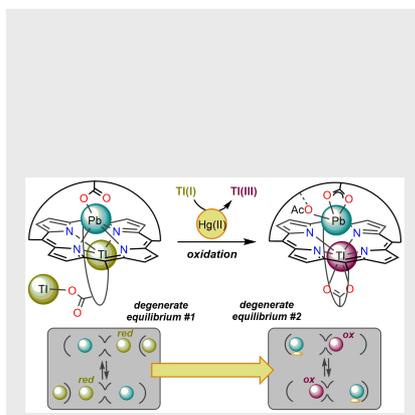
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- [15] At UV-vis concentration ($\sim 5 \cdot 10^{-6} \text{ M}^{-1}$), addition of 1 equiv. of $\text{Pb}(\text{OAc})_2$ to **1** leads to three Soret bands with maxima at 422, 472 and 484 nm. They correspond respectively to **1**, **1_{Pb}** and **1_{Pb2}** (structure in Figure 3b). The latter bridged complex is not observed at NMR concentration ($\sim 5 \cdot 10^{-3} \text{ M}^{-1}$).
- [16] The Hg(II)-mediated TI(I)-to-TI(III) oxidation is considerably boosted by the presence of DMAP, see ref 12.
- [17] The broad ^1H and ^{205}Tl NMR signatures of **1_{Tl(III)}** formed by oxidation with mercury is likely due to the presence of various chemicals in the NMR tube (DMAP, Pb(II), TlO^+ , AcO^- and eventually Hg(II) and TI(I)), possibly interacting with the complex in different manners (carboxylate of the strap, metal centre...) and affecting the TI(III) intraligand dynamic (funneling motion).

Entry for the Table of Contents

FULL PAPER

Porphyrin plays a mean pinball!

Targeting new devices based on coupled translocations of metal ions, Pb(II)/Tl(I) and Pb(II)/Tl(III) heteromultimetallic porphyrin complexes have been prepared and their metal exchange dynamics evaluated. A unique Hg(II)-mediated oxidation process allowed Pb(II)/Tl(I)-to-Pb(II)/Tl(III) conversion, changing thereby the intrinsic fluxionality of the system.



Stéphane Le Gac,^{*} Victoria Ndoiyom,
Luca Fusaro, Vincent Dorcet, and
Bernard Boitrel^{*}

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**Hg(II)-Mediated Tl(I)-to-Tl(III)
Oxidation in Dynamic Pb(II)/Tl
Porphyrin Complexes**