Identification of Zr(IV)-based architectures generated from ligands incorporating the 2,2′-biphenolato unit†

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The structural identification in solution of the Zr(IV) complexes involving two 2,2-biphenol-based proligands is reported. The proligand L1H2 contains one 2,2-biphenol unit whereas L2H4 incorporates two 2,2-biphenol units linked by a para-phenylene bridge. Diffusion Ordered Spectroscopy (DOSY) combined with electrospray mass spectrometry analysis and density functional theory (DFT) allowed for determining the molecular structures of such Zr(IV)-based architectures. It is proposed that [Zr(OPri)4(HOPri)] in the presence of L1H2 generates an octahedral complex formulated as [ZrL1\textsubscript{3}H\textsubscript{2}]. Concerning the self-assembled architecture incorporating the L\textsubscript{2} ligand, the analytical data highlight the formation of an unprecedented neutral Zr(IV) triple-stranded helicate ([ZrL2\textsubscript{2}H\textsubscript{4}]). Insight into the geometry of these complexes is obtained via DFT calculations. Remarkably, the helicate structure characterized in solution strongly contrasts with the triple-stranded structure of the complex that crystallizes.

In this manuscript we report the liquid state characterisation of the architectures resulting from the reactions of the Zr(IV) centre with 2,2′-biphenol-based compounds. The proligands L1H\textsubscript{2} and L2H\textsubscript{4} involved in this study are depicted in Fig. 1. As mentioned above, this set of 2,2′-biphenol derivatives has been shown to generate complex controlled assemblies in the presence of the Ti(IV) centre. For instance, L1H2 leads to a monomeric C\textsubscript{2v}-symmetric complex constructed around an octahedral titanium centre. This compound is formulated as [Ti(L1\textsubscript{2})(HOPri)\textsubscript{2}]\textsuperscript{4+}. Concerning the strand L2H4, helical neutral assemblies named [Ti\textsubscript{2}(L2\textsubscript{2})(HOPri)\textsubscript{2}] and [Ti\textsubscript{2}(L2)(L2H)(OPri) (HOPri)]\textsuperscript{2+} were characterised. Having proved that these ligands are well suited for displaying a rich Ti(IV) coordination chemistry, we examine now the role of the metal ion size on the resulting assemblies. Thus, it appeared to us particularly relevant to study the coordination chemistry of these two compounds, i.e. L1H\textsubscript{2} and L2H\textsubscript{4} in the presence of zirconium(IV). Compared to Ti(IV), Zr(IV) is known for being bigger with a Pauling ionic radius ratio between Zr(IV) and Ti(IV) equal to

![Fig. 1. Compounds L1H2 and L2H4.](image-url)
Thus, $r(\text{Zr}(\text{iv})) / r(\text{Ti}(\text{iv})) = 1.15$. Thus, Zr(\text{iv})-complexes with coordination numbers higher than six are rather common in comparison with Ti(\text{iv})-complexes. Also, the large ionic radius of Zr(\text{iv}) permits accommodation of bulky ligands around this metallic centre.

Hereafter, we report the methodology allowing to elucidate the formula of the compounds resulting from the reactions of L$^1$H$_2$ or L$^3$H$_4$ with Zr(\text{iv}). We show that DOSY supported by mass spectrometry analysis and DFT calculations are a key combination to elucidate the nature of these species formed in situ. This study shows that the structures incorporating the Zr(\text{iv}) ions are dissimilar from those already mentioned for Ti(\text{iv}). In particular, this investigation highlights that Zr(\text{iv}) accommodates three bidentate oxygenated L$^1$ ligands. This particular feature allows the formation of an assembly composed of two Zr(\text{iv}) centres and three strands when Zr(\text{iv}) reacts with L$^3$H$_4$. DFT calculations suggest for the dinuclear assembly a triple-stranded helicate structure formulated as Zr$_2$L$^2$H$_4$. Finally, we show that this metallo-supramolecular chemistry conducted with Zr(\text{iv}) and L$^3$H$_4$ generates in the solid state an assembly strongly dissimilar from the one characterized in solution.

**Results and discussion**

**ZrL$^1$H$_3$**

The zirconium source employed to conduct this study was the “classical” [Zr(OPri)$_4$(HOPri)$_2$] alkoxide complex. It is noteworthy that this species adopts a dimeric structure involving δ-μ-isopropoxo bridges ([Zr$_2$(OPri)$_8$(HOPri)$_2$]). This structure in solution and in the solid state with two intramolecular hydrogen bonds characterized for this compound. First, several reaction conditions were tested by reacting [Zr(OPri)$_4$(HOPri)$_2$] with 1, 2 and 3 equivalents of L$^1$H$_2$ in CD$_2$Cl$_2$. The resulting uncoloured mixture were analysed by $^1$H NMR (see the ESI†). Surprisingly, these coordination reactions were not efficient as the L$^1$H$_2$ compound was largely predominant in solution for the three molar ratios tested. Also, the final composition of these mixtures was not really affected when these samples were heated. The most promising result was obtained when [Zr(OPri)$_4$(HOPri)$_2$] reacted with two equivalents of L$^1$H$_2$. New large signals different from those observed for the initial components were clearly identified by $^1$H NMR as shown in Fig. 2, highlighting the formation of a Zr-based complex. A conversion ratio of about 51% could be estimated by $^1$H NMR after integration of the most deshielded signal of the unreacted L$^1$H$_2$ and the methine proton signal ($\delta = 3.93$ ppm, broad signal). We explain this conversion by the dimeric structure of [Zr$_2$(OPri)$_8$(HOPri)$_2$] rendering this precursor moderately reactive. The aliphatic region of the $^1$H NMR spectrum displays two intense very broad resonances at $\delta = 3.89$ ppm and 1.09 ppm (see the ESI†). Overall, the shape of these signals suggests an exchange process with free alcohol generated in the course of the coordination step of L$^1$H$_2$ and the ligands of the dimeric [Zr$_2$(OPri)$_8$(HOPri)$_2$] precursor.

A single deshielded signal ($\delta = 155.0$ ppm) was observed by $^{13}$C NMR spectroscopy (Fig. 2c) and d), in the region corresponding to a chemical shift typical to the C–O–Zr resonance. Consequently, this $^{13}$C NMR spectrum is in full accordance with the formation of a single highly symmetrical complex in solution. It is worth noticing that this complex appears to be unstable in solution as the $^1$H NMR aromatic region spectrum of a mixture analysed after one day of its preparation reveals only the presence in solution of the initial L$^1$H$_2$ molecule.

Among all the available analytical techniques permitting to evaluate the nature of self-assembled architectures or coordination compounds, Diffusion Ordered Spectroscopy (DOSY) experiments$^{11}$ are becoming increasingly popular to elucidate these metallo-supramolecular complexes. In the absence of structural data for a given species, this non-invasive technique permits to gain crucial information about the size and the shape of a compound in solution since the diffusion coefficient measured in the course of a DOSY experiment is correlated to the hydrodynamic radius ($R_h$) of the species in solution according to the Stokes–Einstein equation. Therefore, DOSY became a routine technique to analyse metallo-supramolecular aggregates in solution. For instance, this NMR method has been successfully applied to analyse helicates,$^{14}$ cyclic inorganic clusters,$^{15}$ cages,$^{16}$ rotaxanes,$^{17}$ catenanes$^{18}$ or metallo-prisms.$^{18}$ Thus, DOSY appeared to us as a well adapted technique to analyse the mixtures obtained when Zr(\text{iv}) reacts with L$^1$H$_2$ and later with L$^3$H$_4$. Table 1 gathers the diffusion coefficients measured for the species in solution and
**Table 1** Diffusion coefficients in \( \mu m^2 \ s^{-1} \) measured at room temperature from the mixtures of \( L^1H_2 \) or \( L^2H_4 \) with \([Zr(OPr')_4(HOPr')]\). Diffusions are given for measurement in \( CD_2Cl_2 \). \( R_h \) values are calculated from these diffusions. The \( R_h \) values are determined according to the Stokes–Einstein equation with \( \eta = 4.603 \times 10^{-4} \) Pa s at 298 K for the viscosity of \( CD_2Cl_2 \). The diffusion and \( R_h \) are given at \( \pm 10\% \). Let’s recall for the previously reported titanium complexes that isopropanol ligands are decoordinated at room temperature for these two complexes in solution. The diffusions given for \( L^1H_2 \) or \( L^2H_4 \) in \( CD_2Cl_2 \) are given for measurement in CD2Cl2.

| Complex in solution | Diffusion (\( \mu m^2 \ s^{-1} \)) | \( R_h \) (Å) |
|---------------------|---------------------------------|------------|
| \([ZrL^1H_2]^{a}\) | 680                            | 7.0        |
| \([ZrL^1H_2]^{b}\) | 505                            | 9.4        |
| References          |                                 |            |
| \( L^1H_2 \)         | 1150                           | 4.1        |
| \( L^2H_4 \)         | 830                            | 5.7        |
| \([TiL^1](HOPr')_2]^{a}\ | 780        | 6.1        |
| \([TiL^1](L^1H)(HOPr')(HOPr')]\ | 630 | 7.5        |

*The following stoichiometry has been applied to generate the complex in situ: \( 2L^1H_2 + [Zr(OPr')_4(HOPr')] \). The following stoichiometry has been applied to generate the complex in situ: \( L^2H_4 + [Zr(OPr')_4(HOPr')] \).*

The diffusion coefficients measured for the previously reported Ti(IV)-based references. These references were synthesized by using analogous conditions as those reported here. For the experiment conducted with two equivalents of \( L^1H_2 \) and one equivalent of \([Zr(OPr')_4(HOPr')]\), only two species containing aromatic protons are detected by DOSY; \( L^1H_2 \) and a new species assumed for being a Zr(IV)-complex (see the ESI†). The diffusion measured for the complex corresponds only to aromatic proton resonances showing that the Zr(IV) ion is not coordinated to isopropanol or isopropoxo ligands. The complex formed in situ is around 4.7 times more voluminous than the \( L^1H_2 \) compound (estimated volumes: \( V(Zr(IV)-complex) = 1420 \) Å\(^3\), \( V(L^1H_2) = 300 \) Å\(^3\), where \( V \) is calculated from \( R_h \) values with the relation \( V = 4/3 \cdot \pi \cdot R_h^3 \) assuming a spherical shape of the molecules). A volume ratio of 1.5 is found between the Zr(IV)-based complex in solution and a previously reported complex with \( V(Zr(IV)-complex) = 1420 \) Å\(^3\) and \( V([Ti-(L^1)_4(HOPr')]_2) = 940 \) Å\(^3\) highlighting a Zr(IV)-complex containing three ligands. Finally, electrospray ionization mass spectrometry (ESI-MS) analysis allows the unambiguous identification of the complex. As shown in Fig. 3, two intense peaks are detected by ESI-MS. According to the peak observed at high \( m/z \) (\( m/z = 1123.2561 \)), a formula \([ZrL^1H_2]^{a}\) could be proposed for this Zr(IV)-based compound formed in situ.

**Zr\(_2\)L\(_2\)H\(_4\)**

Having determined the formula of the Zr(IV) complex formed in situ with \( L^1H_2 \), the reaction involving the \( L^2H_4 \) proligand was studied. In this case, \( L^2H_4 \) reacts with one equivalent of \([Zr(OPr')_4(HOPr')]\) at room temperature. Neither \(^1\)H NMR nor \(^13\)C NMR analysis permitted us to extract useful information about the species formed in situ. The \(^1\)H NMR spectrum indicates the presence of free \( L^2H_4 \) in solution with also the presence of large and complex broad signals in the aromatic region too complex to be analysed (see the ESIf). Herein, the coordination process is rather efficient. A conversion of 87% was estimated by integrating the para-phenylene bridge proton signal of the unreacted \( L^2H_4 \) (δ = 7.68 ppm, singlet) and the methylene proton signal (δ = 3.93 ppm, broad septuplet). The \(^13\)C NMR spectrum only displays signals relative to \( L^2H_4 \) in the region of aromatic carbons. By DOSY, in addition to the diffusion attributed to the unreacted \( L^2H_4 \) strand, only one diffusion associated to the formation of a Zr(IV)-based assembly incorporating the ligand \( L^2 \) is noticed for the analysed solution. This observation highlights the high selectivity of the self-assembly process. Indeed in this particular case, the molecular volumes could not be estimated accurately for this species, as the shape of the complex in solution is unknown.

**Fig. 3** ESI mass spectrum of the mixture obtained after mixing two equivalents of \( L^1H_2 \) with \([Zr(OPr')_4(HOPr')]\) in \( CD_2Cl_2 \). The experimental peak (top) at \( m/z = 1123.2561 \) is shown in the insert picture with the isotopic profile (bottom) simulated for \([ZrL^1H_2 + Na]^+ \) (calcd for \( C_{42}H_{50}NaO_5Zr; m/z = 1123.2547 \)). The peak at \( m/z = 699.2470 \) is attributed to \([2L^1H_2 + Na]^+ \) (calcd for \( C_{49}H_{50}NaO_4; m/z = 699.2511 \)).
However, owing to the order of magnitude of the $R_h$ values (see Table 1), it appears that the Zr(IV)-based assembly is more voluminous than the titanium(IV) dinuclear double stranded helicate already reported.\textsuperscript{5} ESI-MS analysis of the crude mixture proves the formation of a dinuclear assembly built up from three strands. The ESI-MS mass spectrum and the simulated isotopic profile for the peak at $m/z = 2006.4081$ are shown respectively in Fig. 4a and b. The two more intense peaks at $m/z = 1214.4673$ and $m/z = 1813.6810$ are originated from LH\textsubscript{4}. Peaks at $m/z = 1984.4188$ and 2006.4081 are attributed to a species formed by two zirconium ions and three strands. In addition to these parent peaks, a peak at $m/z = 1898.5531$ is detected. This peak is originated from a monomeric complex bearing two strands partially protonated and one strand fully protonated ([ZrL\textsubscript{2}\textsubscript{3}H\textsubscript{8}(H\textsubscript{2}O)])\textsuperscript{+}). Now, the dinuclear architecture formed in situ could be assigned as Zr\textsubscript{3}L\textsubscript{2}H\textsubscript{4}. This result is in agreement with the conclusion made for the experiment conducted with the L\textsubscript{1}H\textsubscript{2} ligand.

### Molecular modeling

In order to gain detailed information about the Zr(IV)-based architectures generated from L\textsubscript{1}H\textsubscript{2} and L\textsubscript{2}H\textsubscript{4}, molecular models were computed and their energies minimized using density functional theory (DFT) with the hybrid exchange correlation functional B3LYP. The structures of the mononuclear and dinuclear complexes were modelled on the basis of the conclusion drawn by the DOSY experiments and the mass spectrometry analysis. The monomeric complex is designed knowing that the metallic centre is linked to three bidentate ligands. Owing to the reason that in this complex two phenol sub-units compose the Zr(IV) coordination sphere, the three

Fig. 4  (a) ESI mass spectrum of the mixture obtained after reacting two equivalents of L\textsubscript{2}H\textsubscript{4} with [Zr(OPri\textsubscript{4})\textsubscript{4}(HOPri\textsubscript{4})\textsubscript{4}] in CD\textsubscript{2}Cl\textsubscript{2}. Peaks at $m/z = 1214.4673$ and 1813.6810 are attributed to L\textsubscript{1}H\textsubscript{4} (calcd for [3L\textsubscript{2}H\textsubscript{4} + H\textsubscript{2}O]\textsuperscript{+} = 1813.6566 and calcd for [2L\textsubscript{2}H\textsubscript{4} + H\textsubscript{2}O]\textsuperscript{+} = 1214.4388). Peaks at $m/z = 1984.4188$ and 2006.4081 correspond to an assembly incorporating two Zr(IV) centres and three L\textsubscript{2} ligands (calcd for [Zr\textsubscript{2}L\textsubscript{2}H\textsubscript{4}(H\textsubscript{2}O)\textsubscript{8}](C\textsubscript{126}H\textsubscript{84}O\textsubscript{13}Zr\textsubscript{2}) = 1984.4040 (see the ESI for the isotopic simulation) and calcd for [Zr\textsubscript{2}L\textsubscript{2}H\textsubscript{4}(H\textsubscript{2}O)Na\textsubscript{8}](C\textsubscript{126}H\textsubscript{83}NaO\textsubscript{13}Zr\textsubscript{2}) = 2006.3825). The simulated isotopic profile for the C\textsubscript{126}H\textsubscript{83}NaO\textsubscript{13}Zr formula (bottom) and the enlargement of the peak (top) at $m/z = 2006.4081$ are given in (b). The peak at $m/z = 1898.5531$ is assigned to [ZrL\textsubscript{2}H\textsubscript{8}(H\textsubscript{2}O)]\textsuperscript{+} (calcd for C\textsubscript{126}H\textsubscript{88}O\textsubscript{13}Zr, $m/z = 1898.5272$) (simulated isotopic profile is given in the ESI).
structures [ZrL₁,L₁H₂], [cis-ZrL₁(L₁H)₂] and [trans-ZrL₁(L₁H)₂] were optimized (a schematic representation of these isomers is shown in Fig. 5). The calculated structure corresponding to [cis-ZrL₁(L₁H)₂] is presented in Fig. 6, and the structures of [ZrL₁,L₁H₂] and [trans-ZrL₁(L₁H)₂] are shown in the ESL.

The [cis-ZrL₁(L₁H)₂] isomer appears to be the most stable structure. The energetic difference between [cis-ZrL₁(L₁H)₂] and [trans-ZrL₁(L₁H)₂] is found to be 39 kJ mol⁻¹, while between [cis-ZrL₁(L₁H)₂] and [ZrL₁,L₁H₂] an energy difference of 47 kJ mol⁻¹ is determined. As shown in Fig. 6, the [cis-ZrL₁(L₁H)₂] model indicates that the metallic centre is large enough to accommodate the three ligands leading to a metallic coordination sphere composed of six oxygen atoms. As expected the Zr−O bond lengths are not equivalent as Zr−O(phenolato) bonds (Zr−O(phenolato) = 2.01 ± 0.03 Å) are shorter comparatively to Zr−O(phenol) bonds (Zr−O(phenol) = 2.35 ± 0.04 Å). By using the same procedure as the one used for the theoretical Rh value of cis-[ZrL₁(L₁H)₂], a computed hydrodynamic radius of Rh = 9.7 ± 0.5 Å is determined from the model of the [ZrL₁,L₁H₂] helicate. Again, this computed radius is in good agreement with the one observed by DOSY for the complex in solution (Rh = 9.4 ± 0.9 Å).

Crystal structure
Having evidenced the formation of defined architectures formed in situ when L₁H₄ or L₁H₂ react with [Zr(OPr)₄(HOPr)], solid-state characterisation of these zirconium-based compounds was undertaken. Crystals suitable for X-ray diffraction analysis were obtained only in the case of ligand L₁H₂. Few white crystals were isolated after several weeks when vapours of diethyl ether were allowed to slowly diffuse in a dichloromethane solution composed of L₁H₄ (3 eq.) and [Zr(OPr)₄(HOPr)] (2 eq.). The molecular structure obtained from X-ray diffraction analysis is shown in Fig. 8. The bond valence sum permitted addition of several missing H-atoms not located during refinement of the structure and the complex formula [Zr₄(L₁)₃(L₁H)(μ₂-OH)₂(HOOPr)₃] could be
proposed. Importantly, this species was not detected by ES-MS in the course of the liquid state investigation. The \([\text{Zr}_4(\text{L}^2)^2(\text{L}^2\text{H})(\mu_2\text{-OH})_3(\text{HO}^\prime\text{Pr})_3]\) complex incorporates three strands with one phenol group belonging to the \(\text{L}^2\text{H}\) strand that is not coordinated to a zirconium centre. The three strands are wrapped around a zirconium hydroxo-ladder composed of four metallic centres. This particular arrangement leads to a helical architecture. Each zirconium centre is 6-fold coordinated with pseudo-octahedral coordination geometry as revealed by continuous shape measurements (\(\text{Zr}1(\text{CShM}) = 1.615; \text{Zr}2(\text{CShM}) = 2.756, \text{Zr}3(\text{CShM}) = 2.317; \text{Zr}4(\text{CShM}) = 1.1182\)).\(^{25}\) Four zirconium atoms form the inorganic core of the complex. The two central metallic atoms (\(\text{Zr}2\) and \(\text{Zr}3\)) are \(\mu_2\)-hydroxo bridged by one another and are also respectively di-\(\mu_2\)-hydroxo bridged with a terminal zirconium(IV) centre (\(\text{Zr}1\) or \(\text{Zr}4\)). Also, we notice that two and one isopropanol molecules coordinate with \(\text{Zr}1\) and \(\text{Zr}4\) respectively. It is noteworthy that the chain-like structure adopted by the inorganic core of the complex is rather original\(^{26}\) in comparison with the zirconium hydroxo- or oxo-clusters already reported. Here, the chain-like structure contrasts with the spherical or ovoid shapes of the inorganic cores usually found in zirconium-based aggregates.\(^{27}\) Undoubtedly, the chain-like structure found in \([\text{Zr}_4(\text{L}^2)^2(\text{L}^2\text{H})(\mu_2\text{-OH})_3(\text{HO}^\prime\text{Pr})_3]\) is templated by the \(\text{L}^2\) strands.

The structural difference observed between the structure formed in solution and the one observed in the solid-state is obviously related to the occurrence during crystallization of a partial hydrolysis of some \(\text{Zr}–\text{OPh}\) bonds followed by a classical olation reaction leading to \(\text{Zr}(\mu\text{-OH})_2\text{Zr}\) bridges. As the occurrence of a \([\text{Zr}_2(\text{L}^2)^2(\text{L}^2\text{H})]\) helicate in solution cannot be doubted, the first step could be the hydrolysis of two \(\text{Zr}–\text{OPh}\) bonds allowing the formation of the classical di-\(\mu_2\text{-OH}\) bridge causing departure of the fully protonated ligand (\(\text{L}^2\text{H}^4\)) with addition of two alcohol molecules in order to conserve the sixfold coordination of \(\text{Zr}\)-atoms:

\[
\frac{1}{2}\text{Zr}_2(\text{L}^2)^2(\text{L}^2\text{H}^4) + 2\text{H}_2\text{O} + 2\text{ROH} \\
\rightarrow [(\text{ROH})_2(\text{L}^2\text{H}_2)]\text{Zr}(\mu\text{-OH})_2\text{Zr}(\text{L}^2) + \text{L}^2\text{H}_4
\]

The next step could be a further partial hydrolysis of the \((\text{L}^2\text{H}^2)\) ligand according to:

\[
[(\text{ROH})_2(\text{L}^2\text{H}_2)]\text{Zr}(\mu\text{-OH})_2\text{Zr}(\text{L}^2) + \text{H}_2\text{O} \\
\rightarrow [(\text{ROH})_2(\text{L}^2\text{H}_3)(\eta^1\text{-OH})]\text{Zr}(\mu\text{-OH})_2\text{Zr}(\text{L}^2)
\]

The solid-state structure could now be obtained through a single olation reaction between one (\(\text{L}^2\text{H}^2\))-based and one (\(\text{L}^2\text{H}_3\))-based hydrolysed dimers assisted by proton transfer between the \((\text{L}^2\text{H}^2)\) and \((\text{L}^2\text{H}_3)\) moieties in order to allow for departure of another neutral \(\text{L}^2\text{H}_4\) ligand:
be formulated as a negatively charged $[\text{Zr}_4(L^2)_3]^{4-}$ helicate with 4 protons acting as counter-ions and delocalized over the whole structure. These "free" protons would then be able to catalyse the slow condensation of two alcohol molecules with the liberation of one water molecule: $\text{ROH} + \text{HOR} \rightarrow \text{R-O-R} + \text{H}_2\text{O}$. In such a case, the water necessary for the formation of the tetramer would be formed in situ preventing the isolation of the helicate in the crystalline state. Further theoretical work is thus needed in order to clarify this point.

### Conclusion

We have described herein a coordination chemistry involving one of the most employed zirconium alkoxide precursors, i.e. $[\text{Zr(OPr)}_4(\text{HOPr})]_3$, and two proligands incorporating the 2,2'-biphenol entities. The DOSY investigation supported by mass spectrometry and DFT calculations allowed us to suggest highly plausible structures for the complexes formed in situ. The coordination reaction involving the $\text{L}^2\text{H}_4$ proligand with $\text{Zr(IV)}$ is less efficient comparatively to the one performed with $\text{Ti(IV)}$. Nevertheless, we have established that the $\text{Zr(IV)}$-based complex formed from $\text{L}^2\text{H}_4$ incorporates three bidentate entities according to DOSY and ESI-MS analysis. DFT calculations indicate the formation of the $[\text{cis-ZrL}^2(\text{L}^1\text{H})_5]$ isomer among three possible stereoisomers. Concerning the self-assembled architecture derived from the strand $\text{L}^2\text{H}_4$, the DOSY and mass spectrometry analysis proved the formation of a dinuclear assembly formed with three strands. Remarkably, computational modelling proposes an unprecedented triple-stranded helicate structure that incorporates two distorted octahedral $\text{ZrO}_6$ units for the $\text{Zr(IV)}$-assembly. This structure evidence for the complex in solution contrasts strongly with the one obtained for the complex upon crystallization. In this case, a helical architecture constructed around an original chain-like inorganic core displaying the $[\text{Zr}_4(L^2)_2(\text{L}^1\text{H})_5]^{4-}$ formula is characterized. It has been proposed that $[\text{Zr}_4(L^2)_2(\text{L}^1\text{H})(\text{p}-\text{OH})(\text{HO})_3]$ may in fact be formed during crystallization owing to a partial hydrolysis/condensation reaction of the dimeric helicates mediated by water molecules.

Overall, we have demonstrated the deep impact of the ionic size on the resulting self-assembled architecture formed with the strand $\text{L}^2$ as with $\text{Ti(IV)}$ only double-stranded helicates were obtained. Meanwhile, we have shown that the combination of $\text{Zr(IV)}$ with the 2,2'-biphenol-based proligands leads to a less effective coordination chemistry to create stable and easily characterized self-assemblies in comparison with the one already developed with $\text{Ti(IV)}$.

### Experimental part

#### NMR spectroscopy

Bruker Avance-300, Avance-400 and Avance-500 were used for solution NMR spectroscopic analysis. $^1\text{H}$ NMR DOSY measurements were performed at 500.13 MHz with a 5 mm
\[ \text{[Zr}_2\text{L}_2\text{H}_4] \]

The reaction was conducted under a nitrogen atmosphere. In a vial, \( \text{L}_2\text{H}_4 \) (10 mg, 0.016 mmol), and \([\text{Zr}(\text{OPr})_4(\text{HOPr}_2)]\) (6.45 mg, 0.016 mmol) were mixed in dry \( \text{CD}_2\text{Cl}_2 \) (0.75 mL). The resulting uncoloured mixture was analysed by \(^1\text{H} \) NMR, \(^{13}\text{C} \) NMR, DOSY and mass spectrometry. \(^1\text{H} \) NMR was too complex to be analysed. ES-MS: \( \text{m/z} = 2006.4081 \) \([\text{Zr}_2\text{L}_2\text{H}_4(\text{H}_2\text{O})]^- \) (calcd for \( \text{C}_{126}\text{H}_{83}\text{NaO}_{13}\text{Zr} = 2006.3825 \)). DOSY: \( D = 505 \mu\text{m}^2 \text{s}^{-1} \).

\[ \text{[Zr}_4(\text{L}_2^3)^2(\text{L}_2\text{H})_2(\text{OPr})_2(\text{HOPr})_2] \]

The reaction was conducted under a nitrogen atmosphere. Few colourless single crystals were obtained after several weeks by slow vapour diffusion of diethyl ether on a dry \( \text{CH}_2\text{Cl}_2 \) solution (1.5 mL) composed of \( \text{L}_2\text{H}_4 \) (15 mg, 2.5 \( \times \) \( 10^{-5} \) mol), and \([\text{Zr}(\text{OPr})_4(\text{HOPr}_2)]\) (6.5 mg, 0.66 eq.).

X-ray data: empirical formula: \( \text{C}_{285}\text{H}_{344}\text{Cl}_6\text{O}_{45}\text{Zr}_9 \)
(2\( (\text{Cl}_{1.5}\text{H}_{100}\text{O}_{22}\text{Zr}_9) \), 3\( (\text{C}_3\text{H}_16\text{O}) \), 3\( (\text{C}_2\text{H}_2\text{Cl}_2) \), 2\( (\text{H}_2\text{O}) \)); formula mass: 5331.25 g mol\(^{-1} \); crystal system: triclinic; space group: \( P\overline{1} \); unit cell dimensions: \( a = 17.0968(8) \) Å, \( b = 19.1728(8) \) Å, \( c = 21.3835(8) \) Å; \( \alpha = 81.24(2)^\circ \), \( \beta = 68.379(2)^\circ \), \( \gamma = 87.843(2)^\circ \), \( V = 6425.4(5) \) Å\(^3 \); \( Z = 1 \); density (calcd): 1.378 g cm\(^{-3} \); crystal size: 0.050 \( \times \) 0.060 \( \times \) 0.060 mm\(^3 \); \( \theta \) range for data collection: 1.28 to 30.15\(^\circ \); reflections collected: 33 659; independent reflections: 33 659; \( R \) indices: 0.0638; refinement method: full-matrix least squares on \( F^2 \); data/weights/parameters: 33 659/23/1565; goodness-of-fit on \( F^2 \): 1.009; final \( R \) indices \([ I > 2 \sigma(I) ] \): \( R_1 = 0.0791, \) \( wR_2 = 0.2240; \) \( R \) indices (all data): \( R_1 = 0.1358, \) \( wR_2 = 0.2446. \) CCDC number: 1451432.

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