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# Spontaneous Symmetry Breaking during Self-Assembly of a Double Stranded Biphenolate-Based Ti(IV)-Helicate

**Carine Diebold,**[†] **Pierre Mobian,***[,†] **Clarisse Huguenard,**[†] **Lionel Allouche,**[‡] **and Marc Henry***[,†]

[†]*Laboratoire de Chimie moléculaire de l'Etat Solide, UMR 7140 and* [‡]*Service de RMN, Institut de Chimie, Université de Strasbourg, 67000, Strasbourg, France*

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A binuclear Ti(IV)-based helicate synthesized from a symmetric tetrahydroxyheptaphenylene strand was self-assembled in solution and shown to undergo a spontaneous head-to-tail differentiation according to single-crystal X-ray diffraction.

Spontaneous symmetry breaking occurs when the effect simply has less symmetry than the cause.[1] It is an ubiquitous phenomenon seen in nature to generate fresh information from the molecular chaos, thereby decreasing the local entropy of an evolving system. As a decrease in entropy is a prerequisite for the emergence of living entities,[2] an understanding of how such phenomena may occur at a molecular scale is of crucial importance. Among all spontaneous symmetry breaking processes, emergence of chirality from the isotropic molecular chaos through spontaneous self-assembly is also essential for life apparition. Focusing on metallo-supramolecular self-assembled architectures, helicates[3] are obvious candidates for studying such self-assembly processes owing to their structures reminiscent of DNA,[4] their inherent chirality,[5] their DNA binding properties,[6] their use as precursor for the synthesis of topological nontrivial molecules,[7] their potential application in catalysis[8] and material science,[9] and the search for new functional devices.[10]

We present here an extension of the helicates based on the family of catecholato-titanium(IV) complexes[11] to a Ti(IV)-helicate based on a biphenolate ligand. The choice of the biphenolate-based ligand to design helicates was motivated by the importance of the chemistry of the Ti−O bond in materials science, in enantioselective catalysis as well as its full compatibility with biological living matter. As 2,2′-biphenoxide derivatives constitute one of the most important ligand classes in titanium chemistry,[12] this led us to study the coordination properties of a novel ditopic ligand $\mathbf{LH_4}$ (Figure 1) in the presence of $Ti(OPr^i)_4$. From $^1H$ NMR $\mathbf{LH_4}$ was found to have $C_{2v}$ symmetry in solution whereas $Ti(OPr^i)_4$ was known from $^{47,49}Ti$ NMR[13] as well as EXAFS/XANES measurements,[14] to display tetrahedral symmetry in solution. Owing to the perfect match between the Ti(IV) valence state and the number of phenolic moieties ideally disposed to behave as a double bidentate ligand coupled to the strong reactivity of titanium(IV) isopropoxide toward polyphenols, self-assembly of a double stranded Ti(IV) helicate of $C_2$ symmetry was anticipated. As shown below, this prediction was fully confirmed by experiments, the surprise being an unexpected symmetry breaking down to $C_1$ symmetry due the simultaneous occurrence of a 6-fold and a 5-fold coordinated Ti-atom within the same helicate.

As shown in Figure 1, ligand $\mathbf{LH_4}$ contains two 2,2′-biphenol entities, *ortho*-monosubstituted by a phenyl group, and linked together by a *para*-phenylene spacer. Addition of $Ti(OPr^i)_4$ in a dry $CD_2Cl_2$ solution of $\mathbf{LH_4}$ (1 equiv) resulted immediately in the formation of a red-orange mixture. According to the room-temperature $^1H$ NMR spectrum of the crude mixture, an efficient reaction occurred, since the

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*To whom correspondence should be addressed. E-mail: henry@unistra.fr (M.H.), mobian@unistra.fr (P.M.).

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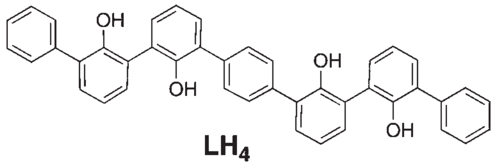

$\mathbf{LH_4}$

**Figure 1.** Representation of the tetrahydroxyheptaphenylene strand $\mathbf{LH_4}$.

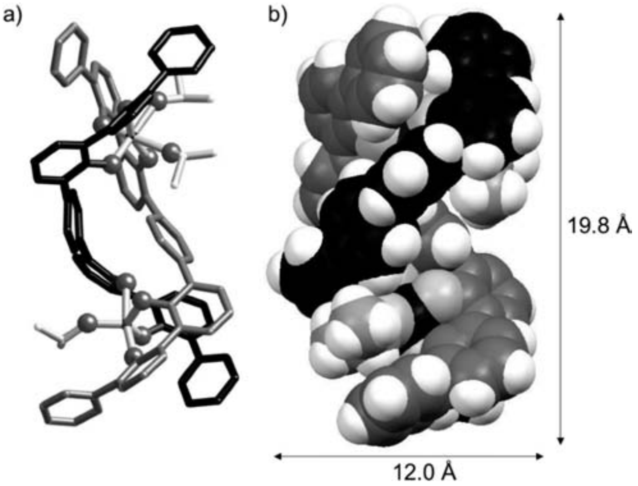

**Figure 2.** Molecular structure of $\mathbf{H_3[Ti_2(L)_2(OPr^i)_3]}$. On the ball and stick model (a), hydrogens are omitted for clarity. Compactness of the structure is revealed by the space filling model (b). In both representations, the two strands L are differently colored (gray and black) for clarity.

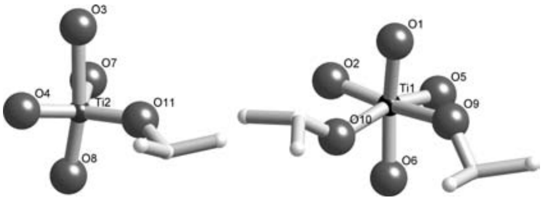

**Figure 3.** Two complex subunits extracted from the structure of $\mathbf{H_3[Ti_2(L)_2(OPr^i)_3]}$. Ti−O distances (Å) obtained from the structure. Sites believed to be protonated are bold. Ti(1)−O: **Ti(1)−O(10) = 2.193(5)**, **Ti(1)−O(9) = 2.154(4)**, Ti(1)−O(6) = 1.920(4), Ti(1)−O(1) = 1.892(4), Ti(1)−O(2) = 1.844(4), Ti(1)−O(5) = 1.810(4). Ti(2)−O: **Ti(2)−O(3) = 2.249(4)**, Ti(2)−O(7) = 1.866(4), Ti(2)−O(4) = 1.851(4), Ti(2)−O(8) = 1.828(4), Ti(2)−O(11) = 1.783(4).

two singlets of the hydroxyl functions located at $\delta = 5.91$ ppm and 5.83 ppm for the free ligand have almost disappeared (see Figure 1 in Supporting Information). However, from the extremely complex aromatic region of the spectrum, it was impossible to extract further useful information. Fortunately, after performing complexation in toluene at room temperature, red-orange platelike crystals appeared after two days and could be isolated from the mother liquor with a yield of 30%. A single crystal suitable for X-ray diffraction was randomly chosen. The compound crystallizes in the triclinic crystal system with the achiral space group ($P\bar{1}$). A first refinement of the structure has confirmed the formation of dinuclear Ti-based helicate and evidenced the presence of 11 toluene molecules per unit cell in the crystal. Owing to the much too high refinement factor of the fully solvated structure (R1 = 19%), the SQUEEZE command was used for the structural resolution,[15] leading to a structure free of solvent molecules and dispaying a $Ti_2O_{11}C_{93}H_{73}$ stoichiometry. The bond valence sum[16] around each Ti-atom being 4.1 and 3.9, it was safely concluded that this helicate was a Ti(IV) derivative and should thus be formulated as $\mathbf{H_3[Ti_2(L)_2(OPr^i)_3]}$ with three missing H-atoms not located during refinement of the structure.

The nanosized helicate (Figure 2) is characterized by a Ti−Ti separation of 8.75 Å. As the selected molecular strand $\mathbf{LH_4}$ allows a good turn of the helicate, a pitch of the helix of 15 Å could be estimated from the structure.[17] The molecular motif is noncentrosymmetric ($C_1$) and describes a rare example of a homometallic helicate built around two different coordination geometries.[18] The absence of any 2-fold axis of symmetry here, usually present in homotopic helicates, comes from the fact that the two titanium(IV) centers adopt a distorted octahedral geometry and a trigonal bipyramid geometry, respectively, as shown in Figure 3. For the octahedral complex subunit, the metal is coordinated by two bidentate entities with a $C_2$ local symmetry and two cis positions occupied by monodentate ligands. Concerning the trigonal bipyramidal complex, the metal is surrounded by two bidentate units, and a third monodentate ligand completes the coordination sphere of the titanium center. As imposed by neutrality of the complex, three protonated OH sites have to be identified now. Concerning the nature of the monodentate ligands linked to the metallic centers, that is, isopropanol or isopropoxy ligands, large Ti−O distance differences between these two coordination modes could be determined from the 5.29 release of the Cambridge Crystallographic Database. Average distances of 1.772 Å and 2.172 Å were respectively observed for the isopropanol or isopropoxy Ti−O distances.[19] A comparison of these characteristic distances with the ones measured in the helicate (Figure 3) shows that two isopropanol molecules are coordinated to the octahedral metallic center. As a result of the short Ti−O distance (1.783(4) Å), it is then reasonable to view one position of the trigonal bipyramidal center as occupied by an isopropoxy group. The third protonated site of the complex appears then to be the phenolic-type Ti(2)−O(3) distance that is actually rather long (2.249(4) Å), evidencing the presence of a rarely observed coordination link between a titanium center and a phenol group.[19] As a further check of this assignment, the same location of these missing H-atoms was obtained using Brown's bond valence sums around each of the oxygen atoms.[20]

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(17) To the best of our knowledge $\mathbf{H_3[Ti_2(L)_2(OPr^i)_3]}$ is a unique example of a double-stranded titanium complex showing helical chirality. For double-stranded titanium complex where a "meso"-relation stands for the two complex units see: Albrecht, M.; Napp, M.; Schneider, M.; Weis, P.; Fröhlich, R. *Chem.—Eur. J.* **2001**, *7*, 3966–3975.

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(19) The Ti-$O_{OPr^i}$ distance of 1.772 Å ($\sigma$ = 0.017) was obtained from 89 distances measured from 19 structures. The selected structures were titanium(IV) complexes containing biphenolate ligands and isopropoxy ligands. An average Ti-$OH_{OPr^i}$ distance of 2.16 Å ($\sigma$ = 0.078) is obtained from 16 structures where isopropanol is coordinated to the titanium.

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Therefore according to the solid state analysis, the helicate should now be definitively formulated as $[\mathbf{Ti_2}(\mathrm{L})(\mathbf{LH})(\mathbf{HOPr_i})_2(\mathbf{OPr^i})]$.

To check that the selected single crystal was not a synthetic artifact, the $^{13}$C CPMAS spectrum of the as-synthesized powder was recorded (see Figure 2 in Supporting Information). It showed the presence of a well-crystallized and unique phase and was interpreted in full agreement with the single-crystal XRD analysis. Signals were most conveniently attributed by analogy with a previously studied Ti(IV) complex, obtained from 3,3′-diphenyl-2,2′-biphenol and Ti(OPr$^i$)$_4$, where a single octahedral Ti(IV) center is complexed by isopropanol and phenolate ligands only.[21] Three distinct signals for CH groups were detected in the helicate, evidencing as expected three inequivalent monodentate ligands. Signals at 71.3 and 69.8 ppm have been attributed to isopropanol ligands and the third CH signal, at significantly different chemical shift (80.7 ppm), to the isopropoxy ligand of the pentacoordinated metallic center. From the XRD structure, seven phenolate and one phenol CO signals were expected corresponding to NMR signals found between 152.6 and 162.2 ppm, leaving a signal at 147.4 ppm attributed the phenol-type COH site. A further fine match between solid state NMR and single-crystal XRD data was noted, as one phenolate signal stands out, due to its relatively low chemical shift (152.6 ppm). It was attributed to O(6)-based phenolate characterized by a Ti−O(6) distance (1.920(4) Å) significantly longer than other Ti−O links of phenolate-type (average length: 1.85 ± 0.03 Å). Having firmly established the solid-state structure of the $[\mathbf{Ti_2}(\mathrm{L})(\mathbf{LH})(\mathbf{HOPr^i})_2(\mathbf{OPr^i})]$ helicate, a check of its stability in the gaseous and liquid phases was undertaken. Crystals of the helicate were thus dissolved in $CH_2Cl_2$, and the resulting solution was submitted to positive high-resolution electrospray ionization mass spectrometry. The resulting spectrum reveals that the analyzed species were composed of two ligands L and two titanium(IV) ions. Moreover, the isotopic patterns and the proposed formulas are in perfect agreement (see Figure 3 in Supporting Information). It is worth noting that no traces of complex with coordinated isopropanol or isopropoxy ligand were detected, suggesting the rather weak coordination of these ligands to the metal center. Next, due to the complex $^1$H NMR signature of the complex formed in situ, we thus have turned to diffusion ordered spectroscopy (DOSY). Performing a DOSY experiment at room temperature on the complex formed in situ in $CD_2Cl_2$ revealed the presence of at least four species in solution (see Figure 5a in Supporting Information). However, no hydrodynamic value obtained from the diffusion coefficient of the species in solution matches with the mean radius 9.2 ± 0.5 Å of the helicate $[\mathbf{Ti_2}(\mathrm{L})(\mathbf{LH})(\mathbf{HOPr^i})_2(\mathbf{OPr^i})]$ evaluated from its crystalline structure using a standard set of van der Waals radii.[22] This could be explained by a partial decoordination of the isopropanol ligands at room temperature as already characterized in a previous study[21] leading to a conformational change of the helicate. Indeed, after lowering the temperature from +25 °C down to −68 °C, a splitting of the signals attributed to the monodentate isopropanol or isopropoxyde ligands bonded to the metals was observed from 3.8 ppm to 2.8 ppm (methine protons) and from 1 ppm to −0.2 ppm (methyl groups). Despite the fact that the evolution of these signals is extremely difficult to monitor due to the complexity of the spectra, these observations match fairly well with the diastereotopic nature of these protons as observed in the single-crystal XRD structure (see Figure 4 in Supporting Information). Futhermore, a DOSY experiment performed at 193 K shows now a good agreement between the crystalline radius 9.2 ± 0.5 Å[22] and the observed hydrodynamic radius $r = 8.8 \pm 0.5$ Å computed for the largest diffusing species characterized by the diffusion coefficient $D = 100 \pm 5\ \mu\mathrm{m}^2\cdot\mathrm{s}^{-1}$ for a viscosity of 1.60 ± 0.05 mPa·s (see Figure 5b in Supporting Information).

In summary, we have reported here the rational synthesis of a chiral double-stranded titanium(IV)-helicate bearing as substructural motif two monomeric bis-biphenolate-Ti(IV) complexes. It is worth stressing that in great contrast with other similar complexes that are known to oligomerize leading to the formation of titanium clusters via the formation of oxo and/or alcoxo-bridges,[23] we have demonstrated here the possibility to incorporate biphenolate-Ti(IV) motifs in a predictable way into self-assembled molecular structures. Theoretical calculations will be performed to identify the origin of the observed spontaneous symmetry breaking leading to the helix where the "head" (6-fold-coordinated Ti-atoms) is clearly different from the "tail" (5-fold-coordinated Ti-atoms).

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**Supporting Information Available:** X-ray diffraction data, NMR experimental, $^1$H NMR spectra, DOSY maps, $^{13}$C CPMAS spectrum, and ES-MS mass spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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