way for application of sol–gel processing to encapsulation, coatings, or net-shape casting. Current efforts are being directed at expanding this family of ROP monomers and determination of the mechanical properties of the gels.

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Template-Directed Self-Recognition of Alkyl-Bridged Bis(catechol) Ligands in the Formation of Helicate-Type Complexes[**]

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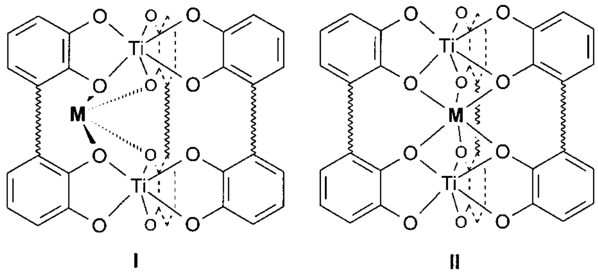
(Metallo-)supramolecular aggregates are formed in spontaneous self-assembly processes. Hereby the steric and electronic information that is embedded in each single molecular component often forces the system to follow a program which affords only one defined supramolecular species.[1–3] Self-recognition of linear ligand strands during the formation of double- or triple-stranded helicates from mixtures of different ligands leads to the self-assembly of structurally well-defined coordination compounds out of a number of different possibilities. Mixtures of complexes are formed that contain only one type of ligand per complex.[4–6] "Hetero"-recognition, on the other hand, leads to compounds that are composed of different ligands.[7, 8]

Lehn et al. described examples in which the self-recognition of ligands in the formation of helicates is influenced by 1) the number of binding sites of the ligands or 2) the preferred coordination geometry of the metal ions in combination with an appropriate structure of the ligands.[4] On the other hand, Raymond et al. performed a study in which the self-recognition during the self-assembly of triple-stranded homoleptic helicates from a mixture of ligands is based on the length of different rigid spacers which bridge two catecholamide moieties.[5] Self-recognition also can be controlled by the chirality of the organic ligands.[6, 7] Herein we describe investigations on the self-recognition of alkyl-bridged bis(catechol) ligands **1**-H$_4$ and **2**-H$_4$ on the formation of a mixture of dinuclear titanium(IV) complexes. During this process binding of the countercations to the tetraanionic complexes plays a crucial role in the selective formation of specific coordination compounds (Scheme 1).



Scheme 1. Possible binding modes of alkali metal cations **M** by which dinuclear helicate-type complexes are stabilized: "Outside" coordination (**I**)[9] or "inside" coordination (**II**).[10]

In principle, reaction of a 1:1 mixture of **1**-H$_4$ and **2**-H$_4$ (1.5 equiv of each) with two equivalents titanium(IV) ions (Ti(OMe)$_4$ or (acac)$_2$TiO) in the presence of alkali metal carbonate (2 equiv) as base could lead to the homoleptic dinuclear complexes **A1** and **A2**, the heteroleptic dinuclear complexes **B1** and **B2**, the homoleptic oligomeric complexes **C1** and **C2**, and/or the heteroleptic oligomeric complexes **D** (Scheme 2). In earlier investigations we already isolated and characterized the lithium and sodium salts of the *meso*-helicate **A1**. With potassium cations only the oligomeric (but still soluble!) complex **C1** was obtained.[9] The dinuclear helicate **A2** was formed in the presence of lithium, sodium, potassium as well as many other countercations.[10]

For entropic reasons the formation of the dinuclear complexes **A** and **B** should be favored over the oligonuclear species **C** and **D**.[5] However, the binding of the countercations to the anionic coordination compounds either stabilizes the dinuclear complexes or destabilizes them leading to the formation of the oligomers **C** or **D**.[9, 11]

A red soluble solid is obtained when a 1:1 mixture of **1**-H$_4$ and **2**-H$_4$ with Ti(OMe)$_4$ (methanol, reflux or (acac)$_2$TiO, methanol, room temperature) is treated with potassium carbonate as base and the solvent is removed. The ^{1}H and ^{13}C NMR spectra (in [D$_4$]methanol) of this red solid show only signals of the homoleptic helicate **A2** (positive-ion FAB MS (3-nitrobenzyl alcohol (3-NBA) matrix): m/z: 940 $\{K_3H[(\mathbf{2})_3Ti_2]\}^+$). Signals of a titanium complex of ligand **1** are not observed. This is attributed to the formation of the oligomeric species **C1**, which leads to very broad signals in the NMR spectrum, as described previously.[9] However, the presence of titanium complexes of **1** was shown by acidic hydrolysis (2 N HCl) of the red solid obtained. After extraction of the aqueous phase with diethyl ether, the

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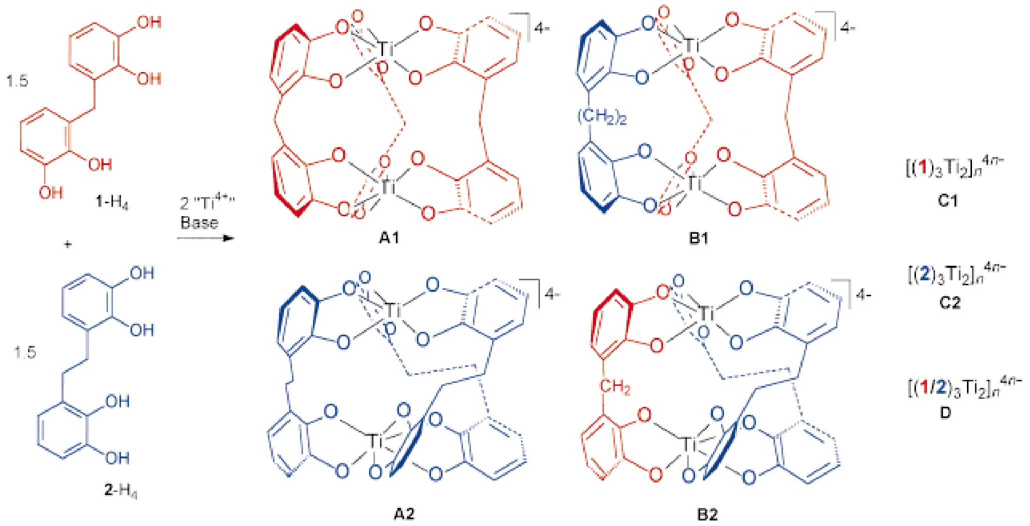


Scheme 2. Possible homoleptic (**A1**, **A2**) and heteroleptic (**B1**, **B2**) dinuclear and oligomeric (**C1**, **C2**, **D**) complexes obtained from a 1:1 mixture of the ligands **1**-H_4 (1.5 equiv) and **2**-H_4 (1.5 equiv) by reaction with titanium(IV) ions (2 equiv) in the presence of alkali metal carbonates (2 equiv) as base.

organic phase contained a 1:1 mixture (by ^1H NMR spectroscopy) of the free ligands **1**-H_4 and **2**-H_4. This indicates that a sorting of the ligands takes place during the formation of the titanium complexes leading in a self-recognition process to a mixture of the two thermodynamically most favored species **A2** and **C1** which both contain only one kind of ligand. The formation of the oligomer **C1** is favored over the formation of **A1** because potassium ions bind to internal oxygen atoms of ligand **1** and thus destabilize the dinuclear titanium complex.

When sodium carbonate is used instead of potassium carbonate, a different result is obtained. In this case a mixture of the two homoleptic dinuclear complexes **A1** (positive-ion FAB MS (3-NBA matrix): *m*/*z*: 873 $\{Na_4H[(\mathbf{1})_3Ti_2]\}^+$) and **A2** (positive-ion FAB MS (3-NBA matrix): *m*/*z*: 892 $\{Na_3H[(\mathbf{2})_3Ti_2]\}^+$) is formed. In contrast to the potassium ion, the sodium ion is able to stabilize the dinuclear complex **A1**[9] and no oligomer **C1** is formed. Thus, in the presence of Na^+ the template-directed self-recognition process affords a mixture of the homoleptic *meso*-helicate **A1** as well as the helicate **A2**.

With lithium carbonate as base, again a red soluble solid is obtained quantitatively. The NMR spectra at room temperature show the signals of the two homoleptic coordination compounds **A1** and **A2**, as well as additional signals of a metal complex (Figure 1). The compound displays resonances of diastereotopic methylene protons of coordinated ligand **1** as doublets at $\delta = 2.91$, 3.11, 4.09, and 4.62 (ratio 1:1:1:1). The appearance of four signals for alkyl protons indicates that in addition to the homoleptic dinuclear complexes **A** the heteroleptic coordination compound **B1** is formed. However, no defined signals are observed for the ligand **2** of **B1** at room temperature. ^1H NMR spectroscopy at 333 K reveals defined signals for the protons of the alkyl bridges. Besides the signals of **A1** ($\delta = 4.15$, 3.04 , 2d) and **A2** ($\delta = 2.75$, s) the resonances of **B1** are observed at $\delta = 4.64$, 4.07, 3.10, 3.02, 2.91, and 2.54 (6d, intensity ratio: 1:1:1:2:1:2). The doublets at $\delta = 3.02$ and 2.54 ($J = 8.5$ Hz) correspond to the spacer protons of the ligand strand **2**. Due to a fast inversion of **2** (Scheme 3) only two signals can be observed for this ligand. The two ligands **1** are rigid and the shifts of the spacer protons are not influenced by the temperature.

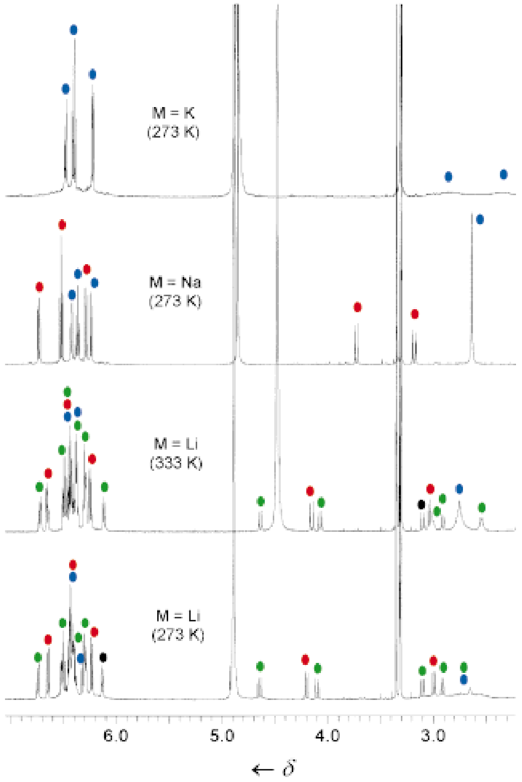
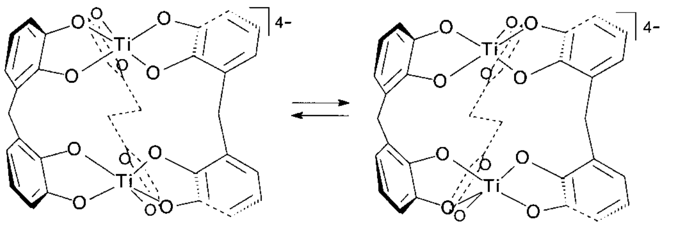


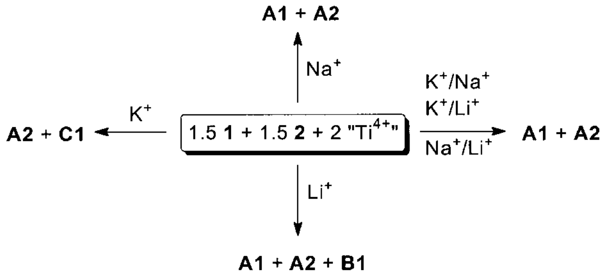
Figure 1. ^1H NMR spectra ([D$_4$]methanol, 500 MHz) of the complexes obtained from a 1:1 mixture of **1**-H_4 and **2**-H_4 and titanium(IV) ions in the presence of M_2CO_3 (M = K, Na, Li). Blue: signals of **A2**; red: signals of **A1**; green: signals of **B1**. Different NMR shifts and line width are observed for similar dinuclear titanium complexes due to the different countercations which bind to the anions. The signals of the lithium salts were assigned on the basis of NOESY and COSY NMR spectroscopy.

The positive-ion FAB-MS (3-NBA matrix) shows in addition to signals of the **A** type complex salts at *m*/*z* 851 ($\{Li_4H[(\mathbf{2})_3Ti_2]\}^+$) and 815 ($\{Li_5(\mathbf{1})_3Ti_2]\}^+$) a peak at *m*/*z* 823 which is assigned to the heteroleptic complex {Li$_4$H-



B1

Scheme 3. Dynamic behavior of **B1:** The flexible ligand **2** can switch between two different orientations, while the two rigid ligands **1** are fixed in one position.



Scheme 4. Overview of the dinuclear and oligomeric complexes obtained with different cations and mixtures of cations.

$[(\mathbf{1})_2(\mathbf{2})\mathrm{Ti}_2]\}^+$ (**B1**+4Li+H). **B1** also is formed if the two complex salts $\mathrm{Li}_4[(\mathbf{1})_3\mathrm{Ti}_2]$ and $\mathrm{Li}_4[(\mathbf{2})_3\mathrm{Ti}_2]$ (1:1) are dissolved in [D$_4$]methanol and heated for several days. However, the ratio of the coordination compounds is different to that observed in the case of complexation of the ligand mixture.

The formation of the dinuclear titanium complex **B1**, which contains two ligands **1** and one ligand **2**, might be due to the ability of lithium ions to bind to the "square" of the four internal oxygen atoms of ligand **1** that is formed upon coordination to titanium(IV) ions.[9] By this binding the cation stabilizes the dinuclear complex. In case of **B2** such a binding site for Li^+ is not present.

Besides the experiments with pure alkali metal carbonates as base, reactions were performed with 1:1 mixtures of two different carbonates. Thus the reaction of a mixture of sodium carbonate and potassium carbonate with **1**-H$_4$ and **2**-H$_4$ and titanium(IV) ions produced a red material which contains the complexes **A1** and **A2**. The ^{1}H NMR spectroscopic shifts of the methylene protons of **A1** are similar to those observed for the pure salt $\mathrm{Na}_4[(\mathbf{1})_3\mathrm{Ti}_2]$. This indicates that the *meso*-helicate structure here is stabilized by binding of sodium ions to the tetraanion. The hydrogen resonances observed for **A2** are similar to those observed for $\mathrm{K}_4[(\mathbf{2})_3\mathrm{Ti}_2]$ in the presence of sodium salts.[10]

Similarly, if a mixture of lithium carbonate and potassium carbonate is used for the deprotonation of the ligands, only signals of the dinuclear complexes **A1** and **A2** are detected by ^{1}H and ^{13}C NMR spectroscopy. In contrast to the complex formation in the presence of pure potassium carbonate as base (resulting in **A2** and **C1**), in the latter cases besides K^+, templates are present (Li^+ or Na^+) that can stabilize **A1** and thus favor its assembly. No indication for the formation of oligomeric material **C1** is found. To obtain a complete picture, the complexation of the ligand mixture was also performed in the presence of a mixture of lithium carbonate and sodium carbonate. Again only the two titanium complexes **A1** and **A2** were observed.

In conclusion, the self-assembly of dinuclear helicates and *meso*-helicates from ligands **1**-H$_4$ and **2**-H$_4$ and titanium(IV) ions proceeds with self-recognition of the ligands. Hereby the formation of homoleptic dinuclear complexes (**A**) strongly depends on the countercations, which act as templates (Scheme 4). With sodium ions or with mixtures of cations (Na/K, Na/Li, Li/K) only the dinuclear homoleptic complexes **A1** and **A2** are obtained. With Li^+ ions the heteroleptic complex **B1** is formed in addition to the homoleptic complexes **A**. In the presence of potassium ions self-recognition takes place but leads to the dinuclear complex **A2** and the oligomer **C1**. The results presented represent an unprecedented example for a new control mechanism in self-recognition of linear ligands upon formation of helicate-type complexes. In the future, mechanisms like the one discussed might allow the construction of complex supramolecular aggregates starting from simple building blocks but using different directing forces to control and influence the supramolecular construction plan.

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