Self-Assembly of Dinuclear CH_2-bridged Titanium(IV)/Catecholate Complexes: Influence of the Counterions and of Methyl Substituents in the Ligand

Markus Albrecht*

Abstract: The spontaneous self-assembly of methylene-bridged dinuclear Ti^{IV} complexes $M_4[L_3Ti_2]$ (L = **1**–**3**) from CH_2-bridged di(catechol) ligands (**1-H$_4$**–**3-H$_4$**) was found to proceed in the presence of lithium or sodium carbonate acting as a base (M = Li, Na). In contrast, only an unspecific mixture of coordination compounds was obtained in the presence of potassium carbonate. This difference in behavior is due to the ability of Li^+ or Na^+ to stabilize the triple-stranded dinuclear titanium(IV) species $[L_3Ti_2]^{4-}$ In the solid state, $Li_4[(\mathbf{1})_3Ti_2]$ exhibits a highly symmetric structure with three lithium cations bound to the *meso*-helicate tetraanion. ^6Li NMR together with ^1H NMR studies at variable temperature revealed that, in solution, an unsymmetrical "bowl-shaped" species is formed with only two Li^+ bound to the anion. A methyl substituent on the methylene spacer of the di(catechol) ligand (ligand **2**) led to supramolecular systems with new stereocenters and thus a higher content of information. However, only one of the four possible diastereoisomeric metal complexes of $[(\mathbf{2})_3Ti_2]^{4-}$ was observed. A third type of ligand, with a methyl group attached to one terminus of the linear ligand, was also investigated. The synthesis of such an unsymmetrical ligand, **3-H$_4$**, was readily achieved starting from 2,3-dimethoxybenzyl alcohol (**4**) and 2,3-dimethoxybenzaldehyde (**6**). Upon complexation, the ligand **3-H$_4$** led to a statistical mixture of the two possible isomers of the dinuclear titanium(IV) complex $[(\mathbf{3})_3Ti_2]^{4-}$.

Keywords
alkali metals · catechol ligands · NMR spectroscopy · supramolecular chemistry · titanium

Introduction

Supramolecular architectures are formed from molecular components in spontaneous self-assembly processes,[1] whereby noncovalent interactions between complementary building blocks lead to the formation of specific aggregates. In metallosupramolecular chemistry the selective formation of defined species in thermodynamically controlled processes is achieved by the simple mixing of metal ions with appropriate organic donor molecules (ligands) in solution. This metal-directed self-assembly can be influenced by various factors, for example the preorganization of the ligands, preferred coordination geometries of the metals, or templating effects.[2, 3]

Linear coordination compounds can be formed from two or three oligodentate ligands and two or more metal ions. These complexes possess either a chiral helical ("helicate")[4–7] or an achiral nonhelical ("*meso*-helicate")[8] structure. Recently, we reported the formation of a tetraanionic *meso*-helicate from three methylene-bridged di(catecholate) ligands and two titanium(IV) ions.[9] The self-assembly of this dinuclear complex is induced by the counterions: lithium or sodium cations lead to defined coordination compounds; no specific product is observed if potassium carbonate is used. The X-ray structural analysis of the lithium salt indicates that here the templating effect is not due to the encapsulation of the Li^+ ion. A more complicated structure is obtained, in which three of the counterions bind to the anion to form an empty "molecular box" (Figure 1).

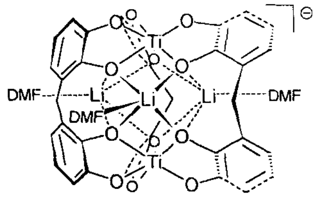

Figure 1. Structure of the anion $\{Li_3[(\mathbf{1})_3Ti_2]\cdot 3\,DMF\}^-$ as observed in the solid state [9].

The main objective of this paper is to investigate the factors that are important in the self-assembly of methylene-bridged dinuclear catecholate/titanium(IV) complexes. These complexes were investigated by ^6Li NMR and ^1H NMR studies at variable temperature. Additionally, the influence of methyl substituents on the spacer methylene (i.e. the introduction of new stereocenters upon complex formation) and on one of the two catechol moieties of the ligand on the formation of different isomers was tested. The results obtained are discussed in this paper.

Results and discussion

Ligand syntheses: The ligands **1-H$_4$** and **2-H$_4$** were prepared as previously reported.[10] The directional ligand **3-H$_4$**, which bears a methyl group as a "marker" at one of the two catechol

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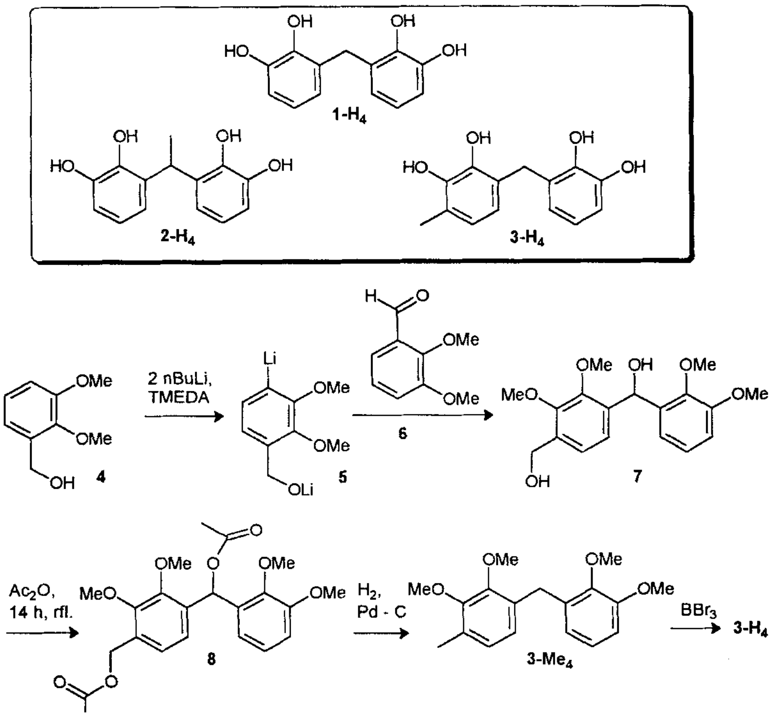
moieties, was synthesized from 2,3-dimethoxybenzyl alcohol (**4**) and 2,3-dimethoxybenzaldehyde (**6**). Benzylic alcohol **4** was deprotonated twice by reaction with two equivalents of *n*BuLi in the presence of TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) in ether to give the dianion **5**. This was subsequently trapped with 2,3-dimethoxybenzaldehyde (**6**) to afford diol **7** as a yellow oil in 32% yield after chromatographic workup (Scheme 1).



Scheme 1. Ligands discussed in this study and the synthesis of **3-H$_4$**.

Abstract in German: *Durch spontane Selbstorganisation entstehen zweikernige methylenverbrückte Titan(IV)-Komplexe $M_4[L_3Ti_2]$ (L = 1–3) aus entsprechenden Di(brenzkatechin)-liganden* ***1-H$_4$*** *–* ***3-H$_4$*** *in Anwesenheit von Lithium- oder Natriumcarbonat als Base (M = Li, Na). Mit Kaliumcarbonat wird nur ein unspezifisches Gemisch an Koordinationsverbindungen erhalten. Dies liegt an der Fähigkeit von Lithium- oder Natriumionen, das dreisträngige, zweikernige Tetraanion $[(1)_3Ti_2]^{4-}$ zu stabilisieren. Im Festkörper weist $Li_4[(1)_3Ti_2]$ eine hochsymmetrische Struktur auf, bei der drei der Lithiumgegenionen an das meso-Helicat-artige Tetraanion gebunden sind. ^6Li- und ^1H-NMR-spektroskopische Untersuchungen bei mehreren Temperaturen zeigen jedoch, daß in Lösung eine unsymmetrische Verbindung vorliegt, bei der nur zwei Lithiumionen gebunden sind. Methylsubstituenten an der Alkylbrücke des Di(brenzkatechin)-liganden führen zu supramolekularen Systemen mit erhöhtem Informationsgehalt. Während der Metallkomplexierung von* ***2*** *werden neue Stereozentren gebildet. Es wird jedoch nur einer der vier möglichen diastereomeren Metallkomplexe $[(2)_3Ti_2]^{4-}$ beobachtet. Ausgehend von 2,3-Dimethoxybenzylalkohol (4) und 2,3-Dimethoxybenzaldehyd (6) läßt sich der direktionale Ligand* ***3-H$_4$****, der eine Methylgruppe an einem Terminus trägt, einfach darstellen. In Koordinationsstudien führt dieser Ligand zu einem statistischen Gemisch der isomeren zweikernigen Titankomplexe $[(3)_3Ti_2]^{4-}$*

The ^1H NMR spectrum of diol **7** (in $CDCl_3$) displays characteristic signals for the benzylic alkyl groups at $\delta = 6.33$ (s, 1 H, CH) and 4.63/4.59 (2 d, $J = 11.0$ Hz, each 1 H, diastereotopic protons, CH_2). The large difference in the shifts of the diastereotopic protons of the CH_2 group suggested that, after initial deprotonation of the OH functionality of **4**, the second attack of *n*BuLi may not have occurred *ortho* to the methoxy group but next to the benzylic alcoholate.[11] However, no NOE could be observed between the C*H*OH and the C*H*$_2$OH protons of **7**. This indicates that only the position *para* to the benzylic alcoholate in **4** is deprotonated during the reaction.

The alcohol **7** was transformed into the corresponding diacetate **8** by reaction with acetic anhydride at 140 °C (84% yield). The two ester functionalities of **8** were removed by hydrogenolytic cleavage to yield the CH_2-bridged ligand precursor **3-Me$_4$** in 93% yield. The final step—cleavage of the methyl ether groups with BBr_3 in dichloromethane at 0 °C—proceeded quantitatively to produce the di(catechol) derivative **3-H$_4$** as a reddish, waxy solid.

$M_4[(1)_3Ti_2]$ (M = Li, Na):

Synthesis of $M_4[(1)_3Ti_2]$ (M = Li, Na): The lithium or sodium salts of $[(1)_3Ti_2]^{4-}$ were prepared as previously reported by reaction of three equivalents of the ligand **1-H$_4$** and two equivalents of $[(acac)_2TiO]$ (acac = acetyl acetonate) in the presence of two equivalents of the alkali metal carbonate in methanol.[9, 12] After evaporation of the solvent, the complex salts were obtained in quantitative yield as red solids. The corresponding ^6Li derivative was prepared by a similar reaction with four equivalents of freshly prepared ^6LiOMe as the base.

The complexes $M_4[(1)_3Ti_2]$ (M = Li, Na) were also obtained in an NMR experiment in which $LiClO_4$ or $NaClO_4$ (4 equiv) was added to a [D$_4$]methanol solution of preformed "$K_4[(1)_3Ti_2]$". This experiment is shown in Figure 2 for the addition of $LiClO_4$. Within one hour characteristic signals of

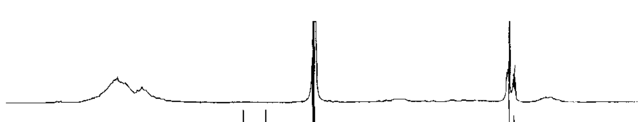


Figure 2. Change in the ^1H NMR spectrum ([D$_4$]methanol) of "$K_4[(1)_3Ti_2]$" upon addition of 4 equiv $LiClO_4$.

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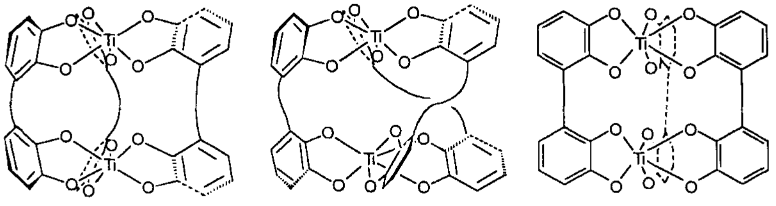
$Li_4[(\mathbf{1})_3Ti_2]$ were observed. After 20 hours this complex was the only detectable coordination compound. This experiment shows that the addition of a "template" like Li^+ or Na^+ induces the self-assembly of a defined supramolecular species. Addition of only one or two equivalents of Li^+ did not lead to clean NMR spectra.

^1H NMR studies at variable temperature: The lithium compound $Li_4[(\mathbf{1})_3Ti_2]$ displays in its ^1H NMR spectrum at room temperature in [D_4]methanol one set of signals for the aromatic protons: $\delta = 6.65$ (dd, $J = 1.3$, 7.6 Hz, 6 H), 6.44 (pseudo-t, $J = 7.6$ Hz, 6 H), and 6.23 (dd, $J = 1.3$, 7.6 Hz, 6 H). The resonances of the diastereotopic protons of the methylene spacer are at $\delta = 4.20$ (d, $J = 12.8$ Hz, 3 H) and 2.99 (d, $J = 12.8$ Hz, 3 H). A similar set of signals is observed for the sodium salt $Na_4[(\mathbf{1})_3Ti_2]$. The presence of signals of diastereotopic alkyl protons indicates that the dinuclear titanium compounds adopt the C_{3h}-symmetric *meso*-helicate structure **A** (Figure 3).[9] In the corresponding D_{3d}-symmetric helicate-type structure **B** only one signal of homotopic protons would be detected for the spacer. A third possibility is a linear dinuclear complex with trigonal-prismatic tris(catecholato)titanium(IV) moieties. Although in a related ethylene-bridged system, the coordination environment of titanium is close to trigonal-prismatic,[7a] the coordination geometry at the transition metal centers of $Li_4[(\mathbf{1})_3Ti_2]$ can be best described as pseudooctahedral. Additionally, a D_{3h} symmetric complex **C** in the ^1H NMR spectrum should lead to only one signal for the CH_2-spacer. Thus, at room temperature, the tetraanion in solution possesses the same symmetry (**A**) as that observed in the solid state[9] (Figure 3).



A
meso-helicate
octahedral coordination
geometry at the metal
(Δ_1,Λ_2-form)
C_{3h}

B
helicate
octahedral coordination
geometry at the metal
(Δ,Δ-form)
D_{3d}

C
linear structure
trigonal-prismatic coordination
geometry at the metal
D_{3h}

Figure 3. Schematic representation of the different structural possibilities for the tetraanion $[L_3Ti_2]^{4-}$ (L: e.g. **1**).

The spectra did not change significantly on heating the NMR samples to 333 K. However, when the $Li_4[(\mathbf{1})_3Ti_2]$ sample was cooled in the NMR instrument, then a splitting of the signals of both the aromatic and alkyl protons was observed (Figure 4). Only broad signals were detected at 223 K. Further cooling led to numerous new signals, which then sharpened.

At 193 K, resonances of the aromatic moieties are detected at $\delta = 6.78-6.62$ (m, 6 H), 6.51–6.40 (m, 6 H), 6.26 (d, $J = 7.1$ Hz, 2 H), 6.19 (d, $J = 7.4$ Hz, 2 H), and 6.15 (d, $J = 7.4$ Hz, 2 H). The signals of the spacer are observed at $\delta = 4.33$ (d, $J = 11.3$ Hz, 2 H), 4.27 (d, $J = 10.3$ Hz, 2 H), 4.05 (d, $J = 10.3$ Hz, 2 H), 3.05 (d, $J = 11.3$ Hz, 2 H), and 2.98 (d, $J = 10.3$ Hz, 4 H) (all signals are broadened at 193 K because of viscosity problems). The observation of three different sets of resonances of the ligand indicates that not a C_{3h}- but a C_s-symmetric species is present in solution. At room temperature only averaged spectra can be detected.

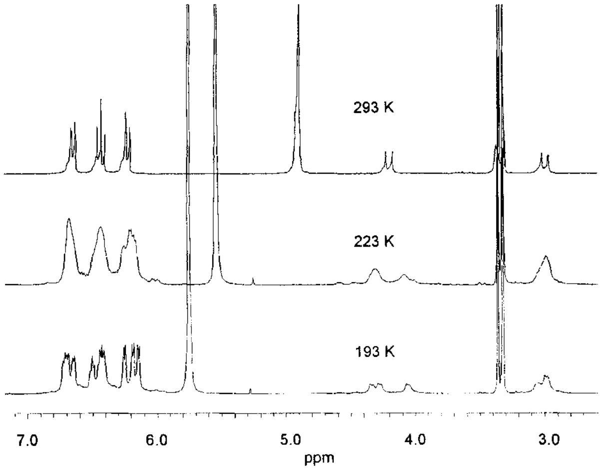


Figure 4. Variable-temperature ^1H NMR spectra of $Li_4[(\mathbf{1})_3Ti_2]$ (in [D_4]methanol).

Cooling of a sample of $Na_4[(\mathbf{1})_3Ti_2]$ in [D_4]methanol also led to a broadening of the ^1H NMR signals. However, no splitting into defined resonances was observed, even at temperatures as low as 193 K.

Heteronuclear NMR spectroscopic investigations: In order to gain a better understanding of the influence of the alkali metal cations in the self-assembly of the dinuclear titanium(IV) complex $[(\mathbf{1})_3Ti_2]^{4-}$, heteronuclear NMR studies were performed at variable temperature by ^{23}Na NMR and ^6Li NMR spectroscopy.

The ^{23}Na NMR spectrum (105 MHz) of $Na_4[(\mathbf{1})_3Ti_2]$ at room temperature in [D_4]methanol shows one signal at $\delta = 0.3$, with a line width of $\Delta\nu_{1/2} = 435$ Hz. Although the line width indicates that an exchange process is taking place, no significant changes of the spectrum are observed upon cooling to 188 K.

The ^6Li NMR spectra (58 MHz) of $^6Li_4[(\mathbf{1})_3Ti_2]$ in [D_4]methanol are presented in Figure 5. At room temperature

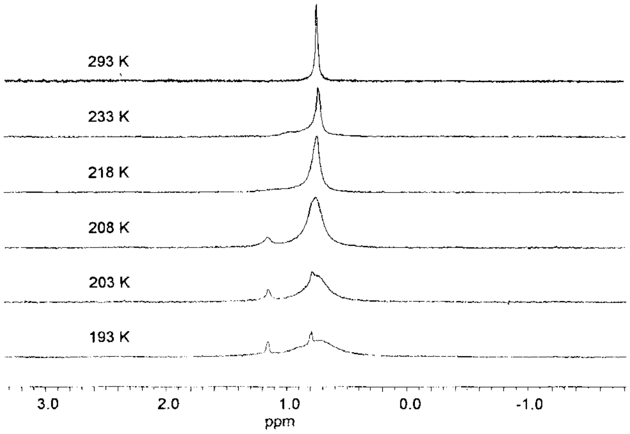


Figure 5. Variable-temperature ^6Li NMR spectra of $^6Li_4[(\mathbf{1})_3Ti_2]$ (in [D_4]-methanol).

only one signal at $\delta = 0.94$ can be detected. However, upon cooling the signal broadens and starts to split at about 233 K. At 193 K two sharp signals are observed at $\delta = 1.15$ and 0.79, in an approximate ratio of 1:1. The resonance at $\delta = 0.79$ is partly hidden by a broad signal at $\delta = 0.73$. This indicates that three different types of lithium cations are present in solution.

The results of both the ^{1}H and ^{6}Li NMR spectroscopy of ^{6}Li$_4$[(**1**)$_3$Ti$_2$] at variable temperature reveal that the highly symmetric species, which is indicated by NMR spectroscopy at room temperature, is not present in solution. These observations indicate that in solution only two of the lithium cations are bound to the tetraanion; this leads to an aggregate with low symmetry. All three ligands are now different and three sets of ligand signals can be observed by ^{1}H NMR spectroscopy at 188 K. The two coordinated lithium atoms are diastereotopic and produce two sharp signals in the ^{6}Li NMR spectrum at 193 K, while the broad resonance at $\delta = 0.73$ can be assigned to two solvated lithium counterions. This is in contrast with the highly symmetric structure which was found in the solid state. Instead of a closed "molecular box" {Li$_3$[(**1**)$_3$Ti$_2$]}$^-$,[9] an open, bowl-shaped aggregate {Li$_2$[(**1**)$_3$Ti$_2$]}$^{2-}$ (Figure 6) is observed in solution.

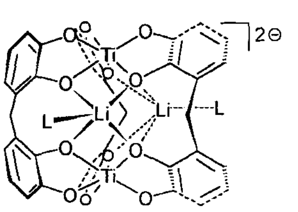


Figure 6. Proposed structure of {Li$_2$[(**1**)$_3$Ti$_2$]}$^{2-}$ in solution (L = ligand/solvent).

Li$_4$[(2)$_3$Ti$_2$]: The ligand **2-H$_4$**, which bears a methyl group attached to the spacer, was used to obtain the dinuclear titanium compound Li$_4$[(**2**)$_3$Ti$_2$] (FAB(+) MS in glycerin: $m/z = 851$ {Li$_4$H[(**2**)$_3$Ti$_2$]}$^+$). As depicted in Figure 7, the methyl group can adopt two different orientations: "in" or "out". Theoretically, four diastereoisomers can be formed in a triple-stranded system: in/in/in, in/in/out, in/out/out, and out/out/out. However, the ^{1}H NMR and ^{13}C NMR spectra in [D$_4$]methanol show that only one of these possible isomers is formed predominantly.

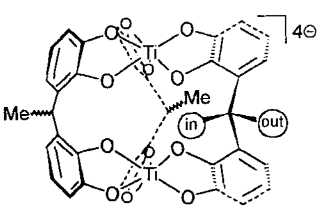


Figure 7. The tetraanion [(**2**)$_3$Ti$_2$]$^{4-}$; the two possible orientations of the methyl group (in/out) are indicated for one ligand strand.

In the ^{1}H NMR spectrum signals of a C_{3h}-symmetric species can be observed at $\delta = 6.78$ (dd, $J = 1.2$, 7.8 Hz, 6H), 6.51 (pseudo-t, $J = 7.8$ Hz, 6H), 6.21 (dd, $J = 1.2$, 7.8 Hz, 6H), 4.67 (q, $J = 7.5$ Hz, 3H), and 1.32 (d, $J = 7.5$ Hz, 9H). Corresponding ^{13}C NMR resonances are detected at $\delta = 157.7$ (C), 156.5 (C), 132.4 (C), 119.2 (CH), 117.7 (CH), 110.4 (CH), 29.0 (CH), and 21.2 (CH$_3$). The symmetry of the coordination compound shows that either the in/in/in or the out/out/out isomer is obtained. For sterical reasons, the out/out/out isomer should be favored.

M$_4$[(3)$_3$Ti$_2$] (M = Li, Na): If a methyl substituent is attached to one of the aromatic moieties the directional ligand, **3-H$_4$** is obtained.[13] This linear ligand bears a "marker" at one end and can thus adopt two different orientations ("up" or "down") in a dinuclear coordination compound. It is possible to obtain a linear triple-stranded complex with two ligands oriented in one and the third in the other direction (C_1 symmetry). On the other hand, an analogous complex with all three ligands oriented in one direction (C_3 symmetry) could be formed. In a coordination study, a mixture of three equivalents of ligand **3-H$_4$** together with two equivalents of [(acac)$_2$TiO] and two equivalents of lithium carbonate or sodium carbonate as a base was stirred in methanol at room temperature for 20 h. The solvent was removed to afford Li$_4$[(**3**)$_3$Ti$_2$] or Na$_4$[(**3**)$_3$Ti$_2$] as red solids. The negative FAB-MS (glycerin as matrix) contains a peak for Li$_3$[(**3**)$_3$Ti$_2$]$^-$ at $m/z = 843$. Corresponding signals are detected for the sodium compound in the FAB(+)-MS (glycerin) at $m/z = 915$ (HNa$_4$[(**3**)$_3$Ti$_2$]$^+$) and 937 (Na$_5$[(**3**)$_3$Ti$_2$]$^+$).

The ^{13}C NMR as well as the ^{1}H NMR spectrum ([D$_4$]methanol, 296 K) of Li$_4$[(**3**)$_3$Ti$_2$] or Na$_4$[(**3**)$_3$Ti$_2$] display a number of resonances. Signals of the CH$_3$ substituents of Li$_4$[(**3**)$_3$Ti$_2$] are observed at $\delta = 15.9$, 15.8, and 15.7 and 2.08, 2.07, and 2.05 (intensity 1.0:1.8:1.0), respectively. This indicates that the C_1-symmetric (all three ligands are different, intensity 1.0:1.0:1.0) as well as the C_3-symmetric isomer (all three ligands equivalent, intensity 0.8) are formed. The corresponding ^{1}H NMR spectrum of Na$_4$[(**3**)$_3$Ti$_2$] is shown in Figure 8 and reveals similar features to those discussed for the lithium salt. A ratio of the C_1- to C_3-symmetric isomers of 4:1 can be estimated from the ^{1}H NMR as well as the ^{13}C NMR spectra of M$_4$[(**3**)$_3$Ti$_2$] (M = Li, Na). This observed ratio is close to that expected by statistical formation of the two structures (expected: C_1:C_3 = 3:1)

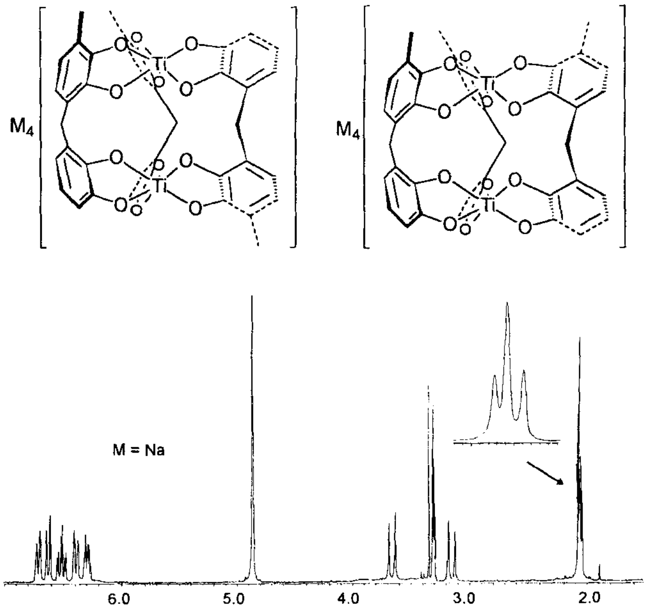


Figure 8. ^{1}H NMR spectrum of Na$_4$[(**3**)$_3$Ti$_2$] in [D$_4$]methanol. The signals of the methyl groups at $\delta = 2.0$–2.1 indicate the presence of a 4:1 mixture of the unsymmetrical (left) and the C_3-symmetrical isomer (right).

This coordination study shows that ligand **3** and titanium(IV) ions form a dinuclear coordination compound [(**3**)$_3$Ti$_2$]$^{4-}$ with a statistical preference for the C_1-symmetric structure.

Conclusions

This paper reports on an example of a self-assembly process in which the formation of a dinuclear triple-stranded tetraanionic *meso*-helicate is influenced by the counterion that is present. Only counterions that can stabilize the tetraanion ($\mathrm{Li^+}$ or $\mathrm{Na^+}$, but not $\mathrm{K^+}$) lead to the formation of defined supramolecular species. For $\mathrm{Li_4[(\mathbf{1})_3Ti_2]}$, stabilization occurs in the solid state by the binding of three of the four lithium cations to the tetraanion. However, NMR spectroscopic studies indicate that in solution only two lithium ions are bound to the anion, leading to a loss of symmetry. The understanding of such templating effects will lead to a deeper insight into self-assembly processes, and should help to understand and to control such processes.[14]

The attachment of substituents to the ligands allows the formation of different isomers and thus leads to systems that contain more information than the unsubstituted derivatives. Reaction with ligand **2** only produced one diastereoisomer of $\mathrm{Li_4[(\mathbf{2})_3Ti_2]}$, while the directional ligand **3** gave $\mathrm{M_4[(\mathbf{3})_3Ti_2]}$ (M = Li, Na) as a statistical mixture of the possible isomers.

Future work will focus on the investigation of control mechanisms, which are important for the selective formation of (metallo)supramolecular species or isomers.[15]

Experimental Section

^{1}H NMR, ^{13}C NMR, ^{6}Li NMR, and ^{23}Na NMR spectra were recorded on a Bruker DRX500, AM400, or WM250 NMR spectrometer using DEPT techniques for the assignment of the multiplicity of carbon atoms. FT–IR spectra were recorded by diffuse reflection (KBr) on a Bruker IFS spectrometer. UV/Vis spectra were recorded in methanol on a Perkin Elmer UV/Vis Lambda2 spectrometer. Mass spectra (EI, 70 eV or FAB(+/−), glycerin as matrix) were taken on a Finnigan MAT90 mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer. Solvents were purified by standard methods. Melting points: Büchi535 (uncorrected). Air-sensitive compounds were prepared and handled under Ar using Schlenk techniques.

(4-Hydroxymethyl-2,3-dimethoxyphenyl)(2,3-dimethoxyphenyl)methanol (7): A solution of *n*BuLi/hexane (1.6 M, 7.5 mL, 12 mmol) at room temperature was added to 2,3-dimethoxybenzyl alcohol (**4**) (1.0 g, 5.94 mmol) and TMEDA (1.5 mL) in ether (20 mL). 2,3-Dimethoxybenzaldehyde (**6**) (990 mg, 5.96 mmol) in ether (20 mL) was added after 4 h and the mixture then stirred overnight. 6 N HCl was added and the phases were separated. The ether phase was dried ($\mathrm{MgSO_4}$) and solvent removed in vacuo. The residue was purified by column chromatography (silica gel, $\mathrm{CH_2Cl_2}$). Yield: 630 mg (32%), yellow oil. (^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 7.06-6.98$ (m, 3H), 6.89 (dd, $J = 1.3$, 7.8 Hz, 1H), 6.84 (dd, $J = 1.3$, 8.1 Hz, 1H), 6.33 (s, 1H), 4.63 (d, $J = 11.0$ Hz, 1H), 4.59 (d, $J = 11.0$ Hz, 1H), 3.83 (s, 6H), 3.69 (s, 3H), 3.66 (s, 3H); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 152.5$ (C), 150.7 (C), 150.1 (C), 146.3 (C), 137.4 (C), 137.1 (C), 134.3 (C), 123.9 (CH), 123.3 (CH), 122.7 (CH), 119.6 (CH), 111.8 (CH), 66.6 (CH), 61.0 ($\mathrm{CH_2}$), 60.5 ($\mathrm{CH_3}$), 60.4 ($\mathrm{CH_3}$), 60.1 ($\mathrm{CH_3}$), 55.7 ($\mathrm{CH_3}$); IR (KBr): $\tilde{\nu} = 3404$, 2938, 2835, 1586, 1480, 1271, 1016, 761 cm^{-1}; MS (EI): m/z (%) = 334 (22) $[M]^+$, 165 (100); HRMS calcd for $\mathrm{C_{18}H_{22}O_6}$: 334.1416, found: 334.1426.

(4-Acetoxymethyl-2,3-dimethoxyphenyl)(2,3-dimethoxyphenyl)methyl acetate (8): Diol **7** (630 mg, 1.88 mmol) was heated (140 °C) in acetic anhydride (10 mL) for 14 h. After evaporation of the solvent, the residue was dissolved in $\mathrm{CH_2Cl_2}$ and washed with sat. aqueous $\mathrm{NaHCO_3}$. The organic phase was dried ($\mathrm{MgSO_4}$) and $\mathrm{CH_2Cl_2}$ removed in vacuo. Yield: 660 mg (84%), yellow oil. ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 7.47$ (s, 1H), 7.05–6.99 (m, 3H), 6.88–6.82 (m, 2H), 5.11 (s, 2H), 3.84 (2s, 3H each), 3.80 (s, 3H), 3.75 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 170.8$ (C), 169.6 (C), 152.8 (C), 151.5 (C), 150.6 (C), 146.8 (C), 134.7 (C), 133.5 (C), 130.0 (C), 124.6 (CH), 123.8 (CH), 122.8 (CH), 119.8 (CH), 112.3 (CH), 67.2 (CH), 61.5 ($\mathrm{CH_2}$), 60.7 ($\mathrm{CH_3}$), 60.4 ($\mathrm{CH_3}$), 60.1 ($\mathrm{CH_3}$), 55.8 ($\mathrm{CH_3}$), 21.2 ($\mathrm{CH_3}$), 21.1 ($\mathrm{CH_3}$); IR (KBr): $\tilde{\nu} = 2940$, 2836, 1742, 1483, 1373, 1234, 1024, 773 cm^{-1}; MS (EI): m/z (%) = 418 (100) $[M]^+$, 285 (49), 165 (56), 151 (60); HRMS calcd for $\mathrm{C_{22}H_{26}O_8}$: 418.1628, found: 418.1614.

(4-Methyl-2,3-dimethoxyphenyl)(2,3-dimethoxyphenyl)methane (3-Me$_4$): Diacetate **8** (580 mg, 1.39 mmol) and Pd/C (200 mg) in methanol/ethyl acetate (1:3, 15 mL) were stirred for 46 h under an atmosphere of $\mathrm{H_2}$ (50 bar). The mixture was filtered and the solvent removed. Yield: 390 mg (86%), yellow oil. ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 6.94$ (t, $J = 7.9$ Hz, 1H), 6.79 (m, 2H), 6.71 (d, $J = 7.8$ Hz, 1H), 6.67 (dd, $J = 1.4$, 7.7 Hz, 1H), 3.98 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 2.23 (s, 3H); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 152.8$ (C), 151.4 (C), 151.2 (C), 147.2 (C), 135.1 (C), 132.7 (C), 130.2 (C), 125.4 (CH), 125.2 (CH), 123.7 (CH), 122.5 (CH), 110.4 (CH), 60.4 ($\mathrm{CH_3}$), 60.2 ($\mathrm{CH_3}$), 60.0 ($\mathrm{CH_3}$), 55.7 ($\mathrm{CH_3}$), 29.5 ($\mathrm{CH_2}$), 15.7 ($\mathrm{CH_3}$); IR (KBr): $\tilde{\nu} = 2935$, 2833, 1481, 1278, 1081, 752 cm^{-1}; MS (EI): m/z (%) = 302 (100) $[M]^+$; HRMS calcd for $\mathrm{C_{18}H_{22}O_4}$: 302.1518, found: 302.1507.

(4-Methyl-2,3-dihydroxyphenyl)(2,3-dihydroxyphenyl)methane (3-H$_4$): At 0 °C a solution of $\mathrm{BBr_3/CH_2Cl_2}$ (1 M, 6.5 mL) was added to a solution of the ligand precursor **3-Me$_4$** (350 mg, 1.16 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL). The mixture was stirred overnight at room temperature and methanol was added (5 mL). The solvent was removed and the residue then dissolved in ether and washed with water. The ether phase was dried ($\mathrm{MgSO_4}$) and the solvent evaporated in vacuo. Yield: 295 mg (93%), slightly red, hygroscopic solid; m.p. 46 °C. ^{1}H NMR ([D$_4$]methanol): $\delta = 6.63-6.55$ (m, 3H), 6.52 (d, $J = 8.0$ Hz, 1H), 6.50 (d, $J = 8.0$ Hz, 1H), 3.83 (s, 2H), 2.15 (s, 3H); ^{13}C NMR ([D$_4$]methanol): $\delta = 146.1$ (C), 144.5 (C), 143.5 (C), 143.4 (C), 129.5 (C), 126.9 (C), 123.8 (C), 122.6 (CH), 122.3 (CH), 121.8 (CH), 120.8 (CH), 114.1 (CH), 31.0 ($\mathrm{CH_2}$), 16.0 ($\mathrm{CH_3}$); IR (KBr): $\tilde{\nu} = 3311$, 3051, 2936, 1476, 1279, 756 cm^{-1}; MS (EI): $m/z = 246$ $[M]^+$, 137, 124; HRMS calcd for $\mathrm{C_{14}H_{14}O_4}$: 246.0892, found: 246.0883; calcd for $\mathrm{C_{14}H_{14}O_4 \cdot {}^1/_3 H_2O}$: C 66.66, H 5.86; found: C 66.54, H 6.06.

General procedure for the preparation of titanium(IV) complexes: Ligand (3 equiv), $\mathrm{M_2CO_3}$ (M = Li, Na; 2 equiv), and $\mathrm{[(acac)_2TiO]}$ (2 equiv) were dissolved in methanol and stirred overnight. The mixture was evaporated to dryness to afford a red solid. The coordination compounds may be purified by chromatography (Sephadex LH-20, methanol), but this was often unnecessary.

"$\mathbf{K_4[(1)_3Ti_2]}$": Yield: 100% red solid as the octahydrate; UV/Vis (methanol): $\lambda = 205$, 273, 369 nm; MS (FAB(−)): m/z (%) = 897 (very low intensity, $\mathrm{K_3[(\mathbf{1})_3Ti_2]^-}$); calcd for $\mathrm{C_{39}H_{24}K_4O_{12}Ti_2 \cdot 8H_2O}$: C 43.34, H 3.73; found: C 43.70, H 4.01.

$\mathbf{Na_4[(1)_3Ti_2]}$: Yield: 100% orange-red solid as the nonahydrate; ^{1}H NMR ([D$_4$]methanol): $\delta = 6.74$ (d, $J = 7.7$ Hz, 6H), 6.53 (pseudo-t, $J = 7.7$ Hz, 6H), 6.29 (d, $J = 7.7$ Hz, 6H), 3.73 (d, $J = 13.5$ Hz, 3H), 3.19 (d, $J = 13.5$ Hz, 3H); ^{13}C NMR ([D$_4$]methanol): $\delta = 158.4$, 155.7, 126.9, 122.8, 120.2, 111.7, 31.5; ^{23}Na NMR ($\mathrm{D_2O}$, 0.1 M, 296 K): $\delta = 0.98$ ($\Delta\nu_{1/2} = 880$ Hz); UV/Vis (methanol): $\lambda = 206$, 273, 366 nm; MS (FAB(+)): $m/z = 895$ ($\mathrm{Na_5[(\mathbf{1})_3Ti_2]^+}$), 873 ($\mathrm{Na_4H[(\mathbf{1})_3Ti_2]^+}$), 851 ($\mathrm{Na_3H_2[(\mathbf{1})_3Ti_2]^+}$), 829 ($\mathrm{Na_2H_3[(\mathbf{1})_3Ti_2]^+}$); calcd for $\mathrm{C_{39}H_{24}Na_4O_{12}Ti_2 \cdot 9H_2O}$: C 45.28, H 4.09; found: C 45.07, H 4.27.

$\mathbf{Li_4[(1)_3Ti_2]}$: Yield: 98% orange-red solid as the nonahydrate; ^{1}H NMR ([D$_4$]methanol): $\delta = 6.65$ (dd, $J = 1.3$, 7.6 Hz, 6H), 6.44 (pseudo-t, $J = 7.6$ Hz, 6H), 6.23 (dd, $J = 1.3$, 7.7 Hz, 6H), 4.20 (d, $J = 12.8$ Hz, 3H), 2.99 (d, $J = 12.8$ Hz, 3H); ^{13}C NMR ([D$_4$]methanol): $\delta = 158.2$, 156.9, 127.6, 121.9, 119.0, 111.0, 31.9; ^{6}Li NMR of $\mathrm{^6Li[(\mathbf{1})_3Ti_2]}$ ([D$_4$]methanol, 296 K): $\delta = 0.94$, (187 K): $\delta = 1.15$, 0.79, 0.73 (br.); UV/Vis (methanol): $\lambda = 205$, 271, 359 nm; MS (FAB(+)): $m/z = 809$ ($\mathrm{Li_4H[(\mathbf{1})_3Ti_2]^+}$), 803 ($\mathrm{Li_3H_2[(\mathbf{1})_3Ti_2]^+}$), 797 ($\mathrm{Li_2H_3[(\mathbf{1})_3Ti_2]^+}$); calcd for $\mathrm{C_{39}H_{24}Li_4O_{12}Ti_2 \cdot 9H_2O}$: C 48.28, H 4.36; found: C 48.16, H 4.76.

$\mathbf{Li_4[(2)_3Ti_2]}$: Yield: 98% orange-red solid as the octahydrate; ^{1}H NMR ([D$_4$]methanol): $\delta = 6.78$ (dd, $J = 1.2$, 7.8 Hz, 6H), 6.51 (pseudo-t, $J = 7.8$ Hz, 6H), 6.21 (dd, $J = 1.2$, 7.8 Hz, 6H), 4.67 (q, $J = 7.5$ Hz, 3H), 1.32 (d, $J = 7.5$ Hz, 9H); ^{13}C NMR ([D$_4$]methanol): $\delta = 157.7$ (C), 156.5 (C), 132.4 (C), 119.2 (CH), 117.7 (CH), 110.4 (CH), 29.0 (CH), 21.2 ($\mathrm{CH_3}$); IR

(KBr): $\tilde{\nu} = 3390, 3059, 2973, 1451, 1254, 924, 725\ \mathrm{cm^{-1}}$; UV/Vis (methanol): $\lambda = 205, 271, 360$ nm; MS (FAB(+)): $m/z = 851$ ($Li_4H[(\mathbf{2})_3Ti_2]^+$); calcd for $C_{42}H_{30}Li_4O_{12}Ti_2 \cdot 8H_2O$: C 50.73, H 4.66; found: C 50.35, H 4.91.

$Na_4[(\mathbf{3})_3Ti_2]$: Yield: 56% red solid as the nonahydrate after chromatography; ^{1}H NMR ([D$_4$]methanol): $\delta = 6.71$ (d, $J = 7.6$ Hz, 3H), 6.59 (d, $J = 7.6$ Hz, 3H), 6.51 (m, 3H), 6.35 (d, $J = 8.0$ Hz, 3H), 6.27 (m, 3H), 3.66 (d, $J = 13.4$ Hz, 3H), 3.15 (d, $J = 13.4$ Hz, 3H), 2.07, 2.06, 2.04 (3s, $\sum$ 9H); ^{13}C NMR ([D$_4$]methanol): $\delta = 158.3$, 156.9, 156.8, 155.8, 127.3, 127.2, 124.5, 124.4, 122.8, 122.5, 122.3, 122.0, 121.8, 120.9, 120.2, 120.0, 111.7, 31.6, 15.9, 15.8, 15.7; MS (FAB(+)): $m/z = 937$ ($Na_5[(\mathbf{3})_3Ti_2]^+$), 915 ($Na_4H[(\mathbf{3})_3Ti_2]^+$); calcd for $C_{42}H_{30}Na_4O_{12}Ti_2 \cdot 9H_2O$: C 46.86, H 4.49; found: C 46.87, H 4.71.

$Li_4[(\mathbf{3})_3Ti_2]$: Yield: 100% orange-red solid as the decahydrate; ^{1}H NMR ([D$_4$]methanol): $\delta = 6.67$ (d, $J = 7.6$ Hz, 3H), 6.59 (d, $J = 7.7$ Hz, 3H), 6.47 (m, 3H), 6.36 (d, $J = 7.6$ Hz, 3H), 6.25 (m, 3H), 4.11 (d, $J = 12.9$ Hz, 3H), 3.03 (d, $J = 12.9$ Hz, 3H), 2.08, 2.07, 2.05 (3s, $\sum$ 9H); ^{13}C NMR ([D$_4$]methanol): $\delta = 157.8$ (3 signals), 156.3 (3 signals), 156.2 (2 signals), 128.1 (2 signals), 128.0, 125.4 (2 signals), 125.3, 122.4, 122.2 (2 signals), 121.9 (2 signals), 121.7 (2 signals), 121.1, 120.9, 120.3, 120.2 (2 signals), 119.3 (2 signals), 119.1 (2 signals), 111.2, 111.1, 32.3, 15.9, 15.8, 15.7; IR (KBr): $\tilde{\nu} = 3587, 2924, 1455, 1261, 1076, 731\ \mathrm{cm^{-1}}$; UV/Vis (methanol): $\lambda = 204$, 271, 342 nm; MS (FAB(−)): $m/z = 843$ ($Li_3[(\mathbf{3})_3Ti_2]^-$); calcd for $C_{42}H_{30}Li_4O_{12}Ti_2 \cdot 10H_2O$: C 48.96, H 4.89; C 48.96, H 5.21.

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