Dicatechol ligands: novel building-blocks for metallo-supramolecular chemistry

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The self-assembly of helicate-type coordination compounds from oligodentate ligands and two or more metal ions is an important part of metallo-supramolecular chemistry. The design of appropriate ligands, the fascinating structures of the self-assembled coordination compounds and the understanding of the mechanisms of metal-directed self-assembly processes are topics which have recently come into the focus of attention. In this paper the formation, characterization and some properties of helicate-type compounds which are formed from oligo-catechol ligands are described.

1 Introduction

Helicity is a motif which is present in many macroscopic natural or artificial objects. Several people, artists or architects as well as scientists, are fascinated and inspired by the beauty of helical structures.[1]

On a microscopic (molecular) level, helicity can be found for example in proteins or in double stranded DNA. A class of artificial helical supramolecular aggregates which has recently come into the focus of attention are the helicates. They are formed by spontaneous and cooperative self-assembly of two or three linear oligo-donor ligand strands and two or more metal ions. Due to the preferred coordination chemistry of the metal centers, double-, triple-, or quadruple-stranded helicates are obtained (Fig. 1). Investigations into the formation, structure, and synthetic use of helicates have been mainly performed with nitrogen-donor ligands and only to a minor extend with oxygen-donors.[1,2]

In 1968 Neilands reported the isolation and characterisation of the siderophore rhodoturulic acid (**1**-H$_2$), the diketopiperazine of δ-*N*-acetyl-L-(*S*)-δ-*N*-hydroxyornithine.[3] **1**-H$_2$ bears two hydroxamic acid units as binding sites for metal ions and forms with iron(III) ions enantiomerically pure binuclear Δ-configured helical complexes [(**1**)$_3$Fe$_2$].[4]

Although [(**1**)$_3$Fe$_2$] was the first isolated triple-stranded helicate, only few examples of analogous oxygen donor complexes are described in the literature. As an example, ligand

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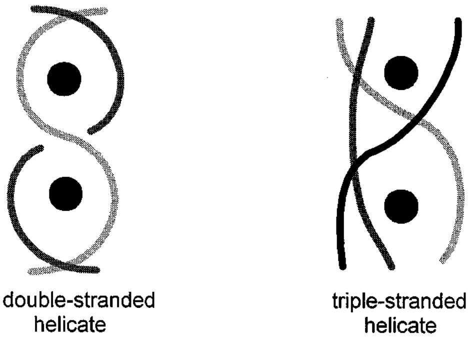
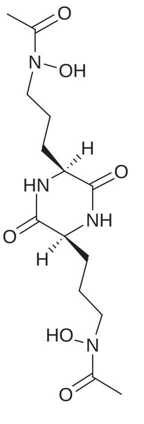
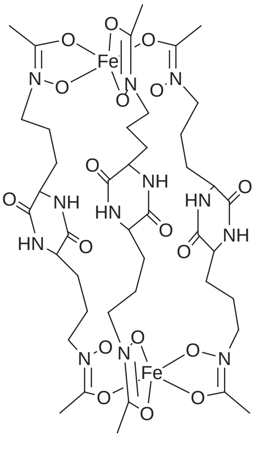


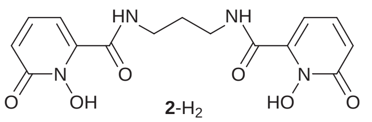
Fig. 1 Schematic representation of a double- and a triple-stranded helicate



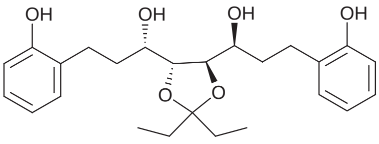
1-H$_2$
(rhodoturulic acid)



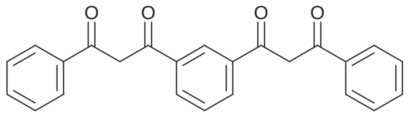
[(**1**)$_3$Fe$_2$]



2-H$_2$



3-H$_4$



4-H$_2$

Ligands **1**-, **2**-, **4**-H$_2$ and **3**-H$_4$ and the first triple-stranded helicate [(**1**)$_3$Fe$_2$]

2-H_2 can be deprotonated twice and is then able to form a neutral triple-stranded helicate with iron(III) ions.[5] Three ligands of **3**-H_4 form in the presence of titanium(IV) ions the enantiomerically pure trinuclear helicate $[(\mathbf{3})_3Ti_3]$.[6] Just recently the ligand **4**-H_2 with two 1,3-dicarbonyl moieties was introduced and its helicates $[(\mathbf{4})_3M_2]$ (M = Ti, V, Mn, Fe) were described.[7] However, most of the oxygen donor ligands which were used for the self-assembly of helicate-type complexes contain catechol units as binding sites for metals. Herein we describe the metal directed self-assembly, structure and some properties of helicate-type coordination compounds which are formed from oligo(catecholato) ligands.

2 Dicatechol ligands

A number of dicatechol ligands which bear different spacers were synthesised to enable the systematic study of the self-assembly of helicates with oxygen donor ligands. One class of such compounds possesses amide linkers in the spacer to connect two catechol units (**5a–f**-H_4).[8–12]

A second class of ligands (**6**-H_4, **7**-H_6) contains pure alkyl chains as spacers.[13–15]

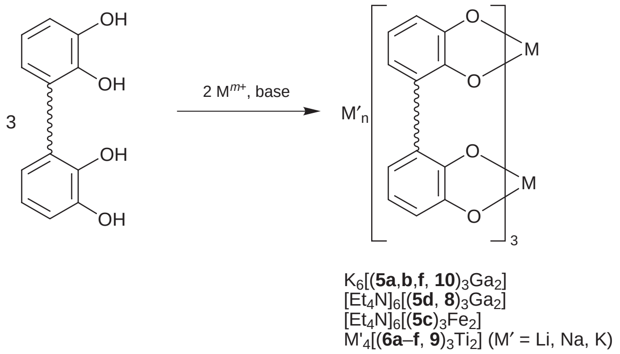
The chiral ligands **8**-H_4–**10a**-H_4 were prepared to investigate their use in the self-assembly of enantiomerically pure helicates.[9,10,16,17]

3 Self-assembly of helicate-type coordination compounds

3a Formation of triple-stranded dinuclear metal complexes from dicatechol ligands

The ligands **5**–**10** were used in metal directed self-assembly processes. In one case a double-stranded helicate $Na_4[(\mathbf{5e})_2(MoO_2)_2]$ was obtained and could be structurally characterised.[12] All other experiments led to dinuclear (**5**, **6**, **8**–**10**)[8–11,15–22] (Scheme 1) or trinuclear (**7**)[23] triple-stranded complexes of gallium(III), iron(III), or titanium(IV).

The dinuclear complexes are obtained in quantitative or close to quantitative yield. Only with the long chain ligands **6g,h**-H_4 is a mixture of isomers or oligomers detected by NMR spectroscopy. However, the species which are formed in these reactions are still soluble. No precipitation of polymeric material is observed. For entropic reasons the dinuclear complexes are favoured with respect to oligomer or polymer formation.

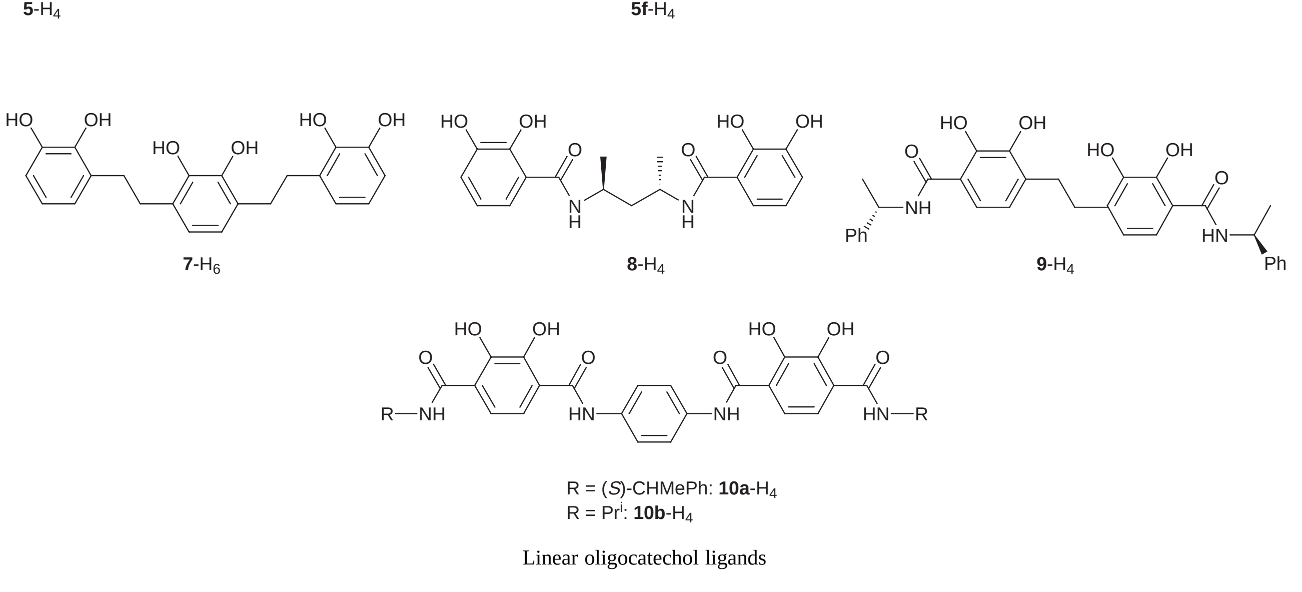


Scheme 1 Formation of dinuclear helicate-type complexes

The enantiomerically pure chiral helicates $M_4[(\mathbf{9})_3Ti_2]$ (M = Li, Na, K),[17] $[(\mathbf{3})_3Ti_3]$,[6] $K_6[(\mathbf{10a})_3Ga_2]$,[16] or $[Et_4N]_6[(\mathbf{8})_3Ga_2]$[10] could be obtained from oxygen donor ligands. A high specific rotation of $[\alpha]_D$ = +970 (±50) (c = 1) is observed for $K_4[(\mathbf{9})_3Ti_2]$ in methanol (free ligand: $[\alpha]_D$ = +53; c = 1, methanol).[17]

The cooperativity of the self-assembly process of the helicate-type complexes was shown for several dinuclear coordination compounds. Reaction of appropriate metal ions with an excess of ligands **5a,b,d,f**-H_4[8,10] or **6b,c**-H_4[18,19] in the presence of base selectively led to the binuclear complexes. No mononuclear species could be observed by NMR spectroscopy or mass spectrometry.

A mixture of the ligands **5a,b,f**-H_4 leads in the presence of gallium tris(acetylacetonate) and potassium carbonate to a

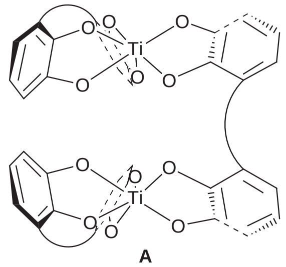


Linear oligocatechol ligands

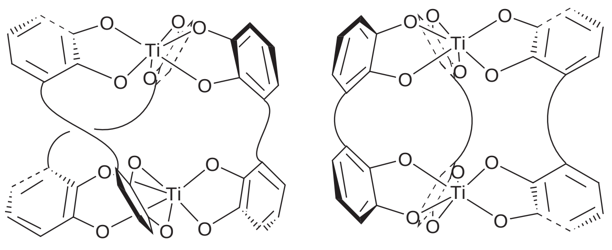
mixture of the three helicates $[(\mathbf{5a})_3Ga_2]^{6-}$, $[(\mathbf{5b})_3Ga_2]^{6-}$, and $[(\mathbf{5f})_3Ga_2]^{6-}$ in which every dinuclear complex contains only one kind of ligand. In this case the molecular self-recognition process is controlled by the different spacer length of the three ligands.[8]

3b The structure of triple-stranded dinuclear metal complexes

The dinuclear coordination compounds can adopt different structures. Due to the spacer length of the ligands **6a,b,c,9**-H_4 binding of both binding sites of one ligand to the same titanium ion should not be possible (structure A).



A



helicate
(Λ,Λ-form)

meso-helicate
(Δ,Λ-form)

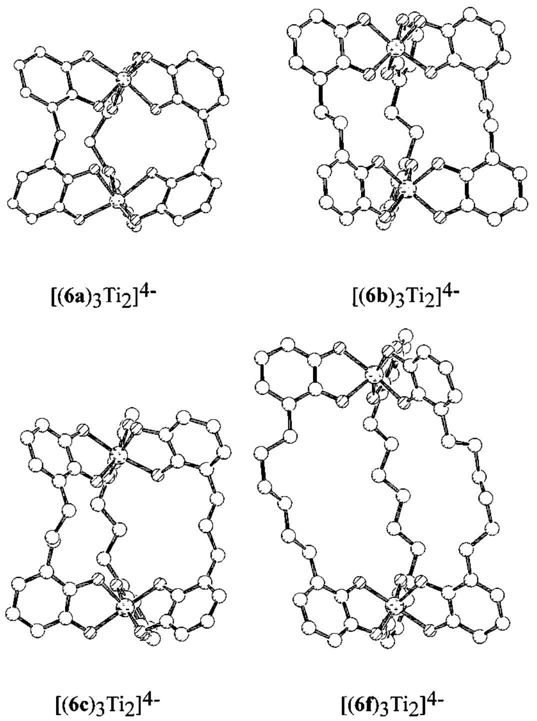
Possible stuctures of dinuclear coordination compounds

However, there are two possible diastereomeric structures. If both complex units possess the same configuration, the triple-stranded helicate is formed. If the two units are differently configured, the corresponding achiral *meso*-compound is obtained: the *meso*-helicate. In the D_3-symmetric helicate the ligands show an 'S'-type conformation while the ligands of the C_{3h}-symmetric *meso*-helicate adopt a 'C'-type conformation.[15,18,20,22]

The helicate- as well as the *meso*-helicate-type structures can be observed for the alkyl-bridged derivatives $[(\mathbf{6})_3Ti_2]^{4-}$. X-Ray structural analyses could be obtained for the dinuclear titanium complexes $Li_4[(\mathbf{6a})_3Ti_2]\cdot 6DMF$,[20] $Li_4[(\mathbf{6b})_3Ti_2]\cdot 6\ DMF\cdot 2H_2O$,[19] $Na_4[(\mathbf{6c})_3Ti_2]\cdot 6DMF\cdot 5H_2O$,[18] and $K_4[(\mathbf{6f})_3Ti_2]\cdot 5\ DMF\cdot 3\ H_2O$.[15]

The tetraanions $[(\mathbf{6})_3Ti_2]^{4-}$ with an odd number of methylene units $\{[(\mathbf{6a})_3Ti_2]^{4-}, [(\mathbf{6c})_3Ti_2]^{4-}\}$ possess the *meso*-helicate structure in the solid state. The same structure is observed in solution. On the other hand, the compounds with an even spacer length $\{[(\mathbf{6b})_3Ti_2]^{4-}, [(\mathbf{6f})_3Ti_2]^{4-}\}$ adopt the helicate structure (Fig. 2). In $[(\mathbf{6f})_3Ti_2]^{4-}$ the stereochemical information is transferred through seven σ-bonds to influence the relative configuration of the complex moieties and form the chiral helicate.

The results discussed above show that it is possible to obtain selectively either the chiral helicates or the achiral *meso*-helicates by choosing an appropriate spacer. The self-assembly process itself is highly diastereoselective (only one stereoisomer is observed) and can be controlled in the case of the alkyl-bridged dicatechol ligands **6**. A ligand with an odd number of methylene units yields the *meso*-helicate while an even number leads to the corresponding helicate.The tetraanions $[(\mathbf{6})_3Ti_2]^{4-}$ represent structures of cage compounds in which internal oxygen atoms are present. The high negative charge and the cryptand type structure should be ideal for the encapsulation of cations. Thus, in the solid state one of the counterions can be observed in the interior of $[(\mathbf{6b})_3Ti_2]^{4-}$ (Li)[19] or $[(\mathbf{6c})_3Ti_2]^{4-}$ (Na).[18] As a representative example the structure of the monomeric species of $Li_4[(\mathbf{6b})_3Ti_2]\cdot 6\ DMF\cdot 2\ H_2O$ is shown in Fig. 3.[19] Three of the lithium ions are located outside of the cryptand type helicate (one is bound to four DMF molecules; two are bound to terminal oxygen atoms of the helicate and to DMF molecules which act as bridges to obtain a linear coordination polymer in the solid state). The fourth lithium cation is found in the interior of the tetraanion binding to two internal oxygen atoms of one of the ethylene linked dicatechol ligands **6b**. Additionally this ion is coordinated to two water molecules which by hydrogen bonding to the remaining internal



$[(\mathbf{6a})_3Ti_2]^{4-}$ $[(\mathbf{6b})_3Ti_2]^{4-}$

$[(\mathbf{6c})_3Ti_2]^{4-}$ $[(\mathbf{6f})_3Ti_2]^{4-}$

Fig. 2 Molecular structures of the tetraanionic helicates $[(\mathbf{6b})_3Ti_2]^{4-}$ and $[(\mathbf{6f})_3Ti_2]^{4-}$ and the corresponding *meso*-helicates $[(\mathbf{6a})_3Ti_2]^{4-}$ and $[(\mathbf{6c})_3Ti_2]^{4-}$

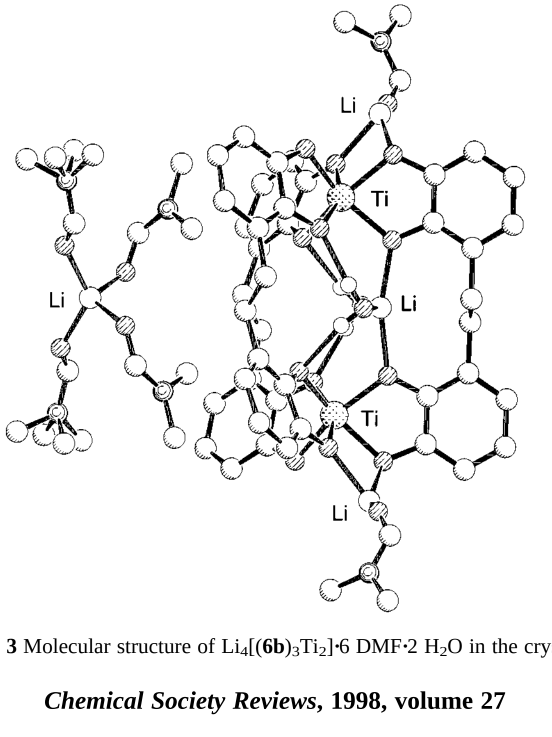


Fig. 3 Molecular structure of $Li_4[(\mathbf{6b})_3Ti_2]\cdot 6\ DMF\cdot 2\ H_2O$ in the crystal

catecholate oxygen atoms are additionally fixed in the interior of this cavity. The arrangement of ligands around this lithium atom allows the stabilisation of an unusual distorted square planar coordination geometry.[19]

In $[(\mathbf{6f})_3\mathrm{Ti}_2]^{4-}$ the cavity is much too large to encapsulate only one cation. Consequently two potassium cations (which are electronically saturated by coordination to DMF or water) are located in the interior of this tetraanionic cryptand in the solid state. $\mathrm{K}_4[(\mathbf{6f})_3\mathrm{Ti}_2]\cdot5\mathrm{DMF}\cdot3\mathrm{H}_2\mathrm{O}$ crystallises in the orthorhombic space group $P2_12_12_1$ with spontaneous separation of the enantiomeric helices.[15]

The X-ray structures of the helicates $\mathrm{K}_6[(\mathbf{5a})_3\mathrm{Ga}_2]$,[9,16] $[\mathrm{Et}_4\mathrm{N}]_6[(\mathbf{5c})_3\mathrm{Fe}_2]$,[11] and $[\mathrm{Et}_4\mathrm{N}]_6[(\mathbf{5d})_3\mathrm{Ga}_2]$[10] are also described in the literature. They all possess a triple-stranded helicate structure. However, no inclusion of guests could be observed for those compounds with amide linkages in the spacer. Only for $[(\mathbf{2})_3\mathrm{Fe}_2]$ could the binding of one molecule of water be shown in the solid state.[5]

The inclusion of sodium cations in the metallacryptands $[(\mathbf{6b,c})_3\mathrm{Ti}_2]^{4-}$ in solution can be shown by ^{23}Na NMR spectroscopy of the corresponding sodium salts. At room temperature a broad signal is observed for the sodium ions. The line width of the signal indicates that an exchange process between different cations takes place. Cooling of the NMR samples ([^{2}H$_4$]methanol) results in a splitting of the signals and at low temperature an intense signal can be observed for 'free' solvated sodium ions $\{\delta = -0.9$ for $[(\mathbf{6b})_3\mathrm{Ti}_2]^{4-}\}$. Additionally a small signal is detected $\{\delta = -15.5$ for $[(\mathbf{6b})_3\mathrm{Ti}_2]^{4-}\}$ which is assigned to encapsulated sodium. The exchange barrier can be estimated to be approximately $\Delta G^{\ddagger} = 32$ kJ mol^{-1}.[1,15]

The observation of alkali metal cations which are bound to the helicates in the solid state and in solution shows that the counterions are part of the supramolecular structures and not just innocent spectators. Therefore those ions should have an influence on the properties as well as on the self-assembly of the cryptand-type helicates and *meso*-helicates.

3c Dynamic behaviour of the dinuclear complexes

A property of the triple-stranded helicates or *meso*-helicates which are formed from oligocatechol ligands is the racemisation or symmetrization of the metal complexes. This inversion process can be monitored by dynamic NMR spectroscopy using either diastereotopic protons of the spacer in the ligands **6** and **7** or of the substituents bound to the ligand **10b**.

Fig. 4 shows the ^{1}H NMR spectra of $\mathrm{K}_4[(\mathbf{6b})_3\mathrm{Ti}_2]$ in $\mathrm{D}_2\mathrm{O}$ at variable temperature.[19] At room temperature signals of the aromatic units and two multiplets (δ = 2.76 and 2.44) of the diastereotopic spacer protons can be observed. Heating the sample leads to coalescence of the signals of the alkyl protons at 328 K and at higher temperature only one sharp singlet is detected. From those results a $\Delta G^{\ddagger}$ value of 64.4 kJ mol^{-1} is estimated. Similar experiments with the alkyl-bridged complexes $[(\mathbf{6})_3\mathrm{Ti}_2]^{4-}$ show that the symmetrization of the helicates or *meso*-helicates is influenced by several different factors:[21]

(1) The inversion barriers of the *meso*-helicates are higher than those observed for the helicates.

(2) Within the helicate or *meso*-helicate series, the free energy barriers are lower for compounds with longer chain lengths.

(3) Due to interaction of the cations with the tetraanions, the cations possess an enormous influence on the inversion behaviour of the dinuclear complexes.

The inversion of $[(\mathbf{6})_3\mathrm{Ti}_2]^{4-}$ [21] as well as of $[(\mathbf{10b})_3\mathrm{Ga}_2]^{6-}$ [9,16] proceeds by a non-dissociative mechanism. Thus, no ligand exchange can be observed in the presence of excess ligand. For $[(\mathbf{10b})_3\mathrm{Ga}_2]^{6-}$ it could be shown that the inversion barrier $\Delta G^{\ddagger} = 80$ kJ mol^{-1} is only 1.2 times higher than the one observed for the analogous mononuclear complex $[(\mathbf{11})_3\mathrm{Ga}]^{3-}$.[24]

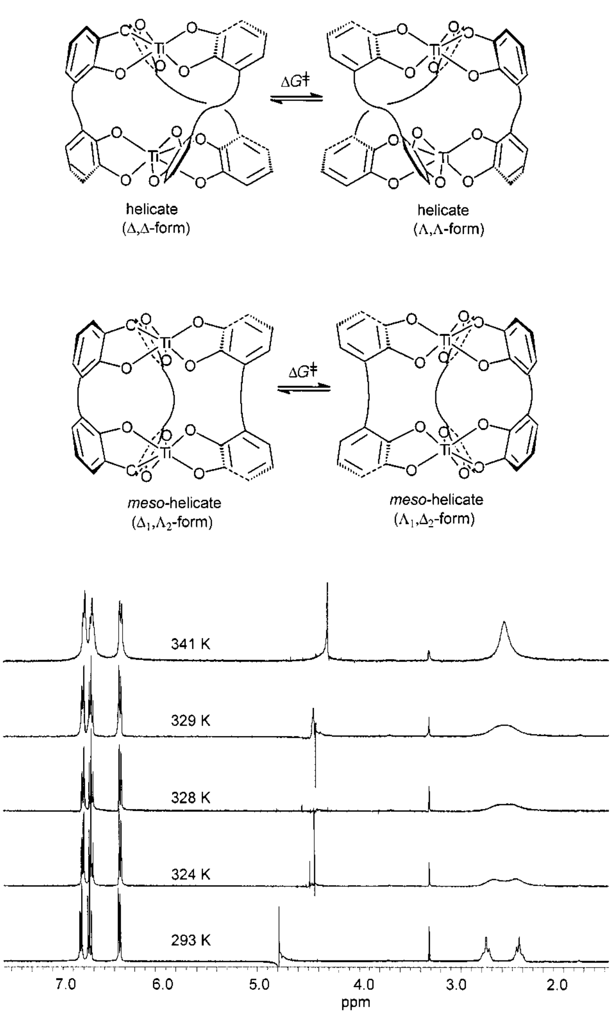
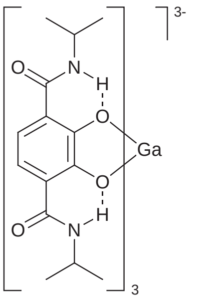


Fig. 4 Schematic representation of the inversion of dinuclear helicates and *meso*-helicates and the observation of the racemisation of $\mathrm{K}_4[(\mathbf{6b})_3\mathrm{Ti}_2]$ by dynamic ^{1}H NMR spectroscopy (in $\mathrm{D}_2\mathrm{O}$)



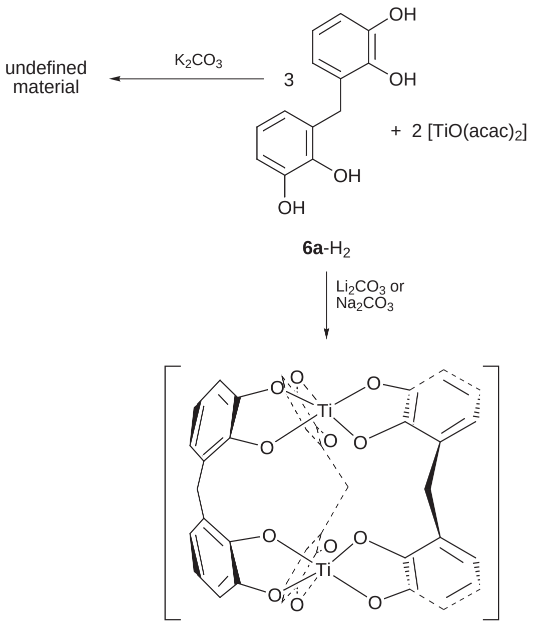
$[(\mathbf{11})_3\mathrm{Ga}]^{3-}$

This indicates that the inversion of the helicate $[(\mathbf{10b})_3\mathrm{Ga}_2]^{6-}$ proceeds by a stepwise mechanism with a *meso*-helicate structure as intermediate. The analogous complex $[(\mathbf{12})_3\mathrm{Ga}_2]^{6-}$ does not show interconversion of the C_1- and C_3-symmetric isomers during racemisation. This again shows that the inversion follows an intramolecular mechanism.[9,16] The dinuclear and trinuclear helicates $\mathrm{M}_4[(\mathbf{6b})_3\mathrm{Ti}_2]$ and $\mathrm{M}_6[(\mathbf{7})_3\mathrm{Ti}_3]$ (M = Na or K) possess approximately the same inversion barrier and therefore again a consecutive inversion of the metal complex units takes place. This means for the trinuclear complex $\mathrm{M}_6[(\mathbf{7})_3\mathrm{Ti}_3]$ that the inversion starts at one end of the helicate followed by inversion of the central unit and finally of the second terminus.[23]

3d Template-assisted self-assembly

In the alkyl-bridged helicate- and *meso*-helicate-type complexes $M_4[(\mathbf{6})_3Ti_2]$ the counterions are part of the molecular structure of the complexes and are not only innocent spectators. Therefore they should play an active part in the self-assembly process which leads to the dinuclear coordination compounds.

For $[(\mathbf{6a})_3Ti_2]^{4-}$ this could be shown by a series of experiments. If a mixture of ligand **6a**-H_4, $[TiO(acac)_2]$ (acac = acetyl acetonate) and alkali metal carbonate is stirred in methanol overnight, one would expect to obtain the dinuclear *meso*-helicate. However, with potassium carbonate, only a mixture of undefined products can be obtained which probably contains a variety of different oligomers. With sodium or lithium carbonate only one defined species can be observed in the NMR spectra. The same spectra are obtained by addition of, respectively $LiClO_4$ or $NaClO_4$, to the mixture of oligomers which was originally produced in the presence of potassium carbonate.[20,22]

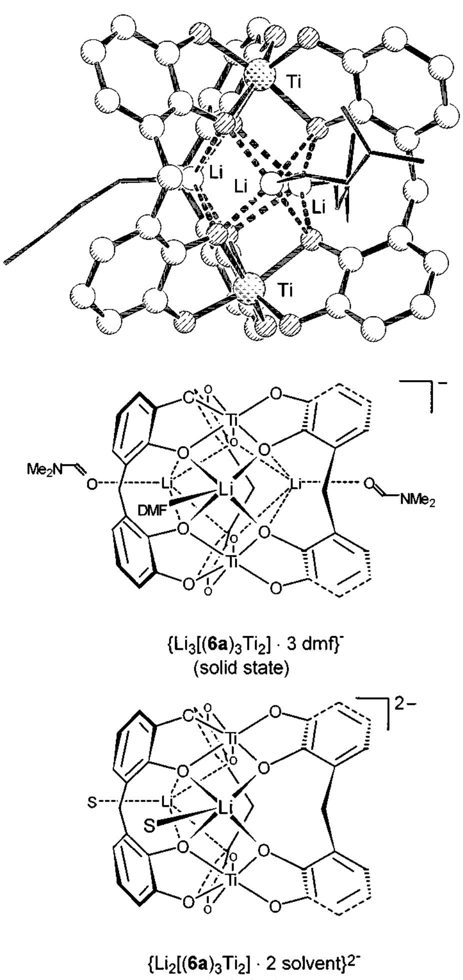


Scheme 2 Template-directed self-assembly of $[(\mathbf{6a})_3Ti_2]^{4-}$

The small cations (Li^+, Na^+) are able to stabilise the *meso*-helicate structure by binding to the oxygen atoms of the catecholate ligands. Potassium is too large and no stabilisation of the dinuclear complex can occur. Therefore lithium and sodium can act as a template while potassium cannot. However, this templating does not proceed by inclusion of one cation in the interior of the cryptand-type *meso*-helicate. The X-ray structural analysis of $Li_4[(\mathbf{6a})_3Ti_2]$ reveals that no lithium ion is bound in the interior but three cations bind to the periphery of the tetraanion and form a 'molecular box' (Fig. 5).[20]

In solution a different situation is found (Fig. 5). As was shown by ^6Li and ^1H NMR spectroscopy at low temperature only two of the lithium cations bind to the tetraanion. In the ^6Li NMR spectrum of $^6Li_4[(\mathbf{6a})_3Ti_2]$ at 193 K two sharp signals can be observed at δ = 1.36 and 0.99 for the two diastereotopic ions which are bound to the *meso*-helicate $[(\mathbf{6a})_3Ti_2]^{4-}$. Additionally a broad signal can be detected at δ = 0.90 for the two solvated lithium ions. In the ^1H NMR spectrum the signals split at low temperature to form three sets of signals due to the loss of symmetry.[22]

In the case of the self-assembly of $[(\mathbf{6a})_3Ti_2]^{4-}$ a templating effect by the counterions is observed (Scheme 2). The lithium or sodium cations can act as template while potassium is not able to induce a self-assembly process to form defined complexes. Similar template-assisted self-assembly processes also seem to be important in the formation of various other supramolecular species.[25,26]



$\{Li_3[(\mathbf{6a})_3Ti_2] \cdot 3\ dmf\}^-$
(solid state)

$\{Li_2[(\mathbf{6a})_3Ti_2] \cdot 2\ solvent\}^{2-}$
(solution)

Fig. 5 The molecular structure of $Li_3[(\mathbf{6a})_3Ti_2]^-$ in the solid state and of $Li_2[(\mathbf{6a})_3Ti_2]^{2-}$ in solution

4 Self-assembly of dinuclear coordination compounds from directional and sequential ligands

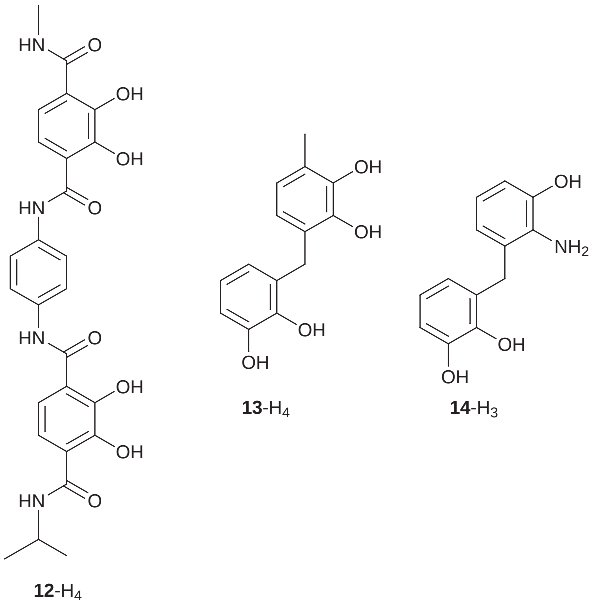
Supramolecular systems with a high content of information are obtained if directional or sequential ligands are used for the self-assembly of helicate type complexes. The ligands **12**–**14**[9,16,22,27] possess two different binding sites for metal ions and thus two different orientations of the ligands are possible. Two isomeric coordination compounds can be formed.

Different binding sites at the ligands (ambident chelating ligands) should enable the selective binding of different metals which in a triple-stranded system would lead to a situation as depicted in Fig. 6, Type 1 structure. Selective binding of the metal ions to the different binding sites of the ligand occurs. On the other hand, if only one kind of metal ion is used a Type 2 structure should be obtained in a self-assembly process. In such a homobinuclear complex the two metal ions have a very similar electronic situation and charge separation is minimised.[27]

4a Directional systems

The directional ligand **12**-H_4 with $Ga(acac)_3$ in the presence of KOH yields the dinuclear helicate $K_6[(\mathbf{12})_3Ga_2]$ as a mixture of the C_3- (*cis*) and C_1-symmetric (*trans*) isomers in a ratio of 1.00 : 2.86 which is close to the statistical mixture. Variable temperature NMR studies in D_2O show that the two isomers racemise ($\Lambda\Lambda \leftrightarrow \Delta\Delta$) independently without reorientation of the ligands (*cis–trans* isomerization).[9,16]

A mixture of the C_3- and C_1-symmetric *meso*-helicate-type complexes $M_3[(\mathbf{13})_3Ti_2]$ (M = Li, Na) was obtained from ligand **13**-H_4 and $[TiO(acac)_2]$ in the presence of M_2CO_3. Again



The directional ligands **12**-H_4, **13**-H_4 and **14**-H_3

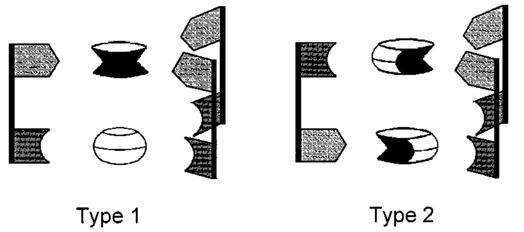
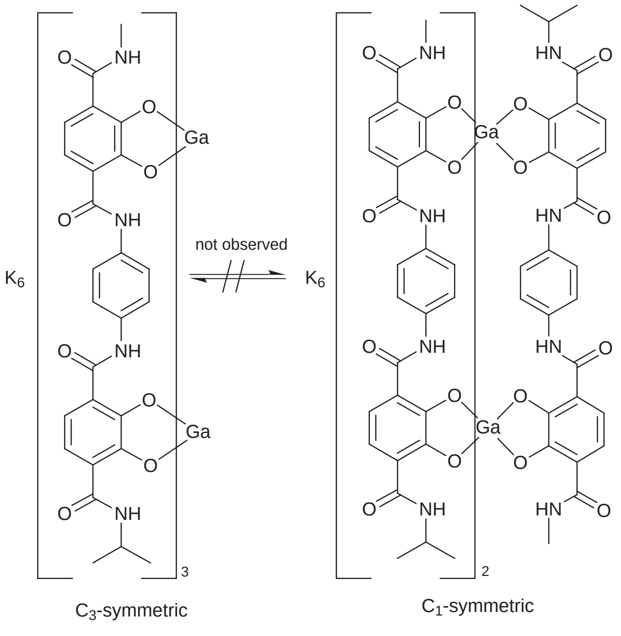


Fig. 6 Schematic representation of the relative orientation of sequential ligands in triple-stranded dinuclear coordination compounds

a close to statistical distribution (found: 1 : 4; expected: 1 : 3) of the two isomers could be observed.[22]

No significant selectivity can be found in the self-assembly of triple-stranded dinuclear helicate-type complexes from the directional ligands **12**-H_4 and **13**-H_4. The unsymmetric C_1 and the C_3-symmetric isomers are formed close to the statistical ratio (3 : 1). The reason for this is that the two binding sites of the directional ligands geometrically and electronically are too similar which does not lead to a discrimination between the two binding sites during self-assembly.



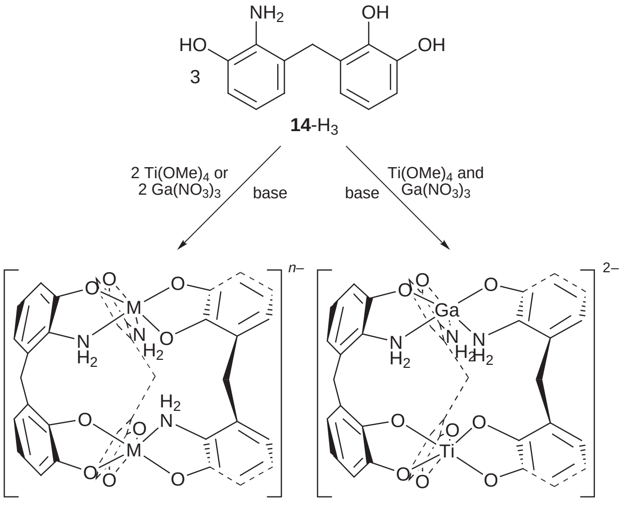
$K_6[(\mathbf{12})_3Ga_2]$

Possible isomerisation of $K_6[(\mathbf{12})_3Ga_2]$

4b Sequential systems

A sequential ligand in which the two binding sites possess different denticity was first realised by Piguet and co-workers.[28] The orientation of this sequential ligand upon complexation is controlled by the preferred coordination geometry of the metals which were used.[28]

A ligand which possesses two geometrically very similar binding sites for metals which are different in their electronic features is **14**-H_3.[27]



$[(\mathbf{14})_3M_2]^{n-}$
M = Ti (n = 1),
M = Ga (n = 3)

$[(\mathbf{14})_3GaTi]^{2-}$

Scheme 3 Formation of dinuclear coordination compounds from the sequential ligand **14**-H_3

Self-assembly of pseudo-*meso*-helicate type homodinuclear complexes $[(\mathbf{14})_3M_2]^{n-}$ (M = Ga, Ti; n = 3, 1) proceeds by mixing of three equivalents of **14**-H_3 with two equivalents of $Ti(OMe)_4$ or $Ga(acac)_3$ in the presence of alkali metal carbonate as base (Scheme 3). NMR spectroscopy reveals that the dinuclear complexes possess no symmetry (C_1) and a full set of signals is observed for the triple-stranded complexes (39 carbon atoms in the ^{13}C NMR spectra). This is in accordance with a Type 2 structure (Fig. 6) which was expected for a homodinuclear complex. Two of the ligands **14** are oriented in one, the third in the opposite direction. No signals of a homodinuclear complex which adopts a Type 1 structure can be detected by NMR spectroscopy. If a 1 : 1 mixture of $Ti(OMe)_4$ and $Ga(acac)_3$ is reacted with **14**-H_3 and alkali metal carbonate, the heterodinuclear complex $[(\mathbf{14})_3TiGa]^{2-}$ (Fig. 7) is exclusively formed in a cooperative self-assembly process. By FAB MS spectrometry only the heterodinuclear complex and no homodinuclear complexes can be observed. The ^1H as well as ^{13}C NMR spectra of $[(\mathbf{14})_3TiGa]^{2-}$ are very simple which indicates that a C_3-symmetric Type 1 complex is formed. Only one set of ligand signals can be detected by NMR spectroscopy. The formation of $[(\mathbf{14})_3TiGa]^{2-}$ can also be observed in an NMR experiment by mixing of the heterodinuclear compounds $[(\mathbf{14})_3Ga_2]^{3-}$ and $[(\mathbf{14})_3Ti_2]^{-}$ in a ration of 1 : 1.[27]

The X-ray structural analysis of $K_2[(\mathbf{14})_3TiGa]$·6 DMF·diethyl ether shows the same Type 1 structure in the solid state as was observed for the dianion $[(\mathbf{14})_3GaTi]^{2-}$ in solution. The titanium is bound to three catecholate units while three aminophenolato ligands are coordinated to gallium. The complex experiences an additional stabilisation through internal hydrogen bonding of the amines to the internal oxygen atoms of

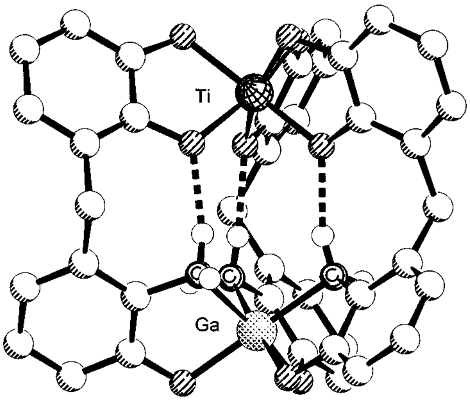


Fig. 7 Molecular structure of $[(\mathbf{14})_3\mathrm{TiGa}]^{2-}$ in the solid state

the catechols. Therefore no templating by alkali metal cations needs to take place.[27]

5 Conclusions

Linear oligocatechol ligands which bear either amide or alkyl spacers are excellent organic building blocks for the self-assembly of metallo-supramolecular architectures. In this review we discussed a number of aspects of this chemistry:

(i) Triple-stranded helicate-type oligonuclear complexes are obtained in cooperative self-assembly processes.

(ii) Self-recognition can lead to defined coordination compounds from a mixture of differently sized ligands.

(iii) The relative stereochemistry of the complex units can be controlled in the case of alkyl-bridged systems and racemisation or inversion of the compounds can be observed by NMR spectroscopy.

(iv) Helicate-type complexes with a cryptand-type structure are able to bind alkali or alkaline earth metal cations in their interior.

(v) The self-assembly process can be assisted by certain templates (*e.g.* appropriate counterions).

(vi) With directional or sequential ligands two different structures of metal complexes can be obtained. If the two binding sites of the ligand are different, selective formation of Type 1 heterodinuclear and Type 2 homodinuclear complexes can be achieved.

The results which were discussed show the high potential of oxygen donor ligands in metal-directed self-assembly processes and it is expected that even more complex and fascinating structures will be observed in the future.[26,29]

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