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Protonation of Tris(iminocatecholato) Complexes of Gallium(III) and Titanium(IV)

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Dedicated to Professor Dr. H. G. Thomas on the occasion of his 70th birthday

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The coordination behaviour of the chiral tren-type tripodal ligand **3**-H_6 with gallium(III) and titanium(IV) ions was investigated and it was found that only mononuclear complexes are formed. In the presence of Na^+, one of the cations acts as a template and is bound inside the "cap" of $[Na(\mathbf{3})M]^{n-}$ (M = Ga, n = 2; M = Ti, n = 1). If no such cation is present, three protons are bound to the iminocatechol units in order to prevent repulsion between lone pairs at nitrogen and oxygen. To minimize the charge repulsion between the protonated imines of $[H_3(\mathbf{3})M]^{n+}$ (M = Ga, n = 0; M = Ti, n = 1), an enamine/chinomethine mesomeric structure becomes important. The adoption of this unusual mesomeric form by the iminocatecholates was supported by computational methods. In further investigations, we found, that the addition of protons (H_2SO_4) to the dinuclear (catecholimine)titanium helicate $K_4[(\mathbf{4})_3Ti_2]$ leads to protonation of the imine part of the iminocatechol. An excess of acid results in the hydrolysis of the complexes as well as of the imine units.

Introduction

Self-assembly processes depend strongly on the geometry of molecular building blocks, which are able to form well-defined aggregates by non-covalent or coordinative interactions.[1] The outcome is often predictable, if rigid moieties are used.[2] However, with flexible units, prediction is still challenging, because many different steric, electronic, and entropic aspects need to be taken into account, which may counterbalance each other to some extent and thus make it difficult to estimate their final net effect.

During the last couple of years we and others have been investigating the coordination chemistry of tris(catechol) ligands which have been able to form supramolecular tetrahedra of the M_4L_4 type.[3] Starting with rigid ligand systems like **1**-H_6, we easily obtained the desired container molecule $[Ti_4\mathbf{1}_4]^{8-}$, which shows interesting host–guest chemistry.[4]

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Ligand **2**-H_6 (Figure 1), on the other hand, is more flexible. Therefore, it either can form a mononuclear

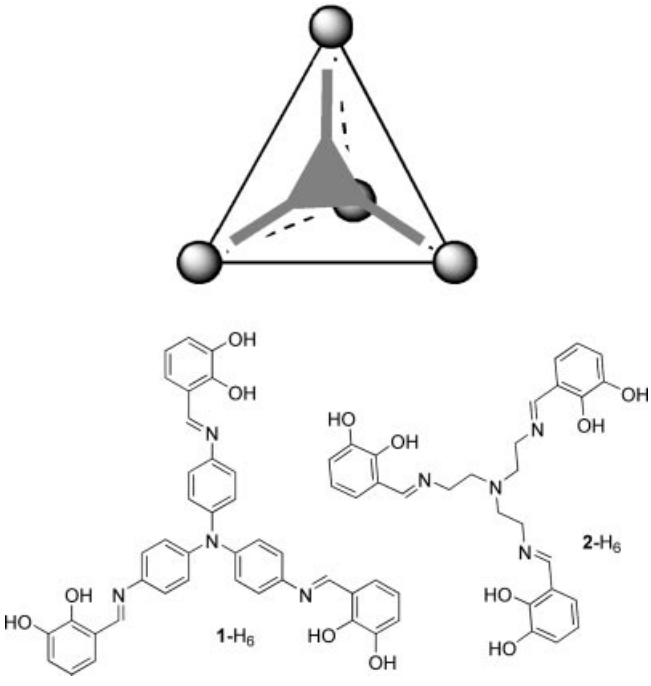


Figure 1. Schematic representation of a metallosupramolecular tetrahedon and appropriate triangular ligands.

"[Ti(**2**)]$^{2-}$" complex or a tetrahedron [Ti$_4$**2**$_4$]$^{8-}$ depending on the templating cation which is present. The smaller sodium cation nicely fits into the cavity formed when all catecholato units coordinate to the same metal center and thus template the formation of mononuclear complexes, while the potassium ion, whose size exceeds that of this cavity, favours the formation of the tetrahedron in dmso.[5]

Although a simple tetrahedron is not chiral, the self-assembled M_4L_4 tetrahedra possess twisted chiral complex units as cornerstones. In order to generate chiral enantiomerically pure tetrahedra, we now investigated triangular ligands **3**-H_6 based on the chiral tren-type platform, developed by Moberg et al.,[6] which can be considered to be a chiral variant of **2**-H_6. However, coordination studies with titanium(IV) and gallium(III) cations show the bulkiness of the isopropyl substituents at the ligand to be so high that the ligand cannot adopt the appropriate extended conformation with the triangular geometry required to occupy a face of the tetrahedron. Consequently, the ligand forms only mononuclear complexes. If no appropriate template cation is present to fill the cavity, the mononuclear complex is highly basic and takes up three protons in order to compensate the repulsion between electron pairs at the imine nitrogen atom and the internal catecholato oxygen atom. Similar hydrogen bonding can be observed in the complexes of catecholamides.[7]

This protonation behaviour cannot only be observed for the tritopic ligand **3**-H_6, but also in the case of a titanium helicate formed from the ditopic ligand **4**-H_4.[8] A gallium(III) complex of the monotopic **5**-H_2 seems to show a similar behaviour, but protonation is accompanied by decomposition (Figure 2).[9]

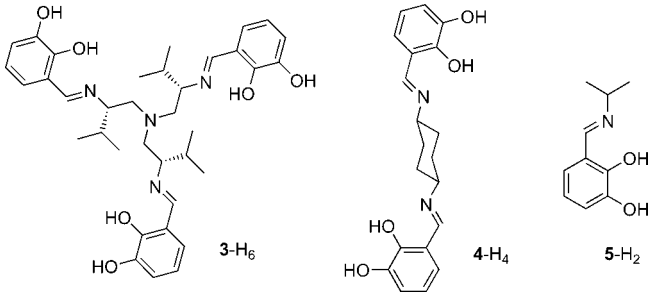


Figure 2. Ligands discussed in this study.

Results and Discussion

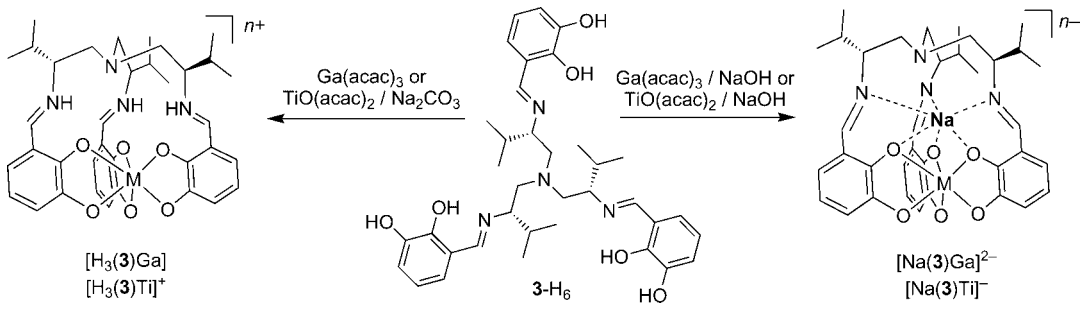
Coordination Chemistry of Ligand 3-H_6 with Titanium(IV) and Gallium(III)

The chiral tritopic ligand **3**-H_6 was prepared by utilizing Moberg's procedure[6] for the synthesis of the tetraamine precursor followed by imine condensation with 3 equiv. of 2,3-dihydroxybenzaldehyde (Scheme 1).[10]

Reaction of ligand **3**-H_6 with 1 equiv. of gallium(III) acetylacetonate in the presence of 1.5 equiv. of sodium carbonate does not only yield the desired mononuclear complex Na_2[Na⊂{(**3**)Ga}]. Instead, the ^{1}H NMR spectrum in [D_6]-dmso indicates the presence of two different species. One set of low-field signals at δ = 7.89 (s, CH_{imine}), 6.06 (d, J = 7.7 Hz, H_{cat}), 6.02 (d, J = 7.7 Hz, H_{cat}) and 5.91 (t, J = 7.7 Hz, H_{cat}) ppm can be assigned to Na_2[Na⊂{(**3**)Ga}] by comparison with the chemical shifts observed for the already known compound Na[Na⊂{(**2**)Ti}].[5] The second set of signals for catechol protons appears at δ = 6.40 (m, 6 H) and 6.33 (m, 3 H) ppm. The most intriguing feature is the appearance of the imine CH resonance at δ = 8.62 ppm as a doublet with J = 13.5 Hz and of an additional doublet of doublets at δ = 12.5 (J = 13.5, 11.1 Hz) ppm. According to the coupling pattern and the far low-field shift of this signal, we assign it to a proton at the imine nitrogen atom. As shown in Figure 4, both species can also be obtained in pure form. Use of the stronger base NaOH allows the formation of Na_2[Na⊂{(**3**)Ga}], while in the absence of base only the protonated species is obtained.

Using titanium(IV) as the central metal ion, we obtained similar results. With NaOH, the complex Na[Na⊂{(**3**)Ti}] is formed, while use of the weaker base sodium carbonate leads to the formation of only the species showing the protonated imine signals at δ = 12.0 (m, =NH) and 9.05 (d, J = 14.6 Hz, =CH) ppm.[11]

According to those results, we propose, that both gallium and both titanium compounds are mononuclear complexes of ligand **3**. According to earlier crystal structure investigations of iminocatecholato complexes,[12] conformation **I** (Figure 3) is preferred over structure **II** due to electron-pair repulsion. However, molecular models suggest conformation **I** not to be achievable for the mononuclear complexes studied here due to the restrictions imposed by the tren subunit connecting the catecholate units. Consequently, the



Scheme 1.

parent compounds $[(\mathbf{3})Ga]^{3-}$ and $[(\mathbf{3})Ti]^{2-}$ should significantly suffer from the repulsion of the electron pairs at the imine nitrogen atoms and at the internal catecholato oxygen atoms.

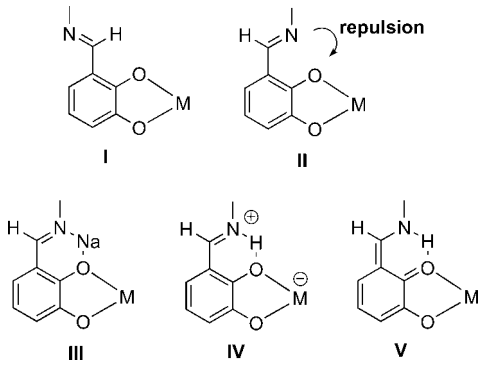


Figure 3. Different binding modes of the catecholimine ligand.

The formation of the mononuclear complexes is nevertheless possible, when the repulsion is taken care of by a cation (sodium) chelated by the imine group and the internal catecholato oxygen atom as in **III** or by protonation of the imine group, thus creating a hydrogen bond to the adjacent oxygen atom as shown in the two mesomeric structures **IV** and **V**.

According to the ^1H NMR spectra as shown in Figure 4 (d–f), a situation like that described by structures **IV** and **V** is present in our complexes.[13] The resonances at low field are due to the hydrogen bonds between N and O, which show a coupling with the imine CH group as well as with the CH group of the spacer. Complexes of similarly protonated salicylimines are frequently found, e.g. in the work by Binnemans et al. on mesogenic lanthanide complexes.[14] In the present case, this protonation needs to occur three times within the cavity of the complex in order to waive all three unfavorable N/O interactions in $[(\mathbf{3})M]^{n-}$ (M = Ga, n = 3; M = Ti, n = 2). This should lead to a high accumulation of positive charge in the triply protonated counterparts $[H_3(\mathbf{3})M]^{n+}$ (M = Ga, n = 0; M = Ti, n = 1), which is, however, at least to some extent compensated by the negatively charged metal complex units. In addition, the charges can be distributed over the respective aromatic system with the enaminone **V** as a "neutral" mesomeric structure.[15] These factors make the imine nitrogen atoms rather basic sites which are not fully deprotonated during complex formation with carbonate.

The gallium complex $[H_3(\mathbf{3})Ga]$ is soluble in D_2O. Hereby the acidic protons are exchanged by deuterium resulting in the disappearance of the corresponding signal and the appearance of a singlet for the imine proton.

The triply protonated compound $[H_3(\mathbf{3})Ga]$ is neutral and thus not directly detectable by mass spectrometry without attaching an additional – and potentially interfering – charge. The corresponding sodium complex $[Na(\mathbf{3})Ga]^{2-}$ on the other hand is a dianion, which again may cause problems due to charge repulsion in the gas phase. Therefore, we focused on the corresponding titanium(IV) species $[H_3(\mathbf{3})Ti]^+$ and $[Na(\mathbf{3})Ti]^-$ which should both be easily detected by electrospray ionization Fourier-transform ion-cy-

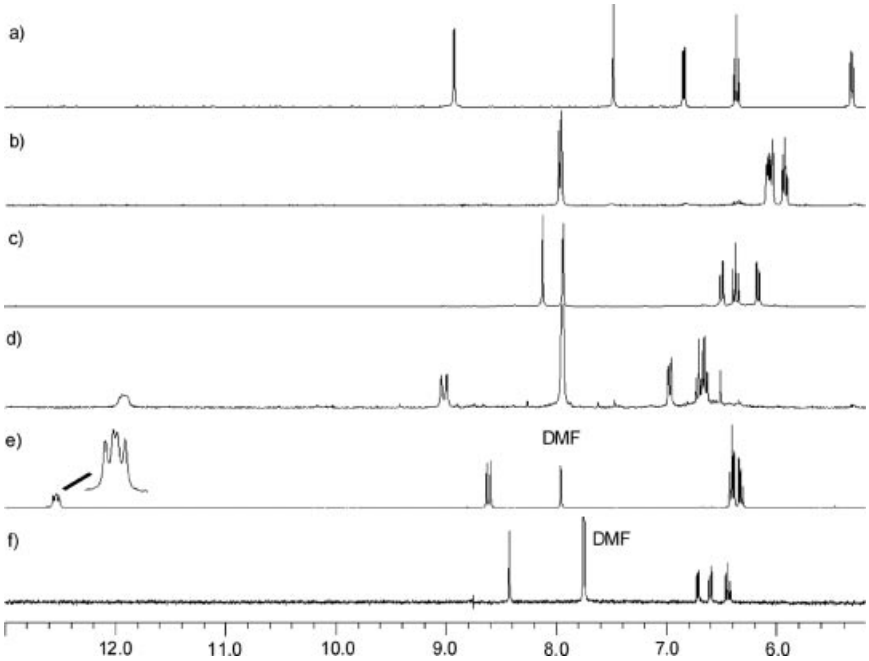


Figure 4. ^1H NMR spectra of the low-field region of **3**-H_6 (a), $Na_2[Na(\mathbf{3})Ga]$ (b), Na $[Na(\mathbf{3})Ti]$ (c), $[H_3(\mathbf{3})Ti]^+$ (d), and $[H_3(\mathbf{3})Ga]$ (e) in $[D_6]$dmso and of $[D_3(\mathbf{3})Ga]$ in D_2O (f).

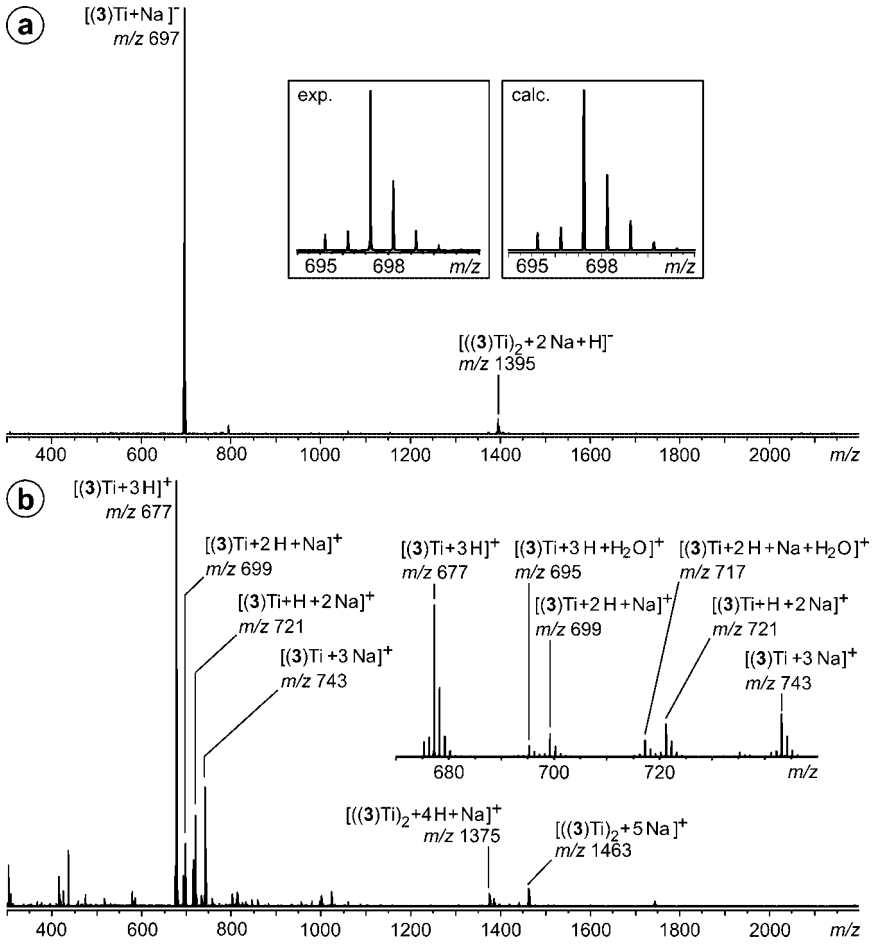
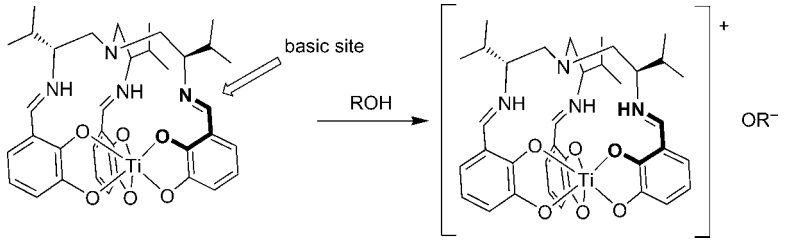


Figure 5. a) ESI FT-ICR mass spectrum of a 100 μM solution of Na[Na(**3**)Ti] in thf (negative mode). The insets show the observed and calculated isotope patterns. b) ESI FT-ICR mass spectrum of a 100 μM solution of Na[Na(**3**)Ti] in thf (positive mode). The region *m/z* = 670–750 is expanded. The water adducts and sodium/proton exchange products can be traced back to some residual water in the solvent.

clotron-resonance (ESI FT-ICR) mass spectrometric experiments (Figure 5).[16]

In the negative mode, a 100 μM solution of Na[Na(**3**)Ti] in thf gives rise to a signal corresponding to the anion [Na(**3**)Ti]⁻ as the by far dominating peak. The only other signal is due to {[Na(**3**)Ti]$_2$H}⁻ at *m/z* = 1395, which we attribute to an unspecific proton-bonded dimer. In the positive detection mode, a more complex spectrum is obtained, which exhibits signals for ions that underwent Na^+/H^+ exchange reactions up to the $[H_3(\mathbf{3})Ti]^+$ cation, where all sodium ions have been replaced. Although the source of the protons can only be residual water contained in the thf used as the spray solvent, the $[H_3(\mathbf{3})Ti]^+$ cation is the most prominent ion observed in the spectrum indicating a high tendency for protonation of the imine groups.

In a neutral, doubly protonated species [H$_2$(**3**)Ti], one imine site still suffers from a repulsion between N and O electron pairs, thus leading to a highly basic position within the complex (see Scheme 2). This site is able to deprotonate slightly acidic compounds like alcohols or water. In order to study this aspect further, *negative*-mode mass spectra of Na$_2$[(**3**)Ti] in thf were recorded in the presence of differently substituted alcohols (Figure 6). Besides the signal of the expected [Na(**3**)Ti]⁻ anion, several signals for anions appear



Scheme 2.

in which the sodium cation has been replaced by a proton: $[H(\mathbf{3})Ti]^-$, $[H_2(\mathbf{3})Ti]\cdot RO^-$, $[H_2(\mathbf{3})Ti]\cdot Cl^-$, and $[H_3(\mathbf{3})Ti]^+\cdot RO^-\cdot Cl^-$ (likely, the chloride is background chloride as often found in the negative-mode mass spectra). The latter three anions correspond to doubly protonated neutral or triply protonated cationic complexes in which an appropriate number of anions provides the overall negative charge necessary for the experiment in the negative mode. It is intri-

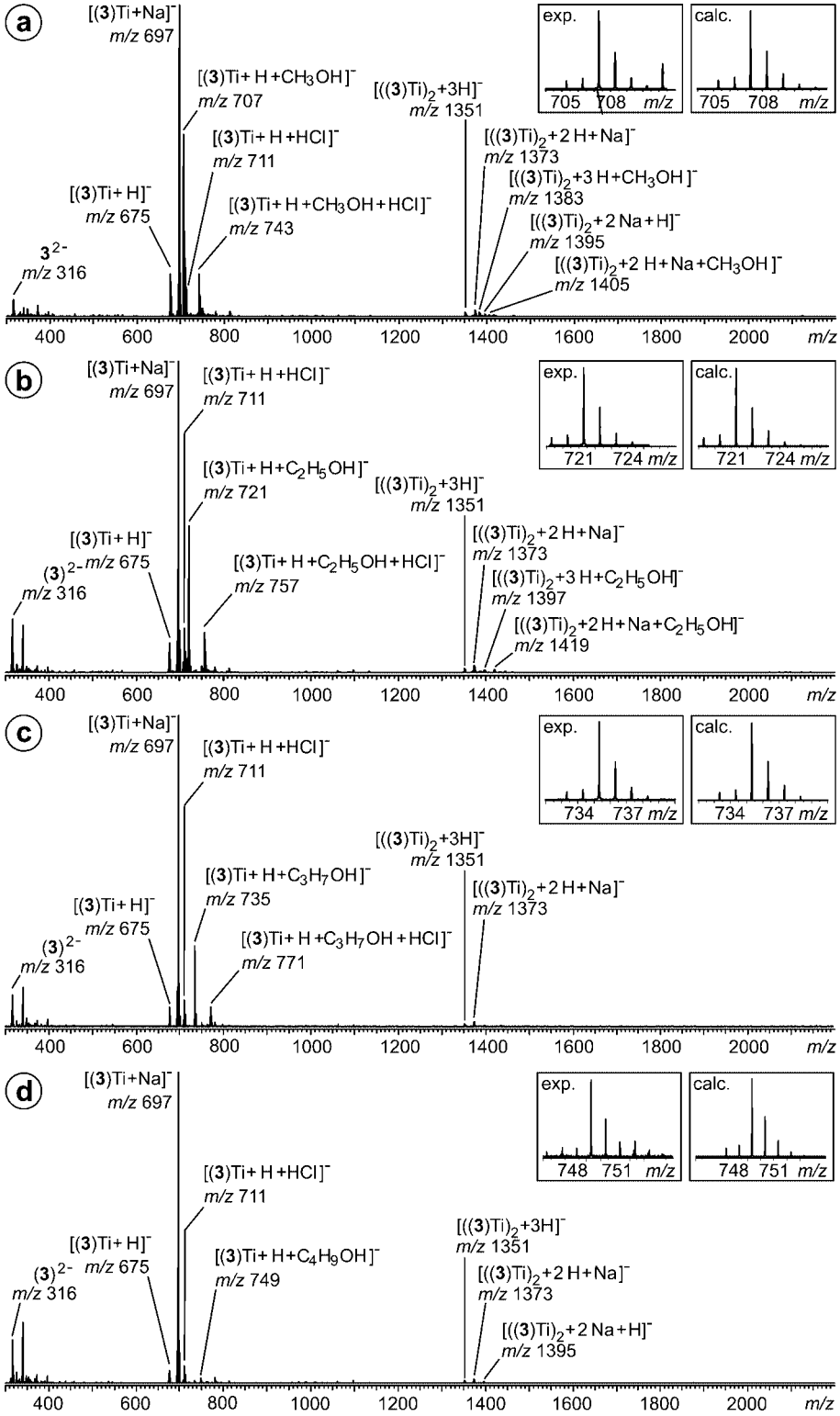


Figure 6. ESI FT-ICR mass spectrum of a 100 μM solution of $Na_2[(\mathbf{3})Ti]$ in thf (negative mode) in the presence of the same amount of different alcohols: (a) methanol, (b) ethanol, (c) 2-propanol, (d) *tert*-butyl alcohol. The observed and calculated isotopic patterns of the species with alcohol are shown. All spectra were measured under exactly the same conditions.

guing to see that the intensity ratios among these four complexes do not change much irrespective of the nature of the alcohol, while the ratio of the sum of all protonated complexes relative to the sodiated complexes undergoes a drastic change with increasing size of the substituent R on the alcohol. This trend follows the solution acidities of the alcohols (pK_a values for alcohols determined in water: MeOH: 15.49; EtOH: 15.90; *i*PrOH: 16.57; *t*BuOH: 16.84).[17] Methanol as the most acidic one in this series yields the most intense signals for the protonated complexes; *tert*-butyl alcohol as the least acidic one gives rise only to signals of very low intensities for the protonated complexes relative to the sodiated ones. The observed trend, however, does not follow the gas-phase proton affinities (MeO^-: 1596 kJ/mol; EtO^-: 1583 kJ/mol; $iPrO^-$: 1569 kJ/mol; $tBuO^-$: 1568 kJ/mol),[18] which would – in contrast to the experiment – lead to the expectation that methanol protonates the complex less easily and thus does not form complexes such as [H_2(**3**)Ti]·RO^- with higher abundance than *tert*-butyl alcohol. Consequently, we conclude that the mass spectrometric experiments provide some insight into the solution-phase protonation equilibria.

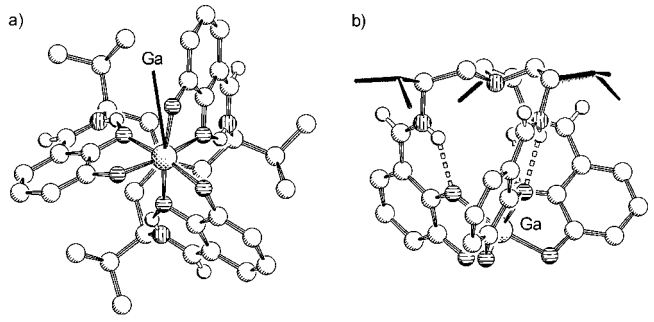


Figure 7. Molecular structure of [H_3(**3**)Ga] in the crystal. (a) View along the Ga–N_{amine} C_3 axis. (b) Side view (isopropyl groups are only indicated). Hydrogen atoms other than imine CH and N–H···O are omitted for clarity.

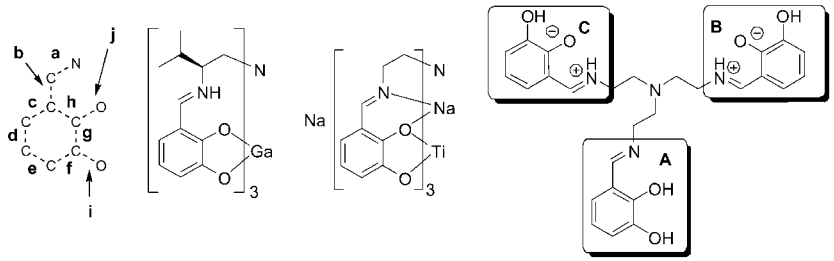
Fortunately, we were able to obtain X-ray quality crystals of [H_3(**3**)Ga] from dmf/diethyl ether. The structure is shown in Figure 7. The compound crystallizes in the hexagonal space group $P6_3$ (No. 173) and was refined to $R = 0.051$. The molecule is located on an axis of threefold symmetry.

Figure 7 shows the molecular structure of [H_3(**3**)Ga]. The chiral tripodal ligand **3** is coordinating the gallium(III) ions and induces the Δ-configuration at the tris(catecholato) complex unit. The chiral "tren analogue" spacer is forming a close-to-planar platform with the isopropyl groups located in this plane, pointing to the outside. In this way, the sterically least crowded conformation is adopted. The imine units are protonated (the proton positions could be refined) forming hydrogen bonds to the internal oxygen atoms of the catecholato unit, as it was discussed in Figure 3 (**IV**/**V**).

A deeper insight into the structural features of this compound can be given by comparing the bond lengths with those of the related compounds **2**-H_6[19] and Na[Na(**2**)Ti],[5] as it is done in detail in Table 1.

For the catecholimine **A** of **2**-H_6, the bond lengths are in the expected range. The imine bond (**a**) is a typical C=N bond with a length of 1.280 Å. The distance $C(sp^2)_{imine}$–$C(sp^2)_{aromatic}$ is 1.450 Å (**b**). Within the aromatic system typical C–C bond lengths of approximately 1.38 Å (**c**–**h**) are found and the C–$O_{catechol}$ distances are about 1.36 Å (**i**, **j**). A similar situation is observed for the complex Na[Na(**2**)-Ti]. However, in the units **B** and **C** of **2**-H_6, a significant alternation of bond lengths can be observed for the aromatic units (**c**–**h**), while the C–O bond lengths are different, e.g. **B**: C–OH 1.360 Å (**i**), C=O 1.299 Å (**j**). The alternation of the aromatic bond lengths is even more pronounced in [H_3(**3**)Ga] so that the mesomeric structure **V** in Figure 3 significantly contributes to an accurate description of this

Table 1. Comparison of the bond lengths (Å) of the iminocatechol units of [H_3(**3**)Ga], Na[Na(**2**)Ti] and **2**-H_6 in the crystal. In Na[Na(**2**)Ti], the moieties are crystallographically independent and therefore the shortest and longest values are given. In **2**-H_6 one "normal" iminocatechol unit is observed (**A**) while the two others (**B**, **C**) show proton transfer from the catechol OH group to the imine nitrogen atom. Data for Na[Na(**2**)Ti][5] and **2**-H_6[19] were taken from the literature.



	[H_3(**3**)Ga]	Na[Na(**2**)Ti]	**2**-H_6 (**A**)	**2**-H_6 (**B**)	**2**-H_6 (**C**)
a	1.298	1.263–1.272	1.280	1.287	1.295
b	1.425	1.442–1.478	1.450	1.420	1.424
c	1.426	1.375–1.412	1.398	1.416	1.411
d	1.358	1.377–1.405	1.377	1.360	1.365
e	1.408	1.361–1.405	1.390	1.400	1.402
f	1.383	1.350–1.385	1.375	1.366	1.365
g	1.439	1.398–1.424	1.393	1.428	1.428
h	1.419	1.387–1.405	1.399	1.424	1.424
i	1.333	1.348–1.371	1.373	1.360	1.367
j	1.296	1.316–1.344	1.355	1.299	1.291

complex. Here, we observe four relatively long C–C distances of 1.408–1.439 Å and two short ones with 1.358 and 1.383 Å. A remarkable difference can be also observed for the $C_{catecholate}$–O bonds. The internal one is relatively short with 1.296 Å due to its increased double-bond character, while the other one is significantly longer (1.334 Å).

The Protonation Behaviour of $K_4[(4)_3Ti_2]$

Attempts to obtain analogous protonated helicates of iminocatecholates by reaction of either gallium(III) acetylacetonate or titanoyl(IV) acetylacetonate with ligand **4**-H_4 in the absence of base were not successful. Therefore, we used the preformed helicate $K_4[(4)_3Ti_2]$[8] [the corresponding dinuclear gallium(III) helicate can unfortunately not be obtained] and protonated it by stepwise addition of sulfuric acid in [D_6]dmso.

The ^{1}H NMR resonances (Figure 8) of the catechol protons of $K_4[(4)_3Ti_2]$ (**A**) appear at δ = 6.86, 6.29, and 6.07 ppm and that of the imine group at δ = 8.58 (s) ppm. Upon addition of sulfuric acid in steps of 1 equiv. H^+ (0.5 equiv. H_2SO_4), the spectrum changes drastically. This is best monitored by the shift of the imine CH signal (Figure 9). Initially a partial protonation occurs, which leads to a dynamic species (protonation ↔ deprotonation). Upon addition of 5–8 equiv. of protons, a final spectrum is obtained which corresponds to **B** in Figure 8.

The catechol signals of **B** are observed at δ = 7.04, 6.67, and 6.57 ppm and the imine resonance is found as a doublet at δ = 7.40 (J = 15.7 Hz)ppm which couples with a signal at δ = 11.95 (dd, J = 15.7, 5.2 Hz) ppm. The observed spectrum is in accordance with a protonated species $[H_6(4)_3Ti_2]^{2+}$, in which the six protons are fixed in the interior of the triple-stranded helicate in the same way as dis-

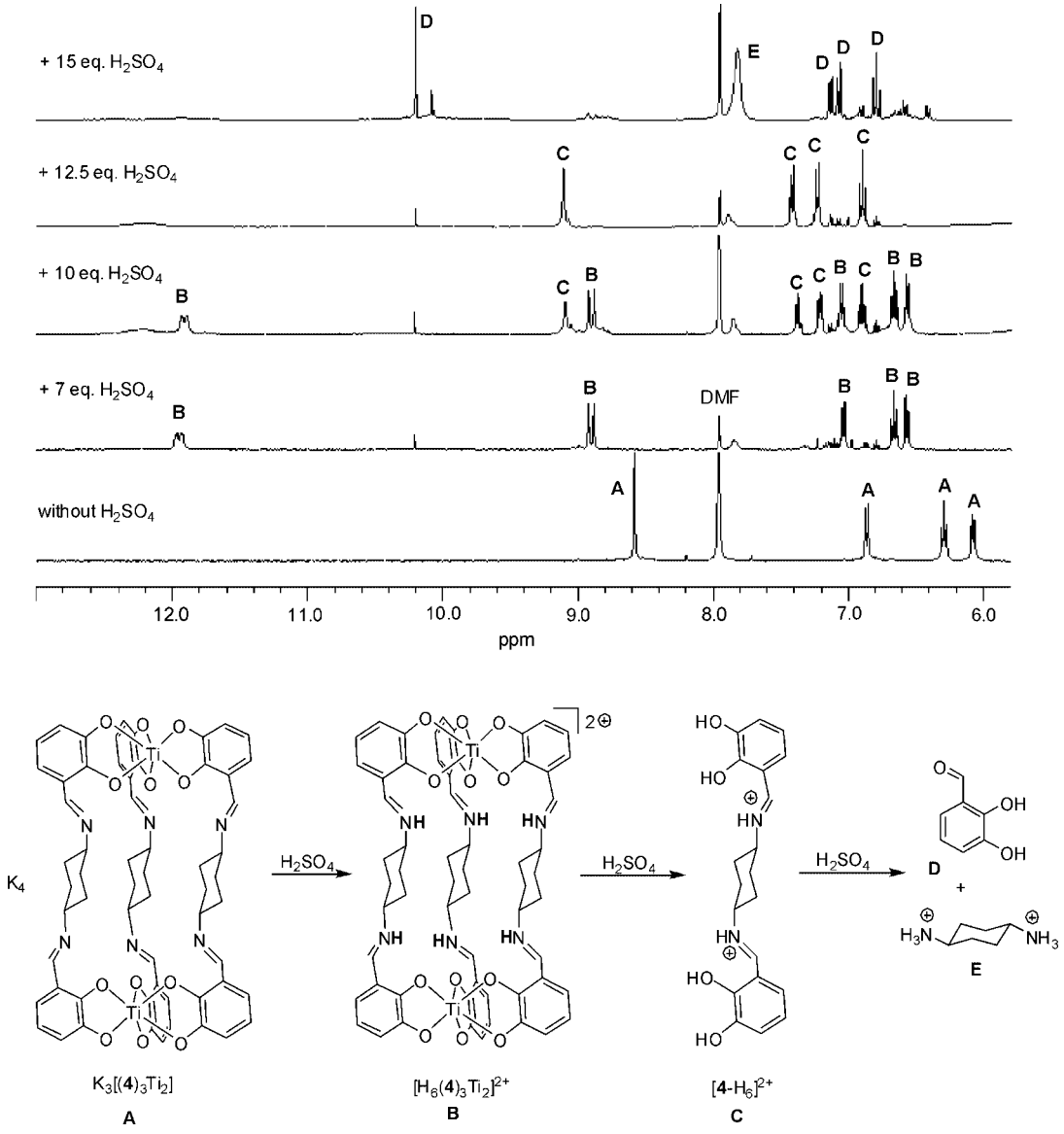


Figure 8. Change of the low-field region of the ^{1}H NMR spectrum of $K_4[(4)_3Ti_2]$ in [D_6]dmso upon controlled addition of H_2SO_4 in [D_6]-dmso.

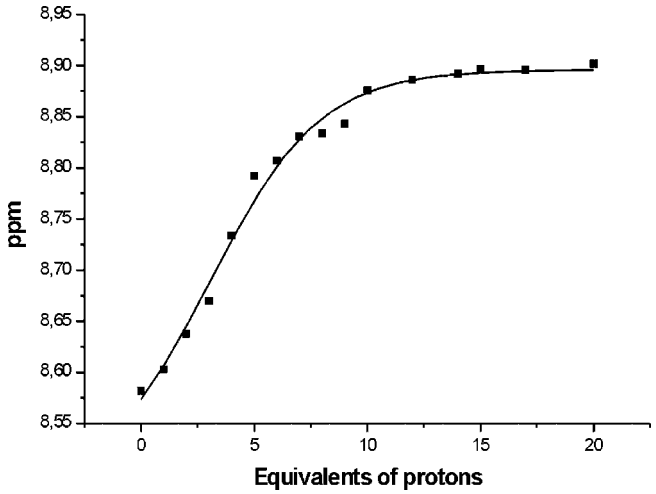


Figure 9. Change of the chemical shift of the imine CH resonance of $[(\mathbf{4})_3Ti_2]^{4-}$ in $[D_6]$dmso upon successive addition of protons (H_2SO_4).

cussed for the mononuclear complexes above. This compound can be observed by ESI MS at *m*/*z* = 1151.6 ($[\mathbf{4}_3Ti_2H_5]^+$), 1256.1 ($[\mathbf{4}_3Ti_2H_6SO_4Li]^+$), and 1452.5 ($[\mathbf{4}_3Ti_2H_6SO_4(H_2SO_4)_2Li]^+$).

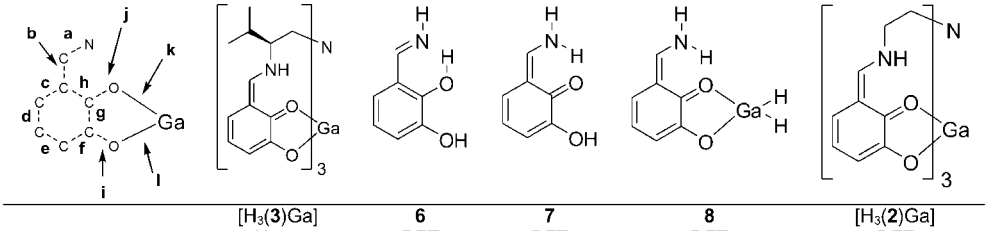
Further addition of sulfuric acid generates a new species which – at 12.5 equiv. – becomes the major one (**C**). Here, the complex is decomposed and the free protonated ligand $[\mathbf{4}\text{-}H_6]^{2+}$ is liberated. The same spectrum is obtained by protonation of **4**-H_4 in $[D_6]$dmso in the absence of any metal ions. Further addition of acid leads to the hydrolysis of the imine groups by residual water in the solvent, and 2,3-dihydroxybenzaldehyde (**D**) and protonated *trans*-1,4-diaminocyclohexane (**E**) are formed.

The protonation of corresponding mononuclear complexes[20] is rather difficult, due to the lability of the complexes in the presence of protons. For $K_2[(\mathbf{5})_3Ti]$ and $K_3[(\mathbf{5})_3Ga]$, no reliable results were obtained. However, we were able to observe NMR resonances for $K_3[(\mathbf{5})_3Ga]$ with the characteristic pattern of an imine species. Unfortunately, we could not obtain pure compounds due to decomposition of the complex simultaneous to protonation.

Computational Considerations

In order to obtain a deeper insight into the bonding behaviour of the iminocatecholates, we performed a computational study. The most simple model for the ligand we considered is the iminocatechol **6**. We calculated **6** and its enaminone tautomer **7** using the hybrid B3LYP density functional method (DFT) with the TZVP basis set[21] and the second-order Moller-Plesset perturbation theory (MP2) employing the 6-311G(d,p) basis set.[22] The imine is found to be more stable than the enaminone by 25 kJ/mol at the MP2 level of theory. The same result is obtained for the mono-deprotonated species. The X-ray data are more consistent with the enaminone structure **7** rather than with the iminocatechol **6**. The bond lengths are listed in Table 2. We analysed computationally the stability of both tautomeric forms in various metal complexes and found in those with gallium(III) ions no stable imine structure at all but only the enaminone. This can be understood in terms of a weakening of the O–H bond when the complex with the metal ion is formed. The most simple complex we considered was **8** for which the calculated bond lengths show very good agreement with the X-ray data of $[H_3(\mathbf{3})Ga]$. The largest complex we calculated on the B3LYP/TZVP level was the tren derivate $[H_3(\mathbf{2})Ga]$. The Ga atom was treated with a scalar relativistic effective core potential (ECP). For the small complexes such as **8** we employed the MDF10 ECP[23] with the corresponding cc-pVTZ-PP basis set.[24] In all complexes with three catecholato units the simpler ECP SDF28 was used with the corresponding basis set.[25] The

Table 2. Comparison of the bond lengths (Å) of the iminocatechol units of $[H_3(\mathbf{3})Ga]$ as found by X-ray crystallography and of **6**, **7**, **8**, and $[H_3(\mathbf{2})Ga]$ as obtained by computational methods.



	$[H_3(\mathbf{3})Ga]$ X-ray	**6** DFT	**7** DFT	**8** DFT	$[H_3(\mathbf{2})Ga]$ DFT
a	1.298	1.282	1.324	1.320	1.326
b	1.425	1.451	1.390	1.397	1.395
c	1.426	1.406	1.433	1.434	1.435
d	1.358	1.381	1.360	1.365	1.365
e	1.408	1.398	1.426	1.418	1.422
f	1.383	1.384	1.363	1.385	1.383
g	1.439	1.403	1.448	1.444	1.444
h	1.419	1.406	1.448	1.430	1.432
i	1.333	1.359	1.352	1.309	1.311
j	1.296	1.348	1.264	1.296	1.289
k	2.020	n/a	n/a	2.070	2.080
l	1.947	n/a	n/a	1.920	1.916

bond lengths of $[H_3(\mathbf{2})Ga]$ do not deviate significantly from the simpler model complex **8** demonstrating that interactions of the three catecholato units do not change the bonding in this case. Very similar results were also obtained for gallium tris(catecholate)s with three simple imine-type ligands.

A closer inspection of Table 2 reveals a deviation of the computed and measured distances for the imine group. The X-ray $C_{aromatic}$–C_{imine} and C_{imine}–N distances are about halfway between the imine structure **6** and the enamine structure **7**. The existence of the enamine tautomer rather than the imine form has been established computationally. As a tautomeric form of the enamine the protonated imine has to be considered. With the computational methods used here we can only predict that the enamine form dominates the protonated imine by analysing the order of the molecular orbitals, but more elaborate methods would be required to assess the contribution of the second mesomer.

The results of the computational chemistry strongly support the interpretations of our experimental findings. In the (iminocatecholato)gallium complexes an enamine/quinomethine-type structure is the dominating mesomeric form.

Conclusions

Our earlier results on the formation of the molecular tetrahedron $[(\mathbf{2})_4Ti_4]^{8-}$ from the flexible ligand **2** made us believe, that we have an easy entry for the preparation of related derivatives, to which we can attach substituents, e.g. in order to introduce chiral information. However, the conformation of ligand **2** is controlled by electronic influences: the repulsion between the free imine nitrogen and catecholato oxygen electron pairs or by the ability of this unit to chelate a metal cation. On the other hand, for ligand **3** additional steric effects become dominant (Figure 10).

For the formation of a tetrahedron vs. a mononuclear complex, two different conformations of the ligand have to be considered. The tetrahedron is formed, if the ligand can spread out to form a triangle with the catechol units located at the corners. This is possible with ligand **2**-H_6. In case of **3**-H_6 this conformation is "sterically encumbered" due to the bulky isopropyl groups (see Figure 10). The most relaxed conformation is the "cap-type" structure, in which the three catechol moieties are predisposed for tripodal binding of one metal ion. In a 1:1 complex between **3** and a metal ion [e.g. gallium(III)] repulsion between the free electron pairs occurs. This can be overcome either by addition of sodium cations as templates or by proton extraction from solvent (alcohol or water). In the latter case, a high positive charge is now accumulated in the "cap" of the compound which is compensated by adopting an enaminone/chinomethine mesomeric structure.

In dinuclear helicate-type (and mononuclear noncapped) complexes, it is possible to obtain similar protonated structures by addition of mineral acids. However, addition of an excess of acid leads to the decomposition of the complex and finally to the hydrolysis of the imine ligands.

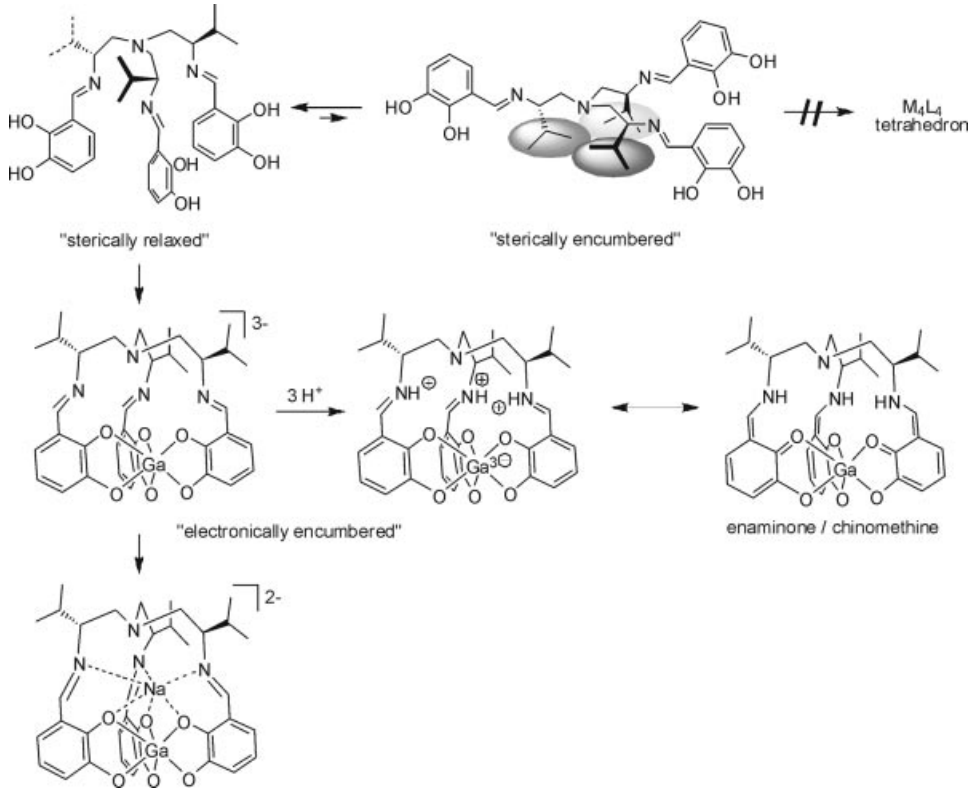


Figure 10. Stabilizing and destabilizing influences that control the sodium- or proton-templated formation of mononuclear gallium(III) complexes.

The experimental findings of this study were supported by high-level ab initio and density functional calculations on the simple mesomeric catechol structures **6** and **7**, and the complexes **8** and [H_3(**2**)Ga].

This study shows that subtle influences can control the outcome of a metallosupramolecular coordination study. Steric constraints at ligands, geometry of metal coordination, influence of templates, solvent effects, pH, electronic effects, steric effects are only few aspects, which have to be considered in order to rationally control the self-assembly of sophisticated supramolecular aggregates. The present study is only a small step in order to achieve this goal, but it demonstrates the power of several of the mentioned aspects to interfere in the assembly process.

Experimental Section

General: NMR spectra were recorded with a Varian Mercury 300 or Inova 400 spectrometer. FT-IR spectra were recorded with a Bruker IFS spectrometer. Mass spectra were taken with a Thermo Deca XP mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyser. ESI MS spectra were measured in thf using a Bruker APEX IV fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer with an Apollo electrospray ion source described in detail earlier.[26] The chiral tren derivative was prepared as described by Moberg et al.[6]

3-H_6: The (2*S*)-N^1,N^1-bis[(*S*)-2-amino-3-methylbutyl]-3-methylbutane-1,2-diamine (0.118 g, 0.43 mmol) and 2,3-dihydroxybenzaldehyde (0.185 g, 1.34 mmol, 3.1 equiv.) were dissolved in distilled methanol (10 mL), and the mixture was stirred overnight. The tris(catechol) **3**-H_6 precipitated as yellow solid. It was collected by filtration and was washed with cold methanol. Yield: 0.126 g (0.20 mmol, 46.4%). M.p. 259 °C. ^{1}H NMR (400 MHz, [D_6]dmso): δ = 14.06 (s, 3 H, OH), 8.92 (s, 3 H, OH), 7.47 (s, 3 H, $CH_{aldehyde}$), 6.84 (dd, *J* = 1.4, 7.8 Hz, 3 H, CH_{arom}), 6.36 (t, *J* = 7.8 Hz, 3 H, CH_{arom}), 5.33 (dd, *J* = 1.4, 7.8 Hz, 3 H, CH_{arom}), 2.84 (m, 3 H, CH_{alkyl}), 2.70 (dd, *J* = 13.5, 8.5 Hz, 3 H, CH_{alkyl}), 2.57 (d, *J* = 13.5 Hz, 3 H, CH_{alkyl}), 1.79 (m, 3 H, CH_{alkyl}), 0.85 (d, *J* = 6.9 Hz, 9 H, CH_{alkyl}), 0.80 (d, *J* = 6.6 Hz, 9 H, CH_{alkyl}). IR (KBr): $\tilde{\nu}$ = 3392, 3290, 2961, 2877, 1636, 1544, 1522, 1465, 1395, 1230, 1055, 1016, 856, 780, 736, 490, 465 cm^{-1}. MS (EI, 70 eV): *m*/*z* = 632.3 [M^+], 440.2 [$C_{25}H_{35}N_3O_4^+$], 303.1 [$C_{17}H_{25}N_3O_2^+$], 318.1 [$C_{18}H_{28}N_3O_2^+$], 192.1 [$C_{11}H_{11}NO_2^+$], 123.0 [$C_7H_7O_2^+$]. $C_{36}H_{48}N_4O_6$ (632.79) calcd. C 68.33, H 7.65, N 8.85; found C 67.68, H 7.43, N 8.38.

Na_3[(3)Ga]: The ligand **3**-H_6 (30 mg, 0.0474 mmol), gallium(III) acetonylacetonate (170 mg, 0.0474 mmol) and sodium hydroxide (0.0057 g, 0.142 mmol) were dissolved in dimethylformamide (40 mL), and the mixture was stirred overnight. Then, the solvent was removed and the red-orange solid was dried under high vacuum. Yield: 0.042 g (0.0474 mmol, >99%). ^{1}H NMR (400 MHz, [D_6]dmso): δ = 7.89 (s, 3 H, NCH_{imine}), 6.06 (d, *J* = 7.7 Hz, 3 H, CH_{arom}), 6.02 (d, *J* = 7.7 Hz, 3 H, CH_{arom}), 5.91 (t, *J* = 7.7 Hz, 3 H, CH_{arom}), 2.90 (m, 3 H, CH_{alkyl}), 2.77 (t, *J* = 11.5 Hz, 3 H, CH_{alkyl}), 1.91 (m, 3 H, CH_{alkyl}), 1.43 (m, 3 H, CH_{alkyl}), 0.76 (d, *J* = 6.6 Hz, 9 H, CH_{alkyl}), 0.69 (d, *J* = 6.9 Hz, 9 H, CH_{alkyl}). IR (KBr): $\tilde{\nu}$ = 3428, 2956, 2872, 2826, 2298, 1664, 1622, 1458, 1386, 1247, 1055, 867, 738 cm^{-1}. MS: positive ESI (dmf/MeOH): *m*/*z* = 721.5 [**3**GaH_3Na^+], 743.4 [**3**$GaNa_2H_2^+$], 1421.2 [$\mathbf{3}_2Ga_2H_6Na^+$], 1465.2 [$\mathbf{3}_2Ga_2H_4Na_3^+$]; negative ESI (dmf/MeOH): *m*/*z* = 632.1 [**3**H^-], 697.8 [**3**GaH_2^-], 719.8 [**3**$GaNaH^-$], 1395.2 [$\mathbf{3}_2Ga_2H_5^-$], 1419.2 [$\mathbf{3}_2Ga_2H_4Na^-$]. $C_{36}H_{42}GaN_4Na_3O_6$·dmf·5H_2O (928.62): calcd. C 50.44, H 6.40, N 7.54, found C 50.21, H 6.41, N 7.49.

H_3[(3)Ga]: The ligand **3**-H_6 (30 mg, 0.0474 mmol) and gallium(III) acetonylacetonate (17 mg, 0.0474 mmol) were dissolved in dimethylformamide (40 mL), and the mixture was stirred overnight. Then, the solvent was removed and the red-orange solid was dried under high vacuum. Yield: 0.045 g (0.0474 mmol, >99%). ^{1}H NMR (400 MHz, [D_6]dmso): δ = 12.53 (dd, *J* = 13.5, 11.1 Hz, 3 H, CNH_{imine}), 8.62 (d, *J* = 13.5 Hz, 3 H, NCH_{imine}), 6.40 (m, 6 H, CH_{arom}), 6.33 (m, 3 H, CH_{arom}), 4.05 (m, 3 H, CH_{alkyl}), 2.65 (dd, *J* = 13.5, 11.1 Hz, 3 H, CH_{alkyl}), 2.11 (m, 3 H, CH_{alkyl}), 1.78 (m, 3 H, CH_{alkyl}), 0.80 (d, *J* = 6.6 Hz, 9 H, CH_{alkyl}), 0.68 (d, *J* = 6.6 Hz, 9 H, CH_{alkyl}). ^{1}H NMR (400 MHz, D_2O): δ = 8.43 (s, 3 H, CNH_{imine}), 6.40 (d, *J* = 7.2 Hz, 3 H, CH_{arom}), 6.33 (d, *J* = 7.7 Hz, 3 H, CH_{arom}), 6.44 (apt, *J* = 7.7 Hz, 3 H, CH_{arom}), 3.85 (m, 3 H, CH_{alkyl}), 2.62 (apt, *J* = 12.2 Hz, 3 H, CH_{alkyl}), 2.25 (m, 3 H, CH_{alkyl}), 1.65 (m, 3 H, CH_{alkyl}), 0.68 (d, *J* = 6.9 Hz, 9 H, CH_{alkyl}), 0.53 (d, *J* = 6.9 Hz, 9 H, CH_{alkyl}). ^{1}H NMR (400 MHz, CD_3OD): δ = 8.46 (s, 3 H, NCH_{imine}), 6.74 (dd, *J* = 7.4, 1.1 Hz, 3 H, CH_{arom}), 6.54 (dd, *J* = 8.2, 0.9 Hz, 3 H, CH_{arom}), 6.44 (apt, *J* = 7.8 Hz, 3 H, CH_{arom}), 3.95 (m, 3 H, CH_{alkyl}), 2.86 (apt, *J* = 12.1 Hz, 3 H, CH_{alkyl}), 2.31 (dd, *J* = 12.5, 5.6 Hz, 3 H, CH_{alkyl}), 1.84 (m, 3 H, CH_{alkyl}), 0.89 (d, *J* = 6.9 Hz, 9 H, CH_{alkyl}), 0.76 (d, *J* = 6.9 Hz, 9 H, CH_{alkyl}). IR (KBr): $\tilde{\nu}$ = 3431, 2957, 2868, 1665, 1631, 1496, 1383, 1325, 1249, 1089, 1021, 873, 733, 593, 555 cm^{-1}. MS: positive ESI (dmf/MeOH): *m*/*z* = 699.6 [**3**GaH_3H^+], 721.5 [**3**GaH_3Na^+], 1399.5 [$\mathbf{3}_2Ga_2H_6H^+$], 1421.4 [$\mathbf{3}_2Ga_2H_6Na^+$]; negative ESI (dmf/MeOH): *m*/*z* = 697.9 [**3**GaH_2^-]. $C_{36}H_{45}GaN_4O_6$·3dmf·H_2O (936.80): calcd. C 57.70, H 7.32, N 10.47; found C 57.94, H 7.15, N 10.21.

X-ray Crystal Structure Analysis of H_3[(3)Ga]: $C_{36}H_{45}GaN_4O_6$·3C_3H_7NO, *M* = 918.77, orange crystal 0.40 × 0.04 × 0.03 mm, *a* = 12.216(1), *c* = 19.119(1) Å, γ = 120°, *V* = 2470.9(3) Å^3, $\rho_{calcd.}$ = 1.235 g cm^{-3}, μ = 0.614 mm^{-1}, empirical absorption correction (0.791 ≤ *T* ≤ 0.982), *Z* = 2, hexagonal, space group $P6_3$ (No. 173), λ = 0.71073 Å, *T* = 198 K, ω and ϕ scans, 10869 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.62 Å^{-1}, 3070 independent (R_{int} = 0.039) and 2581 observed reflections [$I \geq 2\sigma(I)$], 194 refined parameters, *R* = 0.051, wR^2 = 0.082, Flack parameter 0.01(2), max. residual electron density 0.44/–0.30 e·Å^{-3}, hydrogen atom at N18 from difference Fourier map, others calculated and refined as riding atoms. Data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[27] absorption correction Denzo,[28] structure solution SHELXS-97,[29] structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, 1997). CCDC-628295 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

Na_2[(3)Ti]: The ligand **3**-H_6 (30 mg, 0.0474 mmol), $TiO(acac)_2$ (12 mg, 0.0474 mmol) and sodium carbonate (5.1 mg, 0.0481 mmol) were dissolved in dimethylformamide (40 mL), and the mixture was stirred overnight. Then, the solvent was removed and the red-orange solid was dried under high vacuum. Yield: 0.041 g (0.0474 mmol, quant.). ^{1}H NMR (300 MHz, [D_6]dmso): δ = 8.14 (s, 3 H, NCH_{imine}), 6.51 (dd, *J* = 7.7, 1.1 Hz, 3 H, CH_{arom}), 6.38 (t, *J* = 7.7 Hz, 3 H, CH_{arom}), 6.18 (dd, *J* = 7.7, 1.1 Hz, 3 H, CH_{arom}), 3.10 (m, 3 H, CH_{alkyl}), 2.89 (m, 3 H, CH_{alkyl}), 2.08 (dd,

J = 11.5, 3.6 Hz, 3 H, CH_{alkyl}), 1.57 (m, 3 H, CH_{alkyl}), 0.78 (d, J = 6.7 Hz, 9 H, CH_{alkyl}), 0.75 (d, J = 6.9 Hz, 9 H, 3 H, CH_{alkyl}) ppm. IR (KBr): $\tilde{\nu}$ = 3433, 2956, 2868, 1663, 1622, 1552, 1449, 1383, 1244, 1095, 1073, 865, 743, 655, 565, 523 cm^{-1}. MS: positive ESI (dmf/MeOH): m/z = 700.7 [**3**TiH_2Na^+], 677.7 [**3**TiH_3^+]; negative ESI (dmf/MeOH): m/z = 676.8 [**3**TiH_2^-]. $C_{36}H_{42}N_4Na_2O_6Ti$·dmf·$4H_2O$ (865.79): calcd. C 54.11, H 6.64, N 8.09, found C 54.17, H 6.42, N 8.88.

H_3[(3)Ti]OH: The ligand **3**-H_6 (25 mg, 0.0395 mmol), $TiO(acac)_2$ (10 mg, 0.0395 mmol) and potassium carbonate (5.5 mg, 0.0395 mmol) were dissolved in dimethylformamide (40 mL), and the mixture was stirred overnight. Then, the solvent was removed and the red-orange solid was dried under high vacuum. Yield: 0.040 g (quant.). ^{1}H NMR (400 MHz, [D_6]dmso): δ = 11.95 (m, 3 H, NH), 9.04 (d, J = 14.6 Hz, 3 H, CH_{imine}), 6.98 (d, J = 7.7 Hz, 3 H, CH_{arom}), 6.72 (t, J = 7.7 Hz, 3 H, CH_{arom}), 6.66 (d, J = 7.7 Hz, 3 H, CH_{arom}), 4.30 (m, 3 H, CH_{alkyl}), 2.85 (m, 3 H, CH_{alky}), 2.40 (m, 3 H, CH_{alkyl}), 2.00 (m, 3 H, CH_{alkyl}), 0.81 (d, J = 6.3 Hz, 18 H, CH_{alkyl}) ppm. IR (KBr): $\tilde{\nu}$ = 3425, 2956, 2873, 1648, 1549, 1486, 1385, 1250, 1216, 1084, 1053, 966, 782, 742, 668, 611, 504 cm^{-1}. MS: positive ESI (dmf/MeOH): m/z = 697.2 [**3**$TiNa^+$], 715.2 [**3**TiH_2ONa^+], 1392.1 [$\mathbf{3}_2Ti_2H_4ONa^+$]; negative ESI (dmf/MeOH): m/z = 675.6 [**3**TiH^-], 1351.6 [$\mathbf{3}_2Ti_2H_3^-$]. No correct elemental analysis was obtained.

5-H_2: 2,3-Dihydroxybenzaldehyde (0.5 g, 3.6 mmol) was dissolved in isopropylamine (5 mL). The solvent was distilled off to obtain the imine as a yellow-brown solid. Yield: 0.646 g (3.6 mmol, quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 (s, 1 H, NCH), 6.86 (d, J = 7.4 Hz, 1 H, CH_{arom}), 6.64 (d, J = 7.9 Hz, 1 H, CH_{arom}), 6.49 (dd, J = 7.9, 7.4 Hz, 1 H, CH_{arom}), 3.64 (sept, J = 6.4 Hz, 1 H, CH_{alkyl}), 1.31 (d, J = 6.4 Hz, 6 H, CH_{alkyl}). IR (KBr): $\tilde{\nu}$ = 3214, 3038, 2972, 2925, 1642, 1543, 1518, 1465, 1402, 1362, 1230, 1127, 1021, 900, 862, 749, 718, 490 cm^{-1}. MS (EI, 70eV): m/z = 179.0 [**5**-H_2^+], 137.0 [$C_7H_7NO_2^+$], 136.0 [$C_7H_6NO_2^+$], 109.0 [$C_6H_5O_2^+$]. $C_{10}H_{13}NO_2$ (179.22): calcd. C 67.02, H 7.31, N 7.82; found C 67.29, H 7.00, N 7.89.

Acknowledgments

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