

Controlling the Orientation of Sequential Ligands in the Self-Assembly of Binuclear Coordination Compounds

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Received September 16, 1996[⊗]

Abstract: The sequential ligand **5**-H₃, which contains one catechol and one aminophenol unit, was prepared in a four-step sequence. The two electronically different binding sites of **5** are able to control the metal-directed self-assembly of binuclear coordination compounds with different ligand orientations. In coordination studies with titanium(IV) or gallium(III) ions, this ligand **5** was used to obtain anionic homobinuclear complexes [(**5**)₃Ti₂][−] and [(**5**)₃Ga₂]^{3−} with two ligands orientated in one and the third in the opposite direction (type II structure). On the other hand, if the ligand **5** reacts with a 1:1 mixture of titanium(IV) and gallium(III) ions exclusively, the heterobimetallic complex [(**5**)₃GaTi]^{2−} is formed in a cooperative process. In this coordination compound the three ligands are orientated in one direction (type I structure). For K₂[(**5**)₃GaTi]·6DMF·ether, space group *P*2₁/*c*, *a* = 12.868(3) Å, *b* = 19.902(2) Å, *c* = 27.063(2) Å, β = 102.22(1)°, *V* = 6774(2) Å³, *Z* = 4, and *R* = 0.071. The structural analysis shows that titanium(IV) binds to the catecholate moieties while gallium(III) prefers the aminophenolate binding site of the ligand **5**. Internal hydrogen bonding enhances the stability of the ΛΔ configured binuclear complex.

Introduction

Molecular recognition plays an important role in biochemical processes like protein folding, enzyme–substrate interaction, or the assembling of the double-stranded DNA. Thereby protons very often act as the connecting species between units of complementary shape.¹ In artificial supramolecular systems the small cation H⁺ may be substituted by larger main group or transition metal cations. In contrast to the proton, those cations may possess a specific shape by means of charge, size, hardness, or preferred coordination geometry and thus might play an active part in the molecular recognition process. Strong interactions only can occur with “complementary donor molecules” (ligands). Molecular recognition between metal ions and appropriate ligands in self-assembly processes leads to the formation of polynuclear supramolecular coordination compounds. Hereby the steric and electronic information which is contained in each single molecular component forces the system to follow a

program to form only one defined species in high selectivity.^{2,3}

The formation of oligonuclear helical coordination compounds (helicates) is an excellent example where the assembly of the supramolecular aggregates is controlled by the properties of the molecular building blocks.⁴ The structure of the obtained species is influenced by the nature of the metal (e.g., double-⁵ versus triple-stranded compounds⁶) and the ligand (e.g., helicate^{5,6} versus meso-helicate⁷). If sequential ligand strands are introduced,⁸ heterobinuclear complexes can be formed which possess two or three ligands orientated in one direction (type I, Figure 1). On the other hand, combination of sequential ligands with only one kind of metal should lead to a type II situation as depicted in Figure 1.⁹ The metal is able to bind to both different ligand subunits, and this should lead to different

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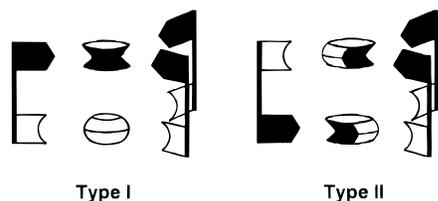
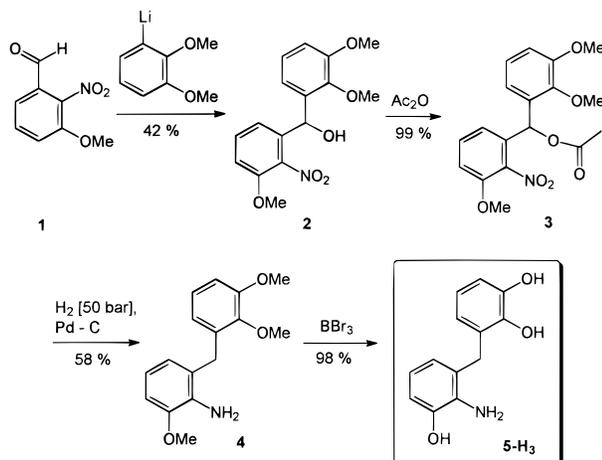


Figure 1. Schematic representation of the two orientations of sequential ligands in triple-stranded binuclear metal complexes.

Scheme 1



orientations of the ligand strands in the binuclear complex. Similar metal centers try to be as similar as possible.

In recent studies, Piguet and Williams took advantage of the different coordination geometries and numbers of metal ions to obtain double- or triple-stranded type I as well as type II helicates from sequential ligands which contain bi- and tridentate chelating units.¹⁰

Inspired by our results in the metal-directed self-assembly of alkyl-bridged bis(catecholate) ligands,^{11,12} we synthesized (2-amino-3-hydroxyphenyl)(2,3-dihydroxyphenyl)methane (**5-H₃**) as a precursor for the sequential ligand **5**. Ligand **5** contains two electronically different binding sites with very similar sterical demands. Thus, **5** should be ideal to test the possibility to obtain coordination compounds of type I or type II from only

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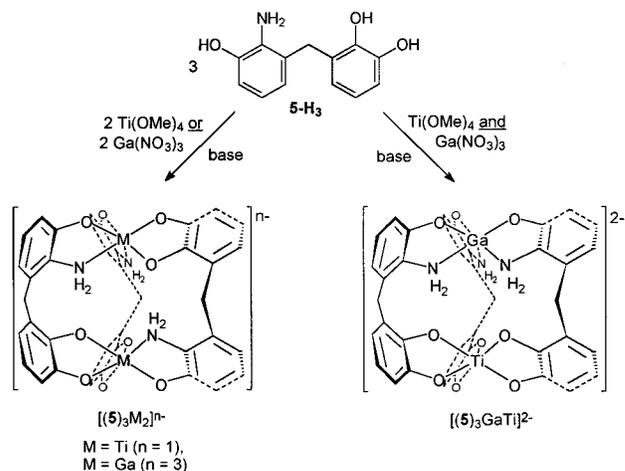
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Scheme 2



one kind of ligand in a self-assembly process which is controlled by the electronic features of the two different binding sites.

Results and Discussion

Synthesis of Ligand 5-H₃. Ligand **5-H₃** was synthesized in a four-step sequence¹³ as outlined in Scheme 1. Addition of 2-nitro-3-methoxybenzaldehyde (**1**) to (2,3-dimethoxyphenyl)lithium, which was generated in situ by reaction of 1,2-dimethoxybenzene with *n*BuLi in ether,¹⁴ affords—after hydrolytic workup—the carbinol **2** in 42% yield. The alcohol **2** by reaction with acetic anhydride at 100 °C quantitatively (99%) is transformed into the acetate **3**. In the following reaction step simultaneous reductive removal of the acetate and reduction of the nitro group with hydrogen (50 bar) in the presence of Pd—C gives the aniline derivative **4** in 58% yield. Finally, the methyl ethers are cleaved quantitatively (98%) to afford **5-H₃**, which is the precursor for the sequential ligand **5**.

Synthesis of Coordination Compounds. The bis(titanium) complex $K[(5)_3Ti_2]$ is prepared by stirring a mixture of **5-H₃** (3 equiv), $Ti(OMe)_4$ (2 equiv), and potassium carbonate (0.5 equiv) for 4 days in methanol. After removal of the solvent, $K[(5)_3Ti_2] \cdot 6H_2O$ is obtained as a red hygroscopic solid in 93% yield (Scheme 2). The corresponding binuclear gallium complex also is formed quantitatively (by NMR) by reaction of **5-H₃** (3 equiv), $Ga(NO_3)_3 \cdot 9H_2O$ (2 equiv), and lithium carbonate (4.5 equiv). $LiNO_3$ is removed by extraction with THF to give analytically pure $Li_3[(5)_3Ga_2] \cdot 10H_2O$ in 50% yield.

The heterobinuclear coordination compound $K_2[(5)_3GaTi] \cdot 6H_2O$ is formed when ligand **5-H₃** (3 equiv) together with a mixture of $Ga(NO_3)_3 \cdot 9H_2O$ and $Ti(OMe)_4$ (1 equiv each) and potassium carbonate (2.5 equiv) is stirred in methanol for 4 days and solvent is removed. Analytically pure $K_2[(5)_3GaTi] \cdot 6H_2O$ is obtained after chromatography (Sephadex LH-20, methanol) in 73% yield. The dianion $[(5)_3GaTi]^{2-}$ also is formed, when $K[(5)_3Ti_2]$ and $Li_3[(5)_3Ga_2]$ are dissolved in methanol-*d*₄. After 1 week, characteristic signals for $[(5)_3GaTi]^{2-}$ are observed by ¹H NMR.

The compounds $Na_3[(5)_3Ga_2]$, $K_3[(5)_3Ga_2]$, $Li[(5)_3Ti_2]$, $Li_2[(5)_3GaTi]$, and $Na_2[(5)_3GaTi]$ were prepared and characterized by NMR spectroscopy to show that the alkali metal cations don't have an influence on the self-assembly of the binuclear anionic complexes (vide infra).¹² Identical spectra are obtained for the anions if different cations are present. However, the complex salts were not isolated in analytically pure form.

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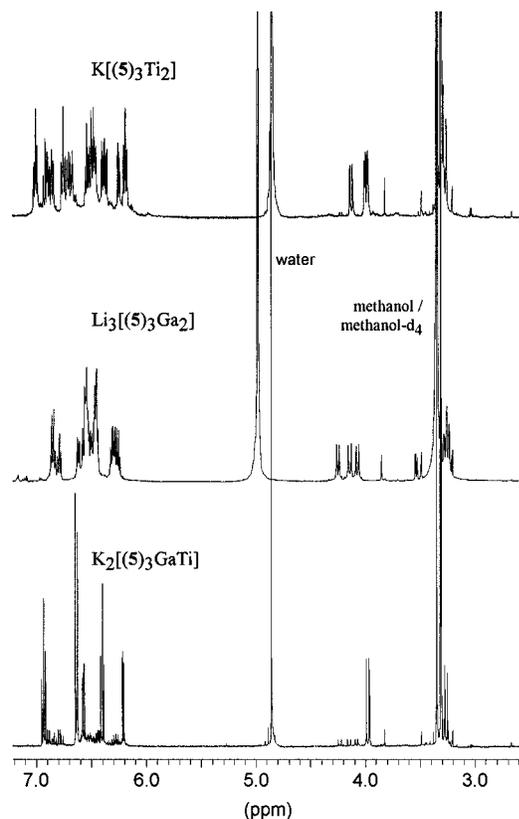


Figure 2. ^1H NMR spectra (500 MHz) of the crude products of $\text{K}[(\mathbf{5})_3\text{Ti}_2]$, $\text{Li}_3[(\mathbf{5})_3\text{Ga}_2]$, and $\text{K}_2[(\mathbf{5})_3\text{GaTi}]$ in methanol- d_4 .

FAB Mass Spectrometric Investigations. The composition of the complexes $\text{K}[(\mathbf{5})_3\text{Ti}_2]$, $\text{Li}_3[(\mathbf{5})_3\text{Ga}_2]$, and $\text{K}_2[(\mathbf{5})_3\text{GaTi}]$ is well demonstrated by their FAB mass spectra. For $\text{K}[(\mathbf{5})_3\text{Ti}_2]$ the peak of the anion $[(\mathbf{5})_3\text{Ti}_2]^-$ can be observed in its negative ion FAB mass spectrum in glycerine at $m/z = 780$. A positive ion FAB MS was taken for $\text{Li}_3[(\mathbf{5})_3\text{Ga}_2]$ (glycerine as matrix). Peaks at $m/z = 846$ ($\text{HLi}_3[(\mathbf{5})_3\text{Ga}_2]^+$) and 852 ($\text{Li}_4[(\mathbf{5})_3\text{Ga}_2]^+$) are observed. A peak at $m/z = 840$ can be detected for the heterobimetallic species $\text{K}[(\mathbf{5})_3\text{GaTi}]^-$ (FAB(-) MS, glycerine), which shows that indeed a binuclear titanium/gallium complex is formed. No peaks of homobinuclear complexes are observed in this case.

NMR Spectroscopic Studies of $\text{K}[(\mathbf{5})_3\text{Ti}_2]$ and $\text{Li}_3[(\mathbf{5})_3\text{Ga}_2]$. In its ^1H NMR spectrum in methanol- d_4 , $\text{K}[(\mathbf{5})_3\text{Ti}_2]$ displays signals at δ 7.01 (2 H), 6.91 (2 H), 6.76 (3 H), 6.48 (5 H), 6.45 (2 H), 6.26 (2 H), and 6.19 (2 H) for aromatic protons, three doublets at δ 4.13, 3.99, and 3.98 (each $J = 13.0$, each 1 H), and a multiplet at δ 3.25 (3 H) (Figure 2). The observation of three doublets at about 4.0 ppm and a multiplet at 3.25 ppm for the spacer shows that the three ligands $\mathbf{5}$ are magnetically different. In the ^{13}C NMR spectrum, signals of 36 aromatic carbon atoms and of three methylene units are detected (see the Experimental Section; Figure 3). A CH-correlation NMR experiment shows that the three protons with resonances in the region 4.13–3.98 ppm are bound to carbon atoms of different methylene groups. The observation of three different sets of proton signals for the methylene spacer and of a resonance for every single carbon atom of the complex indicates that the formed coordination compound possesses low symmetry. The binuclear gallium compound $\text{Li}_3[(\mathbf{5})_3\text{Ga}_2]$ gives rise to similar spectra (for details see the Experimental Section; Figures 2 and 3) and thus possesses a similar structure as its titanium analogue.

The discussed spectroscopic findings unambiguously show that with titanium(IV) or gallium(III) exclusively coordination compounds with the C_1 symmetric type II structure are obtained.

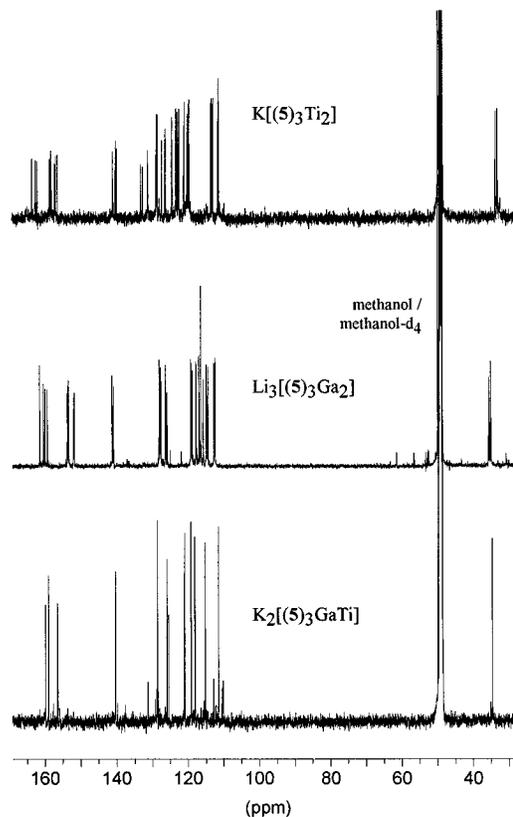


Figure 3. ^{13}C NMR spectra (125 MHz) of the crude products of $\text{K}[(\mathbf{5})_3\text{Ti}_2]$, $\text{Li}_3[(\mathbf{5})_3\text{Ga}_2]$, and $\text{K}_2[(\mathbf{5})_3\text{GaTi}]$ in methanol- d_4 .

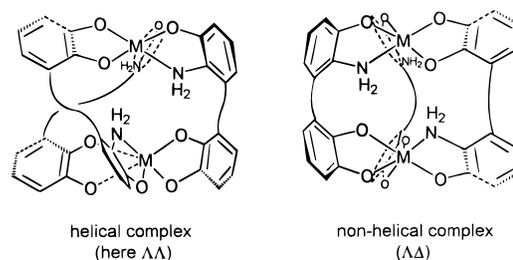


Figure 4. Helical and nonhelical structure of type II coordination compounds $[(\mathbf{5})_3\text{Ti}_2]^-$ or $[(\mathbf{5})_3\text{Ga}_2]^{3-}$ (the spacers are only indicated).

Two of the ligands $\mathbf{5}$ are orientated in one and the third in the opposite direction, leading to a loss of symmetry. Thus, as proposed, type II binuclear coordination compounds are formed by thermodynamically controlled self-assembly of three sequential ligands and two identical metal ions.

Due to the two different complex units of this type II complex, it is not possible to distinguish by NMR between a helical ($\Delta\Delta$ or $\Delta\Delta$) or a nonhelical ($\Delta\Delta$)¹⁵ structure of $[(\mathbf{5})_3\text{Ti}_2]^-$ or $[(\mathbf{5})_3\text{Ga}_2]^{3-}$, respectively. However, in accordance with earlier findings^{7,12} and because of the presence of rigid CH_2 spacers, it has to be assumed that the binuclear coordination compounds possess the nonhelical $\Delta\Delta$ structure.

NMR Spectroscopic Studies of $\text{K}_2[(\mathbf{5})_3\text{GaTi}]$. The ^1H NMR (Figure 2) and ^{13}C NMR spectra (Figure 3) of $\text{K}_2[(\mathbf{5})_3\text{GaTi}]$ in methanol- d_4 display only one set of signals for the coordinated ligands (see the Experimental Section). By ^1H NMR only two doublets can be detected for the protons of the alkyl spacer [3.97, 3.26 ($J = 12.9$ Hz, 3 H each)]. This shows that in contrast to the C_1 symmetric homobinuclear complexes now a C_3 symmetric binuclear type I coordination compound is formed. The three ligands $\mathbf{5}$ are magnetically equivalent.

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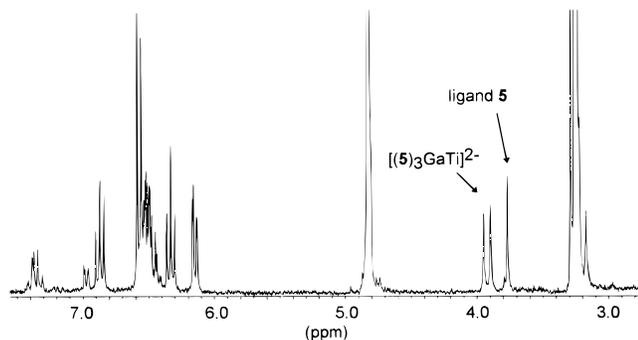


Figure 5. Formation of $K_2[(5)_3GaTi]$ in methanol- d_4 (1H NMR, 250 MHz) in the presence of an excess of $5 \cdot H_3$.

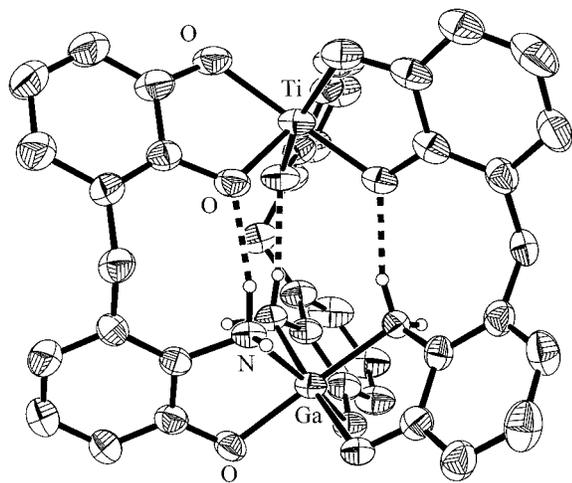


Figure 6. ORTEP diagram of $[(5)_3GaTi]^{2-}$ (only amine hydrogen atoms are shown).

Traces of a type II complex which can be detected in the crude product (Figures 2 and 3) are due to a slightly incorrect titanium to gallium ratio (for a spectrum with correct Ga:Ti ratio see Figure 5).

An additional experiment was performed with a non-stoichiometric ligand to metal ratio. Therefore a 1:1 mixture of titanium(IV) and gallium(III) was reacted with approximately 5 equiv of ligand **5**. The obtained 1H NMR spectroscopic results indicate that the self-assembly of $[(5)_3GaTi]^{2-}$ proceeds with positive cooperativity.¹⁶ Only signals of the heterobinuclear complex and of free ligand **5** can be measured in methanol- d_4 (Figure 5). No signals of mononuclear or homobinuclear metal complexes are observable.

Crystal Structure of $K_2[(5)_3GaTi] \cdot 6DMF \cdot Ether$. X-ray quality crystals of $K_2[(5)_3TiGa] \cdot 6DMF \cdot ether$ were obtained by slow diffusion of ether into a solution of the salt in DMF. The structural analysis shows that the bis-anionic heterobinuclear titanium/gallium complex contains one pseudo-octahedral tris(catecholate) titanium(IV) complex unit¹⁷ and one pseudo-octahedral tris(*o*-aminophenolate) gallium(III) moiety¹⁸ ($Ti \cdots Ga = 5.101 \text{ \AA}$). The latter adopts a facial geometry to enable the formation of defined molecular species. The two different complex units are connected by three methylene linkages. The X-ray structure (Figure 6) shows the same C_3 symmetry of the dianion that can be observed in solution. Thus, the three

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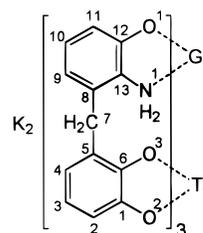


Figure 7. Atomic numbering scheme for $K_2[(5)_3GaTi]$.

sequential ligands **5** are orientated in one direction and a type I coordination compound is formed. Due to the presence of methylene groups as alkyl spacers the two chiral complex units show opposite configuration ($\Lambda\Delta$). This observation is in accordance with results of investigations on the stereochemistry of the metal-directed self-assembly of helicates and meso-helicates of alkyl-bridged bis(catecholate) ligands.^{11,12}

The stability of the supramolecular architecture of the anion $[(5)_3GaTi]^{2-}$ is further enhanced by hydrogen-bonding interactions of the NH_2 groups with internal oxygen atoms of the titanium(IV) tris(catecholate) unit ($N-H = 0.91 \text{ \AA}$; $H \cdots O = 1.94-1.98 \text{ \AA}$; $N-H \cdots O = 163-165^\circ$).¹⁹ Therefore no templating by alkali metal cations has to take place. The hydrogen bridges of $[(5)_3GaTi]^{2-}$ have a similar stabilizing function as the alkali metal counterions of the dinuclear titanium compound of a methylene-bridged bis(catecholate) ligand which is analogous to **5**.¹²

The potassium cations are exohedrally coordinated to the "ends" of the anionic binuclear complex ($K_2 \cdots Ga = 3.573(2) \text{ \AA}$; $K_1 \cdots Ti = 3.472(2) \text{ \AA}$) with six oxygen atoms (of the anion $[(5)_3GaTi]^{2-}$ and of DMF) coordinating to each of the K^+ ions (distorted octahedral coordination geometry). Four of the cations form a linear arrangement with $K \cdots K$ distances of $3.795(2)$ or $3.705(3) \text{ \AA}$. A part of this network is presented in Figure 8 showing the relative orientation of the anions $[(5)_3GaTi]^{2-}$ and the positions of the potassium cations.

Conclusions

In this paper we described a facile synthesis of the sequential ligand **5**, which possesses two electronically different binding sites. With titanium(IV) or gallium(III) ions this ligand spontaneously forms binuclear triple-stranded coordination compounds. In the homobinuclear complexes two of the three ligands are orientated in one and the third in the other direction (type II). If the metal-directed self-assembly process is performed with a mixture of titanium and gallium ions (1:1) another type of coordination compound is obtained. Now one of the binding sites of the ligand coordinates to one kind of metal ion and the second binding site to the other kind of metal. A C_3 symmetric complex (type I) is obtained in which all three sequential ligands are orientated in one direction. The X-ray structural analysis reveals that in the binuclear titanium/gallium complex the titanium only binds to catecholate units and the gallium only to aminophenolate moieties. The complex possesses a nonhelical pseudo-meso-type structure.

The discussed self-assembly processes cleanly lead to the formation of two different types of structures of coordination compounds (type I or type II complex). Thus, ligand **5** together with gallium and/or titanium ions represents an example of a programmed supramolecular system where different combinations of the same building blocks enable the selective self-

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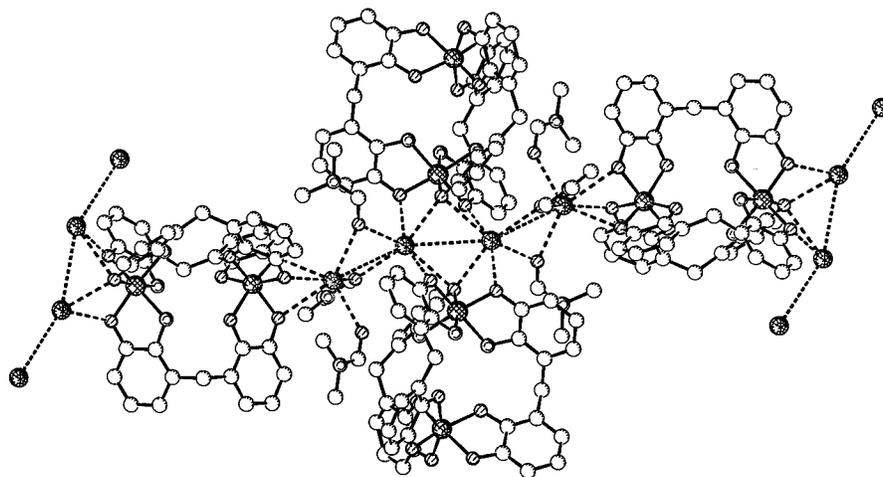


Figure 8. Representation of the polymeric network (SCHAKAL) of $K_2[(5)_3GaTi] \cdot 6DMF \cdot ether$ in the solid state.

Table 1. Selected Bond Length (\AA) and Angles (deg) for $K_2[(5)_3GaTi] \cdot 6DMF \cdot Ether$

	first ligand	second ligand	third ligand
Ga—O1	1.944(5)	1.954(5)	1.932(5)
Ga—N1	2.058(5)	2.098(5)	2.086(6)
Ti—O2	1.948(5)	1.951(5)	1.953(5)
Ti—O3	1.969(5)	1.968(5)	1.970(5)
N1—Ga—O1	83.5(2)	82.6(2)	83.4(2)
O2—Ti—O3	80.0(2)	80.0(2)	79.7(2)
C5—C7—C8	118.2(6)	117.1(6)	116.1(7)

assembly of two structurally different aggregates. This means that here two different supramolecular programs are available.²⁰

Experimental Section

General Remarks. 1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 500, AM 400, or WM 250 NMR spectrometer using DEPT techniques for the assignment of the multiplicity of carbon atoms. FT-IR spectra were recorded by diffuse reflection (KBr) or on NaCl plates on a Bruker IFS spectrometer. UV-vis spectra were recorded in methanol on a Perkin Elmer UV-vis Lambda 2 spectrometer. Mass spectra (EI, 70 eV or FAB(+/-), glycerine as matrix) were taken on a Finnigan MAT 90 mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer. Solvents were purified by standard methods. Melting points: Büchi 535 (uncorrected). Air-sensitive compounds were prepared and handled under Ar using Schlenk techniques.

(2,3-Dimethoxyphenyl)(2-nitro-3-methoxyphenyl)methanol (2). 2,3-Dimethoxybenzene (1.60 g, 11.6 mmol) and 1.6 mL of Tmeda (tetramethylethylenediamine) are dissolved in ether (30 mL) and 7.8 mL of a 1.6 M solution of *n*BuLi in hexane are added at room temperature.¹⁴ The mixture is stirred for 4 h, and solid 3-methoxy-2-nitrobenzaldehyde (**1**) (2.07 g, 11.4 mmol) is added in several portions. After the solution is stirred overnight, 6 N aqueous HCl is added and the phases are separated. The ether phase is dried ($MgSO_4$) and solvent is removed. Column chromatography (silica gel, CH_2Cl_2) affords 1.52 g (42%) of **2** as a yellow oil: 1H NMR ($CDCl_3$) δ 7.36 (t, $J = 8.2$ Hz, 1 H), 7.05 (t, $J = 8.0$ Hz, 1 H), 7.00–6.88 (m, 4 H), 6.11 (s, 1 H), 3.88 (s, 3 H), 3.86 (s, 3 H), 3.65 (s, 3 H), 3.10 (br, 1 H, OH); ^{13}C NMR ($CDCl_3$) δ 152.5 (C), 150.8 (C), 146.2 (C), 140.4 (C), 136.8 (C), 134.9 (C), 131.1 (CH), 124.0 (CH), 119.9 (CH), 119.4 (CH), 112.6 (CH), 111.7 (CH), 67.7 (CH), 60.4 (CH₃), 56.5 (CH₃), 55.8 (CH₃); IR (KBr) $\nu = 3418, 2940, 1839, 1534, 1480, 1281, 762$ cm^{-1} ; MS (EI, 70

eV) $m/z = 319$ (29%) $[M]^+$, 167 (95%), 84 (100%); HRMS ($C_{16}H_{17}NO_6$) calcd 319.1056, found 319.1041.

(2,3-Dimethoxyphenyl)(2-nitro-3-methoxyphenyl)methyl Acetate (3). The carbinol **2** (1.52 g, 4.76 mmol) is dissolved in 20 mL of acetic anhydride, and the mixture is heated overnight to 100 °C. Volatiles are removed in vacuo, and the residue is dissolved in CH_2Cl_2 . The solution is washed with saturated aqueous $NaHCO_3$ and dried ($MgSO_4$), and solvent is evaporated to yield 1.70 g (99%) of **3** as an off-white solid: mp 81–82 °C; 1H NMR ($CDCl_3$) δ 7.32 (t, $J = 8.2$ Hz, 1 H), 7.25 (s, 1 H), 7.05 (t, $J = 8.0$ Hz, 1 H), 6.97 (d, $J = 8.2$ Hz, 1 H), 6.90 (dd, $J = 8.2/1.4$ Hz, 1 H), 6.85 (dd, $J = 8.0/1.3$ Hz, 1 H), 6.81 (d, $J = 8.0$ Hz, 1 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 3.82 (s, 3 H), 2.11 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.3 (C), 152.6 (C), 151.0 (C), 146.6 (C), 140.2 (C), 132.8 (C), 131.7 (C), 130.7 (CH), 124.1 (CH), 120.3 (CH), 119.3 (CH), 112.8 (CH), 112.2 (CH), 68.1 (CH), 60.4 (CH₃), 56.5 (CH₃), 55.7 (CH₃), 20.6 (CH₃); IR (KBr) $\nu = 2942, 2840, 1748, 1535, 1482, 1371, 1281, 1226, 767$ cm^{-1} ; MS (EI, 70 eV) $m/z = 361$ (19%) $[M]^+$, 43 (100%); HRMS ($C_{18}H_{19}NO_7$) calcd 361.1162, found 361.1148. Elemental anal. Calcd for $C_{18}H_{19}NO_7$: C, 59.83; H, 5.30; N, 3.88. Found: C, 59.64; H, 5.28; N, 4.39.

(2,3-Dimethoxyphenyl)(2-amino-3-methoxyphenyl)methane (4). The acetate **3** (1.70 g, 4.71 mmol) is dissolved in ethyl acetate/methanol (3:1). Pd-C (480 mg) is added, and the mixture is stirred under a hydrogen atmosphere (50 bar) for 18 h. After filtration over silica gel, solvent is removed and the residue is applied to column chromatography (silica gel, CH_2Cl_2) to obtain 740 mg (58%) of **4** as a slightly red solid: mp 62 °C; 1H NMR ($CDCl_3$) δ 6.98 (t, $J = 7.9$ Hz, 1 H), 6.78 (m, 3 H), 6.71 (m, 2 H), 4.28 (br., 2 H), 3.92 (s, 2 H), 3.87 (s, 3 H), 3.86 (s, 3 H), 3.83 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 152.6 (C), 147.2 (C), 146.5 (C), 134.5 (C), 133.4 (C), 125.3 (C), 124.2 (CH), 122.7 (CH), 122.0 (CH), 117.2 (CH), 110.3 (CH), 108.4 (CH), 60.8 (CH₃), 55.6 (CH₃), 55.5 (CH₃), 31.1 (CH₂); IR (KBr) $\nu = 3473, 3375, 2937, 2835, 1619, 1583, 1482, 1277, 1083, 1008, 751, 736$ cm^{-1} ; MS (EI, 70 eV) $m/z = 273$ (3%) $[M]^+$, 196 (30%), 154 (100%), 139 (51%); HRMS ($C_{16}H_{19}NO_3$) calcd 273.1365, found 273.1348. Elemental anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.09; H, 7.14; N, 5.37.

(2,3-Dihydroxyphenyl)(2-amino-3-hydroxyphenyl)methane (5-H₃). At 0 °C, 1 M BBr_3/CH_2Cl_2 (13.7 mL) is added to amine **4** (725 mg, 2.66 mmol) in CH_2Cl_2 (20 mL). The mixture is allowed to warm to room temperature and stirred overnight. Methanol is added, and volatiles are removed in vacuo. The residue is dissolved in ether, washed with saturated aqueous $NaHCO_3$, and dried ($MgSO_4$), and solvent is evaporated to obtain 615 mg (98%) of **5-H₃** as a yellow hygroscopic foam: mp 39–41 °C; 1H NMR (methanol-*d*₄): δ 6.65–6.54 (m, 6 H), 3.84 (s, 2 H); ^{13}C NMR (methanol-*d*₄): δ 146.7 (C), 146.0 (C), 143.9 (C), 133.2 (C), 129.4 (C), 128.2 (C), 122.6 (CH), 122.0 (CH), 120.5 (CH), 120.1 (CH), 114.0 (CH), 113.4 (CH), 32.0 (CH₂); IR (KBr) $\nu = 3372, 2977, 1620, 1592, 1475, 1281, 744$ cm^{-1} ; MS (EI, 70 eV) $m/z = 231$ (100%) $[M]^+$, 109 (95%); HRMS ($C_{13}H_{13}NO_3$) calcd 231.0895, found 231.0907. Elemental anal. Calcd

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for $C_{13}H_{13}NO_3 \cdot 1/4H_2O$: C, 66.23; H, 5.77; N, 5.94. Found: C, 66.17; H, 5.62; N, 6.15.

K[(5)₃Ti₂]. A suspension of **5-H₃** (49 mg, 0.21 mmol), Ti(OMe)₄ (24 mg, 0.14 mmol), and K₂CO₃ (5.0 mg, 0.036 mmol) in methanol (20 mL) is stirred until a red solution is formed (4 days). Solvent is removed, and the residue is dried in vacuo to obtain 60 mg (93%) of K[(5)₃Ti₂] as a hygroscopic red solid: ¹H NMR (methanol-*d*₄) δ 7.01 (m, 2 H), 6.91 (m, 2 H), 6.76 (m, 3 H), 6.48 (m, 5 H), 6.45 (m, 2 H), 6.26 (m, 2 H), 6.19 (m, 2 H), 4.13 (d, *J* = 13.0 Hz, 1 H), 3.99 (d, *J* = 13.0 Hz, 1 H), 3.98 (d, *J* = 13.0 Hz, 1 H), 3.25 (m, 3 H); ¹³C NMR (methanol-*d*₄) δ 163.5 (C), 162.5 (C), 162.0 (C), 158.6 (C), 158.2 (C), 158.1 (C), 157.1 (C), 156.8 (C), 156.4 (C), 140.9 (C), 140.1 (C), 139.8 (C), 133.1 (C), 132.5 (C), 131.1 (C), 128.8 (CH), 128.6 (CH), 128.5 (CH), 127.2 (C), 126.3 (C), 126.1 (C), 124.3 (CH), 123.2 (CH), 123.0 (CH), 122.6 (CH), 122.3 (CH), 121.0 (CH), 120.0 (CH), 119.8 (CH), 119.6 (CH), 113.4 (CH), 113.0 (CH), 112.9 (CH), 111.5 (CH), 111.4 (CH), 111.2 (CH), 33.7 (CH₂), 33.2 (CH₂), 33.1 (CH₂); IR (KBr) ν = 3183, 3056, 1615, 1584, 1458, 1270, 1249, 746 cm⁻¹; UV-vis (methanol) λ = 198, 275, 344 nm; MS (FAB(-), glycerine) *m/z* = 780 [M - K]⁻. Elemental anal. Calcd for C₃₉H₃₀N₃Ti₂KO₉·6H₂O: C, 50.50; H, 4.56; N, 4.53. Found: C, 50.75; H, 4.47; N, 4.63.

Li[(5)₃Ti₂]: ¹H NMR (methanol-*d*₄) δ 7.04 (m, 2 H), 6.91 (m, 2 H), 6.78 (m, 3 H), 6.5–6.2 (br m, 9 H), 6.18 (m, 2 H), 4.13 (d, *J* = 13.0 Hz, 1 H), 3.99 (d, *J* = 13.1 Hz, 1 H), 3.98 (d, *J* = 13.0 Hz, 1 H), 3.26 (m, 3 H).

Li₃[(5)₃Ga₂]. Ligand **5-H₃** (107 mg, 0.45 mmol), Ga(NO₃)₃·9H₂O (125 mg, 0.30 mmol), and Li₂CO₃ (51 mg, 0.69 mmol) in methanol are stirred for 28 h. Solvent is evaporated and LiNO₃ is removed by extraction with THF to obtain 76 mg (50%) of Li₃[(5)₃Ga₂] as a beige hygroscopic solid: ¹H NMR (methanol-*d*₄) δ 6.85 (m, 2 H), 6.79 (t, *J* = 7.8 Hz, 1 H), 6.61 (d, *J* = 7.3 Hz, 1 H), 6.58–6.44 (m, 11 H), 6.27 (m, 3 H), 4.25 (d, *J* = 12.6 Hz, 1 H), 4.14 (d, *J* = 12.5 Hz, 1 H), 4.07 (d, *J* = 12.5 Hz, 1 H), 3.26 (m, 3 H); ¹³C NMR (methanol-*d*₄) δ 161.5 (C), 160.5 (C), 160.1 (C), 159.3 (C), 153.8 (C), 153.6 (C), 153.4 (C), 153.3 (C), 152.0 (C), 151.9 (C), 141.3 (C), 140.9 (C), 140.8 (C), 128.1 (CH), 128.0 (CH), 127.8 (C), 127.7 (CH), 127.5 (C), 126.4 (C), 126.2 (C), 125.8 (C), 119.2 (CH), 119.1 (CH), 118.8 (CH), 117.8 (CH), 117.6 (CH), 116.9 (CH), 116.4 (CH, double intensity), 115.7 (CH), 114.9 (CH), 114.7 (CH), 114.4 (CH), 112.7 (CH), 112.5 (CH), 112.4 (CH), 35.5 (CH₂), 35.1 (CH₂), 35.0 (CH₂); IR (KBr): ν = 3269, 3057, 1463, 1256, 743 cm⁻¹; MS (FAB(+), glycerine) *m/z* = 846 [M + H]⁺, 852 [M + Li]⁺. Elemental anal. Calcd for C₃₉H₃₀N₃Ga₂Li₃O₉·10H₂O: C, 45.70; H, 4.92; N, 4.10. Found: C, 45.39; H, 4.61; N, 3.80.

Na₃[(5)₃Ga₂]: ¹H NMR (methanol-*d*₄) δ 6.87–6.75 (br m, 4 H), 6.60–6.43 (m, 11 H), 6.30 (m, 3 H), 4.23 (d, *J* = 12.6 Hz, 1 H), 4.15 (d, *J* = 12.6 Hz, 1 H), 4.09 (d, *J* = 12.5 Hz, 1 H), 3.22 (m, 3 H).

K₃[(5)₃Ga₂]: ¹H NMR (methanol-*d*₄) δ 6.86–6.74 (br m, 4 H), 6.60–6.42 (m, 11 H), 6.29 (m, 3 H), 4.24 (d, *J* = 12.7 Hz, 1 H), 4.14 (d, *J* = 12.6 Hz, 1 H), 4.08 (d, *J* = 12.5 Hz, 1 H), 3.15 (m, 3 H).

K₂[(5)₃GaTi]. A mixture of ligand **5-H₃** (52 mg, 0.22 mmol), Ti(OMe)₄ (12 mg, 0.070 mmol), Ga(NO₃)₃·9H₂O (31 mg, 0.075 mmol), and K₂CO₃ (26 mg, 0.188 mmol) is stirred for 4 days in methanol. Solvent is removed, and the residue is purified by chromatography (Sephadex LH-20, methanol) to obtain 53 mg (73%) of K₂[(5)₃GaTi] as a red hygroscopic solid: ¹H NMR (methanol-*d*₄) δ 6.93 (t, *J* = 7.9

Hz, 3 H), 6.63 (d, *J* = 7.9 Hz, 6 H), 6.57 (dd, *J* = 7.7/1.5 Hz, 3 H), 6.40 (t, *J* = 7.7 Hz, 3 H), 6.21 (dd, *J* = 7.7/1.5 Hz, 3 H), 3.97 (d, *J* = 12.9 Hz, 3 H), 3.26 (d, *J* = 12.9 Hz, 3 H); ¹³C NMR (methanol-*d*₄) δ 159.8 (C), 158.9 (C), 156.5 (C), 140.3 (C), 128.6 (CH), 125.9 (C), 125.4 (C), 121.0 (CH), 119.2 (CH), 118.0 (CH), 115.1 (CH), 111.4 (CH), 34.6 (CH₂); IR (KBr) ν = 3275, 3051, 1610, 1583, 1295, 1271, 1252, 744 cm⁻¹; UV (methanol) λ = 200, 282, 380 nm; MS (FAB(-), glycerine) *m/z* = 840 [M - K]⁻. Elemental anal. Calcd for C₃₉H₃₀N₃TiGaK₂O₉·6H₂O: C, 47.38; H, 4.28; N, 4.25. Found: C, 47.63; H, 4.47; N, 4.24.

Li₂[(5)₃GaTi]: ¹H NMR (methanol-*d*₄) δ 6.95 (t, *J* = 7.6 Hz, 3 H), 6.65 (dd, *J* = 7.6 Hz, 6 H), 6.57 (dd, *J* = 7.6/1.2 Hz, 3 H), 6.40 (pseudo t, *J* = 7.6 Hz, 3 H), 6.21 (dd, *J* = 7.6/1.2 Hz, 3 H), 3.98 (d, *J* = 12.8 Hz, 3 H), 3.25 (d, *J* = 12.8 Hz, 3 H); ¹³C NMR (methanol-*d*₄) δ 159.4, 158.7, 156.3, 140.3, 128.5, 125.6, 125.3, 122.2, 119.7, 119.0, 115.0, 111.3, 34.5.

Na₂[(5)₃GaTi]: ¹H NMR (methanol-*d*₄) δ 6.95 (t, *J* = 8.3 Hz, 3 H), 6.65 (d, *J* = 8.2 Hz, 6 H), 6.58 (dd, *J* = 7.7/1.5 Hz, 3 H), 6.40 (pseudo t, *J* = 7.7 Hz, 3 H), 6.22 (dd, *J* = 7.6/1.2 Hz, 3 H), 3.96 (d, *J* = 13.1 Hz, 3 H), 3.27 (d, *J* = 13.1 Hz, 3 H); ¹³C NMR (methanol-*d*₄) δ 159.5, 158.8, 156.2, 140.1, 128.5, 125.6, 125.3, 122.2, 119.7, 119.0, 115.1, 111.4, 34.4.

X-ray Structural Analysis of K₂[(5)₃GaTi]·6DMF·Ether. X-ray quality crystals of K₂[(5)₃TiGa]·6DMF·ether were obtained by slow diffusion of ether in a DMF solution of K₂[(5)₃TiGa]. Crystal data for K₂[(5)₃TiGa]·6DMF·ether: formula C₆₁H₈₂N₉O₁₆GaTiK₂, formula weight 1393.18, red blocks (0.5 × 0.4 × 0.3 mm³), monoclinic space group *P*2₁/*c* (No. 14); *a* = 12.868(3) Å, *b* = 19.902(2) Å, *c* = 27.063(2) Å, β = 102.22(1)°, *V* = 6774(2) Å³, *Z* = 4, *F*(000) = 2920, *T* = 223 K, ρ_{calcd} = 1.366 g cm⁻³, μ = 7.09 cm⁻¹, empirical absorption correction from ψ scans (C_{min}/C_{max} = 0.901/0.999), Enraf-Nonius MACH3 diffractometer, λ = 0.710 73 Å, ω/2θ scans, 9642 reflections measured (-*h*, +*k*, ±*l*), 2θ_{max} = 45.5°, 9163 independent and 5723 observed [*I* ≥ 2σ(*I*)], 765 refined parameters, *R* = 0.071, *wR*² = 0.187; the largest peaks in the residual electron density map [max 1.71(-1.35) e Å⁻³] were located near the disordered solvent molecules. The structure was solved by direct methods (SHELXS-86) and refined against *F*² (SHELXL-93); hydrogens were introduced in their calculated positions and refined isotropically as riding atoms. Two of the three DMF molecules not located in the K coordination are disordered. The molecules were refined by using geometric and thermal restraints where the non-disordered one served as a structural model.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie (Liebig Stipendium for M.A.) and the Deutsche Forschungsgemeinschaft.

Supporting Information Available: X-ray crystallographic data for K₂[(5)₃GaTi]·6DMF·ether, including tables of positional parameters, anisotropic thermal parameters, and bond distances and angles (14 pages). See any current masthead page for ordering and Internet access instructions.

JA963265F