DOI: 10.1002/ejoc.201101725

Supramolecular $[M_4L_4]$ Tetrahedra Based on Triangular Acylhydrazone Catechol Ligands

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Keywords: Cage compounds / Ligand design / Self-assembly / Gallium / Titanium / Hydrazones

The ligands **1**-H_6 and **2**-H_6 are prepared by condensation of the triangular triamines **5** and 2,3-dihydroxybenzoic acid hydrazide **7**. The ligands form container-type tetrahedral coordination compounds M_x [(**1** or **2**)$_4$M′$_4$] (M = Li, Na, K; M′ = Ti, x = 8; M′ = Ga, x = 12). The complexes are characterized by NMR spectroscopy and ESI mass spectrometry. Despite the relatively labile acyl hydrazone unit, the complexes show high stability in water. Ligand **3**-H_6 is prepared from the trisacyl hydrazide **8** and 2,3-dihydroxybenzaldehyde **9** but does not form well-defined coordination compounds with gallium(III) or titanium(IV) ions.

Introduction

Container molecules are of immerging importance due to their ability to form inclusion complexes in which highly reactive species are stabilized or chemical reactions are catalyzed. Molecular containers are formed either through covalent approaches or can be obtained by noncovalent self-assembly through hydrogen bonding or metal coordination. The latter approach, especially, results in easily accessible, stable compounds.[1] Spectacular examples in this field are the cages described by Fujita[2] or the $[M_4L_6]$ tetrahedron described by Raymond, which is formed from six biscatechol ligands and four gallium(III) ions.[3]

An efficient approach to $[M_4L_4]$ metallosupramolecular tetrahedra is the coordination of four triangular ligands to four metal centers. The ligands span the faces of the tetrahedron while the metals are located on the corners of the polyhedron (Figure 1). This approach was first exemplified by use of the ligands **A**–**C** (Figure 2). However, the obtained compounds did not provide an internal cavity with which to encapsulate guests.[4] Thus, ligand **D** was designed. This compound forms a very large tetrahedron that accommodates different guest species in its interior. The connecting imine units are easily formed by condensation of an aldehyde with an amine, but their instability in protic solvents limits the use of ligand **D**.[5]

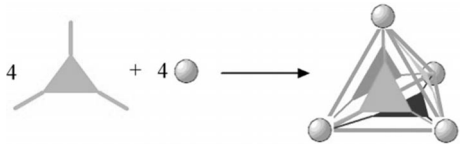

Figure 1. Self assembly of $[M_4L_4]$ supramolecular tetrahedra from triangular ligands and appropriate metal ions.

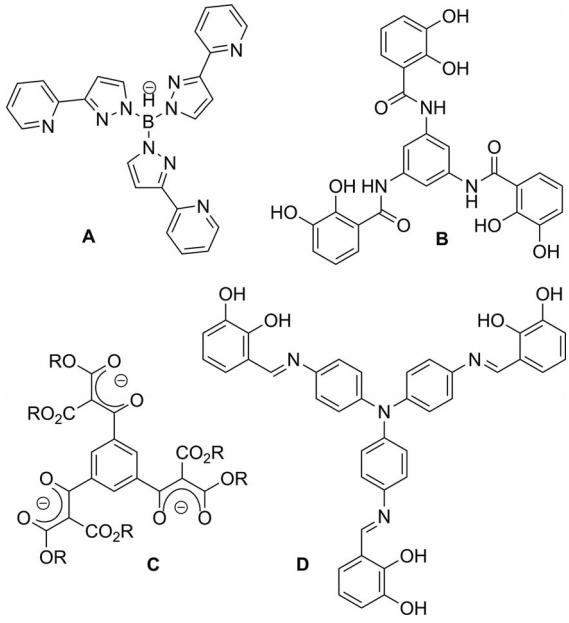

Figure 2. Triangular ligands that form $[M_4L_4]$ supramolecular tetrahedra.

Different approaches can be envisaged to obtain more stable ligands.[6] In this study, the imine unit of **D** has been substituted and the related acyl hydrazone connected triscatechol ligands were prepared.[7] The preparation of the ligands **1**-H_6–**3**-H_6 (Figure 3) and their coordination chem-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201101725.

istry with titanium(IV) and gallium(III) ions is described. The molecular tetrahedra obtained are characterized by NMR spectroscopy as well as ESI mass spectrometry.

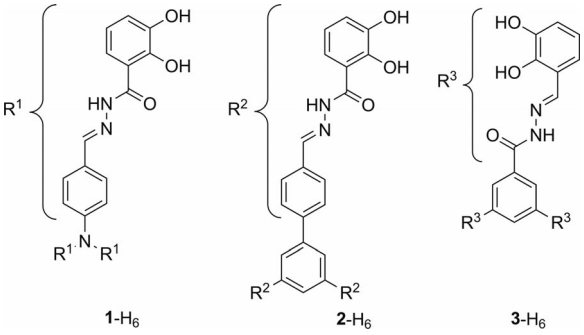


Figure 3. Ligands synthesized in this study. Only one of the catechol bearing acylhydrazone side arms connected to the C_3 symmetric central nitrogen (**1**-H_6) or arene (**2**-H_6, **3**-H_6) unit is shown.

Results and Discussion

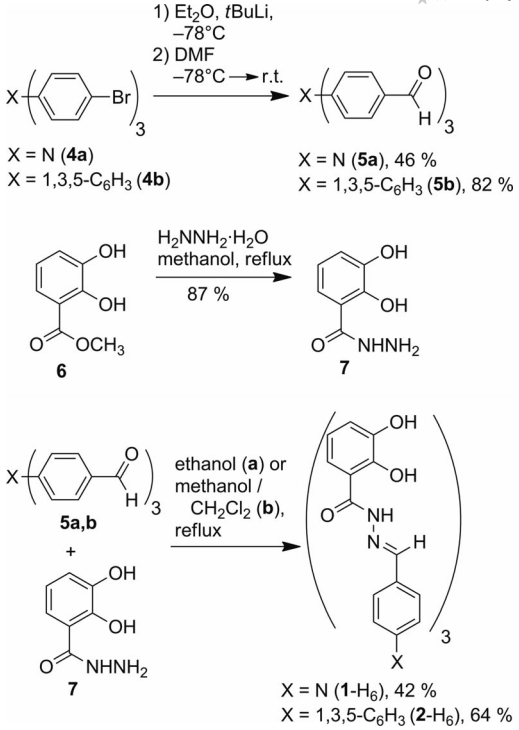
Preparation of Ligands 1-H_6, 2-H_6 and 3-H_6

In **1**-H_6 a central amine bearing the three side-chains terminated by catechol units introduces the idealized C_3 symmetry. In **2**-H_6 and **3**-H_6, 1,3,5-substituted arenes act as a C_3-symmetric backbone. Ligands **1**-H_6 and **2**-H_6 are based on acyl hydrazones formed from the hydrazide of 2,3-dihydroxybenzoic acid and a central triangular trisaldehyde. In **3**-H_6 the situation is reversed, with the acyl unit connected to the central backbone and the hydrazone bound to the catechol.

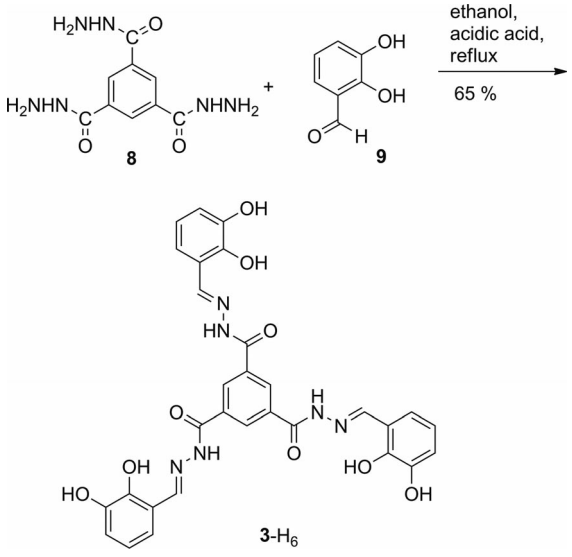
For the hydrazone condensation to obtain ligands **1**-H_6 and **2**-H_6, building blocks **5a**, **5b** and **7** were required. The trisaldehydes **5a** and **5b** were obtained by halogen–metal exchange of the corresponding bromides **4a** and **4b** using *t*BuLi in diethyl ether at –78 °C. The intermediate organometallic species were quenched with *N*,*N*-dimethylformamide (DMF) to give the desired derivatives in 46 (**5a**) or 82% (**5b**) yield, respectively.[8] Reaction of methyl 2,3-dihydroxybenzoate (**6**) with hydrazine hydrate in methanol resulted in the formation of acylhydrazine **7** in 87% yield. Due to precipitation of the product, the selection of appropriate solvents in the final condensation step was crucial for success. The amine-based ligand **1**-H_6 was obtained from ethanol in 42%, whereas **2**-H_6 formed in methanol/dichloromethane in 64% (Scheme 1).

The obtained compounds were characterized by standard techniques. For example, **1**-H_6 gave rise to the expected, characteristic signals in its ^{1}H NMR spectrum (recorded in [D_6]DMSO).

The synthesis of ligand **3**-H_6 is depicted in Scheme 2. 1,3,5-Benzenetricarboxylic acid could be easily transformed into the ester and subsequently into hydrazide **8**,[9] which was condensed with 2,3-dihydroxybenzaldehyde **9** to form trishydrazone **3**-H_6 in 65% yield. The reaction was performed in ethanol containing traces of acetic acid. Derivative **3**-H_6 gave rise to a characteristic ^{1}H NMR spectrum.



Scheme 1. Preparation of ligands **1**-H_6 and **2**-H_6.

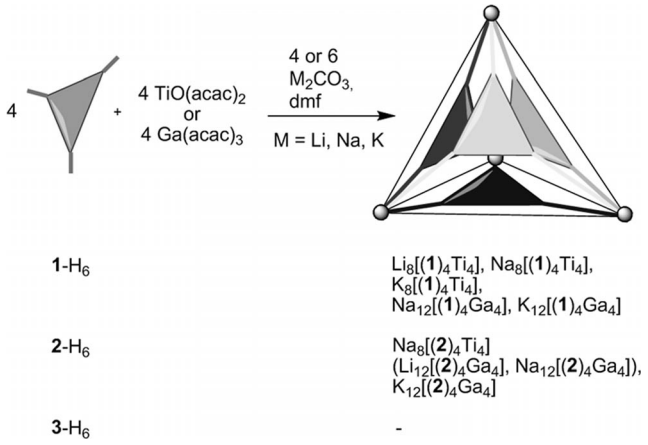


Scheme 2. Preparation of ligands **3**-H_6.

Coordination Studies to Obtain Metallosupramolecular Tetrahedra of 1-H_6, 2-H_6 and 3-H_6 with Titanium(IV) and Gallium(III) Ions

Coordination compounds of ligands **1**-H_6–**3**-H_6 were prepared either from 1:1:1 mixtures of the ligand, titanoyl bisacetylacetonate [TiO(acac)$_2$] and alkali metal carbonate, or from 1:1:1.5 mixtures of ligand, gallium trisacetylacetonate [Ga(acac)$_3$] and alkali metal carbonate in DMF as solvent (Scheme 3). During the reaction, the colour of the solution turned red (Ti) or yellow (Ga), indicating the formation of complexes. With ligands **1**-H_6 and **2**-H_6, the de-

sired $[M_4L_4]$ complexes could be isolated, with the exception of $Li_{12}[(\mathbf{1})_4Ga_4]$ and $Li_8[(\mathbf{2})_4Ti_4]$. The latter are probably minor components within a complex mixture of species. Complexes $Li_{12}[(\mathbf{2})_4Ga_4]$ and $Na_{12}[(\mathbf{2})_4Ga_4]$ could be characterized by spectroscopic techniques, but were not obtained in analytically pure form. It has to be mentioned that, due to the large cavities, all complexes contained large amounts of solvents. Rigorous drying resulted in decomposition (probably oligomerization) of the cages and only insoluble materials were obtained. The high content of solvent in the crystal was certainly a drawback in obtaining X-ray crystal structures. Although nice single crystals were obtained, we were not able to record sufficient numbers of reflections for the solution of a structure. Ligand **3**-H_6 did not afford characterizable derivatives. In this case, probably polymeric or oligomeric compounds were formed.



Scheme 3. Self-assembly of $[M_4L_4]$ tetrahedra.

Figure 4 shows the ^{1}H NMR spectra of ligand **1** and of its titanium(IV) complexes in $[D_6]$DMSO. All signals are significantly shifted upon coordination of titanium(IV), whereas no remarkable differences are found in the spectra obtained with different alkali metal counterions. The downfield shifting of the hydrazone CONH-signal is indicative for formation of a hydrogen bond to the internal oxygen atom of the titanium coordinated catechols.

ESI MS is a powerful tool to reveal the composition of charged supramolecular aggregates.[10] A representative example the spectrum of $Li_8[(\mathbf{1})_4Ti_4]$ in methanol is shown in Figure 5. The dominating peaks at m/z = 822.7 and 1097.2 are assigned to $\{H_4[(\mathbf{1})_4Ti_4]\}^{4-}$ and $\{H_5[(\mathbf{1})_4Ti_4]\}^{3-}$, respectively. The sodium $Na_8[(\mathbf{1})_4Ti_4]$ and the potassium salt $K_8[(\mathbf{1})_4Ti_4]$ also show characteristic signals in their ESI MS spectra.

Similar results to those obtained for titanium(IV) were obtained with gallium(III). As a representative example, the ^{1}H NMR spectrum of $Na_{12}[(\mathbf{1})_4Ga_4]$ and the free ligand are compared in Figure 6. Again, a characteristic shift of the NH resonance to higher ppm values is observed due to the intramolecular hydrogen bond. The corresponding potassium salt $K_{12}[(\mathbf{1})_4Ga_4]$ leads to a very similar spectrum.

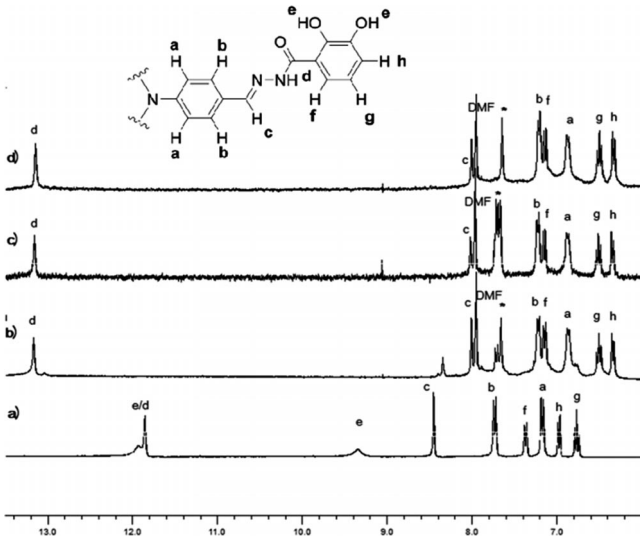


Figure 4. ^{1}H NMR spectra of **1**-H_6 (a) and $M_8[(\mathbf{1})_4Ti_4]$ with M = Li (b), Na (c) or K (d) in $[D_6]$DMSO.

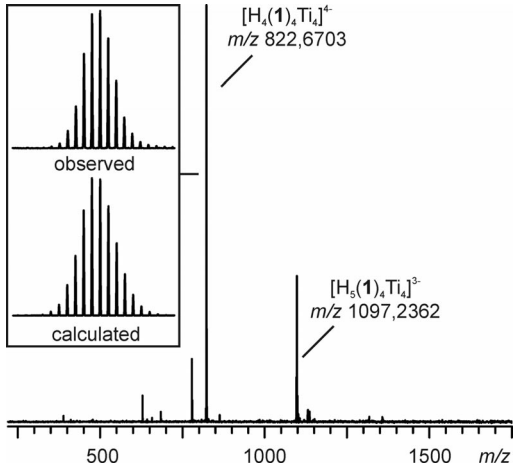


Figure 5. ESI MS of $Li_8[(\mathbf{1})_4Ti_4]$.

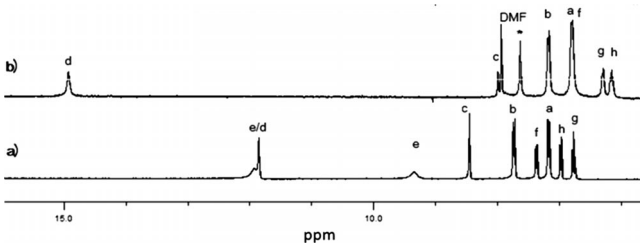


Figure 6. ^{1}H NMR spectra of **1**-H_6 (a) and $Na_{12}[(\mathbf{1})_4Ga_4]$ (b) in $[D_6]$DMSO.

Negative ESI MS sprayed from methanol reveals characteristic signals for the tetrahedral tetranuclear metal complexes, for example, at m/z = 1134.7 $\{H_8Na[(\mathbf{1})_4Ga_4]\}^{3-}$ and 1127.2 $\{H_9[(\mathbf{1})_4Ga_4]\}^{3-}$. In addition, peaks are detected that indicate that methanol is strongly attached to the container (e.g., m/z = 1152.7 $\{H_7Na_2[(\mathbf{1})_4Ga_4]MeOH\}^{3-}$). The solvent molecules are probably encapsulated in the interior of the cavity.

The coordination studies with ligand **2**-H_6 resulted in the formation of related titanium(IV) or gallium(III) metallosupramolecular tetrahedra that were characterized by ^{1}H NMR and ESI MS analyses. As a representative example, the ^{1}H NMR spectrum of $Na_8[(\mathbf{2})_4Ti_4]$ is compared to the corresponding ligand spectrum in Figure 7 (due to different solubility of the compounds the spectra were recorded in different solvents). Again, a downfield shift of the NH proton is observed due to intramolecular hydrogen-bonding.

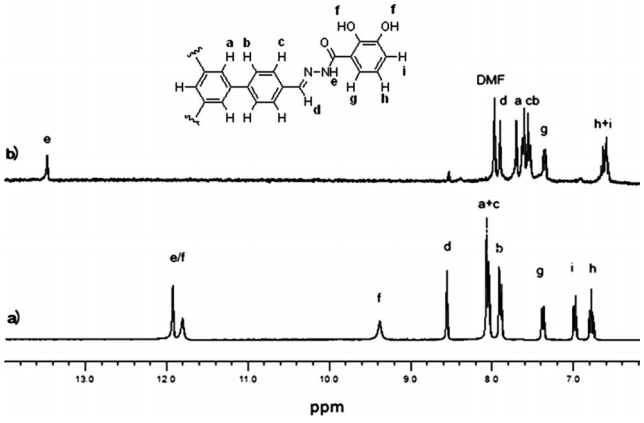


Figure 7. ^{1}H NMR spectra of **2**-H_6 in [D_6]DMSO (a) and $Na_8[(\mathbf{2})_4Ti_4]$ in CD_3OD (b).

The composition of the complexes is again revealed by ESI MS studies (methanol); for example, characteristic peaks are observed at m/z = 905.63 $\{Na_4[(\mathbf{2})_4Ti_4]\}^{4-}$, 917.5 $\{H_6Li_2[(\mathbf{2})_4Ga_4](MeOH)_4\}^{4-}$, or 941.55 $\{H_3Na_5[(\mathbf{2})_4Ga_4](MeOH)\}^{4-}$.

The water stability of the tetrahedral complexes of ligand **1** and **2** with titanium(IV) or gallium(III) was tested. To this end, the complexes were dissolved in D_2O and ^{1}H NMR spectra were measured. Well-resolved resonances of the container molecules were obtained (Figure 8 shows as representative example the spectra of $K_8[(\mathbf{2})_4Ga_4]$). The measurement of the sample was frequently repeated over the time period of one week and no change in the spectra was observed. This experiment demonstrates the long-term stability of the complexes in water at ambient temperature.

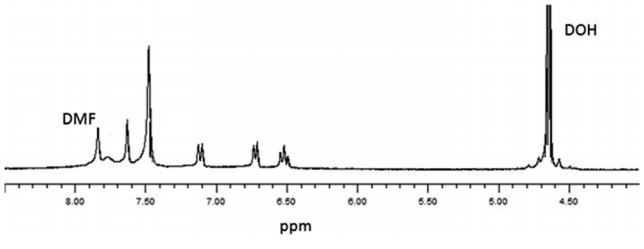


Figure 8. ^{1}H NMR spectrum of $K_8[(\mathbf{2})_4Ga_4]$ in D_2O.

Conclusions

In this study, the preparation of triangular triscatechol ligands based on acylhydrazone linkages was described. The ligands are readily available, however, only ligands **1**-H_6 and **2**-H_6 are good candidates for the self-assembly of metallosupramoecular tetrahedra. According to our design, ligands **1**-H_6 and **2**-H_6 form the corresponding complexes $M_x[(\mathbf{1/2})_4(Ti/Ga)_4]$, which can be characterized by NMR and ESI MS analyses . MS as well as elemental analyses show that the containers are able to uptake solvent molecules. Unfortunately, so far it was not been possible to observe the inclusion of added guest species, but the described results indicate that the containers are filled with solvent molecules and probably with counter cations. The compounds show high stability in water. Use of ligand **3**-H_6 does not result in tetrahedral coordination compounds. In this case, as a working hypothesis, we assume that repulsion between the lone pair of the hydrazone nitrogen atom and of the coordinated catechol oxygen atom prevents formation of the desired complexes.

The introduction of hydrazone linkages in this chemistry paves the way to ligands that are easily generated and that lead to complexes with high stability even in water.

Experimental Section

General: NMR spectra were recorded with a Varian Mercury 300 spectrometer. FTIR spectra were recorded with a Bruker IFS spectrometer. Mass spectra were recorded with a Thermo Deca XP mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyser. Compounds **4a**, **4b**,[8] and **8**[9] were prepared following literature procedures.

General Procedure for the Preparation of Aldehydes 5a and 5b: A solution of *t*BuLi (1.5 M in pentane, 12.5 mL, 6 equiv.) was added dropwise to a solution of bromide **4a** or **4b** (3 mmol, 1 equiv.) in anhydrous solvent (**a**: diethyl ether; **b**: THF; 30 mL) precooled to –78 °C under N_2. The reaction mixture was stirred at this temperature for 1 h followed by dropwise addition of anhydrous DMF (1.4 mL, 6 equiv.). The reaction suspension was allowed to reach room temperature and stirred for 2 h. The reaction was quenched by the slow addition of saturated NH_4Cl. After evaporation of organic solvent, the aqueous phase was exacted with dichloromethane (3×20 mL). The combined organic extracts were dried (Na_2SO_4), evaporated to dryness and purified by silica column chromatography (**5a**: hexane/ethyl acetate, 1:1; **5b**: dichloromethane/ethyl acetate, 10:1) to obtain **5a** (46%) or **5b** (82%) as white solids.

Compound 5a: ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 9.94 (s, 3 H), 7.91 (AA′BB′, J = 8.7 Hz, 6 H), 7.28 (AA′BB′, J = 8.7 Hz, 6 H) ppm. MS (EI, 70 eV): m/z (%) = 329.1 (100) $[M]^+$.[8]

Compound 5b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.04 (s, 3 H), 7.96 (AA′BB′, J = 8.4 Hz, 6 H), 7.84 (s, 3 H), 7.81 (AA′BB′, J = 8.4 Hz, 6 H) ppm.[8]

Synthesis of 7: Ester **6** (345 mg, 2 mmol) was dissolved in methanol (30 mL), and 98% hydrazine solution (0.4 mL, 8 mmol) was added to the reaction mixture, which was heated to reflux overnight. The mixture was concentrated and EtOAc was added. After storage in a refrigerator for 3 d, a white precipitate was obtained that was filtered and dried under vacuum; yield 269 mg (1.6 mmol, 78%). ^{1}H NMR (300 MHz, CD_3OD): δ = 7.18 (dd, J = 7.9, 1.5 Hz, 1 H), 6.91 (dd, J = 7.9, 1.5 Hz, 1 H), 6.70 (t, J = 7.9 Hz, 1 H) ppm. MS (EI, 70 eV): m/z (%) = 168.1 (25.7) $[M]^+$.

Synthesis of 1-H_6: Compounds **7** (164 mg, 0.99 mmol) and **5a** (80 mg, 0.24 mmol) were dissolved in ethanol (90 mL) and heated to reflux for 7 d. The solvent was evaporated and the residue was heated to reflux in methanol for 1 h. The product **1**-H_6 was collected by filtration; yield 76.8 mg (0.10 mmol, 42%); m.p. 245 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 11.93 (s, 3 H), 11.84 (s, 3 H), 9.34 (s, 3 H), 8.45 (s, 3 H), 7.73 (d, J = 8.4 Hz, 6 H), 7.37 (d, J = 7.5 Hz, 3 H), 7.17 (d, J = 8.4 Hz, 6 H), 6.97 (d, J = 7.5 Hz, 3 H), 6.78 (t, J = 7.5 Hz, 3 H) ppm. MS (ESI$^-$): m/z = 778.13 [M – H]$^-$. IR (KBr): $\tilde{\nu}$ = 3234, 3068, 1639, 1591, 1501, 1456, 1318, 1263, 1169, 1078, 987, 962, 939, 836, 800, 737 cm^{-1}. $C_{42}H_{33}N_7O_9 \cdot 3H_2O$: C 60.50, H 4.71, N 11.76; found C 60.77, H 4.50, N 11.76.

Synthesis of 2-H_6: To a solution of hydrazide **7** (90 mg, 0.53 mmol) in methanol (20 mL) was added a solution of aldehyde **5b** (52 mg, 0.13 mmol). The mixture was heated to reflux for 2 d and then cooled to room temperature. From the resulting suspension, a white precipitate formed slowly during the next two weeks that was filtered and dried under vacuum; yield 71 mg (0.08 mmol, 64%); m.p. 226. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 11.94 (s, 3 H), 11.82 (s, 3 H), 9.39 (s, 3 H), 8.56 (s, 3 H), 8.08 (m, 9 H), 7.91 (m, 6 H), 7.38 (d, J = 7.8 Hz, 3 H), 6.99 (d, J = 7.8 Hz, 3 H), 6.78 (t, J = 7.8 Hz, 3 H) ppm. MS (ESI$^-$): m/z = 839.1 [M – H]$^+$. IR (KBr): $\tilde{\nu}$ = 3426, 3261, 3033, 2322, 2106, 1640, 1597, 1545, 1456, 1369, 1317, 1229, 1159, 1075, 1018, 983, 940, 880, 822, 798, 735 cm^{-1}. $C_{48}H_{36}N_6O_9 \cdot 2H_2O$: C 65.75, H 4.60, N 9.58; found C 65.82, H 4.47, N 9.51.

Synthesis of 3-H_6: 1,3,5-Benzenetricarbohydrazide **8** (504 mg, 2.0 mmol) and 2,3-dihydroxybenzaldehyde **9** (912 mg, 6.6 mmol) were dissolved in ethanol (150 mL). After addition of acetic acid (ca. 1 mL) the mixture was heated at reflux for 24 h. The white precipitate was filtered, washed with ethanol and dried in vacuo. Ligand **3**-H_6 (787 mg, 1.3 mmol, 65%) was obtained as a white powder. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 12.42 (s, 3 H), 10.97 (s, 3 H), 9.27 (s, 3 H), 8.71 (s, 3 H), 8.64 (s, 3 H), 7.00 (dd, J = 7.7, 1.2 Hz, 3 H), 6.86 (dd, J = 7.7, 1.2 Hz, 3 H), 6.74 (t, J = 7.7 Hz, 3 H) ppm. ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 162.0 (C), 149.5 (CH), 146.1 (C), 145.7 (C), 133.7 (C), 130.1 (CH), 119.9 (CH), 119.3 (CH), 118.9 (C), 117.6 (CH) ppm. MS (ESI$^-$): m/z = 610.99 [M – H]$^-$.

General Procedure for the Preparation of Titanium(IV) Complexes: Ligand (1 equiv.), [TiO(acac)$_2$] (1 equiv.) and M_2CO_3 (M = Na, K, Li; 1 equiv.) were dissolved in DMF (50 mL) and stirred overnight. After evaporation of the solvent a red solid was obtained.

Li_8[(1)$_4$Ti$_4$]: Yield quant. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 13.16 (s, 12 H), 8.00 (s, 12 H), 7.22 (d, J = 7.0 Hz, 24 H), 7.14 (d, J = 7.7 Hz, 12 H), 6.87 (d, J = 7.0 Hz, 24 H), 6.54 (t, J = 7.7 Hz, 12 H), 6.34 (d, J = 7.7 Hz, 12 H) ppm. MS (ESI$^-$): m/z = 822.67 {H$_4$[(**1**)$_4$Ti$_4$]}$^{4-}$, 1097.24 {H$_5$[(**1**)$_4$Ti$_4$]}$^{3-}$. IR (KBr): $\tilde{\nu}$ = 3284, 3062, 2972, 2934, 1653, 1591, 1546, 1500, 1465, 1439, 1382, 1321, 1280, 1215, 1176, 1150, 1077, 1055, 1009, 955, 935, 885, 851, 815, 742, 672 cm^{-1}. $C_{168}H_{108}N_{28}O_{36}Ti_4Na_8 \cdot 14DMF \cdot 17H_2O$: C 53.99, H 5.18, N 12.59; found C 54.15, H 5.51, N 12.24.

Na_8[(1)$_4$Ti$_4$]: Yield quant. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 13.14 (s, 12 H), 7.95 (s, 12 H), 7.21 (d, J = 7.5 Hz, 24 H), 7.14 (d, J = 7.9 Hz, 12 H), 6.86 (d, J = 7.5 Hz, 24 H), 6.50 (t, J = 7.9 Hz, 12 H), 6.33 (d, J = 7.9 Hz, 12 H) ppm. MS (ESI$^-$): m/z = 1097.24 {H$_5$[(**1**)$_4$Ti$_4$]}$^{3-}$, 1104.16 {H$_4$Na[(**1**)$_4$Ti$_4$]}$^{3-}$, 1130.55 {H$_2$Na$_3$[(**1**)$_4$Ti$_4$](H$_2$O)$_2$}$^{3-}$, 1135.87 {H$_2$Na$_2$K[(**1**)$_4$Ti$_4$](H$_2$O)$_2$}$^{3-}$, 1746.84 {H$_3$Na$_3$[(**1**)$_4$Ti$_4$](MeOH)$_2$(H$_2$O)$_4$}$^{2-}$, 1754.83 {H$_3$Na$_2$K[(**1**)$_4$Ti$_4$](MeOH)$_2$(H$_2$O)$_4$}$^{2-}$. IR (KBr): $\tilde{\nu}$ = 3290, 2932, 1652, 1592, 1547, 1501, 1464, 1439, 1384, 1323, 1281, 1247, 1215, 1177, 1146, 1078, 1054, 1008, 955, 933, 886, 852, 815, 743, 671 cm^{-1}. $C_{168}H_{108}N_{28}O_{36}Ti_4Na_8 \cdot 12DMF \cdot 16H_2O$: C 52.86, H 4.87, N 12.09; found C 52.94, H 5.36, N 12.05.

K_8[(1)$_4$Ti$_4$]: Yield quant. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 13.14 (s, 12 H), 8.00 (s, 12 H), 7.20 (d, J = 7.2 Hz, 24 H), 7.13 (d, J = 7.8 Hz, 12 H), 6.87 (d, J = 7.2 Hz, 24 H), 6.49 (t, J = 7.8 Hz, 12 H), 6.32 (d, J = 7.8 Hz, 12 H) ppm. MS (ESI$^-$): m/z = 886.5 {K$_4$[(**1**)$_4$Ti$_4$](MeOH)(H$_2$O)$_4$}$^{4-}$. IR (KBr): $\tilde{\nu}$ = 3396, 2975, 2881, 1650, 1592, 1548, 1500, 1464, 1438, 1383, 1322, 1281, 1245, 1213, 1177, 1148, 1076, 1054, 1007, 955, 933, 885, 852, 814, 742, 670 cm^{-1}. $C_{168}H_{108}N_{28}O_{36}Ti_4K_8 \cdot 9DMF \cdot 27H_2O$: C 49.38, H 4.78, N 10.93; found C 49.39, H 4.73, N 10.97.

Na_8[(2)$_4$Ti$_4$]: Yield quant. ^{1}H NMR (300 MHz, CD$_3$OD): δ = 13.48 (s, 12 H), 7.91 (s, 12 H), 7.71 (s, 12 H), 7.62 (d, J = 7.9 Hz, 24 H), 7.55 (d, J = 7.9 Hz, 24 H), 7.36 (m, 12 H), 6.62 (m, 24 H) ppm. ^{1}H NMR (300 MHz, D$_2$O): δ = 7.99 (s, 12 H), 7.91 (s, 12 H), 7.65 (m, 48 H), 7.44 (d, J = 8.1 Hz, 12 H), 6.89 (t, J = 8.1 Hz, 12 H), 6.79 (d, J = 8.1 Hz, 12 H) ppm. MS (ESI$^-$): m/z = 905.63 {Na$_4$[(**2**)$_4$Ti$_4$]}$^{4-}$, 909.63 {Na$_3$K[(**2**)$_4$Ti$_4$]}$^{4-}$. IR (KBr): $\tilde{\nu}$ = 3473, 2928, 2879, 2325, 2111, 1652, 1602, 1542, 1507, 1464, 1439, 1385, 1353, 1287, 1245, 1213, 1145, 1080, 1055, 1009, 934, 887, 853, 826, 801, 742, 668 cm^{-1}. $C_{192}H_{120}N_{24}O_{36}Ti_4Na_8 \cdot 11DMF \cdot 10H_2O$: C 57.51, H 4.65, N 10.43; found C 57.66, H 4.29, N 10.35.

General Procedure for the Preparation of Gallium(III) Complexes: A mixture of ligand (1 equiv.), [Ga(acac)$_3$] (1 equiv.) and M_2CO_3 (M = Na, K; 1 equiv.) in DMF (50 mL) were stirred overnight at room temperature. The solvent was removed and the complex was obtained as a red solid.

Na_{12}[(1)$_4$Ga$_4$]: Yield 97%. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 14.94 (s, 12 H), 7.94 (s, 12 H), 7.19 (m, 24 H), 6.80 (m, 36 H), 6.30 (m, 12 H), 6.16 (m, 12 H) ppm. MS (ESI$^-$): m/z = 1127.70 {H$_9$[(**1**)$_4$Ga$_4$]}$^{3-}$, 1134.70 {H$_8$Na[(**1**)$_4$Ga$_4$]}$^{3-}$, 1137.70 {H$_9$[(**1**)$_4$Ga$_4$](MeOH)}$^{3-}$, 1145.03 {H$_8$Na[(**1**)$_4$Ga$_4$](MeOH)}$^{3-}$, 1147.69 {H$_9$[(**1**)$_4$Ga$_4$](MeOH)$_2$}$^{3-}$, 1152.69 {H$_7$Na$_2$[(**1**)$_4$Ga$_4$](MeOH)}$^{3-}$. IR (KBr): $\tilde{\nu}$ = 3377, 3058, 2928, 2885, 1652, 1590, 1545, 1499, 1468, 1439, 1384, 1356, 1322, 1281, 1210, 1176, 1144, 1061, 1004, 954, 933, 886, 852, 831, 811, 735, 662 cm^{-1}. $C_{168}H_{108}N_{28}O_{36}Ga_4Na_{12} \cdot 14DMF \cdot 22H_2O$: C 49.76, H 4.97, N 11.60; found 49.73, H 5.34, N 11.25.

K_{12}[(1)$_4$Ga$_4$]: Yield quant. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 14.90 (s, 12 H), 7.94 (s, 12 H), 7.18 (m, 24 H), 7.02 (m, 12 H), 6.82 (m, 24 H), 6.50 (m, 12 H), 6.28 (m, 12 H) ppm. MS (ESI$^-$): m/z = 1127.35 {H$_9$[(**1**)$_4$Ga$_4$]}$^{3-}$, 1137.67 {H$_9$[(**1**)$_4$Ga$_4$](MeOH)}$^{3-}$, 1147.34 {KNaH$_7$[(**1**)$_4$Ga$_4$]}$^{3-}$. IR (KBr): $\tilde{\nu}$ = 3376, 3058, 2931, 2883, 1655, 1591, 1545, 1499, 1467, 1441, 1383, 1356, 1321, 1282, 1210, 1176, 1144, 1060, 1003, 954, 932, 885, 852, 831, 809, 736, 662 cm^{-1}. $C_{168}H_{108}N_{28}O_{36}Ga_4K_{12} \cdot 14DMF \cdot 12H_2O$: C 49.63, H 4.56, N 11.57; found C 49.98, H 5.04, N 11.38.

K_{12}[(2)$_4$Ga$_4$]: Yield quant. ^{1}H NMR (300 MHz, CD$_3$OD): δ = 7.87 (s, 12 H), 7.71 (s, 12 H), 7.62 (m, 24 H), 7.54 (m, 24 H), 7.18 (d, J = 8.1 Hz, 12 H), 6.72 (d, J = 7.5 Hz, 12 H), 6.40 (d, J = 7.5 Hz, 12 H) ppm. ^{1}H NMR (300 MHz, D$_2$O): δ = 7.96 (s, 12 H), 7.76 (s, 12 H), 7.61 (m, 48 H), 7.24 (d, J = 7.8 Hz, 12 H), 6.85 (d, J = 7.8 Hz, 12 H), 6.64 (t, J = 7.8 Hz, 12 H) ppm. MS (ESI$^-$): m/z = 1261.18 {K$_2$H$_7$[(**2**)$_4$Ga$_4$](MeOH)$_2$(H$_2$O)}$^{3-}$. IR (KBr): $\tilde{\nu}$ = 3417, 2925, 2884, 2322, 2114, 1653, 1541, 1507, 1467, 1440, 1386, 1352, 1290, 1259, 1209, 1143, 1061, 1004, 934, 887, 855, 825, 799, 738, 661 cm^{-1}. $C_{192}H_{120}N_{24}O_{36}Ga_4K_{12} \cdot 12DMF \cdot 15H_2O$: C 52.31, H 4.51, N 9.63; found C 52.32, H 4.75, N 9.58.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra of ligands and complexes.

Acknowledgments

Support by the Deutsche Forschungsgemeinschaft (DFG) (international training school Seleca) and the Fonds der Chemischen Industrie are gratefully acknowledged.

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Received: November 30, 2011
Published Online: March 7, 2012

