Linear Oxygen-Donor Ligands Derived from Gallic Acid Methyl Ester: Ligand Synthesis and Preliminary Coordination Studies

M. Albrecht* and **M. Schneider**

Karlsruhe, Universität, Institut für Organische Chemie

Abstract. The new ligands **3a-c-H$_4$** with two catechol-type oxygen-donor binding sites and ether-linked spacers are synthesized in three step procedures starting from gallic acid methyl ester **4**. After protection of two OH-functions as benzophenone ketale, a Williamson ether synthesis introduces the spacer, and finally the ketale is removed again. Preliminary coordination studies with **3a** (or **3b**, **3c**) and titanium(IV) ions show that dinuclear triple-stranded complexes M$_4$[(**3a**)$_3$Ti$_2$] (and K$_4$[(**3b/c**)$_3$Ti$_2$]) are formed in the presence of alkali metal (M = Li, Na, K, Cs) as well as ammonium cations (M = NH$_4$, PhCH$_2$NH$_3$, i-Pr$_2$NH$_2$).

Helicates as well as *meso*-helicates are intensive studied metallo-supramolecular targets. On the one hand it is of interest to investigate into the structure and the self-assembly of the oligonuclear supramolecular coordination compounds [1–3]. On the other hand the use of helicates for the preparation of materials with special physical properties [4] or of topologically interesting molecules [5] has to be investigated. For the latter linear organic donor molecules have to be designed and synthesized which bear reactive functional groups to enable further derivatization of the ligands or of the self-assembled metal complexes.

Many investigations towards the formation and properties of helicate-type structures were performed with oligo-nitrogen-donor ligands [2]. Corresponding oxygen-donors were investigated to a minor extend [3]. Hereby mainly oligo-catechol units that were connected by different types of spacers were used as the metal coordination sites [6–10].
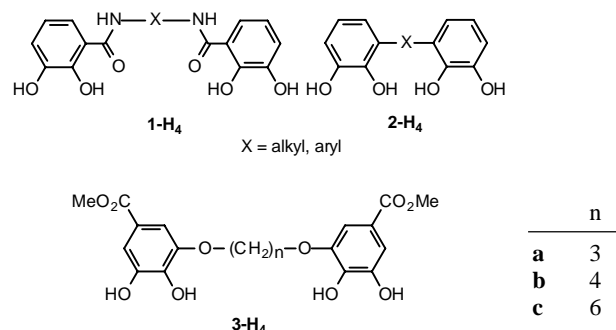
Recently, Raymond [7], Stack [8], and Duhme [9] described dicatechol ligands **1-H$_4$** with amide linkages of the aryl or alkyl spacers to the catechol moieties while we investigated into derivatives **2-H$_4$** where the alkyl and aryl bridges are connected directly to the coordinating units [10]. In this paper we present a simple approach to a novel type of dicatechol ligands **3a–c-H$_4$** which possess ether bridges in the spacer and ester groups as substituents at the aromatic units. Additionally, we describe preliminary coordination studies with titanium(IV) ions in the presence of alkali metal cations or ammonium cations.

Results and Discussion

The synthesis of the ligands **3a–c-H$_4$** is achieved in a three step procedure starting from gallic acid methyl ester **4**. Initially two out of the three hydroxy groups of the ester **4** are protected by formation of the benzophenone ketal **5**. As described by Jurd [11], heating of gallic acid methyl ester **4** in the presence of an equimolar amount of dichlorodiphenylmethane for 5 min to 175 °C affords compound **5** as a white solid in 91% yield (Scheme 1).

Reaction of the ketal **5** (2 eq.) with 1,3-diiodopropane, 1,4-diiodobutane, or 1,6-diiodohexane (1 eq.) in acetone in the presence of potassium carbonate at reflux leads overnight in a Williamson ether synthesis to the ligand precursors **6a** (61% yield), **6b** (80% yield) and **6c** (71% yield). In the final step the ketal moieties are cleaved by heating of **6a–c** in acetic acid. The acetic acid is evaporated *in vacuo*, and the benzophenone is removed by extraction with ether and *n*-hexane. The ligands **3a/b-H$_4$** are both obtained in 86% yield and **3c-H$_4$** in 97% yield as white solids.

As an alternative, the ketal **6a** also can be transformed into the ligand **3a-H$_4$** by stirring a mixture of **6a** and of palladium on charcoal in dichloromethane for 15 h under an atmosphere of 55 bar of hydrogen (autoclave!) [12]. By filtration, removal of the solvent and washing with acetone (to remove diphenylmethane), **3a-H$_4$** is
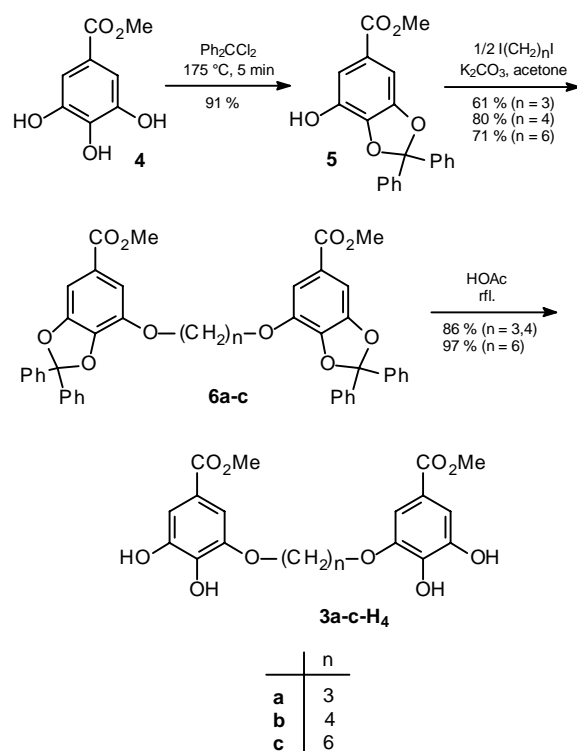
Scheme 1 Synthesis of the ligands **3a–c-H$_4$**.

obtained in 40% yield. The hydrogenolytic reduction of the ketal was only applied to the (CH$_2$)$_3$-bridged system (**a**). Due to the higher yields acidic cleavage of the ketals of **6a–c** is preferred to obtain the free ligands **3a-H$_4$**, **3b-H$_4$**, or **3c-H$_4$**, respectively.

In preliminary studies towards the self-assembly of dinuclear triple-stranded helicate-type complexes from ligand **3a-H$_4$** we dissolved the ligand (3 eq.) in methanol and added titanoyl bisacetylacetonate [(acac)$_2$TiO] and alkali metal carbonate (2 eq.). If lithium or sodium carbonate are used as base, the metal complexes Li$_4$[(**3a**)$_3$Ti$_2$] (87% yield) and Na$_4$[(**3a**)$_3$Ti$_2$] (76% yield) are obtained by evaporation of methanol and penta-2,4-

dione and are purified by washing with dichloromethane. With potassium and cesium carbonate the dinuclear complexes K$_4$[(**3a**)$_3$Ti$_2$] (71% yield) or Cs$_4$[(**3a**)$_3$Ti$_2$] (67% yield) precipitate, and the orange solids can be isolated by filtration.

As representative examples the potassium salts K$_4$[(**3b,c**)$_3$Ti$_2$] are prepared from **3b–c-H$_4$**, [(acac)$_2$TiO] and potassium carbonate in 27% (b) and 74% (c) yield. The obtained dinuclear complexes M$_4$[(**3a–c**)$_3$Ti$_2$] are characterized by standard spectroscopic methods. *E.g.*, in the ^{1}H NMR spectrum of Li$_4$[(**3a**)$_3$Ti$_2$] (methanol-d$_4$) the signals of the aromatic protons are detected at δ/ppm = 7.08 and 6.82 (d, J = 1.9 Hz). At δ/ppm = 3.78 a singlet is observed for the methyl ester and the resonances of the spacer protons can be found at δ/ppm = 4.23 (t, J = 6.1 Hz) and 2.20 (m). Corresponding NMR spectra are observed for the Na-, K-, and Cs-salts. Positive FAB MS (3-NBA as matrix) shows that the compounds are triple-stranded dinuclear complexes. Characteristic peaks are detected at m/z = 1337 [HLi$_4$(**3a**)$_3$Ti$_2$]$^+$ and 1401 [HNa$_4$(**3a**)$_3$Ti$_2$]$^+$. Due to their insolubility in common matrices, no FAB MS spectra could be obtained for the potassium and cesium salts.

The spectroscopic results do not allow an assignment of the relative stereochemistry of the two complex units. However, due to the very flexible ether linkages it is expected that a fast equilibrium between the helicate and the *meso*-helicate structure is present in solution [10]. Furthermore, the position of the alkali metal cations can not be defined by the presented spectroscopic results. In analogy to our earlier results it is expected that cations are bound in the interior of the triple-stranded bistitana-cryptands [(**3a–c**)$_3$Ti$_2$]$^{4-}$ [13]. Unfortunately, we were not yet able to obtain crystals of the complex salts which are suitable for an X-ray structure analysis.

In addition to our complexation studies in the presence of alkali metal cations we synthesized dinuclear
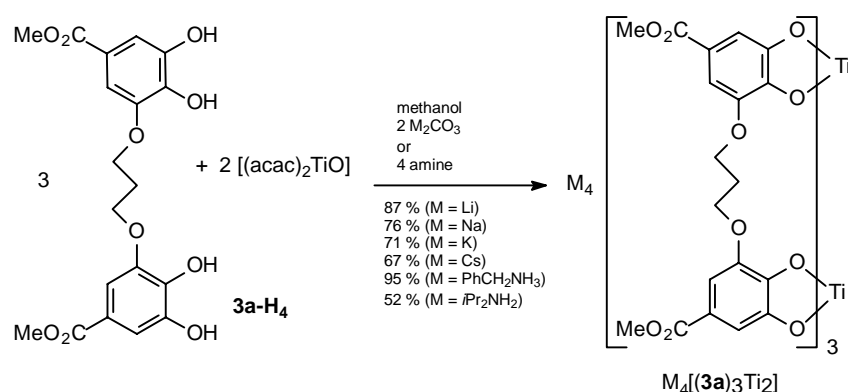
M$_4$[(**3a**)$_3$Ti$_2$]

Scheme 2 Preparation of dinuclear titanium(IV) complexes from the ligand **3a-H$_4$** and [(acac)$_2$TiO] in the presence of alkali metal carbonates (M = Li, Na, K, Cs) or amines (M = PhCH$_2$NH$_3$, *i*-Pr$_2$NH$_2$) as base. The corresponding complex [NH$_4$]$_4$[(**3a**)$_3$Ti$_2$] is prepared in the presence of ammonium acetate but can not be obtained in analytically pure form.

coordination compounds with ammonium cations as counterions. Thus, we prepared the helicate-type complexes $[(3a)_3Ti_2]^{4-}$ in the presence of ammonium acetate, benzyl amine, or diisopropyl amine as base. Although the complex with NH_4^+-cations could not be isolated in analytically pure form, all three complex salts gave characteristic ^1H and ^{13}C NMR spectra. In the case of $[PhCH_2NH_3]_4[(3a)_3Ti_2]$ a positive FAB MS spectrum could be obtained which shows the signal of $[H_5(3a)_3Ti_2]^+$ at $m/z = 1313$ and of $[H_4(PhCH_2NH_3)(3a)_3Ti_2]^+$ at $m/z = 1419$. The latter gives an indication that the benzyl ammonium cation by hydrogen bonding may be tightly bound to the tetraanionic dinuclear complex. Hereby, the cationic moiety might be encapsulated by the cryptand-type titanium complex, while the benzyl substituent is located outside of the cavity [14]. In the presence of diisopropy amine the dinuclear titanium(IV) complex $[i\text{-}Pr_2NH_2]_4[(3a)_3Ti_2]$ is obtained. However, from our findings no comment can be made on the positions of the ammonium cations.

In conclusion, we presented a simple three step procedure for the preparation of ether-linked dicatechol-type ligands **3a-c-H₄** starting from gallic acid methyl ester. The syntheses which were discussed open the way to the preparation of numerous other derivatives which might bear different functionalities or chiral groups in the spacer. Additionally, the ester group of the ligand can be transformed into other moieties. Our preliminary coordination studies show that the ligands **3a-c-H₄** can act as building blocks for metallo-supramolecular chemistry and are able to form dinuclear helicate-type titanium(IV) complexes in the presence of alkali metal as well as ammonium cations.

Experimental

Melting points were measured on a Büchi 535 (uncorrected). IR spectra were obtained on a Bruker IFS 88 spectrometer (diffuse reflection, KBr). EI MS/HRMS (70 eV) or FAB MS spectra (matrix: 3-nitrobenzoic acid (3-NBA)) were detected on a Finnigan MAT 90 spectrometer. For ^1H NMR and ^{13}C NMR (BB/DEPT) a Bruker DRX 500 or a AM 400 spectrometer were used (internal standard: $CHCl_3$, DMSO-d$_5$ or HCD_2OD). UV-Vis spectra were obtained on a Perkin Elmer UV-Vis Lambda 2 spectrometer.

Methyl 7-hydroxy-2,2-diphenylbenzo[d]1,3-dioxolane-5-carboxylate (5)

The benzophenone ketal was obtained from gallic acid methyl ester (**4**) and dichlorodiphenylmethane in 91% yield as described in the literature [11].

Preparation of the Ketal-Protected Ligands (6a–c) (General Procedure)

Dioxolane **5** (5.49 g, 15.8 mmol), diiodo alkane (8.00 mmol), and potassium carbonate (6.6 g, 47.8 mmol) in acetone (200 ml) are refluxed overnight. After cooling to r.t. the precipitate is removed by filtration, and acetone is evaporated *in vacuo*. The residue is purified by column chromatography (silica gel, dichloromethane).

Methyl 7-(3-(6-(methoxycarbonyl)-2,2-diphenylbenzo[2,3-d]1,3-dioxolan-4-yloxy)propoxy)-2,2-diphenylbenzo[d]1,3-dioxolane-5-carboxylate (6a)

Yield 3.54 g (61%) of a white solid. *m.p.* 75 °C. – ^1H NMR (CDCl$_3$): δ/ppm = 7.56 (m, 8 H), 7.35 (m, 14H), 7.28 (d, $J = 1.4$ Hz, 2H), 4.37 (t, $J = 6.1$ Hz, 4H), 3.85 (s, 6 H), 2.31 (quin, $J = 6.1$ Hz, 2H). – ^{13}C NMR (CDCl$_3$): δ/ppm = 166.3 (C), 148.2 (C), 142.1 (C), 139.4 (C), 139.3 (C), 129.2 (CH), 128.1 (CH), 126.2 (CH), 124.1 (C), 118.3 (C), 111.6 (CH), 103.9 (CH), 66.0 (CH$_2$), 52.0 (CH$_3$), 29.1 (CH$_2$). – IR (KBr): $\tilde{v}$/cm^{-1} = 3063, 2951, 1719, 1633, 1508, 1435, 1328, 1206, 1118, 1020, 764, 700. – MS (EI, 70 eV): m/z = 736 (100%) [M]$^+$. – HRMS calcd. for $C_{45}H_{36}O_{10}$ (M$^+$): 736.2308, found: 736.2289.

| $C_{45}H_{36}O_{10}$ | Calcd.: | C 73.36 | H 4.93 |
| (736.8) | Found: | C 73.28 | H 4.99. |

Methyl 7-(4-(6-(methoxycarbonyl)-2,2-diphenylbenzo[2,3-d]1,3-dioxolan-4-yloxy)butoxy)-2,2-diphenylbenzo[d]1,3-dioxolane-5-carboxylate (6b)

Yield 2.57 g (80%) of a white solid. *m.p.* 180–181 °C. – ^1H NMR (CDCl$_3$): δ/ppm = 7.59 (m, 8H), 7.36 (m, 12H), 7.33 (d, $J = 1.5$ Hz, 2H), 7.28 (d, $J = 1.5$ Hz, 2H), 4.22 (m, 4H), 3.85 (s, 6H), 2.02 (m, 4H). – ^{13}C NMR (CDCl$_3$) δ/ppm = 166.5 (C), 148.4 (C), 142.5 (C), 139.7 (C), 139.5 (C), 129.4 (CH), 128.3 (CH), 126.4 (CH), 124.2 (C), 118.4 (C), 111.7 (CH), 104.0 (CH), 69.3 (CH$_2$), 52.2 (CH$_3$), 25.9 (CH$_2$). – IR (KBr): $\tilde{v}$/cm^{-1} = 3071, 2960, 2875, 1710, 1634, 1436, 1209, 700.

| $C_{46}H_{38}O_{10} \cdot H_2O$ | Calcd.: | C 71.86 | H 5.24 |
| (750.8) | Found: | C 72.03 | H 4.91. |

Methyl 7-(6-(6-(methoxycarbonyl)-2,2-diphenylbenzo[2,3-d]1,3-dioxolan-4-yloxy)hexoxy)-2,2-diphenylbenzo[d]1,3-dioxolane-5-carboxylate (6c)

Yield 1.6 g (71%) of a white solid. *m.p.* 159 °C. – ^1H NMR (CDCl$_3$): δ/ppm = 7.60 (m, 8H), 7.36 (m, 12H), 7.32 (d, $J = 1.4$ Hz, 2H), 7.28 (d, $J = 1.4$ Hz, 2H), 4.15 (t, $J = 6.6$ Hz, 4H), 3.86 (s, 6H), 1.84 (m, 4H), 1.55 (m, 4H). – ^{13}C NMR (CDCl$_3$): δ/ppm = 166.4 (C), 148.2 (C), 142.4 (C), 139.5 (C), 139.3 (C), 129.2 (CH), 128.2 (CH), 126.3 (CH), 124.1 (C), 118.2 (C), 111.6 (CH), 103.7 (CH), 69.5 (CH$_2$), 52.0 (CH$_3$), 29.1 (CH$_2$), 25.6 (CH$_2$). – IR (KBr): $\tilde{v}$/cm^{-1} = 3067, 2940, 2875, 1714, 1635, 1512, 1436, 1337, 1212, 1125, 1020, 699.

| $C_{48}H_{42}O_{10}$ | Calcd.: | C 74.02 | H 5.44 |
| (778.9) | Found: | C 73.53 | H 5.42. |

Deprotection of the Ligands (3a–c-H₄) (General Procedure)

The ketal protected derivatives **6** (3.67 mmol) are dissolved in 40 ml of glacial acetic acid and 10 ml of water. The mixture is refluxed overnight, and solvents are removed *in va-*

cuo. The residue is washed with ether and *n*-hexane and dried *in vacuo*.

Methyl 3-(3-(2,3-dihydroxy-5-(methoxycarbonyl)phenoxy)propoxy)-4,5-dihydroxybenzoate (3a-H₄)

Yield 86% of a white hygroscopic solid. *m.p.* 200 °C.
¹H NMR (DMSO-d₆): δ/ppm = 7.08 (d, *J* = 1.8 Hz, 2H), 7.04 (d, *J* = 1.8 Hz, 2H), 4.18 (t, *J* = 6.1 Hz, 4H), 3.75 (s, 6H), 2.18 (quin, *J* = 6.1 Hz, 2H). – ¹³C NMR (dmso-d₆): δ/ppm = 166.3 (C), 147.1 (C), 145.5 (C), 139.6 (C), 119.2 (C), 110.5 (CH), 105.6 (CH), 65.3 (CH₂), 51.8 (CH₃), 28.8 (CH₂). – IR (KBr): $\tilde{v}$/cm⁻¹ = 3562, 3407, 2954, 1701, 1626, 1529, 1443, 1342, 1237, 1092, 763.
C₁₉H₂₀O₁₀ · 2H₂O   Calcd.: C 51.35   H 5.44
(408.4)   Found: C 51.06   H 5.37.

Methyl 3-(4-(2,3-dihydroxy-5-(methoxycarbonyl)phenoxy)butoxy)-4,5-dihydroxybenzoate (3b-H₄)

Yield 86% of a white hygroscopic solid. *m.p.* 224 °C. –
¹H NMR (dmso-d₆): δ/ppm = 7.09 (d, *J* = 1.6 Hz, 2H), 7.04 (d, *J* = 1.6 Hz, 2H), 4.03 (m, 4H), 3.75 (s, 6H), 1.09 (m, 4H).
– ¹³C NMR (DMSO-d₆): δ/ppm = 166.3 (C), 147.2 (C), 145.5 (C), 140.0 (C), 119.2 (C), 110.5 (CH), 106.0 (CH), 68.4 (CH₂), 51.8 (CH₃), 25.5 (CH₂). – IR (KBr): $\tilde{v}$/cm⁻¹ = 3439, 3403, 3094, 2950, 1691, 1442, 1339, 1254, 1082, 766.
C₂₀H₂₂O₁₀ · 0.5H₂O Calcd.: C 55.68   H 5.37
(422.4)   Found: C 55.24   H 5.33.

Methyl 3-(6-(2,3-dihydroxy-5-(methoxycarbonyl)phenoxy)hexoxy)-4,5-dihydroxybenzoate (3c-H₄)

Yield 97% of a white hygroscopic solid. *m.p.* 191 °C. –
¹H NMR (dmso-d₆): δ/ppm = 7.08 (d, *J* = 1.6 Hz, 2H), 7.01 (d, *J* = 1.6 Hz, 2H), 3.96 (t, *J* = 6.3 Hz, 4H), 3.74 (s, 6H), 1.73 (m, 4H), 1.47 (m, 4H). – ¹³C NMR (DMSO-d₆): δ/ppm = 166.3 (C), 147.2 (C), 145.6 (C), 140.2 (C), 118.9 (C), 110.4 (CH), 106.0 (CH), 68.6 (CH₂), 51.7 (CH₃), 28.8 (CH₂), 25.3 (CH₂). – IR (KBr): $\tilde{v}$/cm⁻¹ = 3524, 3400, 2953, 2875, 1693, 1622, 1445, 1333, 1227, 1076, 761.
C₂₂H₂₆O₁₀ · H₂O   Calcd.: C 56.41   H 6.02
(450.4)   Found: C 56.37   H 5.64.

Preparation of Dinuclear Titanium Complexes with Alkali Metal Cations as Counterions

Three eq. of the ligand **3a(b,c)-H₄**, two eq. of [(acac)₂TiO], and two eq. of alkali metal carbonate are dissolved in methanol and stirred at r.t. After 15 h the orange precipitate is collected by filtration, washed with a small amount of methanol and dried *in vacuo*.

Tetralithium[tris(μ-1,3-bis(5-(methoxycarbonyl)catecholato-3-oxy)propane)bistitanate] (Li₄[(3a)₃Ti₂])

The complex is obtained after removal of the solvent and of penta-2,4-dione from the reaction mixture. Yield 87%. –
¹H NMR (methanol-d₄): δ/ppm = 7.08 (d, *J* = 1.9 Hz, 6H), 6.82 (d, *J* = 1.9 Hz, 6H), 4.23 (t, *J* = 6.1 Hz, 12H), 3.78 (s, 18H), 2.20 (m, 6H). – ¹³C NMR (methanol-d₄): δ/ppm = 170.2 (C), 160.3 (C), 155.3 (C), 144.8 (C), 118.9 (C), 111.0 (CH), 109.2 (CH), 68.8 (CH₂), 53.0 (CH₃), 31.4 (CH₂). – IR (KBr): $\tilde{v}$/cm⁻¹ = 3429, 2952, 2678, 1691, 1582, 1486, 1435, 1342, 1226, 1100, 1005, 871, 827, 766, 618. FAB(+) MS (3-NBA):

m/z = 1337 [Li₄(**3a**)₃Ti₂H]⁺, 1331 [Li₃(**3a**)₃Ti₂H₂]⁺. – UV-Vis (methanol): λ/nm = 215, 300.
C₅₇H₄₈Li₄O₃₀Ti₂ · 14H₂O Calcd.: C 43.09   H 4.82
(1336.6)   Found: C 42.97   H 4.75.

Tetrasodium[tris(μ-1,3-bis(5-(methoxycarbonyl)catecholato-3-oxy)propane)bistitanate] (Na₄[(3a)₃Ti₂])

The complex is obtained after removal of the solvent and of penta-2,4-dione from the reaction mixture. Yield 76%. –
¹H NMR (methanol-d₄): δ/ppm = 7.16 (d, *J* = 1.8 Hz, 6H), 7.84 (d, *J* = 1.8 Hz, 6H), 4.21 (t, *J* = 5.3 Hz, 12H), 3.79 (s, 18H), 2.20 (m, 6H). – ¹³C NMR (methanol-d₄): δ/ppm = 170.1 (C), 159.6 (C), 153.7 (C), 145.0 (C), 119.2 (C), 109.2 (CH), 109.1 (CH), 69.1 (CH₂), 52.0 (CH₃), 30.2 (CH₂). – IR (KBr): $\tilde{v}$/cm⁻¹ = 3437, 2951, 2678, 1693, 1578, 1483, 1435, 1342, 1224, 1099, 1007, 871, 824, 765, 617. – FAB(+) MS (3-NBA): *m/z* = 1401 [Na₄(**3a**)₃Ti₂H]⁺, 1379 [Na₃(**3a**)₃Ti₂H₂]⁺. – UV-Vis (methanol): λ/nm = 214, 231, 300.
C₅₇H₄₈Na₄O₃₀Ti₂ · 13H₂O Calcd.: C 41.87   H 4.56
(1400.8)   Found: C 41.77   H 4.47.

Tetrapotassium[tris(μ-1,3-bis(5-(methoxycarbonyl)catecholato-3-oxy)propane)bistitanate] (K₄[(3a)₃Ti₂])

Yield 71%. – ¹H NMR (DMSO-d₆): δ/ppm = 6.98 (d, *J* = 1.3 Hz, 6H), 6.52 (d, *J* = 1.3 Hz, 6H), 4.08 (m, 12H), 3.72 (s, 18H), 21.8 (m, 6H). ¹³C NMR (dmso-d₆): δ/ppm = 167.2 (C), 159.5 (C), 152.8 (C), 143.1 (C), 116.3 (C), 106.8 (CH), 106.2 (CH), 69.0 (CH₂), 51.3 (CH₃), 28.7 (CH₂). – IR (KBr): $\tilde{v}$/cm⁻¹ = 3511, 2950, 1997, 1577, 1482, 1436, 1347, 1223, 1104.
C₅₇H₄₈K₄O₃₀Ti₂ · 6H₂O   Calcd.: C 43.52   H 3.84
(1465.2)   Found: C 43.41   H 3.72.

Tetrapotassium[tris(μ-1,4-bis(5-(methoxycarbonyl)catecholato-3-oxy)butane)bistitanate] (K₄[(3b)₃Ti₂])

Yield 27%. – ¹H NMR (DMSO-d₆): δ/ppm = 6.92 (br, 6H), 6.55 (br, 6H), 3.90 (m, 12H), 3.75 (s, 18H), 1.95 (m, 12H).
C₆₀H₅₄O₃₀Ti₂K₄ · 9H₂O   Calcd.: C 43.17   H 4.35
(1407.3)   Found: C 43.36   H 4.28.

Tetrapotassium[tris(μ-1,6-bis(5-(methoxycarbonyl)catecholato-3-oxy)hexane)bistitanate] (K₄[(3c)₃Ti₂])

Yield 74%. – ¹H NMR (DMSO-d₆): δ/ppm = 6.84 (d, *J* = 1.4 Hz, 6H), 6.49 (d, *J* = 1.4 Hz, 6H), 3.79 (m, 12H), 3.70 (s, 18H), 1.82 (m, 12H), 1.51 (m, 12H). – ¹³C NMR (DMSO-d₆): δ/ppm = 167.4 (C), 159.3 (C), 153.4 (C), 143.1 (C), 115.8 (C), 106.4 (CH), 104.0 (CH), 67.8 (CH₂), 51.2 (CH₃), 29.1 (CH₂), 26.0 (CH₂). No correct elemental analysis could be obtained.

Tetracesium[tris(μ-1,3-bis(5-(methoxycarbonyl)catecholato-3-oxy)propane)bistitanate] (Cs₄[(3a)₃Ti₂])

Yield 67%. – ¹H NMR (dmso-d₆): δ/ppm = 6.87 (d, *J* = 1.8 Hz, 6H), 6.45 (d, *J* = 1.8 Hz, 6H), 4.03 (t, *J* = 5.6 Hz, 12H), 3.70 (s, 18H), 2.01 (m, 6H). – ¹³C NMR (dmso-d₆): δ/ppm = 167.2 (C), 160.0 (C), 154.8 (C), 142.6 (C), 115.8 (C), 108.4 (CH), 106.4 (CH), 66.3 (CH₂), 51.1 (CH₃), 39.1 (CH₂). – IR (KBr): $\tilde{v}$/cm⁻¹ = 3399, 2949, 2668, 1696, 1574, 1479, 1434, 1344, 1222, 1097, 1009, 868, 824, 754, 609. –

UV-Vis (dmso): λ/nm =249, 312.

$C_{57}H_{48}Cs_4O_{30}Ti_2 \cdot 5H_2O \cdot 5MeOH$
(1840.4)   Calcd.: C 35.62   H 3.76.
               Found: C 35.67   H 3.77.

Tetraammonium[tris(μ-1,3-bis(5-(methoxycarbonyl)cate-cholato-3-oxy)propane)bistitanate] ([NH$_4$]$_4$[(**3a**)$_3$Ti$_2$])

The ligand **3a-H$_4$** (56 mg, 0.14 mmol), [(acac)$_2$TiO] (24 mg, 0.09 mmol), and ammonium acetate (14 mg, 0.18 mmol) are dissolved in 30 ml of methanol. The solution is stirred. After 3 d the orange precipitate is filtered off and dried *in vacuo* to obtain 10 mg of [NH$_4$]$_4$[(**3a**)$_3$Ti$_2$]. – ^{1}H NMR (DMSO-d$_6$): δ/ppm = 7.12 (br, 16H), 6.85 (d, J = 1.4 Hz, 6H), 6.44 (d, J = 1.4 Hz, 6H), 4.02 (t, J = 5.4 Hz, 12H), 3.69 (s, 18H), 2.03 (m, 6H). – ^{13}C NMR (dmso-d$_6$): δ/ppm = 167.2 (C), 159.9 (C), 154.6 (C), 142.4 (C), 115.9 (C), 108.5 (CH), 106.3 (CH), 66.5 (CH$_2$), 51.1 (CH$_3$), 29.1 (CH$_2$). – IR (KBr): $\tilde{v}$/cm^{-1} = 3 195, 2 950, 1 697, 1 579, 1 482, 1 435, 1 346, 1 221, 1 100, 1 008, 825, 753, 609. – UV-Vis (dmso): λ/nm =247, 314. No correct elemental analysis could be obtained.

Preparation of Dinuclear Titanium Complexes with Alkyl Ammonium Cations as Counterions

The ligand **3a-H$_4$** (3 eq.), [(acac)$_2$TiO] (2 eq.), and an excess of amine (approx. 10 eq.) are dissolved in methanol and stirred overnight. The solvent is removed, and the remaining solid is washed with dichloromethane or *n*-hexane and dried *in vacuo*.

Tetra(benzylammonium)[tris(μ-1,3-bis(5-(methoxycarbonyl)-catecholato-3-oxy)propane)bistitanate]([PhCH$_2$NH$_3$]$_4$[(**3a**)$_3$Ti$_2$])

Yield 95% of an orange solid. – ^{1}H NMR (methanol-d$_4$): δ/ppm = 7.22 (m, 20H), 7.04 (d, J = 1.8 Hz, 6H), 6.86 (d, J = 1.8 Hz, 6H), 4.21 (s, 8H), 3.92 (t, J = 5.4 Hz, 12H), 3.78 (s, 18H), 1.72 (m, 6H). – ^{13}C NMR (methanol-d$_4$): δ/ppm = 170.0 (C), 159.9 (C), 153.7 (C), 145.1 (C), 134.9 (C), 130.1 (CH), 129.9 (CH), 129.8 (CH), 119.6 (C), 109.5 (CH), 109.2 (CH), 69.5 (CH$_2$), 52.1 (CH$_3$), 47.6 (CH$_2$), 30.2 (CH$_2$). – FAB(+) MS (3-NBA): m/z = 1419 [(PhCH$_2$NH$_3$)(**3a**)$_3$Ti$_2$H$_4$]$^+$, 1313 [(**3a**)$_3$Ti$_2$H$_5$]$^+$. – IR (KBr): $\tilde{v}$/cm^{-1} = 3 451, 2 949, 1 705, 1 573, 1 481, 1 434, 1 339, 1 262, 1 217, 1 100, 1 010, 822, 753, 700, 610. – UV-Vis (methanol): λ/nm = 191, 209, 231, 304.

$C_{85}H_{88}N_4O_{30}Ti_2 \cdot 4H_2O$ Calcd.: C 56.30 H 5.34 N 3.09
(1741.5)   Found: C 56.08 H 5.63 N 2.47.

Tetra(diisopropylammonium)[tris(m-1,3-bis(5-(methoxy-carbonyl)catecholato-3-oxy)propane)bistitanate] ([*i*-Pr$_2$NH$_2$]$_4$[(**3a**)$_3$Ti$_2$])

Yield 52% of an orange solid. – ^{1}H NMR (methanol-d$_4$): δ/ppm = 7.10 (d, J = 1.8 Hz, 6H), 6.79 (d, J = 1.8 Hz, 6H), 4.19 (t, J = 5.6 Hz, 12H), 3.79 (s, 18H), 2.99 (br, 16H), 2.19 (br, 6H), 1.63 (m, 16H), 0.87 (t, J = 7.5 Hz, 24H). – ^{13}C NMR (methanol-d$_4$): δ/ppm = 170.2 (C), 160.6 (C), 154.7 (C), 144.9 (C), 118.9 (C), 110.0 (CH), 108.9 (CH), 69.1 (CH$_2$), 52.0 (CH$_3$),50.8 (CH$_2$), 31.4 (CH$_2$), 21.2 (CH$_2$), 11.3 (CH$_3$). – IR (KBr): $\tilde{v}$/cm^{-1} = 3 441, 2 965, 2 880, 2 109, 1 701, 1 576, 1 477, 1 433, 1 340, 1 216, 1 098, 1 010, 823, 754, 607. – UV-Vis

(methanol): λ/nm = 215, 232, 302.

$C_{81}H_{112}N_4O_{30}Ti_2 \cdot 8H_2O$ Calcd.: C 52.26 H 6.93 N 3.01
(1717.6)   Found: C 52.06 H 6.65 N 2.74.

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Address for correspondence:
Priv.-Doz. Dr. Markus Albrecht
Universität Karlsruhe Institut für Organische Chemie,
Richard-Willstätter-Allee
D-76131 Karlsruhe
Fax: Internat. code (0)721 698 529
E-mail: albrecht@ochhades.chemie.uni-karlsruhe.de