Alkali-Metal Cation Binding by Self-Assembled Cryptand-Type Supermolecules

Markus Albrecht,* Herbert Röttele, and Peter Burger

Abstract: Reaction of three equivalents of alkyl-bridged biscatechol ligands (**1**–**3**)-H_4 with two equivalents of [$(acac)_2TiO$] in the presence of two equivalents of alkali-metal carbonate (M = Na, K) affords helicate- or *meso*-helicate-type supramolecular coordination compounds by spontaneous self-assembly processes. The cryptand-type structure of the binuclear tetraanions $[(\mathbf{1})_3Ti_2]^{4-}$ or $[(\mathbf{2})_3Ti_2]^{4-}$ permits inclusion of sodium cations; this was observed by ^{23}Na NMR spectroscopy in solution. Competition experiments with potassium or lithium cations revealed that potassium but not lithium easily displaces the sodium ions from the cavity. Titration experiments indicated that the binding constant for potassium is significantly higher than for sodium. On the other hand, for the large tetraanion $[(\mathbf{3})_3Ti_2]^{4-}$ with hexamethylene spacers, no binding of alkali-metal ions could be observed by NMR spectroscopy in solution. In the solid state, however, two potassium ions could be incorporated in the interior of the cryptand-type helicate.

Keywords
catechols · cryptates · helicates · NMR spectroscopy · titanium complexes

Introduction

Metal-directed multi-component self-assembly is one way to develop new materials with novel properties and structural features. The species obtained can behave as supramolecular devices with further functions (e.g., molecular recognition or electron transfer). Thus, the coordination chemistry of late transition metals in combination with relatively soft oligonitrogen donor ligands has recently become an intensely studied field of supramolecular chemistry.[1–3] To a much lesser extent, early transition metals and hard oxygen donors are also under investigation.[4] During our work on the metal-directed self-assembly of oligocatecholate ligands with hard metal ions, we isolated and structurally characterized a tetraanionic helicate[5] and a corresponding *meso*-helicate (Fig. 1).[6,7]

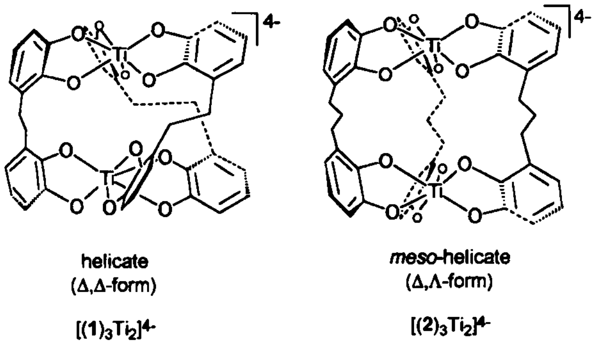
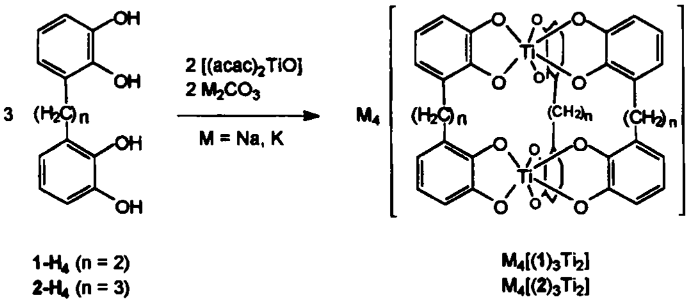


Fig. 1. Structure of the helicate $[(\mathbf{1})_3Ti_2]^{4-}$ and the *meso*-helicate $[(\mathbf{2})_3Ti_2]^{4-}$.

In the solid state, the tetraanions bind one of the alkali counterions in cryptate fashion to form the complex salts $[Li]_3[Li \subset ((\mathbf{1})_3Ti_2)]$[5] and $[Na]_3[Na \subset ((\mathbf{2})_3Ti_2)]$.[6] The inclusion of sodium or lithium in the solid state made us wonder whether the cation-binding properties of $[(\mathbf{1})_3Ti_2]^{4-}$ and of the larger $[(\mathbf{2})_3Ti_2]^{4-}$ were still present in solution.[8,9] Thus, we decided to use high-resolution ^{23}Na NMR spectroscopy as an analytical method for the determination of cryptate formation.[10–12] Additionally, we stretched the tetraanionic binuclear coordination compounds to obtain a cavity much too large for the encapsulation of only one alkali-metal cation.

Results and Discussion

Formation of $M_4[(\mathbf{1})_3Ti_2]$ and $M_4[(\mathbf{2})_3Ti_2]$: The complex salts $M_4[(\mathbf{1})_3Ti_2]$ and $M_4[(\mathbf{2})_3Ti_2]$ (M = Na, K) are formed in quantitative yields from three equivalents of the corresponding alkyl-bridged biscatechol ligand **1**-H_4 or **2**-H_4, respectively,[13] two equivalents of [$(acac)_2TiO$] (acac = acetyl acetonate), and two equivalents of alkali-metal carbonate in a spontaneous self-assembly process (Scheme 1). If only one equivalent of



Scheme 1. Spontaneous self-assembly of $[(\mathbf{1})_3Ti_2]^{4-}$ and $[(\mathbf{2})_3Ti_2]^{4-}$

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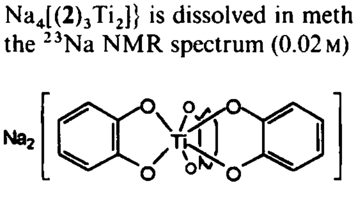
$[(acac)_2TiO]$ and alkali-metal carbonate is used, unreacted ligand **1** or **2** can be detected by NMR besides the binuclear coordination compounds. This shows that the formation of the supramolecular complexes proceeds with positive cooperativity.[14]

^{23}Na NMR spectroscopic studies: If the salt $Na_4[(\mathbf{1})_3Ti_2]$ {or $Na_4[(\mathbf{2})_3Ti_2]$} is dissolved in methanol/[D$_4$]methanol (1:1) and the ^{23}Na NMR spectrum (0.02 M) is measured at room temperature, only one broad signal at $\delta_{Na} = -3.5$ {$\delta_{Na} = -0.6$} can be detected. The mononuclear tris(catecholate) titanium complex $Na_2[(\mathbf{4})_3Ti]$[15] (**4**-H$_2$ = catechol) shows a resonance under the same conditions at $\delta_{Na} = -2.7$ (0.04 M solution). However, cooling of a sample of $Na_4[(\mathbf{1})_3Ti_2]$ (Fig. 2) {$Na_4[(\mathbf{2})_3Ti_2]$} to 188 K resulted in the splitting into two signals at $\delta_{Na} = -0.9$ {-0.7} and -15.5 {-16.0}. The former can be assigned to solvated sodium ions. The signals at $\delta_{Na} = -15$ to -16 appear in the same region as the Na$^+$ complex of the 2.2.2-cryptand ($\delta_{Na} = -11.4$).[12] This indicates that in solution, as already observed in the solid state,[5, 6] cations are located in the cavity of the tetraanions $[(\mathbf{1})_3Ti_2]^{4-}$ or $[(\mathbf{2})_3Ti_2]^{4-}$. Coalescence of the signals occurs at 193–198 K for $Na_4[(\mathbf{1})_3Ti_2]$ and 198–203 K for $Na_4[(\mathbf{2})_3Ti_2]$; a free energy barrier of $\Delta G^{\neq} = 7.5–8.5\ kcal\,mol^{-1}$ can be estimated for the exchange of bound and free Na$^+$ (compare $[(2.2.2\text{-cryptand})Na]^+$: $\Delta G^{\neq} = 15.4\ kcal\,mol^{-1}$).[12]



$Na_2[(4)_3Ti]$

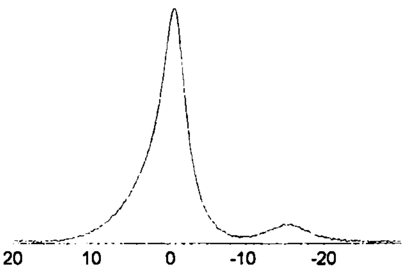


Fig. 2. ^{23}Na NMR spectrum of $Na_4[(\mathbf{1})_3Ti_2]$ at 188 K (methanol/[D$_4$]methanol).

In addition to the low-temperature investigations, some competition experiments with Li$^+$ and K$^+$ were carried out in D$_2$O/H$_2$O (0.005 M solutions; 295 K) (Figs. 3–5). The broad ^{23}Na NMR signals of $Na_4[(\mathbf{1})_3Ti_2]$ ($\delta_{Na} = -1.1$, $\Delta\nu_{1/2} = 290$ Hz) or $Na_4[(\mathbf{2})_3Ti_2]$ ($\delta_{Na} = -0.2$, $\Delta\nu_{1/2} = 75$ Hz) compared with that of mononuclear $Na_2[(\mathbf{4})_3Ti]$ ($\delta_{Na} = -0.2$, $\Delta\nu_{1/2} = 7$ Hz) again indicate a fast exchange of encapsulated and solvated sodium ions. Addition of four equivalents of lithium chloride (one equivalent with respect to sodium ions) led to a slight sharpening of the signals ($\Delta\nu_{1/2} = 255$ Hz for $[(\mathbf{1})_3Ti_2]^{4-}$; $\Delta\nu_{1/2} = 52$ Hz for $[(\mathbf{2})_3Ti_2]^{4-}$). A similar effect was observed upon addition of four equivalents of NaCl. The changes in the spectra were much larger when four equivalents of potassium chloride were added. The lines sharpened dramatically to $\Delta\nu_{1/2} = 35$ Hz for $[(\mathbf{1})_3Ti_2]^{4-}$ and $\Delta\nu_{1/2} = 30$ Hz for $[(\mathbf{2})_3Ti_2]^{4-}$. In a more detailed ^{23}Na NMR study we titrated $Na_4[(\mathbf{1})_3Ti_2]$ in D$_2$O (0.055 M) with KCl at room temperature (Fig. 4). The signal sharpened and shifted to lower field until about one equivalent of potassium ions had been added (Fig. 5). This shows that only one equivalent of potassium ions is needed to remove the sodium from the interior of the binuclear titanium complex. Thus,

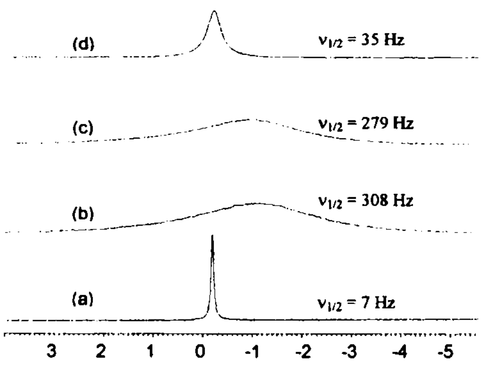


Fig. 3. ^{23}Na NMR spectra (296 K, D$_2$O/H$_2$O) of a) $Na_2[(\mathbf{4})_3Ti]$, b) $Na_4[(\mathbf{1})_3Ti_2]$, c) $Na_4[(\mathbf{1})_3Ti_2]$ + 4 LiCl, and d) $Na_4[(\mathbf{1})_3Ti_2]$ + 4 KCl.

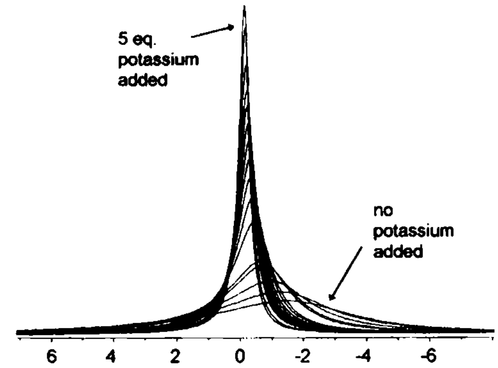


Fig. 4. Titration of $Na_4[(\mathbf{1})_3Ti_2]$ in D$_2$O [0.055 M] with KCl monitored by ^{23}Na NMR.

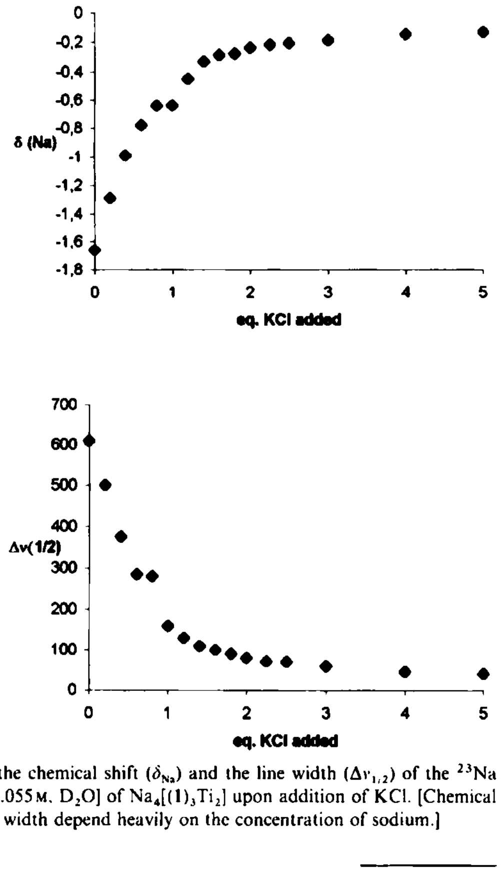
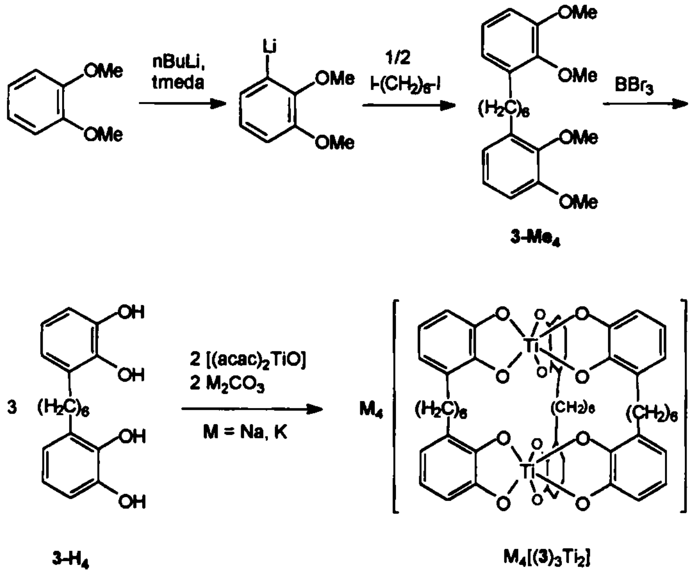


Fig. 5. Change in the chemical shift (δ_{Na}) and the line width ($\Delta\nu_{1/2}$) of the ^{23}Na NMR resonance [0.055 M, D$_2$O] of $Na_4[(\mathbf{1})_3Ti_2]$ upon addition of KCl. [Chemical shift as well as line width depend heavily on the concentration of sodium.]

the binding of potassium is highly favored.[16] The fact that the exchange of the alkali-metal cations proceeds without dissociation of the tetraanion can be shown by mixing $Na_4[(1)_3Ti_2]$ and **1-H$_4$** in [D$_4$]methanol. No dynamic behavior could be observed by ^1H NMR up to 330 K.

Synthesis of 3-H$_4$ and M$_4$[(3)$_3$Ti$_2$]: To explore the limitations of the cation-binding abilities of the binuclear catecholate complexes, we synthesized the ligand **3-H$_4$** from 2,3-dimethoxyphenyl lithium[17] and 1,6-diiodohexane followed by ether cleavage (BBr_3) as depicted in Scheme 2 and prepared the corresponding titanium compounds $M_4[(3)_3Ti_2]$ (M = Na, K).



Scheme 2. Preparation of **3-H$_4$** and $M_4[(3)_3Ti_2]$.

The ^{23}Na NMR spectra (0.02 M solution, methanol/[D$_4$]methanol) of $Na_4[(3)_3Ti_2]$ at room temperature as well as at 188 K show only one signal at $\delta_{Na} = -1.8$ (296 K). This means that the cavity formed by three ligands **3** and two titanium ions is too large to encapsulate sodium ions fully. Exchange of incorporated and solvated sodium ions proceeds fast with respect to the NMR timescale. However, an inclusion compound can be observed for $K_4[(3)_3Ti_2]$ in the solid state.

Molecular structure of K$_4$[(3)$_3$Ti$_2$]·5DMF·3H$_2$O: Figure 6 shows the molecular structure of $K_4[(3)_3Ti_2]\cdot 5DMF\cdot 3H_2O$. Both octahedrally coordinated titanium centers exhibit the same configuration and a triple-stranded helicate-type[3-5] coordination compound is formed (Fig. 6a). As shown earlier,[5-7] the relative chirality of the titanium tris(catecholate) moieties depends on the length of the alkyl spacer. The latter prefers to adopt a zigzag structure, as observed for one of the chains in the crystal. In the case of an even number of methylene units this leads to the helicate-type structure. In $[(3)_3Ti_2]^{4-}$ the chiral information is transferred through seven σ-bonds from one complex unit to the other. The observed orthorhombic space group $P2_12_12_1$ shows that the complex crystallizes with spontaneous chiral resolution and only one of the two enantiomeric helicates is present in the crystal.[3c] However, owing to the length of the alkyl spacer, a fast equilibrium between the helicate- and the *meso*-helicate-type structures should be present in solution.

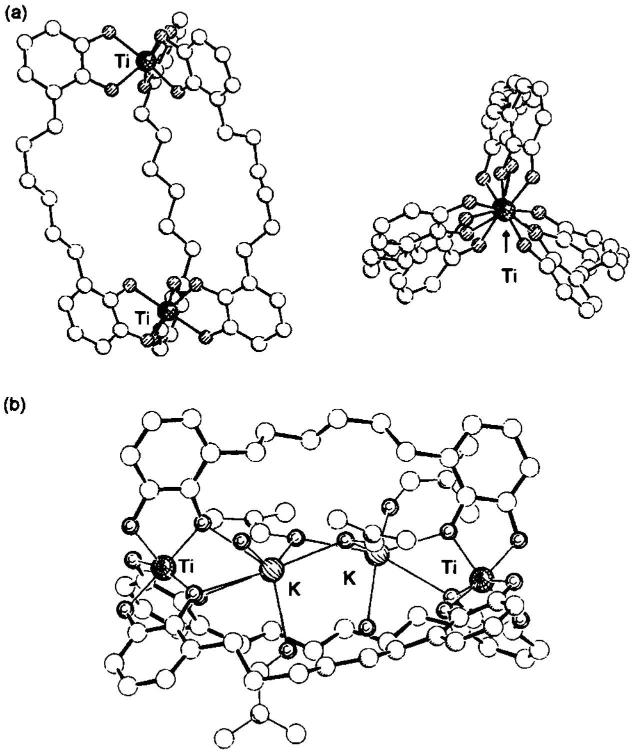


Fig. 6. SCHAKAL representation of a) the tetraanionic helicate $[(3)_3Ti_2]^{4-}$: side view (left) and view along the Ti–Ti axis (right) and b) a part of the molecular structure of $K_4[(3)_3Ti_2]\cdot 5DMF\cdot 3H_2O$ (two potassium ions, one DMF molecule, one water molecule, and all hydrogen atoms are omitted for clarity).

The cavity of the tetraanion is big enough for the inclusion of two potassium ions (Fig. 6b).[18] They are endohedrally bound to oxygen atoms of the catecholates of the titanium complex moieties. Vacant binding sites of the alkali-metal ions are saturated by DMF and water molecules. Two further K^+ ions are coordinated to the ends of the catecholate compound, bridging to another anion. Thus, an infinite chain is formed in the solid state.

Conclusion

The results of the ^{23}Na NMR spectroscopic studies clearly show that incorporation of sodium ions by self-assembled tetraanionic binuclear tris(biscatecholate) titanium(IV) complexes $[(1)_3Ti_2]^{4-}$ and $[(2)_3Ti_2]^{4-}$ takes place in solution.[19] The relatively large cavities of the two helicate-type tetraanions are more appropriate for the uptake of potassium ions than for sodium or lithium (cavity size [X-ray]: $[(1)_3Ti_2]^{4-} \approx 270$ pm,[5] $[(2)_3Ti_2]^{4-} \approx 340$ pm;[6] ionic size:[20] Li^+ 136 pm, Na^+ 190 pm, K^+ 266 pm). The large hexamethylene-bridged helicate $[(3)_3Ti_2]^{4-}$ does not show significant binding properties in solution, but the inclusion of *two* potassium ions can be observed in the solid state.

The work presented in this paper has shown that the counterions of anionic helicates or *meso*-helicates formed from biscatecholate ligands and titanium(IV) ions are not merely innocent spectators but a part of the molecular structure of the supramolecular species. Therefore they should be considered to play an important role in the self-assembly process itself.[21] Future work will focus on the investigation of the influence of the counterions on the formation of supramolecular coordination compounds.

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Experimental Section

Melting points (uncorrected): Büchi 535. IR: Bruker IFS. MS: Finnigan MAT90. UV/Vis: Perkin Elmer UV-Vis LAMBDA 2. ^{1}H NMR and ^{13}C NMR (BB/DEPT): AM400 or WM250, $T = 296$ K; internal standard: chloroform or [D_3]methanol. ^{23}Na NMR spectra were obtained on the AM400 at 105.8 MHz in D_2O, D_2O/H_2O (1:1), or methanol/[D_4]methanol (1:1); external standard: 1 M NaCl in D_2O. All reactions were carried out under argon. For the preparation and characterization of $M_4[(2)_3Ti_2]$ see ref. [5].

1,6-Bis(2,3-dimethoxyphenyl)hexane (**3-Me$_4$**): To 1,2-dimethoxybenzene (1.00 g, 7.24 mmol) and TMEDA (*N,N,N′,N′*-tetramethyl-1,2-ethanediamine, 1 mL) in 20 mL of ether was added *n*BuLi/hexane (1.6 M, 4.7 mL, 7.52 mmol) [17]. After 3 h, 1,6-diiodohexane (1.21 g, 3.58 mmol) in 20 mL of ether was added over a period of 1 h. The mixture was stirred for 15 h and then 20 mL of water and 1 mL of conc. HCl were added. The ethereal phase was separated and dried over $MgSO_4$, and solvent was removed in vacuum. The residue was purified by column chromatography (silica gel, hexane/dichloromethane 1:1) to obtain a colorless oil (0.33 g, 26%). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 6.98$ (t, $J = 7.9$ Hz, 2H), 6.76 (m, 4H), 3.86 (s, 6H), 3.82 (s, 6H), 2.63 (t, $J = 7.7$ Hz, 4H), 1.60 (m, 4H), 1.41 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, BB/DEPT): $\delta = 152.7$ (C_{qual}), 147.1 (C_{qual}), 136.8 (C_{qual}), 123.7 (CH), 121.9 (CH), 109.9 (CH), 60.6 (CH_3), 55.7 (CH_3), 30.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2); IR (neat): $\tilde{\nu} = 2932, 1584, 1481, 1085, 1013, 748$ cm^{-1}; MS (EI, 70 eV): $m/z = 358$ (100%, M^+); HRMS for $C_{22}H_{30}O_4$ calcd.: 358.2144, found: 358.2131.

1,6-Bis(2,3-dihydroxyphenyl)hexane (**3-H$_4$**): To **3-Me$_4$** (170 mg, 0.47 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C, 1 M BBr_3/CH_2Cl_2 (2 mL) was added. The mixture was allowed to warm to room temperature and was stirred for 14 h. 5 mL of methanol were added and the solvent was removed under vacuum. After addition of 20 mL of water the suspension was extracted with ether (40 mL). Drying ($MgSO_4$) and evaporation of the solvent yielded a gray hygroscopic solid (140 mg, 99%). M.p. 132 °C; ^{1}H NMR ([D_4]methanol, 400 MHz): $\delta = 6.60$ (m, 2H), 6.55 (m, 4H), 2.57 (t, $J = 7.6$ Hz, 4H), 1.58 (m, 4H), 1.37 (m, 4H); ^{13}C NMR ([D_4]methanol, 100 MHz, BB/DEPT): $\delta = 145.9$ (C_{quat}), 144.2 (C_{quat}), 130.7 (C_{quat}), 121.9 (CH), 120.1 (CH), 113.6 (CH), 31.1 (CH_2), 31.0 (CH_2), 30.5 (CH_2); IR (KBr): $\tilde{\nu} = 3451, 3365, 3069, 2928, 1627, 1589, 1480, 1293, 945$ cm^{-1}; MS (EI, 70 eV): $m/z = 302$ (84%, M^+), 123 (100%, $[C_7H_7O_2]^+$); HRMS for $C_{18}H_{22}O_4$, calcd.: 302.1518, found: 302.1532; calcd. for $C_{18}H_{22}O_4 \cdot {}^1/_4 H_2O$ (306.7): C 70.45, H 7.39; found: C 70.66, H 7.32.

General procedure for the preparation of titanium(IV) complexes: Ligand (3 equiv), M_2CO_3 (M = Na, K; 2 equiv), and $[(acac)_2TiO]$ (2 equiv) were dissolved in methanol and stirred overnight. The mixture was evaporated to dryness, and a red solid was obtained. The coordination compounds may be purified by chromatography (Sephadex-LH20, methanol) but this is often unnecessary.

$K_4[(1)_3Ti_2]$: Yield: 80% as pentahydrate (after chromatography); ^{1}H NMR ([D_4]methanol, 250 MHz): $\delta = 6.52$ (dd, $J = 1.5/7.6$ Hz, 6H), 6.44 (t, $J = 7.6$ Hz, 6H), 6.26 (dd, $J = 1.5/7.6$ Hz, 6H), 2.7 (m, 6H), 2.4 (m, 6H); ^{13}C NMR ([D_4]methanol, 100 MHz, BB/DEPT): $\delta = 159.2$ (C_{quat}), 157.8 (C_{quat}), 126.6 (C_{quat}), 120.1 (CH), 118.6 (CH), 110.4 (CH), 33.5 (CH_2); IR (KBr): $\tilde{\nu} = 3397, 2926, 1453, 1262$ cm^{-1}; UV/Vis (methanol): $\lambda = 209, 274, 363$ nm; FAB(+)MS (glycerin): $m/z = 941$ ($K_3H_2[(1)_3Ti_2]^+$), 979 ($K_4H[(1)_3Ti_2]^+$), 1017 ($K_5[(1)_3Ti_2]^+$); calcd. for $C_{42}H_{30}Ti_2K_4O_{12} \cdot 5H_2O$: C 47.19, H 3.77; found: C 47.42, H 4.10.

$Na_4[(1)_3Ti_2]$: Yield: 93% as dodecahydrate; ^{1}H NMR ([D_4]methanol, 250 MHz): $\delta = 6.47$ (dd, $J = 1.8/7.3$ Hz, 6H), 6.41 (t, $J = 7.3$ Hz, 6H), 6.28 (dd, $J = 1.8/7.3$ Hz, 6H), 2.68 (s, 12H); IR (KBr): $\tilde{\nu} = 3370, 2925, 1453, 1263, 739$ cm^{-1}; UV/Vis (methanol): $\lambda = 209, 274, 363$ nm; FAB(+)MS (glycerin): $m/z = 871$ ($Na_2H_3[(1)_3Ti_2]^+$), 893 ($Na_3H_2[(1)_3Ti_2]^+$), 915 ($Na_4H[(1)_3Ti_2]^+$), 937 ($Na_5[(1)_3Ti_2]^+$); calcd. for $C_{42}H_{30}Ti_2Na_4O_{12} \cdot 12H_2O$: C 44.62, H 4.81; found: C 44.69, H 4.82.

$K_4[(3)_3Ti_2]$: Yield: 97% as undecahydrate; ^{1}H NMR ([D_4]methanol, 400 MHz): $\delta = 6.36$ (t, $J = 7.4$ Hz, 6H), 6.30 (d, $J = 7.4$ Hz, 6H), 6.23 (d, $J = 7.4$ Hz, 6H), 2.34 (m, 12H), 1.43 (m, 12H), 1.26 (m, 12H); ^{13}C NMR ([D_4]methanol, 100 MHz, BB/DEPT): $\delta = 159.6$ (C_{quat}), 158.4 (C_{quat}), 126.5 (C_{quat}), 119.3 (CH), 117.9 (CH), 110.0 (CH), 30.2 (CH_2), 29.2 (CH_2), 27.8 (CH_2); IR (KBr): $\tilde{\nu} = 3369, 3050, 2853, 1566, 1452, 1255, 737$ cm^{-1}; UV/Vis (methanol): $\lambda = 202, 276, 375$ nm; FAB(+)MS (glycerin): $m/z = 1147$ ($K_4H[(3)_3Ti_2]^+$), 1185 ($K_5[(1)_3Ti_2]^+$); calcd. for $C_{54}H_{54}O_{12}Ti_2K_4 \cdot 11H_2O$: C 48.21, H 5.69; found: C 48.14, H 5.54.

$Na_4[(3)_3Ti_2]$: Yield: 99% as tetradecahydrate; ^{1}H NMR ([D_4]methanol, 250 MHz): $\delta = 6.38$–6.31 (m, 12H), 6.21 (dd, $J = 2.1/7.0$ Hz, 6H), 2.47 (m, 12H), 1.39 (brm, 24H); IR (KBr): $\tilde{\nu} = 3405, 2927, 1451, 1254, 737$ cm^{-1}; UV/Vis (methanol): $\lambda = 203, 276, 375$ nm; FAB(+)MS (glycerin): $m/z = 1061$ ($Na_3H_2[(3)_3Ti_2]^+$), 1083 ($Na_4H[(3)_3Ti_2]^+$), 1105 ($K_5[(3)_3Ti_2]^+$); calcd. for $C_{54}H_{54}O_{12}Ti_2Na_4 \cdot 14H_2O$: C 48.58, H 6.19; found: C 48.63, H 6.32.

Single-crystal structure analysis of $K_4[(3)_3Ti_2] \cdot 5DMF \cdot 3H_2O$: $C_{54}H_{54}O_{12}K_4Ti_2 \cdot 5DMF \cdot 3H_2O$, $M_r = 1566.70$, orange-red parallelepiped, $0.2 \times 0.3 \times 0.4$ mm^3, $a = 1431.3(3)$, $b = 1597.8(3)$, $c = 3483.1(3)$ pm, $V = 7966(2) \times 10^6$ pm^3 ($T = 173$ K), $\rho_{calcd} = 1.306$ g cm^{-3}, orthorhombic, $P2_12_12_1$ (no. 19), $Z = 4$, Siemens-Nicolet four-circle diffractometer, $Mo_{K\alpha}$ radiation, $\mu = 0.478$ mm^{-1}, 9465 measured reflections between $4° < 2\theta < 54°$, of which 9429 were independent and 9419 were used for refinement. Structure solution by direct methods (SHELXS-86), refinement vs F^2 (SHELXL-93), 901 parameters, $w = 1/[\sigma^2(F_0)^2 + (0.0916P)^2]$, R for $3756\,F_0 < 4\sigma(F_0) = 0.0895$, $wR2$ for all 9419 data = 0.2297, GoF = 0.929, residual electron density $0.391/-0.323$ e Å^{-3}. The heavy atoms were anisotropically refined. Hydrogen atoms were calculated in geometrically optimized positions and refined isotropically by means of a riding model with fixed $U_{eq} = 0.08$. Three residual peaks (1.7–1.9 e Å^{-3}) due to a highly disordered solvent molecule were accounted for by the squeeze (bypass) procedure of the Platon program package as described [22,23].

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