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Two- and Three-Dimensional Coordination Polymers From the Reaction of Bis- and Tris(2-aminoethyl)amine with Titanium and Zirconium Alkoxides

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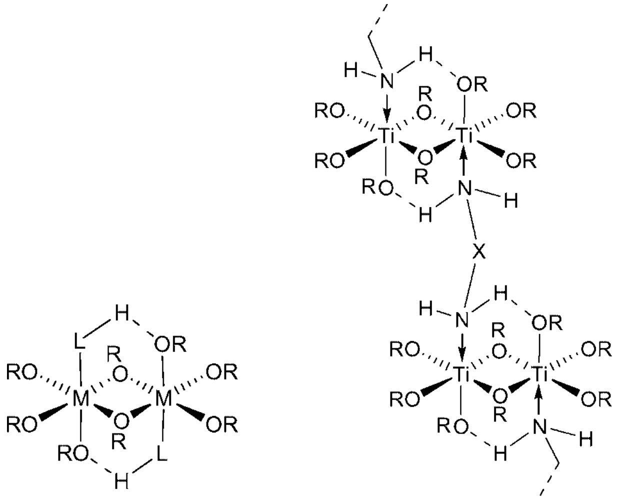
Dedicated to Professor Bernhard Kräutler on the occasion of his 60th birthday

Keywords: Titanium / Zirconium / Coordination polymers / N ligands

The reaction of bis(2-aminoethyl)amine with M(O*i*Pr)$_4$ (M = Ti, Zr) affords the chain-like coordination polymers [M$_2$(O*i*Pr)$_8$(H$_2$NCH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$)]$_\infty$, where only the NH$_2$ groups of the amine are coordinated to the M$_2$(O*i*Pr)$_8$ units. 2D NMR spectroscopy shows that the adducts dissociate into the starting compounds when dissolved in CD$_2$Cl$_2$ but are slowly re-formed in solution over a period of two weeks. Puckered layers of condensed six-membered rings of [Ti$_2$(O*i*Pr)$_8$]$_3$[N(CH$_2$CH$_2$NH$_2$)$_3$]$_2$ are formed when [Ti(O*i*Pr)$_4$] is treated with tris(2-aminoethyl)amine. The voids in the center of the rings are filled by non-coordinated Ti$_2$(O*i*Pr)$_8$ guest molecules. In contrast, chains of [Zr$_2$(O*i*Pr)$_8$(H$_2$NCH$_2$CH$_2$NR′CH$_2$CH$_2$NH$_2$)]{R′=CH$_2$CH$_2$NH$_2$[Zr$_2$(O*i*Pr)$_8$(HO*i*Pr)]} are formed upon treatment of tris(2-aminoethyl)amine with [Zr(O*i*Pr)$_4$].

Introduction

An understanding of the Lewis acidity of metal alkoxides is the key for understanding their chemistry, for example in sol–gel processes or as catalysts. One consequence of the acidic properties of the metal center in these alkoxides is their tendency to form oligomers [M(OR)$_x$]$_n$ with alkoxido bridges between two or three metal atoms, i.e. by interaction of the Lewis basic alkoxido groups with the Lewis acidic metal centers. The physical properties as well as the chemical reactivity of the metal alkoxides are influenced by the degree of aggregation. In alcoholic solution, for instance, addition of solvent molecules to the metal center competes with the formation of alkoxido bridges. The stability of the adducts increases for given alkoxido groups with increasing Lewis basicity of the alcohol, increasing Lewis acidity of the metal atom, and increasing coordination number of the metal. Thus, the adducts [M$_2$(O*i*Pr)$_8$(*i*PrOH)$_2$] (M = Ce,[1,2] Zr,[2] Hf[2,3]) can be isolated, whereas the analogous adducts [Ti$_2$(OR)$_8$(ROH)$_2$] are only stable when the Lewis acidity of the metal is raised by more electronegative substituents.[4–6] The metal atoms in the dimeric adducts [M$_2$(OR)$_8$(ROH)$_2$] are octahedrally coordinated owing to both the formation of alkoxido bridges and the coordination of alcohol molecules (Scheme 1, LH = ROH). The coordinated alcohol is stabilized by hydrogen bonding with the neighboring alkoxido ligand.



Scheme 1. General structure of the adducts [Ti$_2$(OR)$_8$(LH)$_2$] (LH = R′OH or R′NH$_2$; --- represents hydrogen bonds) and polymeric [Ti$_2$(OR)$_8$(NH$_2$XNH$_2$)].

The stability of the adducts can also be increased by stronger Lewis bases. We recently succeeded in crystallizing a number of amine adducts [M$_2$(OR)$_8$(NH$_2$R′)$_2$] (M = Ti, Zr) when M(OR)$_4$ was treated with the corresponding primary amines.[7,8] These amine adducts (Scheme 1, LH = R′NH$_2$) have similar structures to the alcohol adducts [M$_2$(OR)$_8$(ROH)$_2$], including the hydrogen bond between the amino group and the adjacent OR ligand. However, comparison of the adducts of different amines showed that

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the Lewis basicity of the amine nitrogen is not the decisive parameter for the stability of the adducts. Instead, the strength of the NH···O hydrogen bond appears to be the main parameter. Any electronic or steric effect weakening the hydrogen bond thus weakens the stability of the adducts.

The general structure of $[\mathrm{Ti_2(O}i\mathrm{Pr)_8(NH_2R')_2}]$ was extended to insoluble coordination polymers with the chain structures shown in Scheme 1 when $[\mathrm{Ti(OR)_4}]$ was treated with diamines $\mathrm{H_2NXNH_2}$ (X = hydrocarbon spacer).[7–9] An open question of previous work was whether the observed structures are retained in solution and whether coordination equilibria exist, because the obtained ^{15}N NMR spectra were rather inconclusive. The use of $\mathrm{NH(CH_2CH_2NH_2)_2}$ and $\mathrm{N(CH_2CH_2NH_2)_3}$ has now allowed us to answer this question. This is discussed in this paper, together with the interesting structural chemistry of the corresponding adducts.

Results and Discussion

Solid-State Structures

When bis(2-aminoethyl)amine was treated with an equimolar amount, or a slight excess, of $[\mathrm{Ti(O}i\mathrm{Pr)_4}]$ in 2-propanol or $[\mathrm{Zr(O}i\mathrm{Pr)_4}]$ in heptane, the compounds $[\mathrm{M_2(O}i\mathrm{Pr)_8(H_2NCH_2CH_2NHCH_2CH_2NH_2)}]$ (**1**: M = Ti; **2**: M = Zr) were obtained in high yield. Although the starting amine contains three basic nitrogen atoms, only the two primary amino groups were found by X-ray structure analysis to coordinate to the metal alkoxide moieties. As a result, chain-like coordination polymers are formed (Figures 1 and 2), as previously found for $[\mathrm{Ti_2(O}i\mathrm{Pr)_8(H_2NXNH_2)}]_\infty$ with hydrocarbon spacers (X) between the primary amino groups.

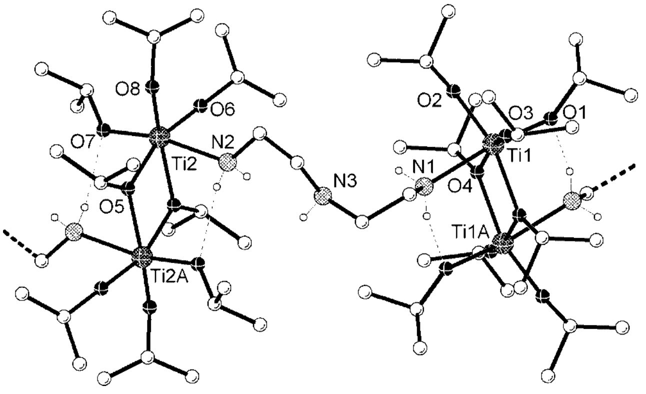


Figure 1. The chain structure of $[\mathrm{Ti_2(O}i\mathrm{Pr)_8(H_2NCH_2CH_2NHCH_2CH_2NH_2)}]_\infty$ (**1**). The dotted lines represent NH···O hydrogen bonds. Selected bond lengths [pm] and angles [°]: Ti(1)–N(1) 229.2(2), Ti(1)–O(3) 180.7(2), Ti(1)–O(4) 205.0(2), Ti(1)–O(4A) 208.8(2), Ti(1)–O(1) 183.9(2), Ti(1)–O(2) 183.9(2), N(1)···O(1) 294.1(3), Ti(2)–N(2) 229.9(2), Ti(2)–O(7) 186.6(2), Ti(2)–O(5) 204.9(2), Ti(2)–O(4A) 209.8(2), Ti(2)–O(6) 181.4(2), Ti(2)–O(8) 182.6(2), N(2)···O(7) 293.7(3); N(1)–Ti(1)–O(1) 169.56(8), N(2)–Ti(2)–O(7) 168.65(9), N(1)–Ti(1)–Ti(1A) 77.97(6), N(2)–Ti(2)–Ti(2A) 76.75(7), O(1)–Ti(1)–Ti(1A) 91.75(6), O(7)–Ti(2)–Ti(2A) 92.42(7).

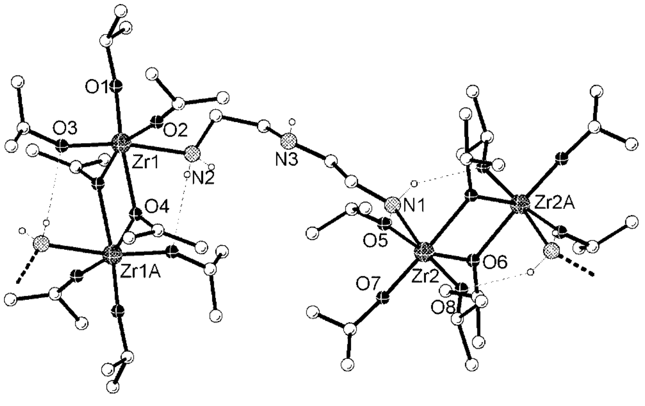


Figure 2. The chain structure of $[\mathrm{Zr_2(O}i\mathrm{Pr)_8(H_2NCH_2CH_2NHCH_2CH_2NH_2)}]_\infty$ (**2**). The dotted lines represent NH···O hydrogen bonds. Selected bond lengths [pm] and angles [°]: Zr(1)–N(2) 241.7(3), Zr(1)–O(3) 196.9(3), Zr(1)–O(4) 219.0(2), Zr(1)–O(4A) 220.2(3), Zr(1)–O(1) 195.0(3), Zr(1)–O(2) 195.5(3), N(2)···O(3) 315.2(5), Zr(2)–N(1) 243.9(4), Zr(2)–O(8) 198.4(3), Zr(2)–O(6) 219.3(3), Zr(2)–O(6A) 219.2(3), Zr(2)–O(5) 195.1(3), Zr(2)–O(7) 195.0(3), N(1)···O(8) 308.8(5); N(2)–Zr(1)–O(3) 170.0(1), N(1)–Zr(2)–O(8) 168.4(1), N(2)–Zr(1)–Zr(1A) 76.77(9), N(1)–Zr(2)–Zr(2A) 76.24(9), O(3)–Zr(1)–Zr(1A) 93.41(9), O(8)–Zr(2)–Zr(2A) 92.70(9).

We have observed previously that secondary amines are less prone to coordinate to $\mathrm{M(OR)_4}$ and have attributed this finding to the less pronounced ability of secondary amines to engage in the hydrogen bonding that stabilizes the M–N interaction.[8] Although the NH group in **1** and **2** does not interact with the metal alkoxides, it is probably responsible for the much better solubility of **1** and **2** compared to related coordination polymers with hydrocarbon spacers X. As will be discussed later, this fact allows us to investigate the solution structures by NMR spectroscopy.

Apart from different conformations of the bis(2-aminoethyl)amine units, the polymeric structures of **1** and **2** follow the same construction principle. The amine is a two-directional linker for the $\mathrm{M_2(O}i\mathrm{Pr)_8}$ units, i.e. each $\mathrm{NH_2}$ group of bis(2-aminoethyl)amine is coordinated to another $\mathrm{M_2(O}i\mathrm{Pr)_8}$ unit. The chains are close-packed, with an interchain distance of about 870 pm in **1** and 910 pm in **2**

The metal alkoxide units are centrosymmetric dimers of the general composition $\mathrm{M_2(OR)_8(NH_2R)_2}$ in which the octahedrally coordinated metal atoms are bridged by two OR groups. The amines are coordinated axially to the $\mathrm{M_2(\mu\text{-}OR)_2}$ ring and hydrogen-bonded to neighboring alkoxido ligands (see Scheme 1 and Figures 1 and 2). The N···O separations [293.7(3) and 294.1(3) pm for **1**; 308.8(5) and 315.2(5) pm for **2**] are in the typical range of NH···O hydrogen bonds.[10] To enable hydrogen bonding, the M–M–N angles are reduced to 76–78° by bending of the amino ligand towards the center of the $\mathrm{M_2(\mu\text{-}OR)_2}$ ring. The M–O distances *trans* to the amine ligand are in between the (long) M–O distances of the bridging OR groups and the (short) M–O distances of the equatorial terminal OR groups.

When [Ti(O*i*Pr)$_4$] was treated with 0.67 molar equivalents of tris(2-aminoethyl)amine, colorless crystals of [{Ti$_2$(O*i*Pr)$_8$}$_3$-{N(CH$_2$CH$_2$NH$_2$)$_3$}$_2$·Ti$_2$(O*i*Pr)$_8$] (**3**) were obtained after recrystallization from CH$_2$Cl$_2$. All NH$_2$ groups of tris(2-aminoethyl)amine coordinate to Ti$_2$(O*i*Pr)$_8$ units. The crystal structure of **3** is thus a two-dimensional coordination polymer with N(CH$_2$CH$_2$NH$_2$)$_3$ as a three-directional linker and the Ti$_2$(OR)$_8$ units as two-directional connectors. The framework of **3** is formally related to that of black phosphorus, i.e. the framework of **3** is a puckered layer of condensed six-membered, centrosymmetric rings (Figures 3 and 4) with CH$_2$CH$_2$NH$_2$[Ti$_2$(O*i*Pr)$_8$]NH$_2$CH$_2$CH$_2$ edges and pyramidal nitrogen atoms as the corners. The geometry of the Ti$_2$(O*i*Pr)$_8$(NH$_2$R)$_2$ units of the framework structure corresponds to the general structure shown in Figure 1 (left), including the hydrogen bonds (N···O 297–302 pm). Furthermore, the Ti–N distances in **3** [230.5(4)–231.9(5) pm] are the same as in molecular or chain-like complexes with mono- or diamines.

The [Ti$_2$(O*i*Pr)$_8$]$_3$[N(CH$_2$CH$_2$NH$_2$)$_3$]$_2$ network structure contains a large free volume due to the very large ring size (about 1.4 nm in diameter). In the crystals obtained in the reaction of [Ti(O*i*Pr)$_4$] with N(CH$_2$CH$_2$NH$_2$)$_3$, the voids in the center of the rings are filled with Ti$_2$(O*i*Pr)$_8$ guest molecules, which do not undergo any bonding interaction with the host structure. The Ti–Ti vectors of the Ti$_2$(O*i*Pr)$_8$

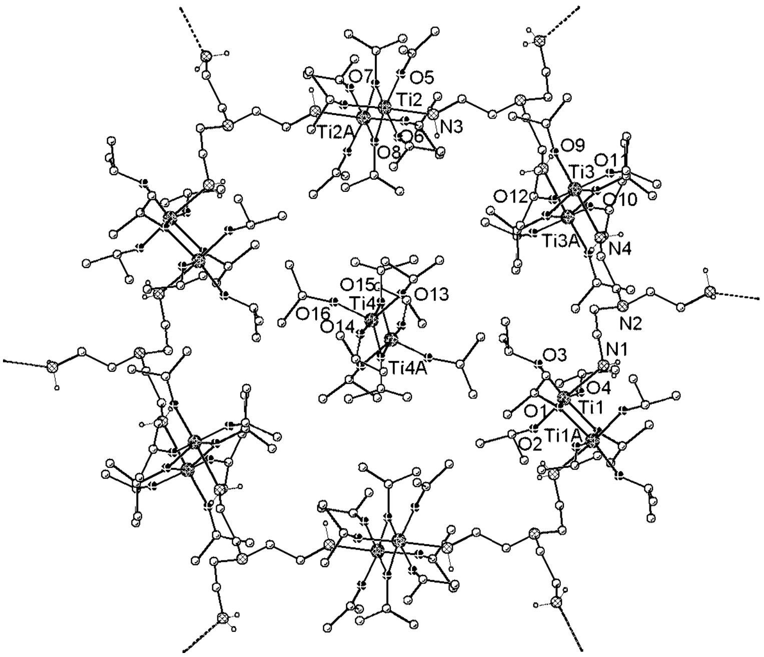


Figure 3. Perspective view (approximately perpendicular to the layer) of a six-membered ring from which the layer structure of **3** is composed. Most hydrogen atoms have been omitted for clarity. Selected bond lengths [pm]: Ti(1)–N(1) 233.5(5), Ti(2)–N(3) 231.4(4), Ti(3)–N(4) 231.7(4), N(1)···O(2) 302.0(6), N(3)···O(6) 296.7(6), N(4)···O(9) 298.2(6).

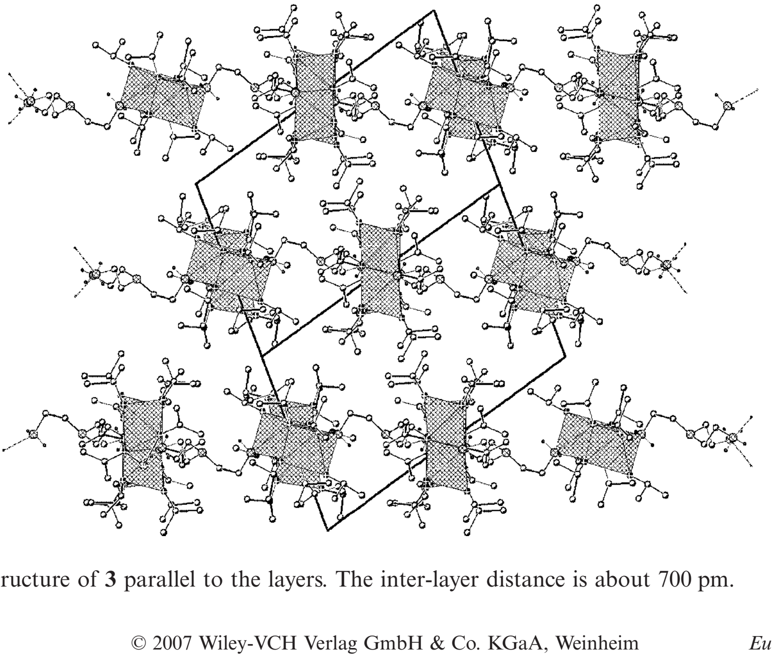


Figure 4. View of the layer structure of **3** parallel to the layers. The inter-layer distance is about 700 pm.

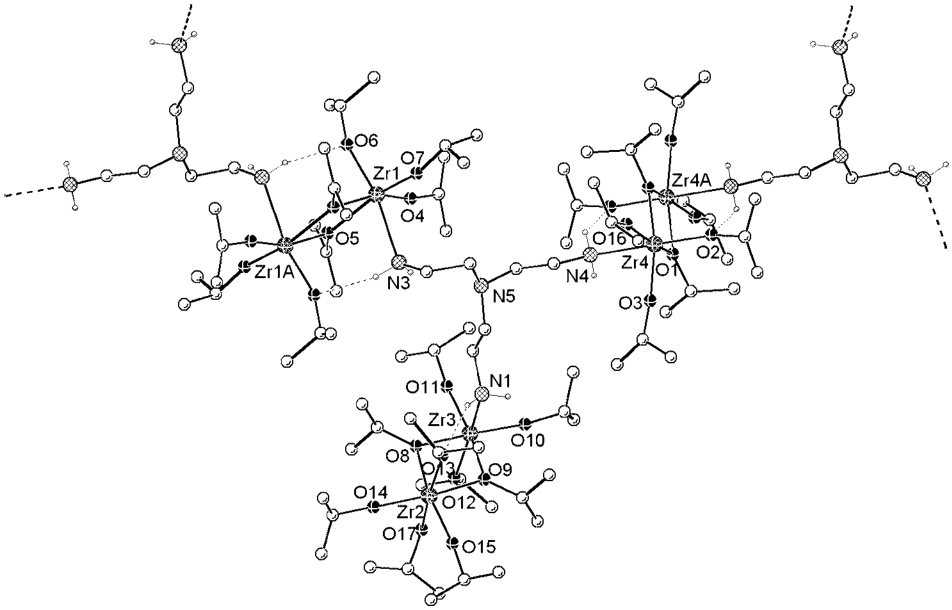


Figure 5. The chain structure of $[\{Zr_2(OiPr)_8\}\{Zr_2(OiPr)_8(HOiPr)\}\{(H_2NCH_2CH_2)_3N\}]_\infty$ (**4**). Selected bond lengths [pm]: Zr(1)–N(3) 244.8(6), Zr(3)–N(1) 243.0(7), Zr(4)–N(4) 243.3(6), Zr(2)–O(17) 232.1(6) (coordinated *i*PrOH), N(1)···O(13) 308(1), N(3)···O(6) 309.2(9), N(4)···O(2) 308(1), O(17)···O(12) 270.6(8).

guests are approximately perpendicular to the layer of the host structure. The structure of the entrapped titanium alkoxide dimers can be described as two trigonal bipyramids sharing a common axial–equatorial edge. Related structures of dimeric, nonsolvated titanium alkoxides with five-coordinate titanium atoms are known for bulky OR groups, such as $[Ti_2(OCH_2tBu)_8]$,[11] $[Ti_2(OiPr)_6(OAr)_2]$ (Ar = 2,4,6-$Me_3C_6H_2$[12] or 2,6-$iPr_2C_6H_3$[13]) and $[Ti_2(OiPr)_4\{OCH(CF_3)_2\}_4]$.[4] The crystal structure of **3** thus contains two structurally different $Ti_2(OiPr)_8$ moieties: the guest molecules with five-coordinate titanium atoms and the $Ti_2(OiPr)_8$ units with six-coordinate titanium atoms being part of the framework structure. Framework structures such as **3** have not yet been observed in the chemistry of transition metal alkoxides. It may be speculated that other guests could be incorporated in the same way into the host structure of $[Ti_2(OiPr)_8]_3[N(CH_2CH_2NH_2)_3]_2$.

The analogous reaction of $[Zr(OiPr)_4]$ with tris(2-aminoethyl)amine resulted in a compound with different composition and crystal structure. The structure of the obtained complex $[Zr_2(OiPr)_8][Zr_2(OiPr)_8(HOiPr)][(H_2NCH_2CH_2)_3N]$ (**4**) can be formally derived from the layer structure of **3** by decoordinating one NH_2 group per $N(CH_2CH_2NH_2)_3$ and replacing it with an 2-propanol molecule. This results in a chain structure of the type $Zr_2(OiPr)_8(H_2NCH_2CH_2NR'CH_2CH_2NH_2)$, where R′ is a $CH_2CH_2NH_2[Zr_2(OiPr)_8(HOiPr)]$ moiety (Figure 5). Formation of a layered structure is thus inhibited because one coordination site at one zirconium is blocked by an alcohol molecule. As mentioned in the Introduction, alcohol adducts of $[Zr(OiPr)_4]$ are stable while those of $[Ti(OiPr)_4]$ are not; this allows the alcohol to compete with the amine for coordination. It is interesting to note at this point that reaction of $M(OiPr)_4$ with benzylamine results in the same structure $[M_2(OiPr)_8(NH_2CH_2Ph)_2]$ for both Ti and Zr.[8] The bond lengths and angles of the zirconium atoms in **4** coordinated to NH_2 groups are basically the same as those in **2**, while those of the sixth zirconium atom, to which an 2-propanol molecule is coordinated, are very similar to those in $[Zr_2(OiPr)_8(iPrOH)_2]$, including the hydrogen bond between the coordinated alcohol and the adjacent O*i*Pr ligand.[2]

NMR Investigations in Solution

The coordination polymers **1**–**4** described above can be recrystallized, which is a strong indication that the amine adducts are relatively stable and may persist in solution. Nevertheless, coordination equilibria may exist upon dissolution of the compounds. This is not simply an academic question but is also important for the use of metal alkoxides in sol–gel processes, where coordination polymers may offer the possibility to pre-organize metal alkoxides prior to hydrolytic polycondensation.

A section of the ^1H NMR spectrum of the dissolved crystals of **1** is reproduced at the top of Figure 6. The $^1H/^{13}C$ HSQC spectrum shows one correlation at δ = 4.51 (^1H) and 76.5 ppm (^{13}C) for a CH unit of the time-averaged isopropoxide ligands and two correlations at δ = 2.84 (^1H)/52.8 ppm (^{13}C) and 2.54 (^1H)/42.2 ppm (^{13}C) corresponding to the two CH_2 units of the amine ligand. The latter two signals are very similar to the signals of the free ligand at δ = 2.57/2.68 ppm (^1H) and 41.7/57.7 ppm (^{13}C), respectively. The $^1H/^{15}N$ HMBC spectrum of **1** (Figure 7, left) shows two correlations at δ = 9.1 (NH) and –3.2 ppm (NH_2), which are almost the same as the shifts for the uncoordinated ligand (δ = 9.1 and –2.3 ppm). The two protons of the NH_2 groups appear as a broad signal at δ = 1.09 ppm. This indicates that most of the amine ligand is not coordinated to the metal center.

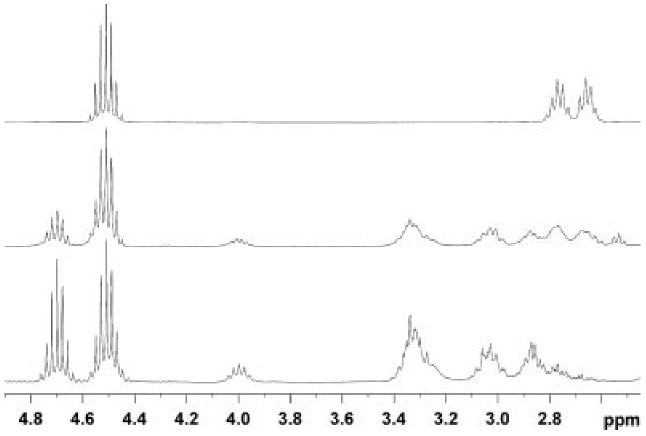


Figure 6. ^1H NMR spectra of $[Ti_2(OiPr)_8(NH_2CH_2CH_2NHCH_2CH_2NH_2)]$ (**1**) in CD_2Cl_2. Top: immediately after dissolving the crystals; center: after one week; bottom: after two weeks.

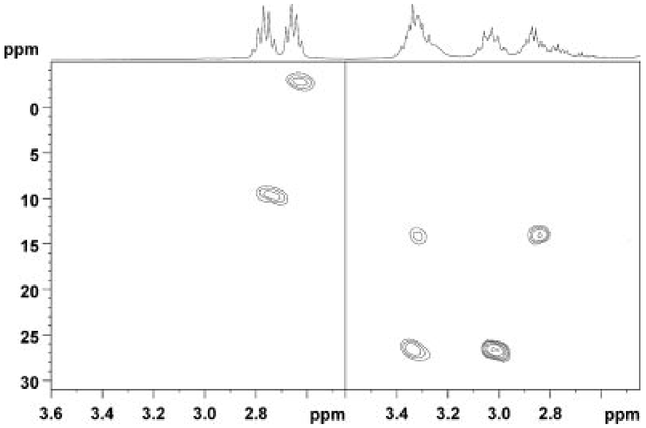


Figure 7. $^1H/^{15}N$ HMBC spectrum of **1** in CD_2Cl_2. Left: immediately after dissolving the crystals; right: after two weeks.

This picture changed completely when NMR spectra of the same solution were recorded again after one week. The CH_2 region of the amine now showed five new broad and unresolved multiplets beside the previous two signals, which were broader (Figure 6, center) and with lower intensity. In a third spectrum measured after two weeks (Figure 6, bottom), nearly no starting signals were left, but instead four new broad multiplets were observed. The signals for the two nitrogen atoms had shifted to δ = 14.0 (typical shift range for coordinated NH_2) and 26.5 ppm (NH) (Figure 7, right). This indicated strongly that the amine is now coordinated. This conclusion was supported by the pair-wise splitting of the proton signals of the CH_2 groups in the $^1H/^{13}C$ HSQC spectrum (Figure 8). Correlations were found at δ = 3.32/2.86 (^1H) and 48.7 ppm (^{13}C) as well as δ = 3.33/3.02 (^1H) and 39.6 ppm (^{13}C). The splitting of the proton resonance is due to the fact that the protons become non-equivalent upon coordination of the NH_2 groups to the metal centers. The two protons of the NH_2 group are also split into two broad signals (proton trace in Figure 8) at δ = 5.69 and 2.39 ppm. This is evidence for the formation of stable N–H···O hydrogen bonds, as observed in the solid-state structure. Four different signals of isopropoxide groups were identified in the $^1H/^{13}C$ HSQC spectrum at this point (Figure 8). Two signals overlap in the proton region at δ = 4.69 ppm (^1H) and show ^{13}C correlations to the signals at δ = 78.3 and 76.7 ppm; the third is located at δ = 4.51 (^1H) and 76.1 ppm (^{13}C). The signals at δ = 3.97 (^1H) and 64.1 ppm (^{13}C) are due to non-coordinated *i*PrOH. The NMR spectra after two weeks, especially the number and intensity ratio of the O*i*Pr ligand signals, correspond with the local symmetry [two axial O*i*Pr (*trans* to NH_2), four equatorial and two bridging] of **1** in the solid-state structure. The presence of noncoordinated 2-propanol is either due to incomplete removal of adsorbed alcohol during drying of the crystals or minor hydrolysis during the long measuring period.

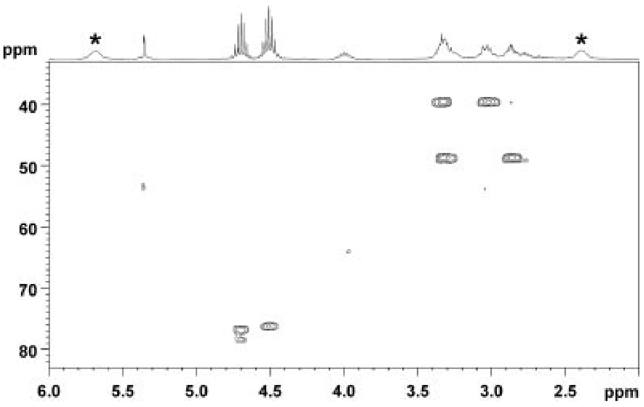


Figure 8. $^1H/^{13}C$ HSQC spectrum of **1** in CD_2Cl_2 after two weeks. The two proton signals marked with an asterisk are from NH_2.

We interpret the spectroscopic findings by proposing that the polymeric adduct of **1** dissociates into $[Ti_2(OiPr)_8]$ and $NH(CH_2CH_2NH_2)_2$ upon dissolution in CD_2Cl_2. The NMR spectra measured immediately after dissolution of the crystals thus correspond to a mixture of the starting compounds. The adduct is formed again in a slow reaction in solution, and the NMR spectra after two weeks correspond to the amine adduct **1**. This notion was supported by the following experiment. When $[Ti(OiPr)_4]$ and bis(2-aminoethyl)amine were mixed in a 2:1 ratio (same Ti:amine ratio as in crystalline **1**) in CD_2Cl_2 the same changes in the spectra were observed over a period of two weeks as when crystals of **1** were dissolved. Only the signals of the starting materials were present after mixing, whereas an identical signal pattern was observed after two weeks as for the dissolved crystals.

The corresponding complex $[Zr_2(OiPr)_8(NH_2CH_2CH_2NHCH_2CH_2NH_2)]$ (**2**) shows almost the same solution behavior as **1**, with the exception that **2** is less soluble, which leads to rather faster crystallization in the NMR tube. The crystals recovered from the NMR tube had identical cell parameters as the original crystals.

As a result of the NMR investigations described above, it is now possible to prove adduct formation even if the compounds do not crystallize and thus no solid-state structures are available. Figure 9 shows the NMR spectra of a 1:1 mixture of [Ti(O*i*Pr)$_4$] and *N*-(trimethoxysilylpropyl)-ethylenediamine in CD_2Cl_2. To prove whether coordination occurs in solution, spectra were recorded over a period of two months. New signals were observed one week after mixing the starting compounds (Figure 9, center), and after two months (Figure 9, bottom) almost no signals of the starting compounds were left. ^{15}N NMR signals at δ = 14.3 (NH) and 2.7 ppm (NH$_2$) were found after mixing the compounds, compared to δ = 13.4 (NH) and –4.0 ppm (NH$_2$) for the ethylenediamine derivative before addition of [Ti(O*i*Pr)$_4$], which shifted to δ = 37.8 (NH) and 31.3 ppm (NH$_2$) after two months. The signals for the *i*OPr ligands after two months correspond roughly to the symmetry of a [Ti$_2$(O*i*Pr)$_8$(NH$_2$R)$_2$] complex. These NMR spectra thus strongly indicate that the ligand is almost completely coordinated and compound **5** is formed.

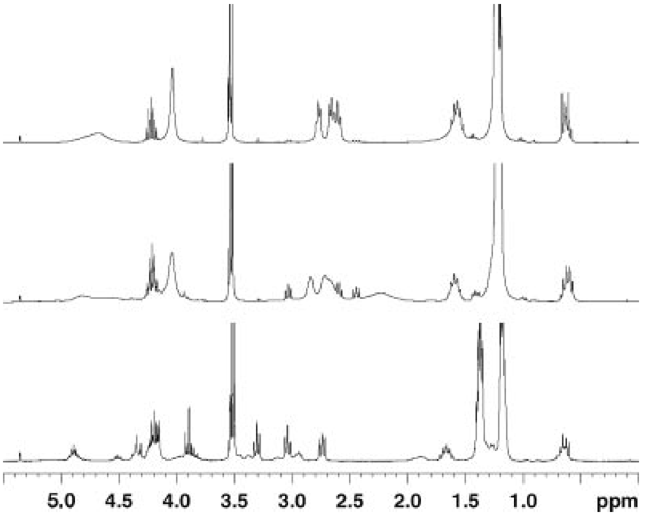
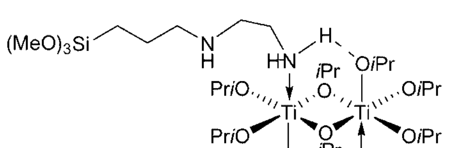


Figure 9. ^{1}H NMR spectrum of [Ti(O*i*Pr)$_4$] and $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OMe)_3$ in a 1:1 ratio in CD_2Cl_2. Top: after mixing; center: after one week; bottom: after two months.



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In the ^{1}H NMR spectrum of [{Ti$_2$(O*i*Pr)$_8$}$_3$-{N(CH$_2$CH$_2$NH$_2$)$_3$}$_2$·Ti$_2$(O*i*Pr)$_8$] (**3**) (Figure 10, top) four broad multiplets were observed between δ = 3.40 and 2.80 ppm immediately after dissolving the crystals, and the CH$_2$ region in the ^{1}H/^{13}C HSQC spectrum (Figure 11) showed four different pairwise correlations to ^{13}C atoms, with two of them belonging to the same CH$_2$CH$_2$ unit (δ = 36.4–53.3 and 38.6–60.0 ppm). An EXSY spectrum of this compound showed exchange peaks between these CH$_2$CH$_2$ units along the diagonal. An explanation for this observation might be that not all three CH$_2$CH$_2$ units are coordinated in solution and therefore show time-averaged ^{1}H and ^{13}C signals. The ^{15}N signals were found at δ = 36.3 (N) and 14.8 ppm (coordinated NH$_2$).

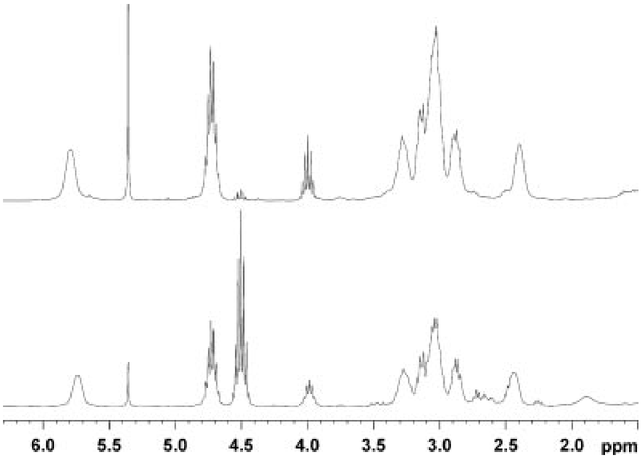

Figure 10. Top: ^{1}H NMR spectrum of [{Ti$_2$(O*i*Pr)$_8$}$_3$-{N(CH$_2$CH$_2$NH$_2$)$_3$}$_2$·Ti$_2$(O*i*Pr)$_8$] (**3**) immediately after dissolving the crystals in CD_2Cl_2. Bottom: [Ti(O*i*Pr)$_4$] and tris(2-aminoethyl)-amine in CD_2Cl_2 mixed in a 2:1 ratio after two weeks.

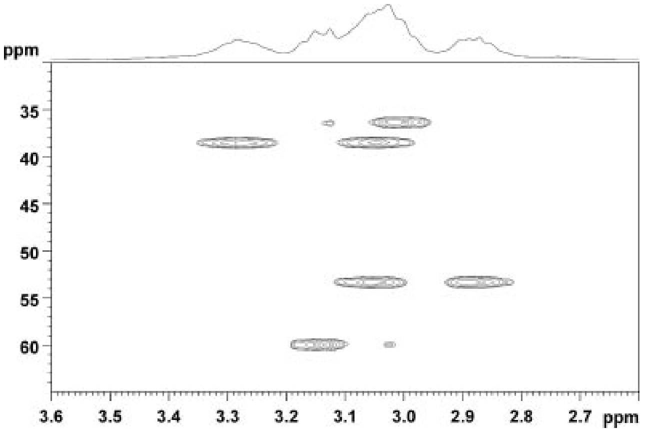

Figure 11. ^{1}H/^{13}C HSQC spectrum of the CH$_2$ region of **3** in CD_2Cl_2.

Mixing [Ti(O*i*Pr)$_4$] and tris(2-aminoethyl)amine in a 2:1 ratio in CD_2Cl_2 again showed a very similar peak pattern for the CH$_2$ region of the amine after two weeks (Figure 10, bottom). It is worth mentioning that the signals in the CH region of the isopropoxide ligand have different intensities, which might be due to either different concentrations of the product or to different amounts of free 2-propanol. The spectra of **3** suggests that this compound does not dissociate (completely) into the starting compounds, contrary to what had been observed for **1** and **2**. We cannot exclude that part of the NH$_2$ groups dissociate, but the observed spectra after dissolution of the crystals of **3** are distinctly different to a mixture of [Ti(O*i*Pr)$_4$] and tris(2-aminoethyl)-amine. The interpretation of the O*i*Pr signals in the spectra was complicated by the presence of the Ti$_2$(O*i*Pr)$_8$ guests in the crystal lattice.

The corresponding zirconium derivative **4** is almost insoluble in CD_2Cl_2, therefore no detailed NMR investigations were carried out.

Conclusions

We have shown that the previously observed formation of chain-like coordination polymers upon reaction of $[M(OR)_4]$ (M = Ti, Zr) with diamines can be extended to the formation of layered structures. Layers of $[Ti_2(O\mathit{i}Pr)_8]_3[N(CH_2CH_2NH_2)_3]_2$, consisting of condensed six-membered rings, are obtained from $[Ti(O\mathit{i}Pr)_4]$ and tris(2-aminoethyl)amine. The voids of the rings are occupied by $Ti_2(O\mathit{i}Pr)_8$ nonsolvated guest molecules.

The amine adducts of $[M(OR)_4]$ (M = Ti, Zr) are retained in solution. Although **1** and **2** dissociate into $[M(O\mathit{i}Pr)_4]$ and bis(2-aminoethyl)amine when dissolved in CD_2Cl_2, the adducts slowly form again in solution. We are aware that this may be different in other solvents. There is strong spectroscopic evidence that the network structure of **3** is retained upon dissolution of the crystals, at least partially.

An important consequence for sol-gel processing is that amine adducts must be taken into account when $[M(OR)_4]$ is used in the presence of compounds with NH_2 groups. Adduct formation will probably influence the reactivity of the alkoxides and may also result in morphological changes of the gels. We will further investigate the possibility to preorganize gels by di- and triamine adducts.

Experimental Section

All operations were carried out in a moisture- and oxygen-free atmosphere of argon. $[Ti(O\mathit{i}Pr)_4]$ (97%, Aldrich), $[Zr(O\mathit{i}Pr)_4]$ (70–75% in heptane, ABCR), bis(2-aminoethyl)amine (99%, Aldrich) and tris(2-aminoethyl)amine (96%, Aldrich) were used as received. The solvents were dried and purified by standard techniques.

Synthesis of $[Ti_2(O\mathit{i}Pr)_8(H_2NCH_2CH_2NHCH_2CH_2NH_2)]$ (1): Bis(2-aminoethyl)amine (315 mg, 3.05 mmol) was added, whilst stirring, to a solution of $[Ti(O\mathit{i}Pr)_4]$ (882 mg, 3.10 mmol) in 1 mL of 2-propanol at room temperature. The clear reaction solution was then stored at 4 °C and colorless crystals were obtained after 12 h. The product was recrystallized twice from CH_2Cl_2 and dried in vacuo. Yield: 736 mg (83%).

Dissolved Crystals or Mixture of Starting Compounds: ^1H NMR (CD_2Cl_2, 21 °C): δ = 4.51 (sept, J = 6.1 Hz, $OC\mathit{H}Me_2$), 2.84–2.54 (m, $C\mathit{H_2}C\mathit{H_2}NH_2$), 1.26 [d, J = 6.1 Hz, $OCH(C\mathit{H_3})_2$], 1.08 (br., $N\mathit{H_2}$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ = 76.5 ($O\mathit{C}HMe_2$), 52.8 [$HN(\mathit{C}H_2)_2$], 42.2 [$H_2N(\mathit{C}H_2)_2$], 26.5 [$OCH(\mathit{C}H_3)_2$] ppm. $^{15}N\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ = –3.2 ($H_2\mathit{N}$), 9.1 ($\mathit{N}H$) ppm.

After Two Weeks at Room Temperature: ^1H NMR (CD_2Cl_2, 21 °C): δ = 5.68 (br., $N\mathit{H_2}/N\mathit{H}$), 4.70, 4.51 (sept, J = 6.1 Hz, $OC\mathit{H}Me_2$), 4.00 (sept, J = 6.1 Hz, $HOC\mathit{H}Me_2$), 3.43–2.58 (m, $C\mathit{H_2}C\mathit{H_2}NH_2$), 2.39, 1.56 (br., $N\mathit{H_2}/N\mathit{H}$), 1.26 [d, J = 6.1 Hz, $OCH(C\mathit{H_3})_2$], 1.19 [d, J = 6.1 Hz, $HOCH(C\mathit{H_3})_2$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ = 78.3, 76.7, 76.2 ($O\mathit{C}HMe_2$), 64.1 ($HO\mathit{C}HMe_2$), 48.7 ($HN\mathit{C}H_2$), 39.6 ($H_2N\mathit{C}H_2$), 26.1 [$OCH(\mathit{C}H_3)_2/HOCH(\mathit{C}H_3)_2$] ppm. $^{15}N\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ = 14.0 ($H_2\mathit{N}$), 26.5 ($\mathit{N}H$) ppm.

Synthesis of $[Zr_2(O\mathit{i}Pr)_8(H_2NCH_2CH_2NHCH_2CH_2NH_2)]$ (2): Bis(2-aminoethyl)amine (209 mg, 2.03 mmol) was slowly added, whilst stirring, to 1029 mg (2.20 mmol) of a 70–75% solution of $[Zr(O\mathit{i}Pr)_4]$ in *n*-heptane that was diluted with 2 mL of *n*-heptane. The resulting white precipitate was dissolved in a mixture of 4 mL of 2-propanol and 2 mL of CH_2Cl_2 under reflux. The product was recrystallized twice from CH_2Cl_2 and dried in vacuo. Yield: 972 mg (94%).

Dissolved Crystals: ^1H NMR (CD_2Cl_2, 21 °C): δ = 4.91, 4.39 (sept, J = 6.1 Hz, $OC\mathit{H}Me_2$), 3.98 (sept, J = 6.1 Hz, $HOC\mathit{H}Me_2$), 2.80 [br., $HN(C\mathit{H_2})_2$], 2.69 [br., $H_2N(C\mathit{H_2})_2$], 1.32, 1.30 [d, J = 6.1 Hz, $OCH(C\mathit{H_3})_2$], 1.20 [d, J = 6.1 Hz, $HOCH(C\mathit{H_3})_2$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ = 69.8, 69.2 ($O\mathit{C}HMe_2$), 63.6 ($HO\mathit{C}HMe_2$), 42.1 [$H_2N(\mathit{C}H_2)_2$], 52.6 [$HN(\mathit{C}H_2)_2$], 32.1, 27.2 [$OCH(\mathit{C}H_3)_2$], 24.8 [$HOCH(\mathit{C}H_3)_2$] ppm.

Synthesis of $[\{Ti_2(O\mathit{i}Pr)_8\}_3\{(H_2NCH_2CH_2)_3N\}_2\cdot Ti_2(O\mathit{i}Pr)_8]$ (3): Tris(2-aminoethyl)amine (365 mg, 2.50 mmol) was added dropwise, whilst stirring, to a solution of 1051 mg (3.70 mmol) of $[Ti(O\mathit{i}Pr)_4]$ in 2 mL of CH_2Cl_2 at room temperature under argon. The colorless solution was refluxed for 5 min and then concentrated to half its volume. The vessel was then stored at 4 °C to afford colorless crystals after 3 d. The product was recrystallized twice from CH_2Cl_2 and dried in vacuo. Yield: 732 mg (62%). The same product, but in lower yields, was obtained when 2-propanol was used as the solvent.

Dissolved Crystals: ^1H NMR (CD_2Cl_2, 21 °C): δ = 5.81 (br., $N\mathit{H_2}$), 4.73, 4.51 (sept, J = 6.1 Hz, $OC\mathit{H}Me_2$), 3.41–2.66 [m, $N(C\mathit{H_2}C\mathit{H_2}NH_2)_3$], 2.40 (br., $N\mathit{H_2}$), 1.26 [d, J = 6.1 Hz, $OCH(C\mathit{H_3})_2$], 0.96 (b, $N\mathit{H_2}$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ = 79.0, 76.9, 76.3 ($O\mathit{C}HMe_2$), 60.2 (non-coordinated), 53.5 [$N(\mathit{C}H_2CH_2NH_2)_3$], 38.5 (non-coordinated), 36.5 [$N(CH_2\mathit{C}H_2NH_2)_3$], 26.0 [$OCH(\mathit{C}H_3)_2$] ppm. $^{15}N\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ = 36.8 (N), 14.2, 13.5 ($\mathit{N}H_2$) ppm.

Synthesis of $[Zr_2(O\mathit{i}Pr)_8][Zr_2(O\mathit{i}Pr)_8(HO\mathit{i}Pr)][(H_2NCH_2CH_2)_3N]$ (4): Tris(2-aminoethyl)amine (207 mg, 1.42 mmol) was slowly added, whilst stirring, to 737 mg (1.58 mmol) of a 70–75% solution of $[Zr(O\mathit{i}Pr)_4]$ in *n*-heptane that was diluted with 3 mL of 2-propanol. The reaction solution was refluxed for 5 min and then concentrated to half its volume. The closed vessel was then stored at room temperature to yield colorless crystals after three weeks. The product was recrystallized twice from CH_2Cl_2 and dried in vacuo. Yield: 461 mg (89%).

Dissolved Crystals: ^1H NMR (CD_2Cl_2, 21 °C): δ = 4.48, 4.35, 4.22 (sept, J = 6.1 Hz, $OC\mathit{H}Me_2$), 3.13 (br., $C\mathit{H_2}CH_2NH_2$), 2.98 (br., $CH_2C\mathit{H_2}NH_2$), 1.44–0.98 [m, $OCH(C\mathit{H_3})_2/HOCH(C\mathit{H_3})_2$] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ = 71.4, 70.8, 70.3, 68.9 ($O\mathit{C}HMe_2$), 52.5 [$N(\mathit{C}H_2CH_2NH_2)_3$], 37.4 [$N(CH_2\mathit{C}H_2NH_2)_3$], 26.6, 26.3, 25.4 [$OCH(\mathit{C}H_3)_2$] ppm. $^{15}N\{^1H\}$ NMR (CD_2Cl_2, 21 °C): δ = 30.85 (N), 9.09 ($H_2\mathit{N}$) ppm.

X-ray Structure Analyses: The crystals were mounted on a Siemens SMART diffractometer (area detector) and measured in a nitrogen stream. Mo-K_α radiation (λ = 71.069 pm, graphite monochromator) was used for all measurements. The data collection at 173 K covered a hemisphere of the reciprocal space, by a combination of three or four sets of exposures. Each set had a different ϕ angle for the crystal, and each exposure took 15 or 20 s and covered 0.3° in ω. The crystal-to-detector distance was 5 cm. Further details can be found in Table 1. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was employed. The cell dimensions were refined with all unique reflections. The structures were solved by direct methods

Table 1. Crystallographic parameters of **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{28}H_{69}N_3O_8Ti_2$	$C_{28}H_{69}N_3O_8Zr_2$	$C_{108}H_{260}N_8O_{32}Ti_8$	$C_{57}H_{138}N_4O_{17}Zr_4$
Formula weight	671.7	758.3	2566.4	1516.3
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [pm]	9.6371(6)	18.144(4)	1234.4(5)	12.269(3)
b [pm]	12.2646(7)	18.238(4)	1846.8(7)	18.244(4)
c [pm]	17.055(1)	12.366(3)	1858.2(7)	18.958(4)
α [°]	99.820(1)	90	63.522(7)	90.875(4)
β [°]	95.970(1)	92.98(3)	83.637(8)	92.723(5)
γ [°]	104.461(1)	90	88.171(9)	108.513(4)
Volume [10^6 pm^3]	1900.5(2)	4087(1)	3767(2)	4017(2)
Z	2	4	1	2
Calcd. density [g cm^{-3}]	1.174	1.233	1.131	1.254
μ [mm^{-1}]	0.463	0.550	0.464	0.560
Crystal size [mm]	0.26 × 0.24 × 0.22	0.05 × 0.03 × 0.02	0.29 × 0.22 × 0.19	0.21 × 0.18 × 0.15
2θ range [°]	2.42–25.00	2.78–25.00	2.02–25.00	2.11–25.00
Reflections collected/unique	15342/6657	14118/7184	20312/13064	20751/13995
Data/parameters	6657/374	7184/375	13064/703	13995/740
GOF on F^2	1.054	1.039	1.01	0.888
R [$I > 2\sigma(I)$]	0.050	0.050	0.088[a]	0.078
wR_2	0.135	0.138	0.140	0.155
Largest diff. peak/hole [e Å^{-3}]	1.233/–0.729	0.957/–0.562	0.929/–0.601	0.784/–0.922

[a] The high R values of **3** are due to disorder of the guest $Ti_2(OiPr)_8$ molecule.

(SHELXS-97). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL-97) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined as riding on the corresponding atom. The C–O and C–C distances of the $Ti_2(OiPr)_8$ guest molecule in **3** were refined using geometric restraints (DFIX, DANG).

CCDC-616750 (for **1**), -616751 (for **2**), -269602 (for **3**) and -616752 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

NMR Investigations: All NMR spectra were recorded with a Bruker Avance 300 spectrometer (^{1}H at 300.13, ^{13}C at 75.47 MHz, ^{15}N at 30.41 MHz) equipped with a 5 mm, inverse-broadband probe head with a z-gradient unit at room temperature. 2D NMR spectra (EXSY, mixing time was usually 1 s; HSQC; HMBC) were measured with Bruker standard pulse sequences. Gas-tight Young tubes were used for all measurements, and CD_2Cl_2 (99.8 %, euriso-top) was used as the solvent. ^{15}N shifts were referenced externally against an aqueous solution of $^{15}NH_4Cl$. To remove most of the residual amine and free alcohol previous to the measurement, the crystals were dissolved in CD_2Cl_2, the solvent was removed again in vacuo, and the residue was dried for more than 8 h at 4×10^{-4} mbar. The dried precipitate was then used for NMR investigations.

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