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Contributions to the Structural Chemistry of 2-Amino Alcoholate Derivatives of Titanium and Zirconium Alkoxides and Their Partial Hydrolysis Products

Helmut Fric,[a] Michael Puchberger,[a] and Ulrich Schubert*[a]

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The structures of $Ti_2(OiPr)_6(OCHMeCH_2NH_2)_2$ and $Ti_2(OiPr)_6(OCH_2CHMeNH_2)_2$, obtained by reaction of $Ti(OiPr)_4$ with the corresponding amino alcohols, were investigated to elucidate the structural influence of the organic substituents at the amino alcohol. A methyl group at the OH-substituted carbon atom results in a larger distortion of the structure than a methyl group at the NH_2-substituted carbon. The disubstituted compound $Ti_2(OiPr)_4(OCH_2CH_2NH_2)_4$ was formed, when $NaTi(OiPr)_5$ was reacted the amino ethanol. While one $OCH_2CH_2NH_2$ ligand is chelating, the oxygen atom of the second bridges the titanium atoms, and the NH_2 group is dangling. The structures of the partial hydrolysis products $Ti_4O_4(OiPr)_4(OCHPhCHMeNHMe)_4$ and $Ti_8O_6(OEt)_{12}(OCH_2CH_2NH_2)_8$ were also investigated. The former contains an incomplete double-cube Ti_4O_4 cluster core, the latter is made of two $Ti_4O_3(OEt)_6(OCH_2CH_2NH_2)_4$ sub-units, with a nearly planar $Ti_4(\mu_2\text{-}O)_2(\mu_3\text{-}O)(\mu_2\text{-}OEt)_2$ ring system, connected by two OEt bridges. $Zr(OCH_2CH_2NH_2)_4$ is a mononuclear compound with four chelating amino alcoholate ligands. The structure of $Zr_6(OBu)_{18}(OCH_2CH_2NH_2)_6$ is assembled from two $Zr_2(OBu)_5(OCH_2CH_2NH_2)_3$ and two $Zr(OBu)_4$ sub-units, which are associated by alkoxo bridges.

Introduction

A common way to moderate the reactivity of metal alkoxides, $M(OR)_x$, in sol-gel processes is the use of "chemical additives".[1] Acetic acid or acetylacetone is mainly employed, but other compounds, such as various carboxylic, phosphonic, phosphinic or sulfonic acids, as well as β-diketones, β-keto esters, amino alcohols, oximes, etc. are occasionally used. Such "additives" have in common that they are protic compounds and can thus substitute one or more OR groups of $M(OR)_x$ with concomitant ROH elimination [Equation (1)]. Furthermore, the corresponding anions act as bidentate (or multidentate) ligands (BL) and thus block coordination sites at the metal. This results in a lower reactivity of the new precursors $M(OR)_{x-y}(BL)_y$ towards nucleophiles compared with the parent alkoxides $M(OR)_x$.[2] In most practical sol-gel protocols, the organically modified precursors $M(OR)_{x-y}(BL)_y$ are prepared in situ without being isolated or characterized.

$$M(OR)_x + y\ BL\text{-}H \rightarrow M(OR)_{x-y}(BL)_y + y\ ROH \qquad (1)$$

Upon reaction with water, the OR groups of $M(OR)_{x-y}(BL)_y$ are preferentially hydrolyzed, because the BL are more strongly bonded due to the chelate effect. The organic ligands BL are thus retained in the obtained gels unless forcing conditions are employed. This opens the possibility to use the BL not only to control the reactivity of $M(OR)_x$, but also to introduce organic functionalities in the gels via substituted BL,[3,4] an option which is hardly exploited in sol-gel processing.

Despite their wide-spread use and huge impact on the formation and structure of the derived gels, the basic chemistry of only few organically modified precursors, essentially carboxylate- and β-diketonate-substituted compounds, has been investigated in some detail. Although the versatility of such oxygen-based ligands is out of question, they also have some disadvantages. Reaction of $M(OR)_x$ often results in oxo clusters $M_aO_b(OH/OR)_c(OOCR')_d$ instead of substituted alkoxo compounds, due to concomitant formation of ester and water. Although the clusters are interesting building blocks for materials syntheses themselves,[5] their formation renders the structure of sol-gel materials derived from carboxylate-substituted metal alkoxides somewhat unpredictable on a molecular and nanometer scale. Modification of $M(OR)_x$ by simple β-diketones is straightforward, but possibilities to introduce functional organic groups are limited. Furthermore, substitution in the 3-position renders β-diketones more susceptible to hydrodeacylation reactions when treated with metal alkoxides.[6]

These restrictions led us to investigate alternatives for the organic modification of metal alkoxides. In this article we are reporting some basic structural chemistry of 2-amino alcoholate derivatives of $Ti(OR)_4$ and $Zr(OR)_4$ and allied initial hydrolysis products. Apart from avoiding the chemical problems encountered with carboxylates and β-diketonates, there are more options for the modification of

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[a] Institute of Materials Chemistry, Vienna University of Technology,
Getreidemarkt 9, 1060 Wien, Austria

2-aminoethanolate ligands, viz. at the nitrogen atom, at the CH_2 group next to N, or at the CH_2 group next to O.

Little attention was paid to 2-amino-alcoholate-substituted metal alkoxide derivatives, although the first examples were already prepared in the 1960s, mainly by the group of R. C. Mehrotra.[7–10] It was claimed that all alkoxo ligands of $Ti(OR)_4$ or $Zr(O\mathit{i}Pr)_4$ can be replaced successively, i.e. that all $Ti(OR)_{4-x}(OCH_2CH_2NR'_2)_x$[8,9] or $Zr(O\mathit{i}Pr)_{4-x}(OCH_2CH_2\text{-}NR'_2)_x$ derivatives[11] (R' = H, Me) with x = 1–4 can be obtained.

The available structural information on such derivatives can be summarized as follows: We have previously confirmed by X-ray structure analyses that the mono-substituted (x = 1) NH_2 derivatives $Ti(OR)_3(OCH_2CH_2NH_2)$ (R = *i*Pr, Et), are dimeric in the solid state, viz. $Ti_2(\mu_2\text{-}OR)_2(OR)_4(OCH_2CH_2NH_2)_2$ [= $Ti_2(OR)_6(OCH_2CH_2NH_2)_2$][12] (in the following, mono-, di-substitution etc. refers to the number of aminoethanolate ligands per Ti atom). Variable-temperature NMR spectra of the mono-substituted (x = 1) NMe_2 compound $Ti(O\mathit{i}Pr)_3(OCH_2CH_2NMe_2)$ in benzene solution indicated a monomer–dimer equilibrium.[10] The disubstituted (x = 2) NMe_2 compound $Ti(O\mathit{i}Pr)_2(OCH_2CH_2NMe_2)_2$ was shown to be monomeric both in benzene solution and the gas phase,[10] while $Ti(O\mathit{i}Pr)_2(OCH_2CH_2NH_2)_2$ is dimeric in benzene solution.[8] The structures of the more highly substituted titanium derivatives, i.e. $Ti(OR)_{4-x}(OCH_2CH_2NR'_2)_x$ (x = 3 and 4), and those of zirconium derivatives are not known.

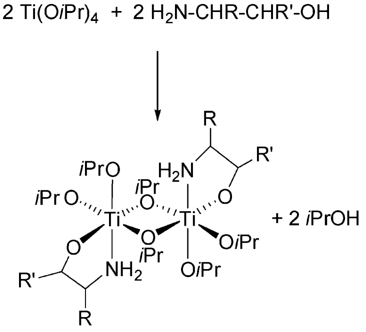
The only structural information available for partial hydrolysis products of amino alcoholate derivatives of titanium alkoxides is the tetrameric cluster $[TiO(OCH_2CH_2NMe_2)_2]_4$, obtained by hydrolysis of $Ti(OCH_2CH_2NMe_2)_4$. It contains both μ and μ_3 oxo ligands and only two aminoethanolate ligands per titanium atom, one $OCH_2CH_2NMe_2$ being chelating and the other monodentate.[13]

Results and Discussion

Titanium Derivatives

The crystalline, dimeric derivatives $Ti_2(\mu_2\text{-}OR)_2(OR)_4(OCH_2CH_2NH_2)_2$ [R = *i*Pr (**1**), Et] were previously obtained by reaction of $Ti(O\mathit{i}Pr)_4$ or $Ti(OEt)_4$ with 2-aminoethanol. The titanium atoms are octahedrally coordinated and bridged by two OR groups. The amino groups of the chelating aminoethanolate ligand are perpendicular to the $M_2(\mu\text{-}OR)_2$ ring and *trans* to each other. The structure of $Ti_2(OR)_6(OCH_2CH_2NH_2)_2$ is thus related to that of amine adducts $Ti_2(OR)_8(NH_2R)_2$,[14] where the NH_2R ligands occupy the same position as the amino group of the aminoethanolate derivatives. While bonding of the amine ligand in the amine adducts is supported by a hydrogen bridge between the N–H group and the neighboring axial OR ligand [N···O distance in $Ti_2(O\mathit{i}Pr)_8(PrNH_2)_2$ 295.2(2) pm[14]], incorporation of the NH_2 group in a chelate ring in the amino alcoholate derivatives does not require stabilization by a hydrogen bond. Thus, the N···O distances in the amino alcoholate derivatives are relatively long [e.g. 308.3(4)–330.2(4) pm in **2**].

We first turned our attention to the question whether the structure of the *mono-substituted* derivative is influenced by organic substituents attached to one of the CH_2 groups of the aminoethanolate ligand. The methyl-substituted derivatives (*S*)-(+)-1-amino-2-propanol and (*S*)-(+)-2-amino-1-propanol were used as model compounds and were reacted, in slight excess, with $Ti(O\mathit{i}Pr)_4$ [Equation (2)].



2a: R = H, R' = Me

2b: R = Me, R' = H (2)

The aminoethanolate derivatives **2a** and **2b** were obtained in high yields. The basic features of their molecular structures (Figure 1 and Figure 2) were essentially the same than that of the unsubstituted derivative **1**, which was elsewhere discussed in detail.[12] However, unlike **1**, **2a** and **2b** are not centrosymmetric due to the chiral ligands; at one

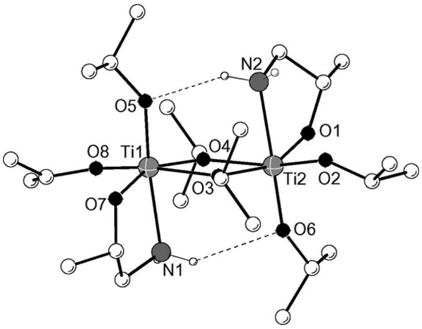


Figure 1. Molecular structure of $Ti_2(O\mathit{i}Pr)_8(OCHMeCH_2NH_2)_2$ (**2a**). The hydrogen atoms were omitted for clarity. The dashed lines indicate weak hydrogen bridges. Selected bond lengths [pm] and angles [°]: Ti(1)–O(3) 211.2(2), Ti(1)–O(4) 200.4(2), Ti(1)–O(5) 183.8(2), Ti(1)–O(7) 186.7(2), Ti(1)–O(8) 181.3(2), Ti(1)–N(1) 229.2(3), Ti(2)–O(2) 184.4(2), Ti(2)–O(1) 187.3(2), Ti(2)–O(3) 201.4(2), Ti(2)–O(4) 210.4(2), Ti(2)–O(6) 180.2(2), Ti(2)–N(2) 227.8(3), N(1)···O(6) 330.2(4), N(2)···O(5) 308.3(4) pm. O(3)–Ti(1)–O(5) 89.8(1), O(3)–Ti(1)–O(7) 89.55(9), O(4)–Ti(1)–O(5) 98.7(1), O(4)–Ti(1)–O(7) 155.18(9), O(5)–Ti(1)–O(8) 100.3(1), O(7)–Ti(1)–O(8) 97.2(1), O(8)–Ti(1)–N(1) 89.3(1), O(5)–Ti(1)–N(1) 169.8(1), O(4)–Ti(1)–N(1) 83.6(1), O(3)–Ti(1)–N(1) 81.3(1), O(1)–Ti(2)–O(2) 95.4 (1), O(1)–Ti(2)–O(3) 157.0(1), O(1)–Ti(2)–O(4) 91.83(9), O(2)–Ti(2)–O(6) 99.8(1), O(3)–Ti(2)–O(6) 100.2(1), O(4)–Ti(2)–O(6) 93.3(1), O(6)–Ti(2)–N(2) 173.0(1), O(2)–Ti(2)–N(2) 85.6(1), O(3)–Ti(2)–N(2) 83.8(1), O(4)–Ti(2)–N(2) 82.3(1), Ti(1)–O(4)–Ti(2) 106.77(8), Ti(1)–O(3)–Ti(2) 106.10(8).

titanium atom the methyl substituent at the chelate ring is pointing towards the neighboring O*i*Pr bridge, and at the other titanium atom in the opposite direction. Variations of the structural parameters in **2b** (with the methyl group bound to the same carbon as the NH_2 group) were only small compared to **1**, and with only minor differences between both halves of the dimer. The largest bond length difference was found between Ti(1)–N(1) [230.0(3) pm] and Ti(2)–N(2) [228.2(3) pm], while bond angle differences were below 1.5°.

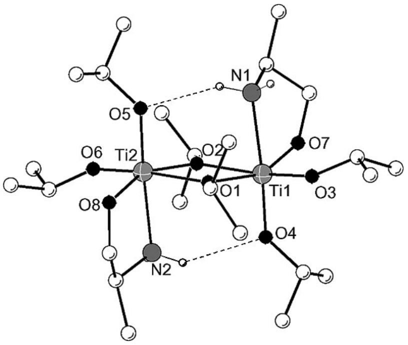


Figure 2. Molecular structure of $Ti_2(OiPr)_8(OCH_2CHMeNH_2)_2$ (**2b**). The hydrogen atoms were omitted for clarity. The dashed lines indicate weak hydrogen bridges. Selected bond lengths [pm] and angles [°]: Ti(1)–O(1) 201.1(2), Ti(1)–O(2) 209.7(2), Ti(1)–O(3) 182.0(2), Ti(1)–O(4) 183.8(3), Ti(1)–O(7) 188.2(3), Ti(1)–N(1) 230.0(3), Ti(2)–O(1) 208.7(2), Ti(2)–O(2) 200.2(2), Ti(2)–O(5) 184.7(2), Ti(2)–O(6) 180.9(2), Ti(2)–O(8) 187.8(2), Ti(2)–N(2) 228.2(3), N(1)···O(5) 312.2(4), N(2)···O(4) 319.1(4) pm. O(1)–Ti(1)–O(2) 73.04(8), O(1)–Ti(1)–O(7) 156.5(1), O(2)–Ti(1)–O(3) 166.9(1), O(2)–Ti(1)–O(4) 90.9(1), O(2)–Ti(1)–O(7) 91.7(1), O(3)–Ti(1)–O(4) 98.3(1), O(3)–Ti(1)–O(7) 96.0(1), O(3)–Ti(1)–N(1) 89.7(1), O(4)–Ti(1)–N(1) 171.5(1), O(1)–Ti(1)–N(1) 83.3(1), O(1)–Ti(2)–O(2) 73.43(8), O(1)–Ti(2)–O(5) 90.17(9), O(1)–Ti(2)–O(8) 89.8(1), O(2)–Ti(1)–N(1) 81.6(1), O(2)–Ti(2)–O(5) 98.3(1), O(2)–Ti(2)–O(8) 155.80(9), O(5)–Ti(2)–O(6) 98.4(1), O(6)–Ti(2)–O(8) 97.4(1), O(6)–Ti(2)–N(2) 89.3(1), O(5)–Ti(2)–N(2) 171.52(9), O(2)–Ti(2)–N(2) 84.1(1), O(1)–Ti(2)–N(2) 82.7(1), Ti(1)–O(1)–Ti(2) 106.8(9), Ti(1)–O(2)–Ti(2) 106.76(9).

Surprisingly, the structural differences between the two halves of **2a** were much more pronounced. The Ti–O and Ti–N bond lengths of the aminoethanolate ligand were 186.7(2)/187.3(2) pm and 229.2(3)/227.8(3) pm, respectively. Even larger differences were found for the two terminal O*i*Pr groups: while the Ti–O bond length of the O*i*Pr group *trans* to N is larger on Ti(1) [Ti(1)–O(5) 183.8(2), Ti(2)–O(6) 180.2(2)], that of the O*i*Pr group in the Ti_2O_2 plane is shorter on Ti(1) [Ti(1)–O(8) 181.3(2), Ti(2)–O(2) 184.4(2)]. Concomitant with the bond length changes, larger bond angle differences were observed compared to **2b**. The structural distortions can be explained by slightly twisting the ligands at Ti(2) away from the bridging O*i*Pr ligand O(4), and the ligands at Ti(1) away from the O*i*Pr ligand O(8), caused by the steric requirements of the methyl groups at the chelate ring.

The reason for the larger structural distortion in **2a** compared with **2b** is rather obvious (Figures 1 and 2). In **2b**, the methyl group at the chelate ring is directed away from the center of the dimer and therefore does not interfere with any other group. In contrast, the methyl groups in **2a** are closer to the more crowded Ti_2O_2 plane and thus interact more strongly with other ligands. Furthermore, the Ti–O distance is much shorter than the Ti–N distance of the aminoethanolate ligands, which additionally pulls the methyl substituents towards the core region of the molecule.

Comparison of the structures of **2a** and **2b** thus allows the following general conclusion: when substituted aminoethanol derivatives are used for the modification of $Ti(OR)_4$, the substituents are better placed at the NH_2-substituted carbon, if a stable linkage is wanted (as in sol-gel reactions). At this position, the substituents are better accommodated than at the O-substituted carbon, especially if bulkier substituents are employed than the CH_3 groups in the model compounds presented in this work.

If the structures of **2a** and **2b** were retained in solution, a maximum of six different sets of O*i*Pr resonances and two different sets of amino alcoholate resonances can be expected in the NMR spectra. The ^1H NMR spectra of $CDCl_3$ solutions of crystalline **2a** or **2b** (see Exp. Sect.) showed a multitude of overlapping resonances, especially in the CH region. Two-dimensional NMR techniques such as COSY, TOCSY and HSQC allowed to assign resonances of four amino alcoholate ligands in both cases, three (**2a**) or four (**2b**) alkoxo groups. The latter undergo intra and/or intermolecular exchange reactions. The large number of resonances can be explained either by the presence of different conformers or isomers in solution or, more likely, by coordination equilibria as described previously in related cases.[10]

The *disubstituted* NMe_2 derivative $Ti(OiPr)_2(OCH_2CH_2NMe_2)_2$ was previously shown to be monomeric both in benzene solution and the gas phase.[10] We were not able to obtain the NH_2 derivative $Ti(OiPr)_2(OCH_2CH_2NH_2)_2$ by analogous reaction of $Ti(OiPr)_4$. Even when an excess of ethanolamine was employed, the mono-substituted dimer **1** crystallized from the reaction mixture. However, the disubstituted derivative $Ti_2(OiPr)_4(OCH_2CH_2NH_2)_4$ (**3**) was formed, when $NaTi(OiPr)_5$[15] was treated with an excess of aminoethanol.

Monomeric structures $Ti(OR)_4L_2$ with R = alkyl and L = $R'NH_2$ are not stable.[4] Therefore, a monomeric compound $Ti(OR)_2(OCH_2CH_2NR'_2)_2$, with two chelating aminoethanolate ligands cannot be expected. The X-ray structure analysis of **3** showed indeed that the compound is a centrosymmetric dimer with only *one* chelating $OCH_2CH_2NH_2$ ligand per Ti atom, i.e. $Ti_2(OiPr)_4(\mu_2\text{-}OCH_2CH_2NH_2)_2(OCH_2CH_2NH_2)_2$. The structure is related to that of the mono-substituted derivative **1**, the alkoxo bridge being formed by the second $OCH_2CH_2NH_2$ ligand. The bond lengths and angles of **1** and **3** are nearly the same. The amino group of the bridging $OCH_2CH_2NH_2$ ligand does not coordinate to the titanium atoms (Figure 3). The distances between the dangling amino group N(3) and both the nitrogen of the chelating aminoethanolate ligand [N(2)···N(3) 3.106(2) pm] and the oxygen of the neighboring O*i*Pr ligand [N(3)···O(3) 3.099(2) pm] indicate that there might be weak hydrogen bond interactions. (The asymmetric unit of **3** contains two halves of centrosymmetric dimers; bond lengths and angles in the other dimer are very similar.) Furthermore, the dangling NH_2 group acts as donor in a N–H···Cl hydrogen bond with a CH_2Cl_2 solvate molecule as indicated by the N3···Cl2 distance of 359.7(2) pm.

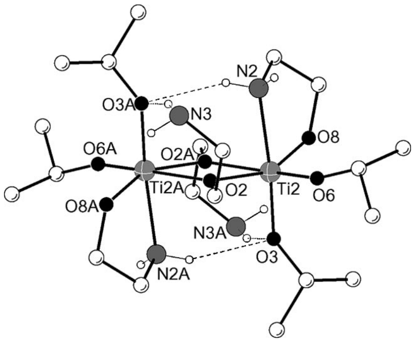


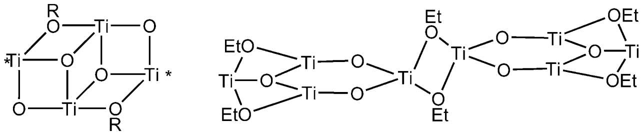
Figure 3. Molecular structure of $Ti_2(OiPr)_4(OCH_2CH_2NH_2)_4$ (**3**). The hydrogen atoms were omitted for clarity. The asymmetric unit contains two halves of centrosymmetric dimers, which are structurally nearly identical. The dashed lines indicate weak hydrogen bridges. Only one set of structural parameters is given. Selected bond lengths [pm] and angles [°]: Ti(2)–O(2) 202.3(1), Ti(2)–O(2)* 207.6(1), Ti(2)–O(3) 186.9(1), Ti(2)–O(6) 179.4(1), Ti(2)–O(8) 187.6(1), Ti(2)–N(2) 226.8(2), N(2)···O(3) 3.107(2), N(2)···N(3) 3.106(2), N(3)···O(3) 3.099(2) pm. O(6)–Ti(2)–O(3) 97.26(6), O(6)–Ti(2)–O(8) 100.65(6), O(3)–Ti(2)–O(8), 100.42(6), O(3)–Ti(2)–O(2) 98.08(5), O(3)–Ti(2)–O(2)* 88.47(5), O(6)–Ti(2)–N(2) 90.86(6), O(3)–Ti(2)–N(2) 171.84(6), O(2)–Ti(2)–N(2) 82.05(5), O(2)*–Ti(2)–N(2)83.76(5), Ti(2)–O(2)–Ti(2)* 106.89(5)°.

The room temperature ^1H-NMR spectra CD_2Cl_2 of **3** only show weakly resolved, broad resonances, which indicate intra- and intermolecular exchange reactions. The signals did not become sharper at lower temperatures. ^{13}C-HSQC experiments allowed the assignment of five different O*i*Pr groups; thus the solution contains different species as in the case of **2**.

Partially Hydrolyzed Titanium Derivatives

In this section, the structures of two partially hydrolyzed amino alcoholate derivatives of $Ti(OR)_4$ are reported. We wish to emphasize that we did not intend, in this stage, to investigate the primary steps in the hydrolysis reaction comprehensively. The crystalline amino alcoholate-substituted oxo titanium derivatives **4** and **5** were obtained in low yields and constitute only part of the (otherwise amorphous and unidentified) reaction products. However, their structures provide preliminary and partial insight on the structural development of the Ti–O units upon hydrolysis.

A compound with a Ti_4O_4 cluster core (Scheme 1), viz. $Ti_4O_4(OiPr)_4(OCHPhCHMeNHMe)_4$ (**4**) (Figure 4), was obtained when ephedrine (HO–CHPh–CHMe–NHMe) was treated with an equimolar amount of $Ti(OiPr)_4$ in the presence of ambient moisture. The structure of **4** [$Ti_4(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(OiPr)_4(\mu_2\text{-}\eta^1\text{-}OCHPhCHMeNHMe)_2(OCHPhCHMeNHMe)_2$] is the same as that of the known cluster $Ti_4O_4(OCH_2CH_2NMe_2)_8$, which was obtained by hydrolysis of $Ti(OCH_2CH_2NMe_2)_4$ or by reaction of $Ti(OiPr)_4$ with 3 molar equivalents of $HOCH_2CH_2NMe_2$ in the presence of water.[13] Each titanium atom is substituted by one terminal O*i*Pr ligand which is *trans* to a μ_3 oxygen [in $Ti_4O_4(OCH_2CH_2NMe_2)_8$ this position is occupied by a monodentate $OCH_2CH_2NMe_2$ ligand]. The titanium atoms marked by an asterisk in Scheme 1 [Ti(1) and Ti(3)] are additionally coordinated by a *chelating* OCHPhCHMeNHMe ligand, while the other Ti atoms [Ti(2) and Ti(4)] are coordinated by the amino group of a *bridging-chelating* (μ_2-η^1) amino alcoholate ligand, the oxygen atom of which bridges two Ti atoms (the “OR” in Scheme 1, left).



Scheme 1. The Ti/O framework of **4** (left) and **5** (right).

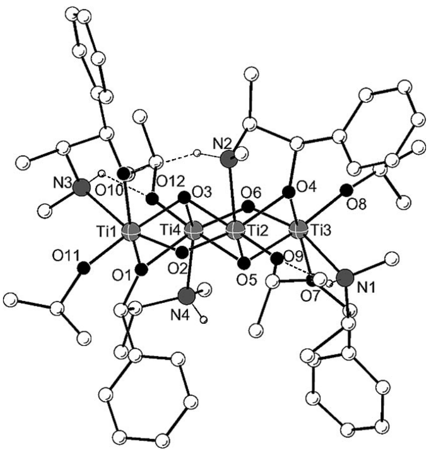


Figure 4. Molecular structure of $Ti_4O_4(OiPr)_4(OCHPhCHMeNHMe)_4$ (**4**). The hydrogen atoms were omitted for clarity. The dashed lines indicate weak hydrogen bridges. Selected bond lengths [pm] and angles [°]: Ti(1)–O(11) 178.6(2), Ti(1)–O(2) 183.8(2), Ti(1)–O(10) 191.5(3), Ti(1)–O(1) 202.9(2), Ti(1)–O(3) 207.9(2), Ti(1)–N(3) 231.8(3), Ti(2)–O(2) 184.1(2), Ti(2)–O(9) 185.5(2), Ti(2)–O(5) 187.1(2), Ti(2)–O(4) 204.3(2), Ti(2)–O(3) 209.3(2), Ti(2)–N(2) 223.0(3), Ti(3)–O(8) 181.2(3), Ti(3)–O(6) 182.9(2), Ti(3)–O(7) 188.6(3), Ti(3)–O(4) 206.4(2), Ti(3)–O(5) 207.8(2), Ti(3)–N(1) 231.5(3), Ti(4)–O(3) 183.6(2), Ti(4)–O(12) 185.8(2), Ti(4)–O(6) 186.8(3), Ti(4)–O(5) 205.6(2), Ti(4)–O(1) 206.8(2), Ti(4)–N(4) 223.4(3). Ti(1)–O(1)–Ti(4) 100.7(1), Ti(1)–O(2)–Ti(2) 107.3(1), Ti(4)–O(3)–Ti(1) 107.2(1), Ti(4)–O(3)–Ti(2) 98.8(1), Ti(1)–O(3)–Ti(2) 90.53(9), C(6)–O(4)–Ti(2) 123.1(2), Ti(2)–O(4)–Ti(3) 100.3(1), Ti(2)–O(5)–Ti(4) 99.0(1), Ti(2)–O(5)–Ti(3) 105.9(1), Ti(4)–O(5)–Ti(3) 91.69(9), Ti(3)–O(6)–Ti(4) 106.7(1).

Structural details have been previously discussed for $Ti_4O_4(OCH_2CH_2NMe_2)_8$.[13] Although **4** is not centrosymmetric due to the chiral ligands the structures are very similar. Two remarks are appropriate in the context of this paper: (i) The structural motif of the central cluster core appears to be rather robust and is hardly influenced by the substituents at the amino alcoholate ligand. This statement is also supported by the fact that both clusters were obtained starting from compounds with very different amino alcohol/Ti ratios. (ii) Crystals of **4** were obtained from a 1:1 mixture of ephedrine and Ti(O*i*Pr)$_4$. This ratio is retained in the oxo cluster **4**. Comparison with the preparation of $Ti_4O_4(OCH_2CH_2NMe_2)_8$[13] indicates that the (structural) chemistry of Ti(OR)$_4$ is mainly influenced by the first amino alcoholate ligand, while a third and forth ligand per titanium atom (possibly also a second ligand, see above) acts as a "normal" OR ligand without major involvement of the amino groups.

The ^{1}H NMR spectrum (Figure 5, top) of **4** shows well resolved signals, and multidimensional NMR spectra allowed the assignment of all ^{1}H, ^{13}C and ^{15}N resonances (see Exp. Sect.).

Four different sets of signals were found for both the ephedrinate and O*i*Pr ligands, as expected for the molecular symmetry, taking the chiral ligands into account. An EXSY spectrum (Figure 5) shows that only two of the four O*i*Pr ligands are mobile and undergo exchange with un-coordinated isopropanol present in the solution as well as with each other. The enantiotopic methyl groups of the two static O*i*Pr ligands are diastereotopic, due to the chiral environment of the ephedrinate ligands, and therefore show separate resonances in the ^{1}H and ^{13}C NMR spectra (1.46/26.7, 1.33/24.7 and 0.71/23.6, 0.83/23.9, respectively). As the methyl protons for one of these O*i*Pr ligands are shifted to higher field (0.71 and 0.83 ppm), this ligand should be in an anisotropic environment of phenyl rings. This is the case for the O*i*Pr ligand bound to Ti(2). The shortest C–C distances between the methyl carbon atoms to carbon-atoms of two neighboring phenyl groups are 370–380 pm, whereas the other mean distances are in the range 400–450 pm. Another reason why this ligand does not show exchange might be a weak hydrogen bond observed in the crystal structure. The O*i*Pr coordinated to Ti(4) shows also two weak hydrogen bonds to neighboring ephedrinate ligands and therefore could be the second static O*i*Pr ligand, also for symmetry reasons.

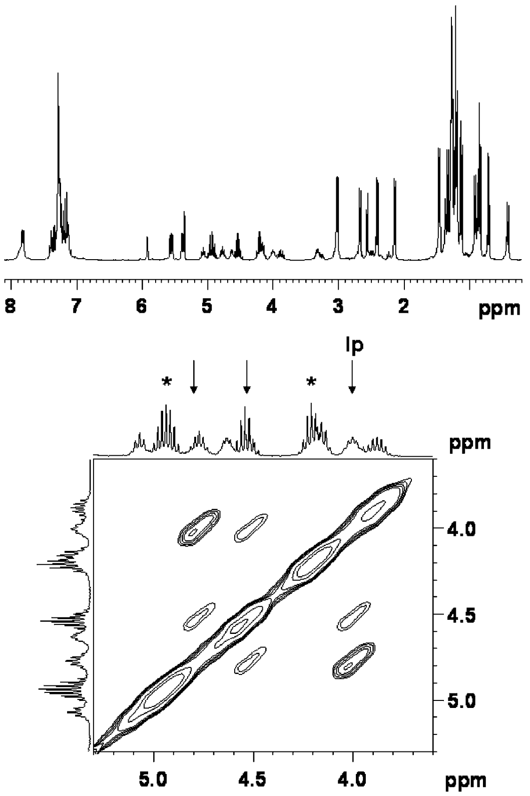


Figure 5. Top: ^{1}H NMR spectrum of **4** in CD_2Cl_2 at room temperature. Bottom: section of an EXSY spectrum of **4** in CD_2Cl_2 at room temperature. The signals marked with an asterisk correspond to the static O*i*Pr ligands, the dynamic O*i*Pr ligands are marked with arrows (Ip = free isopropyl alcohol).

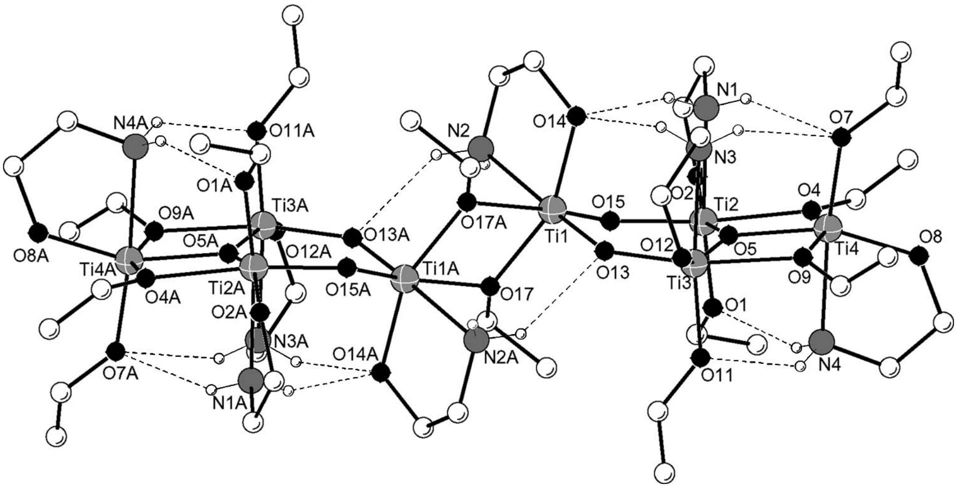


Figure 6. Molecular structure of $Ti_8O_6(OEt)_{12}(OCH_2CH_2NH_2)_8$ (**5**). The hydrogen atoms were omitted for clarity. The dashed lines indicate weak hydrogen bridges. Selected bond lengths [pm] and angles [°]: Ti(1)–O(15) 181.4(2), Ti(1)–O(13) 184.8(2), Ti(1)–O(14) 192.4(2), Ti(1)–O(17) 197.1(2), Ti(1)–O(17)* 212.8(2), Ti(1)–N(2) 225.5(3), Ti(2)–O(1) 183.4(2), Ti(2)–O(15) 185.0(2), Ti(2)–O(2) 188.3(2), Ti(2)–O(5) 196.1(2), Ti(2)–O(4) 210.9(3), Ti(2)–N(1) 227.4(3), Ti(3)–O(13) 181.5(2), Ti(3)–O(11) 183.5(3), Ti(3)–O(12) 191.1(3), Ti(3)–O(5) 196.4(2), Ti(3)–O(9) 211.6(3), Ti(3)–N(3) 227.6(3), Ti(4)–O(7) 183.8(3), Ti(4)–O(8) 184.9(3), Ti(4)–O(5) 193.5(2), Ti(4)–O(4) 197.1(3), Ti(4)–O(9) 197.6(3), Ti(4)–N(4) 228.7(4). Ti(1)–O(15)–Ti(2) 141.5(1), Ti(1)–O(17)–Ti(1)* 106.74(9), Ti(4)–O(9)–Ti(3) 100.5(1), Ti(4)–O(4)–Ti(2) 100.5(1), Ti(4)–O(5)–Ti(2) 107.3(1), Ti(4)–O(5)–Ti(3) 107.7(1), Ti(2)–O(5)–Ti(3) 144.5(1), Ti(3)–O(13)–Ti(1) 140.85(13).

A second crystalline partial hydrolysis product was obtained when water was deliberately added to a solution of equimolar amounts of $Ti(OEt)_4$ and 2-aminoethanol. The chemical composition of the crystalline component in the reaction mixture was $Ti_8O_6(OEt)_{12}(OCH_2CH_2NH_2)_8$ (**5**); the structure is shown in Figure 6. The Ti/aminoethanolate ratio is again 1:1 (as in **4**), but different to **4** all aminoethanolate ligands are chelating, with one chelating ligand per Ti atom. However, the hydrolysis ratio in **5**, i.e. the O/Ti ratio, is smaller than that in **4** (1 in **4** and 0.75 in **5**). Compound **5** is centrosymmetric with two $Ti_4O_3(OEt)_6(OCH_2CH_2NH_2)_4$ units dimerized via two bridging OEt groups (Scheme 1, right) [i.e. $Ti_8(\mu_2\text{-}O)_4(\mu_3\text{-}O)_2(\mu_2\text{-}OEt)_6(OEt)_6(OCH_2CH_2NH_2)_8$]. Compounds with several Ti_4O_x cores have already been observed, with $x = 2$ and 4–6.[13] To the best of our knowledge, compound **5** is the first example for $x = 3$. Each sub-unit of **5** is formed by a nearly planar $Ti_4(\mu_2\text{-}O)_2(\mu_3\text{-}O)(\mu_2\text{-}OEt)_2$ ring system. Each of the three Ti atoms in the sub-unit connected by the μ_3-O group [Ti(2), Ti(3), Ti(4)] are substituted by a chelating $OCH_2CH_2NH_2$ and a terminal OEt group. The octahedral coordination of Ti(1) is accomplished by two bridging OEt (connecting to the second sub-unit), two μ_2-O and the chelating $OCH_2CH_2NH_2$ ligand.

Another way of looking at the structure of **5** is that two Ti_3O units are condensed with a central dimeric $Ti_2(OR)_2$ unit. The structure of the central part of **5** is nearly the same as that of the monosubstituted compounds $Ti_2(OR)_6(OCH_2CH_2NH_2)_2$ discussed above, with only the *terminal* OR groups being hydrolyzed and condensed to the Ti_3O units. Compounds with Ti_3O units are, for example, the carboxylate derivatives $Ti_3O(OR)_8(OOCR')_2$.[16]

Zirconium Derivatives

Only little structural information is available on organically modified zirconium alkoxide derivatives. We also experienced in the current work that amino alcoholate derivatives of $Zr(OR)_4$ are much more difficult to crystallize than the corresponding titanium compounds. Nevertheless, we achieved to crystallize two compounds in small yields. As emphasized for the oxo titanium derivatives above, the

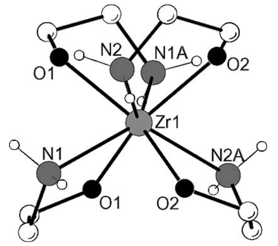


Figure 7. Molecular structure of $Zr(OCH_2CH_2NH_2)_4$ (**6**). The hydrogen atoms were omitted for clarity. Selected bond lengths [pm] and angles [°]: Zr(1)–O(2) 211.7(3), Zr(1)–O(1) 213.2(3), Zr(1)–N(1) 241.4(3), Zr(1)–N(2) 243.3(4). O(2)–Zr(1)–O(2)* 90.0(2), O(2)–Zr(1)–O(1)* 100.3(1), O(2)–Zr(1)–O(1) 146.5(1), O(1)*–Zr(1)–O(1) 88.5(2), N(1)–Zr(1)–N(1)* 135.6(2), N(1)–Zr(1)–N(2)* 127.8(1), N(1)–Zr(1)–N(2) 70.0(1), N(2)*–Zr(1)–N(2) 137.9(2).

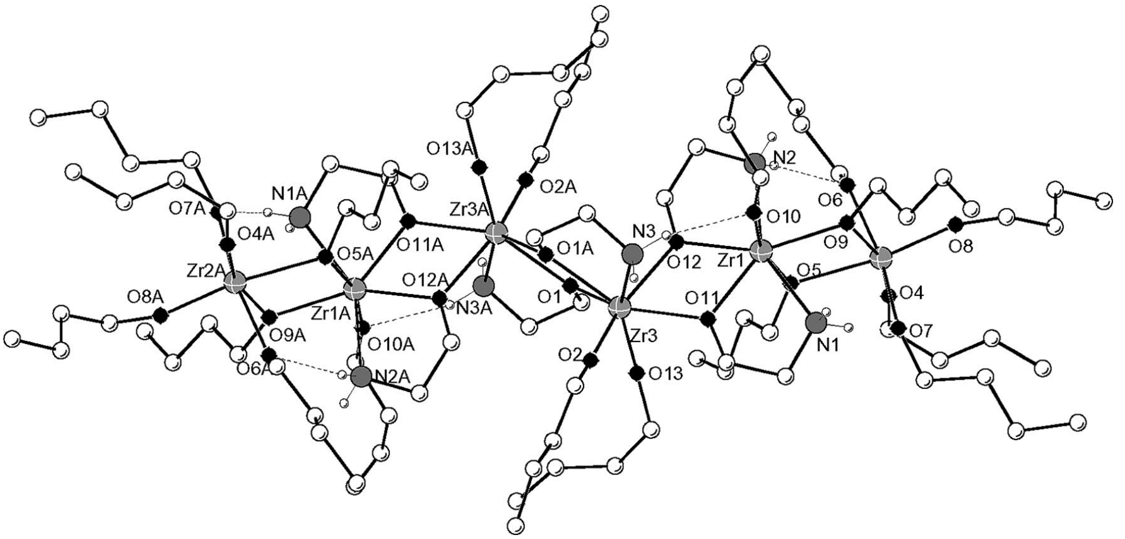


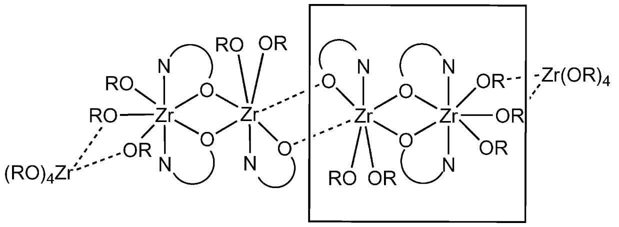
Figure 8. Molecular structure of $[Zr(OBu)_3(OCH_2CH_2NH_2)]_6\cdot 2BuOH$ (**7**). The hydrogen atoms were omitted for clarity. The dashed lines indicate weak hydrogen bridges. Selected bond lengths [pm] and angles [°]: Zr(1)–O(5) 210.7(2), Zr(1)–O(10) 195.8(2), Zr(1)–O(11) 214.7(2), Zr(1)–O(9) 215.7(2), Zr(1)–O(12) 217.5(2), Zr(1)–N(2) 235.0(2), Zr(1)–N(1) 237.9(3), Zr(2)–O(4) 195.1(2), Zr(2)–O(8) 195.8(2), Zr(2)–O(7) 205.5(2), Zr(2)–O(6) 212.5(2), Zr(2)–O(9) 219.6(2), Zr(2)–O(5) 226.0(2), Zr(3)–O(2) 197.2(2), Zr(3)–O(13) 199.4(2), Zr(3)–O(1) 218.2(2), Zr(3)–O(12) 220.1(2), Zr(3)–O(1)* 221.2(2), Zr(3)–O(11) 221.6(2), Zr(3)–N(3) 245.1(2). O(10)–Zr(1)–N(2) 89.12(9), O(5)–Zr(1)–N(2) 87.53(9), O(11)–Zr(1)–N(2) 139.13(8), O(9)–Zr(1)–N(2) 74.67(8), O(12)–Zr(1)–N(2) 71.39(8), O(10)–Zr(1)–N(1) 91.39(9), O(5)–Zr(1)–N(1) 84.61(9), O(11)–Zr(1)–N(1) 70.43(8), O(9)–Zr(1)–N(1) 75.68(8), O(12)–Zr(1)–N(1) 137.23(8), N(2)–Zr(1)–N(1) 150.34(9), O(2)–Zr(3)–O(1) 120.64(8), O(2)–Zr(3)–O(12) 153.90(8), O(13)–Zr(3)–O(1)* 135.66(8), O(1)–Zr(3)–O(11) 141.54(7), O(1)*–Zr(3)–O(11) 140.89(7), O(2)–Zr(3)–N(3) 78.60(9), O(13)–Zr(3)–N(3) 151.42(9), O(1)–Zr(3)–N(3) 128.43(8), O(12)–Zr(3)–N(3) 79.70(8), O(1)*–Zr(3)–N(3) 69.70(8), O(11)–Zr(3)–N(3) 72.24(8), Zr(1)–O(5)–Zr(2) 108.57(8), Zr(1)–O(9)–Zr(2) 109.13(8), Zr(1)–O(11)–Zr(3) 112.86(8), Zr(1)–O(12)–Zr(3) 112.33(8), Zr(3)–O(1)–Zr(3)* 115.60(8).

structures reported in this section do not provide a comprehensive picture of the structural chemistry of these compounds, but rather point out some interesting differences to the titanium derivatives.

When Zr(O*i*Pr)$_4$ was treated with four molar equivalents of 2-aminoethanol, a colorless precipitate was obtained, which yielded a small amount of crystalline $Zr(OCH_2CH_2NH_2)_4 \cdot 2$*i*PrOH (**6**) upon recrystallization. The structure of **6** (Figure 7) is as expected for zirconium with its tendency for higher coordination numbers: all $OCH_2CH_2NH_2$ ligands are chelating and symmetrically arranged, i.e. the oxygen and nitrogen atoms occupy alternating corners in a distorted square antiprism (molecular D_2 symmetry of **6**). The two *i*PrOH solvate molecules are weakly hydrogen bonded to N(2) [N···O 302.5(5) pm]. The structure of **6** is analogous to that of Zr(acetylacetonate)$_4$.[17] As a side remark, a similar structure cannot be expected for $Ti(OCH_2CH_2NH_2)_4$ due to the lower coordination number of the Ti atom.

The second crystalline compound we isolated has a remarkable structure, compared to the titanium compounds of analogous chemical composition. The compound was obtained by reaction of $Zr(OBu)_4$ with 0.82 molar equivalents of 2-aminoethanol and is formally a mono-substitution product ($x = 1$), i.e. $Zr(OBu)_3(OCH_2CH_2NH_2)$. However, unlike the dimeric mono-substitution products of $Ti(OR)_4$ discussed above, the Zr derivative has a complex hexanuclear structure, i.e. $[Zr(OBu)_3(OCH_2CH_2NH_2)]_6 \cdot 2BuOH$ (**7**) (Figure 8).

The structure of **7** $[Zr_6(\mu_2\text{-}OBu)_4(OBu)_{14}(\mu_2\text{-}\eta^1\text{-}OCH_2CH_2NH_2)_6]$ can be rationalized by assembly of smaller sub-units, viz. two $Zr_2(OBu)_5(OCH_2CH_2NH_2)_3$ and two $Zr(OBu)_4$ units each. In the $Zr_2(OBu)_5(OCH_2CH_2NH_2)_3$ sub-unit, the Zr atoms are bridged by the oxygen atoms of two bridging-chelating $OCH_2CH_2NH_2$ ligands. Remarkably, the nitrogen atoms of these ligands are coordinated to the *same* Zr atom [Zr(1)]. Zr(1) is additionally substituted by three OBu ligands and thus reaches a coordination number of seven. The other Zr atom in the dimeric subunit [Zr(3)] is substituted by two terminal OBu groups and one chelating $OCH_2CH_2NH_2$ ligand. The two $Zr_2(OBu)_5(OCH_2CH_2NH_2)_3$ sub-units dimerize via the oxygen atom of the latter ligand, which thus becomes bridging-chelating, and Zr(3) becomes seven-coordinate. Thus, dimerization gives a centrosymmetric $[Zr_2(OBu)_5(OCH_2CH_2NH_2)_3]_2 = Zr_4(OBu)_{10}(OCH_2CH_2NH_2)_6$ unit. The structure of **7** is completed by addition of two $Zr(OBu)_4$ molcules [Zr(2)] to both ends of the Zr_4 unit via OBu bridges (see Scheme 2).



Scheme 2. Schematic construction of **7** from smaller units (see text). A box is drawn around one $Zr_2(OBu)_5(OCH_2CH_2NH_2)_3$ sub-unit. The dashed lines only serve to indicate how the structure of **7** can be constructed form sub-units; in the real structure the dashed lines are also chemical bonds.

Conclusions

Amino alcohols are very versatile reagents for the modification of metal alkoxides, one reason being that they can undergo several stable coordination modes. In this work we have described examples for chelating, bridging and bridging-chelating coordination. Amino alcoholate ligands are thus very adaptable to the requirements of a particular $M(OR)_x$ entity.

The structural chemistry of aminoethanolate derivatives of titanium alkoxides is dominated by dimeric, OR-bridged structures. In the mono-substituted derivatives Ti$_2$(O*i*Pr)$_6$(OCHRCHR′NH$_2$)$_2$, each amino alcoholate ligand chelates one titanium atom, and two O*i*Pr groups are bridging. This structural motif is varied in the disubstituted compound Ti$_2$(O*i*Pr)$_4$(OCH$_2$CH$_2$NH$_2$)$_4$ (**3**) where the bridging O*i*Pr groups are replaced by $OCH_2CH_2NH_2$ groups, with dangling NH_2 groups. Although this dimeric structure appears to be rather robust, it is nevertheless slightly, but significantly influenced by organic substituents attached to either CH_2 group of the $OCH_2CH_2NH_2$ ligand. Comparison of the structures of Ti$_2$(O*i*Pr)$_6$(OCHMeCH$_2$NH$_2$)$_2$ (**2a**) and Ti$_2$(O*i*Pr)$_6$(OCH$_2$CHMeNH$_2$)$_2$ (**2b**) showed that the substituents are better placed at the NH_2-substituted carbon. At this position, they are sterically better accommodated than at the O-substituted C atom.

The structural development of the metal oxide network is a crucial but largely unresolved issue when organically substituted metal alkoxide derivatives are used for sol-gel processing. This refers to structural features of the oxide network itself (because the connectivity is lowered due to the organic ligands) as well as to the directing influence and the positioning of the organic groups. Because hydrolytic condensations are kinetically controlled processes, formation of crystalline intermediates or products is the exception rather than the rule, and information on how the molecular building blocks are connected with each other must therefore be deduced from particular examples, often obtained in a non-rational way. Two such examples were discussed in this work. The structure of Ti$_4$O$_4$(O*i*Pr)$_4$(OCHPhCHMeNHMe)$_4$ (**4**) is the same as that of the previously described compound $Ti_4O_4(OCH_2CH_2NMe_2)_8$,[13] were the terminal OR groups at the Ti_4O_4 cluster core were replaced by O*i*Pr groups. The structure of $Ti_8O_6(OEt)_{12}(OCH_2CH_2NH_2)_8$ (**5**) is made of two $Ti_4O_3(OEt)_6(OCH_2CH_2NH_2)_4$ sub-units connected by two OEt bridges. It represents a new structure motif in the chemistry of titanium oxo derivatives, as it contains a previously unknown nearly planar $Ti_4(\mu_2\text{-}O)_2(\mu_3\text{-}O)(\mu_2\text{-}OR)_2$ ring system.

Nearly no information is available on structural data of 2-amino alcoholate derivatives of zirconium alkoxides. This is probably due to the fact that the zirconium derivatives are much more difficult to crystallize than, for example, the corresponding titanium compounds. The structural characterization of “$Zr(OBu)_3(OCH_2CH_2NH_2)$” in this work shows impressively that simple structural considerations or extrapolations from other metal alkoxides are not applicable. This compound is in fact hexanuclear with one of the most complex structures of “simple” metal alkoxide derivatives. The structure of $Zr_6(OBu)_{18}(OCH_2CH_2NH_2)_6$ (**7**) is assembled from two $Zr_2(OBu)_5(OCH_2CH_2NH_2)_3$ and two $Zr(OBu)_4$ sub-units, which are associated by alkoxo bridges. The compound is thus no real “mono-substitution” product (one aminoethanolate ligand per Zr atom) but contains, in a formal sense, non-, mono- and di-substituted zirconium atoms at the same time.

Experimental Section

General: All operations were carried out in a moisture- and oxygen-free atmosphere of argon using. Ti(O*i*Pr)$_4$ (Aldrich, 97%), Ti(OEt)$_4$ (Aldrich techn.), Zr(O*i*Pr)$_4$ (ABCR, 70–75% in heptane), Zr(OBu)$_4$ in *n*BuOH (Aldrich), 2-aminoethanol (Aldrich 99.9%), (*S*)-(+)-1-amino-2-propanol (isopropanolamine, Aldrich 98%), (*S*)-(+)-2-amino-1-propanol (Aldrich 98%), ephedrine (Aldrich 98%) and NaNH$_2$ (Fluka 99%) were used as received. The solvents were dried and purified by standard techniques.

Synthesis of Ti$_2$(O*i*Pr)$_8$(OCHMeCH$_2$NH$_2$)$_2$ (2a): An amount of 131 mg (1.74 mmol) of (*S*)-(+)-1-amino-2-propanol was added to 452 mg (1.59 mmol) of Ti(O*i*Pr)$_4$. The resulted white precipitate was dissolved in 1 mL of toluene under reflux within 5 min. Colorless crystals were obtained after 4 d at 4 °C, which were dried in vacuo. Yield 343 mg (77%). ^{1}H NMR (CDCl$_3$, 21 °C) Only resonances are given which were clearly assigned by 2D correlations: Amino alcoholate 1: δ = 3.30, 2.74 (NC*H*$_2$), 4.74 (OC*H*Me), 1.23 (CHC*H*$_3$) ppm. Amino alcoholate 2: δ = 3.00, 2.86 (NC*H*$_2$), 4.62 (OC*H*Me) ppm. Amino alcoholate 3: δ = 3.00, 2.86 (NC*H*$_2$), 4.58 (OC*H*Me) ppm. Amino alcoholate 4: δ = 3.14, 2.59 (NC*H*$_2$), 4.35 (OC*H*Me), 1.13 (CHC*H*$_3$) ppm. Alkoxide 1: δ = 4.69 (OC*H*), 1.23 (CHC*H*$_3$). Alkoxide 2: δ = 4.59 (OC*H*), 1.27 (CHC*H*$_3$). Alkoxide 3: δ = 4.03 (OC*H*), 1.26 (CHC*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 21 °C) Amino alcoholate 1: δ = 48.7 (N*C*H$_2$), 75.9 (O*C*HMe), 19.7 (CH*C*H$_3$) ppm. Amino alcoholate 2: δ = 51.6 (N*C*H$_2$), 76.5 (O*C*HMe) ppm. Amino alcoholate 3: δ = 49.8 (N*C*H$_2$), 76.2 (O*C*HMe) ppm. Amino alcoholate 4: δ = 50.9 (N*C*H$_2$), 75.8 (O*C*HMe), 21.8 (CH*C*H$_3$) ppm. Alkoxide 1: δ = 73.2 (O*C*H), 25.4 (CH*C*H$_3$). Alkoxide 2: δ = 76.5 (O*C*H), 26.5 (CH*C*H$_3$). Alkoxide 3: δ = 64.5 (O*C*H), 26.6 (CH*C*H$_3$).

Synthesis of Ti$_2$(O*i*Pr)$_8$(OCH$_2$CHMeNH$_2$)$_2$ (2b): An exothermic reaction was observed when 134 mg (1.78 mmol) of (*S*)-(+)-2-amino-1-propanol was added to 455 mg (1.60 mmol) of Ti(O*i*Pr)$_4$. The obtained precipitate was re-crystallized twice from CH$_2$Cl$_2$ and then dried in vacuo. Yield 370 mg (81%). ^{1}H NMR (CDCl$_3$, 21 °C) Only resonances are given which were clearly assigned by 2D correlations: Amino alcoholate 1: δ = 4.40, 3.82 (OC*H*$_2$), 3.49 (NC*H*Me), 1.15 (CHC*H*$_3$), 2.04, 3.47 (N*H*$_2$) ppm. Amino alcoholate 2: δ = 4.23, 3.92 (OC*H*$_2$), 3.20 (NC*H*Me), 1.14 (CHC*H*$_3$), 2.91, 3.18 (N*H*$_2$) ppm. Amino alcoholate 3: δ = 4.14, 3.87 (OC*H*$_2$), 3.32 (NC*H*Me), 1.21 (CHC*H*$_3$), 1.47, 4.12 (N*H*$_2$) ppm. Amino alcoholate 4: δ = 4.02, 3.94 (OC*H*$_2$), 4.49 (NC*H*Me), 1.19 (CHC*H*$_3$) ppm. Alkoxide 1: δ = 4.71 (OC*H*), 1.26 (CHC*H*$_3$). Alkoxide 2: δ = 4.65 (OC*H*), 1.24 (CHC*H*$_3$). Alkoxide 3: δ = 4.50 (OC*H*), 1.22 (CHC*H*$_3$). Alkoxide 4: δ = 4.04 (OC*H*), 1.14 (CHC*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 21 °C) Amino alcoholate 1: δ = 76.6 (O*C*H$_2$), 50.9 (N*C*HMe), 19.2 (CH*C*H$_3$) ppm. Amino alcoholate 2: δ = 75.5 (O*C*H$_2$), 51.2 (N*C*HMe), 19.4 (CH*C*H$_3$) ppm. Amino alcoholate 3: δ = 77.2 (O*C*H$_2$), 52.8 (N*C*HMe), 19.3 (CH*C*H$_3$) ppm. Amino alcoholate 4: δ = 77.5 (O*C*H$_2$), 52.3 (N*C*HMe), 19.7 (CH*C*H$_3$) ppm. Alkoxide 1: δ = 74.4 (O*C*H), 26.5 (CH*C*H$_3$). Alkoxide 2: δ = 73.5 (O*C*H), 26.3 (CH*C*H$_3$). Alkoxide 3: δ = 76.3 (O*C*H), 25.5 (CH*C*H$_3$). Alkoxide 4: δ = 64.5 (O*C*H), 26.6 (CH*C*H$_3$).

Synthesis of Ti$_2$(O*i*Pr)$_4$(OCH$_2$CH$_2$NH$_2$)$_4$ (3): Na[Ti(O*i*Pr)$_5$] was prepared according to ref.[15] To this end, an amount of 223 mg (5.72 mmol) of NaNH$_2$ was dispersed in 10 mL of heptane. Then 1476 mg (5.19 mmol) of Ti(O*i*Pr)$_4$ was added dropwise at –40 °C whilst stirring. The yellow solution was warmed to room temperature within 1 h and was then separated from unreacted NaNH$_2$. An amount of 910 mg (14.90 mmol) of 2-aminoethanol was added slowly. Colorless crystals were obtained after a few minutes. The product was re-crystallized from *n*-heptane and dried in vacuo. Yield 457 mg (31%). ^{1}H NMR (CD$_2$Cl$_2$, 21 °C): δ = 4.82, 4.22, 4.21, 4.16 (b, OC*H*Me$_2$), 4.00 (br., HOC*H*Me$_2$), 2.99 (br., NC*H*$_2$, OC*H*$_2$), 1.32, 1.31, 1.30, 1.24, 1.19 [m, OCH(C*H*$_3$)$_2$/HOCH(C*H*$_3$)$_2$], 4.25/2.27, 4.10/2.42 (*H*$_2$N) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 21 °C): δ = 75.4, 74.9, 72.9, 71.3 (O*C*HMe$_2$), 64.1 (HO*C*HMe$_2$), 45.2 (O*C*H$_2$*C*H$_2$NH$_2$), 32.0, 29.3, 26.2, 25.3, 22.8 [m, OCH(*C*H$_3$)$_2$/HOCH(*C*H$_3$)$_2$] ppm.

Synthesis of Ti$_4$O$_4$(O*i*Pr)$_4$(OCHPhCHMeNHMe)$_4$ (4): An amount of 1008 mg (3.55 mmol) of Ti(O*i*Pr)$_4$ was added slowly to a solution of 586 mg (3.55 mmol) ephedrine in 2 mL of CH$_2$Cl$_2$ under Ar. The solution was heated under reflux for 5 min and then stored at 4 °C. Colorless crystals of **4** were obtained after one week. Yield 122 mg (21%). ^{1}H NMR (CD$_2$Cl$_2$, 21 °C) Amino alcoholate 1: δ = 5.92 (OC*H*), 3.03 (NC*H*Me), 1.21 (CHC*H*$_3$), 2.42 (NC*H*$_3$), 2.51 (N*H*$_2$) ppm. Amino alcoholate 2: δ = 5.56 (OC*H*), 3.88 (NC*H*Me), 0.83 (CHC*H*$_3$), 3.02 (NC*H*$_3$), 2.51 (N*H*$_2$) ppm. Amino alcoholate 3: δ = 5.53 (OC*H*), 3.32 (NC*H*Me), 0.93 (CHC*H*$_3$), 2.68 (NC*H*$_3$), 4.63 (N*H*$_2$) ppm. Amino alcoholate 4: δ = 5.39 (OC*H*), 3.28 (NC*H*Me), 0.93 (CHC*H*$_3$), 2.55 (NC*H*$_3$), 2.56 (N*H*$_2$) ppm. Alkoxide 1: δ = 4.93 (OC*H*), 1.46, 1.33 (CHC*H*$_3$). Alkoxide 2: δ = 4.77 (OC*H*), 1.28 (CHC*H*$_3$). Alkoxide 3: δ = 4.55 (OC*H*), 1.12 (CHC*H*$_3$). Alkoxide 4: δ = 4.20 (OC*H*), 0.71, 0.83 (CHC*H*$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 21 °C) Amino alcoholate 1: δ = 80.4 (OC*H*), 66.2 (NC*H*Me), 13.0 (CHC*H*$_3$), 36.8 (NC*H*$_3$) ppm. Amino alcoholate 2: δ = 84.7 (OC*H*), 60.6 (NC*H*Me), 12.3 (CHC*H*$_3$), 33.4 (NC*H*$_3$) ppm. Amino alcoholate 3: δ = 81.9 (OC*H*), 62.1 (NC*H*Me), 8.0 (CHC*H*$_3$), 32.8 (NC*H*$_3$) ppm. Amino alcoholate 4: δ = 83.9 (OC*H*), 61.1 (NC*H*Me), 13.9 (CHC*H*$_3$), 33.5 (NC*H*$_3$) ppm. Alkoxide 1: δ = 72.7 (O*C*H), 26.7, 24.7 (CH*C*H$_3$). Alkoxide 2: δ = 75.0 (O*C*H), 25.4 (CH*C*H$_3$). Alkoxide 3: δ = 73.5 (O*C*H), 24.8 (CH*C*H$_3$). Alkoxide 4: δ = 74.3 (O*C*H), 23.6, 23.9 (CH*C*H$_3$). ^{15}N NMR (CD$_2$Cl$_2$, 21 °C): δ = 32.0 (amino alcoholate 1), 30.7 (amino alcoholate 2), 32.9 (amino alcoholate 3), 32.5 (amino alcoholate 4) ppm.

Synthesis of Ti$_8$O$_6$(OEt)$_{12}$(OCH$_2$CH$_2$NH$_2$)$_8$ (5): An amount of 10 µL of H$_2$O was dissolved in 4 mL of EtOH under Ar. A solution of 496 mg (2.17 mmol) of Ti(OEt)$_4$ in 5 mL of EtOH was then added dropwise via a rubber septum followed by 139 mg (2.28 mmol) of 2-aminoethanol. The solution was heated under reflux for 10 min and then stored at 4 °C. The solution was concentrated several times at reflux temperature to 10% of the original volume. Few crystals of **5** were obtained after 30 d.

Synthesis of Zr(OCH$_2$CH$_2$NH$_2$)$_4$·2*i*PrOH (6): An amount of 393 mg (6.43 mmol) 2-aminoethanol was added slowly whilst stirring to 764 mg (1.63 mmol) of a 70–75% solution of Zr(O*i*Pr)$_4$ in

Table 1. Crystallographic and structural parameters of **2**–**7**.

	2a	**2b**	**3**·CH_2Cl_2	**4**	**5**	**6**·$2C_3H_8O$	**7**
Empirical formula	$C_{24}H_{58}N_2O_8Ti_2$	$C_{24}H_{58}N_2O_8Ti_2$	$C_{20}H_{52}N_4O_8Ti_2\cdot CH_2Cl_2$	$C_{52}H_{84}N_4O_{12}Ti_4$	$C_{40}H_{108}N_8O_{26}Ti_8$	$C_8H_{24}N_4O_4Zr\cdot 2C_3H_8O$	$C_{92}H_{218}N_6O_{26}Zr_6$
Formula weight	598.5	598.5	657.4	1148.8	1500.5	451.7	2372.0
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$C2/c$	$P2_1/n$
Unit cell dim.							
a [pm]	959.68(5)	1109.41(7)	847.31(5)	1228.13(6)	952.00(7)	2443.5(3)	12.2685(10)
b [pm]	1271.30(6)	1492.40(9)	948.63(5)	1427.85(7)	1288.4(1)	896.29(8)	17.8016(14)
c [pm]	1364.17(7)	1145.95(7)	2160.9(1)	3664.9(2)	1687.0(1)	1075.0(1)	30.316(2)
α [°]			79.152(1)		86.790(2)		
β [°]	92.239(1)	118.153(1)	88.021(1)		78.028(2)	114.108(3)	90.419(2)
γ [°]			76.461(1)		81.380(2)		
Volume [pm^3]·10^6	1663.1(1)	1672.9(2)	1658.3 (2)	6426.7(5)	2000.7(3)	2148.9(4)	6620.9(9)
Z	2	2	2	4	1	4	2
Calcd. density [g/cm^3]	1.195	1.188	1.317	1.187	1.245	1.396	1.190
Absorption coeff. μ [mm^{-1}]	0.521	0.518	0.686	0.533	0.820	0.545	0.513
Crystal size [mm]	0.20×0.09×0.08	0.20×0.09×0.05	0.32×0.28×0.20	0.21×0.19×0.18	0.25×0.20×0.18	0.05×0.04×0.02	0.24×0.23×0.21
θ range [°]	2.12–25.00	2.02–25.00	2.47–25.00	2.26–25.00	2.05–25.00	2.45–25.00	2.38–25.00
Reflections coll./unique	13465/5757	13466/5880	17688/5778	45461/11221	10788/6946	3643/1359	35554/11623
Data/parameters	5757/325	5880/325	5778/344	11221/649	6946/370	1359/114	11623/586
GOF on F^2	1.055	1.035	1.044	0.999	1.011	0.988	1.069
R [$I > 2\sigma(I)$]	0.037	0.039	0.031	0.049	0.054	0.048	0.040
$wR2$	0.096	0.099	0.083	0.116	0.148	0.110	0.103
Largest diff. peak/hole [e Å^{-3}]	0.572/–0.275	0.398/–0.189	0.832/–0.518	0.670/–0.295	0.695/–0.394	0.715/–0.544	0.729/–0.524

n-heptane. The resulting white precipitate was separated and dissolved in 2 mL of CH_2Cl_2 under reflux. Colorless crystals were obtained upon storage at 4 °C after 12 h. The product was re-crystallized twice from CH_2Cl_2.

Synthesis of [Zr(OBu)$_3$(OCH$_2$CH$_2$NH$_2$)]$_6$·2BuOH (7): An amount of 107 mg (1.75 mmol) of 2-aminoethanol was added to 1023 mg (2.13 mmol) of a 80% solution of $Zr(OBu)_4$ in butanol. The reaction solution was heated to reflux for 5 min and was then stored at –20 °C. After two month few colorless crystals of **7** were obtained. ^1H NMR ($CDCl_3$, 21 °C): δ = 4.35–3.83 (m, $OCH_2CH_2NH_2$) 3.69 (m, $OCH_2CH_2CH_2Me$), 3.23–2.69 (b, $OCH_2CH_2NH_2$), 1.54 (OCH_2CH_2Me), 1.38 ($OCH_2CH_2CH_2$), 0.96 (m, $OCH_2CH_2CH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C): δ = 68.7 ($OCH_2CH_2NH_2$), 62.9 ($OCH_2CH_2CH_2Me$), 44.5 ($OCH_2CH_2NH_2$), 37.4 ($OCH_2CH_2CH_2Me$), 19.2 ($OCH_2CH_2CH_2Me$), 14.2 ($OCH_2CH_2CH_2CH_3$) ppm.

X-Ray Structure Analyses: Data collection (Table 1): The crystals were mounted on a Siemens SMART diffractometer with an 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. 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 the Patterson method (SHELXS97). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL97) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Residual electron density in **5** of disordered solvent molecules could not be assigned to atom positions and was removed by the program package PLATON (Squeeze).

CCDC-663010 (for **2a**), -663011 (for **2b**), -663012 (for **3**), -663013 (for **4**), -663014 (for **5**), -663015 (for **6**) and -663016 (for **7**) 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.

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[1] J. Livage, M. Henry, C. Sanchez, *Progr. Solid State Chem.* **1988**, *18*, 259.

[2] D. C. Bradley, R. C. Mehrotra, D. P. Gaur, *Metal Alkoxides*, Academic Press, London, **1978**; D. C. Bradley, R. C. Mehrotra, I. P. Rothwell, A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Academic Press, London, **2001**; N. Ya. Turova, E. P. Turevskaya, V. G. Kessler, M. I. Yanovskaya, *The Chemistry of Metal Alkoxides*, Kluwer, Boston, **2002**.

[3] Review article: U. Schubert, N. Hüsing, A. Lorenz, *Chem. Mater.* **1995**, *7*, 2010.

[4] U. Schubert, *Acc. Chem. Res.* **2007**, *40*, 730.

[5] Review article: U. Schubert, *Chem. Mater.* **2001**, *13*, 3487.

[6] M. Puchberger, W. Rupp, U. Bauer, U. Schubert, *New J. Chem.* **2004**, *28*, 1289.

[7] Selected articles on metal alkoxide monoamino alcoholate derivatives: R. C. Mehrotra, R. K. Mehrotra, *J. Indian Chem. Soc.* **1962**, *39*, 677; R. C. Mehrotra, G. Srivastava, *J. Indian Chem. Soc.* **1962**, *39*, 521; R. C. Mehrotra, G. Chandra, *Indian J. Chem.* **1965**, *3*, 497; R. C. Mehrotra, V. D. Gupta, *Indian J. Chem.* **1967**, *5*, 643; B. S. Sankhla, R. N. Kapoor, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1381; R. C. Mehrotra, P. N. Kapoor, *Indian J. Chem.* **1967**, *5*, 505; R. C. Mehrotra, P. N. Kapoor, *J. Indian Chem. Soc.* **1967**, *44*, 467; R. K. Mittal, R. C. Mehrotra, *Z. Anorg. Allg. Chem.* **1967**, *351*, 309; B. P. Baranwal, P. C. Bharara, R. C. Mehrotra, *Transition Met. Chem.* **1977**, *2*, 204; R. Duggal, R. C. Mehrotra, *Inorg. Chim. Acta* **1985**, *98*, 121; S. C. Goel, K. S. Kramer, M. Y. Chiang, W. E. Buhro, *Polyhedron*

1990, *9*, 611; A. K. Jain, R. C. Mehrotra, S. Nagar, S. Sharma, *Heteroat. Chem.* **2003**, *14*, 518.

[8] D. M. Puri, R. C. Mehrotra, *J. Indian Chem. Soc.* **1962**, *39*, 447.

[9] P. C. Bharara, V. D. Gupta, R. C. Mehrotra, *Z. Anorg. Allg. Chem.* **1974**, *403*, 337; P. C. Bharara, V. D. Gupta, R. C. Mehrotra, *J. Indian Chem. Soc.* **1974**, *51*, 859; T. Ban, Y. Ohya, Y. Takahashi, *J. Sol-Gel Sci. Technol.* **2003**, *27*, 363.

[10] A. C. Jones, T. J. Leedham, P. J. Wright, M. J. Crosbie, K. A. Fleeting, D. J. Otway, P. O'Brien, M. E. Pemble, *J. Mater. Chem.* **1998**, *8*, 1773.

[11] P. C. Bharara, V. D. Gupta, R. C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *7*, 537.

[12] H. Fric, F. R. Kogler, M. Puchberger, U. Schubert, *Z. Naturforsch. Teil B* **2004**, *59*, 1241.

[13] B. F. G. Johnson, M. C. Klunduk, T. J. O'Connell, C. McIntosh, J. Ridland, *J. Chem. Soc. Dalton Trans.* **2001**, 1553.

[14] H. Fric, U. Schubert, *New J. Chem.* **2005**, *29*, 232; H. Fric, M. Puchberger, U. Schubert, *J. Sol-Gel Sci. Technol.* **2006**, *40*, 155; H. Fric, M. Puchberger, U. Schubert, *Eur. J. Inorg. Chem.* **2007**, 376; M. Casarin, A. Vittadini, U. Schubert, *Monatsh. Chem.* **2007**, *138*, 1217.

[15] T. J. Boyle, T. M. Alam, E. R. Mechenbier, B. L. Scott, J. W. Ziller, *Inorg. Chem.* **1997**, *36*, 3293.

[16] T. J. Boyle, R. P. Tyner, T. M. Alam, B. L. Scott, J. W. Ziller, B. G. Potter Jr, *J. Am. Chem. Soc.* **1999**, *121*, 12104; I. Mijatovic, G. Kickelbick, M. Puchberger, U. Schubert, *New J. Chem.* **2003**, *27*, 3.

[17] J. V. Silverton, J. L. Hoard, *Inorg. Chem.* **1963**, *2*, 243.

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