Nona-coordinated MO_6N_3 centers M = Zr, Hf as a stable building block for the construction of heterometallic alkoxide precursors

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In memory of Professor Liliane G. Hubert-Pfalzgraf – a protagonist in the solution and gas phase stability studies of heteroleptic heterometallic alkoxide precursors of oxide materials.

Abstract

The modification of zirconium or hafnium alkoxides with diethanolamine, H_2dea, leads to the formation of unique nona-coordinated $M\{\mu-\eta^3-NH(C_2H_4O)_2\}_3$ cores. The mechanism is used to develop a self-assembly approach to the first thermodynamically stable zirconium–titanium and hafnium–titanium precursors, $Zr\{\mu-\eta^3-NH(C_2H_4O)_2\}_3[Ti(O^iPr)_3]_2$ (**1**) and $Hf\{\mu-\eta^3-NH(C_2H_4O)_2\}_3[Ti(O^iPr)_3]_2$ (**2**). Mass spectrometric characterization of these compounds demonstrates their volatility. In addition to the solution stability of these compounds the volatility makes them attractive single source precursors for MOCVD and ALD applications. These precursors are also interesting candidates for application in sol–gel synthesis of microporous materials as the stability of the core prevents self-assembly of ligands on the outer surface of the primary particles formed during the hydrolysis. A n-propoxide analog of **1** can be prepared from zirconium n-propoxide but does not yield any crystalline material. It is demonstrated that **1** can be prepared from $[Zr(O^nPr)(O^iPr)_3$ $(^iPrOH)]_2$, however, with a lower yield compared to the use of zirconium isopropoxide. The single crystals obtained from systems containing zirconium isopropoxide, titanium isopropoxide and triethanolamine H_3tea turned out to be $Ti_2(O^iPr)_2(\{\mu-\eta^4-NH(C_2H_4O)_3\}_2)_2$ (**4**). Theoretical calculations indicate that the octacoordinate $M\{\mu-\eta^4-N(C_2H_4O)_3\}_2$ core, anticipated in reaction with H_3tea, will have metal–nitrogen bonds that are too long for its stabilization. This explains why the formation of **4** is thermodynamically favored over the formation of heterometallic species.
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1. Introduction

Sol–gel materials based on zirconium, hafnium and titanium oxides are used in a broad spectrum of applications, ranging from mesoporous materials for catalyst supports and membranes [1,2] to high-tech applications as thin films, fibers [3,4], aerogels [5] and (nano-) particles [6–8]. Thin films can be applied as a micro-membrane layer [9–11], high-temperature thermal barrier coatings or ferroelectrics [12]. Interest in materials containing both titanium and its heavy analogs (zirconium and hafnium) in their composition has grown, such as PZT, PLZT and especially recently – the lead-free BZT [13–15]. The mineral srilankite, $ZrTi_2O_6$, has shown very attractive dielectric properties [16]. A strong difference in reactivity and volatility between

the alkoxide derivatives of zirconium or hafnium and titanium urged the search for stable heterometallic alkoxide precursors involving both types of elements. The single-source precursor approach (combination of the elements in a proper ratio within one thermodynamically stable molecule) has been proven to be a powerful tool in the approach to complex oxide materials [17]. Unfortunately, the reported homoleptic heterometallic complexes such as ZrTi(O^{i}Pr)$_8$(^{i}PrOH)$_2$ or Ba$_2$TiZr(OH)$_2$(O^{i}Pr)$_{10}$(^{i}PrOH)$_6$ [18,19] simply turned out to be a scientific mistake and do not really exist [20,21]. To the best of our knowledge three heteroligands have been reported earlier to stabilize heterometallic titanium zirconium/hafnium species. The first such attempt was reported by Caulton's group in 1998, who investigated the interaction of zirconium pinacolate with titanium isopropoxide. Two complexes, TiZr$_2$-(OCMe$_2$CMe$_2$O)$_4$(OCMe$_2$CMe$_2$OH)(O^{i}Pr)$_2$ and Ti$_2$Zr$_2$-(OCMe$_2$CMe$_2$O)$_6$(O^{i}Pr)$_4$ [20] were characterized in solid state and solution and it was found that their stability in solution was limited. The application of these compounds as precursors of mixed metal oxides does not appear promising and has never been reported. Amorphous carbon is easily formed from the pinacolate ligand due to their low thermal stability. A whole family of methacrylate substituted bimetallic complexes, including Ti$_4$Zr$_4$O$_6$(OBu)$_4$-(OMc)$_{16}$, Ti$_2$Zr$_4$O$_4$(OBu)$_2$(OMc)$_{14}$, Ti$_4$Zr$_2$O$_4$(OBu)$_6$(OMc)$_{10}$, and Ti$_2$Zr$_6$O$_6$(OMc)$_{20}$ have been reported in 2001 by Kickelbick and co-workers [22]. These complexes have been successfully applied as cross-linkers for the reinforce;ment of methacrylate polymers, but the small fraction of the hydrolysable alkoxide groups makes them less attractive for sol–gel applications. In addition, no data on their volatility and gas phase stability have been reported. The X-ray single crystal studies of two interesting methyl-diethanolamine derivatives, Zr$_2$Ti$_2$\{MeN(C$_2$H$_4$-O)$_2$\}$_2$(μ-O^{n}Pr)$_4$(O^{n}Pr)$_6$ and ZrTi\{MeN(C$_2$H$_4$O)$_2$\}$_3$(O^{n}Pr)$_2$ have been reported by Kemmitt et al. [23,24] but no data have been provided on their solution or gas phase stability. In our recent study of the diethanolamine modification of zirconium propoxides, we observed a poor solution stability for the analogs of the compounds reported by Kemmitt and their relatively quick transformation into Zr$_3$\{HN-(C$_2$H$_4$O)$_2$\}$_3$(OPr)$_6$ – complexes with a nona-coordinated central zirconium atom [25]. This very unusual coordination of zirconium has only been observed a few times in aqueous environments (and involved water molecules in the coordination sphere) [26–28], but never before under non-aqueous conditions and then with relatively large ligands.

The uncommon geometry of the complexes with a nona-coordinated central zirconium atom inspired us to prepare a new family of heterometallic precursors. The presence of two types of positions in the Zr\{μ-η^3-NH(C$_2$H$_4$O)$_2$\}$_3$-[Zr(O^{i}Pr)$_3$]$_2$(^{i}PrOH)$_2$ molecule, a nona-coordinated and a hexa-coordinated, provides us with the possibility of constructing new species via self-assembly according to the Molecular Structure Design Concept [29]. For example,

the hexa-coordinated position appears to be able to host smaller atoms like titanium, while bigger atoms like zirconium or hafnium should be able to occupy the nona-coordinated position. Moreover, the compounds can be prepared with several alkoxide ligands. In a preliminary communication, we reported the application of this model for the preparation of Zr\{μ-η^3-NH(C$_2$H$_4$O)$_2$\}$_3$[Ti(O^{i}Pr)$_3$] [25].

The Zr\{η^3-μ$_2$-NH(C$_2$H$_4$O)$_2$\}$_3$[Ti(O^{i}Pr)$_3$] precursor has already proven to be attractive for the preparation of composite materials with unique properties. The precursor has the ability to assure the formation of orthorhombic zirconium titanate phases. Srilankite, ZrTi$_2$O$_6$, is obtained upon hydrolysis and subsequent heat treatment at temperatures above 750 °C [30]. Srilankite is of interest for technological applications in optics and dielectrics [31,32]. Up to now, srilankite could only be prepared at high pressures and temperatures [16,33]. ZrTiO$_4$ can be obtained if the precursor is mixed with an equivalent amount of zirconium *n*-propoxide [34]. In addition to the ability to form these attractive phases the morphology of these materials has been proven to be microporous [30,35]. Microporous metal-oxides are of great importance for the preparation of inorganic membranes and the synthesis of these materials has been an objective for over a decade. The Zr\{η^3-μ$_2$-NH(C$_2$H$_4$O)$_2$\}$_3$[Ti(O^{i}Pr)$_3$] precursor has also shown to be suitable for the preparation of nano-sized crystalline particles by RAPET (reactions under autogenic pressure at elevated temperature) [36].

Here we will report the detailed preparation and characterization of a new family of heterometallic complexes with a MO$_6$N$_3$ tri-capped trigonal prismatic core. The solution and gas phase stability of the obtained compounds is evaluated. The stability and the properties of the derived materials is compared to that of commonly used Hacac modified zirconium precursors for the preparation of 'microporous' materials.

2. Experimental

All manipulations were carried out in a dry nitrogen atmosphere using the Schlenk technique or a glove box. Hexane and toluene (Merck, p.a.) were dried by distillation after refluxing with LiAlH$_4$ and isopropanol (Merck, p.a.) was purified by distillation over Al(O^{i}Pr)$_3$. Diethanolamine (H$_2$dea) and triethanolamine (H$_3$tea) (98%) were purchased from Aldrich. Molecular sieves were added to the H$_2$dea to assure that it remained water free. NMR spectra were recorded in *d$_8$*-toluene (99.6%, Aldrich), which was stored with molecular sieves, for all compounds on a Bruker 400 MHz spectrometer at 243 K. Mass-spectra were recorded using a JEOL JMS-SX/SX-102A mass-spectrometer applying electron beam ionization ($U = 70$ eV) with a direct probe introduction.

2.1. Synthesis

The zirconium propoxide precursors used as starting materials in this work are zirconium isopropoxide ([Zr(O^{i}Pr)$_4$-

(^{i}PrOH)]$_2$ 99.9%) and 70 wt% solution of "Zr(O^{n}Pr)$_4$" (both purchased from Aldrich) and [Zr(O^{n}Pr)(O^{i}Pr)$_3$ (^{i}PrOH)]$_2$ which was prepared according to a recently developed technique [37,38] The zirconium isopropoxide was dissolved and recrystallized from toluene prior to use in order to remove impurities. The hafnium isopropoxide was prepared by anodic oxidation of hafnium metal in isopropanol [39] and recrystallized from toluene. The titanium isopropoxide (99.999% pure) and titanium *n*-propoxide (98% pure) were both obtained from Aldrich. Combinations of the different precursors were modified with H$_2$dea or H$_3$tea according to the techniques described below. The exact composition of the single crystals **1**, **2** and **4** was established with single crystal X-ray crystallography.

2.1.1. [Zr{μ-η³-NH(C$_2$H$_4$O)$_2$}$_3$[Ti(O^{i}Pr)$_3$]$_2$] (1)

Zirconium isopropoxide (0.57 g, 1.5 mmol) was dissolved in a 3 ml mixture of hexane/toluene (volume ratio 2:1), subsequently 0.84 g (~3.0 mmol) titanium isopropoxide and 0.46 g (~4.4 mmol) H$_2$dea was added. The sample was dried under vacuum (0.1 mm Hg) and re-dissolved in 2 ml hexane. After cooling overnight in a freezer at −30 °C, the obtained colorless octahedral crystals were separated from the solvent by decantation. The yield was ~1.1 g (~59%) of compound **1**. The yield can be increased significantly when **1** is crystallized from a more concentrated solution. With additional crystallization steps the compound can be obtained in a quantitative yield.

The synthesis was also performed starting with [Zr(O^{n}Pr)-(O^{i}Pr)$_3$(^{i}PrOH)]$_2$ as the precursor. The precursor (0.94 g, ~2.4 mmol) was dissolved in 2 ml hexane and subsequently 1.39 g (~4.8 mmol) titanium isopropoxide and finally 0.78 g (~ 7.2 mmol) diethanolamine was added. The sample was dried under vacuum (0.1 mm Hg) and redissolved in 2 ml hexane. After cooling overnight in a freezer at −30 °C, the obtained colorless octahedral crystals were separated from the solvent by decantation. The yield was ~0.8 g (~26%) of compound **1**.

Analytical samples of crystals of **1** were dried in vacuum (0.1 mm Hg) prior to spectral analysis. *Anal*. Calc. for C$_{30}$H$_{69}$N$_3$O$_{12}$Ti$_2$Zr: C, 42.3; N, 4.9; H, 8.1. Found: C, 41.8; N, 5.0; H, 7.5%. The IR spectra were recorded of the compound in nujol mulls, cm^{-1}: 1358 sh, 1327 w, 1280 w, 1241 w, 1167 sh, 1160 m, 1124 s, 1085 m, 1060s, 1007 w, 988 s, 941 m, 914 s, 879 m, 844 s, 673 sh, 602 s, 571 sh, 447 s.

2.1.2. [Hf{μ-η³-NH(C$_2$H$_4$O)$_2$}$_3$[Ti(O^{i}Pr)$_3$]$_2$] (2)

Hafnium isopropoxide solvate (0.78 g, ~1.65 mmol) was dissolved in a mixture of hexane and toluene (5 ml and volume ratio 1:1). Subsequently, the appropriate amounts of titanium isopropoxide and H$_2$dea (0.94 g (~3.3 mmol) and 0.53 g (~4.9 mmol), respectively) were added. The sequence of solvent removal under vacuum (0.1 mm Hg) and redissolving in 1.5 ml hexane was performed twice. After cooling overnight in a freezer at −30 °C, the obtained colorless octahedral crystals were separated from the sol-

vent by decantation. The yield was ~1.8 g (~80%) of compound **2**.

Analytical samples were dried in vacuum (0.1 mm Hg) prior to spectral analysis. *Anal*. Calc. for C$_{30}$H$_{69}$N$_3$O$_{12}$-Ti$_2$Zr: C, 38.4; N, 4.5; H, 7.3. Found: C, 37.4; N, 4.5; H, 6.8%. The IR spectra were recorded of the compound in nujol mulls, cm^{-1}: 1160 m, 1124 s, 1084 m, 1063s, 988 s, 914 s, 842 s.

2.1.3. [Zr{μ-η³-NH(C$_2$H$_4$O)$_2$}$_3$[Ti(O^{n}Pr)$_3$]$_2$] (3)

Zirconium *n*-propoxde (1.4 g, ~3.6 mmol) was dried and redissolved in 2 ml hexane and subsequently 2.06 g (~7.2 mmol) titanium isopropoxide and 1.17 g (~ 10.8 mmol) diethanolamine were added. The sample was dried under vacuum (0.1 mm Hg) and redissolved in 2 ml hexane and subsequently placed at −30 °C several days for crystallization. The sequence of drying, redissolving and cooling for crystallization was repeated two more times. The composition of the yellowish product is corresponding to that of **3** in the fully dried samples.

2.1.4. Ti$_2$(O^{i}Pr)$_2$({μ-η⁴-N(C$_2$H$_4$O)$_3$}$_2$)$_2$ (4)

0.73 g (1.86 mmol) of zirconium isopropoxide was dissolved in a 3 ml mixture of hexane/toluene (volume ratio 2:1), subsequently 1.08 g (~3.8 mmol) titanium isopropoxide and 0.56 g (~3.8 mmol) H$_3$tea were added. The milk-like sample was refluxed for 30 min and subsequently dried under vacuum (0.1 mm Hg) and redissolved in 2 ml hexane (were it remained a yellow, milk-like solution). After cooling overnight in a freezer at −30 °C, the obtained colorless octahedral crystals were separated from the solvent by decantation. The crystals were characterized as Ti$_2$(O^{i}Pr)$_2$({μ-η⁴-N(C$_2$H$_4$O)$_3$}$_2$)$_2$ by X-ray diffraction. The synthesis was performed in an analogous manner with zirconium isopropoxide, titanium isopropoxide and triethanolamine in a ratio of 1:2:2. Again the obtained single crystals consisted only of Ti$_2$(O^{i}Pr)$_2$({μ-η⁴-N(C$_2$H$_4$O)$_3$}$_2$)$_2$.

Ti$_2$(O^{i}Pr)$_2$({μ-η⁴-N(C$_2$H$_4$O)$_3$}$_2$)$_2$ was also prepared by dissolving titanium isopropoxide (1.84 g, 6.5 mmol) in 4 ml of hexane. Upon the addition of H$_3$tea (0.97 g, 6.5 mmol) the color of the solution changed from colorless to yellow and an increase in temperature of the solution was observed. The solvents were removed under vacuum (0.1 mm Hg). It was attempted to redissolve the obtained solid product in a 4 ml mixture of solvents (toluene and isopropanol in a volume ratio of 1:1). The sample was subsequently refluxed and toluene was added until a clear solution had formed. The sample was cooled overnight in a freezer at −30 °C, and the obtained crystals (almost quantitative yield) were separated from the solvent by decantation. The crystals were characterized and determined to be that of **4**.

2.2. Crystallography

Data collection for single crystals of all compounds was carried out at 22 °C on a SMART CCD 1k diffractometer

with graphite-monochromated Mo Kα radiation. All structures were solved by standard direct methods. The coordinates of the metal atoms as well as the majority of other non-hydrogen atoms were obtained from the initial solutions and for all other non-hydrogen atoms found in subsequent difference Fourier syntheses. The structural parameters were refined by least squares using first isotropic and then also anisotropic approximations. The coordinates of the hydrogen atoms were calculated geometrically and were included into the final refinement in isotropic approximation for all the compounds. All calculations were performed using the SHELXTL-NT program package [40] on an IBM PC.

2.3. Calculations

All quantum chemical calculations were made using the program package GAUSSIAN-03 (Rev. C.02) [41], employing the hybrid density function B3PW91. The basis sets used for H, C, N and O were of 6-311G quality including additional diffusion and polarization functions. The basis sets used for Zr employed quasi-relativistic (MWB) effective-core potentials, thus taking scalar relativistic effects into account, replacing 28 with adapted basis sets of (8s7p6d)/[6s5p3d] quality [42]. All metal complexes and ligands were geometrically optimized to a maximum of symmetry.

3. Results and discussion

The first heterometallic compound prepared, Zr{η^3-μ_2-NH(C_2H_4O)$_2$}$_3$[Ti(O^{i}Pr)$_3$]$_2$ (**1**) (Table 1, TS1) as reported in [25], has a nona-coordinated zirconium central atom and two hexa-coordinated titanium atoms in the terminal position (Fig. 1). The coordination of the central zirconium atom is a very regular tricapped trigonal prism (see Fig. 2) with the oxygen atoms composing the vertices of the prism

(Zr(1)–O(2) 2.196(3) Å, Zr(1)–O(3) 2.199(3) Å and Zr(1)–O(4) 2.210 (3) Å) and the nitrogen ones – the capping vertices (Zr(1)–N(1) 2.440(6) Å, Zr(1)–N(2) 2.439(5) Å). This high-symmetry coordination indicates a high stability of the chelated core with a uniform charge distribution and possibility of a strong covalent contribution to bonding.

The titanium atoms reside in a trigonally distorted octahedron with, in principle, only two types of Ti–O distances: one bridging (Ti–O 2.137(3)–2.147(3) Å) and one terminal (Ti–O 1.836(5)–1.853(4) Å). This coordination is much more symmetric than the octahedral titanium homo- and heterometallic β-diketonate complexes [43,44], where three different bond lengths occur (very short terminal 1.77–1.80 Å, intermediate alkoxide bridging, 1.95–2.05 Å, and slightly longer ones to the oxygen atoms of β-diketonate ligands, 2.02–2.08 Å), which may be the reason for the high solution stability of complex **1** in comparison with these species as will be discussed below.

A typical ^{1}H NMR spectrum of **1** is depicted in Fig. 3a and it can be seen that the spectrum is rather complex. Compound **1** has four different proton containing groups, i.e., *CH*$_3$, and *CH* of the alkoxide ligands and *NCH*$_2$ and *OCH*$_2$ of the diethanolamine ligand. The complete ligand exchange, which is not unusual for zirconium alkoxide complexes, would lead to the presence of only one signal for each of them. However, the crystallographic symmetry allows one to distinguish two types of diethanolamine ligands and three different alkoxide ligands and hence a corresponding number of signals can be expected. Diastereotopic effects may even lead to a higher complexity of the NMR spectra. In addition, some of the signals in the spectrum are due to traces of the hydrocarbon solvents used during the synthesis or to the toluene in the d_8-toluene used as the solvent for the NMR samples. These signals are present between 0 and 2.15 ppm and marked with "*" in Fig. 3a. Two dimensional NMR

Table 1
Crystal data and the diffraction experiments details for compounds **1**, **2** and **4**

| Compound	**1**	**2**	**4**
Chemical composition	$C_{30}H_{69}N_3O_{12}Ti_2Zr$	$C_{30}H_{69}N_3O_{12}Ti_2Hf$	$C_{36}H_{76}N_4O_{16}Ti_4$
Formula weight	850.90	938.17	1012.61
Crystal system	tetragonal	tetragonal	monoclinic
Space group	$P4(3)2(1)2$	$P4(3)2(1)2$	Cc
μ (mm^{-1})	0.650	2.812	1.410
R_1	0.0521	0.0808	0.0431
wR_2	0.1411	0.1514	0.0791
a (Å)	11.6171(12)	11.620(3)	12.3569(17)
b (Å)	11.6171(12)	11.620(3)	13.3690(18)
c (Å)	32.053(5)	31.987(7)	14.448(2)
α (°)	90	90	90
β (°)	90	90	92.176
γ (°)	90	90	90
V (Å^3)	4325.7(9)	4318.9(18)	2385.0(6)
T (K)	295(2)	295(2)	295(2)
Z	4	4	2
Number of independent reflections (R_{int})	5091 (0.0412)	2639 (0.1350)	1864 (0.0644)
Number of observed reflections [$I > 2\sigma(I)$]	3126	1776	1197
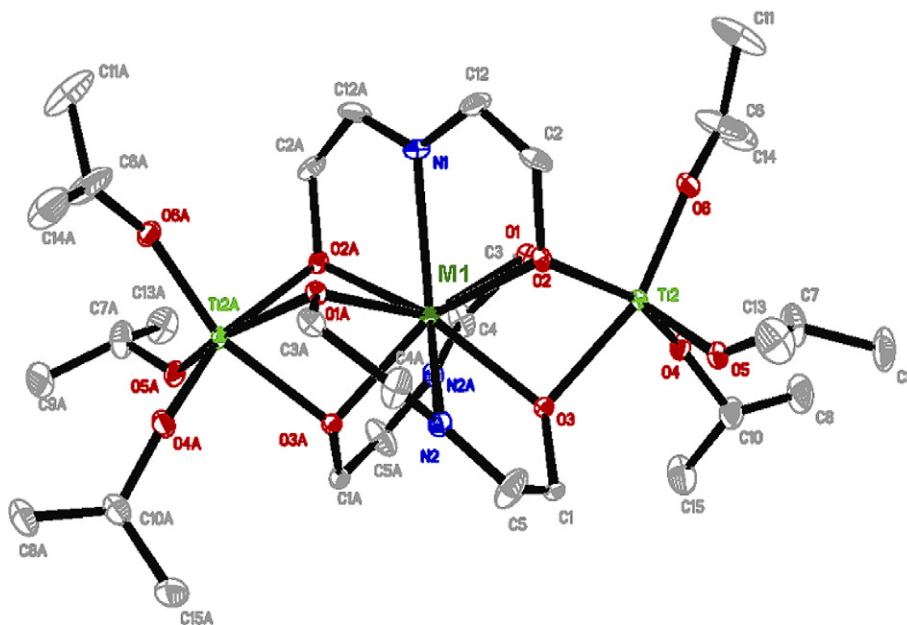
Fig. 1. Molecular structure of M{μ-η³-NH(C₂H₄O)₂}₃[Ti(O^{i}Pr)₃]₂, with M = Zr (**1**) or Hf (**2**).
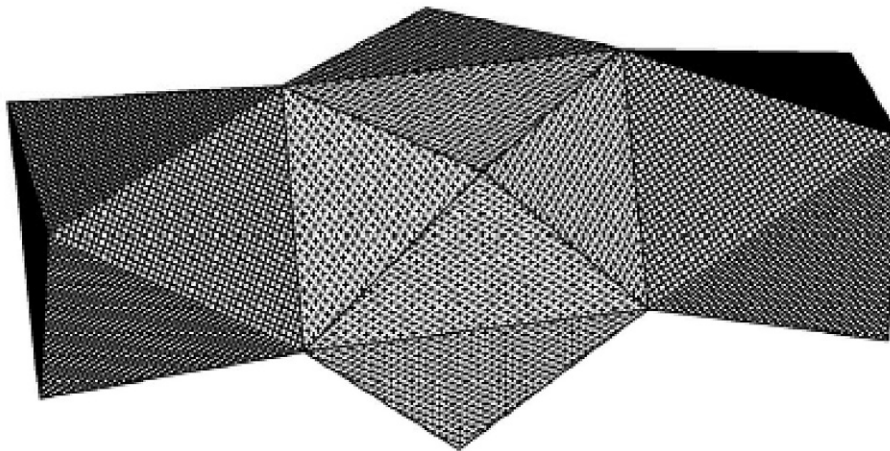

Fig. 2. Polyhedral presentation of the molecular structure of **1**.

was performed to get more insight into the NMR spectra. The proton–proton and proton–carbon coupling experiments (typical spectra are displayed in Fig. 4a and b, respectively) indicated that the signals at 1.45 and 5.0 are due to the CH_3, and CH of the alkoxide ligands, respectively. It was also found that some traces of propanol were present in the sample.

The assignment of signals to the diethanolamine ligands was not possible, since multiple signals were observed. A different carbon chemical shift, i.e., ~50 and 70 ppm, is observed in the proton–carbon coupling spectra for the signals between 2.2–3.4 and 3.7–5.3 ppm (see Fig. 4b). The signals in the respective areas are assigned to the protons of OCH_2 and NCH_2 of the diethanolamine ligands. The integration of the area of all signals assigned to OCH_2 and NCH_2 is in the expected ratio with that of the alkoxide ligands.

We assumed that the presence of various signals due to OCH_2 and NCH_2 of the diethanolamine ligands is caused by alcohol exchange and solvation. In the work on the preparation of homometallic H_2dea modified zirconium precursors, the bonding of alcohol is actually observed in the solid compound Zr{η³-μ₂-NH(C₂H₄O)₂}₃[Zr(O^{i}Pr)₃]₂-(^{i}PrOH)₂ [38]. The proton–proton NMR coupling (Fig. 4a) experiments also support the idea of alcohol exchange and solvation. It seems that the protons in OCH_2 and NCH_2 are in all cases coupled to the same species, but at different chemical shifts. ¹H NMR spectra of two samples from the same batch of crystals from compound **1** were recorded. A drop of isopropanol was added to one of the samples. The spectra displayed a large difference in the position of the signals due to OCH_2 and NCH_2 which confirms the alcohol exchange and solvation of **1** and **2** in the solution.
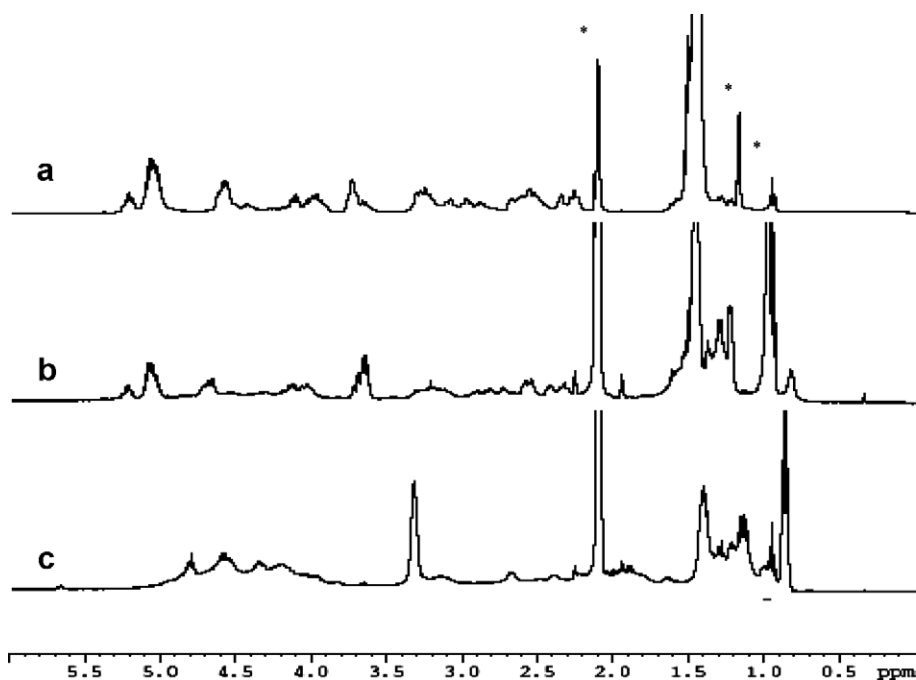
Fig. 3. The proton NMR spectra (a) **1**, (b) **2** and (c) **3**. The signals corresponding to hydrocarbon solvents are marked with "∗".

Identical ^{1}H NMR spectra were obtained for fresh and aged samples of **1**. The aged samples were either stored for 2 months as a solid or for up to one month in toluene. In both cases, the samples were stored at room temperature. Despite the complex nature of the spectra the fact that they do not change over time provides valuable information on the solution stability of this compound. Rearrangement of the heteroleptic ligands in alkoxide precursors can easily be followed in NMR spectra of the compounds (see for example Refs. [45–47]). Thus the unchanged spectra of the aged and fresh samples of compound **1** suggest that no rearrangement of the heteroligands occurs and therefore it is stable upon aging in both solid state and solution.

We showed that it is possible to prepare a compound that has a nona-coordinated central zirconium atom and two hexa-coordinated titanium atoms in the terminal position. It was also of interest to see if the same approach would be valid for hosting a hafnium atom. The main difference between zirconium and hafnium is the smaller atomic radius of the hafnium, resulting from lanthanide contraction. A sample of the aimed compound was prepared according to the procedure described above and the obtained crystals were identified as $Hf\{\eta^3\text{-}\mu_2\text{-}NH\text{-}(C_2H_4O)_2\}_3[Ti(O^iPr)_3]_2$ (**2**) (Table 1, TS2). The molecular structure of **2** is analogous to that of $Zr\{\eta^3\text{-}\mu_2\text{-}NH(C_2H_4O)_2\}_3[Ti(O^iPr)_3]_2$, which is depicted in Fig. 2.

The bond lengths, listed in Table 2, indicate a larger deviation and larger average length in the metal–oxygen bond lengths of the central atom for **2**, i.e., 2.196(3)–2.210(3) Å for compound **1** compared to 2.190(11)–2.237(13) Å for **2**. The distance between the central metal atom and the titanium is, however, shorter for **2**. This is due to the shorter titanium–oxygen bonds, i.e., 2.112(15),

2.119(15), 2.127(14) Å and 2.145(4), 2.147(3), 2.137(3) Å for **2** and **1**, respectively. The alkoxide ligands are more strongly bonded to the titanium atom in **2** compared to **1**, as can be seen from the shorter titanium–oxygen bond lengths. The bond length distribution indicates that the bonds around hafnium have a more pronounced electrostatic character compared to that of zirconium, which results in a higher covalent input for Ti–O bonds.

The ^{1}H NMR spectrum of **2** is depicted in Fig. 4b and is quite similar to that obtained from **1**. At a chemical shift of 0–2.15 ppm the presence of hydrocarbon solvents and some residual alcohol is observed. The effect of alcohol exchange and solvation due to the presence of residual alcohol on the chemical shift of the protons of OCH_2 and NCH_2 of the diethanolamine ligands has already been discussed above. For this reason a quantitative interpretation of the NMR spectra of these compounds is not possible. The behavior of **2** upon aging in solid state and solution was analogous to that described above for **1** and thus this compound is also stable in solid state and solution.

We evaluated the possibility to prepare **1** and **2** by using other (cheaper) homometallic precursors (i.e., using n-propoxides and/or $[Zr(O^nPr)(O^iPr)_3(^iPrOH)]_2$) using alcohol interchange reactions. In addition, we isolated the n-propoxide analog of **1** (hereafter referred to as **3**). In most cases, except when $[Zr(O^nPr)(O^iPr)_3(^iPrOH)]_2$ is used, the anticipated product did not crystallize. The obtained single crystals were identified as **1** on the basis of the determined unit cell parameters. The yield of **1** was in this case significantly lower than when starting from zirconium isopropoxide (26% compared to 59%). This is probably due to the extremely high solubility of the n-propoxide compounds and to the difficulty of removing all of the n-propa-
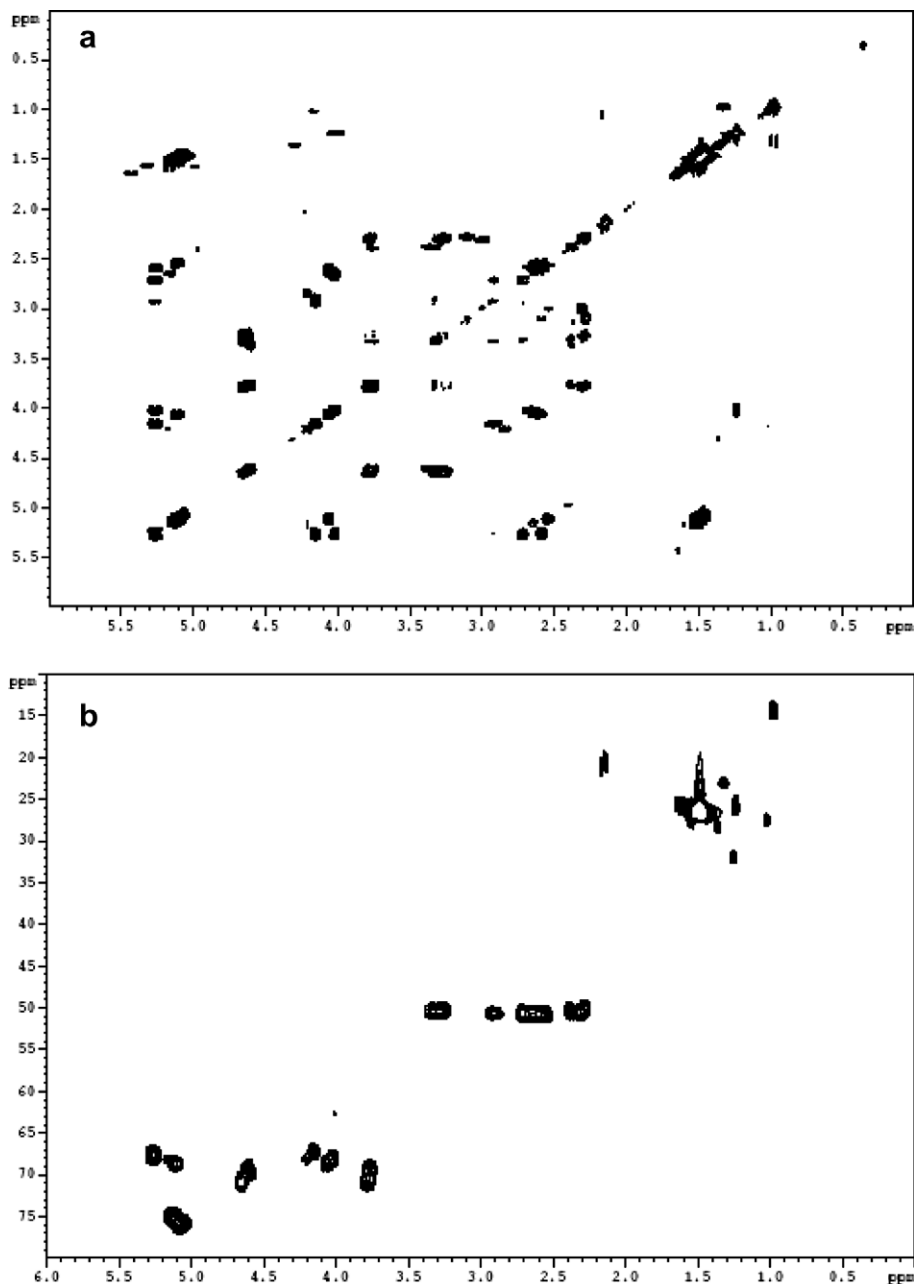
Fig. 4. The proton–proton and proton–carbon coupling NMR spectra of **1**.

nol from the obtained systems. However, the existence of **3** is confirmed in Ref. [30] where it is shown that the derived unique materials of **1** and **3** are identical. The NMR spectrum of **3** (Fig. 3c) contains a large number of unresolved signals. The large signal at 3.3 ppm can be assigned to the parent alcohol; this latter effect is again due to alcohol exchange and solvation.

Compounds **1–3** were also characterized by mass spectrometry. Since the classic works of the late Prof. Hubert-Pfalzgraf [47], electron beam ionization (EI) mass-spectrometry has been recognized as a powerful tool to estimate the gas phase stability of heterometallic alkoxides. This technique is nowadays considered the best tool to evaluate the applicability of precursors in modern

MOCVD techniques (pulse liquid injection assisted MOCVD in particular) [48]. The fragments that are observed in the gas phase provide information on the precursor composition and will also indicate if the compounds are suitable for application in MOCVD and/or ALD. The observed fragments in the spectrum of **1** are in perfect agreement with its molecular structure, though some fragments indicate the presence of a minor amount of a Zr_2–Ti compound. The large signal at 639 m/z(I) (97.1%) is assigned to M–Ti(dea)(OPr) with M = $Zr\{\mu\text{-}\eta^3\text{-NH-}(C_2H_4O)_2\}_3[Ti(O^iPr)_3]_2$ the interpretation of the MS-spectrum for **1** is given in Table 3. In the spectrum of **2**, the same fragment is observed at 727 m/z(I) (81.3%). This fragment and low mass species (i.e., <269 and <290 for

Table 2
Selected bond lengths (Å) of **1** and **2** where M is either Zr or Hf

Compound	1	2
M–O1	2.210(3)	2.190(11)
M–O2	2.196(3)	2.215(12)
M–O3	2.199(3)	2.237(13)
M–N1	2.440(6)	2.43(2)
M–N2	2.439(5)	2.448(17)
M–Ti	3.2035(8)	3.166(4)
Ti–O1	2.145(4)	2.112(15)
Ti–O2	2.147(3)	2.119(15)
Ti–O3	2.137(3)	2.127(14)
Ti–O4	1.836(5)	1.833(17)
Ti–O5	1.849(4)	1.808(15)
Ti–O6	1.853(4)	1.794(17)

compounds **1** and **2**, respectively) are the main species present in the spectra of **1** and **2**. The intensity of these low mass fragments is significantly higher in the spectrum of **2** which indicates that more decomposition occurs for **2**. The spectrum of **3** displayed only low mass fragments, which indicates decomposition of the compound due the electron impact and implies that this compound is not volatile. The presence of a relatively larger amount of high-mass fragments of **1** indicates that the gas phase stability is higher for this compound. However, both compounds seem to be volatile, which in combination with solution stability makes them attractive for MOCVD and ALD applications both with direct evaporation and via liquid injection assisted techniques.

The possibility to prepare heterometallic compounds, using triethanolamine as the modifier, was also briefly examined. The anticipated compounds were expected to be structural analogs of [La(tea)₂{Nb(OⁱPr)₄}₃] [49]. The initial sample consisted of zirconium isopropoxide, titanium isopropoxide and H₃tea in a ratio of 1:2:2. The crystals, which were obtained according to the procedure described in Section 2, were identified by X-ray diffraction as $Ti(O^iPr)_2(\{\mu-\eta^4-NH(C_2H_4O)_3\}_2)_2$ (**4**) (Fig. 5 and Table 1, TS3). The formation of this homometallic compound, earlier reported by Harlow [50], with a high yield, suggests that this compound is thermodynamically favored over the anticipated compound.

Fig. 5. Molecular structure of $Ti_2(O^iPr)_2(\{\mu-\eta^4-NH(C_2H_4O)_3\}_2)_2$.

Quantum chemical calculations were performed to evaluate if there existed any electronic reason why the anticipated compound was not obtained. The binding energy in reaction (1) is about 10 100 kJ/mol

$$Zr^{4+} + 2tea^{2-} \rightarrow Zr(tea)_2^{2-} \qquad (1)$$

Because of the high symmetry we only identified one Zr–O distance of 2.121 Å. The Zr–N distances are quite long, i.e., 3.796 Å. This long Zr–N distances is a probable reason why the formation of **4** is thermodynamically favored over the formation of a heterometallic compound (the Zr–N distances in **4** are 2.317(17) and 2.343(17) Å, and this distance is around 2.4 Å in **1**, respectively).

So far we have demonstrated the formation of thermodynamically stable heterometallic compounds. The stability of **1** and **2** makes these compounds attractive for the

Table 3
Interpretation of m/z(I) spectrum of **1**

TiO(OH)(OC₃H₆)⁺	139 (59.6)	Zr₂(dea)₂(OPr)₃(C₂H₄)⁺	548 (4.4)
Ti(OPr)₂H⁺, ZrO(OPr)(OH)⁺	167 (50.5)	M−Ti(OPr)₃−(OPr)−CH₃	550 (3.7)
TiO(OPr)(OC₃H₆)⁺, ZrO(OPr)(OH)⁺	181 (62.7)	M−dea−3OPr	569 (3.4)
Ti(dea)(OPr)⁺	210 (88.9)	M−Ti(OPr)₃	624 (0.7)
TiO(dea)(OC₃H₆)⁺	225 (100)	M−Ti(dea)(OPr)	639 (97.1)
Zr(dea)O(OCH₂)⁺	239 (27.8)	M−3(OPr)	672 (0.9)
Zr(dea)O(OPr)⁺	252 (6.3)	M−2(OPr)	731 (1.6)
Zr(dea)(OC₂H₄)(OH)⁺	254 (48.6)	Zr₂Ti(dea)₃(OPr)₅⁺	774 (2.0)
Zr(dea)(OPr)(OH)⁺	269 (100)	M−Opr	790 (1.8)
M−Ti(OPr)₂−3(OPr)	447 (2.2)	M−CH₃	834 (1.6)
M−Ti(dea)(OPr)−3(OPr)−H	461 (4.3)	M−H	848 (0.3)
M−Ti(dea)(OPr)−2(OPr)−CH₃	506 (3.2)	Zr₂Ti(dea)₃(OPr)₅(C₂H₄)⁺	876 (0.1)
M−Ti(dea)(OPr)−2(OPr)	521 (6.6)		

preparation of materials and the presence of a stable central core together with only one type of reactive alkoxide ligands attached only to Ti atoms can be a great advantage. The sol–gel applicability of these precursors has already been shown [30,34,35]. However, we would like to underline the uniqueness of this family of precursors for the preparation of microporous materials and orthorhombic zirconium-titanates.

The ability to form microporous materials is of great interest for the preparation of metal-oxide membranes. The preparation of ceramic membranes is commonly performed by sol–gel and there are several reports on the preparation of zirconia membranes using Hacac as a modifier for the precursor [51]. It is thus interesting to compare these latter materials with materials derived from 3.

Sols of both materials were poured out and left to dry in a Petri dish. The solution of the dea-modified heterometallic precursor provided a particulate material where as the Hacac-modified precursor gave material consisting of a film/flakes. This difference is also apparent when the material is examined by a scanning electron microscope (SEM). The zirconium-titanate material from the heterometallic precursor has irregular particle shapes and is strongly 'inter-grown' (Fig. 6a) while the Hacac modified material has the appearance of flakes with flat and smooth surfaces (Fig. 6b). From the SEM images at higher magnifications it can be proved that the surface of the Hacac modified materials is smoother (Fig. 6d) than that derived of 2 (Fig. 6c).

The difference in appearance of the formed materials can be explained by the action of the heteroligands during the sol–gel preparation, a more detailed explanation is provided elsewhere [38,52]. The stability of the central core is able to resist to ligand redistribution in the course of micellar self-assembly [30,52] occurring most often on hydrolysis of the chemically modified metal alkoxides and even observed for the silicon alkoxides in the heterogeneous systems [53]. The conserved ligands ensure reproducible formation of a microporous structure, when they are liberated in the course of a subsequent thermal treatment of the sol–gel deposits [30]. In contrast to this, for heteroleptic acetylacetone modified zirconium alkoxides it is known that ligand redistribution already occurs in both solid state and solution (i.e., they are not thermodynamically stable) [52]. N_2 Sorption measurements on materials derived from Hacac modified zirconium precursor indicate that the materials are predominately dense. The observed microporosity is due to pores that are generated during the film formation and hence not due to intrinsic material properties.

The formation of orthorhombic zirconium-titanates is another unique property of the described class of precursors. Earlier attempts to prepare srilankite from zirconium and titanium alkoxides without diethanolamine as a modifier did not provide the anticipated material [54]. Utilizing heterometallic precursors leads to a more homogeneous distribution of the different metal atoms, since they are incorporated in the particle structure, and thus mixed at an atomic level. Srilankite is of great interest as a dielectric material, but its application has been hindered by the difficulty in its synthesis [31].
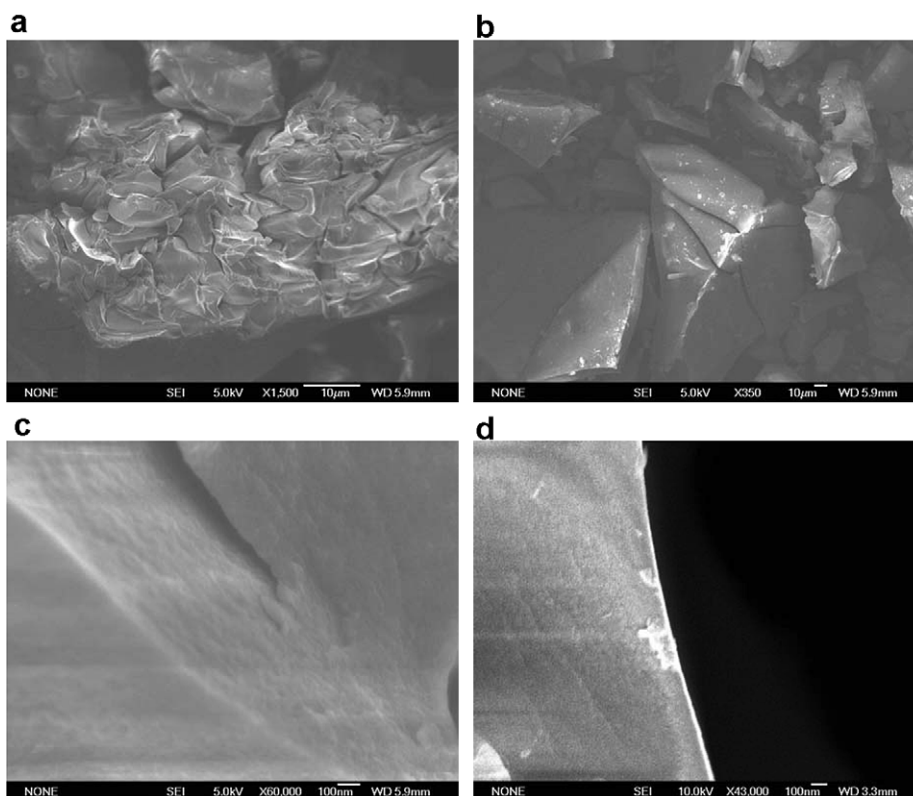

Fig. 6. SEM images of dried sols derived from 3 (a and c) and Hacac modified zirconium precursors (b and d).

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4. Conclusions

We have demonstrated the preparation and characterization of heterometallic alkoxide compounds formed upon modification with diethanolamine (H$_2$dea). The structures of Zr$\{\mu$-η^3-NH(C$_2$H$_4$O)$_2\}_3$[Ti(O^{i}Pr)$_3$]$_2$ (1) and Hf$\{\mu$-η^3-NH(C$_2$H$_4$O)$_2\}_3$[Ti(O^{i}Pr)$_3$]$_2$ (2) were determined by single crystal X-ray diffraction. These trinuclear complexes have a unique nona-coordinated central zirconium or hafnium atom and a hexa-coordinated titanium atom. These compounds are some of the first thermodynamically stable zirconium–titanium and hafnium–titanium precursors. The precursors are also interesting candidates for application in sol–gel. The preparation of the *n*-propoxide analog of 1 did not yield single crystals of the anticipated compound. It has been demonstrated that 1 can be prepared from [Zr(O^{n}Pr)(O^{i}Pr)$_3$(^{i}PrOH)]$_2$, however, in a lower yield compared to when zirconium isopropoxide is used. We evaluated whether or not zirconium–titanium heterometallic compounds can be obtained using triethanolamine as a modifier. Single crystals obtained showed the composition Ti$_2$(O^{i}Pr)$_2(\{\mu$-η^4-NH(C$_2$H$_4$O)$_3\}_2)_2$. Thus, it seems that in this system the formation of a homometallic compound is more favored than a heterometallic one. Quantum chemical calculations indicate that the anticipated compound will have tremendously long metal–nitrogen bond lengths. This is an explanation as to why the formation of 4 is thermodynamically favored. The materials derived of the described precursors have already showed to be very promising. The diethanolamine modified precursors have the ability to produce intrinsic microporous material. In addition, the derived material (ZrTi$_2$O$_6$, srilankite) could up to date only be prepared at much higher temperatures. Srilankite is of great interest as a dielectric material, but its application has been hindered by the difficulty in its synthesis.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.10.022.

References

[1] V.I. Parvulescu, H. Bonnemann, V. Parvulescu, U. Endruschat, A. Rufinska, Ch.W. Lehmann, B. Tesche, G. Poncelet, Appl. Catal. A 214 (2001) 273.

[2] H.C. Zeng, J. Lin, W.K. Teo, F.C. Loh, J.L. Tan, J. Non-Cryst. Solids 181 (1995) 49.

[3] G. De, A. Chatterjee, D. Ganguli, J. Mater. Sci. Lett. 9 (1990) 845.

[4] G. Emig, E. Fitzer, R. Zimmermann-Chopin, Mater. Sci. Eng. A 189 (1994) 311.

[5] A. Lecomte, F. Blanchard, A. Dauger, M.C. Silva, R. Guinebretiere, J. Non-Cryst. Solids 225 (1998) 120.

[6] P. Lobmann, U. Lange, W. Glaubitt, F. Hutter, D. Sporn, High Performance Ceramics (2001), Proceedings Key Engineering Materials 224 (2002) 613.

[7] J. Livage, F. Babonneau, M. Chatry, L. Coury, Ceram. Int. 23 (1997) 13.

[8] M. Chatry, M. Henry, C. Sanchez, J. Livage, J. Sol–gel Sci. Technol. 1 (1994) 233.

[9] R.J. Vacassy, C. Guizard, J. Palmeri, L. Cot, Nanostruct. Mater. 10 (1998) 77.

[10] C.R. Xia, H.Q. Cao, H. Wang, P.H. Yang, G.Y. Meng, D.K. Peng, J. Membr. Sci. 162 (1999) 181.

[11] S. Benfer, U. Popp, H. Richter, C. Siewert, G. Tomandl, Separ. Purif. Technol. 22–23 (2001) 231.

[12] I. Arcon, B. Malic, M. Kosec, A. Kodre, Mater. Res. Bull. 38 (2003) 1901.

[13] C. Gao, J.W. Zhai, X. Yao, Integr. Ferroelectr. 74 (2005) 147.

[14] M. Kobune, K. Yamakawa, T. Yazava, Integr. Ferroelectr. 77 (2005) 69.

[15] W. Zhang, X.G. Tang, K.H. Wong, H.L.W. Chang, Scripta Mater. 54 (2006) 197.

[16] U. Troitzsch, A.G. Christy, D.J. Ellis, J. Am. Ceram. Soc. 87 (2004) 2058.

[17] L.G. Hubert-Pfalzgraf, J. Mater. Chem. 14 (2004) 3113.

[18] M. Veith, S. Mathur, N. Lecerf, V. Huch, T. Decker, H. Beck, W. Eiser, J. Sol-Gel Sci. Technol. 15 (2000) 145.

[19] M. Veith, Dalton Trans. (2002) 2405.

[20] C.A. Zechmann, J.C. Huffman, K. Folting, K.G. Caulton, Inorg. Chem. 37 (1998) 5856.

[21] V.G. Kessler, J. Sol–gel Sci. Technol. 32 (2004) 11.

[22] B. Moraru, G. Kickelbick, U. Schubert, Eur. J. Inorg. Chem. (2001) 1295.

[23] G.J. Gainsford, N. Al-Salim, T. Kemmitt, Acta Crystallogr., Sect. E 58 (2002) m636.

[24] G.J. Gainsford, N. Al-Salim, T. Kemmitt, Acta Crystallogr., Sect. C 28 (2002) m509.

[25] G.I. Spijksma, H.J. M Bouwmeester, D.H.A. Blank, V.G. Kessler, Inorg. Chem. Commun. 7 (2004) 953.

[26] S.M. Harben, P.D. Smith, R.L. Beddoes, D. Collision, C.D. Garner, Angew. Chem., Int. Ed. 36 (1997) 1897.

[27] G.R. Willey, T.J. Woodman, W. Ficher, M.G.B. Drew, Transition Met. Chem. 23 (1998) 467.

[28] W. Ma, H. van Koningsveld, J.A. Peters, T. Maschmeyer, Chem. Eur. J. 7 (2001) 657.

[29] V.G. Kessler, Chem. Commun. (2003) 1213.

[30] G.I. Spijksma, C. Huiskes, N.E. Benes, H. Kruidhof, D.H.A. Blank, V.G. Kessler, H.J.M. Bouwmeester, Adv. Mater. 18 (2006) 2165.

[31] H. Köstlin, G. Frank, G. Hebbinghaus, H. Auding, K. Denissen, J. Non-Cryst. Solids 218 (1997) 347.

[32] International Roadmap of Semiconductor Industry (ITRS). Available from: <http://public.itrs.net/>.

[33] A. Willgallis, H. Harti, Z. Kristallogr. 164 (1983) 59.

[34] S.N. Koc, J. Sol–Gel Sci. Technol. 38 (2006) 277.

[35] U. Aust, S. Benfer, M. Dietze, A. Rost, G. Tomandl, J. Membr. Sci. 281 (2006) 463.

[36] S.V. Pol, V.G. Pol, G.I. Spijksma, Y. Grinblat, R. Kalai Selvan, V.G. Kessler, G.A. Seisenbaeva, S. Gohil, A. Gedanken, J. Phys. Chem. B (submitted for publication).

[37] G.A. Seisenbaeva, S. Gohil, V.G. Kessler, J. Mater. Chem. 14 (2004) 3177.

[38] G.I. Spijksma, Ph.D. Thesis, University of Twente, The Netherlands, 2006.

[39] E.P. Turevskaya, N.I. Kozlova, N.Y. Turova, A.I. Belokon, D. V Berdyev, V.G. Kessler, Y.K. Grishin, Russ. Chem. Bull. 44 (1995) 734.

[40] SHELXTL-NT Program Manual, Bruker AXS, 1998.
[41] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratman, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN-03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
[42] D. Andrae, U. Häussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta 77 (1990) 123.
[43] R.J. Errington, J. Ridland, W. Clegg, R.A. Coxall, J.M. Sherwood, Polyhedron 17 (1998) 659.
[44] V.G. Kessler, S. Gohil, S. Parola, Dalton Trans. (2003) 544.
[45] G.I. Spijksma, H.J.M. Bouwmeester, D.H.A. Blank, A. Fischer, M. Henry, V.G. Kessler, Inorg. Chem. 45 (2006) 4938.
[46] G.I. Spijksma, H.J.M. Bouwmeester, D.H.A. Blank, V.G. Kessler, Chem. Commun. (2004) 1874.
[47] L.G. Hubert-Pfalzgraf, J.G. Riess, Inorg. Chem. 14 (1975) 2854.
[48] T. Haase, N. Bahlawane, J.T. Strong, A. Jakob, Y. Shen, H. Lang, K. Kohse-Höinghaus, in: Proceedings of EUROCVD-15, Electrochemical Society Proceedings, vol. 9, 2005, p. 276.
[49] V.G. Kessler, L.G. Hubert-Pfalzgraf, S. Halut, J.-C. Daran, J. Chem. Soc., Chem. Commun. (1994) 705.
[50] R.L. Harlow, Acta Crystallogr., Sect. C 39 (1983) 1344.
[51] C.R. Xia, H.Q. Cao, H. Wang, P.H. Wang, G.Y. meng, D.K. Peng, J. Membr. Sci. 162 (1999) 181.
[52] V.G. Kessler, G.I. Spijksma, G.A. Seisenbaeva, S. Håkansson, H.J.M. Bouwmeester, D.H.A. Blank, J. Sol-Gel Sci. Tech. 40 (2006) 163.
[53] Bok Yeop Ahn, Sang Il Seok, In Chan Baek, Suk-In Hong, Chem. Commun. (2006) 189.
[54] J.-C. Buhl, A. Willgallis, Cryst. Res. Technol. 24 (1989) 263.