

Molecular design approach to a stable heterometallic zirconium–titanium alkoxide – potential precursor of mixed-oxide ceramics

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Abstract

New heterometallic interesting trinuclear, $Zr\{\eta^3, \mu_2-NH(C_2H_4O)_2\}_3[Ti(O^iPr)_3]_2$ encountering a nona-coordinated central zirconium atom crystallizes at $-30\text{ }^\circ\text{C}$ from a solution of zirconium and titanium isopropoxides and diethanolamine ($Zr:Ti:L = 1:2:3$) in hydrocarbons. Due to its solution stability, this structurally characterized compound is an attractive potential precursor in sol–gel technique for the preparation of mixed metal oxide materials.

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The alkoxides of zirconium are widely used as precursors in the preparation of oxide materials with a tremendously broad spectrum of applications ranging from porous membranes [1–3] and matrices in catalysis [4,5] to dense dielectric or ferroelectric films in electronics [6,7]. In spite of being commonly used, both the homometallic and heterometallic zirconium alkoxide complexes remain insufficiently explored.

Since the application of unmodified zirconium precursors in, for instance, MOCVD or sol–gel is a difficult task, due to extreme sensitivity to hydrolysis and pyrolysis, the precursor is often modified. A generally applied method to moderate the reactivity is the exchange of the alkoxide ligands by chelating organic ligands [8]. In sol–gel studies, acetic acid and acetylacetonone are most

often applied for this purpose [9]. Acetic acid has the undesired ability to react with alcohol upon release of water, and in recent work we showed [10] that the stabilizing effect with acetylacetonone disappears beyond addition of 1 mol equivalent. In our search for a stable modified zirconium precursor we applied diethanolamine, dea, as stabilizing agent. To the best of our knowledge, no reports have been published on zirconium precursor structures formed upon modification with dea. Though, the structure for the modification of zirconium *n*-propoxide with 0.5 mol equivalent of *N*-methyl-diethanolamine has been published [11]. In our study [12] an analogous compound was prepared from zirconium *n*-propoxide with 0.5 mol equivalent dea, but NMR indicated clearly that these compounds are not stable in time. Besides zirconium *n*-propoxide, $[Zr(O^iPr)(O^iPr)_3(^iPrOH)]_2$ [13] and $[Zr(O^iPr)_4(^iPrOH)]_2$ precursors were also utilized and modified with, respectively, 0.5 and 0.5 and 1 mol equivalent of dea. For the latter precursor, for both ratios of modifier, an interesting

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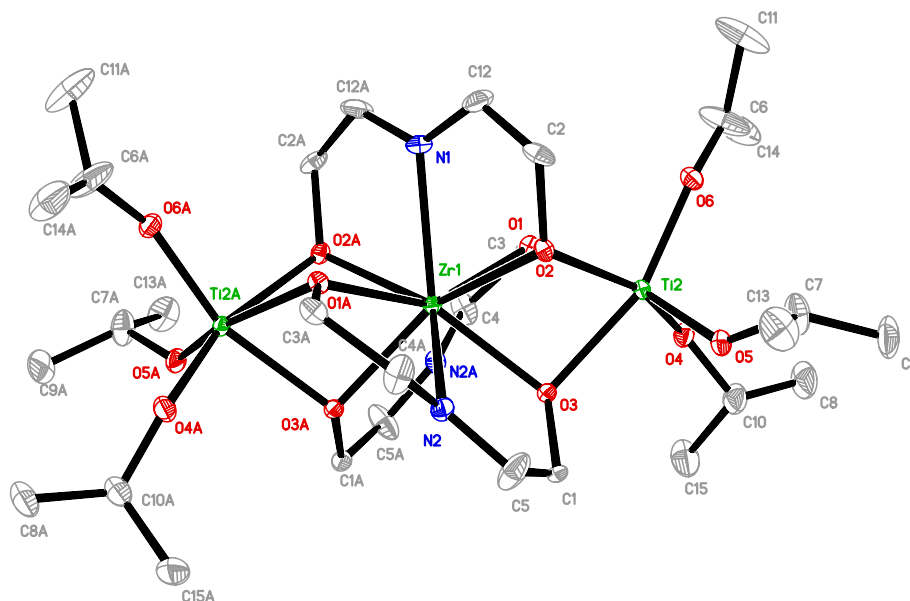


Fig. 1. Molecular structure of $\text{Zr}\{\eta^3, \mu_2\text{-NH}(\text{C}_2\text{H}_4\text{O})_2\}_3[\text{Ti}(\text{O}^i\text{Pr})_3]_2$ (**1**).

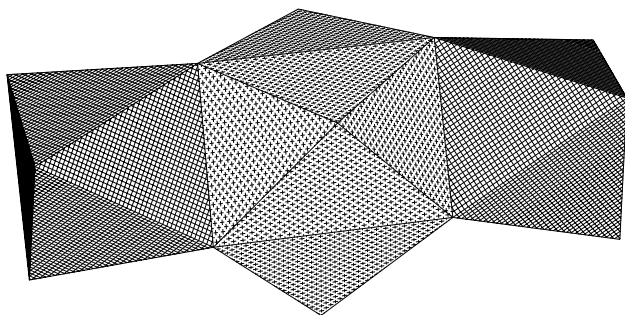


Fig. 2. Polyhedral presentation of the molecular structure of **1**.

hydrocarbon solvent, with cooling overnight at 30 °C provided the anticipated complex in an almost complete yield.¹

The molecular structure of the obtained complex was studied by X-ray crystallography, it was characterized as $\text{Zr}\{\eta^3, \mu_2\text{-NH}(\text{C}_2\text{H}_4\text{O})_2\}_3[\text{Ti}(\text{O}^i\text{Pr})_3]_2$,² depicted in Fig. 1. The coordination of the central Zr atom is very regular tricapped trigonal prismatic (see Fig. 2) with the oxygen atoms composing the vertices of the prism ($\text{Zr}(1)\text{-O}(2)$ 2.196(3), $\text{Zr}(1)\text{-O}(3)$ 2.199(3) and $\text{Zr}(1)\text{-O}(4)$ 2.210(3) Å) and the nitrogen ones – the capping vertices ($\text{Zr}(1)\text{-N}(1)$ 2.440(6), $\text{Zr}(1)\text{-N}(2)$ 2.439(5) Å). This high-symmetry coordination not imposed by the crystallographic elements of symmetry indicates high

trinuclear, $\text{Zr}\{\eta^3, \mu_2\text{-NH}(\text{C}_2\text{H}_4\text{O})_2\}_3[\text{Zr}(\text{O}^i\text{Pr})_3]_2(\text{O}^i\text{Pr-OH})_2$ complex with nona-coordinated central zirconium atom was obtained. This molecule with very unusual but not unique geometry (compare [bis(oxyiminodiacetate)aquazirconium(IV)]²⁻-ion reported by Harben [14]) could be of great interest for the preparation of heterometallic precursors.

The presence of two types of positions, a nona-coordinated and a hexa-coordinated, provides the possibility to construct new species via self-assembly according to Molecular Structure Design Concept [15]. For example, the hexa-coordinated position appeared to be able to host other (and smaller) atoms than zirconium. We report here the application of this model for the preparation of a new Zr–Ti complex.

Mixing of the components, zirconium and titanium isopropoxide and dea, in a ratio of $\text{Zr}:\text{Ti}:\text{L} = 1:2:3$ in

¹ All preparations were carried out in a dry nitrogen atmosphere using Schlenk technique or a glove box. 0.57 g (1.5 mmol) of zirconium isopropoxide was dissolved in a 3-ml mixture of hexane/toluene (volume ratio 2:1), subsequently 0.84 ml (~3.0 mmol) titanium isopropoxide and 0.46 ml (~4.4 mmol) dea was added. After cooling overnight in a freezer at 30 °C, the obtained colorless octahedral crystals were separated from the solvent by decantation. Analytical samples were dried in vacuo prior to spectral analysis. The IR spectra of the compound were recorded in nujol mulls, cm^{-1} : 1358 sh, 1327 w, 1280 w, 1241 w, 1167 sh, 1160 m, 1124 s, 1085 m, 1060 s, 1007 w, 988 s, 941 m, 914 s, 879 m, 844 s, 673 sh, 602 s, 571 sh, 447 s.

² X-ray crystallography data were collected on a Siemens SMART diffractometer. Crystal data: $\text{C}_{30}\text{H}_{69}\text{N}_3\text{O}_{12}\text{Ti}_2\text{Zr}$, $M = 850.90$, tetragonal, $a = 11.6171(12)$ Å, $b = 11.6171(12)$ Å, $c = 32.053(5)$ Å, $V = 4325.7(9)$ Å³, $T = 295$ K, space group $\text{P}4(3)2(1)2$, $Z = 1$, $\mu = 0.650$ mm⁻¹, 25,389 reflections measured, 5091 unique ($R_{\text{int}} = 0.0412$) which were used for refinement. The final discrepancy factors were $R_1 = 0.0521$; $wR_2 = 0.1411$ for 3126 observed reflections ($I > 2\sigma(I)$).

stability of the chelated core with uniform charge distribution and highly covalent bonding.

The coordination of Ti atoms is trigonally distorted octahedral with in principle only two types of Ti=O distances: bridging (Ti–O 2.137(3)–2.147(3) Å) and terminal (Ti–O 1.836(5)–1.853(4) Å). This coordination is much more symmetric than that in octahedral titanium homo- and heterometallic β -diketonate complexes [16,17], where one can observe three types of bond lengths (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 relatively high solution stability of complex **1** in comparison with these species.

^1H NMR on the compound dissolved in toluene remained unchanged after 5 days, which indicates its stability of this compound in hydrocarbon solvents.³ This stability makes this compound attractive for the preparation of materials and the presence of only one type of reactive alkoxide ligands attached only to Ti atoms can be a great advantage. In the literature, we could find that in order to obtain unique or improved properties it has been attempted to prepare composite materials with zirconium and titanium [18, and references herein]. The preparation was performed by, for example, adding zirconium-oxy-nitrate hydrate to titanium alkoxide sols [19]. Utilizing heterometallic precursors will supposedly lead to a more homogeneous distribution, since zirconium is incorporated in the oligomer or particle structure via hydrolysis of stable chelating ligands.

There is, thus, a great potential for heterometallic precursors in the preparation of titanium–zirconium composite materials. The in literature available heterometallic titanium–zirconium precursors [20,21] are considered less suitable compared to the one presented in this paper. They have (different) alkoxide groups attached to both the zirconium and titanium, what again can be a disadvantage due to the different reactivities. Besides that, we have observed for analogous homometallic species a decomposition in time [12], supposedly to the trimeric complex with a nona-coordinated central zirconium atoms. It is, thus, possible to conclude that the bimetallic trinuclear, $\text{Zr}\{\eta^3, \mu_2\text{-NH}(\text{C}_2\text{H}_4\text{O})_2\}_3[\text{Ti}(\text{O}^i\text{Pr})_3]_2$ with nona-coordinated central zirconium atom presented in this work is an attractive potential precursor of mixed metal oxide materials due to its solution stability and the one type of reactive alkoxide groups.

³ The spectra of the dried crystals were initially taken in a solution of CDCl_3 , however within 24 h full decomposition had occurred, resulting in the precipitation of a polymer-like substance. The decomposition of the complex in CDCl_3 is supposedly due to the reactivity of the coordinated amine with a chlorinated solvent.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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