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Influence of Heteroligands on the Composition, Structure and Properties of Homo- and Heterometallic Zirconium Alkoxides

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Abstract. Interaction of the commercial “Zr(OⁿPr)₄” with excess of ⁱPrOH provides with high yields a new solid crystalline but highly soluble precursor Zr₂(μ-OⁿPr)₂(OⁱPr)₆(ⁱPrOH)₂ (**2**). Interaction of 1 eq. of **2** with 1 eq. of Co(acac)₂ results in quantitative transformation in a mixture of Co₂Zr₂(OⁿPr)₄(OⁱPr)₆(acac)₂ (**3**), with a structure representing a fragment of hexagonal packing of metal atoms and alkoxide ligands (typical for derivatives of primary alcohols), and Zr₂(OⁱPr)₆(acac)₂ (**4**). Reaction of 1 eq. of homoleptic zirconium isopropoxide, Zr₂(OⁱPr)₈(ⁱPrOH)₂ (**1**) with 1 eq. of Co(acac)₂ provides a new complex CoZr₂(OⁱPr)₈(acac)₂ (**5**) having a linear chain structure (characteristic of sec-alcohol derivatives) with a quantitative yield. Microhydrolysis of a mixture of 1.5 eq. of **2** and 1 eq. of Co(acac)₂ gave with a moderate yield CoZr₃O(OⁿPr)₃(OⁱPr)₅(acac)₄ (**6**), with a tetrahedral CoZr₃O core characteristic of zirconium sec-oxoalkoxides. Modification of a solution of barium and zirconium isopropoxides in toluene (Ba : Zr = 1 : 1) with 1.5 eq. of Hacac results almost quantitatively in a mixture of insoluble Ba(acac)₂ and soluble and volatile heterometallic alkoxide Ba₂Zr₄(OⁱPr)₁₈(acac)₂ (**7**). Addition of 2 eq. of Hthd to the mixture of barium and zirconium n-propoxides in toluene (Ba : Zr = 1 : 1) gives highly soluble and volatile complex Ba₂Zr₂(thd)₄(OⁿPr)₈(ⁿPrOH)₂ (**8**). Reaction of the in situ obtained Ba(thd)₂ with 0.5 eq. of **2** provided almost quantitatively another highly soluble and volatile precursor

$\text{Ba}_2\text{Zr}_2(\text{thd})_4(\text{O}^n\text{Pr})_2(\text{O}^i\text{Pr})_6$ (**9**). Addition of 2 eq. of Hthd to the mixture of strontium and zirconium isopropoxides in toluene ($\text{Sr} : \text{Zr} = 1 : 1$) gives highly soluble complex $\text{Sr}_2\text{Zr}_2(\text{thd})_4(\text{O}^i\text{Pr})_8$ (**10**) volatilized on heating via complete decomposition into $\text{Sr}(\text{thd})_2$, $\text{Zr}(\text{thd})_2(\text{O}^i\text{Pr})_2$ and non-volatile products. All compounds have been characterized by a variety of spectroscopic techniques, and compounds **1-9** also by X-ray single crystal studies. The principles in construction of zirconium alkoxides and their stability and reactivity are discussed in connection with the sterical role played by the chosen ligands.

Introduction

The alkoxides of zirconium are widely used as precursors in preparation of oxide materials with a tremendously broad spectrum of applications ranging from porous membranes and matrices in catalysis ^{1,2} to dense dielectric or ferroelectric films in electronics ^{3,4}. In spite of being commonly used, both the homometallic and heterometallic zirconium alkoxide complexes remain insufficiently explored. Thus, none of the most common and commercially available homometallic compounds can be considered as an ideal precursor: the cheap *n*-propoxide, “Zr(O^{*n*}Pr)₄”, is at room temperature a tremendously moisture-sensitive waxy solid ⁵, almost always containing oligonuclear oxoalkoxides like Zr₃O(OR)₁₀ and Zr₄O(OR)₁₄ as impurities ⁶ and delivered commercially in the form of 70 wt% solution in ^{*n*}PrOH to overcome (and hide) these disadvantages. Much more stable and well structurally defined zirconium isopropoxide isopropanol solvate, [Zr(O^{*i*}Pr)₄(^{*i*}PrOH)₂]⁷, is rather expensive and poorly soluble in parent alcohol and even in toluene at room temperature. A mixed-ligand alkoxide [Zr(O^{*i*}Pr)(O-*neo*-C₅H₁₁)₃(HO-*neo*-C₅H₁₁)₂]₂ reported by Boyle ⁸ is an attractive precursor for MOCVD, but not for sol-gel due to its high price and impossibility to apply in its parent alcohol. The need in simple, stable, highly soluble and easily accessible zirconium alkoxide precursors urges the search for new compounds.

The chemistry of reported heterometallic zirconium complexes involving alkoxide ligands is very rich and can be traced in two recent books on alkoxide chemistry ^{9,10}. These compounds consist of three major classes: bimetallic chloride alkoxides (often containing alkyl ligands in their molecules) – components in Ziegler-Natta catalysts (reviewed by Sobota in ¹¹), bimetallic alkoxide chlorides – potential homogeneous catalysts (reviewed by Veith in ¹²), and several families of homo- and heteroleptic alkoxide complexes including mainly oxo, carboxylate, and in very few cases even acetylacetonate ligands (reviewed recently by Hubert-

Pfalzgraf ¹³). These are these latter classes that are of major interest for materials science applications as they do not contain halide ligands, which, if remain as impurities after decomposition, damage the properties of oxide materials being of major interest – the oxidation properties of oxide catalysts, the ferroelectric or dielectric properties of capacitor materials, and the homogeneity of stabilized zirconia applied for hard coatings etc. We were focused in the present work on, on one hand, the bimetallic precursors of oxidation catalysts – heterometallic complexes of zirconium and late transition metals and, on the other hand, bimetallic precursors of ferroelectric materials – heterometallic complexes of zirconium and alkaline earth metals, barium and strontium. The data in literature on halide-free bimetallic complexes of late transition metals and zirconium are limited to two series of studies: (a) bimetallic alkoxides and oxoalkoxides of copper and zirconium, $\text{Cu}^{\text{I}}_2\text{Zr}_2(\text{O}^{\text{i}}\text{Pr})_{10}$ ¹⁴, $\text{Cu}^{\text{II}}_4\text{Zr}_4\text{O}_3(\text{O}^{\text{i}}\text{Pr})_{20}$ and $\text{Cu}^{\text{I}}_4\text{Zr}_4\text{O}(\text{O}^{\text{i}}\text{Pr})_{18}$ ¹⁵, which were isolated with relatively low yields (about 40%) via interaction of copper chlorides with specially prepared $\text{K}_4\text{Zr}_2\text{O}(\text{O}^{\text{i}}\text{Pr})_{10}$. Oxo- and copper(II) derivatives have even been obtained by oxidation of copper(I) complex by oxygen gas. (b) Heterometallic alkoxo- and oxoalkoxo-acetylacetonates of cobalt $(\text{Co}_2\text{Zr}_2(\text{acac})_2(\text{O}^{\text{n}}\text{Pr})_{10})$ and $\text{Zr}_2\text{Co}_4(\mu_6\text{-O})(\mu_2\text{-O}^{\text{n}}\text{Pr})_8(\text{O}^{\text{n}}\text{Pr})_2(\text{acac})_4$ ¹⁶ and iron, $\text{FeZr}_3\text{O}(\text{acac})_3(\text{O}^{\text{n}}\text{Pr})_{10}$ ¹⁷, obtained in extremely low yields (and, in case of cobalt, unselectively) by reaction of late transition metal acetylacetonates with zirconium normal propoxide in the parent alcohol. The lack in selectivity was caused supposedly by the presence of oxoalkoxides impurities in the applied commercial zirconium n-propoxide.

Bimetallic solutions of barium and zirconium alkoxides have been very successfully applied for the preparation of powders and coatings of BaZrO_3 and $\text{Ba}(\text{Zr,Ti})\text{O}_3$ in the 1980-es (¹⁸ and refs therein) initially without isolation and characterization of potential precursors. In the 1990-es great efforts have been made in, at first, synthesis of bimetallic isopropoxides via reaction of activated barium metal with $[\text{Zr}(\text{O}^{\text{i}}\text{Pr})_4(\text{iPrOH})]_2$, that provided such

compounds as $\text{BaZr}_4(\text{O}^i\text{Pr})_{18}$, $[\text{BaZr}_2(\text{O}^i\text{Pr})_{10}]_2$, $[\text{BaZr}_2(\text{O}^i\text{Pr})_{10}]_\infty$, and also $\text{BaZr}_4(\text{OH})(\text{O}^i\text{Pr})_{17}$ by the hydrolysis of the first of them, reported by Caulton et al ¹⁹. This work has been followed very soon by the systematic analysis of precursor solutions in parent alcohol (complexation at room temperature) in isopropoxide system, leading to isolation of $\text{BaZr}_4(\text{O}^i\text{Pr})_{18}$, $[\text{BaZr}_2(\text{O}^i\text{Pr})_{10}]_2$, and $\text{Ba}_2\text{Zr}(\text{O}^i\text{Pr})_8(\text{}^i\text{PrOH})_5$ ²⁰, and in the ethoxide system, revealing the existence of such compounds as $\text{BaZr}_4(\text{OEt})_{18}$, $\text{BaZr}_2(\text{OEt})_{10}(\text{EtOH})_4$ and $\text{Ba}_4\text{Zr}_2\text{O}(\text{OEt})_{14}(\text{EtOH})_8$, the latter being formed evidently via partial oxidation of the solutions, reported by Turova et al ²¹. None of these molecules contained metals in 1 : 1 ratio required for the desired perovskite phases and could be regarded as a single-source precursor of these materials. This field was revisited at the end of 1990-es by Veith et al, who have carried the investigation of the tert-butoxide system and reported such new complexes as $\text{BaZr}_2(\text{O}^t\text{Bu})_{10}$ and $\text{BaZr}(\text{O}^t\text{Bu})_6(\text{THF})_2$ – extremely moisture-sensitive compounds that even the authors themselves had difficulties to handle. Partial hydrolysis of the latter compound together with alcohol interchange transformation converted $\text{BaZr}(\text{O}^t\text{Bu})_6(\text{THF})_2$ into $[\text{BaZr}(\text{OH})(\text{O}^i\text{Pr})_5(\text{}^i\text{PrOH})_3]_2$ ²². This latter complex possessed the proper composition but was shown by the authors to decompose on dissolution by NMR. It has been employed for the preparation of BaZrO_3 and $\text{Ba}(\text{Ti,Zr})\text{O}_3$ by the authors ²³ and yielded powders not demonstrating any specific single-source precursor advantages for this compound in comparison with earlier applied alkoxide solutions ²⁴. The value of this precursor for practical application is especially decreased by its extremely irrational five-step synthesis via subsequently dialkylamide and t-butoxide derivatives, while this compound can easily be obtained in a simple one-batch procedure (compare compound **11** below). This urges to continue the search for new solution stable, volatile and easily decomposable single source precursors of zirconate materials that can be achieved by simple and efficient synthetic techniques.

In the present paper we report the application of the recently developed Molecular Structure Design Concept ²⁵ for the stabilization of zirconium n-propoxide via its transformation into a solid crystalline but still highly soluble mixed-ligand propoxide complex, $[\text{Zr}(\text{O}^n\text{Pr})(\text{O}^i\text{Pr})_3(^i\text{PrOH})]_2$, and also for the selective and facile synthesis of a series of highly soluble and volatile cobalt-zirconium, barium-zirconium and strontium-zirconium precursors starting from different zirconium propoxides and applying additional ligands such as oxo- and β -diketonate ones to control the molecular geometry and composition of the complexes. Cobalt-zirconium complexes reported below have already been successfully applied for the preparation of Co-ZrO₂ nanocomposites with core-shell structure for catalytical applications ²⁶.

Experimental

All manipulations were carried out in a dry nitrogen atmosphere using Schlenk technique or a glove box. Water free Co(acac)₂ was obtained by sublimation of Co(acac)₂·xH₂O (Aldrich Chemical Company Inc.) at 110-145°C and 0.1 mm Hg. Barium metal, strontium metal, zirconium isopropoxide, $[\text{Zr}(\text{O}^i\text{Pr})_4(^i\text{PrOH})]_2$ 99.9 %, and 70 wt% solution of $\text{Zr}(\text{O}^n\text{Pr})_4$ were purchased from Aldrich. Room temperature modification of $[\text{Zr}(\text{O}^i\text{Pr})_4(^i\text{PrOH})]_2$ (**1**) was obtained by recrystallization of the commercial product from the minimal amount of toluene : isopropanol = 3 : 1 (vol.) mixture. Isopropanol and n-propanol (Merck, p.a.) were purified by distillation over corresponding Al(OPr)₃, and hexane and toluene (Merck, p.a.) - by distillation over LiAlH₄. Acetylacetone, Hacac, and tetramethylheptanedion, Hthd, were purchased from Aldrich and used without further purification. IR spectra of nujol mulls were registered with a Perkin Elmer FT-IR spectrometer 1720 X. ¹H NMR spectra were recorded for the CDCl₃ solutions of **1-8** and both CDCl₃ and C₆D₅CD₃ solutions for **9** and CD₃CN

solutions for **10** and ^{13}C NMR spectra in CDCl_3 for **4** and **8** on a Bruker 400 MHz spectrometer at 303 K, if not otherwise stated. Mass-spectra were recorded using JEOL JMS-SX/SX-102A mass-spectrometer applying electron beam ionization ($U = 70 \text{ eV}$) with direct probe introduction. The results of microanalysis (C, H) were obtained by Mikrokemi AB, Uppsala, Sweden and by Organic Microanalysis Laboratory at the Moscow State University, Russia, using the combustion technique (at both sites the samples were weighed quickly in an ambient atmosphere before introduction into combustion installation, which explains slightly decreased values of C and H contents observed).

Synthesis

[Zr(*OⁿPr*)(*OⁱPr*)₃(*i*PrOH)]₂ 2. 10 ml of commercial 70 wt% solution of $\text{Zr}(\text{O}^n\text{Pr})_4$ were mixed with 70 ml isopropanol and left for crystallization overnight at -30°C . The resulting transparent crystalline needles were separated by decantation and dried in vacuum (0.1 mm Hg) at room temperature. The separated solution was evaporated to dryness, re-dissolved in 30 ml isopropanol and also left for crystallization overnight at -30°C . The crystals formed (identical according to the spectroscopic data to those from the first step) were added to the previously isolated ones, and the solution evaporated to dryness and re-dissolved in 10 ml isopropanol with subsequent crystallization and addition of the dried crystals from this step to those obtained previously. The total yield was about 90%. Found, %: C 45.9; H 9.5. Calc. For $\text{C}_{30}\text{H}_{72}\text{O}_{10}\text{Zr}_2$, %: C 46.5; H 9.4. IR, cm^{-1} : 3156 m br, 1365 w, 1338 w, 1160 s, 1132 s, 1081 w, 1050 w, 1015 s, 980 m, 953 m, 887 w, 844 m, 820 sh, 579 sh, 556 s, 521 m, 455 s, 431 m. NMR ^1H δ , ppm (interpretation): 5.9 singlet broad (2H, OH), 4.28 septet (8H, CH), 3.36 triplet (4H, CH_2), 1.65 sextet (4H, CH_2), 1.18 doublet (48H, $J_{\text{C-H}} = 6.1 \text{ Hz}$, CH_3 , ^iPr), 0.87 triplet (6H, $J_{\text{C-H}} = 5.9 \text{ Hz}$, CH_3 , ^nPr).

Interaction of $\text{Co}(\text{acac})_2$ with 1 eq. of compound 2

$\text{Co}(\text{acac})_2$ (0.394 g, 1.53 mmol) and **2** (1.187 g, 1.53 mmol) were dissolved on reflux in 4 ml toluene and evaporated to dryness in vacuum. The solid residue was re-dissolved in 4 ml hexane and left for crystallization overnight at -30°C . The bluish purple crystals formed were separated by decantation (Compound **3**, yield 0.651 g, 78 %). The residual solution was slowly evaporated to dryness in vacuum leaving under microscopic observation the analogous bluish purple crystals in a mixture with colorless block-shaped crystals (Compound **4**, no possibility for elementary analysis, the single crystal for X-ray study and spectroscopic characterization were picked up using separation by a syringe needle under microscope). Compound **4** can be obtained in almost quantitative yields by reaction of **1** with 2 eq. of Hacac [Spijksma].

$\text{Co}_2\text{Zr}_2(\text{O}^n\text{Pr})_4(\text{O}^i\text{Pr})_6(\text{acac})_2$ 3. Found, %: C 43.7; H 7.5. Calculated for $\text{C}_{40}\text{H}_{84}\text{Co}_2\text{O}_{14}\text{Zr}_2$, %: C 44.1; H 7.8. IR, cm^{-1} : 1599 s, 1525 s, 1342 m, 1280 w, 1264 w, 1171 s, 1147 sh, 1054 s, 1015 s, 991 w, 972 sh, 952 w, 925 w, 891 m, 848 m, 824 w, 774 m, 657 w, 634 w, 599 m, 575 sh, 556 s, 532 s, 501 s, 455 m, 427 s. M-S, $m/z(\text{I}, \%)$, interpretation: 791(3.3), $[\text{P} - 5 \text{ OR}]^+$; 751(5.8), $[\text{CoZr}_2(\text{acac})_2(\text{OPr})_4(\text{OH})_2(\text{OC}_2\text{H}_4)]^+$; 711(4.1), $[\text{CoZr}_2(\text{OPr})_8]^+$; 642(4.5), $[\text{Co}_2\text{Zr}(\text{acac})_2(\text{OPr})_4]^+$; 524(30.0), $[\text{CoZr}(\text{acac})_2(\text{OPr})_3]^+$; 465(10.0), $[\text{CoZr}(\text{acac})_2(\text{OPr})_2]^+$; 425(6.4), $[\text{CoZr}(\text{acac})(\text{OPr})_3]^+$; 382(6.9), $[\text{CoZrO}(\text{acac})(\text{OPr})_2]^+$; 347(71.2), $[\text{CoZr}(\text{acac})_2]^+$, 307(20.0), $[\text{Zr}(\text{acac})(\text{OPr})_2]^+$, 257(91.7), $[\text{Co}(\text{acac})_2]^+$, 242(100), $[\text{Co}(\text{acac})_2 - \text{CH}_3]^+$.

$[\text{Zr}(\text{acac})(\text{O}^i\text{Pr})_3]_2$ 4. IR, cm^{-1} : 1603 s, 1525 s, 1342 m, 1307 sh, 1276 m, 1167 s br, 1019 s, 980 w, 941 m br, 844 m, 820 m, 774 m, 657 m, 548 s br, 454 s, 427 s. NMR ^1H δ , ppm (interpretation): 5.44 sharp singlet (2H, CH, acac), 4.27 unresolved septet (6H, CH, ^iPr), 1.90 singlet (12H, CH_3 , acac), 1.12 doublet (36H, $J_{\text{C-H}} = 6.1 \text{ Hz}$, CH_3 , ^iPr). M-S, $m/z(\text{I}, \%)$, interpretation: 365(16.4), $[\text{Zr}(\text{acac})(\text{O}^i\text{Pr})_3 - \text{H}]^+$, 307(100), $[\text{Zr}(\text{acac})(\text{OPr})_2]^+$.

Interaction of $\text{Co}(\text{acac})_2$ with 1 eq. of compound 1

$\text{Co}(\text{acac})_2$ (0.538 g, 2.10 mmol) and **1** (1.608 g, 2.07 mmol) were dissolved in 5 ml toluene on reflux and evaporated to dryness. This operation was repeated twice and the final residue was re-dissolved in 2 ml hexane and left for crystallization overnight at -30°C . The violet crystals thus formed were isolated by decantation and dried in vacuum. Yield 1.803 g (84%). The residual solution was slowly evaporated in vacuum leaving the same product under microscopic observation.

$\text{CoZr}_2(\text{O}^i\text{Pr})_8(\text{acac})_2$ 5. Found, %: C 43.9; H 7.4. Calculated for $\text{C}_{34}\text{H}_{70}\text{CoO}_{12}\text{Zr}_2$, %: C 44.8; H 7.7. IR, cm^{-1} : 1603 s, 1525 s, 1334 m, 1276 m, 1179 s, 1159 s, 1128 s, 1015 s, 957 s, 929w, 844 m, 828 m, 774 w, 661 m, 556 s, 501 sh, 458 m, 427 s. M-S, m/z(I, %), interpretation: 751(2.3), $[\text{CoZr}_2(\text{acac})_2(\text{OPr})_4(\text{OH})_2(\text{OC}_2\text{H}_4)]^+$; 524(22.1), $[\text{CoZr}(\text{acac})_2(\text{OPr})_3]^+$; 465(8.4) $[\text{CoZr}(\text{acac})_2(\text{OPr})_2]^+$; 347(90.2), $[\text{CoZr}(\text{acac})_2]^+$, 326(4.1), $[\text{Zr}(\text{O}^i\text{Pr})_4]^+$, 311(100), $[\text{CoZr}(\text{acac})\text{O}(\text{OH})(\text{OCH}_2)]^+$ or $[\text{CoZr}(\text{O}^i\text{Pr})_2(\text{OC}_2\text{H}_4)]^+$, 307(19.6), $[\text{Zr}(\text{acac})(\text{OPr})_2]^+$, 267(18.8), $[\text{Zr}(\text{O}^i\text{Pr})_3]^+$, 257(52.6), $[\text{Co}(\text{acac})_2]^+$, 242(47.5), $[\text{Co}(\text{acac})_2 - \text{CH}_3]^+$.

Interaction of $\text{Co}(\text{acac})_2$ with 1.5 eq. of compound 1 supported by microhydrolysis

$\text{Co}(\text{acac})_2$ (0.416 g, 1.62 mmol) and **2** (1.880 g, 2.43 mmol) were dissolved in 4 ml toluene on reflux, cooled to room temperature and to the purple solution thus formed were added 2.0 ml of wet ethyl ether (upper phase of the ether-water system made by mixing them by shaking in a separation funnel, should contain 1.2 vol% water at room temperature). The solution turned pinkish purple and was immediately evaporated to dryness. The solid residue was re-dissolved in 3 ml hexane and left for crystallization overnight at -30°C . The resulting pinkish purple crystals formed were isolated by decantation and dried in vacuum. Yield 0.426 g (22%).

***CoZr₃O(OⁿPr)₃(OⁱPr)₅(acac)₄* 6.** Found, %: C 43.2; H 7.2. Calculated for C₄₄H₈₄CoO₁₇Zr₃, %: C 43.4; H 7.0. IR, cm⁻¹: 1599 s, 1525 s, 1338 sh, 1280 w, 1256 w, 1171 s, 1147 sh, 1054 s, 1019 s, 976 m, 953 w, 926 m, 887 w, 844 m br, 770 m, 653 sh, 637 m, 595 w, 571 s, 536 s, 521 s, 455 s, 423 s.

Modification of a solution of isopropoxides (Ba : Zr = 1 : 1) in toluene with 1.5 eq. Hacac

Barium metal (0.97 g, 7.08 mmol) was dissolved on reflux in 4 ml ⁱPrOH and **1** (2.74 g, 3.68 mmol) was added to the reaction mixture forming a clear solution. The latter was evaporated to dryness in vacuum and re-dissolved in 7 ml toluene. Acetylacetone (1.00 ml) was slowly added drop wise to the initially clear solution on vigorous stirring. Addition of each small drop led first to formation of a bit of white precipitate that for the first ~ 0.6 ml was then dissolving again giving a clear solution. Addition of the last ~ 0.4 ml was associated with formation of white voluminous precipitate shown by the spectroscopic data to be Ba(acac)₂(ⁱPrOH)_x earlier described by us ¹³. The reaction mixture, viscous slurry, was left at room temperature for 48 h. It turned out then that during this time there occurred precipitation of huge (up to 2-3 mm) rectangular colorless prismatic crystals. The slurry was thinned with 10 ml hexane and removed by syringe. The crystals were washed twice with 5 ml hexane and dried in vacuum. Yield of compound **7** was 2.87 g (82% in relation to **1**).

***Ba₂Zr₄(OⁱPr)₁₈(acac)₂* 7.** Found, %: C 40.1; H 7.2. Calculated for C₆₄H₁₄₀Ba₂O₂₂Zr₄, %: C 40.4; H 7.4. IR, cm⁻¹: 1583 m, 1541 w, 1502 m, 1400 m, 1342 sh, 1249 w, 1190 sh, 1171 s, 1140 sh, 1128 s, 1015 s, 964 s, 949 s, 910 w, 844 m, 828 m, 778 m, 630 w, 571 sh, 552 s, 532 m, 497 w, 470 sh, 455 s. NMR ¹H δ, ppm (interpretation): 5.41 singlet (2H, CH, acac), 4.48 septet (6H, CH, ⁱPr), 7.37 septet (8H, CH, ⁱPr), 4.27 septet (4H, CH, ⁱPr), 1.83 singlet (12H, CH₃, acac), 1.36 doublet (24H, CH₃, ⁱPr), 1.23 doublet (36H, J_{C-H}= 6.1 Hz, CH₃, ⁱPr), 1.17 doublet (48H, J_{C-H}= 6.1 Hz, CH₃, ⁱPr). M-S, m/z(I, %), interpretation: 1145(0.4),

$[\text{Zr}_4\text{O}(\text{OR})_{13}]^+$, 947(3.0), $[\text{BaZr}_2(\text{acac})(\text{O}^i\text{Pr})_9]^+ = [\text{P}^*]^+$, 888(14.7), $[\text{P}^* - \text{OR}]^+$, 848(34.0), $[\text{P}^* - \text{acac}]^+$, 829(13.4), $[\text{P}^* - 2\text{OR}]^+$, 819(12.3), $[\text{Zr}_3\text{O}(\text{OR})_9]^+$, 747(10.9), $[\text{P}^* - \text{acac} - \text{R}_2\text{O}]^+$, 645(4.8), $[\text{P}^* - \text{acac} - 2\text{R}_2\text{O}]^+$, 593(9.6), $[\text{P}^* - 6\text{OR}]^+$ and $[\text{Zr}_2(\text{OR})_7]^+$, 563(60.5), $[\text{BaZr}(\text{acac})(\text{OR})_4]^+$, 491(14.3), $[\text{P}^* - 6\text{OR} - \text{R}_2\text{O}]^+$ or $[\text{Zr}_2\text{O}(\text{OR})_5]^+$, 321(33.6), $[\text{Ba}(\text{acac})_2 - \text{CH}_2]^+$, 237(100), $[\text{Ba}(\text{acac})\text{H}]^+$.

Modification of a solution of n-propoxides (Ba : Zr = 1 : 1) in toluene with 2 eq. Hthd

Barium metal (0.597 g, 4.36 mmol) was added to a solution prepared by dilution of 2.0 ml 70 wt% solution of $^n\text{Zr}(\text{O}^n\text{Pr})_4$ (~ 4.35 mmol) with 3 ml $^n\text{PrOH}$ and subjected to reflux until its complete dissolution. The reaction mixture was evaporated to dryness in vacuum and re-dissolved in 15 ml hexane. Hthd (1.6 ml, ~ 8.7 mmol) was added quickly on vigorous stirring and the solution was left for crystallization overnight at -30°C . Colorless block-shaped crystals thus formed were separated by decantation and dried in vacuum. Yield of compound **8** was 3.07 g (79%).

$\text{Ba}_2\text{Zr}_2(\text{thd})_4(\text{O}^n\text{Pr})_8(^n\text{PrOH})_2$ 8. Found, %: C 48.2; H 8.3. Calculated for $\text{C}_{74}\text{H}_{148}\text{Ba}_2\text{O}_{18}\text{Zr}_2$, %: C 49.8; H 8.4. IR, cm^{-1} : 3148 m br, 1587 s, 1576 s, 1556 s, 1537 s, 1509 s, 1416 s, 1354 s, 1295 w, 1244 m, 1225 m, 1182 m, 1147 m, 1124 m, 1066 s, 1023 m, 988 m, 968 w, 937 vw, 887 w, 867 w, 793 w, 766 sh, 750 w, 731 w, 622 w, 552 m, 525 m, 497 w, 474 m. NMR ^1H δ , ppm (interpretation): (a) at 303 K, 5.81 singlet (2H, CH, thd), 5.44 singlet (2H, CH, thd), 3.83 unresolved multiplet (20H, CH_2 , ^nPr), 1.58 unresolved multiplet (20H, CH_2 , ^nPr), 1.09 singlet (36H, CH_3 , thd), 1.04 singlet (36H, CH_3 , thd), 0.82 unresolved multiplet (30H, CH_3 , ^nPr), (b) at 233 K, 5.96 broad singlet (2H, OH, $^n\text{PrOH}$), 5.74 singlet (2H, CH, thd), 5.40 singlet (2H, CH, thd), 4.03 triplet (8H, CH_2 , ^nPr), 3.50 triplet (12H, CH_2 , ^nPr), 1.79 and 1.52 and 1.34 – incompletely resolved sextets with comparable intensity (in total, 20H, CH_2 , ^nPr), 1.05 singlet (36H, CH_3 , thd), 1.02 singlet (36H, CH_3 , thd), 0.70 triplet (30H, $J_{\text{C-H}} = 5.9$ Hz, CH_3 , ^nPr). M-S,

m/z(I, %), interpretation: 771(4.8), $[\text{BaZr}(\text{thd})_2(\text{OR})_3]^+$, 640(15.9), $[\text{Ba}_2(\text{thd})_2]^+$, 639(25.1), $[\text{Zr}(\text{thd})_3]^+ + [\text{Ba}_2(\text{thd})_2 - \text{H}]^+$, 583(17.5), $[\text{Ba}_2(\text{thd})_2 - \text{H} - \text{C}_4\text{H}_8]^+ + [\text{Zr}(\text{thd})_3 - \text{C}_4\text{H}_8]^+$, 515(100), $[\text{Zr}(\text{thd})_2(\text{OR})]^+$, 459(54.4), $[\text{Zr}(\text{thd})_2(\text{OR}) - \text{C}_4\text{H}_8]^+$.

Reaction of an in situ formed $\text{Ba}(\text{thd})_2$ with 0.5 eq. of compound 2

Barium metal (0.624 g, 4.55 mmol) was dissolved on reflux in a mixture of 1.68 ml Hthd, 3 ml $i\text{PrOH}$ and 5ml toluene and the solution was evaporated to dryness in vacuum. Solid **2** (1.76 g, 2.28 mmol) was added to the waxy residue together with 3 ml hexane and 3 ml toluene. A clear solution thus formed was left for crystallization overnight at -30°C producing a crop of block-shaped colorless crystals, which were separated by decantation and dried in vacuum. Yield of compound **9** was 3.28 g (87%).

$\text{Ba}_2\text{Zr}_2(\text{thd})_4(\text{O}^n\text{Pr})_2(\text{O}^i\text{Pr})_6$ 9. Found, %: C 47.9; H 7.8. Calculated for $\text{C}_{68}\text{H}_{132}\text{Ba}_2\text{O}_{16}\text{Zr}_2$, %: C 49.1; H 8.0. IR, cm^{-1} : 1591 sh, 1576 s, 1560 s, 1541 m, 1509 s, 1412 m, 1361 sh, 1299 sh, 1245 w, 1225 m, 1171 m, 1147 m, 1124 s, 1101 m, 1070 m, 1015 m, 972 s, 953 s, 867 m, 852 w, 824 m, 797 m, 770 w, 750 w, 618 m, 567 s, 536 s, 501 m, 470 s, 451 s, 419 s. NMR ^1H δ , ppm (interpretation): (a) in CDCl_3 (poorer solubility), 5.86 splitted singlet (2H, CH, thd), 5.43 splitted singlet (2H, CH, thd), 4.57 septet (2H, CH, ^iPr), 4.12 septet (2H, CH, ^iPr), 4.02 septet (2H, CH, ^iPr), 3.54 unresolved (4H, CH_2 , ^nPr), 1.59 unresolved (4H, CH_2 , ^nPr), 1.3-1.00 overlapping doublets and singlets with the total intensity of 90H, 0.86 and 0.72 – two triplets of comparable intensity (in total 6H, CH_3 , ^nPr), (b) in $\text{C}_6\text{D}_5\text{CD}_3$ (higher solubility), 5.92 splitted singlet (2H, CH, thd), 5.77 splitted singlet (2H, CH, thd), 4.80 septet (2H, CH, ^iPr), 4.31 unresolved (4H, CH_2 , ^nPr), 3.89 septet (2H, CH, ^iPr), 3.67 septet (2H, CH, ^iPr), 1.58 poorly resolved triplet (4H, CH_2 , ^nPr), 1.30 (72H, CH_3 , thd), 1.22 doublet (12H, $\text{J}_{\text{C-H}} = 6.0$ Hz, CH_3 , ^iPr), 1.14 doublet (24H, $\text{J}_{\text{C-H}} = 6.0$ Hz, CH_3 , ^iPr), 0.96 unresolved (6H, CH_3 , ^nPr). M-S, m/z(I, %), interpretation: 640(18.6), $[\text{Ba}_2(\text{thd})_2]^+$, 639(28.4), $[\text{Zr}(\text{thd})_3]^+ + \text{Ba}_2(\text{thd})_2 - \text{H}]^+$,

583(21.3), $[\text{Ba}_2(\text{thd})_2 - \text{H} - \text{C}_4\text{H}_8]^+ + [\text{Zr}(\text{thd})_3 - \text{C}_4\text{H}_8]^+$, 515(100), $[\text{Zr}(\text{thd})_2(\text{OR})]^+$, 459(58.6), $[\text{Zr}(\text{thd})_2(\text{OR}) - \text{C}_4\text{H}_8]^+$.

Modification of a solution of isopropoxides (Sr : Zr = 1 : 1) in toluene with 2 eq. Hthd

Strontium metal (1.684 g, 19.22 mmol) was dissolved on reflux in a solution of **1** (7.442 g, 10.00 mmol) in 20 ml isopropanol. The solution was evaporated to dryness and re-dissolved in 20 ml toluene and then 8.00 ml Hthd were added to it drop wise on vigorous stirring. The volume of the resulting solution was reduced to ~ 10 ml and 10 ml hexane were added to the mixture, which was left for crystallization overnight at -30°C producing a crop of tiny block-shaped colorless crystals, which were separated by decantation and dried in vacuum. Yield of compound **10** was 10.17 g (68%).

Sr₂Zr₂(thd)₄(OⁱPr)₈ **10**. Found, %: C 52.1; H 8.4. Calculated for C₆₈H₁₃₂Sr₂O₁₆Zr₂, %: C 52.4; H 8.5. IR, cm⁻¹: 1591 s, 1576 s, 1560 s, 1541 m, 1509 s, 1412 s, 1358 s, 1295 w, 1276 vw, 1249 w, 1225 m, 1163 s, 1140 s, 1120 s, 1015 s, 961 sh, 952 s, 918 w, 871 m, 852 w, 820 m, 797 w, 770 w, 754 w, 622 w, 599 vw, 571 m, 536 m, 513 vw, 497 vw, 478 s, 462 s, 439 s, 419 sh. NMR ¹H δ, ppm (interpretation) in CD₃CN: 5.91 singlet (2H, CH, thd), 5.82 singlet (2H, CH, thd), 3.96 septet (6H, CH, ⁱPr), 3.57 septet (6H, CH, ⁱPr), 1.16-1.06 complex unresolved combination of singlets and doublets (total 120H, CH₃, ⁱPr and thd). M-S, m/z(I, %), interpretation: (a) first top in the chromatogram, 639(52.3), $[\text{Zr}(\text{thd})_3]^+$, 583(100), $[\text{Zr}(\text{thd})_3 - \text{C}_4\text{H}_8]^+$, 515(93.9), $[\text{Zr}(\text{thd})_2(\text{OR})]^+$, (b) second top in the chromatogram (>120°C), 725(2.1), $[\text{Sr}_2(\text{thd})_3]^+$, 639(30.6), $[\text{Zr}(\text{thd})_3]^+$, 583(24.6), $[\text{Zr}(\text{thd})_3 - \text{C}_4\text{H}_8]^+$, 515(100), $[\text{Zr}(\text{thd})_2(\text{OR})]^+$, 459(45.8), $[\text{Zr}(\text{thd})_2(\text{OR}) - \text{C}_4\text{H}_8]^+$, 454(2.8), $[\text{Sr}(\text{thd})_2]^+$, 425(32.0), $[\text{Sr}(\text{thd})_2 - \text{C}_2\text{H}_5]^+$, 368(83) $[\text{Sr}(\text{thd})_2 - \text{C}_4\text{H}_9\text{COCH}_2]^+$.

Mass-spectrum of $\text{Ba}_2\text{Ti}_2(\text{thd})_4(\text{OEt})_8(\text{EtOH})_2$ (prepared according to ²⁷), for reference, $m/z(I, \%)$, interpretation: 459(92.4), $[\text{Ti}(\text{thd})_2(\text{OR})]^+$, 414(100), $[\text{Ti}(\text{thd})_2]^+$, 321(93.6), $[\text{Ba}(\text{thd})]^+$ (major component according to the isotope distribution) + $[\text{Ti}(\text{thd})(\text{OR})_2]^+$.

Microhydrolysis of solutions of strontium and zirconium isopropoxides with 1 : 1 metal ratio.

Crystallography

The data collection for all the single crystals of compounds **1-9** and **11** studied was carried out at 22°C on a SMART CCD 1k diffractometer with graphite monochromated MoK_α radiation (for details see Tab. 1). All the structures were solved by direct methods. The coordinates of the metal atoms were obtained from the initial solutions and for all other non-hydrogen atoms found in subsequent difference Fourier syntheses. The structures were refined by least squares first in isotropic and then in anisotropic approximations (except for propyl groups with occupational disorder $^n\text{Pr}/^i\text{Pr}$ in **9** and one isopropyl group in **7** defined by the carbon C(10), C(101) and C(102), with resolved positional disorder, and the groups defined by C(1), C(2) and C(7), subjected to unresolved disorder, which were refined only isotropically). All data collections have been carried out at room temperature, which in combination with quite poor reflectivity for zirconium compounds led to limited volumes of data not permitting to resolve positional and especially rotational disorder characteristic of isopropoxide groups. The structure determination and refinement led to completely converged models leaving no doubt on the connectivity in these molecules. The coordinates of the hydrogen atoms were calculated geometrically (except for hydroxyl protons in **2** and in **11** found in difference Fourier syntheses) and were included into the final refinement in isotropic approximation for

all the compounds. It should be mentioned that the placement of hydrogen atoms can not be considered as definite in the view of unresolved disorder in carbon atoms they are attached to. Their introduction, however, serves to reduce the residual electron density in the structures and improves considerably the quality of resolved models and decreases the observed R-factors. All calculations were performed using the SHELXTL-NT program package²⁸ on an IBM PC.

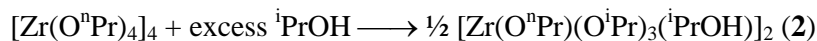
Results and Discussion

Being interested in development of new zirconium alkoxide precursors and providing characterization of their physicochemical properties, including information about their molecular and crystal structures, we started this work with additional purification of the commercially available $[\text{Zr}(\text{O}^i\text{Pr})_4(^i\text{PrOH})]_2$ (**1**) by recrystallization. Having determined the unit cell parameters for the crystals obtained, we were surprised to observe that they did not correspond to those reported in ⁷, but were in this experiment very close to those for $[\text{Hf}(\text{O}^i\text{Pr})_4(^i\text{PrOH})]_2$, which room temperature structure has been reported in ²⁹ and resembled (while deviating considerably) those for the second modification of $[\text{Zr}(\text{O}^i\text{Pr})_4(^i\text{PrOH})]_2$ described by Boyle ³⁰. The molecular structure of **1** (see Fig.1, Tab. TS1) turned to be almost identical to that reported in ⁷. The crystal structure of **1** at room temperature is significantly different from that described in ⁷ and analogous to that observed in ³⁰ with the difference from the latter only caused by increased thermal motion that results in increased unit cell volume. The present study is the first reporting determination of the crystal structure of **1** at room temperature and may be useful for its identification by X-ray powder diffraction (for reference see Fig. FS1).

Development of new precursors was carried out applying the Molecular Structure Design Concept²⁵ based on the choice of a proper metal-oxygen core and its completion with ligands providing both the necessary number of donor atoms and the sterical protection of the chosen core – further development of the Structure Theory proposed by D.C. Bradley^{9,10}. The main aim of this article is to show that zirconium alkoxides as well as other main group, early transition metal and 3d late transition metal alkoxides (such as, for example, aluminium, titanium, niobium, tantalum, molybdenum and tungsten, nickel and cobalt alkoxide precursors reviewed in²⁵) are not rigid clusters but labile oligonuclear complexes, which structure and reactivity can in many cases be predicted and explained on the basis of general and comparably simple thermodynamic principles. Application of these principles is able, as it is described below, to provide simple one-batch synthetic approaches to many new highly soluble and solution and even gas phase stable compounds useful as precursors of oxide materials.

The formation of well structurally defined chain fragments like that of two edge-sharing octahedra in the structure of **1**, M_2O_{10} , is typical of the alkoxide complexes – derivatives of branched or bulky alcohols with the same total number of donor atoms^{9,10}. The alkoxides with normal alkyl chain structure form in the solid most often the aggregates with structure derived from hexagonal packing of metal and alkoxide oxygen atoms with a M_4O_{16} composition as in its first example, the titanium methoxide, $[Ti(OMe)_4]_4$ ³¹. This structure is characteristic also of the zirconium n-propoxide, $[Zr(O^iPr)_4]_4$ ⁵. Six normal chain propoxide ligands are obviously only inefficiently shielding the metal atoms against nucleophilic attack by water molecules, which explains the extreme sensitivity of this compound. We supposed that addition of a sec-alcohol, isopropanol, will lead, as it commonly happens for early 4d and 5d transition elements, to positioning of the branched alkyl groups into terminal, but not

bridging positions and provide a better stable but still not perfectly ordered and highly soluble new dimeric derivative instead of the original tetramer:



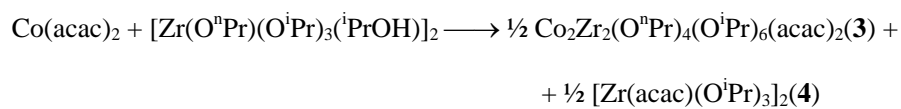
An additional advantage of such transformation lies in obtaining of a solid easy-to-handle precursor with well-defined chemical composition. Conservation of a smaller ligand in the bridging position is a clear thermodynamic advantage and has earlier been observed in alcohol interchange reactions for niobium ³², tantalum ³³ and as mentioned above – also zirconium derivatives ⁸. The difference in the present case lies in the fact that the introduction of bulkier ligands in this case was supposed to change the structure type from M_4O_{16} to M_2O_{10} , and this transformation was really observed. The structure of the compound **2** thus obtained (see Fig. 2, Tab. TS2) was corresponding to our expectations. It is built up of centrosymmetric molecules, one molecule per unit cell, containing two octahedrally coordinated zirconium atoms surrounded by two bridging n-propoxide ligands, two terminal isopropoxide ones in equatorial positions and statistically mixed one terminal ⁱPr-group and one solvating ⁱPrOH molecule in axial positions. This structure is well preserved in solution according to NMR (no observable temperature changes or concentration dependence). It is important to note that even addition of very big excess of isopropanol in the synthesis or repeated treatment are not able to remove the bridging n-propoxide groups and convert **2** to **1**. It is important to notice that the formation of dimeric species in this case can not be considered as any indication of some specific stability characteristic of dimeric zirconium species. Dimeric M_2O_{10} cores are always observed for early transition metal alkoxides, when the ligands providing the proper number of donor atoms and are bulky enough to protect the metal-oxygen core are available. Thus, whole series of $[\text{MoO}(\text{OR})_4]_2$ ³⁴, $[\text{WO}(\text{OR})_4]_2$ ³⁵, $[\text{Nb}(\text{OR})_5]_2$ ^{9,36}, and $[\text{Ta}(\text{OR})_5]_2$ ^{9,37}

with structurally characterized dimeric cores have been described. All these dimeric cores are easily destroyed by modification with chelating ligands or complexation with other alkoxides. For example, the reactions with Hacac transform all of them into monomeric $\text{MO}(\text{OR})_3(\text{acac})$, $\text{M} = \text{Mo}, \text{W}$ ^{25,38} and $\text{M}(\text{OR})_4(\text{acac})$, $\text{M} = \text{Nb}, \text{Ta}$ ^{39,40}. Dimeric, as **1** and **2**, or tetrameric, as $[\text{Zr}(\text{O}^i\text{Pr})_4]_4$, zirconium alkoxides are **no exception**: addition of up to 1 eq. of Hacac per metal atom converts them immediately into $[\text{Zr}(\text{OR})_3(\text{acac})]_2$ as it is corresponding to requirements of the M_2O_{10} type structure, while addition of more than 1 eq. gives immediately monomeric $\text{Zr}(\text{acac})_3(\text{OR})$, disproportionating slowly into $\text{Zr}(\text{acac})_4$ and original alkoxides ⁴¹. The existence of dimeric intermediates with $\text{M}_2(\text{O}^i\text{Pr})_7(\text{acac})(^i\text{PrOH})$ and $\text{M}_2(\text{O}^i\text{Pr})_4(\text{acac})_4$ compositions proposed by Sanchez et al ⁴² has not been confirmed by the experimental data.

It is important to notice also that the reactions of chemical modification and of complex formation should not be considered as the reactions of ligand exchange in one distinct oligomer: the activation energies of ligand exchange in homoleptic alkoxide complexes not containing metal-metal bonds are, according to the ^1H NMR data ^{9, 35, 36}, below or just over the energy of thermal motion (at room temperature). The structure of the product of modification or complexation can thus not be influenced by the structure of the reactant applied, any likeness manifesting only the analogous action of the sterical factors such as the number of donor atoms and volume occupied by the ligand in the coordination sphere and the energy of bonding for the ensemble of bonds in the core. The majority of zirconium-containing molecules, studied so far, contain even numbers of zirconium atoms, which led some researchers to the idea about the existence of specifically stable dizirconiumalkoxide ligands ⁴³. This fact is, however, merely a coincidence: the molecules with single mononuclear $\text{Zr}(\text{OR})_n$ units (such as, for example, $\text{Ba}_2\text{Zr}(\text{O}^i\text{Pr})_8(^i\text{PrOH})_5$ ²⁹ or $\text{Ti}_2\text{Zr}(\text{OCH}(\text{CF}_3)_2)_6$ ⁴⁴) are as easily formed in complexation reactions at room temperature.

Trinuclear $\text{Zr}\{\eta^3\mu_2\text{-NH}(\text{C}_2\text{H}_4\text{O})_2\}_3[\text{Zr}(\text{O}^i\text{Pr})_3]_2$ with nona-coordinated central zirconium atom displaying very unusual but not unique geometry (compare [bis(oxyiminodiacetate)aquazirconium(IV)]²⁻-jon reported by Harben ⁴⁵) is formed at -30°C on addition of 1 eq. of $\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$ to compound **1**, i.e. at the ratio $\text{L} : \text{Zr} = 0.5$ ⁴⁶.

In our search for the new approaches to heterometallic precursors of materials derived from late transition metals and zirconium we investigated the reaction of **2** with cobalt acetylacetonate, analogous to that used by Mosset et al., applying toluene instead of alcohol as solvent. This reaction turned to be selective (no oxoalkoxide byproducts), providing with very high yield only one heterometallic derivative, easily separable from the homometallic byproduct due to its comparably lower solubility:



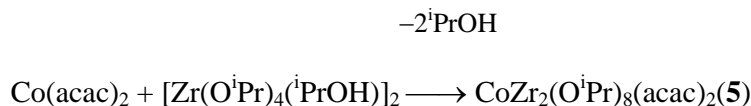
This reaction is an almost quantitative transformation, following exactly the proposed reaction equation. It is necessary to mention that both **3** and **4** have very high solubility in hydrocarbon solvents and are volatile under reduced pressure. The molecular structure of **3** (Fig.3, Tab. TS3) can be considered as derived from the Mo_4O_{16} type by disconnection of two metal atom positions (Co in this case) from the μ_3 -bridges that thus became μ_2 -bridges between Zr atoms. Co atoms have thus become tetrahedrally coordinated surrounded by two oxygen atoms from the acac-ligand and two oxygen atoms from bridging alkoxide ligands. Zr atoms remain hexacoordinated because of their $\sim 0.15 \text{ \AA}$ bigger atomic radius. It is important to note that the composition of this compound is enriched with n-propoxide ligands, which is supposedly necessary to keep this structure type, characteristic of primary alkoxides and alkoxide β -diketonates ^{25, 47}, and still incorporate comparably small Co atoms. The n-propoxide ligands

occupy 4 of 6 available doubly bridging positions, while the terminal ones (with less steric tension) are occupied exclusively by the more bulky isopropoxide ligands. The structures of **3** and of $\text{Co}_2\text{Zr}_2(\text{acac})_2(\text{O}^i\text{Pr})_{10}$ ¹⁶ turned to be very close analogs as it has been proposed initially, the difference being caused by the introduction of bigger size isopropoxide ligands: very long Co- $\mu_3\text{O}(\text{R})$ distance in ¹⁶, 2.453(5) Å, is elongated in **3** to 2.473(5) Å, which can already be considered as a border value between bonding and non-bonding for cobalt(II). In both structures the Co- $\mu_2\text{O}(\text{R})$ distances are quite symmetric (slightly longer 1.944(5) and 1.949(5) Å in **3** and 1.930(6) and 1.934(5) Å in ¹⁶) and the bonds to the acac-ligands asymmetric, influenced by the long contact to the $\mu_3\text{-OR}$ (1.919(5) and 2.001(4) Å in **3** and 1.924(5) and 2.014(6) in ¹⁶). All the bond distances for zirconium atoms in **3** follow the same distribution pattern as in ¹⁶ (longer Zr- $\mu_2\text{O}(\text{R})\text{-Zr}$, shorter Zr- $\mu_2\text{O}(\text{R})\text{-Co}$ and relatively short terminal Zr-OR) but are 0.005-0.008 Å longer because of the application of a bulkier ligand.

The molecular structure of **4** (Fig.4, Tab. TS4) is in fact analogous to that of **1** with one equatorial alkoxide group and one solvating alcohol molecule replaced with a terminal bidentate acac-ligand. The absence of solvating alcohol molecules is supposedly responsible for the strongly increased solubility in hydrocarbon solvents observed for this compound even at low temperatures in contrast to **1** and **2**. It is also important to mention that the introduction of the acac-ligands results in broader distribution of Zr-O bond length for **4** in comparison with **1** and **2**: the stronger ionic contribution to bonding with the acac ligand results in increased length of the corresponding bonds and also the increased asymmetry of the μ_2 -bridges (2.134(3) and 2.258(3) Å compared to 2.110(6) and 2.133(6) Å in **2** and 2.156(6) and 2.171(6) Å in **1**).

As compound **2** reacted with cobalt acetylacetonate in a way characteristic of primary alkoxides, it was interesting to investigate the reactivity of **1**, purely sec-derivative, because it

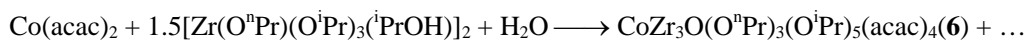
had to lead to a chain type structure. The reaction turned to follow the predicted pathway quantitatively:



The molecular structure of **5** (Fig.5, Tab. TS5) is built up of non-centrosymmetric $(\text{acac})(\text{O}^i\text{Pr})_2\text{Zr}(\mu_2\text{-O}^i\text{Pr})_2\text{Co}(\mu_2\text{-O}^i\text{Pr})_2\text{Zr}(\text{O}^i\text{Pr})_2(\text{acac})$ molecules in centrosymmetric crystal structure with regular tetrahedral coordination for the cobalt atoms, analogous to that in heteroleptic precursors of spinel materials recently developed by our group, $(\text{acac})_2\text{Al}(\mu_2\text{-O}^i\text{Pr})_2\text{M}^{\text{II}}(\mu_2\text{-O}^i\text{Pr})_2\text{Al}(\text{acac})_2$, $\text{M}^{\text{II}} = \text{Mg}, \text{Co}, \text{Ni}$ ⁴⁸ or in the molecules of homoleptic complexes of cobalt and nickel with niobium or tantalum, $(^i\text{PrO})_4\text{M}^{\text{V}}(\mu_2\text{-O}^i\text{Pr})_2\text{M}^{\text{II}}(\mu_2\text{-O}^i\text{Pr})_2\text{M}^{\text{V}}(\text{O}^i\text{Pr})_4$ ⁴⁸. The zirconium atoms display a distorted octahedral coordination, being however much more regular than that in **4**, due supposedly to more uniform negative charge distribution on the oxygen atoms (stronger ionic contribution from less charged and more electropositive Co(II) atoms). It is important to note that the structure of this molecule does not contain any dimeric zirconium unit thus confirming again that the chemistry of heterometallic zirconium derivatives is not relied to the dimeric nature of the homometallic zirconium species applied. Highly symmetric molecular structure results in very high solubility and volatility for **5**, which especially in a view of its more Zr-rich composition, makes it an attractive precursor of catalytic nanocomposite materials with late transition oxide or metal particles distributed in the ZrO_2 matrix. We report the preparation and characterization of such materials from **5** as precursor in a separate publication ²⁶.

Almost all the bimetallic oxoisopropoxide derivatives of zirconium belong to one and the same structure type incorporating a MZr_3O tetrahedral core, such as, for example, in

Gd₂Zr₆O₂(OⁱPr)₂₀(acac)₆⁴⁹ or FeZr₃O(OⁿPr)₁₀(acac)₃¹⁷. It was therefore interesting to attempt the preparation of a representative of this family via reaction of **2** with Co(acac)₂ and introducing oxoligands by microhydrolysis. The desired derivative was obtained by this reaction:

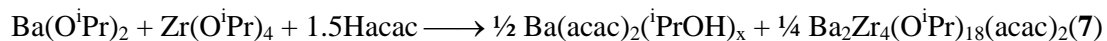


The yield, however, turned to be quite moderate, supposedly, because of the lack of acac ligands in this reaction mixture. It would supposedly be possible to increase it strongly by introduction of two additional equivalents of Hacac into the reaction mixture. The centrosymmetric crystal structure of **6** is built up of non-centrosymmetric molecules (Fig. 6, Tab. TS6) containing a CoZr₃O tetrahedral core. The coordination of metal atoms in it is quite unusual: Co-atoms are pentacoordinated, being connected to the μ₄-O in the center of the molecule, two bridging isopropoxide ligands and two oxygen atoms of an acac ligand attached in a chelating and bridging in η²,μ₂-mode. Zirconium atoms are heptacoordinated, all displaying pentagonal bipyramids as coordination polyhedra. Their coordination spheres are composed of the central μ₄-O, two oxygen atoms of the terminal η²-acac ligands, one terminal OⁱPr group, two μ₂-OⁿPr groups capping the edges of the face of the tetrahedron defined by zirconium atoms only (where the steric tension is as highest) and one μ₂- oxygen atom from either a bridging OⁱPr group, Zr(1) and Zr(2), or a η²,μ₂-acac ligand. The structure of **6** resembles that of FeZr₃O(OⁿPr)₁₀(acac)₃¹⁷ rather much in the coordination of zirconium atoms: it is characterized by quite short distance to the central oxo-ligand (2.085-2.106 Å in **6** compared to 2.110-2.121 Å in the iron compound), strongly elongated μ₂-bridges (2.184-2.216 Å in **6** compared to 2.174-2.204 Å in ¹⁷) and relatively symmetric coordination of the acac-ligand (2.178(15)-2.222(14) Å in **6** compared to 2.155(14)-2.192(16) Å in ¹⁷). The

likeness in coordination of the late transition metal is topological (both are trigonal pyramidal with the axis defined by the μ_4 -oxoligand and the terminal group – one of the oxygen atoms of an acac-ligand in **6** and a terminal alkoxide ligand in ¹⁷), but not metric as the Co(II) atom is ≈ 0.1 Å bigger than Fe(III) one. The direct construction of a molecular analog serves a good confirmation for the action of analogous thermodynamic principles leading to formation of both molecules.

In search for new heterometallic single-source precursors of barium zirconate we had to follow the M_4O_{16} type structure. This structure type is as common and as important for the heterometallic precursors as the perovskite structure type for oxide materials. This fact has been specially underlined already in the first review devoted specifically to the heterometallic alkoxides ⁵⁰. For the barium- or strontium-zirconium precursors this type of structure could be achieved by application of chelating ligands such as β -diketonate ones (4 per core unit) in two possible approaches: either by modification of more sterically demanding derivative of **1** with less sterically demanding acac ligand or less sterically demanding derivatives of **2** or “Zr(OⁿPr)₄” with more sterically demanding thd ligand. The colleagues, sharing our theoretical view on formation of the heterometallic complexes ²⁷, and working actively with zirconium derivatives, have not applied this approach earlier for this system. They were supposedly discouraged by an attempt to apply this approach to barium-cerium alkoxide precursors that resulted in formation of an oxoalkoxide complex, Ba₄Ce₂O(thd)₄(OⁱPr)₁₀, supposedly because of the poor redox-stability of cerium compounds ⁵¹. The first of the proposed synthetic routes appeared to fail as we could observe precipitation (without further re-dissolution) of Ba(acac)₂(ⁱPrOH)_x from the reaction mixture obtained by addition of Hacac to equimolar mixture (Ba : Zr = 1 : 1) of barium and zirconium isopropoxides in toluene. The addition of Acetylacetone was stopped, when approximately 1.5 of the total of 2 equivalents

of it were added. It turned by chance to be the proper stoichiometry for the formation of **7** via following reaction:



Both the crystal and the molecular structure of **7** (Fig. 7, Tab. TS7) is rather close to that of the corresponding homoleptic isopropoxide $\text{Ba}_2\text{Zr}_4(\text{O}^i\text{Pr})_{20}$ reported by Caulton et al in ¹⁹. The main difference lies in the fact that the bridging function between the barium atoms in the center is fulfilled not by two $\mu_2\text{-O}^i\text{Pr}$ but by two $\eta^2, \mu_2, \mu_2\text{-acac}$ ligands, which increases the coordination number of barium atoms from 6 to 8. Such very symmetric chelating doubly μ_2 -bridging coordination of the acac-ligand is rather rare ⁵² and has never been previously observed for heterometallic species. The commonly observed is the η^2, μ_2 -coordination mode (see ^{53, 54}). Zirconium atoms are hexacoordinated by two terminal, two doubly bridging and two triply bridging alkoxide ligands each, which is the most typical coordination in the heterometallic zirconium alkoxide complexes ^{9, 10}. The considerable difference in bonding parameters between **7** and its closest literature analog $\text{Ba}_2\text{Zr}_4(\text{O}^i\text{Pr})_{20}$ ¹⁹ can very logically be explained by the increased coordination number of barium atoms (eight in **7** instead of six in $\text{Ba}_2\text{Zr}_4(\text{O}^i\text{Pr})_{20}$ ¹⁹): the barium atoms display in **7** a square antiprismatic coordination with two shorter and two longer distances at each side (2.763(8), 2.789(7) Å to the μ_2 -alkoxide ligands and 2.783(11), 2.816(11) Å to acac-ligands and 2.821(7), 2.825(6) Å to μ_3 -alkoxide ligands and 2.848(9) and 2.910(10) Å), while in $\text{Ba}_2\text{Zr}_4(\text{O}^i\text{Pr})_{20}$ ¹⁹ they are asymmetrically coordinated with “half of an antiprism” (Ba- μ_2 -OR 2.709-2.788 Å, Ba- μ_3 -OR 2.873-2.895 Å) and two short Ba- μ_2 -OR-Ba contacts of 2.551(8) and 2.591(8) Å. The coordination of zirconium atoms in **7** follows the pattern of bond lengths distribution in $\text{Ba}_2\text{Zr}_4(\text{O}^i\text{Pr})_{20}$ ¹⁹ with exactly the same distances to terminal OR-groups (1.926-1.928 Å) and approximately 0.015

Å shortened distances to all bridging groups reflecting the contraction of this side of the molecule on increase of the Ba-containing fragment. Compound **7** is poorly soluble in hexane but well soluble in toluene, especially on heating, and rather volatile, which makes it an attractive possible precursor of dielectric coatings in both sol-gel and MOCVD techniques.

The approach applying **2** or n-propoxide and a bulky diketonate ligand thd for completion of the structure turned to be fully successful, providing complexes **8** and **9** with very high yields:

toluene



The crystal and molecular structures of compound **8** (Fig. 8, Tab. TS8) and compound **9** (Fig. 9, Tab. TS9) are closely related to each other and also to the structure of $\text{Ba}_2\text{Ti}_2(\text{thd})_4(\text{OEt})_8(\text{EtOH})_2$ published earlier by us²⁷. They belong both to the desired M_4O_{16} core type with hexacoordinated Zr atoms surrounded each by one triply bridging alkoxide ligand, two doubly bridging ones, one terminal alkoxide group and two oxygen atoms from a terminal η^2 -thd ligand. Coordination number for Ba atoms in **8** is seven as it is connected to two triply bridging and two doubly bridging alkoxide ligands, two oxygen atoms from a terminal η^2 -thd ligand and also an oxygen atom of solvating alcohol molecule (the IR spectrum indicates the presence of alcohol in the coordination sphere of barium by the presence of a OH-band at 3148 cm^{-1}). In spite of belonging to the same structure type and displaying the same coordination numbers for barium and for zirconium, the compound **8** possesses a molecular geometry significantly different from that in

$[\text{BaZr}(\text{OH})(\text{O}^i\text{Pr})_5(\text{PrOH})_3]_2^{22}$, which results apparently from quite different charge distribution in the core. The Ba-O distances to terminal ligands in **8** are fairly short (2.533(19) and 2.635(17) Å to the thd-ligand with (-1) charge and 2.721(16) Å to the solvating alcohol in comparison to 2.779-2.892 Å to the terminal alcohol ligands in $[\text{BaZr}(\text{OH})(\text{O}^i\text{Pr})_5(\text{PrOH})_3]_2^{22}$), while those to the alkoxide bridges are much longer (2.691-2.783 Å to doubly and 2.853-3.063 Å to the triply bridging OR in **8** compared to 2.670-2.680 and 2.683-2.717 Å in $[\text{BaZr}(\text{OH})(\text{O}^i\text{Pr})_5(\text{PrOH})_3]_2$). Need in increased coordination originates evidently in too small size of the normal chain radicals insufficient itself to provide the necessary protection of the core. The presence of a number of bulkier isopropoxide ligands in **9** limits the coordination number to six for barium atoms. It is interesting to note that the smaller n-propoxide groups occupy exclusively the doubly bridging positions (in statistics, 50/50 with the isopropoxide ones), where the sterical tension is highest. It is important to note that the structure of **8** and **9** do not confirm either any specific role of dimeric zirconium units in the chemistry of its alkoxides as they contain exclusively monomeric $\text{Zr}(\text{OR})(\text{thd})(\mu_2\text{-OR})(\mu_3\text{-OR})$ units not connected to each other via any common bridging atom. It is interesting to observe that these units can structurally be considered as monomeric $[\text{Zr}(\text{thd})(\text{OR})_4]^-$ anions: all the Zr-OR distances are almost equal independent upon the formal structural function (for example in **8**, 2.021(14) Å to $\mu_3\text{-OR}$, 2.026(16) and 2.050(15) Å to $\mu_2\text{-OR}$ and 2.032(16) Å to the terminal group!). Formation of such monomeric units appears logical as the relatively big size of the thd-ligand provides sufficient shielding and stabilization of a mononuclear MO_6 core. Monomeric molecular compounds $\text{M}^V(\text{OR})_4(\beta\text{-diket})$, $\text{M}^V = \text{Nb}, \text{Ta}$ ^{39,40,47} formed on cleavage of $\text{M}_2(\text{OR})_{10}$ dimers by β -diketones or on transfer of a β -diketonate ligand display almost exactly the same molecular geometries as the $[\text{Zr}(\text{thd})(\text{OR})_4]^-$ anions in **8** and **9**.

Both **8** and **9** are very highly soluble in toluene and parent alcohols, **8** also in hexane. Poor solubility of **9** and **10** (see below) in non-solvating hexane might be caused by their ionic

nature. Both compounds display also very high volatility and will be tested for preparation of ferroelectric layers of BaZrO₃ by pulse liquid injection assisted MOCVD at the University of Paris XI, France.

We have applied the same approach even for the preparation of a strontium-zirconium with isopropoxide only alkoxide ligands, which also turned to be quite successful:

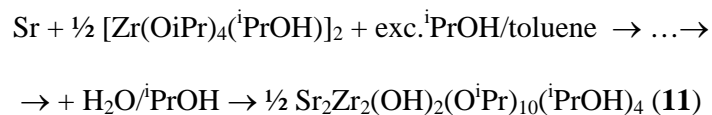


We were not able to fulfill the X-ray single crystal study of **10** because of extensive twinning in their crystals, but this task was not challenging as it was clear that the molecular structure should in this case be very close to that of **9** and completely analogous to that of earlier reported Sr₂Ti₂(thd)₄(OⁱPr)₈⁵⁵ according to the observed NMR data. **10** is very soluble in toluene and isopropanol but almost completely insoluble in hexane.

It appeared interesting to compare the behavior of **8**, **9** and **10** on evaporation in order to understand the role of alkoxide ligand in this process (assuming the analogy between strontium and barium commonly observed for compounds of these two elements). The mass-spectral evidence is limited to only relatively light species, below m/z= 800 because of the technical limitations in this case, but it speaks in favor of the trend for stability of heterometallic species to decrease from **8** through **9** to **10**: in the mass-spectrum of **8** it is possible to trace heterometallic fragments, but not really in that of **9**. Still, the evaporation chromatogram obtained via monitoring of total ion current shows uniform evaporation for both **8** and **9** (all ions follow the total current profile). This is not the case for **10**, where the chromatogram has two distinct tops (lower and higher temperature ones respectively), where the low temperature ions are only the same as those for **9**, while the high temperature ones display a strong fragmentation tree for strontium tetramethylheptanedion derivative,

indicating the thermal decomposition occurring in the solid phase. It is important to note that this decomposition is definitely not a result of electron impact on ionization, as less stable in the gas phase barium-titanium ethoxide complex displays fragmentation trees only for homometallic species but with ion intensities following all the time the total current profile. It is important thus to underline that the volatility and stability on evaporation is a matter of the stability of molecular structure and does not simply increase with the size of alkyl groups in the complexes: higher sterical tension on transition from n- to isopropoxide in this particular case leads to decrease in stability.

In the course of preparation of this paper for publication we have been encouraged by one of the reviewers to seek an unequivocal and ultimate confirmation to the fact that the reactions of chemical modification and complex formation for homoleptic metal alkoxides are self-assembly processes governed by the thermodynamic principles summarized in the Molecular Structure Design Concept and not the reactions of ligand exchange in a complex with defined geometry. To meet the proposal of the reviewer we had obviously to choose a system, where our opponents have developed a long multi-step synthetic approach and achieve the corresponding heterometallic complex by a simple one-batch procedure according to MSDC. We have chosen the strontium-zirconium isopropoxide system – an analog of the barium-zirconium isopropoxide one, where the compound $[\text{BaZr}(\text{OH})(\text{O}^i\text{Pr})_5(^i\text{PrOH})_3]_2$ ²² was obtained via microhydrolysis of initially prepared $\text{BaZr}(\text{O}^t\text{Bu})_6(\text{THF})_2$ (synthesized from individual t-butoxides obtained in advance) with subsequent alcohol interchange with $^i\text{PrOH}$ – expecting the formation of an analogous new compound, which we could confirm by a new X-ray single crystal study. Our supposition turned to be fully correct and the new hydroxo-alkoxide complex $\text{Sr}_2\text{Zr}_2(\text{OH})_2(\text{O}^i\text{Pr})_{10}(^i\text{PrOH})_4$ (**11**) was obtained in a one-batch self-assembly synthesis:



Our major concern in carrying out this reaction was in avoiding a local excess of water that could cause a deeper and irreversible hydrolysis. We introduced water therefore in the form of diluted solution in the parent alcohol. The yield of this first attempt (we had no time for optimization of the conditions of hydrolysis) was not very high, but not less than of $[\text{BaZr}(\text{OH})(\text{O}^i\text{Pr})_5(^i\text{PrOH})_3]_2$ in ²² if the total sequence of the reactions would be taken into account. It means that application of this sequence is totally unnecessary and the idea about ligand exchange in a defined complex does not have any scientific basis. The self-assembly approach is definitely better justified in approach to complex systems.

Conclusions

Efficient one-batch synthetic approaches to highly soluble and volatile homo- and heterometallic zirconium precursors (for Co-Zr and Ba-Zr systems), permitting to control their chemical composition, molecular geometry and physicochemical properties and using inexpensive and commercially available raw materials have been successfully developed applying the Molecular Structure Design Concept. The description of the reactions of chemical modification and complexation of homoleptic metal alkoxides as processes of ligand exchange in a defined molecular structure was shown to be erroneous and unnecessary, complicating the development of synthetic routes to heteroleptic and heterometallic complexes.

The stability of heterometallic complexes on evaporation does not simply improve with the increased size of the alkyl group but depends on the stability of their molecules on heating.

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Supplementary materials. Crystallographic information on compounds **1-9** in the form of CIF-files and also tables of selected bond distances and angles (TS1-TS9) and a figure displaying theoretically calculated X-ray powder pattern for **1** (FS1) are available in Electronic Supplementary.

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Table 1 Crystal data and the diffraction experiments details for compounds **1-5**.

	1	2	3	4	5
Chemical composition	C ₃₀ H ₇₂ O ₁₀ Zr ₂	C ₃₀ H ₇₂ O ₁₀ Zr ₂	C ₄₀ H ₈₄ Co ₂ O ₁₄ Zr ₂	C ₂₈ H ₅₆ O ₁₀ Zr ₂	C ₃₄ H ₇₀ CoO ₁₂ Zr ₂
Formula weight	775.32	775.32	1089.37	735.17	912.27
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2(1)/n	P-1	C2/c
μ/mm^{-1}	0.520	0.513	1.005	0.547	0.803
<i>R</i> 1	0.0700	0.0665	0.0494	0.0451	0.0514
<i>wR</i> 2	0.1999	0.1761	0.1186	0.1016	0.0708
<i>a</i> /Å	12.121(2)	10.153(4)	12.922(5)	9.818(8)	30.601(12)
<i>b</i> /Å	12.191(2)	10.774(4)	16.075(6)	10.639(11)	9.408(4)
<i>c</i> /Å	14.984(3)	11.872(4)	13.415(5)	11.790(12)	17.851(7)
α /°	80.335(4)	112.144(8)	90	87.86(4)	90
β /°	84.806(3)	101.329(6)	95.868(8)	68.83(3)	108.580(8)
γ /°	89.102(4)	104.345(5)	90	64.64(5)	90

$V/\text{\AA}^3$	2173.7(7)	1102.9(7)	2272.1(17)	1027.7(17)	4871(3)
T/K	295(2)	295(2)	295(2)	295(2)	295(2)
Z	2	1	2	1	4
Number of independent reflections	4555 [R(int) = 0.0299]	2044 [R(int) = 0.0664]	3373 [R(int) = 0.0499]	3491 [R(int) = 0.0219]	1403 [R(int) = 0.1846]
Number of observed reflections	2783 [I > 2sigma(I)]	1362 [I > 2sigma(I)]	1192 [I > 2sigma(I)]	2223 [I > 2sigma(I)]	734 [I > 2sigma(I)]

Table 1 (continued) Crystal data and the diffraction experiments details for compounds **6-11**.

	6	7	8	9	11
Chemical composition	$C_{44}H_{84}CoO_{17}Zr_3$	$C_{64}H_{140}Ba_2O_{22}Zr_4$	$C_{74}H_{148}Ba_2O_{18}Zr_2$	$C_{68}H_{132}Ba_2O_{16}Zr_2$	$C_{48}H_{120}O_{18}Sr_2Zr_2$
Formula weight	1217.70	1901.32	1783.04	1662.86	1343.12
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P2(1)/c	P-1	P-1	P-1
μ/mm^{-1}	0.849	1.355	1.092	1.182	1.994
<i>R</i> 1	0.0784	0.0635	0.0861	0.0762	0.0636
<i>wR</i> 2	0.1810	0.1472	0.2012	0.1845	0.1672
<i>a</i> /Å	12.123(7)	18.443(3)	10.820(7)	10.452(7)	10.901(5)
<i>b</i> /Å	12.823(7)	12.546(3)	14.977(9)	14.373(9)	12.732(7)
<i>c</i> /Å	21.622(14)	19.772(4)	16.885(9)	16.179(9)	13.026(7)
$\alpha/^\circ$	81.457(15)	90	104.801(19)	67.072(11)	109.052(19)
$\beta/^\circ$	76.054(9)	97.494(6)	104.294(11)	76.53(2)	100.230(17)

$\gamma/^\circ$	64.937(10)	90	107.671(13)	89.253(15)	99.51(2)
$V/\text{\AA}^3$	2951(3)	4535.7(16)	2359(2)	2169(2)	1632.6(14)
T/K	295(2)	295(2)	295(2)	295(2)	295(2)
Z	2	2	1	1	1
Number of independent reflections	4689 [R(int) = 0.0824]	4276 [R(int) = 0.0447]	3201 [R(int) = 0.0906]	3960 [R(int) = 0.0646]	4230 [R(int) = 0.0315]
Number of observed reflections	2292 [I>2sigma(I)]	2671 [I>2sigma(I)]	1939 [I>2sigma(I)]	2058 [I>2sigma(I)]	2507 [I>2sigma(I)]

Captions to figures:

Fig.1 Molecular structure of $\text{Zr}_2(\text{O}^i\text{Pr})_8(^i\text{PrOH})_2$ (**1**)

Fig.2 Molecular structure of $\text{Zr}_2(\mu\text{-O}^n\text{Pr})_2(\text{O}^i\text{Pr})_6(^i\text{PrOH})_2$ (**2**)

Fig.3 Molecular structure of $\text{Co}_2\text{Zr}_2(\text{O}^n\text{Pr})_4(\text{O}^i\text{Pr})_6(\text{acac})_2$ (**3**)

Fig.4 Molecular structure of $\text{Zr}_2(\text{O}^i\text{Pr})_6(\text{acac})_2$ (**4**)

Fig.5 Molecular structure of $\text{CoZr}_2(\text{O}^i\text{Pr})_8(\text{acac})_2$ (**5**)

Fig.6 Molecular structure of $\text{CoZr}_3\text{O}(\text{O}^n\text{Pr})_3(\text{O}^i\text{Pr})_5(\text{acac})_4$ (**6**) (only first carbon atoms of the propoxide groups are displayed to simplify the view. PP denotes the ^iPr groups and PN – the ^nPr ones).

Fig.7 Molecular structure of $\text{Ba}_2\text{Zr}_4(\text{O}^i\text{Pr})_{18}(\text{acac})_2$ (**7**)

Fig.8 Molecular structure of $\text{Ba}_2\text{Zr}_2(\text{thd})_4(\text{O}^n\text{Pr})_8(^n\text{PrOH})_2$ (**8**)

Fig.9 Molecular structure of $\text{Ba}_2\text{Zr}_2(\text{thd})_4(\text{O}^n\text{Pr})_2(\text{O}^i\text{Pr})_6$ (**9**) (all doubly bridging groups are occupied to 50% by ^iPr groups and to 50% by the ^nPr groups, only one of the possible arrangements being displayed in this picture).

Fig. 1

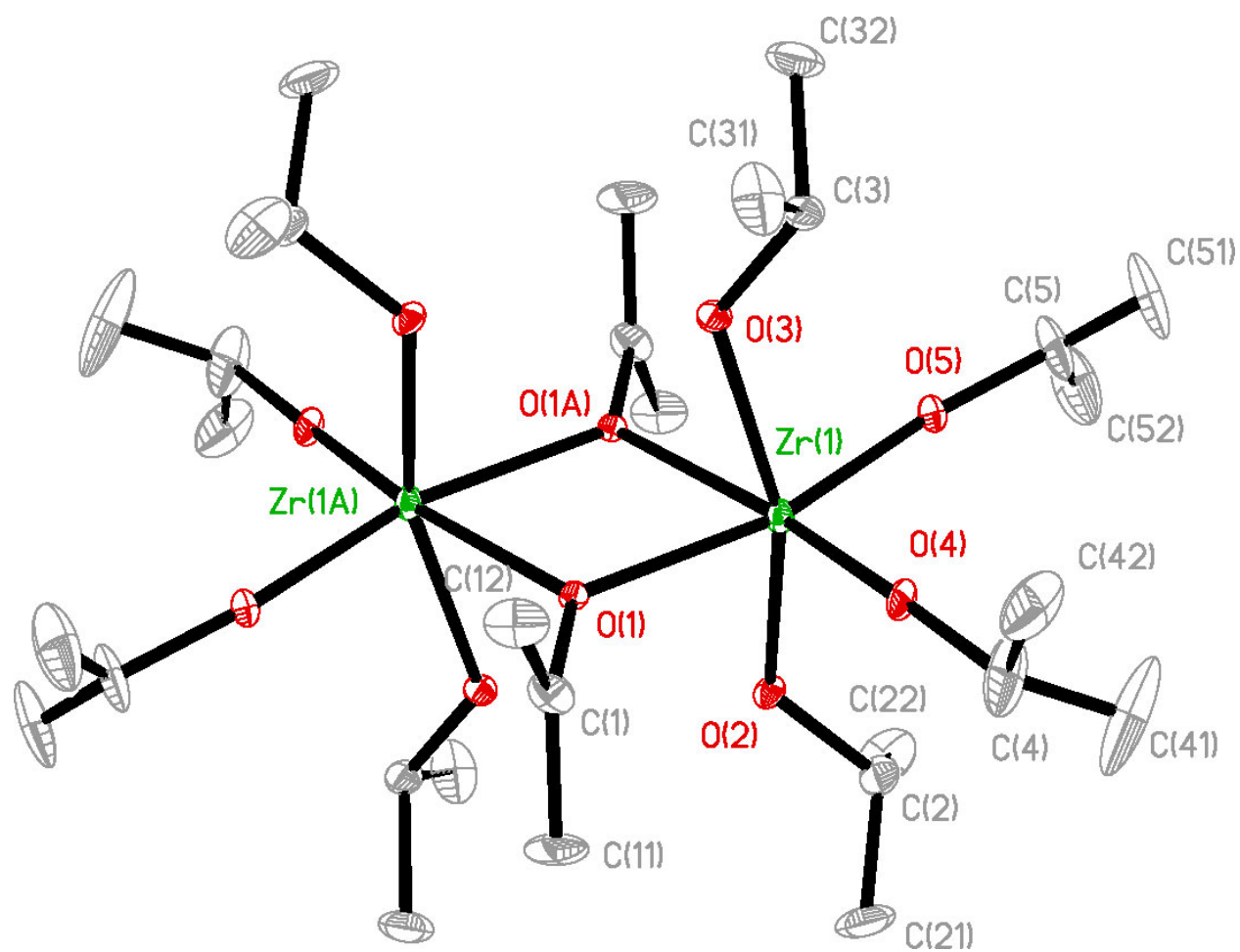


Fig. 2

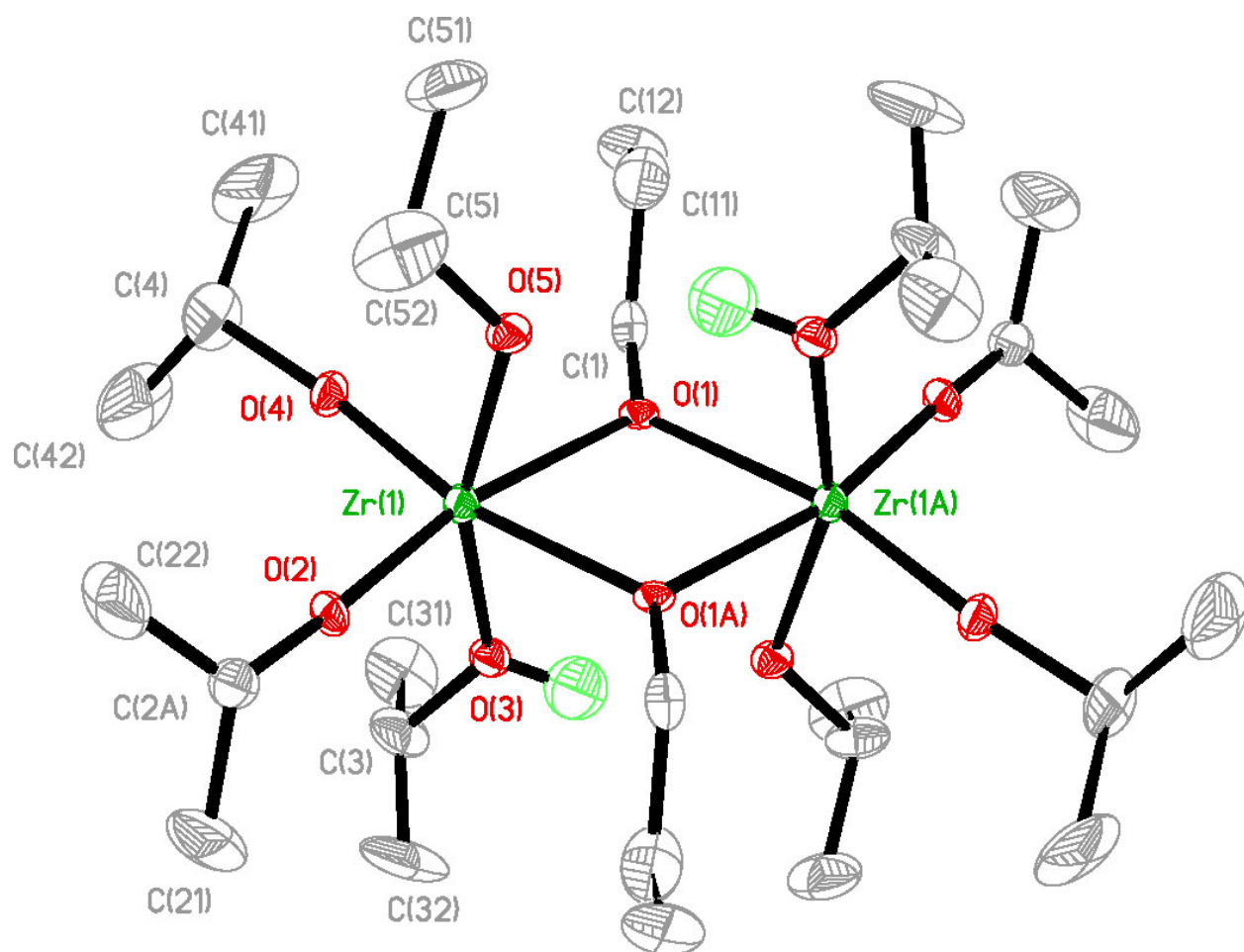


Fig. 3

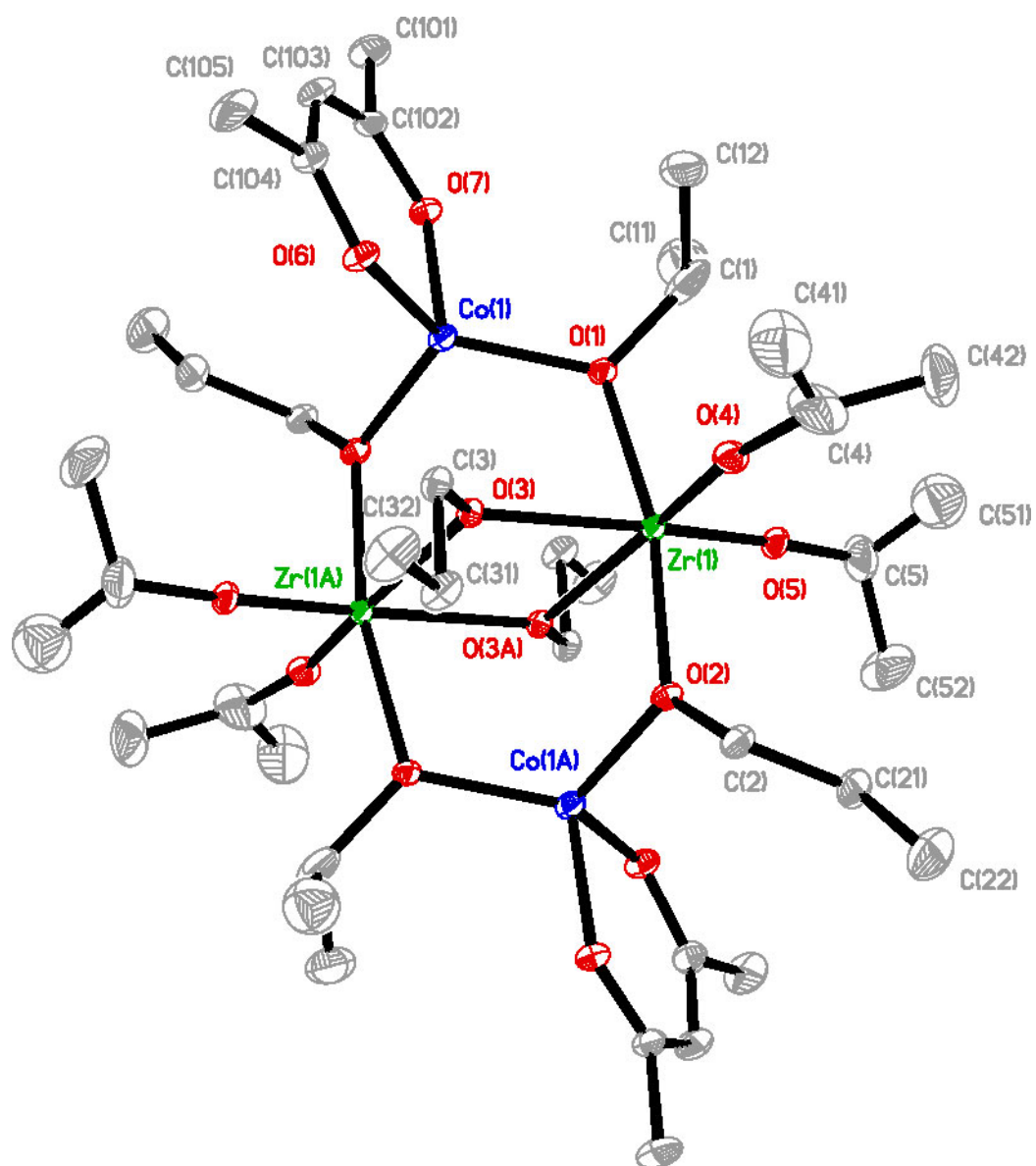


Fig. 4

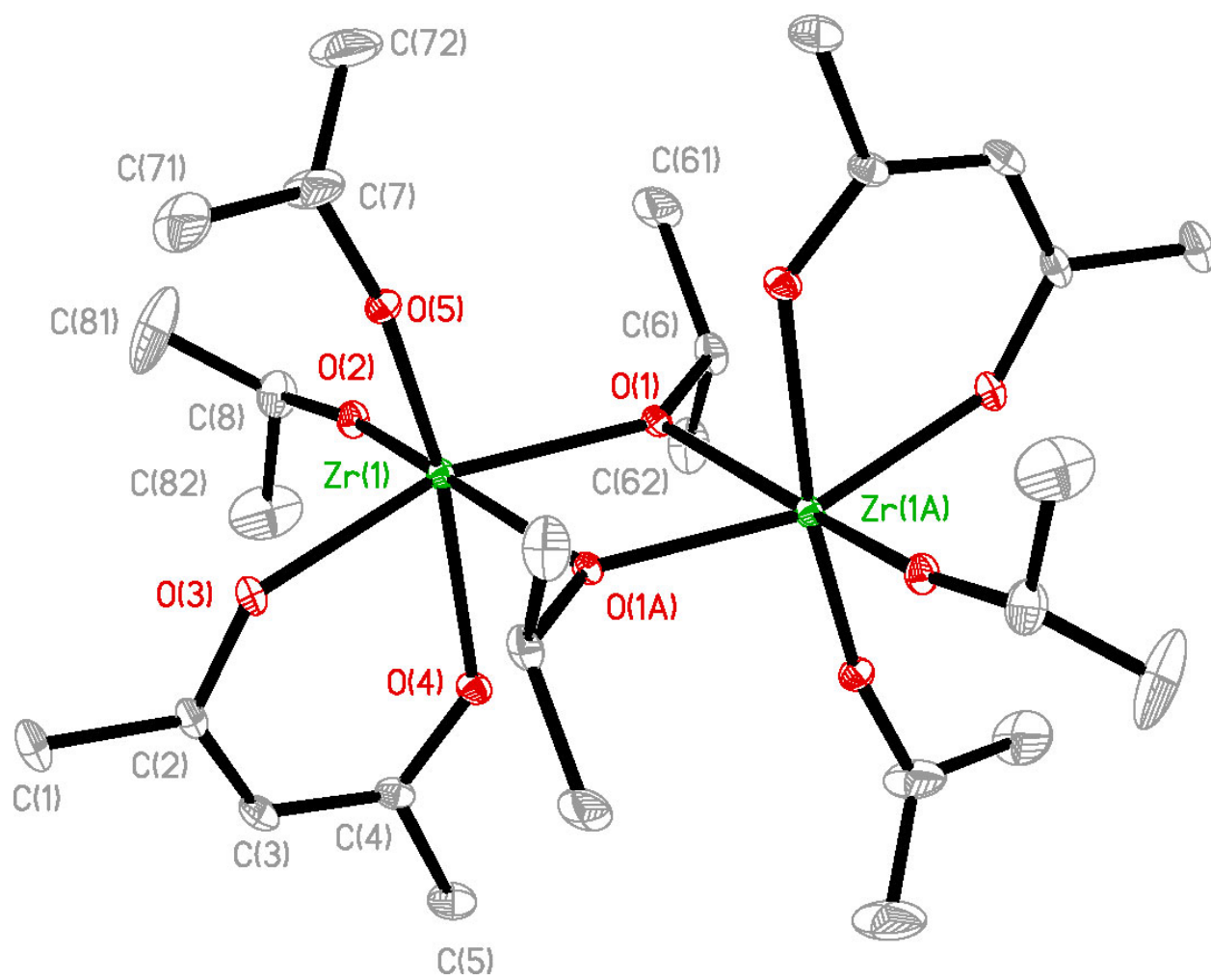
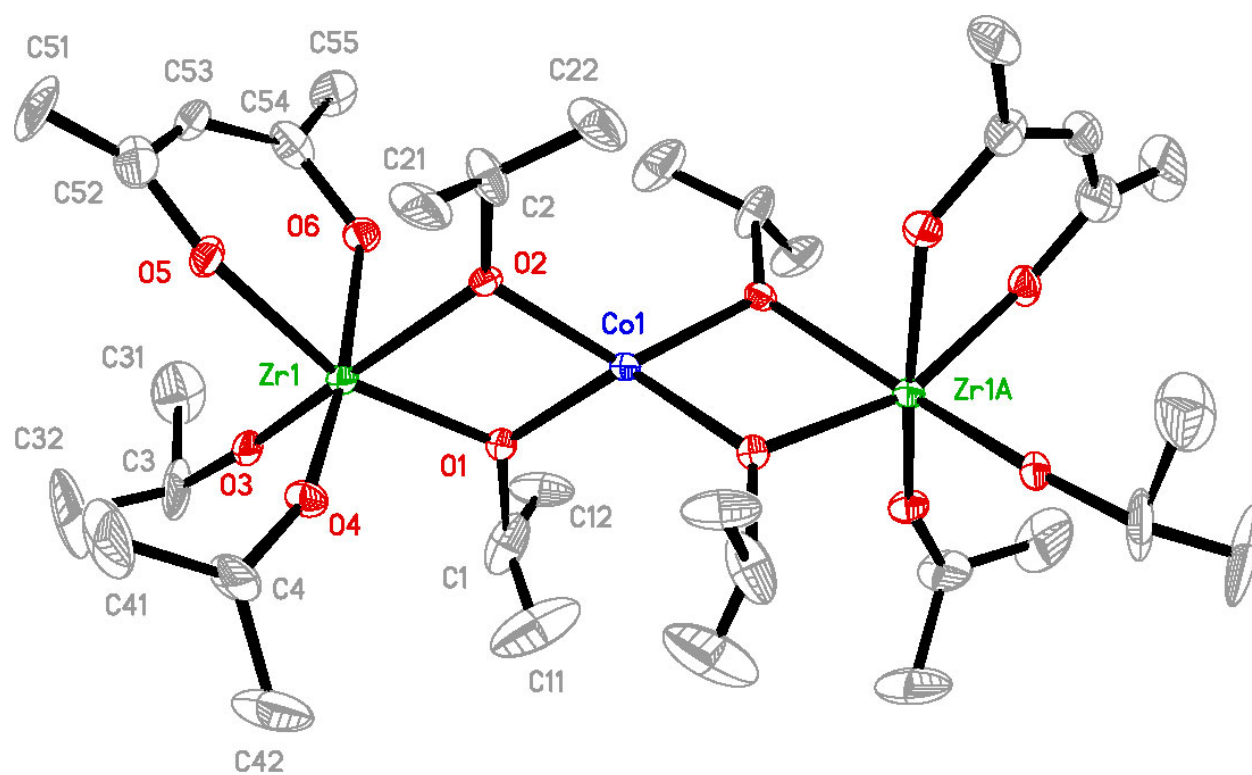


Fig. 5



ORTEP diagram of the molecular structure of the complex. The structure shows three Zr atoms (Zr1, Zr2, Zr3) in green, one Co atom (Co1) in blue, and various C and O atoms. Thermal ellipsoids are drawn at the 50% probability level.

[illegible]

Fig. 8

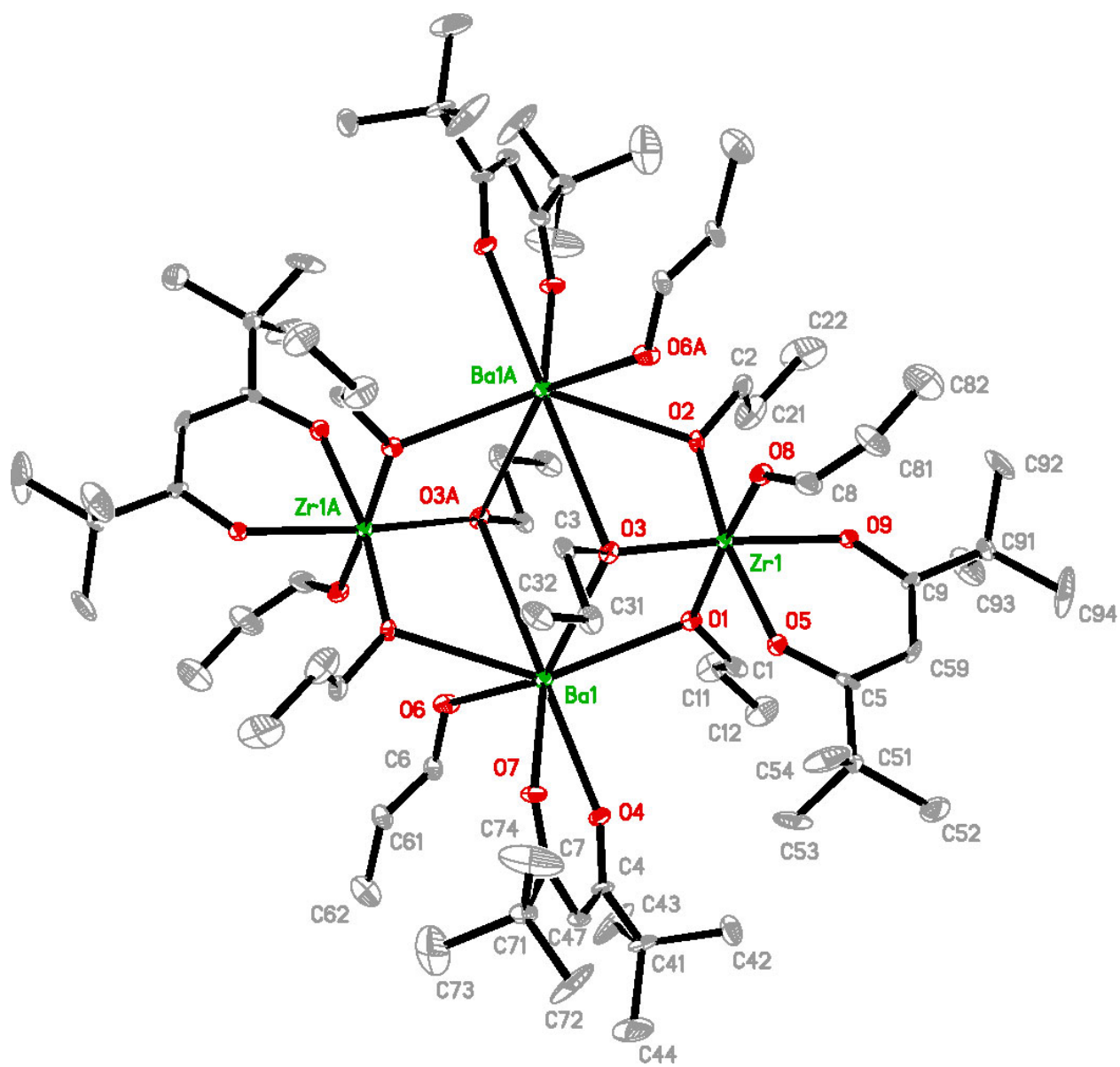


Fig. 9

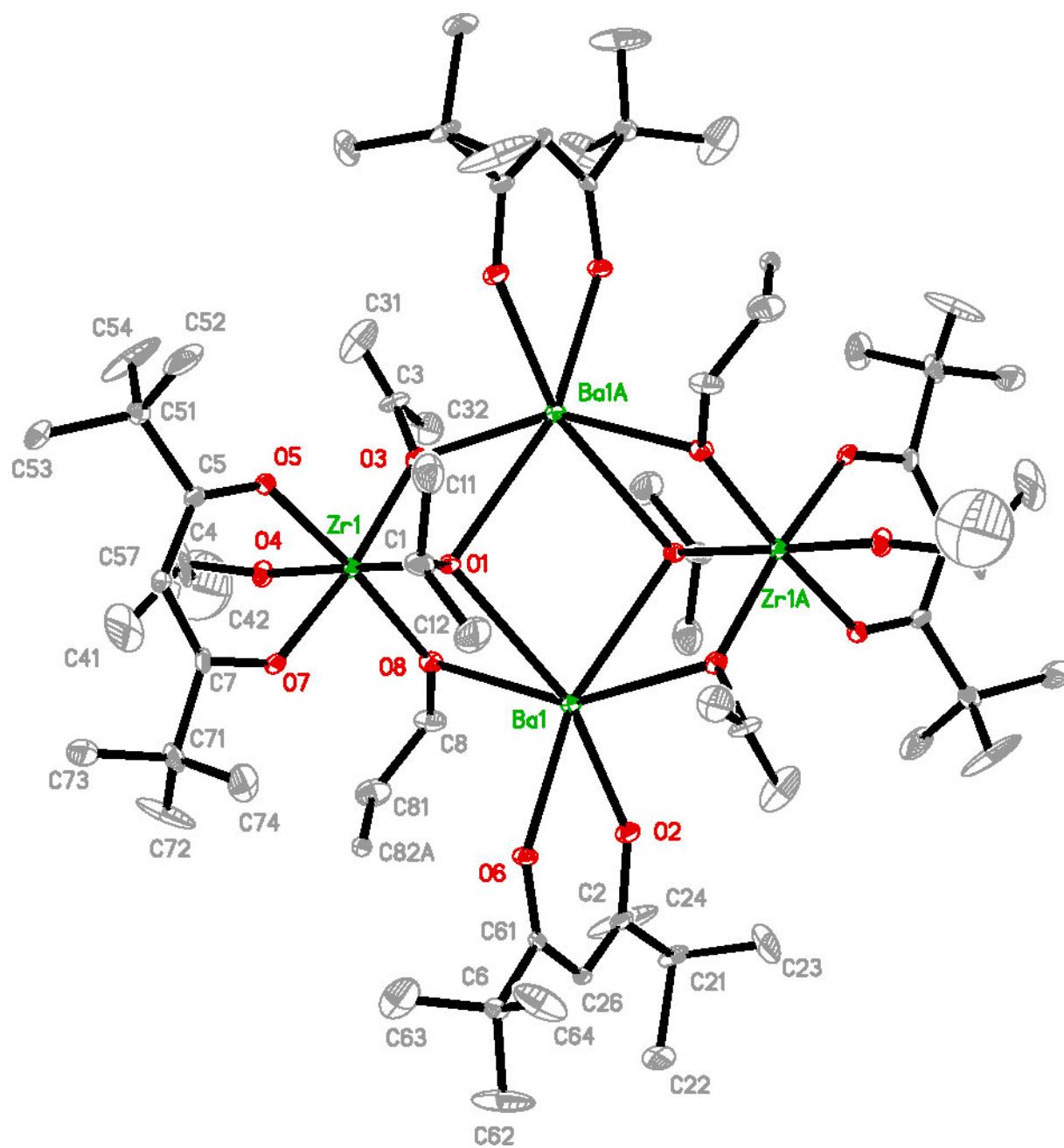


Fig.10

