New zirconium and zirconium–titanium oxo cluster types by expansion or metal substitution of the octahedral Zr₆O₈ structural motif

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1. Introduction

Carboxylate-substituted oxo clusters of the general formula M₆O₈(OR)₆(OOCR)₆ (M = Ti, Zr) are obtained when zirconium or titanium alkoxides, or mixtures thereof, are reacted with carboxylic acids. A variety of different structures was found, with different degrees of substitution (M:COOR ratio) or condensation (M:O ratio). Prominent examples among these oxo clusters are Zr₆O₈(OR)₆(OOCR)₁₂ (Zr₆O₈) [1–6] and Ti₆O₈(OR)₆(OOCR)₆ (Ti₆O₈) [7–12]. Both have an octahedral arrangement of the six metal atoms and were obtained for a variety of carboxylate ligands (Scheme 1).

In the clusters Zr₆O₈(OR)₆(OOCR)₁₂, the eight triangular faces of the M₆ octahedron are alternatively capped by μ₃-O or μ₂-O groups. Each Zr atom is coordinated by eight oxygen atoms. According to quantum mechanical calculations, a structure where the 12 carboxylate ligands bridge the 12 Zr–Zr edges (i.e. an O₈-symmetric cluster) is lowest in energy [13]. In most crystal structures, however, only 9 carboxylate ligands are bridging and three chelate the Zr atoms of one triangular face. Several variations of this structural motif were found, such as the dimeric structures [Zr₆O₈(OR)₆(OOCR)]₁₂ [2,14] in which two Zr₆ units are bridged by carboxylate ligands or clusters [Zr₆O₈(OR)₆(OOCR)]₁₂(LH) where a bridging carboxylate ligand is converted to a η¹-OOCR ligand with concomitant coordination of a water or alcohol molecule (LH) to the emptied coordination site. Coordination of LH is supported by a hydrogen bond to the η¹-OOCR ligand [2,6]. A third possibility to modify the Zr₆O₈ cluster core was demonstrated by Kögerler et al. who showed that two, three or six metal cations (Fe, Mn, Ni, Co) can be coordinated to the μ₃-O sites, with concomitant partial deprotonation of the μ₂-OH groups and adjustment of the ligand sphere [15,16].

In the Ti₆O₈ structure type (Scheme 1), only six triangular faces of the (distorted) Ti₆ octahedron are capped by μ₂-O atoms; two opposite faces are not capped. For this reason the structure of Ti₆O₈ clusters can also be described as a hexagonal prism in which the corners are alternatively occupied by Ti and O atoms. The six carboxylate ligands bridge the edges of the Ti₆ octahedron which connect two Ti₃O triangles. Each titanium atom is octahedrally coordinated by two carboxylate oxygen atoms, three μ₃-O atoms and one terminal OR ligand. The latter are oriented perpendicular to the hexagonal base of the prism. The reason for the difference between the Zr₆O₈ and Ti₆O₈ structures are the different coordination numbers of Ti (c.n. 6) and Zr (c.n. 8). While the total charge of M₆ is the same in both cases, the ligands in Zr₆O₈ must occupy 48 coordination sites, but only 36 in Ti₆O₈.

In this article we report new Zr and mixed Ti/Zr oxo clusters, the structures of which are derived from the Zr₆O₈ structural motif. In the first section Zr clusters are described in which the core of the Zr₆O₈ is expanded by coordination of additional Zr atoms. The structures of the mixed Ti/Zr clusters in the second section are hybrids of the Zr₆O₈ and Ti₆O₈ structures.
2. Results and discussion

2.1. Expansion of the Zr₆O₈ cluster core

Reaction of equal amounts of Zr(OBu)₄ and 4-(chloromethyl)benzoic acid in butanol afforded crystalline Zr₁₀[μ₄-O]₄(μ₃-O)₄(OBu)₈(μ₂-OBu)₈(OOC–C₆H₄–CH₂Cl)₈ (1, Fig. 1). In a formal sense, 1 is formed by condensation of Zr(OBu)₄ units to the μ₃-OH groups of Zr₆O₄(OH)₄(OOCR)₁₂ through bridging OBu groups with partial replacement of four carboxylate ligands (for reasons of charge neutrality). The pyramidal Zr₃(μ₃-OH) groups are thus converted to tetrahedral Zr₄(μ₄-O) units, but otherwise the Zr₆O₈ core is preserved (Fig. 2). The Zr–Zr distances in the central octahedral unit are slightly shorter than in the parent Zr₆O₈ clusters (3.3717–3.5105 Å in 1, 3.480–3.548 Å in Zr₆O₈). The four additional Zr atoms are octahedrally coordinated by two terminal and two bridging OBu groups as well as one bridging carboxylate in addition to the μ₄-O atom. A coordination number of 6 is quite unusual for Zr.

The octahedrally coordinated Zr atoms form a tetrahedron among each other, i.e. the structure of 1 can be described as an octahedral Zr₆ unit inscribed in a larger Zr₄ tetrahedron (Fig. 2). In the parent structure, Zr₆O₄(OH)₄(OOCR)₁₂, the μ₃-OH groups are asymmetrically bonded, with two shorter and one longer Zr–O distance. Although the Zr–O distances of 1 are more uniform, some asymmetry is found in the Zr–O–Zr bond angles between the octahedral (outer) Zr atoms and that of the Zr₄ core: one angle each is in the range 136.0–140.8(2) Å, while the other two are 104.0–107.9(2) Å.

While even structural details of the Zr₆O₈ cluster core are very well preserved upon coordination of the additional Zr atoms, the ligand sphere has undergone some changes. At the first glimpse it appears surprising that different to the symmetric cluster core, the substitution pattern of the Zr atoms is not uniform. The coordination of Zr₁ and Zr₆ is completed by the bridging ligands (two OBu groups and one carboxylate group) to the outer Zr atoms in addition to the μ₁- and μ₄-oxygen atoms. Zr₃ has two bridging OBu groups to outer Zr atoms and two bridging carboxylate ligands to Zr₂ and Zr₄ of the Zr₆ core. Two carboxylate ligands chelate Zr₅. This results in a coordination number of seven for Zr₁, Zr₂, Zr₄ and Zr₆ and a coordination number of eight for Zr₃ and Zr₅ (in the parent cluster all Zr atoms are 8-coordinate). An explanation for this observation might be that this is a compromise between the preferential coordination requirements of the Zr atoms and the number of bidentate ligands available. If all Zr atoms were 8-coordinate, 24 mono-anionic ligands (in addition to the eight μ₁- and μ₄-O) would have to occupy 52 coordination sites; this is not possible with the available ligands (OR and OOCR).

Crystals of Zr₁₀O₈(OBu)₁₈(OOC–C₆H₄–CH₂Cl)₈ (2, Fig. 3) were obtained when water was added to an equimolar mixture of Zr(OBu)₄ and 2-pentynoic acid in BuOH. The core structure of 2 is derived from that of 1 by removing one Zr atom (Zr₅ in 1) together with two (chelating) carboxylate ligands from the central Zr₆ octahedron (Fig. 4). This Zr atom in 1 is connected by two μ₁- and two μ₄-O atoms with the other Zr atoms. In 2, the two μ₄-oxygen atoms become μ₃ and, for charge balancing reasons, the μ₁-O are replaced by μ₃-OBu groups. The remaining carboxylate and OBu ligands coordinate in the same way as in 1, also the Zr–O bond lengths are in the same range.

2.2. Ti/Zr mixed metal clusters

Mixed metal Ti/Zr oxo clusters have been prepared by reaction of metal alkoxide mixtures with methacrylic acid or acetic acid [17,18]. The cores of the known clusters are zigzag chains of [ZrO₂], [ZrO₃] and [TiO₄] polyhedra.

A Ti/Zr oxo cluster with a different structure, namely Ti₂Zr₆[μ₃-O]₄(μ₃-OH)₈(OPt̄₃OPiv₁₁)₂HOPiv (3, HOPiv = pivalic acid, Fig. 5), was obtained from mixtures of various titanium and zirconium alkoxides and varying amounts of pivalic acid. The structure of 3
can be derived from the Zr$_6$O$_8$ structures by replacing two neighboring Zr atoms by Ti (Fig. 6). Because of the different coordination requirements of Ti, this results in a loss of a $\mu_3$-O, as explained for the Ti$_6$O$_6$ structures. The M$_3$ triangle not capped by an oxygen atom is that of the two Ti atoms and Zr$_4$. The distance between Zr$_4$ and the two Ti atoms [Ti1–Zr4 3.688(1), Ti2–Zr4 3.770(1) Å] is about 0.5 Å longer than that between the Ti atoms and the other Zr atoms [3.047(1)–3.285(1) Å].

The best evidence for an assignment of the core oxygens to $\mu_3$-O or $\mu_3$-OH are the M–O bond lengths, which are significantly longer for $\mu_3$-OH groups. Although the spread of distances in $\mu_3$ is much higher than in monometallic clusters, only two core oxygen atoms, O2 (connecting Ti1, Zr1 and Zr2) and O7 (connecting Zr2, Zr3 and Zr4) show longer M–O bond distances compared to the others. Especially Ti1–O2 [2.155(3) Å] is much longer than the other Ti–O distances of the cluster core [1.845(3)–1.945(3) Å]. The effect on the Zr–O bond lengths is weaker but significant [Zr–O2/O7 2.194(3)–2.306(3) Å compared to 2.082(3)–2.173(3) Å for the other core Zr–O bonds]. O2 and O7 are therefore assigned to $\mu_3$-OH groups and the other oxygen atoms to $\mu_3$-O. This assignment is supported by the finding that O2 and O7 undergo strong hydrogen bonds to the C@O groups of two external pivalic acid molecules [O2/C1/C1/C1 O31 2.702(5) Å, O7/C1/C1/C1 O33 2.829(6) Å].

Contrary to the parent Zr$_6$O$_4$(OH)$_4$(OOCR)$_12$ clusters, each Zr atom in 3 is coordinated by a chelating carboxylate ligand. The other OPiv ligands bridging two Zr atoms or Ti and Zr. Ti2 and Zr4 coordinate to three bridging OPiv ligands, all others to two. The coordination sphere of Ti1 is completed by a terminal OPr ligand with a short bond length [Ti1–O8 1.741(3) Å].

It was previously observed that clusters of different composition may be obtained if the precursor composition is slightly varied, such as metal alkoxides with different alkoxo groups [19] or the stoichiometric ratio of the precursors [20]. In the present case we obtained a second Ti/Zr mixed-metal cluster at different reaction conditions, namely Zr$_3$Ti$_2$(Zr$_2$–O)($\mu_3$-OH)$_6$(OBu)$_3$(OPiv)$_{10}$ (Figs. 7 and 4). The structure of 4 is a hybrid of the Zr$_6$O$_8$ and Ti$_6$O$_6$ structure types; one face of the M$_6$ octahedron is
occupied by the three Ti atoms and the opposite face by the three Zr atoms. The corresponding M–O distances clearly show that the Zr faces is capped by a µ3-O [Zr–O 2.093–2.113(2) Å], the three ZrTi3 faces also by a µ3-O [Zr–O 2.107–2.181(2), Ti–O 1.898–1.947(2) Å] and the three ZrTi faces by a µ4-OH each [Zr–O 2.178–2.246(2), Ti–O 2.038–2.136(2) Å]. The Ti face is not capped.

The Ti atoms have the same ligand environment as in the Ti6O8 clusters (including a terminal OR ligand) and the Zr atoms show almost the same coordination as the Zr6O8 clusters (Fig. 7). The only major exception is that only two Zr atoms (Zr2 and Zr3) have chelating ligands, while the third (Zr1) has two µ1-OOPiv ligands which show strong hydrogen bonds to neighboring µ4-OH groups [O2•••O2 2.556(3), O4•••O3 2.484(3) Å]. The third µ4-OH group (O7) is hydrogen-bonded to an external pivalic acid molecule [O7•••O31 2.801(3) Å] (see Fig. 8).

3. Conclusions

The core Zr6O8 of the Zr4(OH)4(OOCR)12 structures can be regarded as the smallest possible structural section of tetragonal zirconia which is stabilized by organic ligands. Along these lines, clusters 1 and 2 are expansions of this embryonic development of the zirconia structure (with one Zr atom missing in 2). Comparison of the Zr6O8 structures with that of 1 also shows that the number and coordination of the organic ligands must be adjusted to the increased cluster size in order to provide sufficient stabilization.

The same line of reasoning applies to the Ti/Zr oxo clusters 3 and 4. The titania–zirconia phase diagram [21] contains several ordered and disordered solid solutions of (Zr,Ti)2O4, the structures of which are not fully understood. We therefore speculate that the cluster cores of 3 and 4 might be structurally related to structural motif(s) in tetragonal (Zr,Ti)2O4 in the same way as Zr6O8 and 1 are related to tetragonal zirconia.

4. Experimental

All experiments were carried out under Ar atmosphere using standard Schlenk techniques. Ti(OPr)4, Ti(OBu)4, Zr(OPr)4, Zr(OBu)4, 4-(chloromethyl)benzoic acid, 2-pentyenoic acid and pivalic acid were all obtained from Aldrich. BuOH was dried prior to use by the following procedure: a 0.5 M solution of BuOH in ether was refluxed with anhydrous sodium wire for 1 h, then distilled under reduced pressure.

Table 1

| Crystal data, data collection parameters and refinement details. |
|---------------------------------------------------------------|
| **1** | **2** | **3** | **4** |
|---------------------------------------------------------------|
| **Empirical formula** | C121H143ClO42Zr10 | C102H192O36Zr9 | C71.58H136.94O34.89Ti2Zr4 | C67H130.75O32.35Ti3Zr3 |
| **Mr** | 3557.54 | 2815.54 | 2016.59 | 1871.43 |
| **Crystal system** | triclinic | monoclinic | monoclinic | monoclinic |
| **Space group** | P1 | P21/c | P21/c | C2/c |
| **a (Å)** | 16.916(1) | 28.459(2) | 30.916(2) | 24.7352 |
| **b (Å)** | 17.072(1) | 28.459(2) | 29.181(2) | 24.7352 |
| **c (Å)** | 30.916(2) | 15.476(6) | 30.042(2) | 21.758(2) |
| **α (°)** | 90 | 94.990(3) | 93.435(2) | 90 |
| **β (°)** | 90 | 93.435(2) | 90 | 90 |
| **γ (°)** | 90 | 90 | 90 | 90 |
| **V (Å3)** | 7538.5(8) | 12762(1) | 18017(2) | 18017(2) |
| **Z** | 2 | 4 | 4 | 8 |
| **Dx (g cm−3)** | 1.563 | 1.465 | 1.339 | 1.380 |
| **µ (mm−1)** | 0.873 | 0.774 | 0.626 | 0.661 |
| **Crystal size (mm)** | 0.045 × 0.35 × 0.25 | 0.39 × 0.35 × 0.34 | 0.25 × 0.20 × 0.17 | 0.25 × 0.17 × 0.13 |
| **Rmin (Å)** | 30.68 | 33.23 | 25.09 | 26.79 |
| **R(F2 >> 2σ(F))** | 0.0789, 0.2198, 1.109 | 0.05513, 1.138, 1.163 | 0.0581, 0.1315, 1.159 | 0.0442, 0.1052, 1.014 |
| **No. of parameters** | 1681 | 1533 | 1114 | 1187 |
| **No. of restraints** | 0 | 0 | 0 | 0 |
| **No. of data observed** | 24 | 24 | 24 | 24 |

\[ \rho_{\text{calc}} = 1/[(\rho_0^2)^2 + (\rho_0^2)^2 + (\rho_0^2)^2], \text{where } P = (\rho_0^2 + 2\rho_0^2)/3. \]
to use by distilling twice from Na. All solvents used for NMR spectroscopy (Eurisotop) were degassed prior to use and stored over molecular sieves. 

1H and 13C solution NMR spectra were recorded on a Bruker AVANCE 250 (250.13 MHz [1H], 62.86 MHz [13C]) equipped with a 5-mm inverse-broadband probe head and a z-gradient unit.

4.1. Zr10O6(OBu)18(OOCCl2H4Cl2)8 (1)

Zr(OBu)4 (643 µl, 1.41 mmol) was added quickly to a suspension of 240 mg (1.41 mmol) of 4-(chloromethyl)benzoic acid in 3 ml of BuOH. The obtained clear solution was briefly heated to reflux and then cooled to room temperature. Crystals of 1 were formed after 2 weeks. Yield 60 mg (12%).

4.2. Zr9O6(OBu)18(OOCCl2)11 (2)

Water (9.6 µl, 0.53 mmol in 1 ml of BuOH) was added to a mixture of 210 mg (2.14 mmol) of 2-pentylocyanoic acid and 1 ml (2.18 mmol) of Zr(OBu)4 in 2 ml of BuOH. After 34 weeks part of the solvent of the clear solution was removed in vacuo. Crystals of 2 were obtained after 8 additional weeks. Yield 250 mg (37%).

4.3. Ti2ZrO2(OH)2(OPr)2(OPiv)12 HOOpiv-0.9BuOH (3)

Pivalic acid (18 mmol, 1.84 g) was added to a mixture of 2 mmol (0.681 g) of Ti(OBu)4 and 2 mmol (0.655 g) of Zr(OPr)4. Colorless crystals were obtained after three months, besides other colorless crystals of poor quality, which could not be identified. The same crystals were obtained after three months, besides other colorless crystals of poor quality, which could not be identified. The same crystals were obtained after three months, besides other colorless crystals of poor quality, which could not be identified.

4.4. Ti2ZrO2(OH)2(OBu)4(OPiv)10 HOOpiv3H2O (4)

A mixture of Ti(OBu)4 (1 mmol, 0.340 g), Zr(OBu)4 (2 mmol, 0.767 g) and pivalic acid (13.5 mmol, 1.38 g) was stirred for 1 h. Colorless crystals of 4 were obtained after 7 months, besides other colorless crystals of poor quality, which could not be identified.

4.5. X-ray structure analyses

Crystallographic data were collected on a Bruker AXS SMART APEX II four-circle diffractometer with k–geometry at 100 K using Mo Kα (λ = 0.71073 Å) radiation. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was employed. The cell dimensions were refined with all unique reflections. SHELXTLPlus software (Bruker Analytical X-ray Instruments, 2007) was used to integrate the frames. Symmetry was then checked with the program PLATON [22].

The structures were solved by charge flipping (SHELX2006). Refinement was performed by the full-matrix least-squares method based on F2 (SHELXS-97 [23]) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Crystal data, data collection parameters and refinement details are listed in Table 1.

Some organic groups in the structures showed disorder. The atom positions were split and their occupancies were refined. The large positive and negative residual electron density in 1 is located close to the CCl bond. Besides two molecules of pivalic acid and one molecule of butanol in 4, residual electron density remained in a void of 280 Å3, which could not be identified. Because the residual density was too far away from the cluster, SQUEEZE by PLATON was applied to remove this electron density.

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Appendix A. Supplementary Material

CCDC 1050491, 1050494, 1050493 and 1050492 contains the supplementary crystallographic data for 1–4. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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