# Methacrylate-Substituted Mixed-Metal Clusters Derived from Zigzag Chains of $[ZrO_8]/[ZrO_7]$ and $[TiO_6]$ Polyhedra

**Bogdan Moraru,[a] Guido Kickelbick,[a] and Ulrich Schubert*[a]**

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Reaction of titanium butoxide and zirconium butoxide with methacrylic acid in different molar ratios results in the formation of the mixed-metal clusters $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$, $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$, $Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$, and $Ti_2Zr_6O_6(OMc)_{20}$ (OMc = methacrylate). The molecular structures of these clusters have been determined by single-crystal X-ray diffraction analysis. They are based on a common structural motif, namely a zigzag chain comprising two terminal $[TiO_6]$ octahedra and two or four central $[ZrO_8]$ dodecahedra or $[ZrO_7]$ pentagonal bipyramids sharing common edges. Two additional $[TiO_6]$ octahedra or $[ZrO_8]$ dodecahedra are condensed at the flank of the main chain.

## Introduction

The so-called POSS-reinforced polymers (POSS = polyhedral oligomeric silsesquioxanes) have recently attracted much interest as a new class of inorganic-organic hybrid materials. They are prepared by the copolymerization of organic monomers with oligomeric $(RSiO_{1.5})_x$ species, mainly the cubic $R_8Si_8O_{12}$ clusters, in which one or (less often) more than one of the organic substituents R incorporates a polymerizable group.[1] The POSS-reinforced polymers show interesting improvements in their thermal and mechanical properties relative to those of the parent polymers.

Additional property modifications can be expected upon reinforcement of organic polymers with metal oxide clusters, especially those of transition metals. Thus, changes in the optical properties may result, or polymers with particular magnetic or catalytic properties may be generated.

However, only a few oxometallate clusters substituted with polymerizable organic ligands are available and, to the best of our knowledge, only $Bu_{12}Sn_{12}O_{14}(OH)_6(OMc)_2$ (OMc = methacrylate),[2] $Ti_3O_2(O\mathit{i}Pr)_5(OCMe{=}CH_2)_3(\mathit{i}PrOH)$,[3] and $[SiW_{10}O_{36}(Si_2R_2O)]^{4-}$ or $[SiW_{11}O_{39}(OSi_2R_2)]^{4-}$ (R = unsaturated organic groups)[4] have hitherto been used as co-monomers in polymerization reactions.[5]

We have recently prepared and structurally characterized several acrylate- or methacrylate-substituted oxotitanium and oxozirconium clusters of differing sizes and shapes, such as $Zr_6O_4(OH)_4(OMc)_{12}$,[6] $Zr_4O_2(OMc)_{12}$,[6,7] $[Zr_6O_4(OH)_4(OAcr)_{12}]_2$ (OAcr = acrylate), $Zr_6O_4(OH)_4(OMc)_{12}(PrOH)$,[8] $Ti_6O_4(OEt)_8(OMc)_8$,[9] $Ti_9O_8(OPr)_4(OMc)_{16}$,[10] and $Ti_4O_2(O\mathit{i}Pr)_6(OAcr)_6$.[11] These crystalline clusters are reproducibly obtained in very high yields by treating $Zr(OR)_4$ or $Ti(OR)_4$ with a defined excess of (meth)acrylic acid. In the first step of this reaction, one or more alkoxide ligands are substituted by carboxylate groups. The alcohol thus liberated then undergoes an esterification reaction. The water produced along with the ester serves to hydrolyze the remaining alkoxide groups and acts as the source of the oxide or hydroxide groups in the clusters. The very slow production of water allows a very controlled growth of the carboxylate-substituted oxometallate clusters.

Small amounts of the clusters $Zr_6O_4(OH)_4(OMc)_{12}$, $Zr_4O_2(OMc)_{12}$, $Ti_4O_2(O\mathit{i}Pr)_6(OAcr)_6$, and $Ti_6O_4(OEt)_8(OMc)_8$, which can be considered as structurally well-defined nanosized building blocks, were then used as co-monomers in radical polymerizations with methyl methacrylate and methacrylic acid. Even small proportions of the clusters (typically 0.5−2 mol-%) were found to efficiently crosslink the organic polymer chains. This results, inter alia, in a controllable swelling behavior, a higher thermal stability, and modified dielectric properties of the resulting inorganic-organic hybrid polymers.[7,12,13] Our initial results indicated that not only the proportion of the cluster, but also its size and shape and the number of polymerizable groups around its core, influence the material properties of the hybrid polymers to some extent. For this reason, our aim was to prepare methacrylate-substituted clusters of different sizes and shapes. In this paper, we report the synthesis and structural characterization of four oblong-shaped mixed-metal oxo clusters of Ti and Zr. Surprisingly, the structures of the clusters turned out to be based on a straightforward common construction principle.

## Results and Discussion

Reaction of $Ti(OBu)_4$, $Zr(OBu)_4$, and methacrylic acid in a 1:1:8.5 ratio resulted in the formation of crystalline $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ (**1**) in almost quantitative yield. The same cluster was obtained when $Ti(OEt)_4$ was employed instead of $Ti(OBu)_4$. The formation of butyl methacrylate could be monitored spectroscopically, which suggested the mass balance given in Equation (1).

[a] Institut für Anorganische Chemie, Technische Universität Wien,
Getreidemarkt 9, 1060 Wien, Austria

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$$4\,Ti(OBu)_4 + 4\,Zr(OBu)_4 + 22\,CH_2{=}C(Me)COOH \rightarrow Ti_4Zr_4O_6(OBu)_4(OMc)_{16}\,(\mathbf{1}) + 6\,CH_2{=}C(Me)COOBu + 22\,BuOH \quad (1)$$

When the $Ti(OBu)_4/Zr(OBu)_4$ ratio was changed from 1:1 to about 1:2, while keeping the total proportion of methacrylic acid constant (4.2 mol methacrylic acid per mol metal alkoxide), the cluster $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$ (**2**) was formed. The compositions of **1** and **2** were verified by X-ray structure analyses (see below). The spectroscopic data, elemental analyses, and powder diffractograms confirmed that **1** and **2** were formed as the sole products of the respective reactions. Assignment of the signals in the $^1H$ and $^{13}C$ NMR spectra to individual ligands proved difficult because they occupy a number of stereochemically different coordination sites. However, the spectra gave a good "fingerprint" of each particular cluster.

Increasing the $Ti(OBu)_4/Zr(OBu)_4$ ratio to 1:3 resulted in a mixture of clusters. In addition to the previously obtained cluster **2**, the clusters $Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$ (**3**) and $Ti_2Zr_6O_6(OMc)_{20}$ (**4**) were also formed. The composition of the mixture was verified by comparison of the powder diffraction patterns calculated from the individual crystal structure analyses with the powder XRD of the product mixture. Cluster **3** was obtained as the sole product when $Ti(OBu)_4$, $Zr(OPr)_4$ (instead of the butoxide), and methacrylic acid were reacted in a 1:1:8.2 molar ratio.

The latter result is remarkable in that it shows that seemingly minor changes in the reaction conditions may result in different clusters (although they are structurally related − see below): The only difference in the reaction conditions leading to **1** and **3**, respectively, is that zirconium *butoxide* is used in the former case, while zirconium *propoxide* is used in the latter. However, as mentioned above, replacing $Ti(OBu)_4$ by $Ti(OEt)_4$ did not result in a different cluster. These observations show that the relative reaction rates of the two alkoxides play an important role, and that the reactivity of the zirconium alkoxide evidently dominates the formation of the cluster nucleus, eventually leading to a particular cluster geometry. This is consistent with the higher reactivity of zirconium alkoxides relative to titanium alkoxides.

Clusters **1** and **4** have the general composition $M_8O_6X_{20}$ ($M = Ti^{IV}$ or $Zr^{IV}$; X = singly negatively charged ligand). The $M_6O_4X_{16}$ composition of **2** and **3** corresponds to a higher degree of condensation. Thus, increasing the $Zr(OBu)_4/Ti(OBu)_4$ ratio in the starting mixture from 1:1 to 3:1 not only favors the formation of the clusters with a higher Zr/Ti ratio, but also the formation of more highly condensed clusters ($M_6O_4X_{16}$ as opposed to $M_8O_6X_{20}$). It should be noted at this point that the previously obtained cluster $Zr_6O_4(OH)_4(OMc)_{12}$, obtained by reacting only $Zr(OPr)_4$ with a 3.8-fold excess of methacrylic acid,[6] also has the $M_6O_4X_{16}$ composition.

The molecular structures of clusters **1**−**4** are based on a common structural motif. This can best be visualized by comparing the cluster cores built up from connected polyhedra (Figure 1). In this representation the carbon atoms have been omitted, i.e. the corners of the polyhedra represent the oxygen atoms (from any ligand).

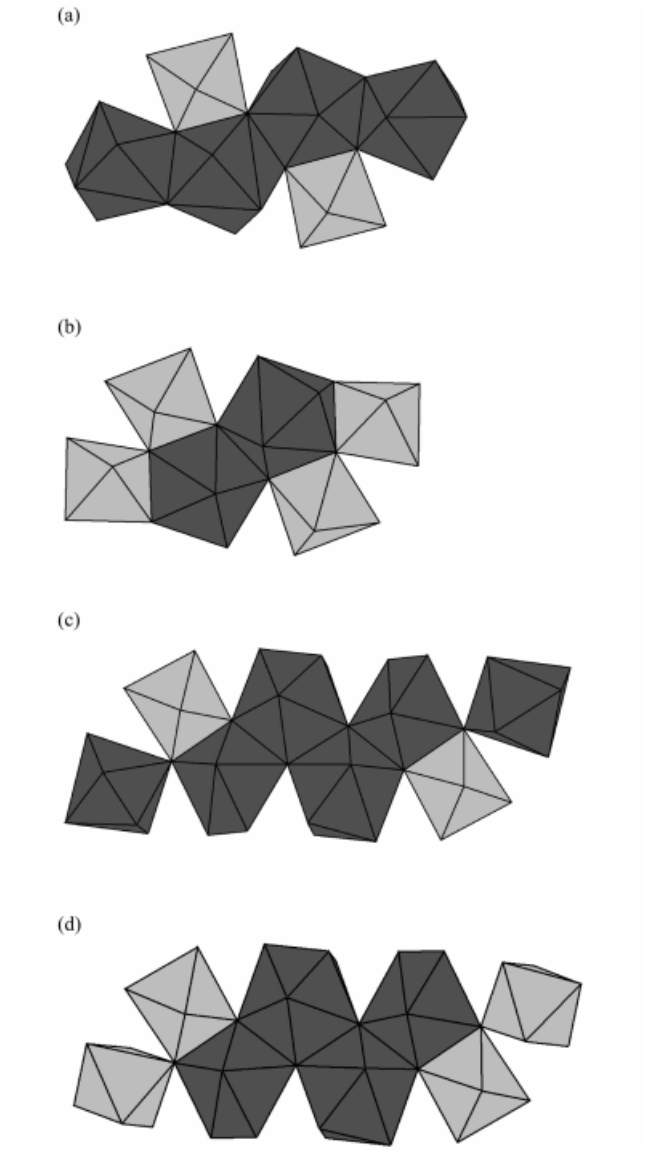


Figure 1. Cores of connected polyhedra present in the clusters **1**−**4**: (a) $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$ (**2**), (b) $Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$ (**3**), (c) $Ti_2Zr_6O_6(OMc)_{20}$ (**4**), (d) $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ (**1**); the central Zr polyhedra in **1** and **4** are 8-coordinate, while the Zr polyhedra bonded to the $[TiO_6]$ octahedra are 7-coordinate

The structural motif common to both six-atom clusters **2** and **3** is a zigzag chain of two $[ZrO_8]$ dodecahedra and two $[TiO_6]$ octahedra, which share common edges. The $[TiO_6]$ octahedra terminate the main chain. The zigzag arrangement is adopted because the central $[ZrO_8]$ dodecahedra share *cis* edges with the neighboring polyhedra (i.e. two $[ZrO_8]$ dodecahedra and one $[TiO_6]$ octahedron are connected by a $\mu_3$-oxygen atom). The main difference between **2** and **3** is the presence of two additional polyhedra condensed onto the $[ZrO_8]$ dodecahedra of the zigzag chain at edges *cis* to the chain-terminating $[TiO_6]$ octahedra. The "extra" polyhedra are $[ZrO_8]$ dodecahedra in **2** and $[TiO_6]$ octahedra in **3**.

In **1** and **4**, the zigzag chain is extended by two oxozirconium polyhedra, but the connectivity is the same. Again, edge-sharing [$TiO_6$] octahedra terminate the main chain, and there are also additional [$ZrO_8$] dodecahedra (in **4**) or [$TiO_6$] octahedra (in **1**) at the flank of the main chain. Contrary to **2** and **3**, the additional polyhedra are condensed onto the main chain through a common corner rather than a common edge. The two polyhedra in **1** and **4** that extend the zigzag chain are distorted [$ZrO_7$] pentagonal bipyramids, located between the terminal [$TiO_6$] octahedra and the central [$ZrO_8$] dodecahedra.

Although both clusters **2** and **3** (composition $M_6O_4X_{16}$) need 16 negatively charged ligands for charge compensation of the $M_6O_4$ core, the 16 ligands have to occupy a different number of coordination sites due to the different coordination numbers of Ti and Zr. Thus, the $Ti_2Zr_4(\mu_3\text{-}O)_4$ core in **2** has 32 coordination sites (6 per Ti, 8 per Zr, minus the coordination sites occupied by the $\mu_3$-O), while the $Ti_4Zr_2(\mu_3\text{-}O)_4$ core in **3** has only 28. Since each of the methacrylate ligands is bidentate (bridging or chelating), both butoxy groups in **2** need to be bridging ($\mu_2$) (Figure 2). The same calculation shows that two of the butoxy groups in **3** must be bridging, while the remaining four are terminal. The latter are located at the titanium atoms (Figure 3). In both cases, the bridging butoxy groups connect the "extra" polyhedra to the zirconium dodecahedron of the zigzag chain [O(4) bridging Zr(1) and Zr(2) in **2**; O(28) bridging Zr and Ti(2) in **3**]. As previously observed for single-metal oxide clusters of Ti or Zr, methacrylate ligands are invariably coordinated to titanium in a bridging mode, but can either bridge or chelate zirconium atoms.

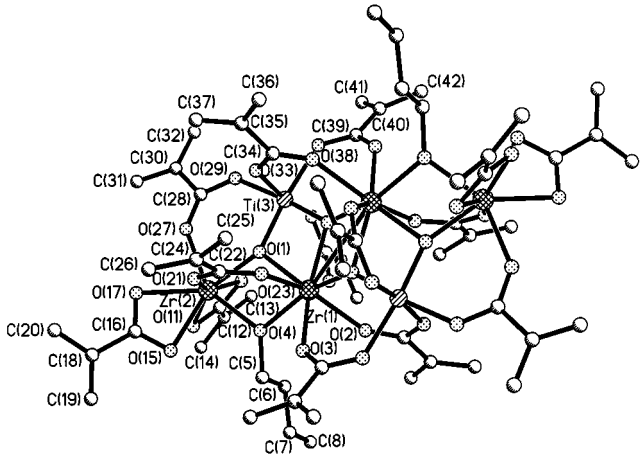


Figure 2. Molecular structure of $Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$ (**2**); hydrogen atoms are omitted for clarity

The 20 ligands of the clusters **1** and **4** (composition $M_8O_6X_{20}$) have to occupy 36 coordination sites in **1** and 40 sites in **4** (in both compounds, two zirconium atoms are only 7-coordinate!). Thus, the four butoxy groups in **1** (Figure 4) must be terminal. They are located at the "extra" titanium atoms. In **4** (Figure 5), the methacrylate ligands occupy all the coordination sites, hence no ligands have to coordinate in a monodentate fashion. This calculation also

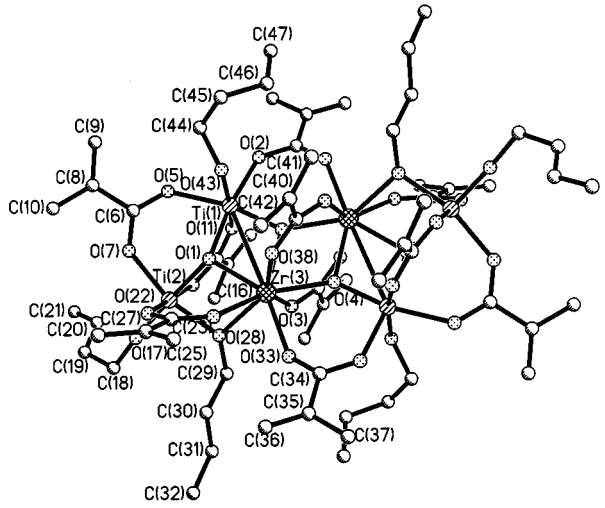


Figure 3. Molecular structure of $Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$ (**3**); hydrogen atoms are omitted for clarity

explains why one of the zirconium atoms in **4** must be 7-coordinate rather than 8-coordinate: the two additional ligands required for 8-coordination could not be compensated by the charge of the cluster core.

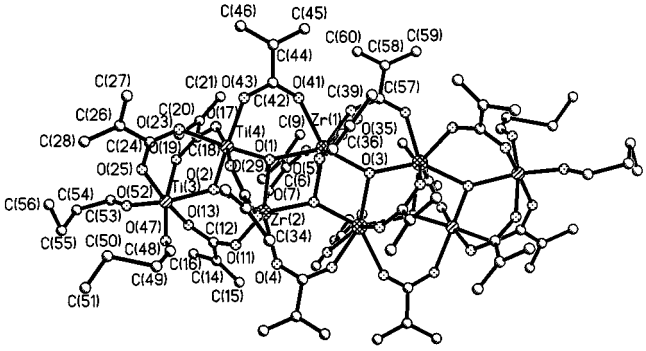


Figure 4. Molecular structure of $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ (**1**); hydrogen atoms are omitted for clarity

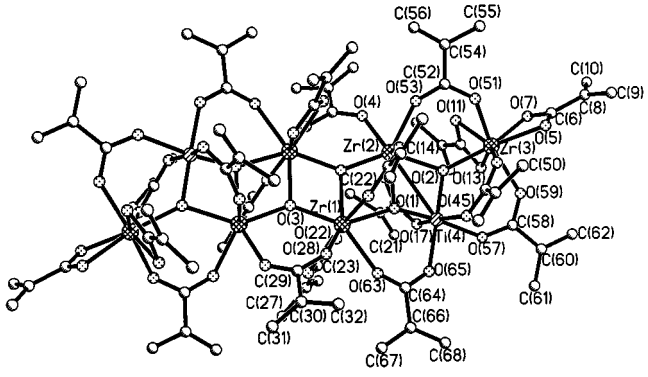


Figure 5. Molecular structure of $Ti_2Zr_6O_6(OMc)_{20}$ (**4**); hydrogen atoms are omitted for clarity

The question arises as to whether it is possible to further extend the zigzag chain observed in the clusters **1** and **4** by the insertion of two additional [$ZrO_7$] or [$ZrO_8$] polyhedra. The composition of the resulting clusters would then be $M_{10}O_8X_{24}$ (i.e. $Ti_2Zr_8O_8X_{24}$ or $Ti_4Zr_6O_8X_{24}$). The 24 singly

negatively charged ligands X would then have to occupy 52 coordination sites in a hypothetical $Ti_2Zr_8O_8X_{24}$ species or 48 coordination sites in $Ti_4Zr_6O_8X_{24}$ (for 8-coordinate Zr). Even if some of the zirconium atoms were to be only 7-coordinate and all of the ligands X were bidentate carboxylate ligands, such a $Ti_2Zr_8O_8X_{24}$ cluster would not be possible because the number of ligands X (a consequence of the charge balance) would be insufficient to occupy the existing coordination sites. A zigzag-shaped cluster of the composition $Ti_4Zr_6O_8X_{24}$ would only be possible if some of the carboxylate ligands coordinated to Ti were to be chelating (which is not the case in the known structures). Therefore, clusters with longer zigzag chains based on the same construction principle as that seen in **1**−**4** cannot be expected.

## Conclusions

We have shown in this paper that a number of clusters with Ti/Zr ratios ranging from 2:1 to 1:3 can be prepared by reacting the metal alkoxides with methacrylic acid. The clusters **1**−**3** can be obtained in high yields without the need for laborious separation procedures. The formation of the clusters is probably due to the slow generation of water by simultaneous ester formation as outlined in the Introduction. The clusters **1**−**4** fill the gap between the single-metal oxotitanium and oxozirconium clusters that we have isolated previously. Using these new methacrylate-substituted clusters as co-monomers in polymerization reactions, we should be able to tune the properties of the resulting hybrid polymers (e.g., refractive index) by varying the inorganic building blocks. The shape and size of the clusters − as inorganic nanoparticles − may also be important with regard to the modification of the polymer properties. SAXS measurements on poly(methyl methacrylate) crosslinked by the clusters $Zr_6O_4(OH)_4(OMc)_{12}$, $Zr_4O_2(OMc)_{12}$, and $Ti_6O_4(OEt)_8(OMc)_8$ have shown that the scattering objects can be approximated by spheres ($Zr_4$ clusters) or discs with diameters of about 1 nm,[12] which corresponds to the crystallographically determined cluster sizes. The clusters described herein are rod-shaped, with lengths between 1.2 (**3**) and 1.8 nm (**1**) (distance between the most distant oxygen atoms) and diameters of about 0.65 nm.

The clusters described in this paper also serve to improve the understanding of the structure evolution in multi-component sol-gel systems, especially those modified by carboxylic acids. Although, as discussed above, the kind of cluster obtained to some extent reflects the reactivity differences of the alkoxides, the formation of the mixed-metal clusters also shows that the organic additives may serve to achieve a homogeneous distribution of the two metals through the formation of carboxylate-bridged extended structures. The only Ti/Zr mixed-metal alkoxide derivatives hitherto reported are the pinacolate derivatives $TiZr_2(OCMe_2CMe_2O)_4(OCMe_2CMe_2OH)_2(OiPr)_2$ and $Ti_2Zr_2(OCMe_2CMe_2O)_6(OiPr)_4$.[14]

## Experimental Section

All operations were carried out in Schlenk tubes under argon. The alkoxides and methacrylic acid were used as received (Aldrich).

**$Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ (1):** A 99% solution of $Ti(OBu)_4$ (1.901 g, 5.53 mmol) in butyl alcohol was mixed with an 80% solution of $Zr(OBu)_4$ (2.681 g, 5.59 mmol) in the same solvent. After the addition of 99% methacrylic acid (4.095 g, 47.1 mmol), the mixture was stored in a closed vessel at room temperature. After 7 d, colorless crystals of **1** had been produced, which were isolated by decanting the mother liquor and drying. Yield 4.23 g (85%); m.p. 124 °C. − $^1$H NMR ($CDCl_3$): δ = 0.88−0.93 (m, 25 H, $OCH_2CH_2CH_2CH_3$), 1.34−1.39 (m, 16 H, $OCH_2CH_2CH_2CH_3$), 1.51−1.56 (m, 16 H, $OCH_2CH_2CH_2CH_3$), 1.83−1.89 [m, 48 H, $=C(CH_3)COO$], 3.61−3.66 (t, 16 H, $OCH_2CH_2CH_2CH_3$), 5.52−5.56 [m, 16 H, *cis*-$CH_2=C(CH_3)COO$], 6.07−6.17 [m, 16 H, *trans*-$CH_2C(CH_3)COO$]. The higher relative intensity of the OBu group signals in the $^1$H NMR spectra indicates the presence of four residual butyl alcohol

Table 1. Crystallographic and structural parameters of **1**−**4**

| | **1** | **2** | **3**·methacrylic acid | **4** |
|---|---|---|---|---|
| Empirical formula | $C_{80}H_{116}O_{42}Ti_4Zr_4$ | $C_{64}H_{88}O_{34}Ti_2Zr_4$ | $C_{71}H_{104}O_{30}Ti_4Zr_2$ | $C_{80}H_{100}O_{46}Ti_2Zr_6$ |
| $M_r$ | 2306.2 | 1862.0 | 1811.6 | 2440.7 |
| Crystal system, space group | monoclinic, *C*2/*c* | triclinic, $P\bar{1}$ | triclinic, $P\bar{1}$ | triclinic, $P\bar{1}$ |
| *a* [pm] | 2776(3) | 1174.29(9) | 1298.0(2) | 1332.67(8) |
| *b* [pm] | 1583.2(8) | 1278.4(1) | 1356.4(2) | 1335.13(8) |
| *c* [pm] | 2674(2) | 1659.6(1) | 1413.4(2) | 1692.1(1) |
| α [°] | | 73.739(1) | 67.787(2) | 97.618(1) |
| β [°] | 117.29(5) | 73.132(2) | 66.829(2) | 91.480(1) |
| γ [°] | | 69.966(2) | 70.926(2) | 104.486(1) |
| Volume [pm$^3$] | 10445(1) × 10$^6$ | 2194.3(3) × 10$^6$ | 2071.1(4) × 10$^6$ | 2883.9(3) × 10$^6$ |
| Z/calcd. density [gcm$^{-3}$] | 4/1.466 | 1/1.409 | 1/1.452 | 1/1.405 |
| μ [mm$^{-1}$] | 0.754 | 0.706 | 0.687 | 0.729 |
| Crystal size [mm] | 0.52 × 0.30 × 0.20 | 0.40 × 0.32 × 0.12 | 0.4 × 0.3 × 0.2 | 0.36 × 0.36 × 0.12 |
| 2θ range | 1.56−23.28 | 1.89−26.36 | 1.97−28.50 | 1.86−24.71 |
| Reflections coll./unique | 24133/7512 | 13399/8887 | 14349/10081 | 15339/9767 |
| Data/parameters | 7512/567 | 8887/470 | 10081/485 | 9767/604 |
| GoF | 1.063 | 1.060 | 1.054 | 1.061 |
| *R*1 [$I > 2\sigma(I)$] | 0.0641 | 0.0503 | 0.0477 | 0.0399 |
| *wR*2 | 0.1658 | 0.1420 | 0.1212 | 0.1192 |
| Largest diff. peak and hole [eÅ$^{-3}$] | 1.519/−0.827 | 1.334/−0.585 | 1.061/−0.742 | 0.853/−0.724 |

molecules per cluster. – $^{13}C$ NMR ($CDCl_3$): δ = 13.8 ($OCH_2CH_2CH_2CH_3$), 18.8 [=C($CH_3$)COO], 30.6 ($OCH_2CH_2CH_2CH_3$), 34.7 ($OCH_2CH_2CH_2CH_3$), 62.7 ($OCH_2CH_2CH_2CH_3$), 125.1–126.9 [$CH_2$=C($CH_3$)COO], 136.5–137.8 [$CH_2$=C($CH_3$)COO], 173.7–176.5 (COO). – $C_{80}H_{116}O_{42}Ti_4Zr_4$4 BuOH (2602.8): calcd. C 44.3, H 5.8; found C 43.7, H 5.2. – $TiO_2/ZrO_2$ from thermogravimetric analysis (TGA): calcd. 35.2%, found 34.3%.

**$Ti_2Zr_4O_4(OBu)_2(OMc)_{14}$ (2):** A 99% solution of $Ti(OBu)_4$ (1.255 g, 3.65 mmol) in butyl alcohol was mixed with an 80% solution of $Zr(OBu)_4$ (3.856 g, 8.04 mmol) in the same solvent. After the addition of 99% methacrylic acid (4.281 g, 49.2 mmol), the mixture was stored in a closed vessel at room temperature. After 7 d, colorless crystals of **2** had been produced, which were isolated by decanting the mother liquor and drying. Yield 7.00 g (67%); m.p. 129 °C. – $^1H$ NMR ($CDCl_3$): δ = 0.88–0.94 (m, 35 H, $OCH_2CH_2CH_2CH_3$), 1.34–1.40 (m, 24 H, $OCH_2CH_2CH_2CH_3$), 1.51–1.56 (m, 24 H, $OCH_2CH_2CH_2CH_3$), 1.91 [m, 42 H, $CH_2C(CH_3)COO$], 3.61–3.66 (t, 24 H, $OCH_2CH_2CH_2CH_3$), 5.52–5.59 [m, 14 H, *cis*-$CH_2$=C($CH_3$)COO], 6.07–6.17 [m, 14 H, *trans*-$CH_2$=C($CH_3$)COO]. The higher relative intensity of the OBu group signals in the $^1H$ NMR spectra indicates the presence of ten residual butyl alcohol molec-

Table 2. Selected bond lengths [pm] and angles [°] in **1** (*: symmetry transformations $-x$, $-y$, $-z + 1$)

| | | | |
|---|---|---|---|
| Zr(1)–O(1) | 218.0(5) | Ti(3)–O(2) | 204.1(5) |
| Zr(1)–O(3) | 207.1(4) | Ti(3)–O(13) | 207.6(5) |
| Zr(1)–O(3)* | 214.8(4) | Ti(3)–O(19) | 211.9(6) |
| Zr(1)–O(5) | 219.2(5) | Ti(3)–O(25) | 198.7(6) |
| Zr(1)–O(35) | 234.1(5) | Ti(3)–O(47) | 179.7(7) |
| Zr(1)–O(37) | 222.3(5) | Ti(3)–O(52) | 187.9(7) |
| Zr(1)–O(41) | 222.7(5) | Ti(4)–O(1) | 178.1(4) |
| Zr(1)–O(56) | 220.7(5) | Ti(4)–O(2) | 184.9(4) |
| Zr(2)–O(1) | 213.3(4) | Ti(4)–O(17) | 199.1(5) |
| Zr(2)–O(2) | 217.8(4) | Ti(4)–O(23) | 205.6(5) |
| Zr(2)–O(3)* | 203.4(5) | Ti(4)–O(29) | 203.8(5) |
| Zr(2)–O(4) | 213.7(5) | Ti(4)–O(43) | 203.4(5) |
| Zr(2)–O(7) | 216.2(5) | | |
| Zr(2)–O(11) | 215.8(4) | | |
| Zr(2)–O(31) | 217.9(5) | | |
| O(1)–Zr(1)–O(3)* | 68.9(2) | O(2)–Ti(3)–O(13) | 88.4(2) |
| O(1)–Zr(1)–O(5) | 76.5(2) | O(2)–Ti(3)–O(19) | 80.7(2) |
| O(1)–Zr(1)–O(37) | 78.3(2) | O(2)–Ti(3)–O(25) | 93.4(2) |
| O(1)–Zr(1)–O(41) | 74.0(2) | O(2)–Ti(3)–O(47) | 90.6(3) |
| O(3)–Zr(1)–O(3)* | 72.1(2) | O(13)–Ti(3)–O(19) | 80.5(2) |
| O(3)–Zr(1)–O(5)* | 80.6(2) | O(13)–Ti(3)–O(47) | 92.0(3) |
| O(3)–Zr(1)–O(35) | 77.7(2) | O(13)–Ti(3)–O(52) | 84.5(3) |
| O(3)–Zr(1)–O(56) | 81.4(2) | O(19)–Ti(3)–O(25) | 87.1(3) |
| O(3)–Zr(1)–O(37)* | 83.5(2) | O(19)–Ti(3)–O(52) | 84.7(3) |
| O(5)–Zr(1)–O(56) | 71.8(2) | O(25)–Ti(3)–O(47) | 100.9(4) |
| O(35)–Zr(1)–O(37) | 56.9(2) | O(25)–Ti(3)–O(52) | 90.6(3) |
| O(35)–Zr(1)–O(41) | 72.5(2) | O(47)–Ti(3)–O(52) | 103.3(4) |
| O(35)–Zr(1)–O(56) | 75.9(2) | O(1)–Ti(4)–O(2) | 86.4(2) |
| O(37)–Zr(1)–O(41) | 87.4(2) | O(1)–Ti(4)–O(17) | 98.3(2) |
| O(41)–Zr(1)–O(56) | 73.0(2) | O(1)–Ti(4)–O(29) | 91.6(2) |
| O(1)–Zr(2)–O(3)* | 71.9(2) | O(1)–Ti(4)–O(43) | 90.5(2) |
| O(1)–Zr(2)–O(2) | 70.4(2) | O(2)–Ti(4)–O(17) | 90.0(2) |
| O(1)–Zr(2)–O(7) | 79.2(2) | O(2)–Ti(4)–O(29) | 91.6(2) |
| O(1)–Zr(2)–O(31) | 80.2(2) | O(2)–Ti(4)–O(23) | 99.1(2) |
| O(2)–Zr(2)–O(31) | 79.1(2) | O(17)–Ti(4)–O(43) | 85.4(2) |
| O(2)–Zr(2)–O(7) | 91.2(2) | O(17)–Ti(4)–O(23) | 88.2(2) |
| O(2)–Zr(2)–O(11) | 81.7(2) | O(23)–Ti(4)–O(29) | 81.8(2) |
| O(3)*–Zr(2)–O(4) | 85.6(2) | O(23)–Ti(4)–O(43) | 84.6(2) |
| O(3)*–Zr(2)–O(7) | 83.6(2) | O(29)–Ti(4)–O(43) | 93.6(2) |
| O(3)*–Zr(2)–O(31) | 92.9(2) | Ti(4)–O(2)–Ti(3) | 125.2(2) |
| O(4)–Zr(2)–O(11) | 72.7(2) | Ti(4)–O(2)–Zr(2) | 98.8(2) |
| O(4)–Zr(2)–O(31) | 75.1(2) | Ti(3)–O(2)–Zr(2) | 135.2(2) |
| O(11)–Zr(2)–O(7) | 75.4(2) | Zr(2)*–O(3)–Zr(1) | 140.4(2) |
| | | Zr(2)*–O(3)–Zr(1)* | 111.7(2) |
| | | Zr(1)–O(3)–Zr(1)* | 107.9(2) |

Table 3. Selected bond lengths [pm] and angles [°] in **2** (*: symmetry transformation $-x + 1$, $-y + 1$, $-z + 1$)

| | | | |
|---|---|---|---|
| Zr(1)–O(1) | 217.0(3) | Zr(2)–O(11) | 223.3(3) |
| Zr(1)–O(2) | 221.0(3) | Zr(2)–O(15) | 227.8(3) |
| Zr(1)–O(3) | 225.2(3) | Zr(2)–O(17) | 224.5(3) |
| Zr(1)–O(4) | 218.8(2) | Zr(2)–O(21) | 216.7(3) |
| Zr(1)–O(23) | 218.7(3) | Zr(2)–O(27) | 218.1(3) |
| Zr(1)–O(45) | 226.8(3) | Ti(3)–O(1) | 182.4(3) |
| Zr(1)–O(49) | 214.8(2) | Ti(3)–O(29) | 203.0(3) |
| Zr(1)–O(49)* | 214.2(2) | Ti(3)–O(33) | 201.3(3) |
| Zr(2)–O(1) | 207.9(2) | Ti(3)–O(38) | 201.1(3) |
| Zr(2)–O(4) | 213.5(3) | Ti(3)–O(43) | 198.6(3) |
| Zr(2)–O(9) | 228.8(4) | Ti(3)–O(49) | 181.5(2) |
| O(1)–Zr(1)–O(4) | 68.3(1) | O(9)–Zr(2)–O(11) | 56.5(1) |
| O(1)–Zr(1)–O(23) | 73.9(1) | O(9)–Zr(2)–O(27) | 77.1(1) |
| O(1)–Zr(1)–O(45) | 74.6(1) | O(11)–Zr(2)–O(15) | 73.7(1) |
| O(1)–Zr(1)–O(49) | 69.4(1) | O(11)–Zr(2)–O(17) | 78.6(1) |
| O(2)–Zr(1)–O(3) | 75.0(1) | O(15)–Zr(2)–O(17) | 57.4(1) |
| O(2)–Zr(1)–O(45) | 68.9(1) | O(15)–Zr(2)–O(21) | 75.1(1) |
| O(2)–Zr(1)–O(49)* | 79.4(1) | O(17)–Zr(2)–O(21) | 77.2(1) |
| O(3)–Zr(1)–O(49)* | 77.3(1) | O(17)–Zr(2)–O(27) | 73.5(1) |
| O(3)–Zr(1)–O(23) | 71.7(1) | O(1)–Ti(3)–O(29) | 90.1(1) |
| O(3)–Zr(1)–O(4) | 76.3(1) | O(1)–Ti(3)–O(33) | 97.9(1) |
| O(4)–Zr(1)–O(45) | 81.7(1) | O(1)–Ti(3)–O(49) | 85.0(1) |
| O(23)–Zr(1)–O(49)* | 77.5(1) | O(1)–Ti(3)–O(43) | 90.4(1) |
| O(23)–Zr(1)–O(49) | 88.5(1) | O(29)–Ti(3)–O(33) | 85.9(1) |
| O(45)–Zr(1)–O(49) | 77.7(1) | O(29)–Ti(3)–O(38) | 94.0(1) |
| O(49)–Zr(1)–O(49)* | 67.5(1) | O(29)–Ti(3)–O(43) | 89.4(1) |
| O(1)–Zr(2)–O(4) | 71.0(1) | O(33)–Ti(3)–O(38) | 87.4(1) |
| O(1)–Zr(2)–O(21) | 77.3(1) | O(33)–Ti(3)–O(49) | 92.6(1) |
| O(1)–Zr(2)–O(27) | 79.7(1) | O(38)–Ti(3)–O(43) | 84.7(1) |
| O(1)–Zr(2)–O(9) | 78.9(1) | O(38)–Ti(3)–O(49) | 91.0(1) |
| O(4)–Zr(2)–O(9) | 86.4(1) | O(43)–Ti(3)–O(49) | 92.8(1) |
| O(4)–Zr(2)–O(15) | 80.2(1) | Zr(1)–O(4)–Zr(2) | 107.5(1) |
| O(4)–Zr(2)–O(21) | 89.4(1) | Zr(1)–O(49)–Zr(1)* | 112.6(1) |

Table 4. Selected bond lengths [pm] and angles [°] in **3** (* symmetry transformation $-x + 1$, $-y + 2$, $-z + 1$)

| | | | |
|---|---|---|---|
| Zr(3)–O(1) | 212.3(2) | Ti(1)–O(4)* | 182.2(2) |
| Zr(3)–O(3) | 219.9(2) | Ti(1)–O(5) | 209.3(2) |
| Zr(3)–O(4) | 212.8(2) | Ti(1)–O(11) | 208.7(2) |
| Zr(3)–O(4)* | 215.4(2) | Ti(1)–O(43) | 181.1(2) |
| Zr(3)–O(24) | 231.7(2) | Ti(2)–O(1) | 195.3(2) |
| Zr(3)–O(28) | 225.6(2) | Ti(2)–O(7) | 202.4(2) |
| Zr(3)–O(33) | 219.3(2) | Ti(2)–O(13) | 204.4(2) |
| Zr(3)–O(38) | 218.6(2) | Ti(2)–O(17) | 176.6(2) |
| Ti(1)–O(1) | 187.9(2) | Ti(2)–O(22) | 198.0(2) |
| Ti(1)–O(2) | 206.0(2) | Ti(2)–O(28) | 194.1(2) |
| O(1)–Zr(3)–O(4)* | 69.52(7) | O(1)–Ti(1)–O(4)* | 82.42(8) |
| O(1)–Zr(3)–O(24) | 75.62(7) | O(1)–Ti(1)–O(5) | 87.83(8) |
| O(1)–Zr(3)–O(28) | 68.38(7) | O(1)–Ti(1)–O(11) | 90.73(8) |
| O(1)–Zr(3)–O(38) | 90.53(7) | O(1)–Ti(1)–O(43) | 102.5(1) |
| O(3)–Zr(3)–O(4) | 76.49(7) | O(2)–Ti(1)–O(4)* | 91.22(8) |
| O(3)–Zr(3)–O(4)* | 77.73(7) | O(2)–Ti(1)–O(5) | 97.05(8) |
| O(3)–Zr(3)–O(28) | 71.88(7) | O(2)–Ti(1)–O(11) | 78.23(9) |
| O(4)–Zr(3)–O(4)* | 71.67(8) | O(2)–Ti(1)–O(43) | 89.7(1) |
| O(4)–Zr(3)–O(33) | 77.26(7) | O(4)*–Ti(1)–O(11) | 92.20(8) |
| O(4)–Zr(3)–O(38) | 75.60(7) | O(4)*–Ti(1)–O(43) | 101.5(1) |
| O(4)*–Zr(3)–O(38) | 77.93(7) | O(5)–Ti(1)–O(11) | 81.54(9) |
| O(24)–Zr(3)–O(28) | 72.92(7) | O(5)–Ti(1)–O(43) | 86.8(1) |
| O(24)–Zr(3)–O(33) | 72.93(7) | O(1)–Ti(2)–O(7) | 86.88(8) |
| O(24)–Zr(3)–O(38) | 69.08(7) | O(1)–Ti(2)–O(13) | 90.02(8) |
| O(28)–Zr(3)–O(33) | 81.90(7) | O(1)–Ti(2)–O(22) | 86.22(8) |
| Ti(1)–O(1)–Ti(2) | 133.2(1) | O(1)–Ti(2)–O(28) | 78.48(8) |
| Ti(1)–O(1)–Zr(3) | 103.58(8) | O(7)–Ti(2)–O(13) | 86.89(9) |
| Ti(2)–O(1)–Zr(3) | 108.61(8) | O(7)–Ti(2)–O(17) | 95.8(1) |
| Ti(1)*–O(4)–Zr(3) | 146.3(1) | O(7)–Ti(2)–O(22) | 93.41(9) |
| Ti(1)*–O(4)–Zr(3)* | 104.41(8) | O(13)–Ti(2)–O(17) | 90.1(1) |
| Zr(3)–O(4)–Zr(3)* | 108.33(8) | O(13)–Ti(2)–O(28) | 88.35(9) |
| | | O(17)–Ti(2)–O(22) | 93.6(1) |
| | | O(17)–Ti(2)–O(28) | 98.9(1) |
| | | O(22)–Ti(2)–O(28) | 90.39(8) |

ules per cluster. – $^{13}C$ NMR ($CDCl_3$): δ = 13.7 ($OCH_2CH_2CH_2CH_3$), 18.4 [$CH_2C(CH_3)COO$], 30.6 ($OCH_2CH_2CH_2CH_3$), 34.8 ($OCH_2CH_2CH_2CH_3$), 62.7 ($OCH_2CH_2CH_2CH_3$), 125.1–127.1 [$CH_2C(CH_3)COO$], 136.5–137.7 [$CH_2C(CH_3)COO$], 173.7–176.5 (COO). – $C_{64}H_{88}O_{34}Ti_2Zr_4$10 BuOH (2603.3): calcd. C 49.2, H 7.1; found C 50.4, H 7.3. – $TiO_2/ZrO_2$ from TGA: calcd. for **2**·10 BuOH 25.0%, found 23.6%.

**$Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$ (3) and $Ti_2Zr_6O_6(OMc)_{20}$ (4):** A 99% solution of $Ti(OBu)_4$ (1.303 g, 3.79 mmol) in butyl alcohol was mixed with an 80% solution of $Zr(OBu)_4$ (5.352 g, 11.25 mmol) in the same solvent. After the addition of 99% methacrylic acid (5.259 g, 60.5 mmol), the mixture was stored in a closed vessel at room temperature. After 7 d, a mixture of colorless crystals of **2**–**4** had been produced, which was recovered by decanting the mother liquor and drying. Yield 7.54 g. Crystals of **4** were manually separated from the mixture for a crystal structure determination.

**$Ti_4Zr_2O_4(OBu)_6(OMc)_{10}$ (3):** A 99% solution of $Ti(OBu)_4$ (1.650 g, 4.80 mmol) in butyl alcohol was mixed with a 70% solution of $Zr(OPr)_4$ (2.144 g, 4.58 mmol) in propanol. After the addition of methacrylic acid (3.363 g, 38.7 mmol), the mixture was stored in a closed vessel at room temperature. After 7 d, colorless crystals of **3** had formed, which were isolated by decanting the mother liquor and drying. Yield 2.361 g (87%); m.p. 133 °C. – $^1H$ NMR ($CDCl_3$): δ = 0.91 (m, 35 H, $OCH_2CH_2CH_2CH_3$), 1.34–1.40 (m, 12 H, $OCH_2CH_2CH_2CH_3$), 1.54–1.58 (m, 12 H, $OCH_2CH_2CH_2CH_3$), 1.91 [m, 30 H, $CH_2C(CH_3)COO$], 3.59–3.63 (m, 6 H, $OCH_2CH_2CH_2CH_3$), 5.52–5.59 [m, 10 H, *cis*-$CH_2C(CH_3)COO$], 6.07–6.17 [m, 10 H, *trans*-$CH_2C(CH_3)COO$]. – $C_{64}H_{86}O_{30}Ti_4Zr_2$ (1709.4): calcd. C 44.5, H 6.1; found C 42.7, H 5.1. – $TiO_2/ZrO_2$ from TGA: calcd. 32.8%, found 31.9%.

Table 5. Selected bond lengths [pm] and angles [°] in **4** (*: symmetry transformation $-x + 2, -y + 1, -z$)

| | | | |
|---|---|---|---|
| Zr(1)–O(1) | 220.2(2) | Zr(3)–O(2) | 208.6(2) |
| Zr(1)–O(3) | 207.6(2) | Zr(3)–O(7) | 225.1(4) |
| Zr(1)–O(3)* | 216.1(2) | Zr(3)–O(5) | 226.7(3) |
| Zr(1)–O(28) | 222.0(2) | Zr(3)–O(11) | 227.9(3) |
| Zr(1)–O(22) | 222.7(2) | Zr(3)–O(13) | 224.1(3) |
| Zr(1)–O(24) | 234.2(2) | Zr(3)–O(47) | 225.3(3) |
| Zr(1)–O(33) | 219.8(2) | Zr(3)–O(51) | 212.4(3) |
| Zr(1)–O(63) | 224.7(2) | Zr(3)–O(59) | 213.1(3) |
| Zr(2)–O(1) | 217.5(2) | Ti(4)–O(1) | 178.2(2) |
| Zr(2)–O(2) | 219.1(2) | Ti(4)–O(2) | 188.9(2) |
| Zr(2)–O(3)* | 204.7(2) | Ti(4)–O(17) | 202.4(2) |
| Zr(2)–O(4) | 214.0(3) | Ti(4)–O(45) | 200.2(3) |
| Zr(2)–O(19) | 217.7(2) | Ti(4)–O(57) | 209.0(2) |
| Zr(2)–O(35) | 216.8(3) | Ti(4)–O(65) | 202.6(3) |
| Zr(2)–O(53) | 217.9(3) | | |
| O(1)–Zr(1)–O(3)* | 69.41(8) | O(5)–Zr(3)–O(47) | 73.7(1) |
| O(1)–Zr(1)–O(22) | 78.76(9) | O(5)–Zr(3)–O(51) | 80.8(1) |
| O(1)–Zr(1)–O(33) | 76.80(9) | O(5)–Zr(3)–O(59) | 80.3(1) |
| O(1)–Zr(1)–O(63) | 73.39(9) | O(7)–Zr(3)–O(11) | 76.5(1) |
| O(3)–Zr(1)–O(3)* | 71.75(9) | O(7)–Zr(3)–O(13) | 76.2(1) |
| O(3)–Zr(1)–O(24) | 77.16(9) | O(11)–Zr(3)–O(13) | 57.6(1) |
| O(3)–Zr(1)–O(28) | 81.29(9) | O(11)–Zr(3)–O(51) | 76.3(1) |
| O(3)*–Zr(1)–O(22) | 84.12(9) | O(13)–Zr(3)–O(59) | 74.0(1) |
| O(3)*–Zr(1)–O(33) | 80.92(9) | O(47)–Zr(3)–O(51) | 78.4(1) |
| O(22)–Zr(1)–O(24) | 57.03(9) | O(47)–Zr(3)–O(59) | 76.8(1) |
| O(22)–Zr(1)–O(63) | 85.8(1) | O(1)–Ti(4)–O(2) | 86.2(1) |
| O(24)–Zr(1)–O(28) | 75.68(9) | O(1)–Ti(4)–O(17) | 91.5(1) |
| O(24)–Zr(1)–O(63) | 73.68(9) | O(1)–Ti(4)–O(45) | 99.1(1) |
| O(28)–Zr(1)–O(33) | 71.17(9) | O(1)–Ti(4)–O(65) | 90.6(1) |
| O(28)–Zr(1)–O(63) | 73.10(9) | O(2)–Ti(4)–O(17) | 91.4(1) |
| O(1)–Zr(2)–O(2) | 70.17(8) | O(2)–Ti(4)–O(45) | 88.3(1) |
| O(1)–Zr(2)–O(3)* | 72.04(9) | O(2)–Ti(4)–O(57) | 99.4(1) |
| O(1)–Zr(2)–O(19) | 78.65(9) | O(17)–Ti(4)–O(57) | 83.9(1) |
| O(1)–Zr(2)–O(35) | 79.45(9) | O(17)–Ti(4)–O(65) | 94.2(1) |
| O(2)–Zr(3)–O(13) | 82.0(1) | O(45)–Ti(4)–O(57) | 85.7(1) |
| O(2)–Zr(2)–O(19) | 78.68(9) | O(45)–Ti(4)–O(65) | 86.7(1) |
| O(2)–Zr(3)–O(51) | 91.0(1) | O(57)–Ti(4)–O(65) | 84.3(1) |
| O(2)–Zr(2)–O(53) | 83.16(9) | Ti(4)–O(1)–Zr(2) | 103.2(1) |
| O(3)*–Zr(2)–O(4) | 85.43(9) | Ti(4)–O(1)–Zr(1) | 150.9(1) |
| O(3)*–Zr(2)–O(35) | 83.44(9) | Zr(2)–O(1)–Zr(1) | 105.63(9) |
| O(4)–Zr(2)–O(19) | 75.6(1) | Ti(4)–O(2)–Zr(3) | 125.0(1) |
| O(4)–Zr(2)–O(53) | 73.1(1) | Ti(4)–O(2)–Zr(2) | 99.1(1) |
| O(35)–Zr(2)–O(53) | 74.6(1) | Zr(3)–O(2)–Zr(2) | 135.3(1) |
| O(2)–Zr(3)–O(11) | 78.0(1) | Zr(2)*–O(3)–Zr(1) | 139.5(1) |
| O(2)–Zr(3)–O(47) | 76.4(1) | Zr(2)*–O(3)–Zr(1) | * 111.9(1) |
| O(5)–Zr(3)–O(7) | 57.2(2) | Zr(1)–O(3)–Zr(1)* | 108.25(9) |

**X-ray Structure Analyses of 1–4:** Selected crystals were mounted on a Siemens SMART diffractometer with a CCD area detector. Graphite-monochromated Mo-$K_\alpha$ radiation (λ = 71.073 pm) was used for all measurements. The crystal-to-detector distance was 4.40 cm. A hemisphere of data was collected by a combination of three sets of exposures at 213 K. Each set had a different φ angle for the crystal; each exposure was of duration 20 s and covered 0.3° in ω. The data were corrected for polarization and Lorentz effects and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined using all unique reflections. The structure was solved by direct methods (SHELXS-86). Refinement was carried out by the full-matrix least-squares method based on $F^2$ (SHELXL-93) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined as riding on the corresponding atom. The asymmetric unit of **3** contains a disordered molecule of methacrylic acid. Only the carbon atoms could be located; they were refined anisotropically without hydrogen atoms attached to them. Crystallographic data (excluding structure factors) for the structures of **1**–**4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-149355 (**1**), -149356 (**2**), -149357 (**3**), and -149358 (**4**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. For additional details see (Table 1–5).


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